MICROENCAPSULATION OF REACTIVE AMINES AND ISOCYANATES AND THEIR APPLICATION TO SELF-HEALING SYSTEMS

BY

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DISSERTATION

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ABSTRACT

Microcapsule-based self-healing systems enable repair of crack damage in polymers and polymer matrix composites. Existing self-healing chemistries are limited by relatively weak chemical bonding between the matrix and the healing material, temperature stability, and side reactions that degrade the active components. We demonstrate for the first time a two-part system that incorporates a healing chemistry similar to the matrix curing chemistry, enabling chemical bonding between the healed material and the matrix material. Amine-containing microcapsules are synthesized by interfacial polymerization of a polyurea about a droplet of amine by means of suspension polymerization. Capsules are subsequently isolated and analyzed for content, and shown to contain reactive amine.

The microcapsules containing reactive amine are employed in concert with microcapsules containing epoxy resin to recover fracture toughness in a cured epoxy. Both capsule types are dispersed in an epoxy resin and the resin is chemically cured. Mechanical load is applied to propagate a crack and rupture microcapsules contained within the cured resin. The average peak load at failure in a virgin specimen is recorded, and compared to the average peak load at failure in the same specimen after a healing period. Recovery of fracture toughness is limited to 15% for specimens healed at temperatures of 50 °C and below, whereas healing efficiencies of up to 60% are observed for specimens healed at temperatures above 80 °C. Control specimens where amine was not present failed to recover.

Microcapsules containing isocyanate are also prepared by means of interfacial polyurea condensation. These capsules are also isolated and analyzed for content, and shown to contain reactive isocyanate. No healing was observed with these capsules, however, due to problems with bonding and long-term stability. With refinement, the isocyanate system is projected for use in polyurethane matrix materials where a moisture-cure could promote the healing reaction.
To my beloved and infinitely supportive wife, Anna, and our wonderful children, and to my mother and in
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# TABLE OF CONTENTS

CHAPTER 1: INTRODUCTION ................................................................................................................. 1

1.1 Healing and Repair in Material Systems.................................................................................... 1

1.2 Development of New Chemistries for Self-Healing............................................................... 3

1.2.1 Chemistry of Epoxy ............................................................................................................. 5

1.2.2 Chemistry of Isocyanates.................................................................................................... 6

1.3 Microencapsulation .................................................................................................................... 7

1.4 Overview of the Dissertation .................................................................................................... 8

CHAPTER 2: MICROENCAPSULATION OF DEH-52, A REACTIVE AMINE ........................................ 10

2.1 Introduction ............................................................................................................................... 10

2.2 Preparation of Microcapsules .................................................................................................. 11

2.3 Reverse Emulsion Stabilization ................................................................................................ 12

2.4 Wall Polymerization Rate ....................................................................................................... 13

2.5 Microcapsule Size Distribution .............................................................................................. 13

2.6 Microscopy of Prepared Microcapsules .................................................................................... 17

2.7 Capsule Analysis ...................................................................................................................... 18

2.8 Reactivity of Core Material ..................................................................................................... 22

2.9 Conclusions ............................................................................................................................. 23

CHAPTER 3: THE AMINE-EPOXY SELF-HEALING SYSTEM ................................................................ 25

3.1 Introduction .............................................................................................................................. 25
3.2 Materials and Methods ................................................................. 26

3.2.1 Materials ................................................................................. 26

3.2.2 Healing Assessment ................................................................. 28

3.2.3 Sample Fabrication ................................................................. 29

3.3 Results and Discussion ............................................................... 32

3.3.1 Reference Specimens .............................................................. 33

3.3.2 Control Specimens ................................................................. 35

3.3.3 Self-Activated Specimens ...................................................... 37

3.3.4 Self-Healing Samples .............................................................. 38

3.4 Effect of Temperature on Healing Efficiency ............................. 39

3.5 Limitations on Healing Efficiency .............................................. 43

3.6 Conclusions ................................................................................. 44

CHAPTER 4: MICROENCAPSULATION OF METHYLENE DIPHENYLDIISOCYANATE, A REACTIVE ISOCYANATE ................................................................. 45

4.1 Introduction ................................................................................. 45

4.2 Materials and Methods ............................................................... 46

4.2.1 Chemicals ................................................................................ 46

4.2.2 Preparation of Microcapsules .................................................. 46

4.2.3 Characterization ...................................................................... 47

4.3 Results and Discussion ............................................................... 48

4.3.1 Capsule Size Control .............................................................. 48
4.3.2 Capsule Morphology........................................................................................................... 50
4.3.3 Core Analysis and Reactivity............................................................................................. 51
4.4 Deposition of Microcapsules in Matrix Materials .............................................................. 54
4.5 Conclusions.......................................................................................................................... 54

CHAPTER 5: CONCLUSIONS AND FUTURE WORK.................................................................. 56
5.1 Conclusions.......................................................................................................................... 56
5.2 Future Work.......................................................................................................................... 57
  5.2.1 Shell Wall Refinements..................................................................................................... 57
  5.2.2 Viscosity.......................................................................................................................... 57
  5.2.3 Alternative Encapsulation Schemes .............................................................................. 58
  5.2.4 Binary Capsule Functionalization ................................................................................. 58

REFERENCES ............................................................................................................................ 59

APPENDIX A: LABVIEW TESTING PROGRAM........................................................................ 68

APPENDIX B: AMINE MICROENCAPSULATION EXPERIMENTATION .................................. 71

AUTHOR’S BIOGRAPHY ............................................................................................................ 72
CHAPTER 1

INTRODUCTION

Brittle thermosetting polymers, like those used in lightweight structural composites and microelectronic devices, are susceptible to crack damage caused by impact, thermal stresses, or fatigue. Small cracks that can develop undetected in a material can quickly compromise the integrity of a matrix, leading to catastrophic failure of the material. If crack growth can be retarded, terminated, or in the optimum scenario, reversed, the working lifetime of a thermosetting material could be dramatically increased. However, manual intervention is costly and requires detection of damage prior to catastrophic failure. Self-healing materials provide an opportunity to solve this problem. In this dissertation, a new binary healing chemistry as well as a one-part healing system is developed with the goal of repairing damage in thermosetting polymers.

1.1 Healing and Repair in Material Systems

Biological systems provided the inspiration for White et al.[1] to propose and create a prototype self-healing system. Natural systems have developed a highly evolved response to damage from external and internal sources. This response varies in sophistication from covering the damage, as in the case of a tree knot, to full-scale repair and remodeling, as in human bone repair. Only recently have similar mechanisms been introduced into engineered materials, where damage occurs as a result of wear, impact, thermal cycling, or other factors. To mitigate this damage, it is desirable to incorporate active functionality to repair or retard the damage that has occurred. Active materials incorporating self-healing functionality have been recently reported in the literature[2-13].
Figure 1.1: The microcapsule self-healing concept.[14] (a) A crack propagates into the matrix, ruptures healing agent reservoirs, and is subsequently polymerized. (b) Self-healing systems include (i) encapsulated monomer and dispersed catalyst, e.g. dicyclopentadiene/Grubbs’ catalyst, (ii) two distinct encapsulated monomers, e.g. epoxide and amine, and (iii) dispersed monomer and encapsulated monomer. (c) Mechanical assessment of healing is performed by comparisons of Mode I fracture loading ($K_{IC}$), or other mechanical properties in the virgin and healed specimens.

Figure 1.1 illustrates the self-healing concept as applied to a microcapsule system. Microcapsules are introduced into a material, and damage stimulates a reaction, as shown in Figure 1.1(a). The first generation of microcapsule based self-healing polymers focused on a two-part system consisting of solid Grubbs’ catalyst and microencapsulated endo-dicyclopentadiene (DCPD)[15]. In the Grubbs/DCPD system (Figure 1.1(b), left), crack healing is accomplished through ring-opening metathesis polymerization (ROMP). Over 90% of the original material’s fracture toughness, as assessed by $K_{IC}$
measurements, is restored[15], even though chemical bonding between the substrate and the poly(DCPD) is not present. The assessment method is summarized in Figure 1.1(c).

In general, repair of a self-healing material is accomplished by the reaction between incorporated healing components in the damaged region. In this work, the material to be healed is a cured epoxy, and the healing components are an epoxy resin and an amine curing agent. Because this system requires two components to mix in order to cause the reaction to occur (Figure 1.1(b)), it is essential that both materials infiltrate the crack plane.

Previously, microcapsules containing DCPD were ruptured by crack damage and DCPD was released into the damaged region and came into contact with the Grubbs’ metathesis catalyst, forming a crosslinked network of poly-DCPD[1, 15-17]. The DCPD chemistry permitted room-temperature crosslinking of DCPD in the presence of the transition metal catalyst. However, the DCPD system suffers from undesirable side reactions, particularly the deactivation of the catalyst in the epoxy matrix. Rule[18] subsequently developed a method to protect the catalyst with wax. A second disadvantage of the DCPD/Grubbs’ catalyst system is its relative expense – making large-scale industrial use cost-prohibitive. The disadvantages discussed above motivated the invention of a novel self-healing system comprising epoxy resin and amine curing agent.

1.2 Development of New Chemistries for Self-Healing

To overcome the limitations of Grubbs’ catalyst, other healing chemistries have been explored. Epoxy resin in conjunction with solvent has been reported to heal epoxy materials. Blaiszik et al.[3, 19] and Caruso et al.[4] demonstrated solvent-mediated post-curing of an undercured epoxy, in which microcapsules containing solvent and additional epoxy were delivered to a crack plane, causing swelling and liberating free polymer endgroups for further reactivity. In a two-part amine-epoxy microcapsule system, developing microcapsules containing epoxy resin and epoxy resins with a solvent is a
fundamental step. However, this approach for self-healing requires chain mobility within the solid substrate that is enhanced by solvent diffusion and a substantially under-cured resin to allow for mobility and further cross-linking to occur. In a fully-cured material, healing is not observed utilizing a single-capsule epoxy system.

A second chemistry that has been applied to self-healing materials is siloxane-based. Cho et al.[20, 21], Keller et al.[5, 22], and Moll et al.[23, 24] demonstrated healing in silicone materials utilizing micro-encapsulated poly(dimethylsiloxane) oligomers with platinum catalyst and vinylsiloxane cross-linking agents. Silicone deforms at low stress, and as such is suitable to healing in elastomers; Moll has also employed siloxane chemistry to seal cracks formed in fiber-reinforced epoxy.

Two additional chemistries aided in motivating the current work. Yin and coworkers[11, 25] developed a system comprising encapsulated epoxy and latent curing agent, in which the curing agent is deposited into the matrix and is inactive until it meets with delivered epoxy. Secondly, the encapsulation of mercaptans for self-healing has been reported[26] previously. Using a latent curing agent requires a deprotection or reactivation step to occur prior to healing, and mercaptans are less desirable due to their disagreeable odor and reaction rate – a mercaptan-based system may fail to fully wet the crack plane before causing ring-opening and solidification of epoxides, hindering its distribution in a damage region.

For the reasons discussed above, none of these systems is equipped to handle a fully-cured epoxy matrix meeting with damage. In this dissertation, new healing chemistries are developed for aerospace grade epoxies and potentially for polyurethanes.
1.2.1 Chemistry of Epoxy

Epoxy resins are characterized by the presence of an epoxide moiety, seen in Figure 1.2. Ring-opening of the epoxide moiety is responsible for hardening and cross-linking of the resin.

![Figure 1.2: (a) Reaction of an epoxide with an amine. Each primary amine can react with two epoxides. When diepoxides and polyamines are employed, a cross-linked structure results. (b) Structure of a common epoxy resin, diglycidyl ether of bisphenol-A (DGEBA).](image)

The resultant hydroxyl group and secondary amine are capable of further reactions at increased temperatures, enhancing cross-link density and limiting degradation due to oxidation or action of corrosive or caustic chemicals by formation of new covalent bonds. Several chemistries can be employed to perform the ring opening; the most common commercial systems employ amines, whereas mercaptans, anhydrides, and Lewis acids find niche applications.

The most common epoxy resin in use is the diglycidyl ether of bisphenol-A (DGEBA), seen in Figure 1.2(b). This resin is a diepoxide, which when reacted with a polyamine such as diethylenetriamine...
(DETA), forms a cross-linked structure due to the multiple reactive sites on DETA. Epoxide-amine systems make up the bulk of industrial epoxy usage, which amounts to millions of tons per annum. Because of this high prevalence of epoxy systems in the marketplace, healing in epoxy systems presents an attractive target commercially.

![Figure 1.3: Primary reactions of isocyanates. Reaction with an alcohol forms a urethane; reaction with amine forms a urea.](image)

### 1.2.2 Chemistry of Isocyanates

Isocyanates are the building block in polyurethane and polyureas. The isocyanates that are most commonly used for commercial polymers are toluene diisocyanate (TDI), isophorone diisocyanate (IPDI) and methylene diphenyldiisocyanate (MDI). The urethane and urea forming reactions are also two-component reactions, similar to the epoxy-amine reaction. An isocyanate and an alcohol react to form
the urethane linkage (Figure 1.3). Ring-opening does not occur; however, like the epoxide reaction above, there are no byproducts to the reaction. A similar reaction occurs between isocyanate and amine, forming a polyurea. The isocyanate moiety is highly reactive, and will react with ambient moisture to release CO$_2$ and produce an amine intermediate, which rapidly reacts to form the polyurea discussed above. Commercial polyurethane systems include foams for insulation and shock absorbance, adhesives, or coatings for material protection against weathering.

The polyurea reaction is very rapid,\cite{27} and as such can be used to form a polymer capsule by interfacial polymerization. This technique was used in both the encapsulation of amine and of MDI.

### 1.3 Microencapsulation

Microencapsulation is the process of passivating or confining a material, generally a liquid, within a solid shell and is an established protocol for passivation or protection of a core material. Literature reports encapsulated materials include oils\cite{1}, epoxies\cite{4, 13, 19, 28}, and heterogeneous catalysts\cite{29}. Capsule wall formation is typically achieved by condensation polymerization of monomers, complex

![Figure 1.4: Microencapsulation of dicyclopentadiene. a) Procedure for preparation of urea-formaldehyde microcapsules containing dicyclopentadiene as developed by Brown\cite{16} b) Relationship between stir rate and microcapsule diameter.](image)
coacervation of large molecules, or precipitation of polymer at an interface.

The technique commonly used in fabricating epoxy microcapsules is polymer condensation of urea and formaldehyde. A stirrer agitates a two-phase suspension, dispersing one phase as droplets in the other in the presence of a surfactant. The oligomers formed by the reaction between these two components proceed *in situ* to the interface between disperse and continuous phase, where they further condense to form a rigid wall membrane, preventing coalescence of dispersed droplets and permitting isolation as a dry powder. This technique was also used for encapsulation of DCPD[16] (Figure 1.4). Similar techniques have been employed for encapsulation of mercaptans[12, 26]. In place of urea, melamine is used and oligomer formation is carried out separately. The oligomers are synthesized neat, then added to the emulsion containing the mercaptan. Oligomers continue to condense about the dispersion, and are later isolated from the solution. Interfacial polymerization of isocyanate and amine in a reverse-phase emulsion[30] has also recently been used to encapsulate a phosphate buffered saline solution and magnetite particles. This method was also employed in the encapsulation of polar solvents in preparation for heterogeneous catalysis within a microcapsule[29].

While other researchers have incorporated microvascular healing into materials[8, 9], such efforts are highly labor-intensive in fabrication. Microcapsule-based self-healing matrices are produced by simple manual mixing of the encapsulated healing components into a liquid matrix for forming into a variety of geometries during the curing process. In this dissertation, reactive amine is successfully encapsulated and utilized to heal crack damage in an epoxy matrix. Reactive isocyanate is also encapsulated and incorporated in a polyurethane, but with no successful healing.

**1.4 Overview of the Dissertation**

In Chapter 2, a protocol for the microencapsulation of reactive amines is introduced, along with the other encapsulation strategies that were tested. Next, the analysis of amine core content as well as ex
situ analysis of healing potential is discussed. The characterization of the microcapsules is provided. Thermal analysis supports the determination of microcapsule contents. Finally, the mass spectrum of the microcapsules is presented, confirming the presence of the desired product.

Chapter 3 discusses the mechanical testing performed on the self-healing epoxy comprising epoxy-amine microcapsules as the healing agents, as well as the difficulties encountered in preparing the capsules for deployment in the cured epoxy matrix. Data is presented illustrating the temperature dependence for healing to occur, and other limitations are discussed.

Chapter 4 describes the microencapsulation of a reactive isocyanate, following a similar protocol to the amine encapsulation discussed in Chapter 2. The details of the encapsulation, including changes required to stabilize the isocyanate capsules are discussed. Additional improvements are recommended prior to deploying this system.

Chapter 5 concludes the dissertation with comparisons between the new epoxy-amine healing system described and external efforts to develop alternative chemistries. Recommendations are given for further improvements in the system.
CHAPTER 2

MICROENCAPSULATION OF DEH-52, A REACTIVE AMINE

Much of the work in self-healing materials has focused on binary systems. In each of these systems, two components meet in the damage region and react, triggering the healing response. Microcapsules comprising the DCPD/Grubbs’ system[1] and a siloxane-based system[5, 22] have been extensively studied. Other binary self-healing techniques incorporate impregnated hollow glass fibers or embedded microchannels containing a vasculature of reactive monomer[8, 9, 33-36]. Due to the robustness of the microvascular preparation, a larger library of monomers, including reactive amines, may be employed in the vascular systems that have previously not been possible in microencapsulated preparations.

Alternative experimentation to the successful amine microencapsulation discussed below can be found in Appendix B.

2.1 Introduction

Preparation of amine containing microcapsules enables the creation of self-healing epoxies in which the microencapsulated healing agents contain the same chemistry as the bulk matrix. Motivated by this objective, we explore microencapsulation strategies to form a polymer shell around a reactive amine to produce a microencapsulated curing agent for epoxide-functionalized healing agents. Previous efforts to encapsulate curing agents has been met with some success: Zhang et al. reported on the encapsulation of a mercaptan and imidazole-based curing agent[12, 26, 37]. Drawing on work in water-in-oil and oil-in-oil emulsion stabilization[29, 38], a protocol was established for interfacial
polymerization of a small-molecule polyamine with a small-molecule diisocyanate to create a cross-linked polymer shell around an amine-containing core.

2.2 Preparation of Microcapsules

Diethylenetriamine (DETA) was used as received from Air Products. Epon Resin 828 was used as received from Miller-Stephenson. DEH-52 curing agent, an adduct of Epon Resin 828 and DETA, was used as received from Dow Chemical. Toluene diisocyanate (TDI), decalin, Span® 85, and polyisobutylene (PIB) were used as received from Sigma-Aldrich. Cloisite 20A nanoclay was used as received from Southern Clay Products. Rhodamine B was purchased as “FLT Industrial Red Dye” from Kingscote Chemicals.

A stock suspension of 5 pph nanoclay in decalin was prepared and the nanoclay was dispersed by sonication for 60 minutes in a water bath. Likewise, 40 g PIB was added to 200 mL of decalin to form a 20 pph stock solution of PIB in decalin. The reactive core material was prepared as a 33 pph solution of DETA in DEH-52.

The water-in-oil emulsion was prepared by adding 5 g of the nanoclay suspension, 10 g each of the PIB stock and core stock, and 30 g decalin and emulsifying at 1500 RPM with a Caframo digital mixer with 3-blade agitator for 10 minutes. The shell-forming reaction was carried out by syringe pump injection of 20 mL of a 20 wt% solution of TDI in decalin at 0.5 mL/min. The polyurea condensation was allowed to proceed at room temperature with continued agitation for 72 h.

Following shell wall synthesis, the capsules were rinsed in decalin to remove excess polyisobutylene, rinsed in ethyl acetate to coacervate the polyisobutylene chains, and subsequently decanted and freeze-dried to remove any remaining solvent. The capsules were recovered by this method in excess of 80% yield based on total capsule weight relative to the amine weight. Capsules were then analyzed by
optical microscopy, thermogravimetric analysis, electrospray ionization-mass spectrometry, and scanning electron microscopy.

Thermogravimetric analysis (TGA) was performed on a Mettler-Toledo TGA851°, calibrated by indium, aluminum and zinc standards. Unless otherwise indicated, a heating rate of 10 °C•min⁻¹ was used in an atmosphere of nitrogen. For each experiment, approximately 5 mg of sample were accurately weighed (± 0.02 mg) into an alumina crucible. The mass loss was recorded during a heating cycle over the temperature range of 25 °C to 650 °C.

Differential scanning calorimetry (DSC) was performed on a Mettler-Toledo DSC821° using a nitrogen atmosphere to measure heat flow (positive exothermal) from 25-400 °C at a heating rate of 10 °C/min.

Mass spectrometry (EI-MS) was performed by electrospray ionization on a 70-VSE through the Mass Spectrometry Facility, SCS, University of Illinois.

Scanning electron micrography (SEM) was performed on Au/Pd sputter-coated samples on a Philips XL-30 FEG at the Imaging Technology Group at the Beckman Institute.

Optical micrographs were acquired by Micropublisher CCD camera with fluorescence and analyzed using NIH ImageJ software.

Solution viscosity was measured by an TA Instruments AR-G2 rheometer with 25 mm diameter aluminum parallel plate geometry at 200% strain in an oscillation frequency sweep from 0.1 – 100 Hz (See Supporting Information).

Titration experiments were performed using a 100 µL Hamilton syringe containing 1.000 N HCl solution from Fisher Scientific. Bromothymol blue was used as the indicator.

2.3 Reverse Emulsion Stabilization

Stabilization of an inverse emulsion presents a challenge in microcapsule synthesis. Initial work focused on chemical surfactants, such as the sorbitol-based Span® series[29], which were unable to
provide the necessary structural stability to prevent emulsified droplets from joining in solution rather than forming a stable microcapsule system. Span® 85 was used to create an emulsion that appeared stable; however, when TDI was added, stable microcapsules were not formed. In order to provide the necessary stabilization, we adopted a hydrophobically-modified nanoclay to form a Pickering emulsion at the polar-nonpolar boundary. Because the nanoclay platelets are several orders of magnitude larger than a chemical surfactant, their presence at the polar-nonpolar interface provided for excellent droplet stabilization.

2.4 Wall Polymerization Rate

The reaction rate between shell wall components is critical to the formation of stable microcapsules. TDI is a highly reactive industrial chemical used in the synthesis of polyurethanes. TDI reacts readily with amines at room temperature to form polyureas. The reaction rate of isocyanates with amines is much faster than the rate of isocyanates with alcohols or water; this results in complete consumption of TDI and polyurea formation at the interface. Bolus addition of TDI to the emulsion was unsuccessful, whereas gradual addition of a TDI solution permitted oligomer formation and precipitation at the emulsion interface, subsequently leading to solidification of the polyurea wall around the amine core. We hypothesize that a single large delivery of TDI caused the emulsified droplets to coalesce, whereas slow addition permitted shell formation. Amine-terminated oligomer formation is stoichiometrically limited in favor of high molecular weight condensation polymerization.

2.5 Microcapsule Size Distribution

The prepared microcapsules were examined by optical and electron microscopy. The mean capsule diameter, measured by electron microscopy, was 26 ± 10 µm (Figure 2.1). Electron micrographs showed
the capsules to be spheroid with some slight irregularities due to the platelet aspect of the nanoclay incorporated in the wall (Figure 2.2), and a distribution of sizes is given in Figure 2.3.

Figure 2.1: Electron micrograph of dried amine-filled capsules prepared at 1750 RPM. The scale bar is 50 µm.
Figure 2.2: Electron micrograph of a single capsule showing small adhesions to an overall-spherical capsule. The scale bar is 10 μm.

Figure 2.3: Size distribution of microcapsules prepared at 1750 RPM. Average capsule diameter is 26 ± 10μm.
Typically, microcapsule diameter is influenced by agitation rate [3, 16] (Figure 2.4). Compared to previous work with a less viscous solution [16], these capsules are several times larger at 1500 RPM, but exhibit similar size to previous capsules prepared at higher speeds. This is likely due to a shear thinning of the continuous phase. Furthermore, due to the increased viscosity of the continuous phase, a critical stir rate exists for our system. Stirring at speeds slower than 1000 RPM did not distribute the isocyanate efficiently through the reaction beaker, causing clumping of soft capsules and precipitation of irregular, semi-solid material. Agitation rates between 1250 and 2000 RPM had a moderate effect on mean capsule diameter.

Viscosity of the stock solution was also critical to capsule formation [40]. When insufficient PIB was added to the emulsion (less than 1.5 g), no microcapsules formed. Instead, bulk polymer was collected from the reaction vessel. Rheological testing of the stock solution gave a viscosity of 15,400 cP at 25 Hz
oscillation, corresponding to the 1500 RPM stir rate. Thus, the solution viscosity is substantially elevated relative to neat decalin, resulting in extended lifetime for the emulsion droplets.

### 2.6 Microscopy of Prepared Microcapsules

Capsules were examined by optical microscopy. Capsules were generally spheroid, with significant adhesions resulting in shape irregularity (Figure 2.5). After drying, capsules could be ruptured by applying force to a coverslip. Capsule rupture caused an observable release of core liquid. Additional syntheses were performed with rhodamine B dye incorporated in the amine core phase. The dye was sequestered to the shell wall, as observed under fluorescence. When force was applied to the dyed capsules, a substantial amount of core material was released as evidenced by a layer of viscous liquid surrounding the fluorescent shell wall (Figure 2.6).

![Figure 2.5: Optical micrograph of capsules in solution illustrating typical shape and adhesions between formed capsules.](image)
2.7 Capsule Analysis

Capsule fill content was assessed by thermogravimetric analysis (Figure 2.7). The stock solution used for the encapsulation showed two distinct weight loss peaks corresponding to DETA and the oligomeric component of DEH-52 (Figure 2.7a). Thermal analysis of the microcapsules (Figure 2.7b) and differential thermal analysis (Figure 2.7c) have clearly resolved peaks matching the stock DETA and DEH-52.

Significant weight loss was also seen corresponding to the polyurea wall material (onset 230 °C, 42%). The residual mass of 6% at elevated temperatures corresponds to inorganic clay and reduced carbon. The capsules were found to be 55% by mass reactive amine core material. Future refinement of the technique will reduce the wall material and enhance the mass fill content.
Figure 2.7: Thermograms of (a) stock amine solution, (b) microcapsules, (c) differential thermal analysis of microcapsules.
Mass spectroscopy by electron ionization was performed to determine the contents of the microcapsules (Figure 2.8). Results indicated the presence of DETA, DEH-52, and TDI-DETA oligomers. This data further indicates that a reaction between DETA and TDI has occurred to create amine-terminated oligomers, and that residual DEH-52 and DETA have been incorporated in the core material, with no remaining TDI in the product.
Figure 2.8: Electrospray Ionization Mass Spectrum with identified peaks.
2.8 Reactivity of Core Material

Capsules were crushed with a mortar and pestle, and were added to neat Epon 828 resin at a 1:1 mass ratio. The resulting slurry was then placed between two glass slides. After resting 72 h at room temperature, the slides could not be manually separated by shear, indicating that a reaction had taken place between ruptured core material and the epoxy resin. In contrast, control slides with only epoxy resin were easily separated and no film was present. Control slides where only amine microcapsules were ruptured under pressure also did not form a solid film.

The slides coated with cured material were separated with a razor blade. Optical microscopy of the film showed no remnant capsules and no discrete fluorescence. A 72 h/100 °C cure cycle was employed to prepare a second film between octadecyltrichlorosilane-treated glass slides (Figure 2.9) for improved visualization.

Figure 2.9: Film of Epon 828 cured by crushed microcapsules. Spherical regions are voids in the film. Scalebar 500 µm.

In a second experiment, the capsules were allowed to osmotically rupture by suspension in water for 1 week, eluting the core material into the aqueous layer since both DETA and DEH-52 are soluble in
water. The solution was then filtered and titrated with acid to determine an amine equivalent weight (AEW) of 254 g capsules/mol NH$_2$. This result indicates a capsule fill ratio of 35 wt%, which is lower than that measured by TGA, suggesting that some residual DEH may have remained in the capsules or had been inadvertently protonated during the digestion, and therefore the actual AEW may be slightly lower than that determined by this process. We note that digestion in acid and back-titration against a base is undesirable due to the potential hydrolysis of the polyurea shell, resulting in a lower AEW than is actually present.

To further determine capsule loading fraction of the core mixture, dynamic DSC was employed to measure the degree of cure ($\alpha = \Delta H/\Delta H_{\text{tot}}$) of an epoxy sample loaded with microcapsules. The neat DEH-52/DETA mixture used as core material was used as a control (40 pph in Epon 828, 100% cure at 250 °C). Microcapsules were ground with a mortar and pestle then delivered into Epon 828 at 40 pph and evaluated immediately by DSC. The degree of cure as measured by heat evolution was 20.8 ± 5.3%, indicating that the microcapsules are 20% efficient at curing epoxy compared to the neat core material. While DETA and DEH-52 compounds are intended to be used at 12 parts per hundred resin (phr) and 25 phr respectively, with AEWs of 34 g/mol NH$_2$ and 90 g/mol NH$_2$, the AEW measured of our microcapsules is substantially higher. By extrapolating the AEWs of DETA and DEH-52 and applying them to published cure cycles, we determine that a nearly 1:1 capsule:resin ratio is required for the optimum stoichiometry of the cured material. Successive generations of this encapsulation strategy will focus on decreasing the AEW of the encapsulated system to improve efficiency and decrease required microcapsule loading levels for effective self-healing.

### 2.9 Conclusions

A method for preparation of microcapsules containing reactive amines has been developed. This method relies on physical stabilization of emulsion droplets for wall formation, and utilizes the rapid condensation of isocyanate with amine to form a stable shell wall. A reverse-phase emulsion was
employed to create discrete amine droplets and interfacial polymerization occurred at the droplet-oil interface. Capsules were determined to contain amine by titration, TGA, and qualitative curing of epoxy resin. Cured adhesive films were formed from the reaction of microcapsules with epoxy resin.
CHAPTER 3

THE AMINE-EPOXY SELF-HEALING SYSTEM

In this chapter, we assess the performance of our capsules through recovery of fracture toughness. A binary microcapsule system was employed for self-healing in an epoxy matrix. Microcapsules containing either an epoxy or an amine hardening agent were dispersed in an epoxy sample and subjected to quasistatic loading to propagate a crack. The crack was subsequently repaired by means of capillary action drawing microcapsule contents into the damaged region, permitting them to react and restore mechanical integrity. Multiple healing temperatures and curing cycles were examined.

3.1 Introduction

Microcapsule-based self-healing is a growing field of interest. Depending on the particular matrix to be healed, multiple chemistries, from poly(dicyclopentadiene)[1, 3, 15, 41, 42] to silicones[23] and epoxy-solid amine[37] or epoxy-mercaptan[12, 13, 26] have been employed within microcapsules to restore fracture toughness following crack propagation. In Chapter 2, we have reported on the fabrication of amine-containing microcapsules utilizing an interfacial polymerization technique[43]. When dispersed in a cured epoxy resin, these amine microcapsules retain active functionality which permits them to further react with added epoxy. Epoxy can be either injected or microencapsulated to produce a healing reaction. When the epoxy is also microencapsulated and dispersed in the resin, an autonomic system is created, capable of restoring fracture toughness and healing the crack with
minimal intervention. Subsequent to fracture and crack propagation, the two microcapsules release their contents into the fracture plane, and the ensuing chemical reaction between the epoxy resin and hardener forms a chemical bond with the specimen, restoring fracture toughness to the specimen.

### 3.2 Materials and Methods

#### 3.2.1 Materials

The amines DEH-52 and DETA were provided by Dow Chemical and Air Products respectively. Cloisite 20A nanoclay was received from Southern Clay Products. Toluene diisocyanate and chlorobenzene were purchased from Sigma-Aldrich. Epon resins and Epikure curing agents were acquired from Miller-Stephenson.

Microcapsules containing 1 part Epon 862 epoxy resin and 1 part chlorobenzene were prepared according to the method of Caruso et al.[4]; microcapsules containing Epon 815C were prepared by the second method of Caruso et al.[44]. A representative image of the microcapsules containing Epon 815C is shown in Figure 3.1. The epoxy resin-containing microcapsules had an average diameter of 85±20 µm.

Microcapsules containing amine were prepared following the method of McIlroy et al.[43], as discussed in Chapter 2. To improve drying and dispersion of the microcapsules, the isolation procedure was modified by depositing microcapsules from the decalin rinse solution directly into hexanes, washing three times, freezing in liquid nitrogen, and then drying *in vacuo* from hexanes. A dry powder resulted. To provide for maximum healing, thermal analysis of residual heat was performed to determine the reactivity of amine microcapsules with excess neat epoxy resin versus neat amine with excess epoxy resin (Figure 3.2). The integration of the exotherms indicates the relative quantity of epoxy capable of
being cured by 25 μm average diameter microcapsules compared to neat amine to be 25%. Thus, using the calculations of Rule[45], a weight ratio of 2 amine:1 epoxy microcapsules provides for a stoichiometric mixture of healing agents. Additionally, microcapsule loading can be compared to the loading prescribed by Rule; utilizing the 25 mm crack channel system, the crack separation is approximately 3 μm, requiring a delivery of 0.3 μL/cm² healing agent[45]. At 15% capsule volume fraction of 25 μm diameter microcapsules, approximately 0.38 μL of healing agent is delivered per cm².

Figure 3.1: Microcapsules containing Epon 815C low-viscosity epoxy resin.
3.2.2 Healing Assessment

To assess fracture toughness of the matrix material and the healed specimen, the tapered double cantilevered beam (as developed by Brown[31], Figure 3.3 and revised by Rule et al.[45], Figure 3.4) is employed. The advantage of this system is that the stress intensity factor in Mode I loading, $K_I$, is constant throughout the length of the fracture. With this constraint in place, the fracture toughness, $K_{IC}$, is independent of crack length, and is related directly to the peak load, $P_c$, at fracture as follows: $P_c = \frac{K_{IC}}{\alpha}$. For the specific geometry we employ, the proportionality constant, $\alpha$, is 11.21 m$^{\frac{3}{2}}$.

Thus, a sample can be fractured, permitted to heal, and then fractured again, and the ratio between virgin and healed fracture toughness is established as the “healing efficiency” of the sample. The ultimate goal of this work is to demonstrate the use of a two-microcapsule system in a cured epoxy matrix to recover fracture toughness as assessed by $K_{IC}$ measurements in quasi-static loading conditions.
Using the method of Brown[31], $K_{IC}$ is measured using the TDCB geometry, with microcapsules localized in the area where the crack is confined.

### 3.2.2.1 Mechanical Test Methodology

A precrack is introduced into the confining region by means of tapping a razor blade into the matrix to establish a sharp crack tip. The beam is then loaded quasistatically under Mode I conditions until fracture occurs. The beam is rejoined and permitted to heal for a designated healing cycle at a controlled temperature for a controlled time. Following the healing cycle, the specimen is re-tested and a healed fracture loading is measured. The ratio between fracture load of the virgin specimen and that of the same specimen following healing is referred to as the healing efficiency, $\eta$, of the system.

### 3.2.2.2 Numerical Assessment of Healing

Numerically, healing is reported as the ratio of virgin fracture toughness, $K_{IC}$, to fracture toughness following the healing cycle. The healing efficiency, $\eta$, is calculated as follows: $\eta = \frac{K_{IC,heated}}{K_{IC,virgin}}$. Under the conditions in Brown et al.\textsuperscript{32}, healing efficiencies of up to $\eta=0.9$ were observed. In the experiments carried out by Caruso et al.\textsuperscript{4}, healing efficiencies of $\eta=1.0$ or better were realized.

### 3.2.3 Sample Fabrication

The epoxy matrix was prepared by mixing Epon 862 and Epikure 3300 at a 100:25 ratio and degassing under vacuum. In order to preserve active materials, the TDCB specimen was prepared in two parts (Figure 3.4). A silicone insert was placed into the mold to maintain space for the inner region. The outer portion, containing no amine or epoxy microcapsules, was molded from Epon 862 and Epikure 3300 at a 100:25 ratio and cured at 50 °C for 18 hours, then the silicone insert was removed. A simple 35 °C cure, like what is performed for DETA/828 systems, results in an extremely brittle matrix. The inner region was likewise composed of Epon 862 and Epikure 3300, mixed with the desired concentration of amine and epoxy microcapsules.
Figure 3.3: Tapered double-cantilever beam. Dimensions in mm. Reproduced from Brown[3].

Figure 3.4: TDCB schematic, dimensions in mm. Purple region is insert region, containing active material if present. Gold region is outer region. Drilled hole is 1.98 mm diameter.
Specimen types are summarized in Table 3.1. Reference specimens were formed from epoxy resin and hardener only, and were healed by addition of 10 µL of stoichiometrically-mixed epoxy/neat amine following virgin fracture. Control specimens incorporated epoxy resin microcapsules within the crack channel, but no amine microcapsules. Self-activated specimens incorporated amine microcapsules within the crack channel and had epoxy injected into the crack channel after the virgin fracture. Active specimens incorporated both epoxy resin microcapsules and amine microcapsules in the crack channel.

<table>
<thead>
<tr>
<th>Specimen type</th>
<th>Cure Temp (°C)</th>
<th>Heal Temp (°C)</th>
<th>$K_{IC}$ (MPa-m$^{0.5}$)</th>
</tr>
</thead>
<tbody>
<tr>
<td>Reference - 35</td>
<td>50</td>
<td>35</td>
<td>0.77±.1</td>
</tr>
<tr>
<td>Reference - 120</td>
<td>120</td>
<td>120</td>
<td>0.60±.1</td>
</tr>
<tr>
<td>Control - 35</td>
<td>50</td>
<td>35</td>
<td>1.66±.17</td>
</tr>
<tr>
<td>Control - 80</td>
<td>50</td>
<td>80</td>
<td>1.66±.17</td>
</tr>
<tr>
<td>Self-Activated</td>
<td>50</td>
<td>35</td>
<td>1.12±.11</td>
</tr>
<tr>
<td>Active - 35</td>
<td>50</td>
<td>35</td>
<td>1.56±.19</td>
</tr>
<tr>
<td>Active - 50</td>
<td>50</td>
<td>50</td>
<td>1.56±.19</td>
</tr>
<tr>
<td>Active - 80</td>
<td>50</td>
<td>80</td>
<td>1.56±.19</td>
</tr>
<tr>
<td>Active - 120</td>
<td>120</td>
<td>120</td>
<td>0.60±.11</td>
</tr>
</tbody>
</table>

The specimens were subsequently cured for 18 hours at 50 °C. Following curing, a 1.98 mm hole was drilled into the sample below the end of the crack channel. The hole traps growing cracks due to its high compliance, and prevents the crack from growing to the end of the sample. A precrack was created in the TDCB specimens by impacting a razor blade into the sample above the localized region. The specimens were then tested in quasistatic tensile loading at 5 µm/sec crosshead displacement to propagate a Mode I crack using the method of Brown et al.[15] In the virgin specimen, samples were loaded until the crack propagated to the end of the crack channel or to the drilled hole. After healing at a specified temperature, the samples were loaded again to complete failure. Figure 3.5 shows a localized TDCB specimen before (a) and after (b) total fracture. When multiple fracture events occurred during a test, an average of all the peak loads associated with stick-slip fracture events was reported as the mean peak load for the specimen.
3.3 Results and Discussion

Each of the different sample types from Table 3.1 were fractured and then allowed to heal for 18 hours at 35 °C. A minimum of 7 samples were tested for each category. Healing was only expected when both the amine and epoxy microcapsules are present. The results for the four different types of samples are summarized in Table 3.2. The maximum possible loading of amine microcapsules in the matrix was 10%, limited by the formation of agglomerates of microcapsules when dispensed into the epoxy resin.

Figure 3.5: Self-activated epoxy TDCB specimen. Scale bar 22 mm. (a) Virgin (b) after complete fracture, post-healing
3.3.1 Reference Specimens

Figure 3.6 depicts the representative loading curve of (a) a reference specimen cured at 50 °C and healed at 35 °C, and (b) one cured and healed at 120 °C. Reference specimens were tested to propagate the crack to the end of the crack channel. The reference specimens exhibited a virgin fracture toughness of 0.8±0.1 MPa-m$^{0.5}$. Immediately following their failure, the reference specimens were healed by applying pre-mixed amine and epoxy directly to the crack plane and then were allowed to heal at 35 °C or 120 °C. The application of a stoichiometrically prepared epoxy to the damage region provided a positive reference for maximum healing possible for the specific chemistry used in this experiment based on ability to bond to the fracture surfaces.

Samples healed by direct application of stoichiometric epoxy recovered an average fracture toughness of 1.1±0.4 MPa-m$^{0.5}$. The resulting healing efficiencies were over 100% due to both crack deviation from the virgin crack and the repair material being tougher than the virgin material. Thus, the amine-epoxy-based healing system has excellent bonding and superior fracture toughness than the plain matrix. Reference samples were also prepared without applying the epoxy-amine mixture to the fracture surface. These negative references exhibited no healing.

Table 3.2: Sample types. Healing efficiencies are given for specimens healed at 35 °C. Fracture toughness is reported for the virgin material.

<table>
<thead>
<tr>
<th>Specimen type</th>
<th>Epoxy capsule wt%</th>
<th>Amine capsule wt%</th>
<th>$K_{IC}$ (MPa-m$^{0.5}$)</th>
<th>Healing Efficiency</th>
</tr>
</thead>
<tbody>
<tr>
<td>Reference</td>
<td>N/A</td>
<td>N/A</td>
<td>0.8±1</td>
<td>150% ± 40%</td>
</tr>
<tr>
<td>Control</td>
<td>15%</td>
<td>0</td>
<td>1.7±2</td>
<td>0</td>
</tr>
<tr>
<td>Self-Activated</td>
<td>0%</td>
<td>10%</td>
<td>1.1±1</td>
<td>30% ± 10%</td>
</tr>
<tr>
<td>Active</td>
<td>5%</td>
<td>10%</td>
<td>1.6±2</td>
<td>14% ± 1%</td>
</tr>
</tbody>
</table>
Figure 3.6: Reference specimen loading curve for specimens (a) cured at 50 °C and healed at 35 °C, (b) cured and healed at 120 °C. Significant change in slope for 120 °C specimen is associated with curing new material in the precrack region. Crack propagation was monitored visually to ensure it did not leave the crack channel on the virgin specimens.
Reference specimens were also cured at 120 °C, then tested and healed at 120 °C (Figure 3.6(b)). Results show that $K_{IC}$ decreases at 120 °C, but the healing efficiency increases due to the lowered virgin fracture toughness. Reference samples cured at 120 °C exhibited a slight discoloration and substantially reduced $K_{IC}$ ($0.60\pm0.1$ MPa-m$^{1/2}$) for the virgin specimens.

### 3.3.2 Control Specimens

Control specimens consisted of 15% w/w microcapsules containing Epon 815C, dispersed in epoxy and deposited in the inner region of the specimen. A representative load-displacement curve for the control samples is shown in Figure 3.7. Virgin fracture toughness of the control samples were $1.7\pm2$ MPa-m$^{1/2}$. This value is significantly higher than the reference specimens described in Section 3.3.1. This toughening is due to the presence of the epoxy capsules acting as a particulate reinforcement that does not affect the stoichiometry of the active region.

No measurable healing was detected in solvent-epoxy control samples healed at 50 °C. Because healing is not present in these controls, any measurable healing at this temperature in a binary system is the result of the reaction between the encapsulated epoxy component and encapsulated amine component in the crack plane.

Control samples were also healed at 80 °C to determine if residual functionality is present in the cured specimen that could lead to healing at elevated temperatures or increased healing duration based on time-temperature superposition. In the controls healed at 80 °C, a modest healing of $17\pm9\%$ was observed, based on a virgin $K_{IC}$ of $1.5\pm0.2$ MPa-m$^{1/2}$. Thus, a small amount of residual reactivity is present that can be healed at elevated temperatures.
Figure 3.7: Representative load-displacement curve for control sample healed at 80 °C.
3.3.3 Self-Activated Specimens

Representative load-displacement data for self-activated specimens (containing only amine microcapsules) is shown in Figure 3.8. Similar to the control specimens, significant toughening was observed after amine microcapsules were introduced. Fracture toughness of the virgin self-activated specimens was 1.1±.1 MPa-m$^{1/2}$. Following fracture of the virgin specimens, 10 µL of 1:1 Epon 862/chlorobenzene was injected into the crack plane and the specimens were allowed to heal at 35 °C. The mean fracture toughness of the healed specimens was 0.3±.1 MPa-m$^{1/2}$, corresponding to a healing efficiency of 30%. Multiple crack propagation events were observed in both the virgin fracture and the
healed fracture. As before, the peak loads at crack propagation events were averaged to produce the nominal fracture toughness of the virgin and healed specimens. Slope of the load-displacement curve was also used to determine if a sample had healed; only peaks that occurred in a healed specimen while the sample exhibited a greater stiffness (as measured by greater slope) than the final virgin slope were included in the average. By eliminating peaks that occur later in the loading, the effect of opening otherwise virgin material was removed.

3.3.4 Self-Healing Samples

Active specimens had both epoxy and amine microcapsules present in the insert region of the specimen. The average fracture toughness was 1.6±2 MPa-m\(^{\frac{1}{2}}\) for the virgin specimens, an increase of 100% over reference value. The increased toughness is due to the presence of 15% particulate reinforcement. In samples with multiple fracture events, averaging was again performed to determine the fracture toughness of the sample. Specimens healed at room temperature exhibited 14±1% healing. Crack propagation events are indicated by arrows, and similar to the self-activated specimens, the slope of the load-displacement plot was used to remove peaks that correspond to opening of new material. Figure 3.9 contains a representative load-displacement plot of a self-healing sample healed at 35 °C for 18 hours.
3.4 Effect of Temperature on Healing Efficiency

Specimen healing temperature plays an important role in the degree of healing. When observing crack planes of self-activated samples healed at 35 °C, the microencapsulated amine appears as a gel inside the cured specimen (Figure 3.10). Raising the temperature permits the epoxy and amine to flow more freely in the crack plane, enhancing mixing and stoichiometric balance. Rheology of the core material demonstrated a significant viscosity dependence on temperature (Figure 3.11). Figure 3.12 contains a representative load-displacement curve for a self-healing sample, cured at 50 °C and healed at 80 °C. Samples healed at 50 °C and 80 °C healed 30±5% and 51±11% respectively, illustrating a relationship between healing temperature and healing efficiency.
Figure 3.10: Crack plane of self-activated specimen. Amine capsules present still contain amine after crack propagation; material is not distributed along crack plane.

Figure 3.11: Relationship between temperature and viscosity of DEH-52 (core material). As temperature increases, viscosity decreases dramatically.
Improved healing was achieved at elevated temperatures. Specimens were healed at a fixed temperature for 18 hours. Figure 3.13 shows the dependence of healing efficiency on temperature for active specimens. Maximum healing occurred at a heal temperature of 120 °C (average healing efficiency 63±12%), however, this temperature was also associated with decreased virgin fracture toughness in the reference specimens. When reference specimens of this particular epoxy system were cured at 120 °C for 18h, the fracture toughness declined to 0.6±1 MPa-m$^{1/2}$, with a healed toughness of 0.7±2 MPa-m$^{1/2}$. Other researchers have also seen declines in fracture toughness in epoxy-matrix composites at elevated temperatures[46]. This result indicates that even at high temperatures, the material used to heal the epoxy specimen is tougher than the virgin material.
Subsequent to healing and fracture, the crack planes of the self-healing specimens were inspected by scanning electron microscopy. Healed material is clearly evident as additional ridges and lines in the vicinity of ruptured capsules on the fracture surface, as shown in Figure 3.14. This evidence confirms that new material is formed in the crack plane as a result of the reaction between released encapsulated components introduced to the damage region.

Figure 3.13: Effect of healing temperature on healing efficiency. Increased temperature causes liquefaction of the amine core material and permits flow and mixing in the crack plane.
3.5 Limitations on Healing Efficiency

One significant limitation of the amine capsule system is the need for elevated temperatures to promote healing. This result is due in part to the high viscosity of the encapsulated amine at room temperature, as seen in Figure 3.11. As the healing temperature is increased, the amine has greater mobility and can flow into the crack plane more easily to react with the epoxy.

A second limitation applies to all binary capsule systems. In order to maximize healing efficiency, the ratios of amine and epoxy delivered must be matched to their stoichiometric ratios. At present, the binary system relies on statistical mixing of the capsules to provide the proper stoichiometry. A superior system would ensure that microcapsules of amine and microcapsules of epoxy are always present and proximal in stoichiometric ratios, e.g. in an A-B-A particle chain[47].
3.6 Conclusions

A two-capsule system employing amine and epoxy was successfully stabilized and dispersed in a localized region of a TDCB and fractured. Modest healing was observed at room temperature. Healing of up to 80% was observed in active healing specimens when healed at elevated temperatures. Control specimens exhibited no healing. The activity of the amine microcapsules to undergo amine-epoxy healing is maintained at temperatures up to 120 °C, and potentially higher, though the matrix itself suffers a reduction in fracture toughness. Temperatures of 50-120 °C improved the healing efficiency of self-healing specimens. These experiments demonstrate that microcapsule-based healing in epoxy samples is a viable autonomic response to damage at mildly elevated temperatures. Future work will focus on improving the delivery of amine to the crack plane at lower temperatures.
 CHAPTER 4

MICROENCAPSULATION OF METHYLENE DIPHENYLDIISOCYANATE, A REACTIVE ISOCYANATE

In this chapter, we discuss the microencapsulation of a monomeric/oligomeric blend of methylene diphenyl diisocyanate (MDI) by interfacial polymerization in silicone oil. The microcapsules prepared by this method were isolated to a dry powder and processed further. Microscopy demonstrated the capsules were spherical in shape with a brittle shell wall. Titration analysis revealed the microcapsule core had a 50% isocyanate yield compared to pure MDI.

4.1 Introduction

Successful microcapsule-based self-healing systems have been discussed in Chapters 1 and 3. Isocyanates in particular present an attractive target for self-healing chemistry due to their commercial prevalence and high reactivity with environmental moisture, leading to the opportunity for a one-component healing system. Isocyanates react with water to form amines and CO₂, and the amines formed can react with other molecules of isocyanate present to form polyurea. By reacting isocyanates with polyamines, a polyurea shell can be formed around a droplet[48-50]. However, past efforts to encapsulate isocyanates have been limited to blocked isocyanates[51-53], until Yang et al.[54] created a method for microencapsulation of isophorone diisocyanate (IPDI). IPDI is an aliphatic isocyanate, and therefore less reactive than aromatic isocyanates such as MDI or toluene diisocyanate (TDI)[27, 55]. Potential matrices for healing applications with isocyanate-based chemistry include polyurethane or polyurea based materials in addition to epoxy. Isocyanates are widely used in commercial foams and
coatings. More than 3 million metric tons of methylene diphenyl diisocyanate (MDI) are produced each year for industrial applications. The protocol for microencapsulating MDI is described below.

4.2 Materials and Methods

The materials and techniques for microencapsulation of the reactive MDI are discussed below. The protocol that was developed borrows heavily from the work in amine encapsulation discussed in Chapter 2.

4.2.1 Chemicals

Baytek Mondur MR, a blend of monomeric and oligomeric MDI, was provided by Bayer Materials Science. Silicone oil (50 cSt) was purchased from Sigma-Aldrich. Aminopropyltrimethoxysilane (APTMS) was purchased from Gelest. Emulsifying Agent 9011 was provided by Dow Corning. Bromothymol blue was purchased from Sigma-Aldrich.

4.2.2 Preparation of Microcapsules

Microcapsules containing MDI were prepared by means of interfacial emulsion polymerization (Figure 4.1). A suspension of Mondur MR was prepared by agitation at 400, 650, or 1000 RPM using an overhead stirrer. The suspension comprised 10 grams MDI in 30 grams 50 cent silicone oil with 0.1% emulsifier. APTMS was prepared as a 10% suspension in 5 g silicone oil with 1% emulsifier. The MDI suspension was stirred for 10 minutes prior to gradual addition of the APTMS suspension, dropwise, to the reaction vessel. Interfacial polymerization of the MDI proceeded by means of isocyanate-amine chemistry to form a shell wall. Stirring was continued for an additional 4 hours. Microcapsules were isolated by washing with hexanes to remove residual silicone oil and repeating the wash 3 times. Capsules were then dried on paper or glass for further analysis.
4.2.3 Characterization

Thermogravimetric analysis (TGA) was performed on a Mettler-Toledo TGA851\textsuperscript{e}, calibrated by indium, aluminum and zinc standards. Unless otherwise indicated, a heating rate of 10 °C min\textsuperscript{-1} was used in an atmosphere of nitrogen. For each experiment, approximately 5 mg of sample were accurately weighed (± 0.02 mg) into an alumina crucible. The mass loss was recorded during a heating cycle over the temperature range of 25 °C to 650 °C.

Scanning electron micrography (SEM) was performed on Au/Pd sputter-coated samples on a Philips XL-30 FEG at the Imaging Technology Group at the Beckman Institute.

Optical micrographs were acquired by Micropublisher CCD camera with fluorescence and analyzed using NIH ImageJ software.
Isocyanate equivalence titrations were performed by suspending microcapsules in acetonitrile with bromothymol blue indicator. Sufficient di-n-butylamine was added to turn the solution blue, and then an endpoint was reached by back-titration with 1.000N HCl solution.

4.3 Results and Discussion

The microcapsules containing MDI were prepared at multiple agitation rates to determine how diameter was affected by agitation rate. Optical and electron microscopy illustrated the capsule morphology. Titration assays were performed to determine the isocyanate content, and the results were supported by thermal analysis.

4.3.1 Capsule Size Control

Microcapsules were produced by continuous stirring during the addition of aminosiloxane. At 650 RPM, the microcapsules prepared had a mean diameter of 42 ± 16 μm. Smaller capsules were prepared at higher agitation rates, though the shape of the distribution was similar. Capsules prepared at 1000 RPM had an average diameter of 23±8 μm, and capsules prepared at 400 RPM had an average diameter of 100±42 μm. The frequency distributions at the different agitation rates are shown in Figure 4.2. The diameter of microcapsules prepared by this method exhibited power-law dependence (RPM$^{1.6}$) on agitation rate (Figure 4.3). Yang et al. found a similar dependence between diameter and agitation rate.[54]
Figure 4.2: Capsule size distributions for 3 preparations of MDI microcapsules at specified agitation rates (RPM).

Figure 4.3: Relationship between capsule diameter and agitation rate. Diameter is proportional to (rate)^{-1.6}.
4.3.2 Capsule Morphology

Optical microscopy revealed yellow colored capsules that could be ruptured by pressure, releasing the MDI within (Figure 4.4). Scanning electron microscopy revealed microcapsules that were spherical in shape with a slightly textured shell (Figure 4.5). The microcapsules prepared by this method have a brittle shell that assembles due to the interfacial reaction between MDI and APTMS. Other oligoaminosiloxanes were employed in an effort to form a shell, however, none formed core-shell morphologies due to the rapid formation of a network polymer. We hypothesize that the shell is formed by self-assembly and condensation of the siloxane groups to form a silica-based polymer shell about the MDI. The methoxy groups on the APTMS condense readily, forming silica-functionalized MDI polymer. The silica then phase-separates to the outside of the MDI droplet and forms a rigid, brittle shell wall.

![Figure 4.4: Optical microscopy of MDI microcapsules (a) on a glass slide (b) crushed](image-url)
4.3.3 Core Analysis and Reactivity

Quantitative determination of the MDI content in the microcapsules was performed both by titration and by TGA. By reacting the neat MDI with a slight excess of di-n-butylamine, a monofunctional amine, and then back-titrating with HCl, the total isocyanate equivalent weight can be obtained. The theoretical value for MDI is 125 g/equiv. The Mondur MR had a value of 148 g/equiv, indicating that a
small amount of oligomeric components were present. The microcapsules were subjected to a similar treatment, but were allowed to soak in the monofunctional amine for 4 hours to ensure complete isocyanate extraction and reaction. The equivalent weight of the microcapsules was 240 g/equiv, indicating the mass fraction of MDI-equivalent oligomer within the microcapsules was approximately 50% (see Table 4.1). Thermogravimetric analysis also supported a value of 35% MDI (Figure 4.6). Polyurea degradation was observed at 250 °C, followed by MDI decomposition between 300-500 °C.

<table>
<thead>
<tr>
<th>Compound</th>
<th>g/equiv NCO</th>
</tr>
</thead>
<tbody>
<tr>
<td>Neat MDI (calc)</td>
<td>125</td>
</tr>
<tr>
<td>Mondur MR</td>
<td>146</td>
</tr>
<tr>
<td>Microcapsules</td>
<td>252</td>
</tr>
</tbody>
</table>

Table 4.1: Titration-determined isocyanate equivalence of MDI and microcapsules containing MDI

Figure 4.6: Thermogravimetric analysis of MDI microcapsules. Weight loss at 250-275°C (35%) corresponds to partial decomposition of MDI. Remaining weight loss prior to 500 °C (35%) corresponds to degradation of polyurea shell.
Qualitative analysis for MDI within the microcapsules was performed by crushing microcapsules, and adding a drop of TAP X-30® Part B polyurethane hardener. In the presence of microcapsules, a foam is produced over the course of 6 minutes by the reaction of MDI with X-30 Part B (Figure 4.7).

Figure 4.7: Images of crushed MDI microcapsules (a) immediately after addition of X-30 Part B and (b) 6 minutes later. A cellular foam has formed due to the reaction between the MDI in the capsules and the X-30 Part B. Scale bar 150 μm.
4.4 Deposition of Microcapsules in Matrix Materials

To test the release of microcapsule contents, capsules were incorporated into polyurethane (Clear-Flex® 50) and epoxy (Epon 828/DETA). In the polyurethane matrix, capsules did not rupture; instead, capsules were observed to debond from the matrix (Figure 4.8(a)). In epoxy matrix, the capsules hardened completely and did not release core material, though they did cleave (Figure 4.8(b)). Because the capsules failed to release core material when deposited in a matrix, additional work is necessary to stabilize the wall and prevent infiltration of species that can react with isocyanates.

4.5 Conclusions

Microcapsules containing MDI were successfully prepared and isolated to a dry powder. Microcapsule diameter is dependent on agitation rate according to a power law relationship. The powdered microcapsules have nearly 50% isocyanate content compared to the neat core material, indicating the potential for delivery of reactive isocyanate from the microcapsules. Microcapsules could be crushed to release reactive isocyanate in a manner that initiated foam formation in a 2-part urethane foam system. Capsules were unable to release material after curing in epoxy or urethane matrices. With refinement, microcapsules containing MDI present an opportunity for 1-part healing systems in epoxies and polyurethanes due to their reactivity with environmental moisture to cure.
Figure 4.8: MDI microcapsules incorporated into (a) Clear-Flex® polyurethane and (b) Epon 828/DETA cured epoxy.
CHAPTER 5

CONCLUSIONS AND FUTURE WORK

5.1 Conclusions

In this dissertation, microencapsulation protocols were created for both reactive amines and reactive isocyanates. Interfacial polymerization created a shell wall to contain the reactive species and permitted dispersion in a thermoset matrix. Capsule morphology was assessed by microscopy. Microcapsules content was characterized by chemical and thermal analyses, and both qualitative and quantitative evidence of their reactivity was obtained. For the amine microcapsules, titration and mass spectroscopy provided quantitative information about the amine remaining in the microcapsule, while curing epoxy delivered to a glass slide by means of microcapsule crushing showed residual reactivity and its potential use for self-healing. For isocyanate microcapsules, titration with di-n-butylamine quantitatively determined the relative reactivity of the remaining core material.

Specimens of epoxy were mechanically tested to determine self-healing ability. Samples were produced by mixing microcapsules containing epoxy resin and microcapsules containing amine hardener into a premixed stoichiometric epoxy system. Following an appropriate cure cycle, tensile loading produced a Mode I fracture within a localized area in the specimen. After permitting the test specimen to heal at an appropriate healing temperature, samples were fractured again to assess healing efficiency. Due to the particular geometry of the samples, healing efficiency was determined by the ratio of peak loading at failure of the specimen. Because multiple fracture events were observed for some samples, the peak loads were averaged for each fracture event for a particular specimen. Samples
containing the full two-part system of microencapsulated resin and encapsulated hardener were capable of healing, whereas samples containing only one component were not. The healing efficiency increased with increasing temperature, indicating that the mobility of the healing agents in the crack plane was improved at elevated temperatures.

5.2 Future Work

The self-healing microcapsule technology described here shows modest healing at room temperature, and enhanced healing at elevated temperatures. However, several improvements can be made to refine the system. In this section, suggestions for future efforts are made for increasing the healing efficiency of the system and stability of the components that are used.

5.2.1 Shell Wall Refinements

The biggest challenge that remains before amine or isocyanate microcapsules can be deployed at a large scale is environmental stability. The amine capsules tended to agglomerate after a short period of storage in a moist environment. Maximum stability was observed when capsules were kept at -20C, keeping the core solid. Capsule stability could be improved by formation of an additional shell wall atop the interfacially-prepared wall. Pores in the interfacial wall could be plugged, agglomeration could be reduced, and environmental stability would increase. The potential chemistries that could be employed include oligomeric isocyanates, acid chlorides, and acid-functionalized siloxanes. All are capable of continued reaction to form a second shell wall. Alternatively, polymers such as polyvinyl alcohol or polyvinyl chloride could be used to form a film around the prepared capsule[56].

5.2.2 Viscosity

Microcapsules demonstrated a significant temperature-healing response. Based on SEM observations of unhealed material in the crack plane, it was determined that the increased viscosity to a near gel-state plays a role in limiting healing. If the viscosity of the amine core material could be
reduced, more material would be able to flow to the damage region, enhancing the healing response. This could be accomplished by changing the diluent ratio in the core material, by incorporating an unreactive diluent, or by forming the shell wall using an alternative reaction that does not result in a gelled core material.

5.2.3 Alternative Encapsulation Schemes

Another potential improvement lies in alternative encapsulation schemes. Microcapsules can be prepared that contain either a volatile solvent that can be removed, e.g. hexanes, or under specific conditions, air can be encapsulated. Under vacuum conditions, the air can be removed and a liquid can be infiltrated into the capsules. This requires capsules that have some porosity, however, and may be susceptible to leaking after filling is accomplished.

Another alternative for encapsulation involves microfluidic flow-focusing devices. With these devices, a droplet of amine could be suspended in a liquid and a shell could be formed around it by UV activation. However, these devices are very low-throughput and require extensive refinement to successfully balance production rate and droplet stability.

5.2.4 Binary Capsule Functionalization

The healing chemistry employed in this dissertation requires appropriate local stoichiometry and dispersion throughout the damage region. The local stoichiometry is dependent on appropriate mixing and dispersion of the microcapsules, even if the global stoichiometry is correct. The stoichiometry problem could be solved by surface functionalization of the microcapsules, encouraging association of the hardener with epoxy in the appropriate ratio in an A-B-A particle fashion. Such functionalization could be accomplished by silane treatment or by a urethane coupling chemistry that would join the polyurea shell of the hardener to the urea-formaldehyde shell of the epoxy resin microcapsules. If performed correctly with chemical control, A-B-A particles could be developed.
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APPENDIX A

LABVIEW TESTING PROGRAM

To perform the mechanical testing, a LabView Virtual Instrument was constructed. The wiring diagram is shown below.
APPENDIX B

AMINE MICROENCAPSULATION EXPERIMENTATION

Besides the successful TDI/Amine protocol for microencapsulation of reactive amines, other microencapsulation techniques were attempted without success. The techniques attempted are summarized below.

*Gelatin-Acacia Coacervation*
Ancamine K54 was suspended in brine and agitated. 1.5 g gelatin was dissolved in 3g hot water to make a sol. 5 g acacia in 20 mL water was added to the stirring Ancamine K54 solution. The gelatin was then added to form a coacervate. Capsules were not formed.

*Acid Chloride Interfacial Polymerization*
DEH-52 was mixed with DETA at 2:1 to create a viscous amine mixture. The mixture was added dropwise into a layered solution of xylenes over 5% adipoyl chloride in chloroform. Solid particles were formed.

*Isocyanate/Acid Chloride Interfacial Polymerization*
DEH-52/DETA 2:1 mixture was agitated in decalin. 0.5 g TDI in 5 g decalin was added, followed by 1.0 g adipoyl chloride in 5 g decalin. The suspension turned pink in color, and polymer was produced, but no capsules were formed.
AUTHOR'S BIOGRAPHY

David A. McIlroy was born in Columbus, Ohio, and grew up in the suburb of Upper Arlington. After high school, he attended the Massachusetts Institute of Technology in Cambridge, MA, to study Materials Science. He interned at Los Alamos National Laboratory, NM in 2001, and at TransForm Pharmaceuticals in Lexington, MA in 2002 and 2003. He earned an S.B. in Materials Science and Engineering in 2003, and worked at TransForm Pharmaceuticals until 2005. Mr. McIlroy came to the University of Illinois at Urbana-Champaign in August, 2005, and joined Prof. Nancy R. Sottos’ research group in 2006 to study the microencapsulation of amines and their application to self-healing epoxy systems. He lives with his wife, Anna, and their two children in Champaign, Illinois. After graduation, Mr. McIlroy will join Ticona Manufacturing as a Product Development Scientist in Florence, Kentucky.