Fabrication and Characterization of Natural Fiber based Self-healing Composite Materials

A thesis submitted in partial fulfillment of the requirements for the degree of

Master of Science in Mechanical Engineering

by

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APPROVAL

The thesis titled “Fabrication and Characterization of Natural Fiber based Self-healing Composite Materials”, submitted by Md. Mahmudul Adil, Student ID: 19MME006P, Session: 2019-20, has been accepted as satisfactory in partial fulfillment of the requirements for the degree of Master of Science in Mechanical Engineering on March 2024.

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ABSTRACT

Recent research has focused on microcapsule-based self-healing polymer composites, offering significant potential for repairing damaged polymeric materials. In this study, microcapsule-based jute fiber-reinforced epoxy self-healing composites were manufactured using the vacuum bagging technique. Epoxy was combined with 3 wt.% of water-insoluble and water-soluble epoxy microcapsules that were synthesized by the in-situ polymerization method. The resulting composite underwent assessment for healing efficiency via impact strength recovery. Incorporating microcapsules within the cracked surface of the composite facilitated healing, demonstrating notable improvements in efficiency. Results indicated that the epoxy composite healed from a 1 mm deep crack exhibited higher impact strength recovery than samples healed from a 1.5 mm deep crack, with healing efficiencies of 83.9% and 78.89%, respectively. Scanning electron microscopic (SEM) analysis showed that the microcapsule size varies from 1.45 µm to 1.83 µm. FTIR spectra confirmed the presence of relevant chemical groups in both microcapsules and the composite.

সারসংক্ষেপ

সাম্প্রতিক গবেষণায় মাইক্রোক্যাপসুল-ভিত্তিক স্ব-নিরাময় পলিমার কম্পোজিটের উপর মনোনিবেশ করা হয়েছে, যা ক্ষতিগ্রস্ত পলিমারিক পদার্থগুলির মেরামতের জন্য গুরুত্বপূর্ণ সম্ভাবনা প্রদান করে। এই গবেষণায়, মাইক্রোক্যাপসুল-ভিত্তিক পাটের ফাইবার এবং ইপোক্সি স্ব-নিরাময় কম্পোজিটগুলি ভ্যাকুয়াম ব্যাগিং কৌশল ব্যবহার করে তৈরি করা হয়েছিল। ইপোক্সির মধ্যে শতকরা ওজন হিসাবে ৩% ইপোক্সি মাইক্রোক্যাপসুল মিশানো হয়েছিল যা ইন-সিটু পলিমারাইজেশন পদ্ধতি দ্বারা সংশ্লেষিত হয়েছিল। প্রভাব শক্তি পুনরুদ্ধারের মাধ্যমে নিরাময় দক্ষতার জন্য ফলস্বরূপ যৌগিক মূল্যায়ন করা হয়েছে। কম্পোজিটের ফাটলযুক্ত পৃষ্ঠের মধ্যে মাইক্রোক্যাপসুলগুলিকে অন্তর্ভুক্ত করা নিরাময়কে সহজতর করে, দক্ষতায় উল্লেখযোগ্য উন্নতি প্রদর্শন করে। ফলাফলগুলি নির্দেশ করে যে ১ মিলিমিটার গভীর ফাটল থেকে নিরাময় করা ইপোক্সি কম্পোজিট ১.৫ মিলিমিটার গভীর ফাটল থেকে নিরাময় করা নমুনার তুলনায় উচ্চ প্রভাব শক্তি পুনরুদ্ধার প্রদর্শন করেছে, যথাক্রমে ৮৩.৩% এবং ৭৮.৮৯% নিরাময় দক্ষতা সহ। স্ক্যানিং ইলেক্ট্রন মাইক্রোস্কোপিক বিশ্লেষণে দেখা গেছে যে মাইক্রোক্যাপসুলের আকার ১.৪৫ মাইক্রোমিটার থেকে ১.৮৩ মাইক্রোমিটার পর্যন্ত পরিবর্তিত হয়। ফুরিয়ার ইনফ্রারেড বর্ণালিবীক্ষণ যন্ত্র স্পেকট্রা মাইক্রোক্যাপসুল এবং যৌগিক উভয় ক্ষেত্রে প্রাসঙ্গিক রাসায়নিক গ্রুপের উপস্থিতি নিশ্চিত করেছে।

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Chapter 1

Introduction

1.1 PREFACE

There has been a growing interest during the past few years on the development of composite materials that possess exceptional mechanical properties and durability. This pursuit has led to notable advancements in the field. The emergence of self-healed composite materials has been recognized as a significant advancement in addressing the detrimental effects of wear, fatigue, and damage experienced by materials over time. This concept presents a groundbreaking methodology for mitigating the aforementioned effects and extending the operational lifespans of various materials. Self-healing composites has attracted significant interest as a result of their ability to independently repair microcracks and fractures. This characteristic offers the potential to enhance the durability and lifespan of structures in diverse sectors such as aerospace, automotive, civil engineering, and more.

1.2 BACKGROUND

Polymer matrix composites are known to experience damage primarily at the interface where the matrix and reinforcement materials meet. This phenomenon often results in interfacial debonding, which is the separation of the two materials at the interface. Autonomic and non-autonomic approaches are used to heal the self-healing composite. Extrinsic methods, intrinsic methods, vascular methods, and microcapsule based self-healing composites are all examples of this type of treatment. In contrast to intrinsic self-healing, which requires no external stimulus to commence repair, extrinsic self-healing can occur independently of any outside influence [1]. In a study conducted in 2001, White et al. [2] introduced the pioneering concept of self-healing materials utilizing microcapsules. Self-healing materials based on capsules include inserting the capsules, which contain healing agents, into composite structures. Damaged capsules necessitate the deployment of crack-healing agents, which are activated when cracks are detected. Through the

utilization of a self-healing mechanism and the integration of self-healing materials, it is possible to restore and recover mechanical properties such as tensile strength and fracture strength [1]. Self-healing materials encompass a diverse range of substances, including metals, concrete, ceramics, polymers, and composites [3,4]. The concept of microcapsule based self-healing is shown in Figure 1.1.

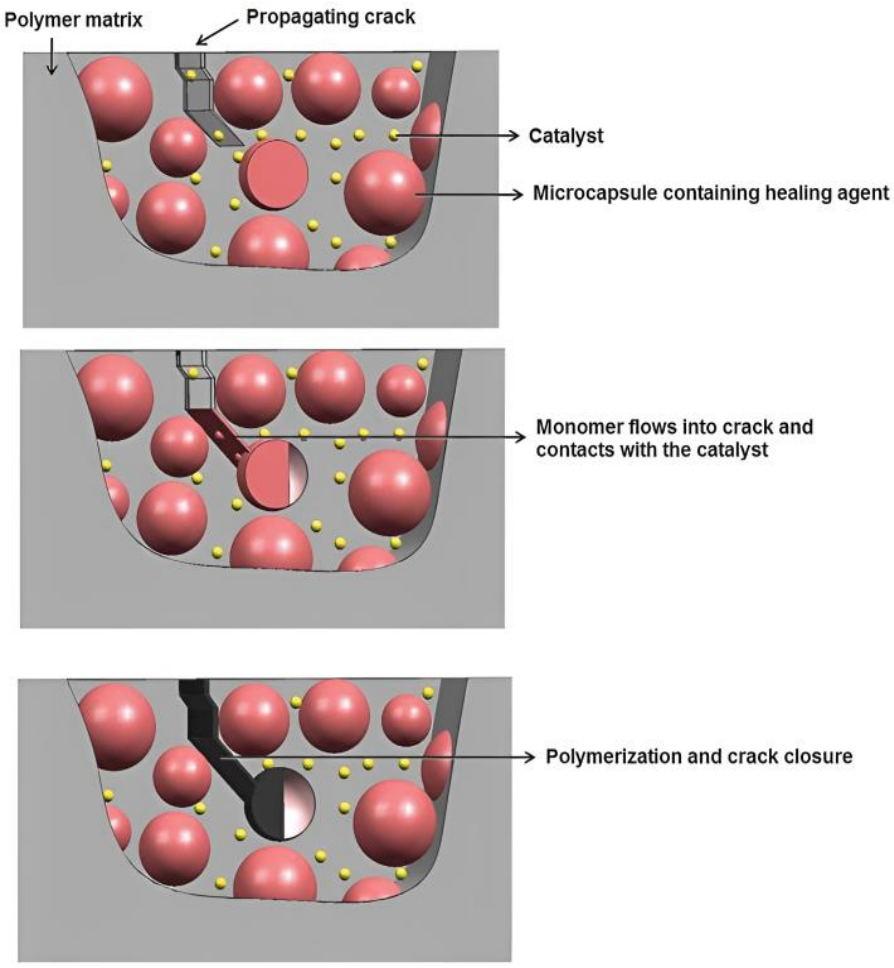


Figure 1.1: Microcapsule based self-healing concept (regenerated from [5])

The self-healing and augmentation mechanisms employed in this study are predicated on two key factors. Firstly, the presence of microcapsules within the material allows for their rupture when subjected to physical damage or internal stress. This rupture facilitates the release of healing or curing agents contained within the microcapsules. Secondly, the reaction between these agents leads to the formation of a polymer network, effectively sealing any cracks that may have formed

within the material. The mechanical properties of self-healing composite films can be significantly restored after sustaining damage [6,7]. The incorporation of self-healing capabilities in matrixes has been found to significantly enhance their longevity and reduce the need for regular maintenance. The commercialization of self-healing techniques, particularly those utilizing microencapsulated healing agents, is progressing at a faster pace compared to other methods. This is primarily due to the advantage of not requiring a modification in the molecular structure of the polymers in order to incorporate self-healing capabilities.

Multiple studies have demonstrated the viability of embedding microcapsules in composite films for damage repair, and promising developments have been made in anticorrosive composites [8–10]. The incorporation of microcapsules into composite coatings has been observed to potentially compromise the mechanical properties of the resulting material which is an important consideration in the design and application of such materials. [11,12]. Furthermore, it is mentioned that microcapsules used for self-healing typically require the use of curing agents or catalysts, which can further impact the mechanical properties of the material. This highlights the importance of carefully balancing the desired self-healing properties with the need for mechanical strength in the design of composite coatings.[13]. Overall, it can be said that microcapsule-based self-healing is a promising approach for improving the durability and longevity of composite coatings, though the trade-offs between self-healing capabilities and mechanical properties should be considered. Ongoing research in this area will likely continue to refine and improve the performance of microcapsule-based composite coatings for various applications.

A good dispersion of microcapsules is necessary for effective and efficient healing of the cracks. In contrast, poor distribution can result in agglomerates and larger particles, which can negatively impact the mechanical properties of the composite film. It is noted that a small number of microcapsules may break during storage or stirring, leading to leakage of the core material and potential agglomeration. Thus, careful handling and processing of microcapsules is important to maintain the effectiveness and avoid negative impacts on the composite film. Overall, the distribution and handling of microcapsules are important considerations in the design and manufacturing of composite films with self-healing capabilities. Further research and development are necessary to optimize these factors and improve the performance of microcapsule-based composite coatings [13].

The early investigations into the restoration of mechanical characteristics in microcapsule-based self-healing materials primarily centered around the examination of a repetitive fracture inspection [2,14] and fatigue testing [15–17] in polymer composites that didn't have fiber reinforcement. In subsequent research, Kessler et al. effectively integrated the self-healing mechanism into a composite material reinforced with woven fibers. They were able to demonstrate the restoration of Mode I fracture toughness [18]. With this breathtaking research they opened the path to incorporate microcapsule with healing agent in other fiber reinforced composite.

1.3 OBJECTIVES

The objectives of this research are listed below:

- To fabricate the microcapsule containing healing agent.
- To fabricate the vacuum bag molded jute fiber reinforced epoxy composite specimens with self-healable microcapsules.
- To investigate the healing efficiency of the healed composite sample.
- To study the morphology and thermal stability of the microcapsules and composite with microcapsules.

1.4 METHODOLOGY

The methodology of this research work is described below through flow chart:

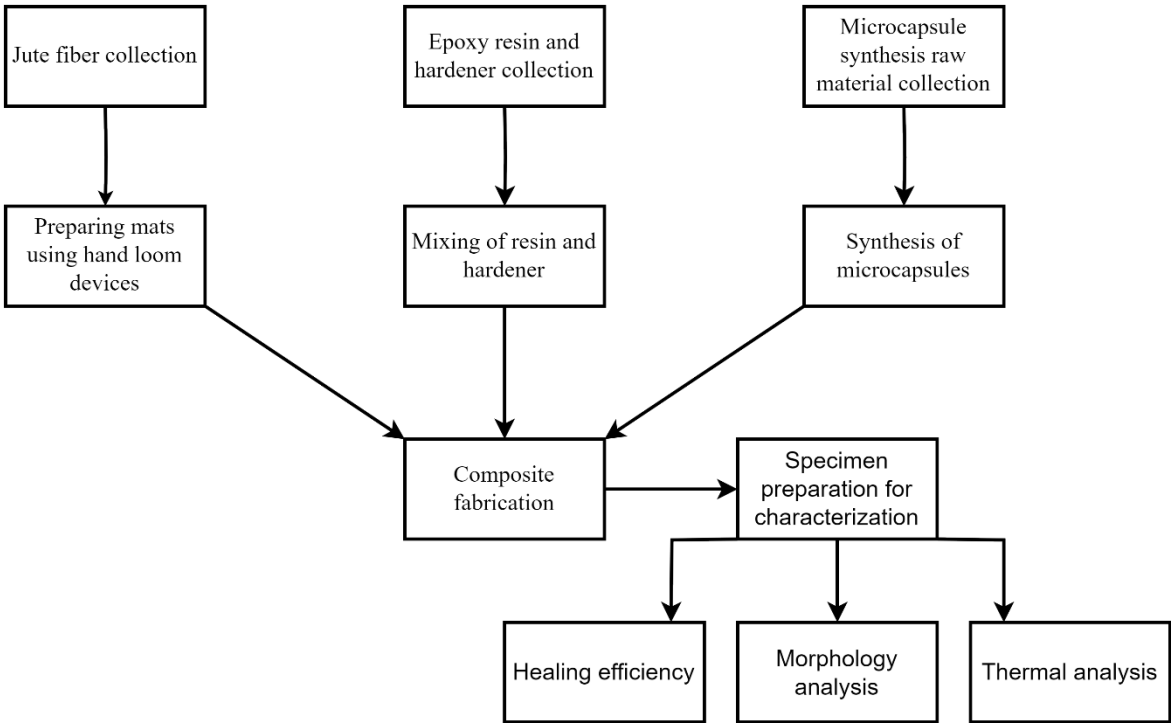


Figure 1.2: Flow chart of working procedure

1.5 OUTLINE

The manner of the chapters of this report is organized by following workflow, which is described below:

Chapter 2 reports the literature review of the current research topic. The notable works are associated with different types of self-healing composites. The vacuum bagging process and the properties from various manufacturing processes are briefly listed in this chapter as well.

Chapter 3 delineates the research method and represents the material used in this thesis. The chapter emphasis to woven jute fiber reinforced microcapsule-based epoxy composites.

Chapter 4 expounds on the data reduction process from physical experiments which was conducted in this work. The physical experiments include impact toughness and the thermal properties test such as and thermogravimetric analysis.

Chapter 5 describes all the experimental results which is the indispensable part of this thesis. The findings of impact strength and thermal characterization such as thermogravimetric analysis and morphology of microcapsules and microcapsule-based composite discussed.

Chapter 6 concludes the thesis works based on the experimental and morphological findings, as well as conveys the recommendation for future works in this research area.

Chapter 2

Literature Review

2.1 INTRODUCTION

Current self-healing composites can be categorized into three groups: capsule-based, vascular and intrinsic self-healing materials. In capsule-based self-healing materials, small capsules containing a liquid able to fill and close cracks are embedded under the material surface. When the material is damaged, cracks cause some capsules to rupture, releasing the liquid and closing the gap. For vascular self-healing materials, the capsules are replaced by a vascular structure similar to a tunnel network, in which various functional liquids flow. These functional liquids will also fill the gap when a crack occurs and breaks the vascular network. The material contained inside a capsule or a vascular network is called a healing agent. The mechanism and behavior of healing agents are fundamental to the recovery process and restoration of mechanical properties.

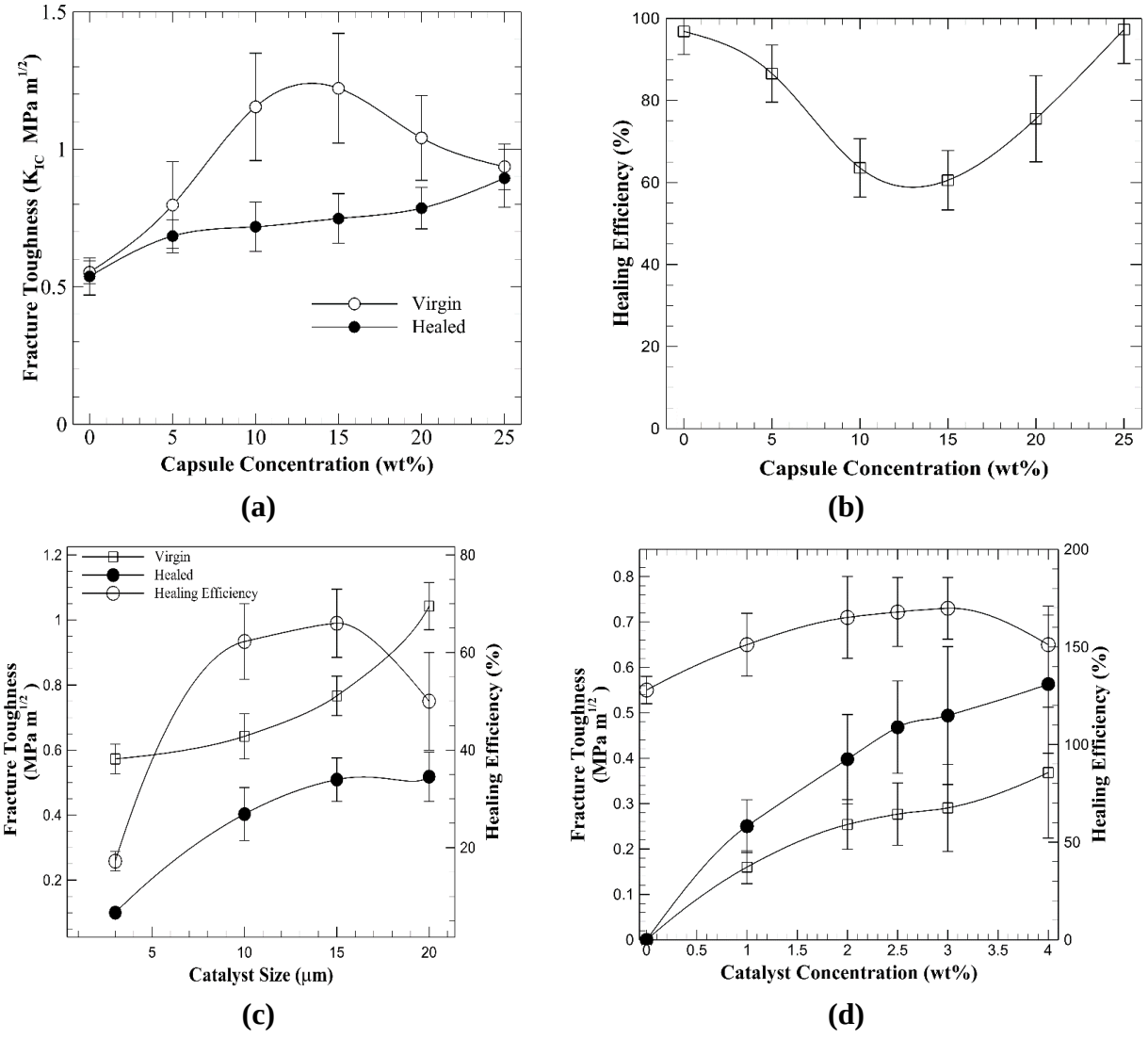
2.2 PREVIOUS WORK ON DEVELOPMENT OF SELF-HEALING SYSTEM

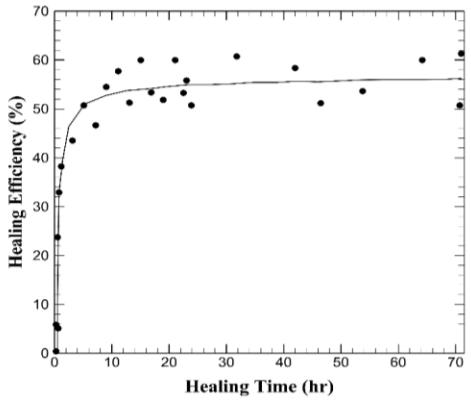
2.2.1. Microcapsule-Catalyst System

Microcapsule-catalyst system involves the incorporation of microencapsulated healing agents and catalysts within an epoxy matrix, thereby enhancing the efficiency of the healing process. In the context of fracture healing, it has been observed that as a fracture approaches the point of rupture, the microcapsules embedded within it may be affected. This phenomenon triggers the release of a healing agent into the area of the fracture, facilitated by the capillary action. Upon contact with the integrated catalyst, the healing agent initiates a process of polymerization, leading to the binding of the fracture faces. The system proposed by White et al. [2] introduced the utilization of dicyclopentadiene (DCPD) monomer as an encapsulated healing agent. Additionally, they employed Ruthenium-based Grubbs' catalyst to initiate the Ring-Opening Metathesis Polymerization (ROMP) of DCPD. In subsequent studies, various researchers have made

significant advancements in the development of microcapsule-catalyst systems, resulting in a diverse range of types with distinct sets of advantages and disadvantages.

A wide variety of variables could affect the effectiveness of self-healing, including the concentration of catalysts and microcapsules used, particles size of catalyst and microcapsule, and the order in which the catalyst is mixed into the matrix along with the epoxy and hardener [14]. Factors affecting healing eficiency and fracture toughness are shown in **Figure 2.1.**





(e)

Figure 2.1: Factors affecting healing eficiency and fracture toughness in case of dcpd-grubbs catalyst microcapsule system (a) capsule concentartion vs. Fracture toughness of virgin and self healing composite, (b) capsule concentartion vs.healing efficiency, (c) catalyst size vs. Fracture tougghness and healing efficiency, (d) catalyst concentartion vs. Fracture tougghness and healing efficiency, (e) healing time vs healing eficiency [14].

Poor dispersion of Grubbs' catalyst and necessity of presence of exact amount of such catalyst, are the limitations of the using DCPD/Grubbs' catalyst system was reported [19] which hinder the healing process. In a study conducted by Rule et al. [19] the researchers embedded the catalyst in a wax microsphere to overcome the weakness of DCPD/Grubbs' catalyst and significant improvement in healing efficiency was observed.

Researchers tried to find the alternate of Grubbs' catalyst because of precious and expensive ruthenium transition metal core [20] and the flammable chemical substances used in the catalyst. To address the challenge, Kamphaus et al. [21] proposed an alternative approach using Tungsten hexachloride (WCl_6) as the catalyst precursor. The utilization of this substitution presents numerous benefits, such as enhanced cost-effectiveness, widespread accessibility, and increased tolerance to moderate fluctuations in temperature. During the study, it was observed that, a modified form of DCPD called Exo-DCPD polymerizes faster than that of DCPD, along with WCl_6 as the catalyst precursor [22]. The healing efficiency achieved was about 20%.

In addition to Exo-DCPD, Ethylidene Norbornene (ENB) draws researcher interest due to its rapid bulk polymerization [23]. Furthermore, unlike DCPD, ENB does not solidify below 15°C [24]. However, it has been identified that the utilization of ENB has a limitation in the form of a linear molecular structure in the resulting polymer achieved through Ring-Opening Metathesis

Polymerization (ROMP), which may not possess adequate physical properties required for efficient micro-crack healing, especially when exposed to elevated temperatures [25]. Lee et al. [26] initially explored the thermal properties of ENB with DCPD combinations. The researchers focused on the hardening process at room temperature using Grubbs' catalyst. It was observed that the addition of ENB blends resulted in improved self-healing properties. This enhancement was attributed to the increased kinetics of the reaction of the ROMP process, which was facilitated by lower catalyst loadings. The investigation of the impact of increasing ENB content on the healing reaction has shown promising results.

The utilization of the DCPD/Grubbs' catalyst has been frequently observed in the field of repairing dissimilar polymer matrices, including bone cement [27], vinyl esters [28] and epoxies. The substitution of DCPD with epoxy resin, specifically with DGEBA, has drawn significant interest due to its potential for enhanced interfacial compatibility [29]. The successful encapsulation of DGEBA epoxy in UF microcapsules and its dispersion with scandium Triflate catalyst has been examined by Coope et al. [30] and he found that DGEBA as a healing agent shows great adhesiveness and compatibility with matrix material. Bolimowski et al. [31] studied the efficiency of this system in fiber-reinforced polymer laminates by filling microcapsules scandium (III) triflate catalysts with DGEBA. Other modifications, such as utilizing Epikote 828 epoxy microcapsule with Aluminum (III) triflate catalyst have been explored by Kosarli et al. [32]. Furthermore, a comprehensive evaluation has been undertaken to analyze the efficacy of a silver-olefin polymer as a catalyst for the self-healing properties of DGEBA epoxy polymers. The findings suggest that there is a notable correlation between the temperature at which the healing process is conducted and the resultant effectiveness of the healing mechanism. Notably, a significant TDCB fracture recovery of approximately 74% was observed after undergoing a 48-hour healing process at a temperature of 70°C [33].

The size of healing agent containers has been identified as a crucial factor in self-healing composite materials. Larger containers may create hollow cavities that can harm the structural material [34]. To address this, Carbon Nanotubes (CNTs) can be used as nanoscale healing agent containers due to their hollow tubular structure. Lanzara et al. [35] investigated CNTs as Nano reservoirs, capable of carrying healing components and serving as filler materials to enhance mechanical properties. The investigation indicate that the mechanical properties remain unchanged when the catalyst's

presence in matrix phase. Furthermore, the conducted thermal analysis in this study demonstrated the potential for having curative abilities in various commercial epoxy resins. The utilization of these resins is prevalent in the manufacturing of traditional materials for composites. Several microcapsule-catalyst systems are listed in the **Table 2.1.**

Table 2.1: Several microcapsule-catalyst systems

Healing agent monomer	**Catalyst**	**Self-healing Mechanism**	**Ref**
DCPD	Grubbs'	ROMP	[2,14–16,36]
DCPD	Grubbs' wax	ROMP	[17,19]
Exo-DCPD	Tungsten (VI) Chloride	ROMP	[21,22]
ENB	Grubbs'	ROMP	[24,25]
ENB+DCP	Grubbs'	ROMP	[26,37]
DGEBA	Scandinium (III) Triflate	ROMP	[30]
DGEBA	Ag-Olefin	ROMP	[31,38]

2.2.2. Dual/multi-Microcapsules System

The dual-microcapsules system developed by Rong et al. [39] to overcome challenges associated with the weak interaction of DCPD and Grubbs' catalysts with host matrix. Problems such as insufficient dissolution of catalysts, improper adhesion between catalysts and healing agents, and interference of the matrix epoxy with the catalyst prompted the development of this approach. This process does not require an extra catalyst because the amine hardener and DGEBA epoxy are encapsulated in different microcapsule. **Figure 2.2** Shows a SEM micrograph of UF encapsulated epoxy and **Figure 2.3** shows a dual-microcapsule system.

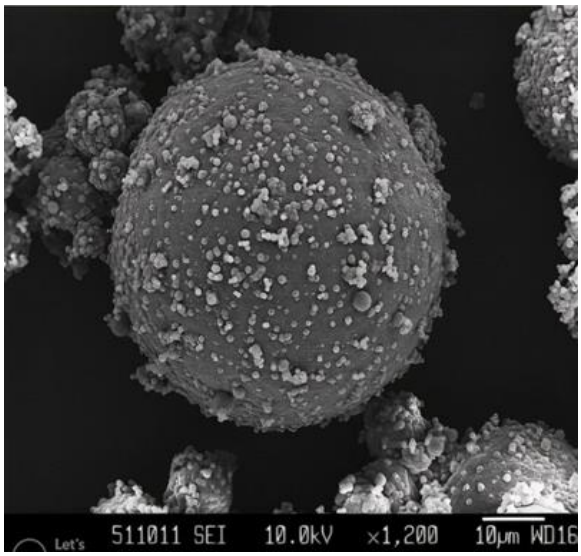


Figure 2.2: SEM micrograph of UF encapsulated epoxy [40].

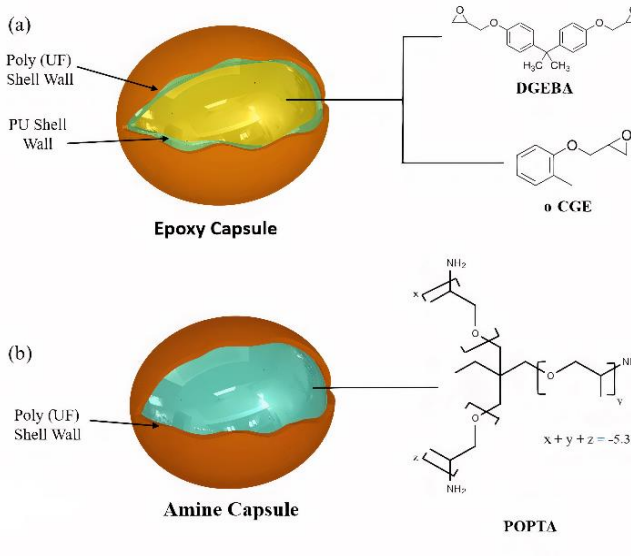


Figure 2.3: Dual-microcapsule system. (a) epoxy capsules consist of a PU-PUF double shell wall and a DGEBA/O-CGE core. (b) amine capsules contain a PUF shell wall and a POPTA core [41].

The interfacial compatibility of the crack region and the healing agent is greatly increased as a outcome of the capsules' core agent being matched with the matrix phase. The method entails pre-integrating a two-component healing material made up of commercially available capsulated imidazole (used as the epoxy hardener) and microencapsulated epoxy into the epoxy matrix. UF is used as the capsule shell wall constituent in a two-step polymerization method in (O/W) emulsion to create the microencapsulated epoxy in advance. Several research outcomes along with the encapsulation techniques are summarized in **Table 2.2.**

Table 2.2: Healing efficiency along with different dual-microcapsule system

Healing agent monomer	**Catalyst/ Hardener**	**Shell wall material**	**Encapsulation Technique**	**Matrix Material**	**Efficiency measuring method and average Healing Efficiency**	**Ref.**
DGEBA epoxy resin	Imidazole (amine hardener)	UF	Oil-in-Water (O/W) emulsion	DGEBA epoxy resin	Fracture toughness test, 106%	[39]

PDMS resin	Platinum	UF	In-situ polymerization process	PDMS resin	Tear strength test, 70–100%	[42]
PDMS resin	Platinum	UF	In-situ microencapsulation	PDMS resin	Torsion fatigue test, 24-54%	[43]
PDMS resin	di-n-butyldilauryl tin	PU	PDMS resin and di-n-butyldilauryl tin were encapsulate by in-situ urea-formaldehyde and interfacial poly-merization consecutively.	PDMS resin	puncture damage test, approximately 100%	[44]
DTHP epoxy resin	Mercaptan as a hardener	MF	(O/W) emulsion	DGEBA epoxy resin	TDCB fracture toughness, More than 100%	[45]
EPON 815C resin	EPIKURE 3274 hardener	UF	EPON 815C microcapsule were encapsulated by in-situ polymerization and EPIKURE 3274 microcapsule were prepared by vacuum infiltration polymerization	EPON 828: DETA epoxy resin	Fracture test, around 91 ± 21% . Six months later, approximately 68%	[46]
Epoxy	PEA as a curing agent	PMMA	O/W emulsion with solvent evaporation technique	Epoxy	Impact test, 93.5%	[47]
DGEBA epoxy	PEA as a hardener	PMMA	W/O/W emulsion with solvent evaporation process	DGEBA epoxy	Tensile test, 84.5%	[48]
Epoxy prepolymer	Mercaptan as a hardener	PMMA	Internal phase separation method	Epikote^{TM} 828	Tensile test, 80%	[49]
EPIDIAN 52 epoxy resin	1-benzyl-2-methylimidazole (Imidazole hardener)	UF for epoxy and PMMA	EPIDIAN 52 was encapsulated by in situ polymeriza-tion in an O/W emulsion and	EPIDIAN 52	Inter laminar fracture toughness, 117.5%	[50]

		for imidazole	imidazole was encapsulated by solvent evaporation technique			
EPON 828 epoxy resin	Amine hardener	PU-UF for epoxy but UF for amine	In-situ polymerization of epoxy and infiltration of hardener	EPON 828	Fracture test, (84 ± 7%)	[41]
DGEBA	EPA	PU/UF	In-situ polymerization with an interfacial microencapsulation	EPON 828	Single-capsule com-pression testing	[51]
Endo-DCPD-	Grubbs' catalyst	UF for DCPD and paraffin wax for Grubbs' catalyst	In-situ poly(urea–formaldehyde)	Mixture of Epicure 3274 and Epon 862 (40:100)	Low velocity impact damage, 51%	[52]

2.2.3. Microcapsules-Latent Curing Agent System

This system was first introduced by Yin et al. [40] as an innovative approach for self-healing. The method described involves the dissolving of the latent curative substance in the matrix phase, while the healing agent is dispersed. This approach addresses the drawbacks of the dual microcapsule system, like potential degradation of mechanical properties and issues related to clustering or inadequate distribution [53]. In this system, imidazole metal complexes work effectively as latent hardeners [54]. Upon release, imidazole exhibits a propensity to engage in a chemical reaction toward the oxirane ring present in the epoxy resin, thereby initiating the formation of a cross-linked network.

In their investigation, Yin et al. [40] examined the effectiveness of copper imidazole complex if it can be used as the alternative of latent hardener in a self-healing system. As a curing agent, DGEBA epoxy resin was used, and an epoxy-based, well-dispersed soluble imidazole as hardener. A compound of 2-methylimidazole and $CuBr_2$ was present in the matrix. This liquid hardener significantly decreased the quantities of epoxy imidazole hardener and healing agents required as compared to discrete encapsulated imidazole. In comparison to discrete encapsulated imidazole,

greater toughness recovery after failure was thus attained [55]. The polymerization of the healing agents requires external heat within a temperature of 120°C to 140°C. This temperature range is crucial for the imidazole complexes to function effectively as hardeners [55].

Previous research has indicated that there is a noticeable disparity in the healing efficiency between aged composite specimens and newly made samples, indicating a decrease in durability of the healing capability for aged composite specimen [56].

In a study conducted by Tripathi et al. [38] the authors investigated various imidazole complexes and epoxy microcapsules on their thermal activation. In this study, the researcher investigated the use of a UF shell to encapsulate cycloaliphatic epoxy resin. Additionally, the epoxy composite samples were treated with two distinct types of latent curing agents, namely nickel and copper imidazole complexes. The findings of the study suggest that nickel imidazole complexes demonstrate superior activity as curing agents and exhibit a lower temperature requirement for curing in comparison to the copper complex. **Table 2.3** consists the summery of development and outcomes of this technique.

Table 2.3: Healing efficiency along with different microcapsule-latent curing agent system

Microcapsule weight %	**Latent Hardener weight %**	**Shell wall material**	**Encapsulation Technique**	**Matrix Material**	**Efficiency measuring method and average Healing Efficiency**	**Ref.**
10 wt.% epoxy loaded (Bisphenol-A) microcapsules	2 wt.% $CuBr_2$ and 2 methylimidazole complex	UF	(O/W) emulsion	epoxy resin (Bisphenol-A)	Fracture toughness 111 %,	[40]
30 wt.% epoxy loaded (Bisphenol-A) microcapsules	2 wt.% $CuBr_2$ and 2 methylimidazole complex	UF	-	epoxy resin (Bisphenol-A)	Interlaminar fracture toughness 79%	[57]
20 wt.% epoxy loaded (Bisphenol-	2 wt.% hardener	PUF	-	epoxy resin (Bisphenol-A)	Compression after impact	[58]

A) microcapsules					(CAI) tests, 100 ± 7%	
30 wt.% epoxy loaded (Bisphenol-A) microcapsules	2 wt.% latent hardener	UF	(O/W) emulsion	epoxy resin (Bisphenol-A)	Fracture toughness, 79%	[59]
30wt.% cycloaliphatic epoxy microcapsule	Nickel and copper imidazole complexes	PUF	In-situ dispersion polymerization technique	Epoxy resin	Impact test, 100 ± 2%	[38]
14 wt.% epoxy microcapsules	2 wt.% $NiCl_2$ $(imidazole)_4$ catalysts	UF	In-situ polymerization	Epoxy resin	Flexural strength 100%	[60]
15wt.% DGEBA epoxy loaded microcapsules	2 wt.% 2MZ-AZINE	PUF	In-situ polymerization	Epoxy resin	Fracture toughness 83%	[61]
8.0 wt.% DGEBA E-51 epoxy	3.0 wt.% Phthalic Anhydride (PAA)	PUF	In-situ polymerization	Epoxy E-44	Impact test, 81.5%	[62]

2.3. INFLUENCIAL PARAMETERS

2.3.1. MICROENCAPCULATION

2.3.1.1 Mixing Parameters

The homogeneity of the capsules as well as their size distribution is affected by the mixing parameters, such as the agitation rate, the stirring time, and the shear forces. It is essential to exercise control over these parameters in order to accomplish homogeneous encapsulation and avoid aggregation as well as particle breaking. There are some important relationships among capsule size, agitation rate, amount of healing materials encapsulated, distribution of microcapsule and healing performance. In order to achieve effective healing, it is crucial for a capsule to contain an adequate amount of healing agent that can adequately fill the gap in the crack region. If the healing agent is insufficient, the healing process may not be successful. Hence large size capsule

contains greater amount of core content (healing agent) compared to small size capsule. In contrast, incorporation of big size capsule reduced the mechanical characteristics of the virgin material due to creation of larger cavity inside the material. The solution of this problem is to disperse small size capsule into the matrix material. Consequently, small size capsule will reduce the chance of maximum healing of a crack as it contains small amount of healing agent. Here an optimal size of capsule should be chosen to solve the challenges related to mechanical properties as well as healing performance [63]. How agitation rate and capsule core content affect microcapsule size is shown in **Figure 2.4**.

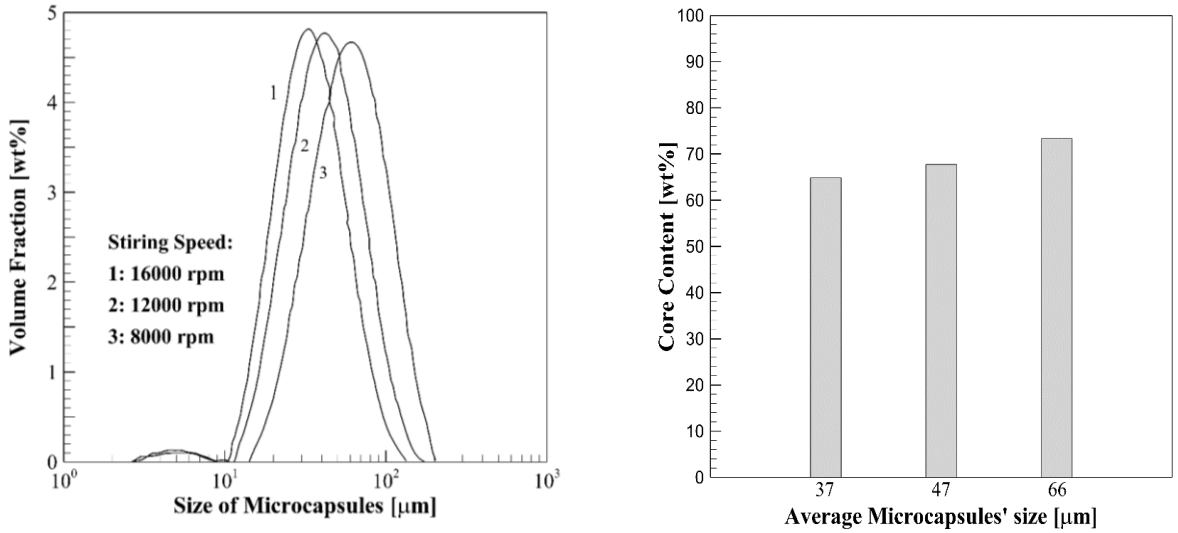
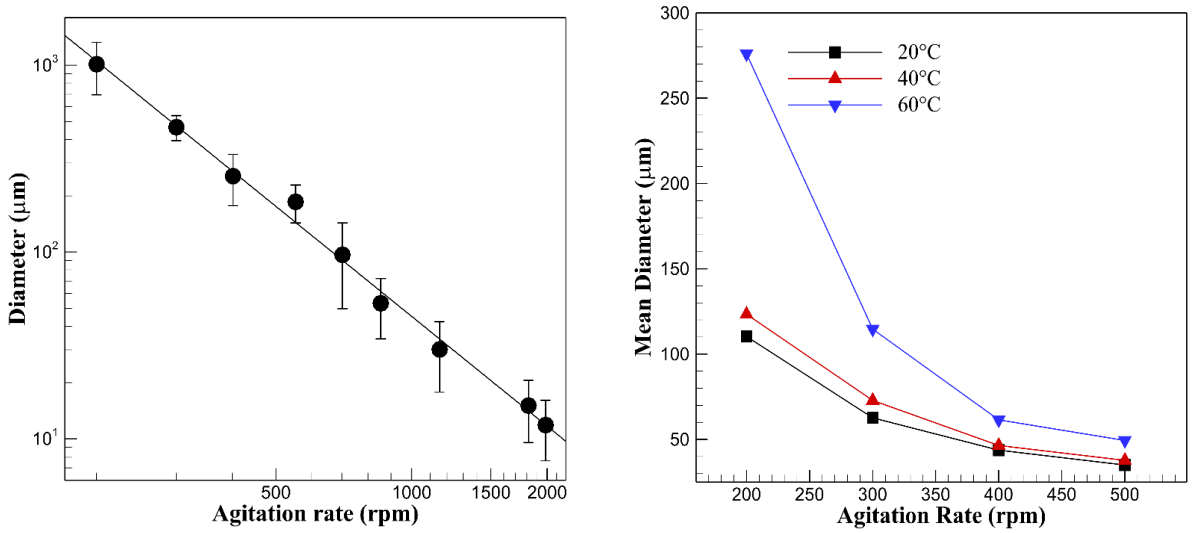


Figure 2.4: (a) Size distribution of the microcapsules containing epoxy healing agent as a function of stirring speed, (b) average microcapsule size vs. core content inside microcapsule [40].

Yin et al. [40] investigated the correlation between agitation rate and capsule size, as well as size distribution. The relationship between microcapsule size and size distribution was observed to be inversely proportional to the rate of stirring. High-speed stirring promotes continual collisions, caused the urea formaldehyde and core content deposition on the reactor wall and stirrer. As a result, the formation of microcapsules are significantly reduced [64]. Additionally, increased droplet collisions during the encapsulation process may lead to increased microcapsule agglomeration, resulting in a reduced total amount of microcapsules [65]. According to the

investigation of Brown et. al [64], average microcapsule diameter and stirring speed are correlated on a log-log linear scale. **Figure 2.5** shows the relationship of agitation rate and microcapsule mean diameter.



(a) **(b)**

Figure 2.5: Effect of agitation rate on capsule mean diameter (a) log-log linear graph of agitation rate vs. Capsule mean diameter [64], (b) influence of agitation speed on the mean diameters of microcapsules prepared under varied temperatures [47].

The dispersion of microcapsules is an essential factor in the production phase. The healing effectiveness of composites is found to be related to the rate of dispersion of microcapsule into the matrix material, which in turn is proportional to the agitation rate during production, as demonstrated by Yuan et al. [66]. The microcapsules and matrix epoxy couldn't be thoroughly mixed due to the weak shearing at the low agitation speed. However, at very high rates of dispersion, microcapsules became deformed or even broke. Stirring time can be considered as another influencing parameter. According to some researchers, a stirring duration of 5 minutes is typically considered adequate for the production of microencapsulated epoxy with a consistent and stable particle size. [40]. It is recommended to keep the capsules size within the range of 63 to 150 μm for development of self-healing coatings [67]. In accordance with previous studies [68], it has been observed that the utilization of microcapsules with a rougher surface and a higher core content can potentially enhance the efficacy of self-healing applications. Effect of agitation speed on microcapsule size and shell wall thickness for various process are listed in **Table 2.4.**

Table 2.4: Effects of agitation speed on microcapsule size

Fabrication Technique	Shell Wall Material	Agitation rate (rpm)	Capsule Mean Diameter (μm)	Shell Wall Thickness (μm)	Ref.
In-situ polymerization	UF	454	220	-	[2]
	PUF	200-300	276	6-10	[61]
	PUF	200-2000	10–1000	0.160-0.220	[64]
	PUF	16000	30–70	-	[40]
	UF	200	50	0.2	[69]
	PMF	500	93.9-92.8		[45]
	PMF	15000	1–10	0.2	[70]
	PMF	350	20-71	0.150-0.270	[71]
	PMF	300	193.2	-	[72]
	Polyphenylene oxide (PPO)	430	118-167	-	[73]
	UF	200	410.9 ± 21.9	-	[63]
		300	306.7 ± 15.3	-	
		400	205.8 ± 26.3	-	
		600	133.5 ± 34.5	-	
		800	64 ± 27.6	-	
Interfacial polymerization	Polyurethane (PU)	350–1100	75-220	0.75-4.4	[74]
	PU	500-1500	40-400	2-20	[75]
	Nickel	2000	36 ± 17	2	[76]
		500-1000	100	4-10	[7]
	Polyurea	1200	0.54	-	[77]
		1800	0.53	-	
		2400	0.39	-	
Electrospraying	Alginate biopolymer	300	364	3-6	[77]

2.3.1.2. Core/shell weight ratio

The concept of core/shell weight (c/s) ratio pertains to the proportionate weight of the core material, which contains the healing agent, in relation to the shell material of the microcapsule [78]. The determination of microcapsule size is a crucial factor in assessing various aspects such as mechanical characteristics and healing capabilities. Higher core material concentrations lead to larger core droplets in emulsions, which substantially increases the size of the microcapsule. A larger size microcapsule contains more healing agent, allowing for a greater release of the agent

upon encountering damage, increasing healing effectiveness. The mechanical characteristics of the microcapsules and the substance they are integrated into can be impacted by the (c/s) ratio. A higher concentration of the healing agent may result from higher core contents, which could change the material's mechanical properties when it heals. This modification may have an impact on properties such as tensile strength, flexibility, and hardness. The core material is shielded from damage by the shell substance. Weight ratio of the core to shell have great impact on the stability of the microcapsules. A balanced (c/s) ratio makes sure that the shell is sufficiently thick and resilient to endure external forces, preventing the healing agent's early release or decomposition. In order to establish a fair balance between compatibility and usefulness, the (c/s) ratio should be tuned. A mismatch in the characteristics of the core and shell might cause problems including early leakage, unstable encapsulation, or inadequate healing. It is noteworthy that the ideal (c/s) ratio can change based on the application, the materials utilized, and the desired therapeutic characteristics. Using a (c/s) ratio of 6.2/1[79] is optimal for UF in-situ polymerization. It is possible to find reports of much higher ratios, such as 6.45/1. This proportion is perfect for producing the spherical microcapsules that improved the mechanical characteristics of the parent material [80]. In a study, some researchers examined the impact of the (c/s) ratio on the manufacturing process of DGEBA-based epoxy resins, specifically LY556 epoxy capsules and CY230 epoxy capsules. The investigation revealed that a 1:1 (c/s) ratio is recommended for the preparation of LY556 epoxy capsules, while a 2:1 (c/s) ratio is deemed ideal for CY230 epoxy capsules. [81]. However, more core substance leads to worse dispersion, and there isn't as much oligomer to form a sturdy coating around the core. As a result, there is a dramatic drop in the total number of microcapsules manufactured. The microcapsules' final form would have a shell wall that was thinner, making them more brittle [82].

2.3.1.3. Monomer viscosity

Self-healing reagents, such as monomers, are preferred due to their low viscosity characteristics. The healing ingredient needs to be able to flow into the micro cracks created when the microcapsules rupture [66]. Yuan et al. [66] interrogated of using epoxy resins of varying viscosities affected the self-healing ability. In the study, undiluted Epoxy 711, Epoxy 731, and EPON 828, resins, were used which had a viscosity of 0.53 Pa.s, 0.85 Pa.s, and 12.5 Pa.s, respectively. The best mixing performance came from the epoxy resin with the lowest viscosity.

Two types of epoxy resins (CY230, LY556) with viscosities of 1.3-2 Pa.s and 10-12 Pa.s, respectively, were encapsulated in methyl methacrylate (PMMA) shell to assess the impact of core material viscosity on self-healing performance [81]. It is found that with the same wt% capsule and same hardener, CY230 encapsulated composite shows better maximum healing efficiency with 74.41% than LY566 encapsulated composite which is 71.94%. In a study it was found that that alginate/epoxy microcapsules exhibited larger core sizes, while alginate/mercaptan microcapsules showed smaller and more uniform core sizes. The higher viscosity of epoxy resin compared to the PETMP/BDMA mixture resulted in the formation of larger epoxy droplets within the alginate solution during the process of oil-in-water emulsion formation [77].

2.3.1.4. Solvent property

Healing agents which are highly viscous need to dilute with other low viscous substance to increase the flow ability. PhCl is a low viscous substance which used to dilute DGEBA epoxy resin [83]. Blaiszik et al. [80] manufactured solvent-epoxy resin microcapsules where chlorobenzene (CIB), phenylacetate (PA), and ethyl phenylacetatefor (EPA) used as solvents (dilutents). The best result was found from EPA-epoxy microcapsules. Wang et al. [84] used N-butyl Glycidyl Ether (BGE) diluents on DGEBA epoxy resin to lower the viscosity. He used different fraction of BGE and the best result was found at 17.5%. Additionally, different solvents can affect the healing efficiency of microcapsules [11]. Some solvents (xylenes and hexyl acetate) are responsible for thermally unstable microcapsules [85]. **Figure 2.6** shows how BGE affecting the viscosity of epoxy resin.

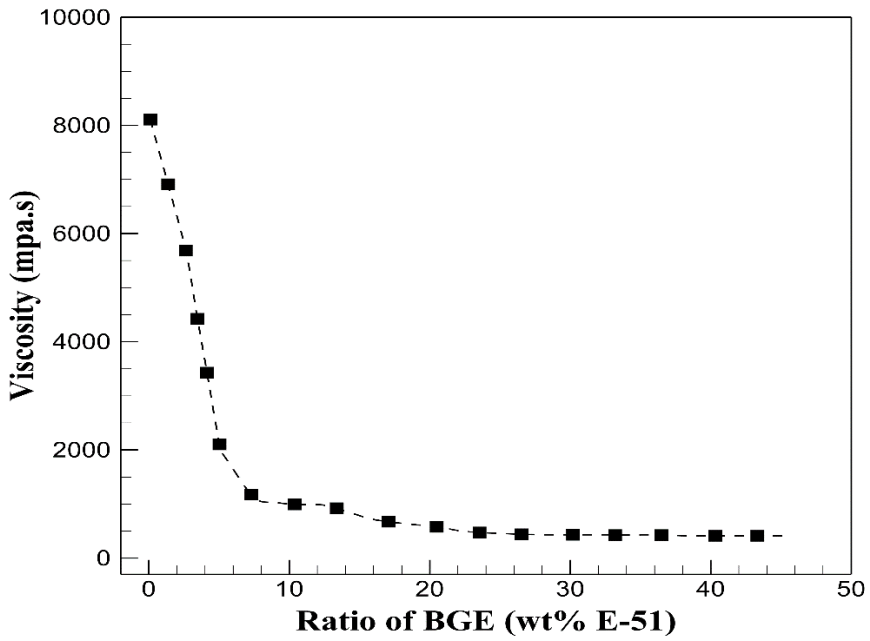


Figure 2.6: Effect of BGE diluent on the viscosity of bisphenol a type epoxy resin e-51 [84].

2.3.1.5. Other parameters

There are other parameters affecting the microencapsulation such as reaction time, temperature, pH, etc. Researcher investigated the synthesis parameter of urea–formaldehyde (UF) microcapsules by altering the parameters such as time, molar ratio, pH and temperature via in-situ polymerization method [86] and listed in **Table 2.5**.

Table 2.5: Synthesis of microencapsulation parameters for UFMs [86]

UF Microcapsules	**Time(h)**	**F/U**	**pH**	**Temperature(°C)**
Microcapsule-1	1	0.94	3	25
Microcapsule-2	4	0.94	7	55
Microcapsule-3	7	0.94	11	85
Microcapsule-4	7	1.88	7	25
Microcapsule-5	1	1.88	11	55
Microcapsule-6	4	1.88	3	85
Microcapsule-7	7	2.81	11	25
Microcapsule-8	7	2.81	3	55
Microcapsule-9	1	2.81	7	85

In the study, all the capsules found thermally stable up to 250°C. Because of high temperature the microcapsule-8 had a smaller number of UF particles around it than microcapsule-4. The ideal pH value was found less than 7 for successful formation of urea-formaldehyde microcapsule [86]. Tong et al. [87] found relatively thinner microcapsule's wall by using lower pH value solution. The investigation of different molar ratios of formaldehyde to urea (F/U) throughout the manufacturing process has revealed significant effects on the formation of microcapsules. The impact observed in this study is attributed to the degree of cross-linking attained during the curing process of resins that have low F/U ratios. It has been observed that the amount of cross-linking in these resins is lower in comparison to resins with higher F/U ratios [86]. When the molar ratio of F/U is inadequate for forming the UF shell wall, it may result in the production of multiple smooth microcapsules instead. [88]. Agitation time can control the size of the microcapsule by controlling the emulsion in the core. By increasing time of the agitation the size of the microcapsules decreased [86].

2.4 HEALING EFFICIENCY

The concept of healing efficiency pertains to the capacity of a composite material to undergo autonomous repair or self-healing following damage. The evaluation of healing efficiency often involves the quantitative analysis of the characteristics of damaged composite materials both before and after undergoing the healing process. This method is widely used in research to assess the effectiveness of healing. The main objective of assessing healing efficiency is to analyze the degree of restoration achieved with respect to mechanical strength, structural integrity, and other pertinent material characteristics.

The healing efficiency of microcapsule-based self-healing composites is often calculated using the following formula:

$$Healing\ Efficiency\ (\%) = \frac{Recovered\ Property\ After\ Healing}{Property\ Before\ Damage} \times 100$$

The equation presented above pertains to the evaluation of various properties of a self-healing composite material, such as tensile property, fracture property, impact property, and so on. The

evaluation of self-healing effectiveness can be conducted using a range of testing mechanisms, as depicted in Figure 2.7.

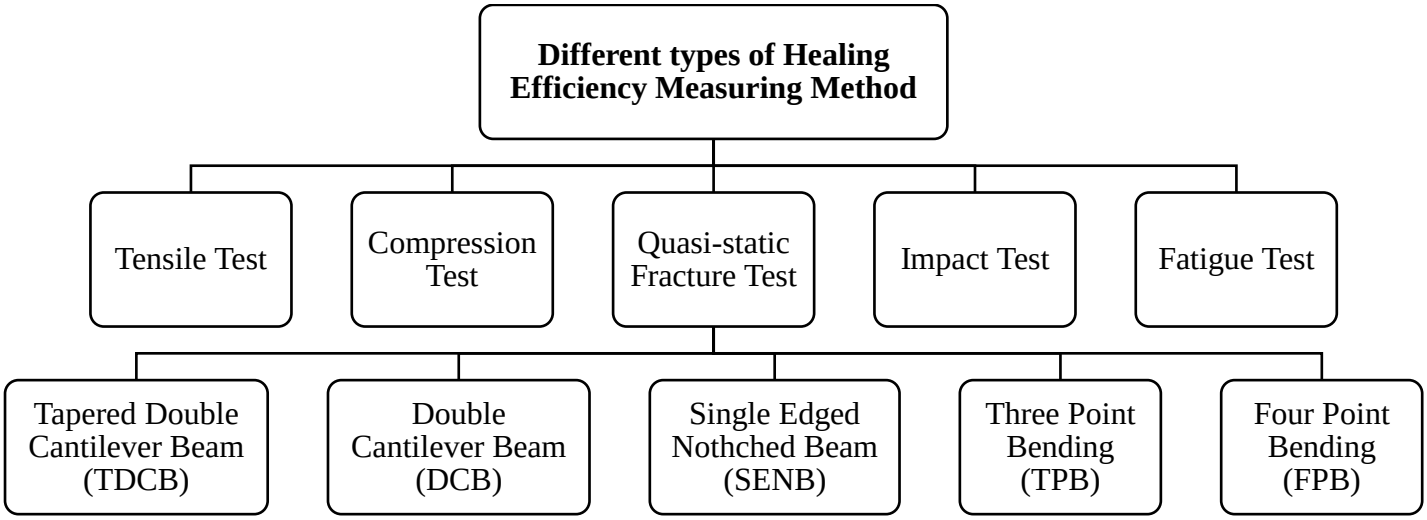
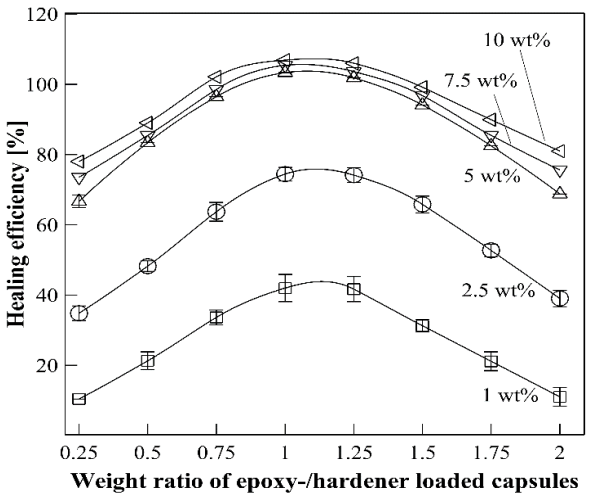
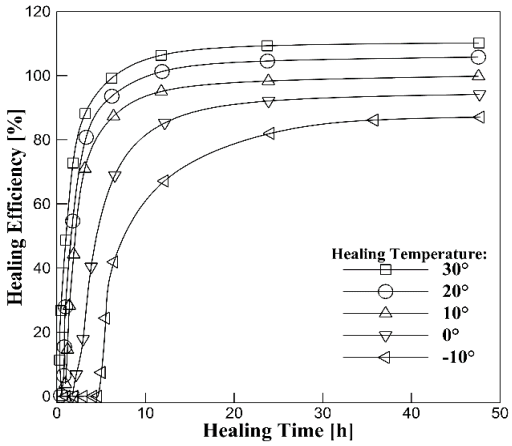


Figure 2.7: Different types of healing efficiency measuring method

The healing efficiency depend on different factors like capsule integrity, capsule distribution, capsule loading, healing agent properties, healing mechanism, healable system, healing temperature, time, environmental conditions, multiple healing cycle [89–91]. Optimizing these factors is essential for developing effective and efficient capsule-based self-healing composites that can significantly extend the lifespan and reliability of various materials in real-world applications. For getting the best healing efficiency there must have an optimal weight ratio of matrix and microcapsule [2,22]. **Figure 2.8** illustrates different factors affecting healing efficiency and fracture toughness and **Table 2.6** represents healing efficiency of some system.



(a)



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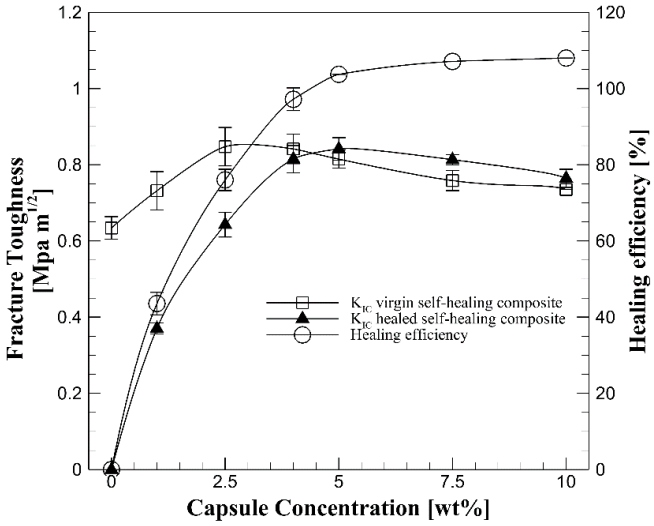


(c)

Figure 2.8: (a) Weight ratio of epoxy-/hardener-loaded capsules vs. healing efficiency, (b) healing efficiency vs. healing time at different temperature (c) the fracture toughness and healing efficiency were studied by varying the concentration of capsules. [45].

Table 2.6: Healing efficiency of some self-healing system

Healing agent	**Catalyst/hardener/latent curing agent**	**Average Healing Efficiency (%)**	**Ref.**
DCPD	Grubbs' catalyst	49	[92]
Urethane prepolymer	Polysiloxane (polydimethylsiloxane) catalyst	100	[93]
ENB 95% and DCPD 5%	-	103	[94]

2.5 THERMAL STABILITY

The investigation of thermal stability in microcapsules utilized in self-healing composites holds significant importance in ensuring their effective implementation. The long-term stability of microcapsules is a crucial characteristic that determines their capacity to endure and preserve their therapeutic substances under high temperatures, without experiencing substantial deterioration or untimely discharge. Thermal stability of microcapsules are affected by several factors like capsule shell wall material, mole ratio, cross linking and curing of the capsule shell wall material, healing agent and capsule size and distribution [95,96]. Decomposition of microcapsule occurs in several stages. Basically, the initial weight loss is caused by the decrease of moisture content and further weight loss is due to the loss of capsule shell wall material. Pittala et. al [81] studied the thermal stability of 3 types of microcapsule with (Poly Methyl Methacrylate) PMMA shell wall material of which two are epoxy resin (LY556, CY230) and one is amine hardener (HY951) microcapsule. It is found that LY556 epoxy capsules shows better stability at temperature greater than 400°C than other microcapsules. **Table 2.7** illustrates the thermal effect of microencapsulation for various technique.

Table 2.7: Thermal stability of different microcapsule based self-healing system

Encapsulation Technique	**Shell Wall Materials**	**Thermal Effets**	**Ref.**
In situ Poly-merization	PUF	The microcapsule wall has less mechanical strength, heat resistance and sealing property than PMF shell wall.	[43, 70]
	PMF	At 25 to 100°C, the PMF microcapsule is thermally stable. But with the increase of temperature the thermal stability decrees. At 270 to 600°C the decomposition of melamine and PMF starts which causes 61% weight loss of the PMF capsule.	[70]

	PMF	Fracture mechanics and fatigue studies suggest that the epoxy composites containing these microcapsules, finding that they were capable of restoring their own properties after being heated to 250°C for 24 hours.	[95]
	PPO	When kept at temperatures below 258°C, the microcapsules maintain their structural integrity, making them suitable for use in thermally demanding applications.	[73]
In-situ emulsification polymerization	UF	Big size capsule remained thermally unstable due to the incomplete polymerization of UF whereas small size capsule found thermally stable at higher temperature, up to 230°C.	[63]
Interfacial polymerization	Polyurea	Double-walled microcapsules had higher heat resistance and thermal stability than single-walled ones, and that their encapsulated ratios were 52% and 43%, respectively.	[77]
Electrospraying	Alginate	The mass loss of blank calcium alginate microcapsules was observed to be up to 40% within the temperature range of 220-430°C, which can be attributed to the decomposition of the glycosidic bond. But, further increased of temperature hinder the decomposition of microcapsules as the calcium carbonate and carbonaceous char acted as the protective barrier.	[96]
O/W emulsion with solvent evaporation technique	PMMA	At temperatures about 140°C, PMMA microcapsules ruptured and release the healing agent and leads to significant weight loss. At 280°C and 325°C, the PMMA shell thermally decomposes, leading to a second and third weight loss, respectively.	[45]

2.6. APPLICATION

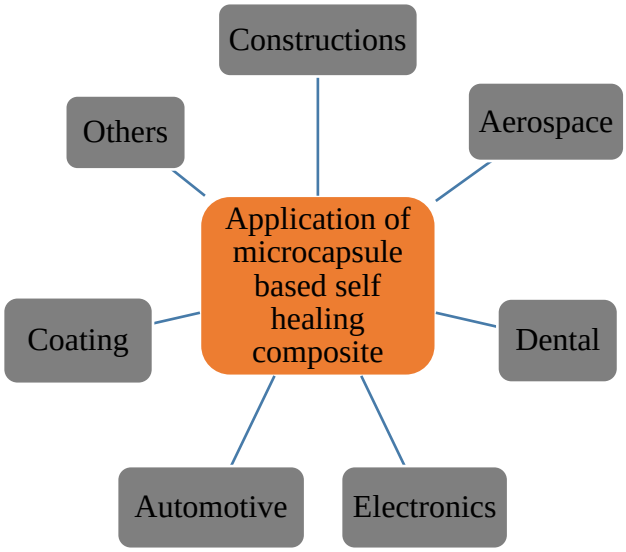
2.6.1 Electronics

Nowadays, different types of composite material are used in electronic devices. In the event of material damage, such as the occurrence of cracks, microcapsules exhibit the remarkable capability of releasing liquid metal. This phenomenon facilitates the filling of the crack, thereby restoring the electric flow within the composite material. Kahar et. al [97] studied the capability of microcapsules to restore electricity in microseconds and he found some outstanding result. He found that 90% samples can restore almost 99% of their original conductivity within this system.

2.6.2 Automotive

Zhang et. al. [98] introduced a novel approach to enhance non-asbestos composite auto brake pad performance. They developed self-healing brake pads by incorporating varying amounts of poly (urea-formaldehyde)/DCPD microcapsules and nano-reinforced fillers. The composites with self-healing microcapsules fulfill the requirements for auto brake pad applications. Additionally, composite with nano fillers (2%) increases the impact and hardness intensity of the formulations. **Figure 2.9** shows different application of microcapsule based self-healing composite.

Figure 2.9: Application of microcapsule based self-healing composite



2.6.3 Aerospace

In contemporary aviation, aircrafts have incorporated a diverse range of composite materials, such as metal matrix composites (MMCs), fiber-reinforced polymer matrix composites (FRPMCs) featuring glass and carbon fibers, and ceramic matrix composites (CMCs). These materials have been selected due to their remarkable capacity to efficiently absorb significant impacts [99,100]. There are some factors which causes damage of materials coating of aircraft such as ultra-violate (UV) radiation, space debris, and thermal cycles [101]. In a study conducted by Zhu et al. [101] UV-responsive microcapsules were synthesized. These microcapsules were designed with an inner polymeric shell that exhibited rapid degradation upon exposure to UV radiation due to their outer TiO_2 shell. The microcapsules rupture upon impact, releasing the healing chemicals, which automatically repair any damage to the coating. Guadagno et. al. [102] developed a self-healing composite that functions actively and effectively at extremely low temperatures down to -50°C, while maintaining the performance of current structural composites.

2.6.4 Constructions

The researchers created different sizes poly(phenol-formaldehyde) (PF) / Dicyclopentadiene (DCPD) microcapsules through in situ polymerization [103]. These self-healing microcapsules were developed for use in cementitious materials, and they include a healing ingredient with good dispersibility. The research showed that mechanical triggers generated by cracks were more likely to occur in the smaller PF microcapsules. Kanellopoulos et al. [4] used a complicated coacervation process to encapsulate sodium silicate (liquid) in gelatin/acacia gum microcapsules for use in self-healing concrete. The microcapsules change shape from ellipsoid (when wet) to perfect spheres (when dry) without compromising their structural integrity. The microcapsules remain stable when in contact with strong alkaline solutions, resembling the alkaline environment of concrete. The system's capacity to switch mechanical states between a rubbery flexible state and a stiff glassy state as a function of moisture content is an intriguing feature. This makes it possible for the microcapsules to withstand being mixed into the cement and to successfully rupture as the composite dries, preventing the cement from leaking out.

2.6.5 Coating

Stankiewicz et. al. [104] investigated different types of self-healing coating like polymeric coating, microcapsule or nanocapsule based coating, hybrid oxide coating. In the past few years the use of microcapsule or nanocapsule based coating has increased dramatically to protect different materials from corrosive environment [104]. The resistance to corrosion of a self-healing epoxy-based coating was evaluated by Behzadnasab et al. [105] utilizing urea-formaldehyde microcapsules of varying sizes. Linseed oil was used as the healing agent with various mixing rates. The study revealed that larger microcapsules exhibited better self-healing performance against corrosion compared to smaller ones. Jialan and his team conducted a study to see how adding microcapsules containing urea formaldehyde (wall material) and epoxy resin (core material) to an epoxy composite coating affects its corrosion resistance [106]. They tested each ratio separately, using 0%, 1%, 2%, and 3% microcapsules, and discovered that the coating with 2% microcapsules had the best resistance. As a result, the coating's effective service life might be four times that of a coating without a microcapsule. **Figure 2.10** illustrates the effect of coating with microcapsule on corrosion resistance**.**

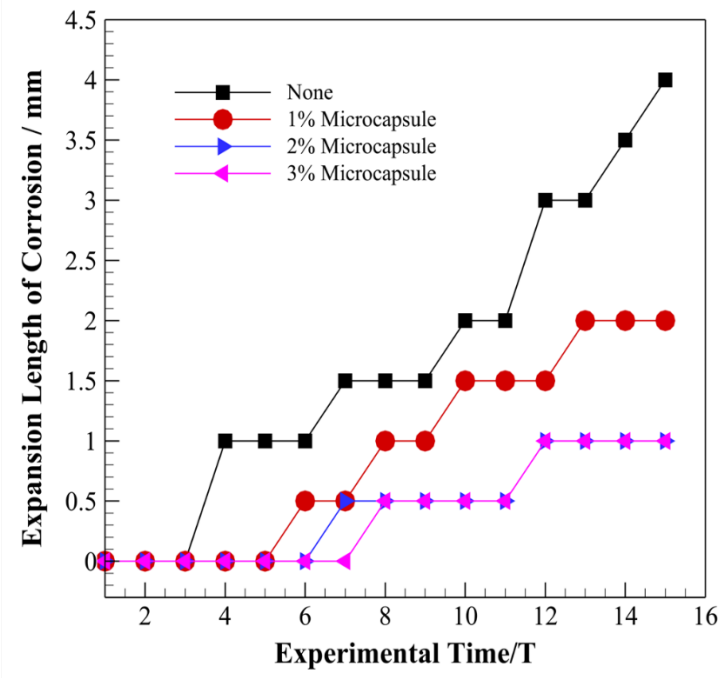


Figure 2.10: Corrosion length of scratches on coatings tested on different salt spray days [106].

2.7 SUMMARY

The main goal of microcapsule based self-healing composite materials is to develop a composite material which will be used in different field to replace other material so that overall performance can be enhanced. In conclusion, the utilization of microcapsule-based self-healing materials has proven to be highly advantageous in various applications, particularly in scenarios where limited accessibility and complex geometries are involved. This has been observed in the aerospace industry [99], underwater piping system [107], reactors (nuclear) [108], and turbine blades [109]. In conclusion, the research on microcapsule based self-healing composite is progressing rapidly, aiming to address the existing limitations and enable the utilization of self-healing materials in the construction of safer infrastructure and sustainable development.

Chapter 3

Method and Materials

3.1 INTRODUCTION

Composites are a type of mixed material that consists of more than one element. These components combine to form a substance that is identical in every way except for its unique combination of physical and chemical properties. Composites, often known as fiber reinforced polymers, are constructed from a fiber reinforcement material and a matrix. When microcapsules with healing agent and catalyst are mixed with a matrix material, a self-healing composite is created. In this present study natural fiber reinforced microcapsule based self-healing polymer composite are manufactured by hand layup and vacuum bagging process where jute was used as fibers. The composite is made by first preparing microcapsules, then mechanically mixing them with epoxy and hardener, and finally casting the solution with the fibers. The purpose of this chapter is to provide an overview on the material involved and the procedure as well.

3.2 MATERIALS

Different types of materials are used to prepare the microcapsule and microcapsules based self-healing composite.

3.2.1 Matrix Material

Lapox Metalam - B is two components modified, epoxy coating system where epoxy resin and hardener are used supplied by Atul Ltd., India. Both epoxy and hardener are collected as liquid form and then used as received. The mixing weight ratio of epoxy and hardener is 2:1. The physical properties of this epoxy and hardener are described in **Table 3.1.**

Table 3.1: Properties of epoxy and hardener

Parameters	Epoxy	Hardener
Description	Clear Transparent Liquid	Clear Transparent Liquid
Viscosity at 25°C (m Pas)	800 - 1,200	300 - 600
Density (g/cc)	1.00 - 1.20	0.95 - 1.00

(a) (b)

Figure 3.1: Matrix materials, (a) epoxy, (b) hardener.

3.2.2 Synthesis of Nano-silica

Silica gel was used to prepare nano silica by ball milling process. A ball mill is a grinding device commonly employed for the purpose of reducing bulk material into particles of nano-scale dimensions. This is achieved through the utilization of zirconium or steel balls of varying sizes, which facilitate the grinding and blending process. The reduction in size is accomplished through

a combination of impact and attrition as the ball falls from near the top of a revolving hollow cylindrical shell. All these oxides are ball milled at a speed of 450 rpm for about 1 hour to achieve the nano-size. After milling a strainer was used to collect the particle in a glass jar. The powder was preserved in a vacuum desiccator for an inert environment. **Figure 3.2** describes SFM-1Desk-Top Planetary Ball Miller machine and different accessories.

(a)

(b)

(c)

Figure 3.2: (a) SFM-1desk-top planetary ball miller machine, (b) planetary disc, (c) nano-silica in ceramic grinding jar

3.2.3 Microcapsule Synthesis Materials

Each component in this technique plays a critical role in the encapsulation process, ultimately leading to the formation of self-healing microcapsules with desirable properties for composite materials. All materials used for microencapsulation was purchased from Sigma Aldrich except Hypermer A-70 which was collected from Croda International, India. The description of different materials for microencapsulation are discussed in **Table 3.2. Figure 3.3** shows different materials used to synthesize microcapsules.

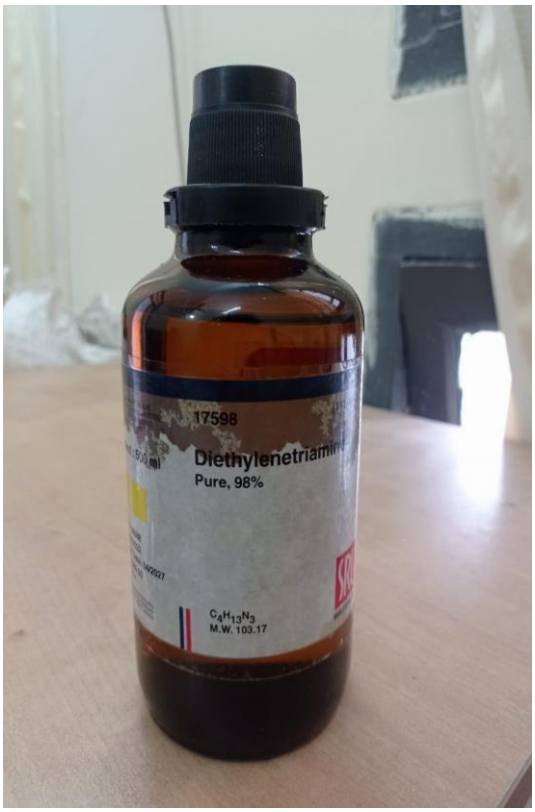
Table 3.2: Materials for microcapsule synthesis

Materials	**Description**
Hypermer A-70	Hypermer A-70 (Polyoxyalkylene modified Random Polyester) is a polymer used as a surfactant of microcapsule. It helps in dispersing the water-soluble epoxy and diethylene triamine in the paraffin oil to form an emulsion. The presence of Hypermer A70 stabilizes the emulsion by reducing interfacial tension between the water and oil phases, thus preventing coalescence of droplets and ensuring uniform encapsulation.
Parafin Oil	Paraffin oil serves as the continuous phase of the emulsion. It provides a non-reactive medium for the encapsulation process. Paraffin oil also aids in controlling the viscosity of the reaction mixture, facilitating stirring and handling during the encapsulation process.
Water-soluble epoxy (1,4-Butane diol diglycidyl ether)	This epoxy resin serves as the core material for the microcapsules. It undergoes polymerization in the presence of diethylene triamine to form a cross-linked polymer network, which constitutes the core of the microcapsules. This network provides mechanical strength and resilience to the microcapsules, allowing them to withstand mechanical stresses and rupture.
Diethylene triamine (DETA)	DETA is a cross-linking agent for the epoxy resin. It reacts with the epoxy groups in the water-soluble epoxy to form a three-dimensional network structure, leading to the formation of a solid core within the microcapsules. This cross-

	linking process imparts mechanical strength and stability to the microcapsules, enabling them to retain their integrity and contents during handling and use.
Pet ether	Pet ether is used as a washing solvent and a dispersing medium. It helps in removing any unreacted or excess reactants, impurities, or by-products from the surface of the microcapsules after centrifugation. Pet ether also aids in dispersing the microcapsules and nano silica during the final stage of the process.
Nano silica	Nano silica, or silica nanoparticles, may serve multiple functions in the microcapsule preparation. It could potentially act as a reinforcing filler, enhancing the mechanical properties of the microcapsules. Additionally, nano silica may contribute to the stabilization of the dispersion and prevent agglomeration of the microcapsules during drying and storage. Moreover, it may also facilitate the interaction between the microcapsules and the surrounding matrix in composite materials, improving their compatibility and adhesion.

(a)

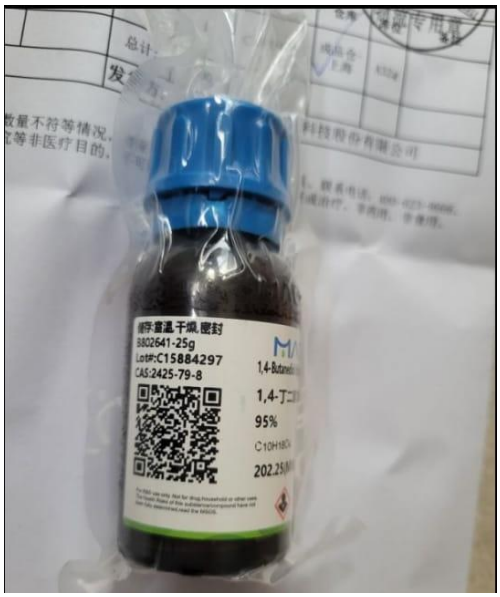
(b)


17598
Diethylenetriamine
Pure, 98%
$C_4H_{13}N_3$
M.W. 103.17

(c)


1.01775.2500
Supelco
EMSURE®ACS,ISO
Petroleum benzine
for analysis
boiling range 40-60°C
Petroleum spirit
Petoleum ehter
UN1268
CAS-No: 64742-49-0
sigmaaldrich.com

(d)



(e)

(f)

Figure 3.3: Materials for microcapsule synthesis: (a) hypermer a-70, (b) parafin oil, (c) water-soluble epoxy (1,4- butane diol diglycidyl ether), (d) diethylene triamine (deta), (e) pet ether, (f) nano silica

3.2.2 Fiber Materials

Jute is an annual crop that is cultivated in Bangladesh's fertile Ganges Delta region to the tune of 80 percent. It is known as "Golden Fiber" due to its golden hue and significance. Jute is an inexpensive natural fiber that is also environmentally beneficial. In contrast to cotton, jute is simple to cultivate, produces high yields per hectare, and requires few pesticides and fertilizers. Jute is the same bast fiber as flax and hemp, and its stems are similarly processed. Another popular source of natural fiber is banana pseudo -stem. Bangladesh cultivates bananas on a yearly basis on 13,335.0 hectares. The trees are left to rot after the fruit is picked, leading to unpleasant odors and environmental damage. So, the remaining trees were gathered by people for use in making fibers. The plant's employees have claimed that one tree can provide 400 grams of fibers. Now many international traders are importing banana fibers from Bangladesh. Jute fiber mats are collected from local market as they are easily available all over the country and raw banana fibers are collected from Narayanganj district, Dhaka. **Figure 3.4** shows the jute fiber extracted from their respective tress.

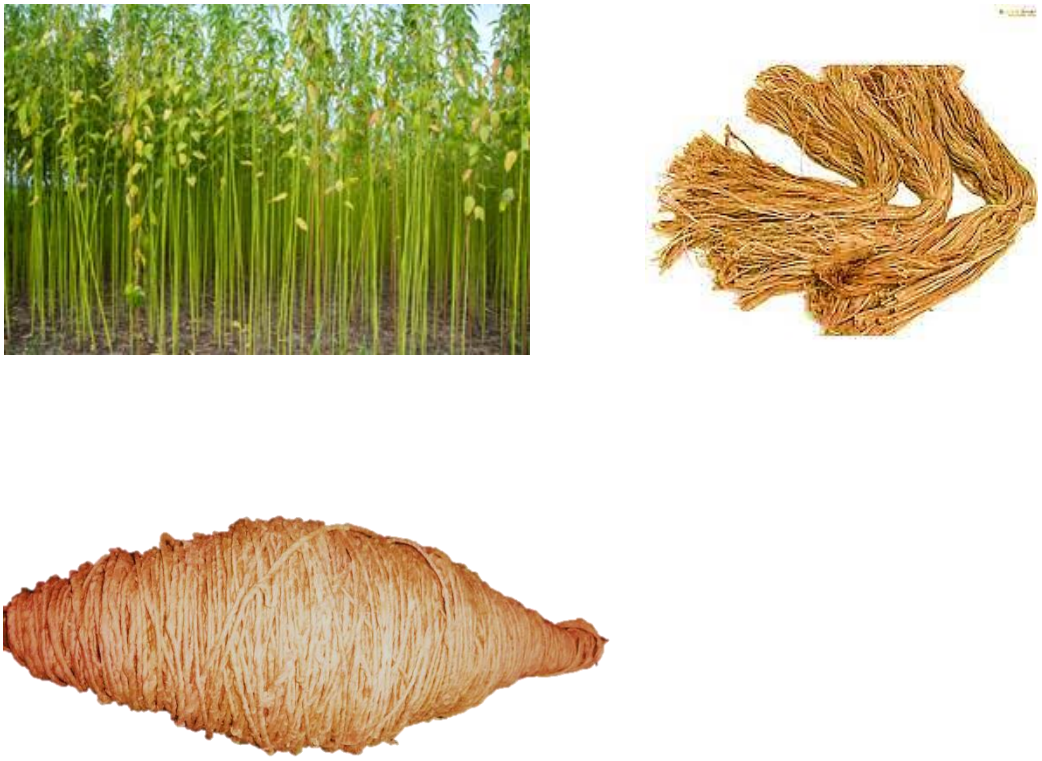


Figure 3.4: Jute trees and fibers

3.2.2.1 Making Jute Fiber Mat

To prepare the woven mat, a special type of Manual loom with the arrangement of some tools is used. The first step would be to select the appropriate type of jute fiber and need to be cleaned, dried, and cut to the appropriate length. Unidirectional woven mats are produced for this research. To produce the unidirectional mat, at first, the yarn is aligned parallel at the table with the help of the sidebars. Jute yarn is woven through parallel aligned yarns with the help of the needle. The yarn is then adjusted by pulling them parallel to one another using the hand bar. The entire mat is generated by repeatedly performing this method. The weaving of mat and the completed mat are shown in **Figure 3.5**.

(a)

(b)

(c)

(d)

Figure 3.5: Weaving of mat

3.2.2.2 Surface Treatment of the Fiber Mat

Reinforcing media in polymer-based matrices, lignocellulose fibers are derived from plants and generally comprise cellulose, hemicellulose, and lignin. To improve its suitability as reinforcement in composite materials, lignocellulose fibers can be chemically modified [80]. In order to enable interlocking between the continuous phase (matrix) and the discontinuous phase (reinforcement), the alkali (Mercerization) treatment process is used for the activation of fiber surface by modifying the surface topology, such as augmenting the surface asperity. NaOH is the most common alkali used for treating cellulose because it solely converts cellulose I to cellulose II [81]. Jute mats were soaked into 5 wt.% of sodium hydroxide solution for 24 hours (1 day). 5 wt.% of sodium hydroxide

solution was made of by mixing crystal NaOH with distilled water. Then the wet mats were dried in the open sun until all the moisture content was removed. **Figure 3.6** shows the fiber mats are soaked in 5% alkali solution.

Figure 3.6: Fiber mats are soaked in 5% alkali solution

3.3 SYNTHESIS OF MICROCAPSULES

Synthesis of microcapsules follows several steps and long hours which was introduced by polo et. al. [110]. The preparation of microcapsules containing epoxy resin which comprises water-insoluble and/or water-soluble components prepared by in-situ polymerization using non-aqueous continuous phase which acts as healing agents for the micro-cracks when embedded in composite structures. The synthesized microcapsules are shown in **Figure 3.7.** The steps of synthesizing microcapsules are discussed below-

Dissolution of Hypermer A70: At first 40 mg of Hypermer A70 was dissolved in 50 gm of paraffin oil to prepare the reaction mixture.

Emulsion Stabilization: A magnetic stirrer with hot plate was used to stir the mixture at 500 rpm for 10 minutes. Then 4.52 gm of water-soluble epoxy (diglycidyl ether of butane diol) was added and stirred for 20 minutes to stabilize the emulsion.

DETA Addition: Then 0.5 gm diethylene triamine (DETA) in 5 gm paraffin oil was added in reaction mixture drop wise over the period of 10 minutes.

Temperature and Stirring: Reaction mixture was then stirred for 30 minutes at 40 °C and then 30 minutes at 50°C. Thereafter temperature was raised to 60°C and stirred for further 4 hours.

Cooling and Overnight Stirring: Then the reaction temperature was brought to 35°C and kept for overnight for stirring for 21 hours.

Pet Ether Addition: After that 90 ml pet ether was added and stirred for 30 minutes.

Centrifugation and Washing: After the completion of reaction, mixture was centrifuged at 3000 rpm for 2 minutes and washed with pet ether.

Microcapsule Dispersion and Nano Silica Addition: Finally, microcapsules were dispersed in 50 ml pet ether and 0.51 gm of nano silica was added.

Evaporation: Then this dispersion was poured into Petri-dish and allowed to be evaporate in air.

Drying: Obtained microcapsules was dried in air for overnight for about 12 hours.

(a) (b)

Figure 3.7: Synthesized microcapsules: (a) in a petri dish before drying, (b) on a paper after drying.

3.4 COMPOSITE PREPARATION

In this work, natural fiber based self-healing composite was prepared by vacuum bag molding process. At the beginning the PVA resin was prepared mixing with distilled water. Then PVA was blended with nano fillers forming a homogenous mixture and filled the space between the laminates of jute and banana mats. All those parts were molded in a vacuum bag and kept under a certain pressure so that a compact material was fabricated.

3.4.1 Compounding

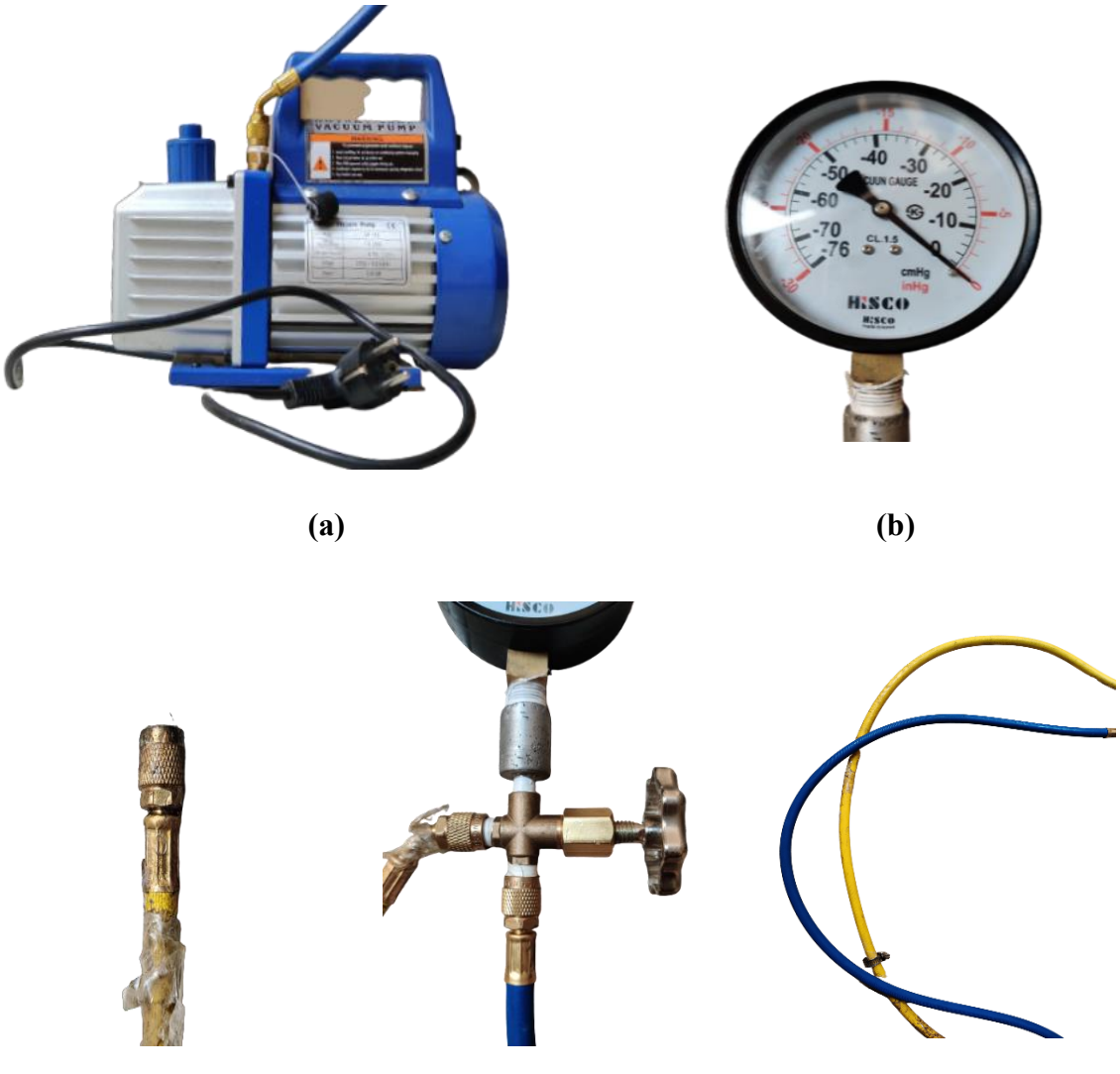
Only one type of composite sample was prepared where 3 weight precent microcapsules was incorporated into the matrix materials. Epoxy, hardener, microcapsule and woven jute fiber in 3 layers, were compounded together to form the self-healing composite. Epoxy and hardener solution without microcapsules was poured and brushed in between each layer to cast the composites. **Table 3.3** illustrates the weight percentage of different constituents.

Table 3.3: Weight percentage of the manufactured composites

% of Woven Jute fiber mass (m/m)	**% of Epoxy mass (m/m)**	**% of Hardener mass (m/m)**	**% of Microcapsules (m/m)**	**Sample/ specimen name**
15	54.67	27.33	3	Pristine

3.4.2 Vacuum Bagging Process

In order to produce composite materials, a vacuum bagging apparatus is required. A vacuum bag that is attached to a vacuum pump is used to seal a composite layup inside of it. Through the removal of air and consolidation of the laminate layers, the composite structure's overall quality and strength are enhanced, adhesion is improved, voids are decreased, and the composite structure is more solid.



(a) **(b)**

(c) **(d)** **(e)**

Figure 3.8: vacuum pump setup (a) vacuum pump (0.25 hp), (b) vacuum gauge, (c) nozzle, (d) vacuum pressure regulator, (e) hose pipes

The reinforcing matrix composite was manufactured using neat and dry fiber mats. In order to be employed in the manufacturing process, epoxy resin and microcapsules were combined in a matrix at a certain weight ratio and homogeneously mixed. After preparing the solution, a brush is used to spread the resin hardener solution in each layer of fiber. The mold is then placed into the vacuum bag. Then vacuum bag molding was used for the fabrication processes. **Figure 3.9** depicts the vacuum bag molding setup.

Figure 3.9: Vacuum bag molding setup

A wood frame mold with a polyethene sheet on top was used for both processes to prevent the resin from sticking to the frame's surface and to help remove the mat after fabrication. Peel Ply was put on the polyethene. Next, fiber mat was laid down and brushed resin on it. There until necessary number of layers were applied, the procedure was repeated. In this work, three layers of fiber mat were used in fabrication. Peel ply as well as a breathing cloth were placed at the top in order to prepare for vacuum bag molding. The mold was then placed inside a vacuum bag and sealed using a both way sealant tape. Under 50-60 cm (Hg) vacuum pressure, the bag's existing air was continuously sucked out for six hours before being kept at room temperature for 14 to 18 hours. The excess matrix solution and air gap were also removed in the vacuum bag molding process. Peel ply and breathing cloth were also applied in the molding process to soak the extra resin.

3.5 CHARPY IMPACT SPECIMEN PREPARATION

The specimens for mentioned tests are cut from the final manufactured products using a CNC machine modeled ARISTO ATEX-H 1325F CNC router shown in Figure 3.11. ASTM standard has flexibility in the thickness of the specimens. Hence the thicknesses of the specimens are not

accordingly to Figure however, the other dimensions are maintained accordingly. Impact specimens are prepared according to the ASTM standards as shown in **Table 3.4.**

Table 3.4: ASTM standard for different tests

Sl. No.	**Tests Name**	**Specimen Standards**
1	Impact test	ASTM D256
2	TGA	Granule sample
3	FTIR	Granule sample

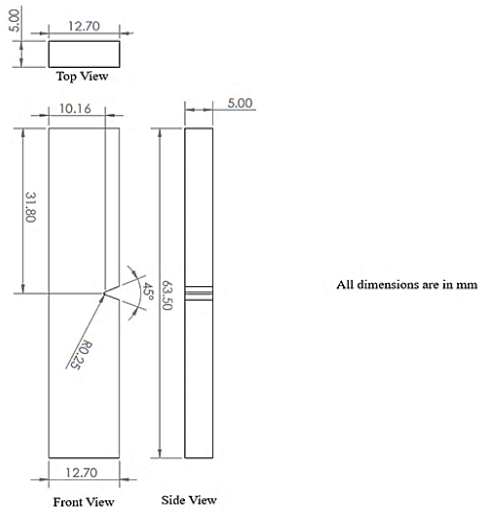
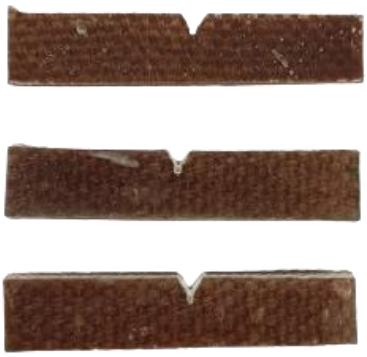


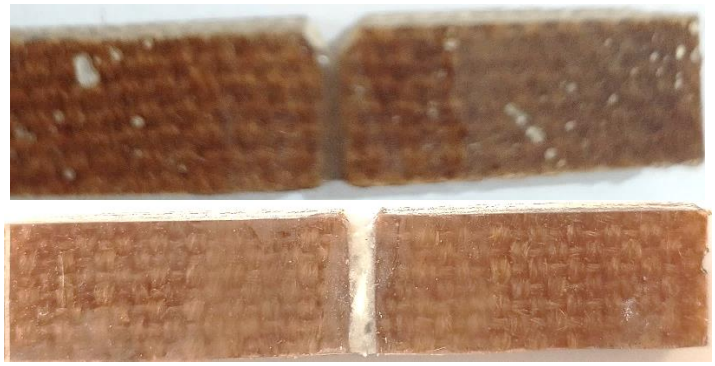
Figure 3.10: ASTM specimens for impact test

Figure 3.11: CNC machine specimen preparation



(a)

(b)



(c)

Figure 3.12: Prepared composite sample (a) pristine sample for impact test, (b) cracked sample for impact test, (c) healed sample

Chapter 4

Data Reductions

4.1 INTRODUCTION

In this chapter, the method for evaluating impact strength for pristine sample, cracked sample and healed sample are explained. Besides, the thermal and physical properties such as Thermogravimetric Analysis (TGA), Fourier-transform infrared spectroscopy (FTIR) are explained.

4.2 IMPACT PROPERTIES

Impact strength is a measure of a material's resistance to damage when subjected to a rapid increase in strain. A material sample of a certain size and configuration is subjected to a rapid load in this test. When a notch, defect, or fracture is present in a material, it usually fails under sudden pressure or impact. The material's impact properties must be investigated in order to understand how it will react under the aforementioned stresses. The impact toughness of a material is measured by the amount of energy absorbed relative to its cross-sectional area when subjected to a high strain rate.

There are two basic types of impact testing methods named Charpy and Izod impact test. In both cases, a simple pendulum with a certain weight strikes the specimens and loses some kinetic energy, from this energy impact strength/toughness is calculated. The fundamental difference between them is, specimen alignment where Charpy conducted horizontal specimen position and Izod conducted vertical specimen position.

In this study, the charpy impact test was done where a V-shaped notch of 2 mm was made at the midpoint of the impact specimens with a notch-tip radius of 0.25 mm. The specimens were then undergone Notched Charpy Impact test (CEAST 9050) compliance to ISO 179 with pendulum

load of 21.3 kg. The impact test was conducted for pristine sample, cracked sample and healed sample. For each case the impact strength was determined and used for healing efficiency evaluation.

4.3 HEALING EFFICIENCY

For self-healing two types of cracks was initiated in two different samples manually with a cutter in the impact specimen along the V-notch, one is 1 mm deep crack and another is 1.5 mm deep crack. After that a self-healing medium was created by mixing microcapsules and catalyst (hardener). The self-healing solution was then kept inside the crack and kept for 24 hours in 40°C for automatic recovery of the crack.

Healing efficiency was measured in terms of impact strength recovery for healed sample. The following equation was used to measure the healing efficiency which is introduced by [111].

$$Healing\ Efficiency\ (\%) = \frac{Impact\ Strength\ After\ Healing}{Impact\ Strength\ of\ Pristine\ Sample} \times 100 \ldots\ldots\ldots\ldots\ldots\ldots (4.1)$$

4.4 FOURIER TRANSFORMATION INFRARED SPECTROSCOPY

Fourier transform infrared spectroscopy (FTIR) is a widely employed method for the identification of functional groups in various materials, including gases, liquids, and solids, by the utilization of infrared light beams. Infrared spectroscopy is a technique used to detect the absorption of infrared radiation by the bonds inside a molecule. This measurement produces a spectrum that is often represented as the percentage of transmitted radiation vs the wavenumber (expressed in reciprocal centimeters, cm^{-1}. A wide variety of materials that possess covalent bonds have the ability to absorb electromagnetic radiation. A certain infrared radiation frequency will be absorbed by a specific bond inside a molecule due to the unique natural vibrational frequency associated with each bond. As an example, the molecule acetic acid (CH_3COOH) consists of several bonds, including C-C, C-H, C-O, O-H, and C=O. Each of these bonds exhibits absorption at distinct

wavelengths and remains unaffected by other interactions. It can be posited that two molecules possessing distinct structures have dissimilar infrared spectra, notwithstanding the possibility of some frequencies coinciding [112]. **Table 4.1** shows different ranges of wavenumbers in particular functional groups.

Table 4.1: Ranges of wavenumbers in particular functional groups [112].

Range (cm^{-1})	**Functional group**
3200–3550	O-H stretching
2500–3000	Carboxylic O-H
3300–3500	N-H stretch, primary amine gives two, secondary one, while tertiary amine gives no peak
3500–3500	O=C-N-H stretch
3500–3500	O=C-N-H stretch
2260–2220	Nitrile (CN)
2950–2850	C-H stretch
3010–3100	=C-H stretch
1620–1680	C=C stretch
1740–1690	Aldehyde C= O
1750–1680	Ketone C = O
1750–1735	Ester C = O
1780–1710	Carboxylic acid C=O
1690–1630	Amide C=O
2800–2700	Aldehyde C-H stretch

Figure 4.1: Perkinelmer FT-IR spectrometer

4.5 THERMOGRAVIMATRIC ANALYSIS

Thermo-gravimetric analysis (TGA) is a commonly employed thermal analysis technique utilized for the examination of the thermal characteristics of materials within a certain temperature range. In this study, SII EXSTAR 6000 TG/DT A6300 thermal analyzer was used to conduct the TGA test. The thermo-gravimetric analysis technique (TG) examines the changes in mass experienced by a substance in response to alterations in temperature. The phenomenon of mass variation often involves a decrease in mass, which arises due to the occurrence of various chemical reactions during the heating process. These events lead to the formation of volatile chemicals. The potential reactions that may occur include combustion, dehydration, decomposition, and others.

TGA analyzed the mass change of the samples from low temperature to high temperature. Here the TGA was conducted with increasing temperature by 5°C in every step from room temperature to 600°C. The mass in the percentage of the sample which remained in the crucible was observed in every step of the temperature. The TGA curves were plotted by Percentage of material that remained versus Temperature. Figure 4.2 shows a thermal analyzer.

Figure 4.2: SII EXSTAR 6000 TG/DT thermal Analyzer

Chapter 5

Results and Discussions

5.1 INTRODUCTION

The present chapter extensively discusses the outcomes of impact strength recovery (healing efficiency) as well as thermal stability of microcapsules and self-healing composite through thermogravimetric analysis.

5.2 HEALING EFFICIENCY

For self-healing two types of cracks was initiated in two different samples manually with a cutter in the impact specimen along the V-notch, one is 1 mm deep crack and another is 1.5 mm deep crack. After that a self-healing medium was created by mixing microcapsules and catalyst (hardener). The self-healing solution was then kept inside the crack and kept for 24 hours in 40°C for automatic recovery of the crack.

Healing efficiency was measured in terms of impact strength recovery for healed sample. The following equation was used to measure the healing efficiency which is introduced by [111].

$$Healing\ Efficiency\ (\%) = \frac{Impact\ Strength\ After\ Healing}{Impact\ Strength\ of\ Pristine\ Sample} \times 100 \ldots\ldots\ldots\ldots\ldots\ldots (5.1)$$

To investigate the healing ability of the composites, impact test was conducted for three specimens which were prepared following the same standard. Impact test was conducted for pristine sample and healed sample. Impact strength is given in **Table 5.1.**

Table 5.1: Impact strength of pristine sample and healed sample

SL	Sample Types	Impact Strength (J/cm^2)
1	Pristine	19.9
2	Cracked (1 mm)	14.2
3	Cracked (1.5 mm)	13.6
4	Healed (1 mm)	16.7
5	Healed (1.5 mm)	15.7

According to equation 5.1 the healing efficiency was found 78.89% for healed sample whose crack was 1.5 mm deep and the healing efficiency was found 83.9% for 1 mm deep crack sample with respect to pristine sample. 1 mm deep crack needs a small amount of healing agent to heal the crack; thus, for the same amount of healing agent for both 1 mm deep crack and 1.5 mm deep crack, 1 mm deep crack appropriately healed and showed higher healing efficiency.

The impact strength of the self-healing composites differs marginally because of the size of the crack. The large size crack shows less recovery than small size crack. **Figure 5.1** and **Figure 5.2 shows** the healing efficiency of healed sample.

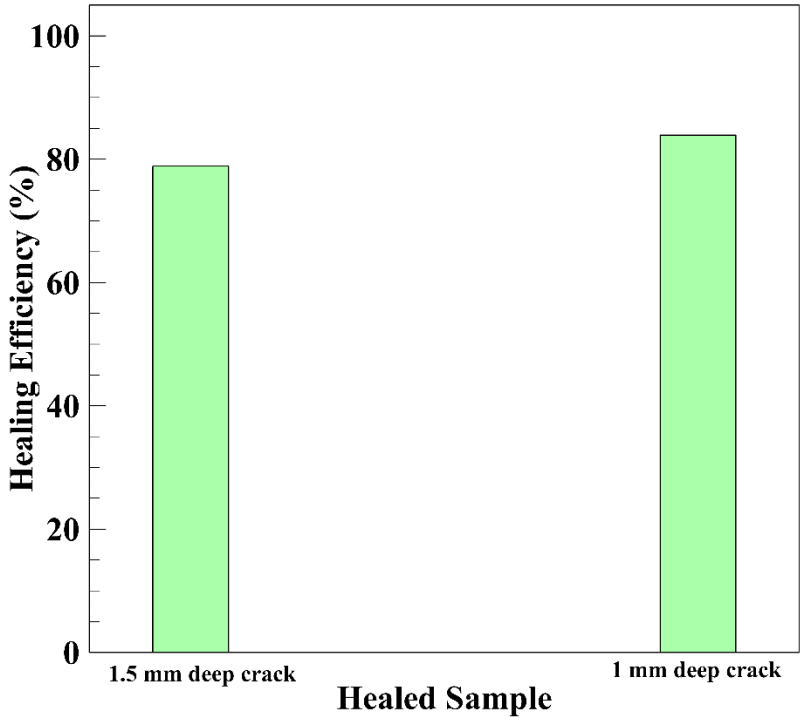


Figure 5.1: Healing efficiency with respect to pristine sample

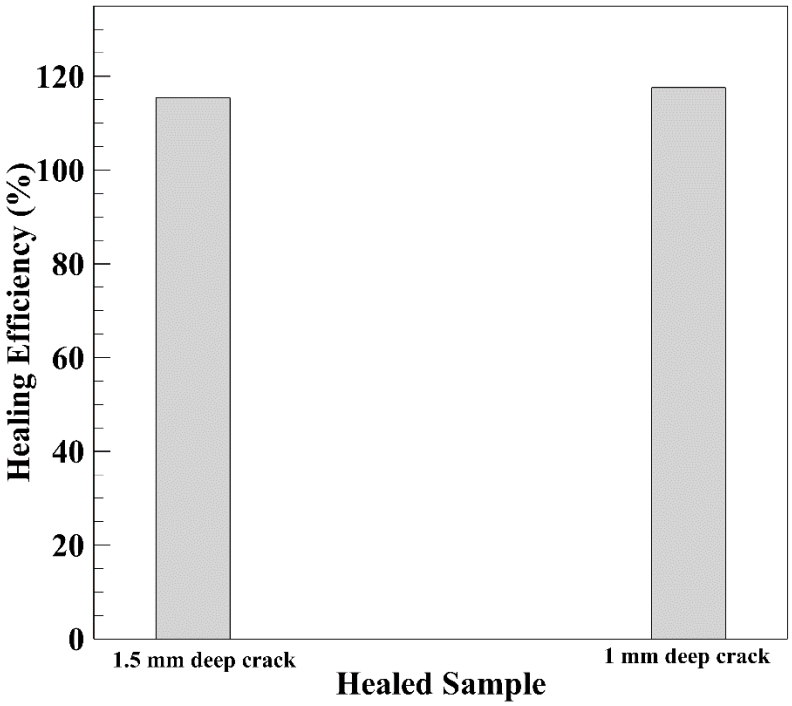


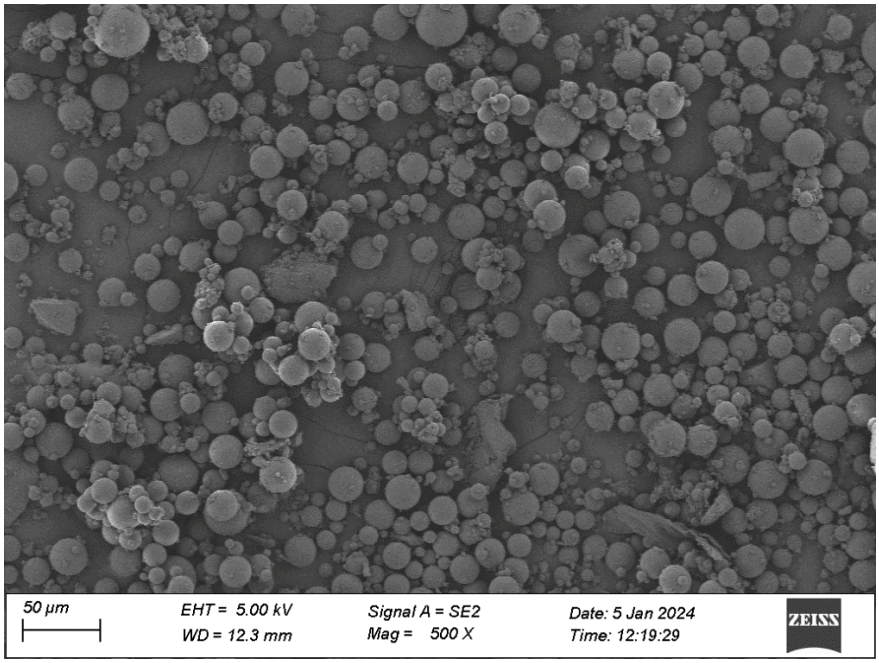
Figure 5.2: Healing efficiency with respect to crack sample

Additionally, according to equation 5.1 the healing efficiency was found 115.44% for healed sample whose crack was 1.5 mm deep and the healing efficiency was found 117.6% for 1 mm deep crack sample with respect to crack sample.

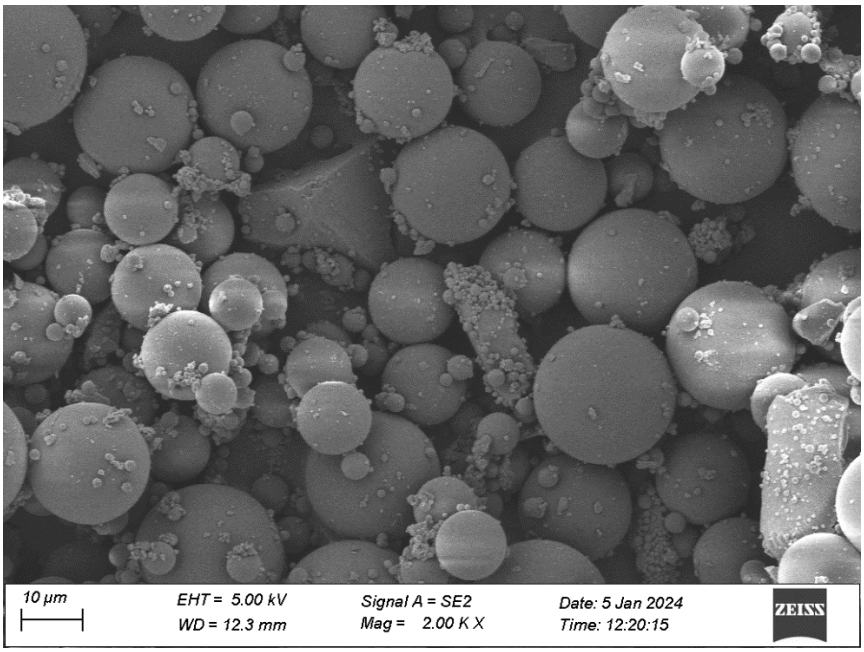
5.3 MORPHOLOGICAL ANALYSIS

5.3.1 Scanning Electron Microscopic Analysis

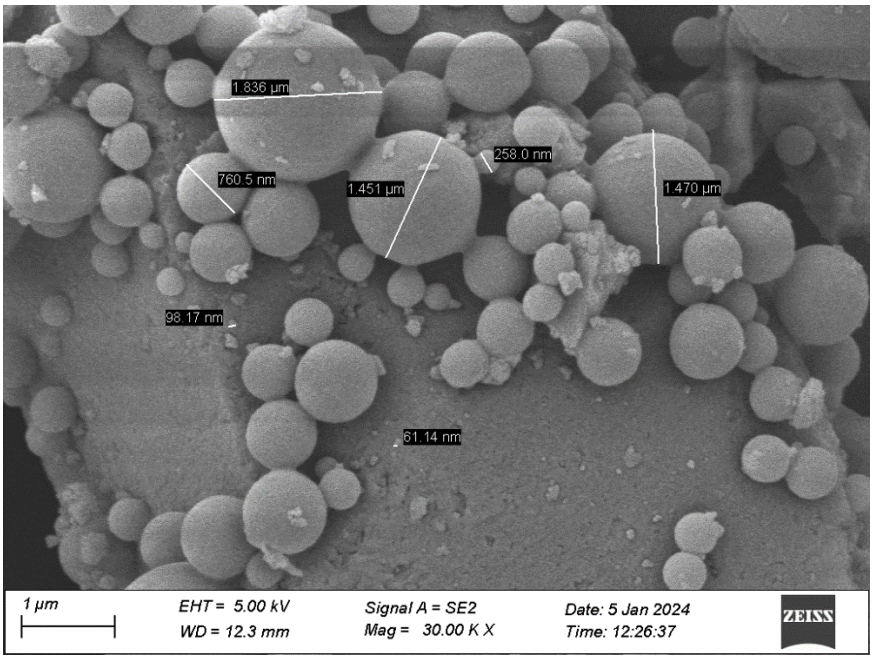
The surface morphology of the prepared microcapsules and microcapsules embedded in composite materials is shown in **Figure 5.3** and **Figure 5.4** respectively. Figure 5.3 and Figure 5.4 illustrates the micrograph of microcapsules and composites at different magnification. From Figure 5.3 (c) it is clearly evident that there are some micro size substances and some nano size substances. The micro size substances are microcapsules and nano size substances are nano silica which used during the microencapsulation process. Figure 5.3 (c) shows that microcapsule size varies from 1.45 µm to 1.83 µm.


50 µm
EHT = 5.00 kV
WD = 12.3 mm
Signal A = SE2
Mag = 500 X
Date: 5 Jan 2024
Time: 12:19:29
ZEISS

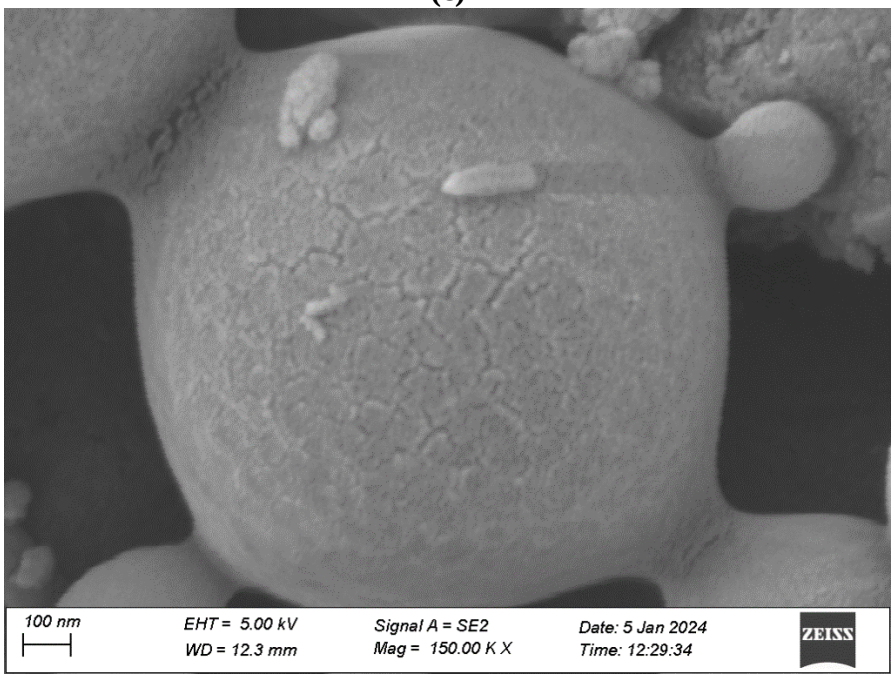
(a)


10 µm
EHT = 5.00 kV
WD = 12.3 mm
Signal A = SE2
Mag = 2.00 K X
Date: 5 Jan 2024
Time: 12:20:15
ZEISS

(b)



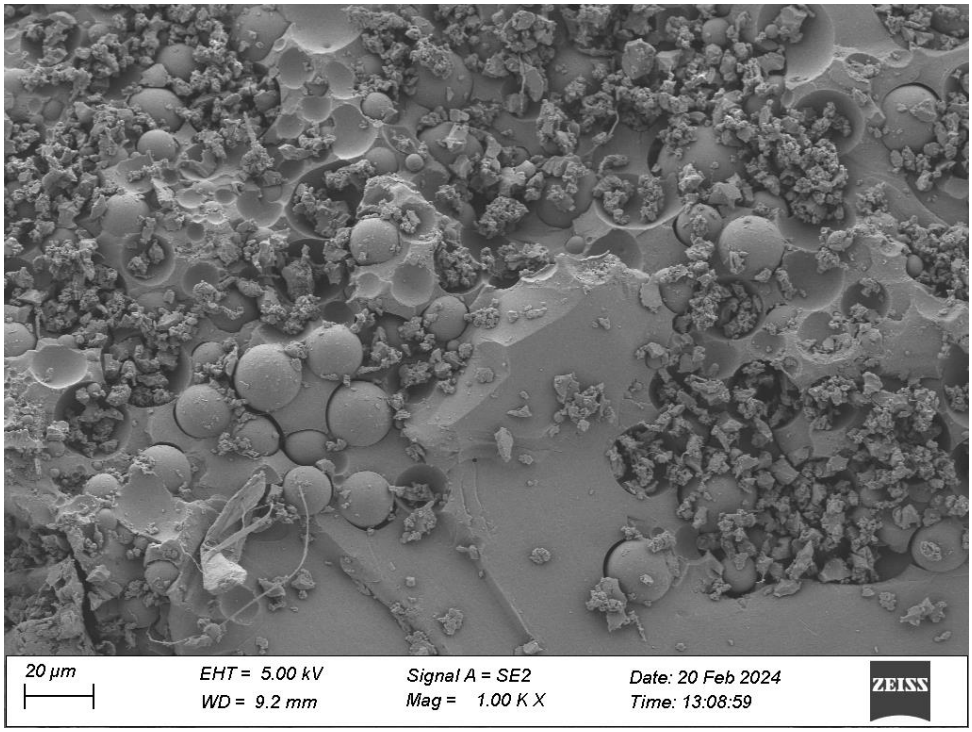
(c)



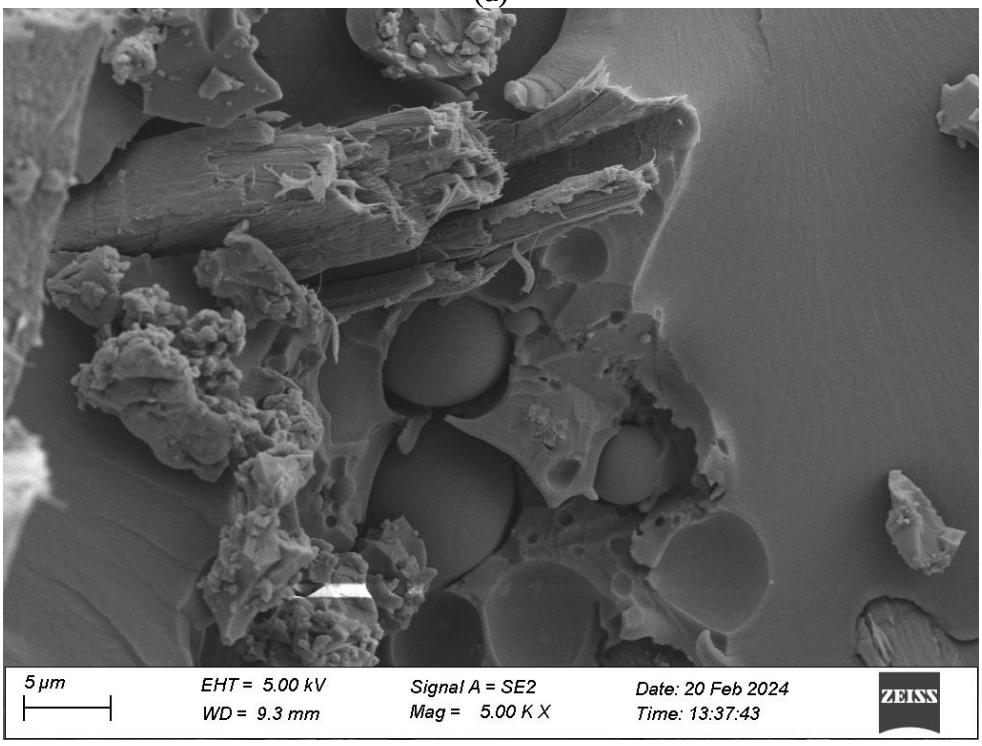
(d)

Figure 5.3: SEM micrograph of prepared microcapsules, (a) 500x magnification; (b) 20000x magnification, (c) 10000x magnification; (d) 30000x magnification, (e) 150000x magnification

Besides there are some agglomerations among microcapsules, this is due to the wet surface of microcapsules.



(a)



(b)

Figure 5.4: SEM micrograph of composite with microcapsules, (a) 1000x magnification; (b) 5000x magnification.

5.3.2 Energy Dispersive X-ray Analysis

Energy dispersive X-ray (EDX) analysis is a commonly used analytical technique in the field of materials science and chemistry. It is utilized to investigate and determine the elemental composition and chemical analysis of microcapsules, particularly those with discernible atomic numbers. **Figure 5.5 and Figure 5.6** illustrates the Energy Dispersive X-Ray Analysis of microcapsules and composite with microcapsules. From figure 5.5 it is observed that there was significant amount of silica. Besides, the presence of nitrogen indicates the presence of diethylene triamine (DETA) which used to synthesize the microcapsule.

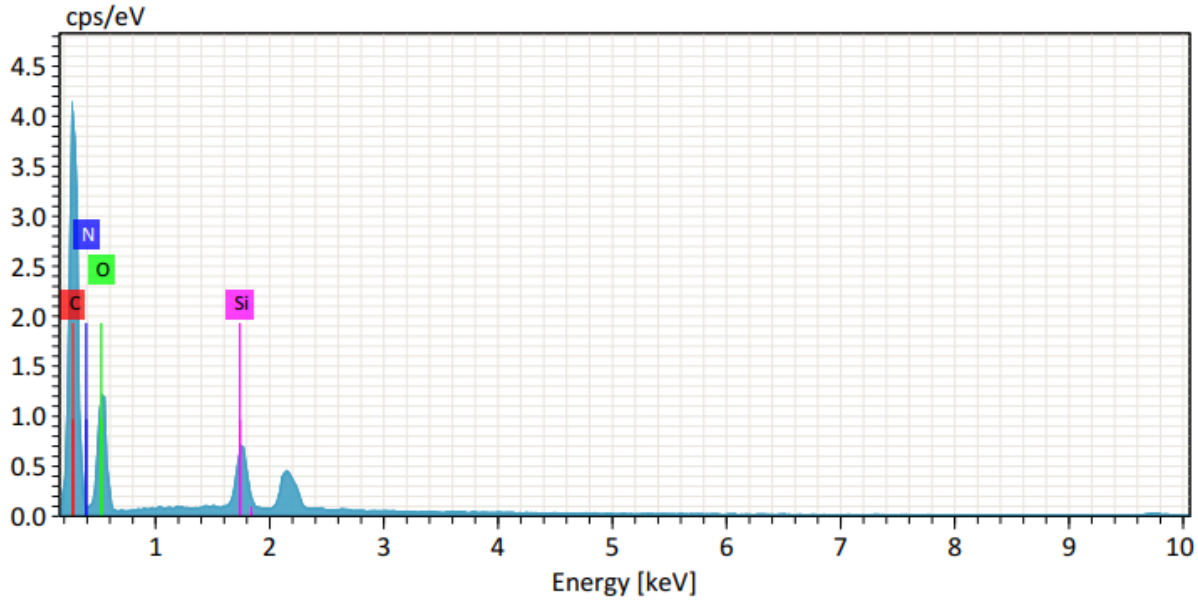


Figure 5.5: EDX micrographs of microcapsules

Figure 5.5 shows all the elements that were present in microcapsules with an additional element that is Na which indicates the presence of NaOH that was used to chemically treat the jute fiber.

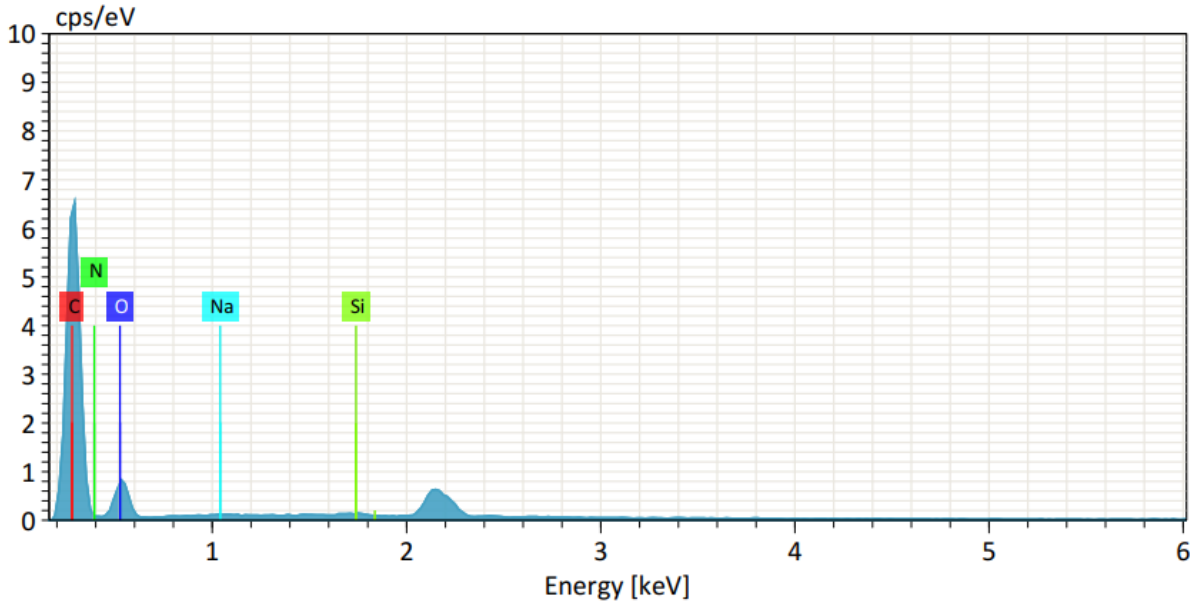


Figure 5.6: EDX micrographs of composite with microcapsules

5.4 Fourier Transformation Infrared Spectroscopy (FT-IR)

In this study, the microstructural properties of the prepared microcapsules and composites with microcapsules were thoroughly examined using FT-IR spectroscopy. The presence of a wide transmission band in the range of 3495-2997 cm^{-1} can be observed in Figure 5.6, indicating the existence of this characteristic in the pure blend is ascribed to the stretching of the hydroxyl groups (OH). It can be seen from Figure 5.7 and Figure 5.8 that the vibration peaks of the C–O–C bond were evident at 1096 and 1015 cm^{-1} which shows the presence of epoxy resin in both microcapsules and composite sample. Si-O-Si stretching bands are found at 1185 cm^{-1}. Stretching bands of C–C and C=C aromatic benzene rings in epoxy resin were obvious at 1591 cm^{-1} and 1435 cm^{-1}. Alkane C-H Stretching present in saturated hydrocarbons such as paraffin oil and pet ether are evident at 3000 cm^{-1}. Amine (N-H) Stretching present in compounds containing amine groups such as diethylene triamine (DETA) are evident at 3340 cm^{-1} and 3329 cm^{-1}. The results show that the microcapsules have been successfully incorporated in epoxy resin.

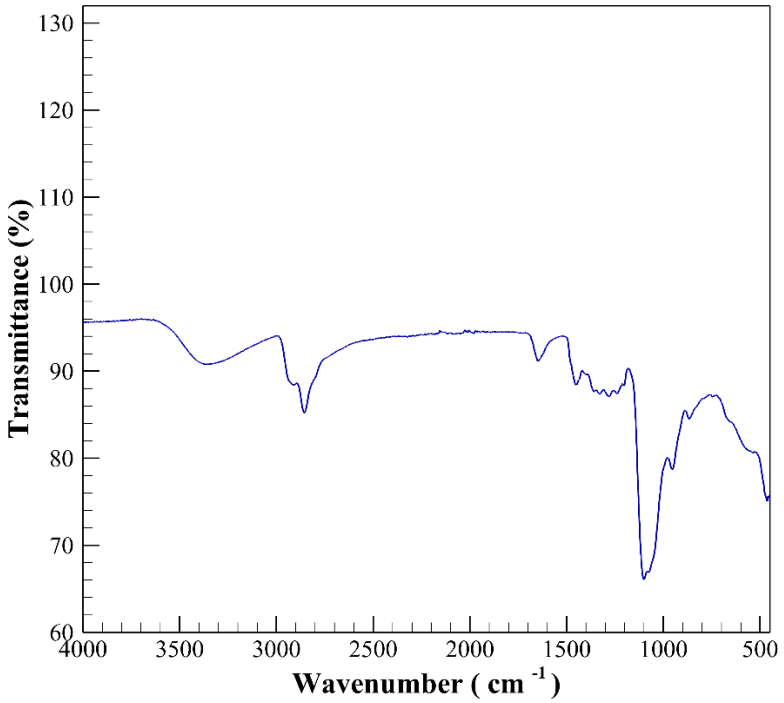


Figure 5.7: The IR spectra of microcapsules

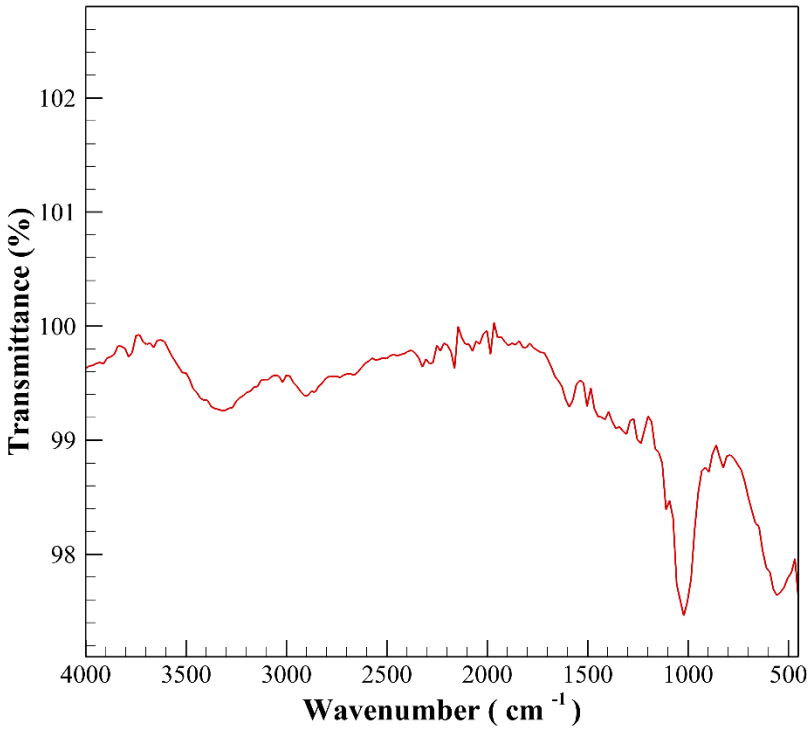


Figure 5.8: The IR spectra of jute fiber epoxy composites with microcapsules

5.5 THERMOGRAVIMATRIC ANALYSIS

Figure 5.9 and Figure 5.10 display the typical curves for Thermogravimetric Analysis (TGA), Differential Thermogravimetric Analysis (DTG), and Differential Thermal Analysis (DTA) of epoxy microcapsules and capsules reinforced self-healing epoxy composite.

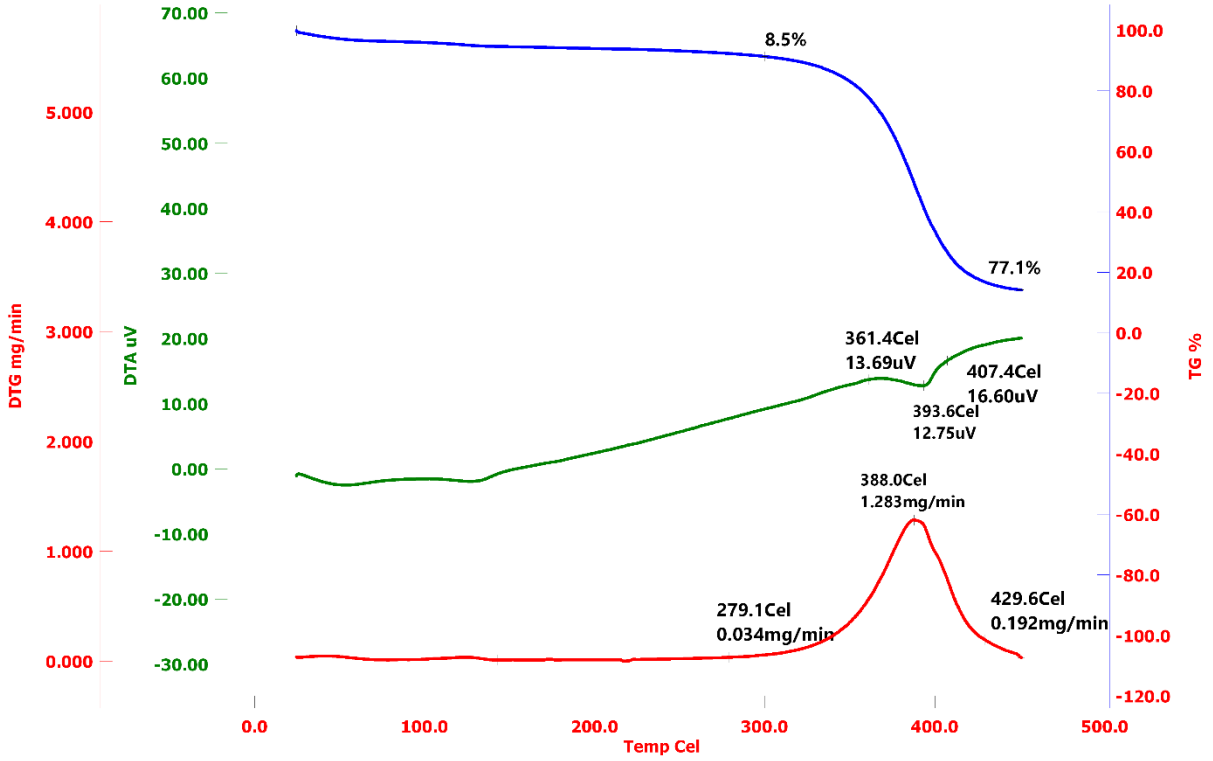


Figure 5.9: Thermal analysis of Microcapsules

Figure 5.9 reveals the distinct three-step decomposition patterns of epoxy microcapsules. Decomposition of epoxy microcapsules is observed in the temperature range of 210°C to 310°C, which is believed to be caused by the degradation of the shell material. Decompositions in the temperature range of 310°C to 420°C and 420°C to 450°C are observed, indicating the degradation of nano silica and epoxy in the capsules, respectively.

From figure 5.10, it is evident that the capsules reinforced self-healing epoxy composite experiences a mass loss of 10.3% during the initial stage of decomposition, occurring between 180°C to 250°C. This can be attributed to the evaporation of water, as well as the hydroxyl groups present in the cellulose structure and other volatile compounds on the fibre surfaces.

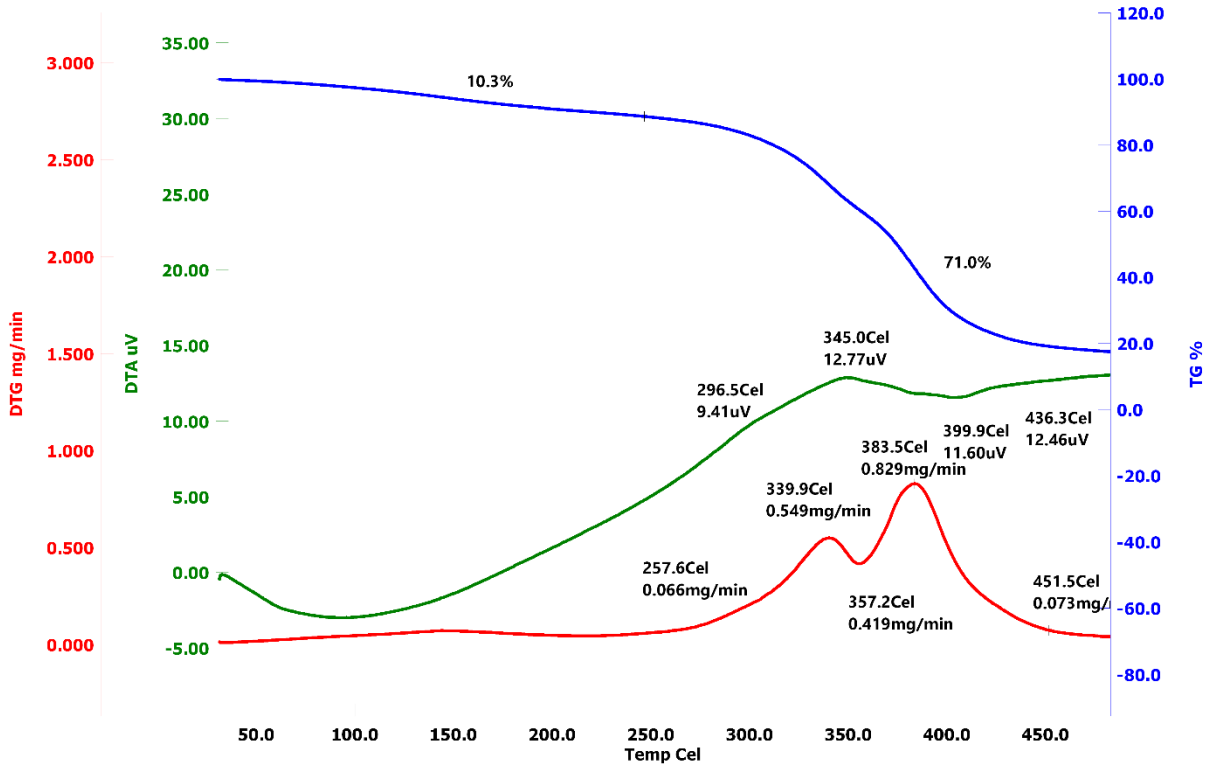


Figure 5.10: Thermal analysis of composite with Microcapsules

In the following stage of degradation, there was a significant decrease in mass observed between temperatures of 250 to 400°C. It is evident that the observed phenomenon is a result of the breakdown of cellulose and hemicellulose. After the initial stages of decomposition, the composites go through a final phase of thermal degradation, usually happening at temperatures of up to 500°C. During this phase, the main component that goes through decomposition is lignin.

Chapter 6

Conclusions and Recommendations

6.1 CONCLUSIONS

The purpose of this study was to synthesize water-insoluble and/or water-soluble epoxy microcapsules containing healing agent and examine the healing efficiency of natural fiber reinforced microcapsule-based epoxy composite. Another aim of this study was to investigate the morphology and physical properties of the microcapsules and microcapsule embedded composite sample. The most challenging aspect of the thesis involved the manufacturing of microcapsules and preparing a self-healing medium so that it can heal a crack. Moreover, the utilization of the vacuum bagging production technique was an additional novel procedure implemented in this thesis, and it was effectively executed. Based on a comprehensive analysis, several conclusions can be drawn:

- Microcapsule and catalyst-based healing medium successfully healed the crack. Healing efficiency was 78.89% for the healed sample whose crack was 1.5 mm deep, and the healing efficiency was 83.9% for the 1 mm deep crack sample with respect to pristine sample. Healing efficiency was found 115.44% for healed sample whose crack was 1.5 mm deep and the healing efficiency was found 117.6% for 1 mm deep crack sample with respect to crack sample.
- SEM analysis clearly indicated the successful manufacturing of microcapsules in the size range of 1.45 μm to 1.83 μm.
- EDX analysis of microcapsules and composite sample showed the presence of nitrogen (N) and silicon (Si) that ensured the use of nano silica and diethylenetriamine (DETA) in preparing microcapsules.
- FTIR analysis revealed the functional groups present in the microcapsules and composite sample. The presence of hydroxyl groups, C–O–C stretching, Si-O-Si bonding, N-H

bonding were the findings of FTIR analysis. The presence of C–O–C stretching in microcapsules and composite sample proved the successful encapsulation of epoxy.

6.2 RECOMMENDATIONS

Based on the results and observations from the thesis, a few recommendations for future works are noted below:

- Microcapsules was synthesized at 500 rpm which can be increased to observe the final microcapsule size as stirring speed affect the microcapsule size.
- Percentage of microcapsules in the composite can be varied to observe the effects of self-healing efficiency. Besides different types of cracks and test method can be employed to observe the self-healing efficiency.
- Thermogravimetric analysis can be done to investigate the thermal stability of the microcapsules and composite.

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