

# **SELF-HEALING POLYMERS**

## **SEMINAR REPORT**

Submitted by

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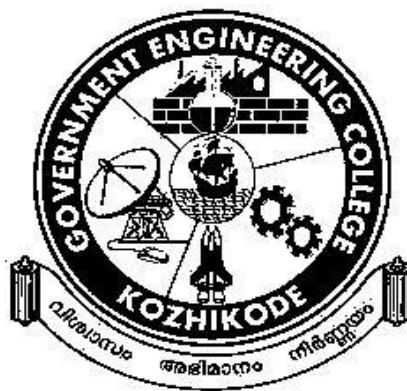
To

the APJ Abdul Kalam Technological University

In partial fulfillment of the requirements for the award of the Degree

of Bachelor of Technology in

*Chemical Engineering*



***Dept. of Chemical Engineering***

*Government Engineering College, Kozhikode*

*November 2023*

## DECLARATION

I undersigned hereby declare that the seminar report “**SELF-HEALING POLYMERS**”, submitted for partial fulfillment of the requirements for the award of the degree of Bachelor of Technology of the APJ Abdul Kalam Technological University, Kerala is a bonafide work done by me under supervision of Dr.Ushakumary E R. This submission represents my ideas in my own words and where ideas or words of others have been included, I have adequately and accurately cited and referenced the original sources. I also declare that I have adhered to ethics of academic honesty and integrity and have not misrepresented or fabricated any data or idea or fact or source in my submission. I understand that any violation of the above will be a cause for disciplinary action by the institute and/or the University and can also evoke penal action from the sources which have thus not been properly cited or from whom proper permission has not been obtained. This report has not been previously formed the basis for the award of any degree, diploma, or similar title of any other University.

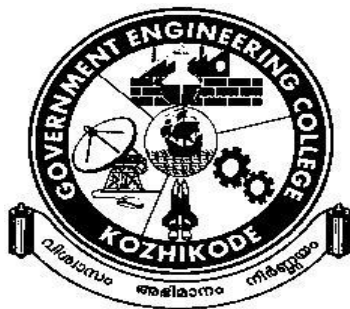
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**CERTIFICATE**

This is to certify that the report entitled  
**“SELF-HEALING POLYMERS”**

Submitted by

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**KKE20CH061**

to the APJ Abdul Kalam Technological University in partial fulfillment of the requirements for the award of the Degree of Bachelor of Technology in Chemical Engineering is a bonafide record of the seminar work carried out by this student under my guidance and supervision. This report in any form has not been submitted to any other University or Institute for any purpose.

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# ABSTRACT

Conventional maintenance and repair methods in structural composites during service are often associated with difficulties and restrictions. These difficulties are prevailed over by the self-healing materials. They are economical and very effective in repairing even Nano-cracks and internal damages without altering their basic properties, and among the materials, polymers are more advantageous in many aspects.

Inspired by the self-healing property of nature, researchers have taken a revolutionary approach to innovating self-healing polymers (SHP) with a range of healing mechanisms, including capsular-based, vascular, and intrinsic self-healing polymers. The development and optimization of self-healing polymers necessitate a robust characterization toolkit, including microscopy techniques (SEM, TEM) for visualizing damage and repair, mechanical testing for assessing mechanical properties, spectroscopic analyses (FTIR, NMR) to probe chemical changes and thermal analysis (DSC, TGA) to investigate phase transitions. Characterization is considered an inevitable tool for elucidating the characteristics and quantifying the self-healing capability of these materials. This seminar briefly summarizes the mechanism and their application in numerous fields with recent advances and mainly focuses on the various characterization techniques.

**Keywords:** self-healing; repair; polymers; characterization; properties.

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## ABBREVIATIONS

1. BDS	- Broadband Dielectric Spectroscopy
2. CFRP	- Carbon Fiber Reinforced Plastic
3. CT	- Computed Tomography
4. CVL	- Crystal Violet Lactone
5. DA	- Diels-Alder
6. DCM	- Dichloro Methane
7. DCPD	- Dicyclopentadiene
8. DSC	- Differential Scanning Calorimetry
9. EMAA	- Ethylene Methacrylic Acid
10. FPR	- Fiber Reinforced Polymer
11. HGF	- Hollow Glass Fibers
12. HIFU	- High Intensity Focused Ultrasound
13. IR	- Infrared Radiation
14. NMR	- Nuclear Magnetic Resonance
15. PAA	- Polyacrylic Acid
16. PBT	- Pressurized Burst Test
17. PCL	- Poly ( $\epsilon$ -caprolactone)
18. PU	- Poly Urethane
19. RF	- Radio Frequency
20. ROMP	- Ring-Opening Metathesis Polymerization
21. SAXS	- Small-Angle X-Ray Scattering
22. SEM	- Scanning Electron Microscopy
23. SENT	- Single Edge Notched Tensile

- 24. SHP - Self-Healing Polymers
- 25. TDCB - Tapered Double Cantilever Beam
- 26. TO - Total Organic
- 27. TRU - Thermoplastic Polyurethane
- 28. UF - Urea-Formaldehyde
- 29. UV - Ultra-Violet
- 30. VSNP - Vinyl Hybrid Silica Nanoparticles
- 31. WAXS - Wide-Angle X-Ray Scattering

# **CHAPTER 1**

## **INTRODUCTION**

Imagine a future where cracked smartphone screens repair themselves, where the wings of an airplane can mend minor damages in mid-flight, and where the durability of everyday objects is vastly extended. This vision of a self-repairing world may seem like science fiction, but it is becoming a reality, thanks to the groundbreaking field of self-healing polymers. In the present world where sustainability and resource conservation are considered to be of paramount importance, self –healing materials have emerged as a game-changer by autonomously repairing damages, enhancing product longevity along with the reduction in waste generation thereby providing a sustainable and resourceful future.

Self-healing materials are those smart materials that after being damaged can repair itself without any human invention. It is an artificially made nature-inspired material that can extend the service life of the product while maintaining or enhancing its functionalities. In the last century, polymers have become basic materials in everyday life for products such as plastics, rubber, films, textiles, and paints. This enormous demand has created a need to extend the reliability and maximum service life, and a new design class of polymeric materials is being envisioned that can recover functionality after damage or fatigue. These polymeric materials can be divided into two groups based on the self-healing mechanisms: intrinsic or extrinsic. Intrinsic SHPs are innate reversibility-based compounds that can heal the damage by increasing the mobility of polymeric chains temporarily. On the other hand, extrinsic type self-healing is triggered by the incorporation of exogenous agents which then help for self-healing from embedded microcapsules on cracking (S.An et., 2018).For the researchers to improve and enhance the performance of a self-healing polymer, characterization techniques are considered to be inevitable as they provide a means to analyze and understand the fundamental properties

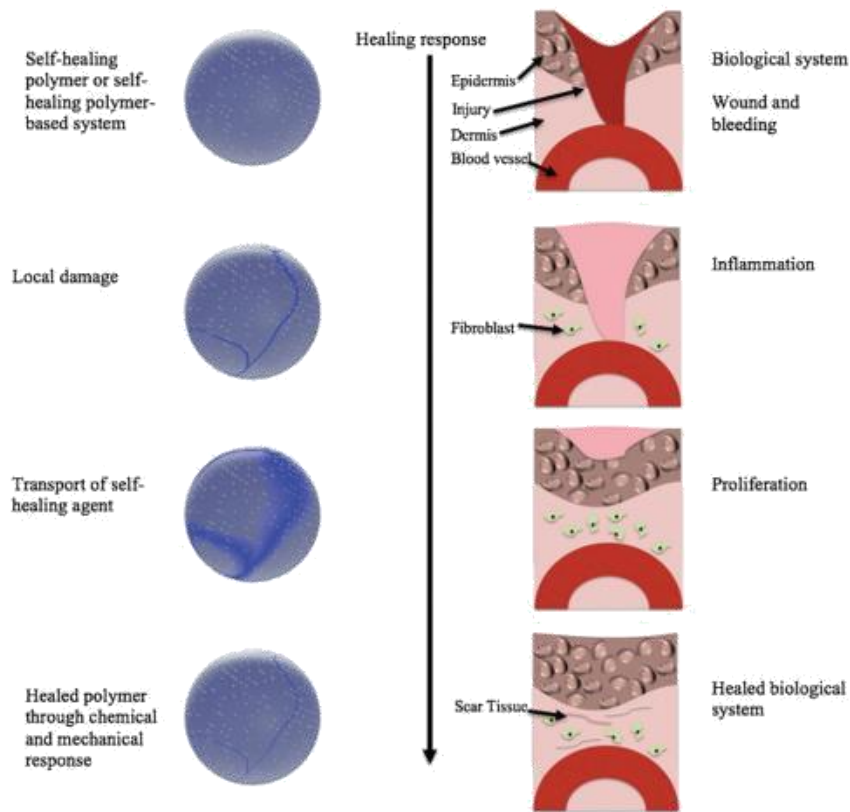
and mechanisms governing these materials' self-repair capabilities. These are several characterization techniques such as mechanical, imaging, spectroscopic, scattering, thermal and rheological techniques.

In this seminar report, we delve deep into the characterization techniques of self-healing polymers and shall explore the underlying principles, mechanisms, recent advancements and potential applications of these remarkable materials. Additionally, we will examine the challenges and prospects that lie ahead in the exciting journey of self-healing polymer research.

## **CHAPTER 2**

### **SELF-HEALING POLYMERS**

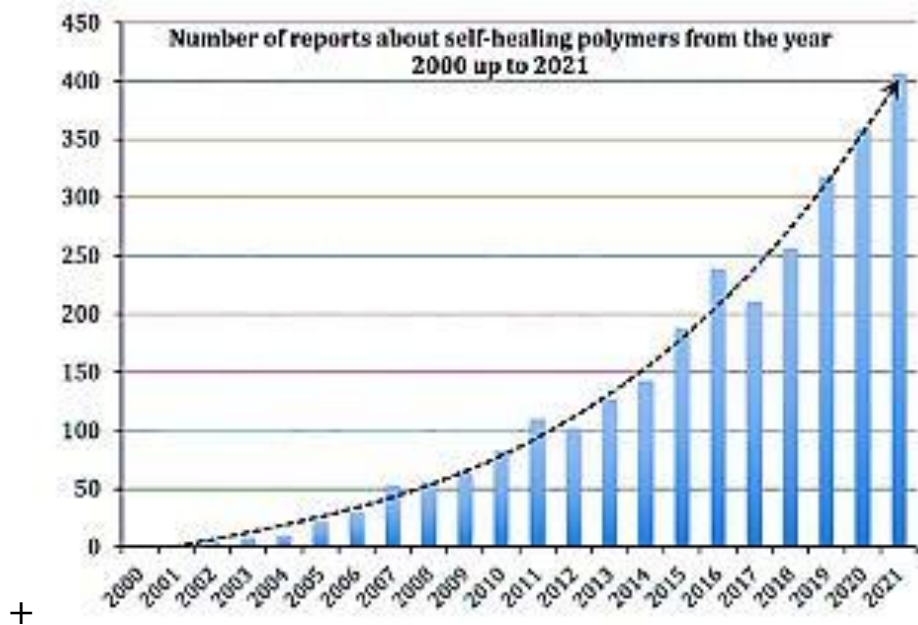
This chapter gives a basic understanding of the topic and its evolution overtime. Materials are often susceptible to fatigue, weaknesses and damage after being exposed to stress and long-term use. These can affect the durability of the material which is why researchers have developed self-healing polymers as a life-changer. Nature has the capacity for self-healing by nature. Researchers have historically innovated new types of materials by imitating nature. Researchers have developed a novel method for treating damage-related losses using self-healing polymers (SHPs) through this practice. Self-healing can be defined as the capability of material to replenish from its own damage or crack without any external help. Among several materials, self-healing polymeric systems are considered advantageous. This is a result of the self-healing polymers' excellent ability to restore component attributes over three basic stages; which are (1) triggering, (2) the healing material is transported to the damage site, and (3) remodeling by the chemical repair process (Dhanasekaran et.,2018). Figure 2.1 shows the basic principle behind self-healing process of a polymer that heals through similar pathways as biological systems.



**Figure2.1:** Healing response by self-healing polymers in comparison to self-healing found in biological systems (El Choufi et al.,2022).

The first demonstration of self-healing in synthetic systems occurred in 1993 using a polymer composite embedded with a single hollow fiber filled with a healing agent (C.M. Dry et al., 1993). When a micro-crack occurs on the surface of the fiber and its corresponding polymer composite, the healing agent, which is a non-reacting adhesive or an air curing agent, leaks and closes the crack. Figure 2.2 shows the development of self-healing polymer based system over the years. The potential of self-healing polymers lies in increasing service life, their repeated use, decreasing the time and cost of maintenance, increasing overall safety, as well as enabling the autonomous healing of parts in remote locations. Furthermore, self-healing polymers can play a crucial role in lowering environmental pollution associated with the use of polymers, as the polymers can regain their functionality after being damaged instead of being replaced. In a future dictated by

global health and climate crises attributed to industrial production along with finite resources, self-healing polymers have a far-reaching scientific and social consequence on how we produce, use, and introduce synthetic polymers into our lives [El Choufi et al.,2022].



**Figure2.2** : Number of articles indexed by Scopus whose titles, abstracts, or keywords include the following terms (“self-healing polymer”) or (“self-healing coating”) or (“healable polymer”) or (“autonomic self-healing”) or (“Self-healing composite”) or (“self-healing” AND “ionomer”) or (“self-healing” AND “microcapsule”) or (“self-healing polymeric”) or (“vascular self-healing”) or (“self-healing” AND "polymer composite") (S.R.White et al., 2001)

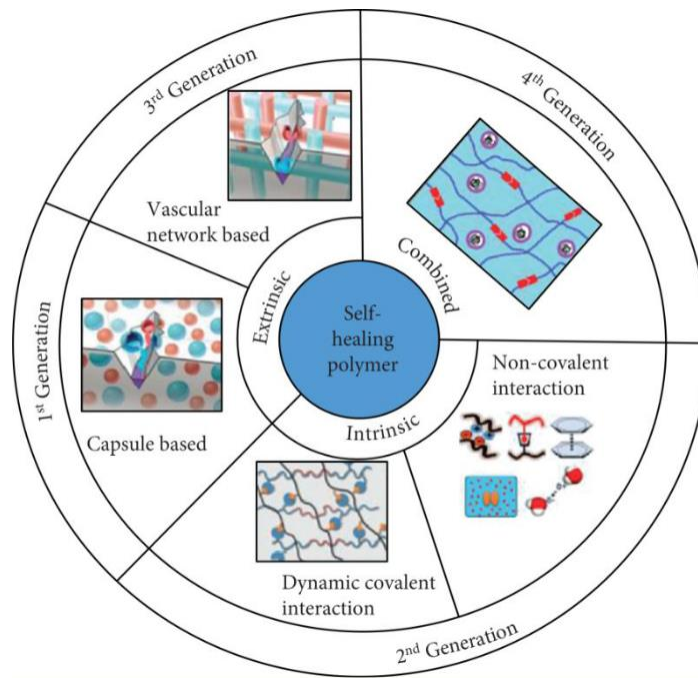
## **CHAPTER 3**

### **MECHANISM OF SELF-HEALING POLYMERS**

Chapter 3 deals with the mechanism behind the synthesis of self-healing polymers. To explain its mechanism is of paramount importance as it provides crucial insights on how these materials respond to damage and repair themselves. These can thereby help researchers to tailor the characterization techniques to improve their performance and efficiency.

Based on the strategies exploited to achieve self-repair, polymers are generally grouped into intrinsic and extrinsic self-healing systems. Intrinsic self-repair is achieved by the synthesis of smart polymers containing functional groups with inherent ability to reversibly polymerize or cross-link their bond in the presence of a stimulus like light or heat (Blaiszik BJ et al., 2010) and by so doing act as healing agents. The processes for obtaining extrinsic self-healing include (a) embedding microcapsules containing curable healing agents into polymer networks; and (b) incorporation of healing agents into polymer networks via micro-vascular channels (Madara S R et al., 2018 ; Bekas D G et al., 2016). The generation and classification based on the mechanism of self-healing polymeric system is as shown in figure 3.1.





**Figure 3.1:** Generation and classification based on the mechanism of SHP (Md. Wasikur Rahman et al., 2021)

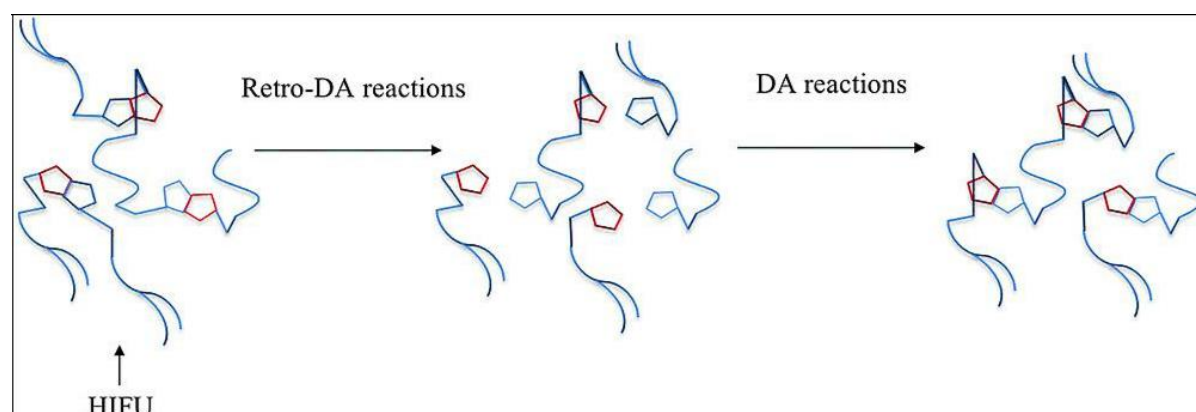
### 3.1 INTRINSIC SELF-HEALING POLYMERIC SYSTEM

Intrinsic self-healing materials do not require the addition of healing agents since healing occurs through their bond reversibility in the polymer (B Jony et al., 2019; A J Garcia et al., 2014). The reversible nature differs between each material and the intrinsic self-healing mechanism has been classified into five different categories: reversible reactions, dispersed thermoplastic, ionomers, supra-molecular material, and molecular diffusion. Intrinsic self-healing mechanism can be stimulated in various ways including ultraviolet (UV) light, temperature, or static load followed by a process of restoration of the chemical or physical bond strength upon stimulus removal.

#### 3.1.1 Intrinsic Healing Based on Reversible Reactions

The self-healing mechanism is enabled by the reversible change of the monomeric state to the cross-linked polymer state with the addition of energy. The first developed polymer composite matrix in 2002 incorporated the Diels-Alder (DA) and retro-Diels-Alder (r-DA) reactions and

since then the thermally aided DA reaction has been one of the most extensively studied intrinsic self-healing systems (X Chen et al., 1998). These reversible reactions occur through dynamic covalent bonds and even after polymerization, these covalent polymers can reform their chemical structure under certain stimuli thus enabling self-healing property and can often exhibit shape memory abilities as well. These reaction mechanism offer greater advantage as the cycle of healing sequence can be theoretically repeated indefinitely. An advancement in this field was the presentation of novel polymers of poly( $\epsilon$ -caprolactone) (PCL) based polyurethane (PU) networks with DA bonds that exhibit shape memory and self-healing mechanisms in response to the ultrasound as shown in **Figure 3.2** using high intensity focused ultrasound (HIFU) (X.Lu et al., 2014)

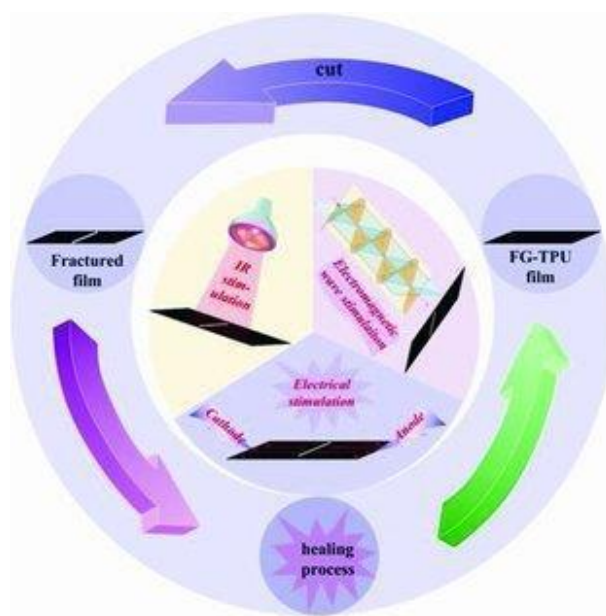


**Figure 3.2:** Schematic illustration of the concept for memory-assisted healing via ultrasound (X.Lu et al., 2014)

### 3.1.2 Intrinsic Healing Based on Thermoplastic Dispersion

Thermoplastic dispersion refers to a system where thermoplastic polymers are dispersed or distributed within a medium, often a liquid, in a homogenous or heterogeneous manner. As thermoplastics have the ability to melt and recast indefinitely, these are integrated into thermoset so that the thermoplastics melt and distribute into the cracks or fracture thereby joining the adjacent composite surfaces providing a self-healing polymer. Thermoplastics can

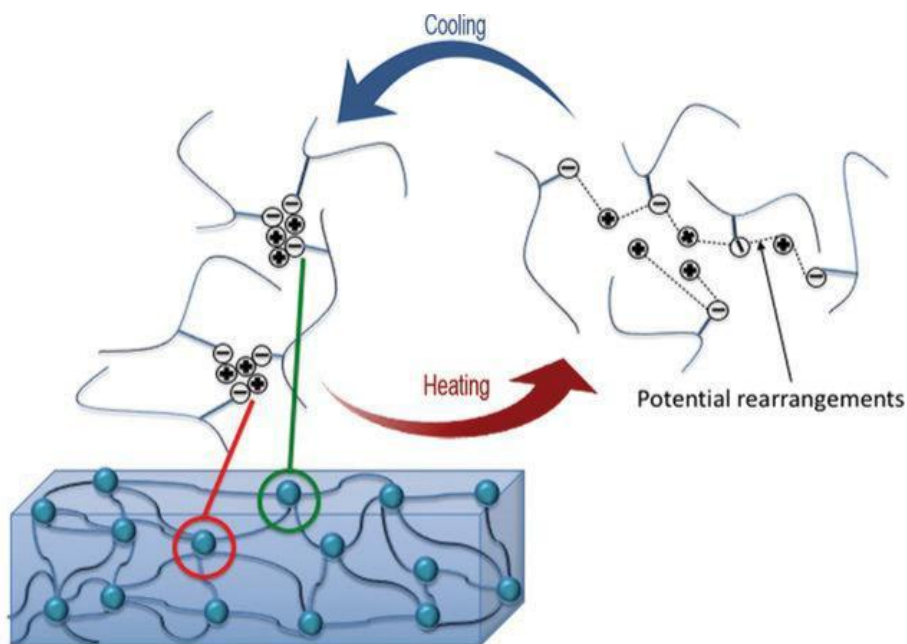
be employed in shapes like fibers, particles, or spheres by heating to a temperature at or above the melting point of thermoplastic. These mixtures have the ability to continually repair damaged areas after they have already healed, in addition to being able to shut macroscopic flaws. Hayes et al., have worked extensively on this topic and the selected thermoplastic poly(bisphenol-A-co-epichlorohydrin) in epoxy resin would regain 70% of its virgin properties (S.A Hayes et al., 2007). This mechanism has extended beyond the thermoset with thermoplastic dispersion and has been used widely in other fields. Most recently it was incorporated in glass fiber reinforced polymer (FRP)-dispersed with magnetic polyamide-6 (PA-6) nanocomposite (PNC) that yielded 84% tensile recovery (R.Gupta et al., 2019). A polymer fabricated from Veriflex polystyrene with dispersed thermoplastic particles leads to healable repeatability of up to 5 cycles before becoming inefficient and a near-total recovery of 65% of the bending load (J.Niji and G.Li, 2010). Another study enhanced few-layered graphene (FG) with dispersed thermoplastic polyurethane (TPU) (L Huang et al., 2013) as shown in figure 3.3. Due to graphene's capacity to absorb Infrared radiation (IR) and electromagnetic waves, the FG-TPU self-healing material was able to heal repeatedly through IR light, electromagnetic waves, and electricity with healing efficiencies higher than 98% .



**Figure 3.3:** Few-layered graphene with dispersed thermoplastic polyurethane (L Huang et.al., 2013)

### 3.1.3 Intrinsic Ionomeric Healing

Ionomers are repetitive units of both electrically neutral molecules and a portion of ionized molecules. They are ion-containing co-polymers. The synthesis of ionomers occurs as a two-step process; initially the non-ionic monomer is copolymerized with the acid-containing monomer and then, metal salts are introduced, either in solution or added to a polymer melt, and ionic pairs form with the metal cations. As a polar ionic pair attracts each other and forms aggregates rich in ionic material. As seen in Figure 3.4, heating causes the aggregate formation's effective crosslinks to lose their attraction, allowing the chains to migrate and self-heal small damage spots and fissures. Ionomers behave like elastomers while they are at room temperature, but when temperatures are raised, they can flow and take on the characteristics of thermoplastics.



**Figure 3.4:** On the right-hand side, the aggregate is shown with the ionic pairs in the center and non-polar chains moving outwards. The healing cycle is correlated to a heating/cooling cycle, as a crack occurs the heat increases and a new ordering of the aggregate occurs as the chains have a greater ability to move, eventually healing the crack as it cools down, and the aggregates reassemble (El Choufi et al., 2022).

Poly(ethylene methacrylic acid) (EMAA) neutralized with various cations was tested as an intrinsic self-healing polymer by conducting multiple types of damages including sawing, cutting, and puncturing (S J Kalista et al., 2007). A razor blade cut or a nail driven through the films did not cause any visible healing for different film thicknesses. The two parts, however, self-bonded to one another after cutting because sawing produced a significant quantity of heat. The fact that successful healing occurred during projectile testing further demonstrated that the healing process has a favorable link with heat. Ionomers subjected to projectile testing have a self-healing mechanism that depends on the pellet heating the sample during puncture. The rise in temperature enables ionic cluster reorganization and their potential rearrangement, which may close the injured spot.

### **3.1.4 Supra-molecular Polymers**

Supra-molecular polymers are formed by the reversible non-covalent interactions between monomeric units. Interactions in supra-molecular polymers include van der Waal forces, hydrogen bonding,  $\pi$ - $\pi$  interaction, metal coordination, and host-guest interactions (T. F. A. de Greef et al., 2009; A W Bosman et al., 2004). The advancement of supra-molecular chemistry and its incorporation into nano-composite materials are the results of these interactions, which enable supra-molecular polymers to show self-healing capabilities thereby influencing the mechanical characteristics and self-healing efficiency. In the majority of cases, carboxyl groups on the polymer side chain play a very important role in forming supra-molecular self-healing materials. Carboxylic groups can take part in electrostatic interactions, hydrogen bonding, and the synthesis of metal complexes. The hydroxyl and carbonyl groups can also combine to produce carboxyl cyclic dimers, which can function as both proton donors and acceptors at the same time. In order to create a polyelectrolyte with excellent stretchability, self-healing, and ionic conductivity, vinyl hybrid silica nanoparticles (VSNP) and polyacrylic acid (PAA) dual cross-linked by hydrogen bonds were used. The films demonstrated approximately 100%

mechanical self-healing efficiency across all 20 healing cycles (Y Huang et al., 2015).

### **3.1.5 Intrinsic Healing by Molecular Diffusion**

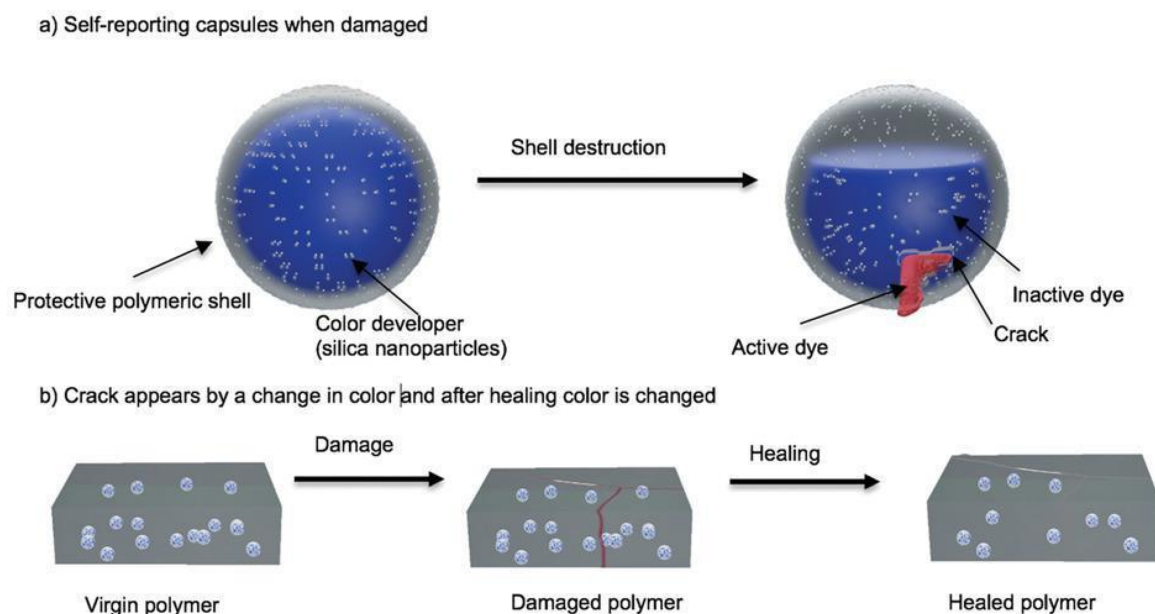
Another method of intrinsic self-healing involves molecular inter-diffusion resulting in polymer-polymer chain entanglement at the crack surface. Dangling chains, mainly seen in weak gels, become the sites of entanglement as they are able to diffuse over longer distances compared to chains in permanent networks that do not allow macroscopic rearrangement. The backbone of self-healing through inter-diffusion is based on Prager et al.'s 1981 work that developed an analysis for the welding process, which occurs when two pieces of the same amorphous polymer are brought into contact at a temperature above the glass transition. The junction surface gradually recovers until it blends in with the bulk polymer after extremely long contact durations. However, this method is not considered efficient due to longer period and the need to reach the glass temperature phase.

## 3.2 EXTRINSIC SELF-HEALING POLYMERIC SYSTEM

### 3.2.1 Capsular-based Self-Healing Polymers

In capsule-based self-healing mechanism, the healing agent is incorporated in a microcapsule which upon damage bursts and the healing agent flows out to react with a catalyst that is embedded in the polymer to fill and heal in the crack. This mechanism was first suggested as a self-healing technique for polymer matrix by White et al. based on the ring-opening metathesis polymerization (ROMP) of dicyclopentadiene (DCPD) via Grubbs' catalyst. Microcapsules with urea-formaldehyde (UF) shell filled with DCPD were dispersed into epoxy matrix with Grubbs' catalyst and the addition of microcapsules and catalyst increased the toughness of the epoxy. When a crack occurs, DCPD leaks out and polymerizes when it comes in contact with the catalyst thereby closing the crack surface. After DCPD loaded microcapsules were successful, several additional research teams adopted the same strategy. In order to monitor the healing cycle of the capsular-based self-healing polymer, a colorant like crystal violet lactone (CVL) was added as shown in figure 3.5 (M Hu et al., 2018). When damage occurs, the capsule break and initially the colorless CVL comes in contact with the silica particles outside the capsule. Color then appears as a result of the reversible opening of the lactone rings owing to a reaction with silica. With the use of various self-healing polymers, the colored damage can be removed while simultaneously returning the dye to its natural colorless state. Color changing allows the healing process to be monitored and the condition of the material over time can be assessed. The ability of the dye to switch back and forth between its active (colored) and inactive (not colored) states, as shown in Figure 3.5 b), is essential for monitoring both the damage and the healing process. This is accomplished when the dye interacts with the color developer when the capsule is broken and changes color while the color is deactivated by the

healing process.



**Figure 3.5** a) Scheme of damage self-reporting capsule through shell destruction and sequestering dye and b) indication of the healing scheme through color development. (M Hu et al., 2018).

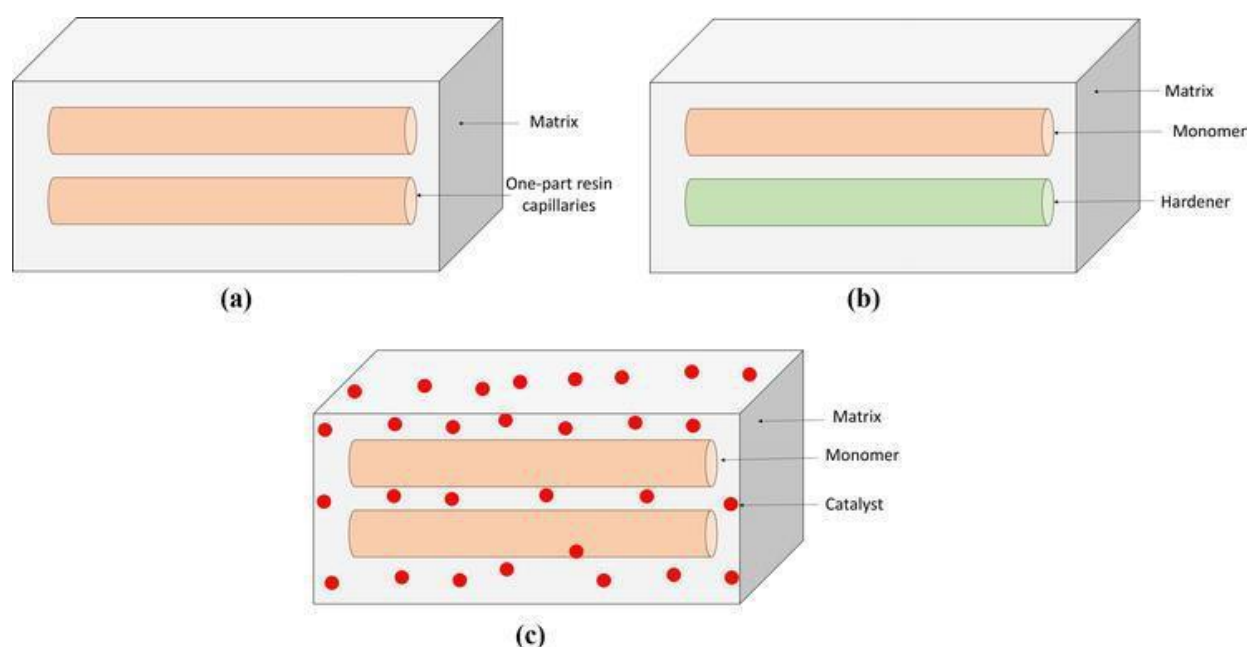
### 3.2.2 Vascular-based Self-Healing Polymers

In this system, the healing agents are encapsulated into capillaries like hollow fibers or hollow tubes and the catalyst is dispersed within the polymer matrix and the resin and the hardener can be encapsulated separately in different capillaries. The damaged areas are recovered when the capillaries break and healing agents flows to micro-crack surfaces. Due to the interconnected vascular network, it can be uni-dimensional, bi-dimensional, or a 3-dimensional network-like structure. In addition, in addition to working as a healing agent container, the vascular networks also act as reinforcement for the polymeric matrices .

Williams et al. used hollow glass fibers (HGF) as storage vessels for a healing agent, infused with a two-part epoxy system and inserted into carbon fiber reinforced plastic (CFRP) beforehand lay-up lamination (Williams GJ et al., 2009). The CFRP showed the ability to



restore compressive strength after low velocity impact damage. Mohammed et al. investigated the self-healing efficiency of a glass fiber/epoxy composite containing microvascular channels, fabricated with polyimide wires. The hollow channels were filled with a three-part healing agent, and after damage, the healing was activated by heating at 130°C for 30 minutes. Healing efficiencies above 50% were reported under tensile and flexural loadings. Radovic et al. investigated the influence of solvent on the stability of the Grubbs' catalyst and the healing efficiency of glass fiber/epoxy composites with embedded filled glass capillaries. Results showed that samples with DCM solvent showed 60% recovery of impact strength after healing, while samples with TO solvent exhibited 51% recovery.



**Figure 3.6** a) One-part resin system, b) resin and hardener encapsulated separately and c) encapsulated resin with dispersed catalyst for vascular network self-healing system (Azevedo do Nascimento, 2022).

## **CHAPTER 4**

### **CHARACTERIZATION OF SELF HEALING POLYMERS**

Characterization techniques in the realm of self-healing polymers are a fundamental toolkit utilized by researchers and scientists to unravel the remarkable properties and behaviors of these innovative materials. These techniques enable a detailed examination of self-healing mechanisms, structural composition, mechanical strength, thermal stability, and other essential characteristics that define the efficiency and applicability of self-healing polymers. By employing a diverse array of specialized methods, scientists gain valuable insights into how these polymers can autonomously repair damage and restore their original properties, resembling the remarkable healing capabilities observed in biological systems.

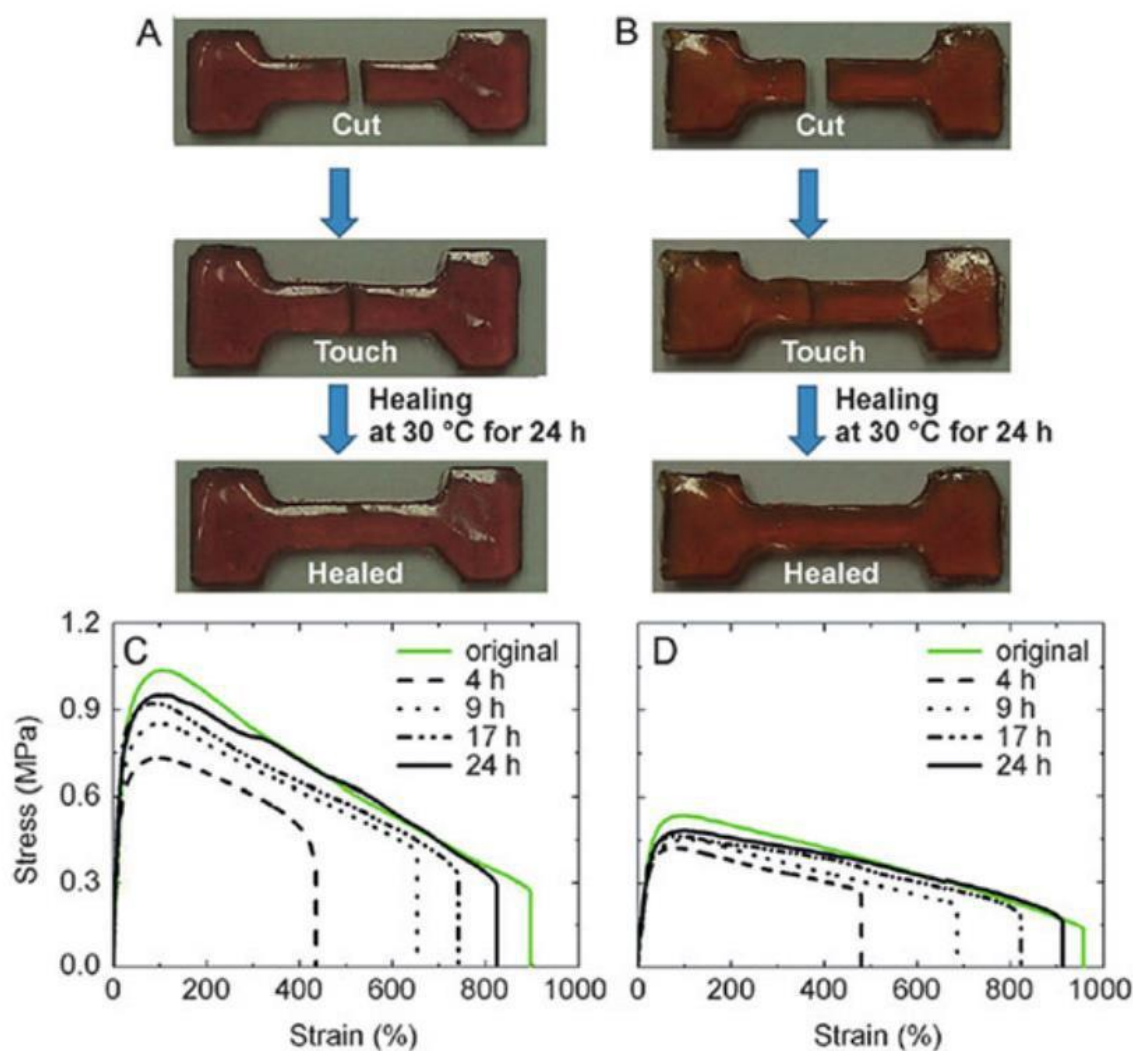
#### **4.1 MECHANICAL CHARACTERIZATION**

##### **4.1.1 Tensile Testing**

A common method for figuring out a material's quasi-static mechanical properties is tensile testing. It provides the opportunity to calculate several parameters as a function of temperature, time, and strain rate, such as tensile strength, tensile stress, elongation, or Young's modulus. It needs specimens that are uniformly rectangular or dog-bone shaped. In order to determine the effectiveness in self-healing, the original and sample material is to be placed under same testing conditions. In the tensile testing procedure for characterizing self-healing polymers, standardized samples of the polymer are securely clamped in a testing machine. The machine then applies a controlled force, gradually stretching the sample until it breaks, allowing measurement of properties like ultimate tensile strength, yield strength, and elasticity, offering crucial insights into the material's mechanical behavior and healing capabilities.

Even though it offers fast first order approximation, this method is not considered ideal as simple comparison of the failure load after damage and healing with that of the virgin material

is incomplete and often misleading, even more so if the damage itself is not quantified and perfectly reproducible. However, this method helps us to crudely assess the time-dependence of the healing process. For example, Binder and coworkers studied tensile failure of polymers with reversible hydrogen bonding groups and demonstrated the progress of the healing process at 30<sup>0</sup>C as a function of time (fig 4.1) (Chen S et al., 2015).



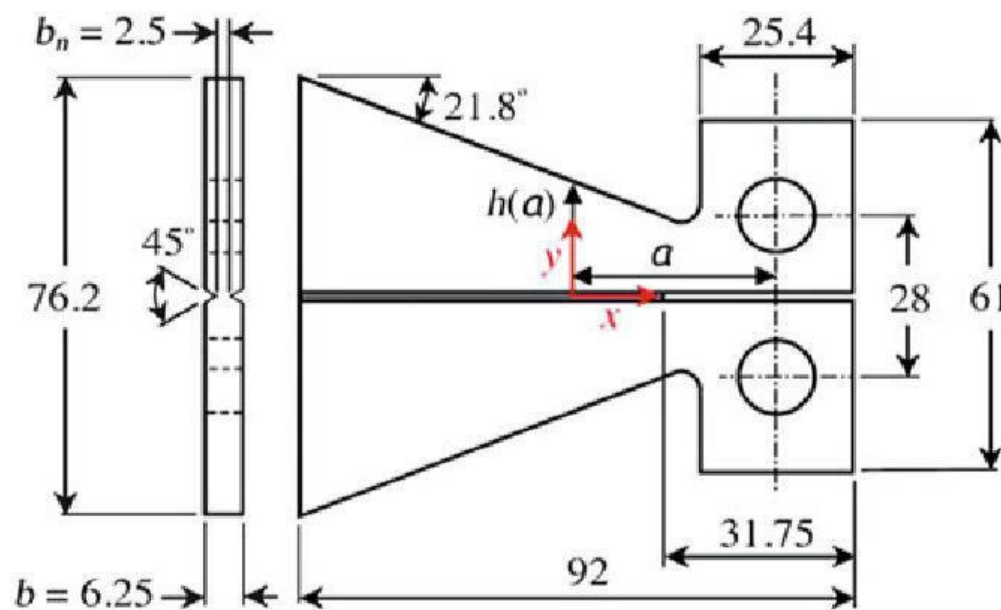
**Figure 4.1.** Two self-healing block polymers based on hydrogen bonds: V-shaped polystyrene-blockpoly(n-butyl acrylate) (left) and H-shaped polystyrene-block-poly(n-butyl acrylate) (right). (a, b) Self-healing behavior of the polymer in tensile testing specimen. (c, d) Recovery of the stress–strain behavior of the polymers (Chen S et al., 2015).

#### 4.1.2 Tapered Double Cantilever Beam

The tapered double cantilever beam (TDCB) is the most suitable technique for studying the

self-healing process in brittle polymers. Fig. 4 shows a schematic illustration of the test specimen. This test geometry enables a more accurate quantification of the healing process than tensile testing because the fracture toughness is independent of the crack length (whereas the crack width is fixed by the plate thickness) (Brown E N, 2011). This is provided that the fracture surfaces are roughly mirror-smooth and that the crack surfaces are accurately repositioned. The ratio between the healed and initial fracture toughness is known as the healing efficiency. Theoretical calculations showed good agreement with the measured results, however minor modifications to the design and the applied load may result in different values in the load-displacement curve.

The use of this sample design has allowed for extensive testing of extrinsic self-healing materials. This approach allowed Kessler et al. to investigate one of the first autonomous self-healing epoxy systems, which included microcapsules holding a liquid healing agent (Kessler M R et al., 2003). Another illustration was given by Liberata et al., who used microcapsules containing a norbornene derivative as a healing agent and investigated the healing effectiveness as a function of time and temperature (Guadagno L et al., 2014).

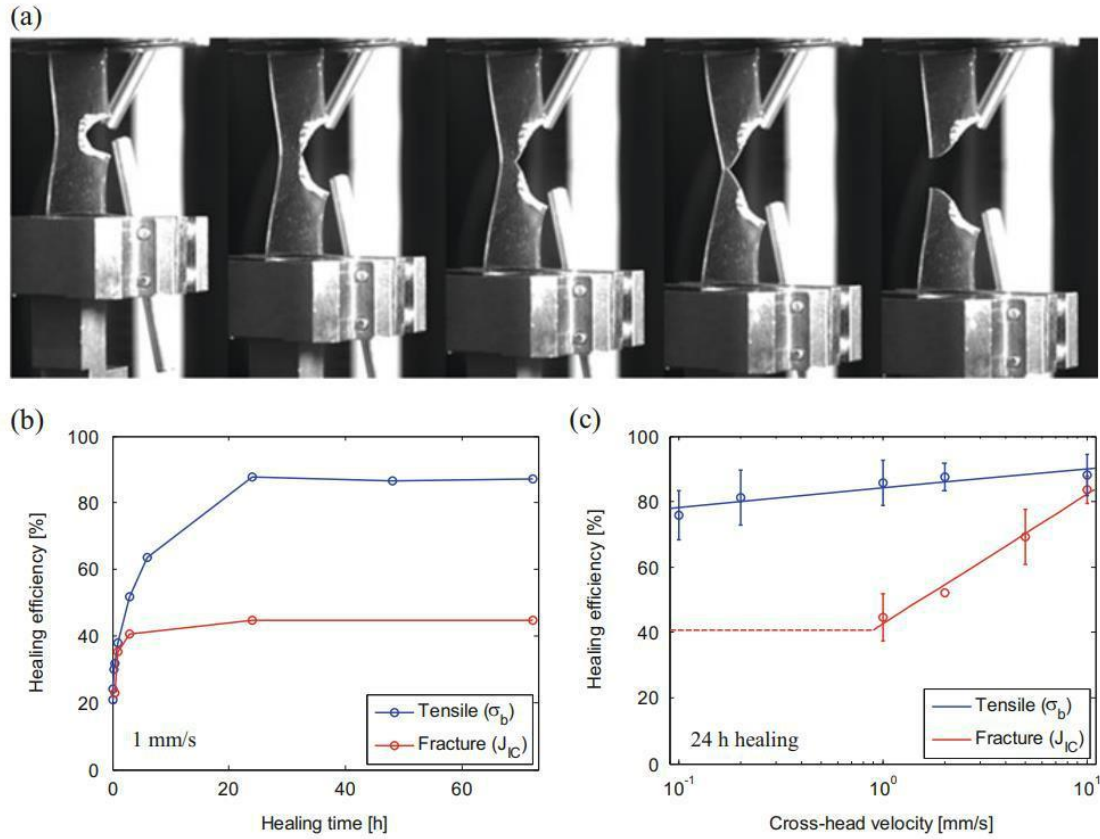


**Figure 4.2** Scheme of the tapered double cantilever geometry (all sizes in mm)

### 4.1.3 Fracture Mechanics

Researchers have traditionally used the recovery of tensile strength of broken samples as a measure of healing in soft polymers. However, this method, based on continuum mechanics, fails to capture the relevant processes at healing surfaces and the effective restoration of mechanical properties. It is important to consider the healing behavior at the interface between two former fracture surfaces as an interfacial phenomenon. Test techniques based on fracture mechanics (such as the TDCB protocol for "stiff polymers") may be able to provide more quantitative data on the healing process. In order to quantify the material's resistance to fracture in the presence of flaws or defects, crack propagation represents an instructive scenario for research into how polymer structure and mechanical properties interact. Rivlin and Thomas conducted early fracture mechanics research on elastomers, proving that tear energy is only a material attribute independent of the sample geometry. Several methods have been created and put to use during the past 20 years to characterize the fracture characteristics of soft polymers, providing information on both the resistance to crack initiation and the resistance to crack propagation. However, fracture mechanics-based tests are hardly used in research works and have only occasionally been used to examine the performance of healable polymers. Grande et al. modified a fracture mechanics testing approach based on the J-integral parameter (Y.Huang et al., 2015) ; M Yamaguchi et al., 2009) to examine the self-healing behavior of a healable supramolecular elastomer (Fig. 5a). The researchers provided a useful comparison between the healing efficiency assessed using conventional tensile experiments and that established by fracture mechanical testing in their work (Fig.4.3). From these findings, it was evident that choosing the appropriate test configurations, along with phenomenologically distinct trials and healing settings, is a necessary step for the creation of new self-healing polymers with enhanced capabilities. Furthermore, it has become obvious that fracture experiments are more important for evaluating the mechanical characteristics of a healed contact. The flaw in the fracture

mechanical assessment of healing effectiveness is that it calls for rather large material volumes, which are not always available for testing experimental polymers.

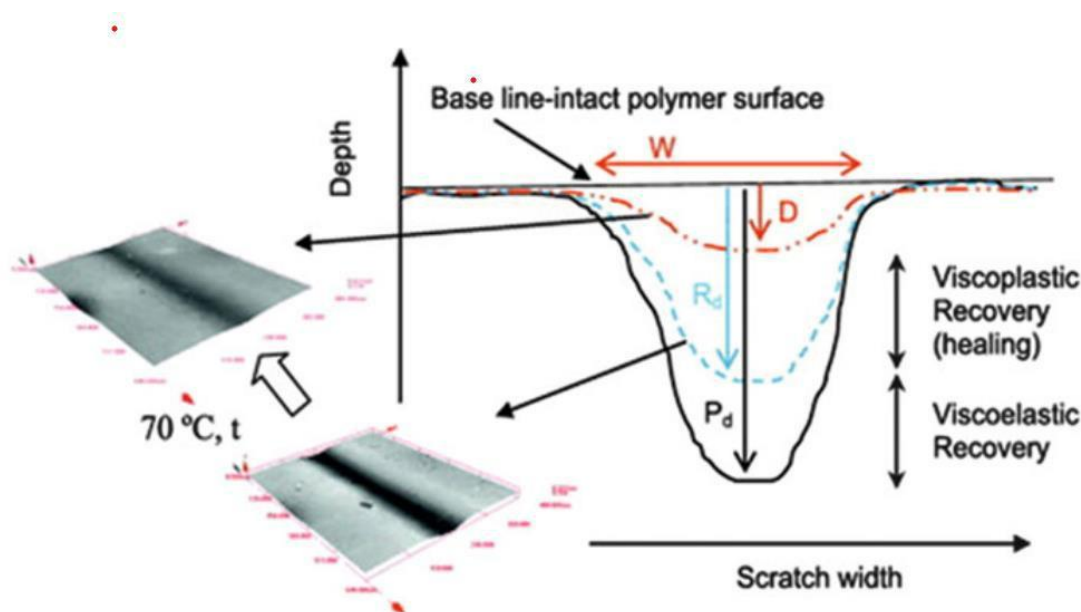


**Fig. 4.3** (a) Single edge notched tensile (SENT) specimen during fracture test. (b, c) Comparison of healing efficiencies obtained in tensile (stress at break,  $\sigma_b$ , recovery) and fracture (fracture toughness, JIC, recovery) experiments. (b) Effect of the healing time: maximum healing efficiencies of around 80% and 40% after 24 h healing in tensile and fracture mode, respectively. (c) Effect of the deformation rate: convergence of tensile and fracture healing efficiencies at the highest cross-head velocity (same failure mechanism) (Y.Huang et al., 2015)

#### 4.1.4 Scratch Healing

Scratch healing is a common self-healing test for polymers, used to evaluate damage healing potential and restore functions like aesthetics and corrosion protection. Intrinsic healing polymers have higher market potential for applications like automotive coatings, optical coatings, and decorative surfaces due to their ability to heal multiple times. Researchers like Garcia and coworkers have developed a micro-scratch tester to create defined scratches for self-

healing polymers (Vega JM et al., 2014). The tester uses a 100  $\mu\text{m}$  radius sphere-conical diamond indenter tip to correct for sample tilting and topology variations. The scratch depth is determined after rapid viscoelastic recovery. The healing efficiency is calculated from changes in the filled volume. Other techniques, such as optical microscopy, atomic force microscopy, scanning electron microscopy, and optical profilometer, have been used to investigate healing of smaller scratches. More recent studies have combined controlled macroscale healing with other techniques to correlate molecular healing with macroscale healing.

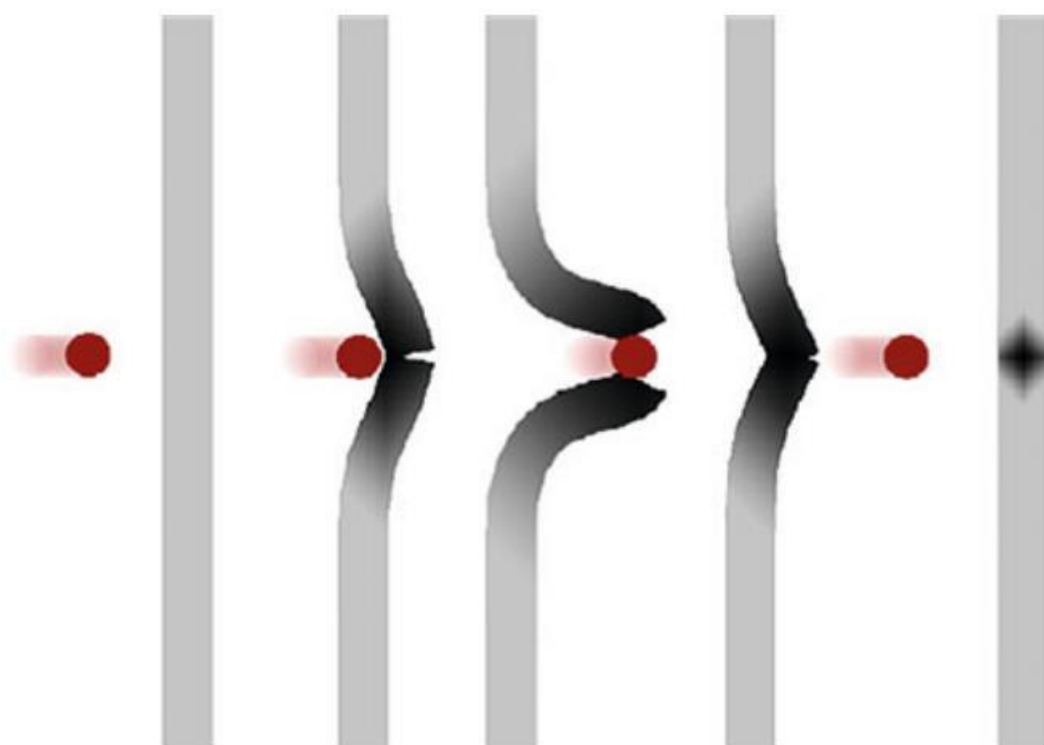


**Figure 4.4** Quantification of scratch healing in term of the changes in scratch size

#### 4.1.5 Ballistic Impact

Kalista and colleagues used a projectile test station to examine the impact damage of self-healing polymer grades on thick ionomer films. They found that during ballistic impact, the polymer heated near the impact site, with the heating effect being more significant for pointed projectiles (Kalista SJ et al., 2007). Using a pressurized burst test (PBT), the degree of healing of samples with closed holes is evaluated. To better understand ionomer healing after ballistic impact, Varley and van der Zwaag created a quasi-static test procedure (Varley R J et al., 2008). According to the testing, the ionic nature of ionomeric ethylene methacrylic acid (EMAA)

copolymers only has a minor impact on the impact zone's local temperature. In order to produce materials with appropriate mechanical qualities and the capacity to heal, blends of ionomers with elastomers or thermoplastics were produced. It was shown that ionomers can heal over a larger range of projectile velocities, and a correlation between the necessary sample thickness and bullet diameter was explained as a crucial geometrical feature. Ballistic tests are relevant for engineering, but it's difficult to comprehend the molecular processes that lead to ballistic healing.



**Figure 4.5** Bullet penetration of thin ionomeric polymer films

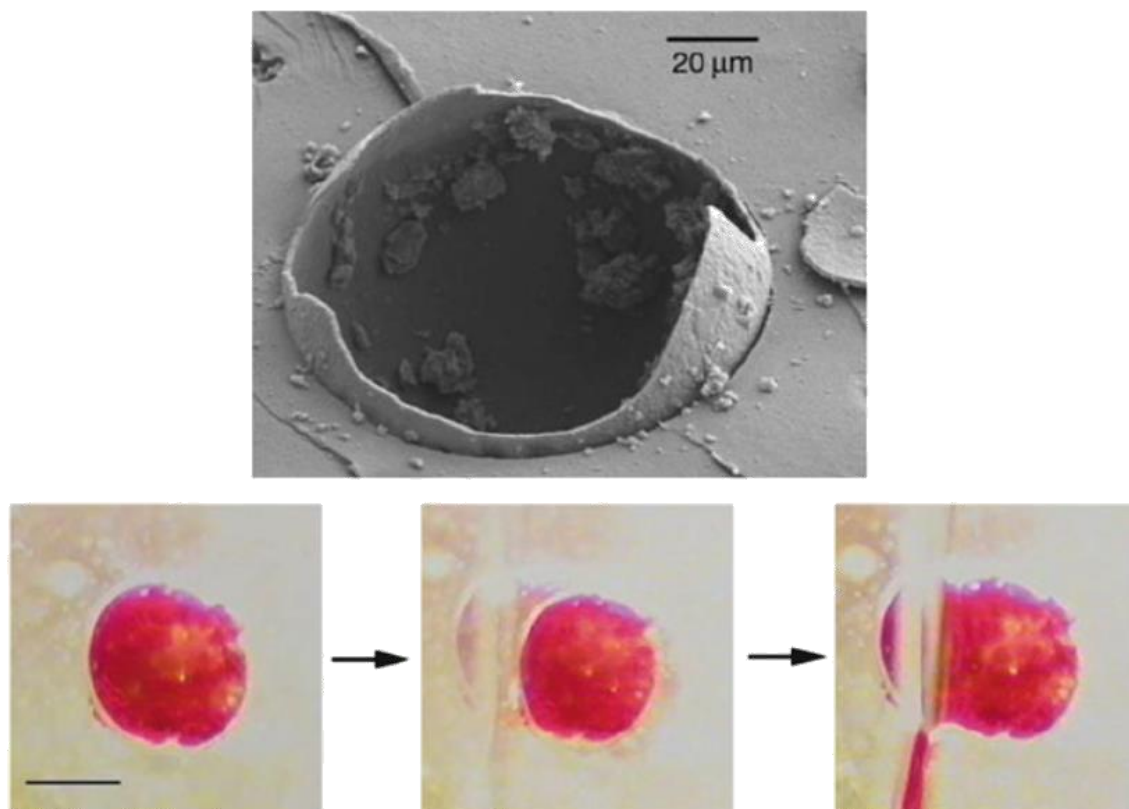


## **4.2 IMAGING TECHNIQUES**

### **4.2.1 Optical Microscopy**

An optical microscope uses visible light to magnify small structures, allowing for detailed observation and analysis of the surface and internal features of materials. It operates on the principle of refraction and reflection of light through lenses, enabling magnification and visualization of structures at the micron and submicron scales. The main components include an objective lens, eyepiece, light source (typically situated under the stage), and a stage to hold and manipulate the sample. The objective lens, often with multiple lenses to achieve high magnification, collects light from the sample and forms an enlarged real image.

The eyepiece further magnifies the image, which the observer views. A light source illuminates the sample. When light hits the specimen, it interacts with its components, revealing details and structures. The objective lens collects light rays from the sample and magnifies them, forming an intermediate real image. The eyepiece further enlarges this image, allowing the observer to view and analyze the sample. Optical microscopy offers direct information on the active molecular mechanism of extrinsic healing, covering length scales higher than intrinsic healing. It can study the release of healing agents from capsules, investigate the effects of size distribution of microparticles, and monitor crack formation after mixing encapsulated solution with a fluorescent dye.



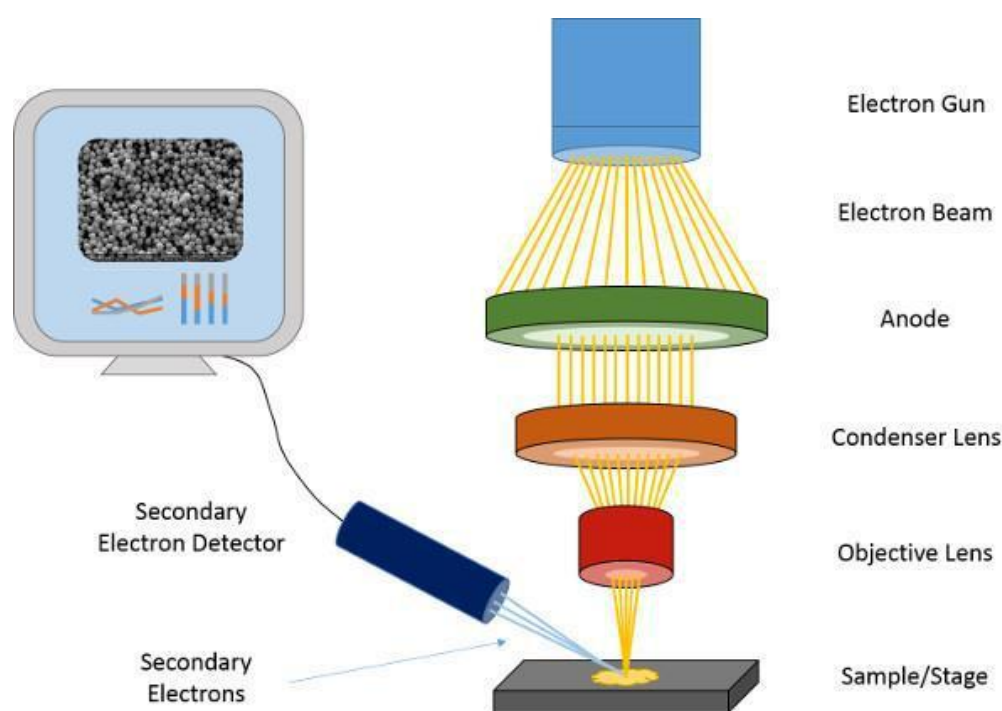
**Figure 4.6** Investigation of the self-healing mechanism of extrinsic self-healing polymers: capsules after disruption and release of healing agent (above) and process of rupture of the capsules and release of the stained healing agent (below) (Stefan Bode, 2015)

#### 4.2.2 Scanning Electron Microscopy

Scanning Electron Microscopy (SEM) uses focused electron beams instead of light to scan the surface of a sample. When the electron beam strikes the sample, it generates various signals, including secondary electrons, backscattered electrons, and X-rays. These signals provide detailed information about the surface topography, composition, and morphology of the sample. Key components include an electron gun, electromagnetic lenses, a sample chamber with a stage, detectors, and a display screen. The electron gun emits an electron beam, focused and scanned over a sample surface. Detectors collect signals from the interaction between the beam and the sample, generating specific signals for each interaction type. These signals create an image with detailed topographical and compositional information of the sample.

distribution of healing agents, and any changes induced by the healing process. SEM enables

high-resolution imaging of self-healing polymers' surface topography, revealing cracks, roughness, and healing-induced changes. It provides detailed information on microstructure, healing agent distribution, and healing-induced changes. Energy-dispersive X-ray spectroscopy (EDS) in SEM aids in elemental analysis, identifying and mapping polymer matrix and healing agent distribution.



**Figure 4.7** Scanning Electron Microscope

### 4.2.3 Micro-Computed Tomography Scanning

Micro Computed Tomography (Micro-CT) is a non-destructive imaging technique that utilizes X-rays to generate a 3D representation of the internal structure of a sample. It's based on the principle of attenuation of X-rays by different materials, where denser materials attenuate more X-rays, producing a contrast in the acquired images. Micro-CT scanners consist of an X-ray source, a rotating stage for sample positioning, X-ray detectors, and a computer for image reconstruction. The X-ray source emits attenuated X-rays that pass through a sample, capturing them using detectors. The rotating stage allows for multiple projections from different angles, allowing for a 3D volume representation of the sample's internal structure. The acquired 2D projections are processed using mathematical algorithms, such as filtered back projection, to

analyze the sample's composition and density.

The very first micro-CT study demonstrating the release of healing agent from fractured microcapsules embedded in an epoxy matrix was that of Mookhoek et al., who used a special micro-CT set-up in an SEM system (Grande AM et al., 2015). Fiber-polymer composite cracks and the release of healing chemicals into the surrounding polymer matrix have both been observed using micro-CT scanning. The visualization of the release of the healing agent is made possible by the differences in fiber, healing agent, and surrounding polymer matrix densities. The compartmented fiber responds to damage gradually, releasing the embedded liquid healing agent during re-loading after a previous healing event, according to a tomographic image of alginate fibers containing healing agent in an unloaded unidirectional pre-impregnated sample. Micro-CT scanning has also been used to examine the effectiveness of extrinsic healing of anticorrosion coatings, measuring the onset of delamination and pitting growth as well as kinetics reduction in an epoxy coating applied to the aluminum alloy 2024-T3 that contained capsules containing a silyl ester healing agent.

## 4.3 SPECTROSCOPIC TECHNIQUES

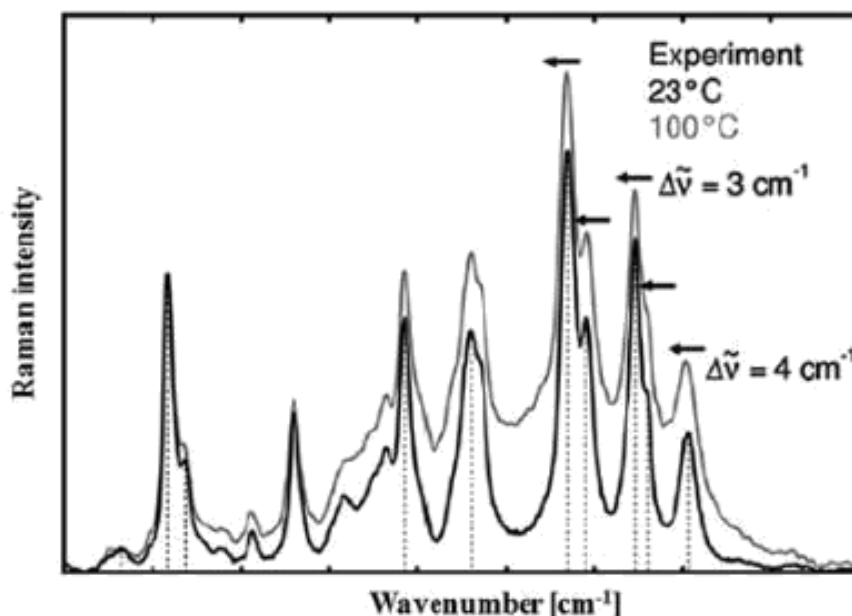
### 4.3.1 Infrared and Raman spectroscopy

Infrared (IR) spectroscopy is a technique that measures the absorption, emission, or reflection of infrared light in a material. This light interacts with molecular vibrations and provides information about the chemical composition, functional groups, and molecular structure of the material. In the context of self-healing polymers, IR spectroscopy is utilized to analyze the polymer's molecular structure and changes during the healing process. IR spectrometer consists of a source of infrared radiation (e.g., a heated filament), a sample compartment, a monochromator to isolate specific wavelengths, and a detector (e.g., thermocouple, bolometer) to measure the intensity of transmitted or absorbed IR light. The IR source emits a broad spectrum of infrared radiation. The IR radiation is passed through the sample, and the sample selectively absorbs certain frequencies of IR light based on its molecular composition and structure. The monochromator selects a specific wavelength of IR light, and the detector measures the intensity of the transmitted or absorbed light. A spectrum is obtained by plotting intensity (absorbance) against the wavelength, which provides information about the molecular vibrations and functional groups in the sample.

Raman spectroscopy is a powerful analytical technique used to study the molecular vibrations and structure of materials, including self-healing polymers, based on the inelastic scattering of light. This method provides valuable insights into molecular compositions and structural changes, making it invaluable for characterizing and understanding the healing mechanisms of self-healing polymers. Raman spectroscopy is based on the principle of inelastic scattering, where a monochromatic light source (commonly a laser) interacts with a sample, causing the atoms or molecules to undergo vibrational transitions. The scattered light is shifted in frequency due to these transitions, and the frequency shift is unique to each molecular bond and provides valuable information about the material's structure. Raman spectroscopy uses a laser as a light source,

emitting monochromatic light in the visible or near-infrared range. The sample undergoes molecular vibrations, generating Raman scattered light. This light is isolated through a monochromator, which records its frequency. A detector records the intensity of the scattered light, and a computerized data analysis system interprets the Raman spectrum. The scattered light contains both original and shifted Raman light due to vibrational transitions in the sample. The intensity is plotted as a function of Raman shift, revealing the sample's vibrational modes and molecular structure.

For detecting and monitoring chemical reactions, including the polymerization of encapsulated monomers, Raman and IR spectroscopy are useful techniques. In metallopolymers, a copolymer crosslinked by terpyridine-iron(II)metal complexes, they have been utilized to examine the mechanism of thermally induced self-healing (Kupfer S et al.,2014). An organic-inorganic dual network featuring disulfide bonds as reversible groups has also been examined using Raman spectroscopy. Utilizing spectroscopic techniques in the infrared (IR) region, further reversible chemical processes exhibiting inherent self-healing ability can be seen. In a polymer made of lauryl methacrylate and two monomers with DA moieties, Bose et al. looked at the connection between self-healing behavior and the reversible Diels-Alder reaction. The chemistry of DA in bulk can be studied using Raman spectroscopic 2D correlation analysis.



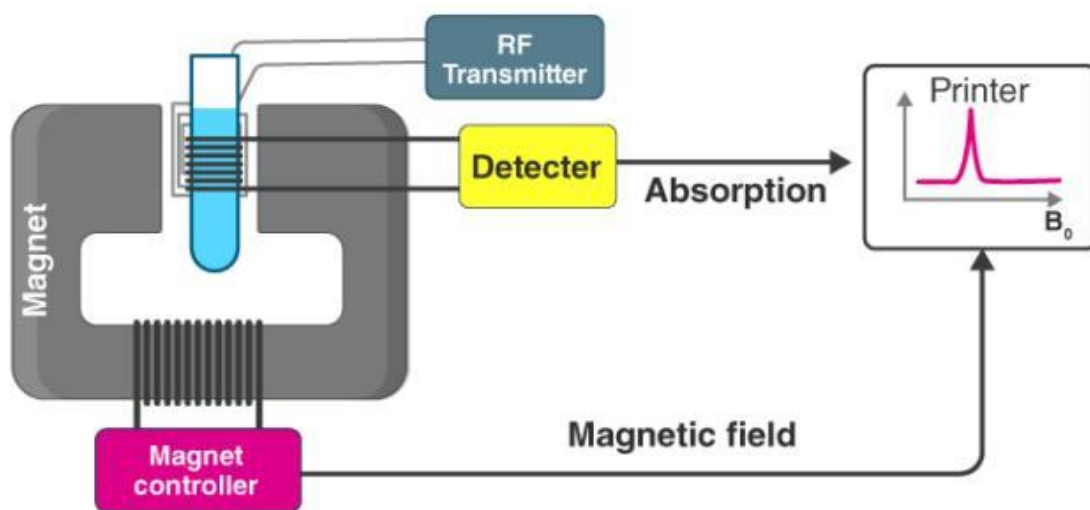
**Figure 4.8** Raman spectrum of a metallopolymer crosslinked by iron(II)-bis-terpyridine metal complexes at 23<sup>0</sup>C and 100<sup>0</sup>C (Kupfer S et al.,2014).

#### 4.3.2 Nuclear Magnetic Resonance

Nuclear Magnetic Resonance (NMR) spectroscopy is a powerful analytical technique used to study the molecular structure, dynamics, and interactions of materials, including self-healing polymers. It uses the principle of nuclear spins aligning in a magnetic field and absorbing and emitting electromagnetic radiation. Atomic nuclei like hydrogen-1 and carbon-13 exhibit nuclear spin, which generates a net magnetic moment when placed in a magnetic field. NMR spectroscopy involves using a strong, uniform magnetic field, typically superconducting magnets, to analyze samples. RF coils are used to apply RF pulses to the sample, detecting the resulting NMR signals. The sample is then placed within the magnet in a sample tube, and detectors capture the emitted signals. A data acquisition system collects and processes the NMR signals to create a spectrum revealing molecular structure and interactions. The sample's nuclear spins align with the magnetic field, and RF pulses perturb these spins, causing transitions between energy levels.

Solid-state NMR spectroscopy is a powerful method for analyzing self-healing polymers, allowing for atomic-level analysis of molecular structure and changes. Wudl and coworkers studied DA-

based self-healing polymers using temperature-dependent  $^{13}\text{C}$ -solid state NMR, revealing reversible opening during heating. Bode et al. used  $^{113}\text{Cd}$ -solid state NMR to show complexation modes of cadmium(II) acetate and cadmium(II) bromide with terpyridine moieties, enhancing self-healing behavior (Bode S et al., 2013).



**Figure 4.9** NMR Spectroscopy

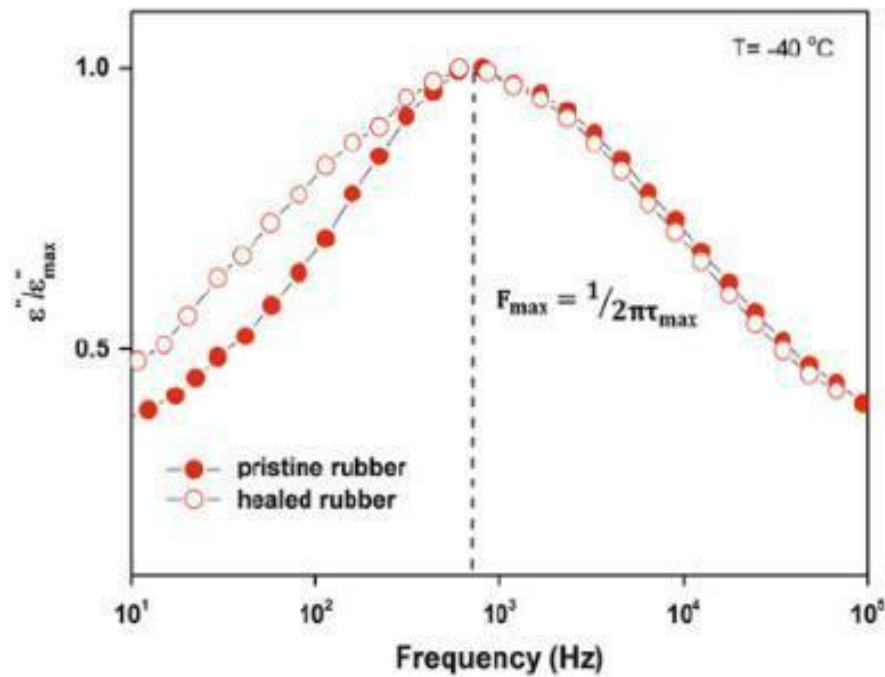
### 4.3.3 Broadband Dielectric Spectroscopy

Broadband Dielectric Spectroscopy (BDS) is a powerful analytical technique used to study the electrical properties of materials, including self-healing polymers. BDS provides insights into the response of materials to varying frequencies of an applied electric field, offering valuable information about their dielectric behavior and molecular dynamics. BDS is based on the principle that materials exhibit distinct electrical responses at different frequencies of an applied electric field. The dielectric properties of a material are characterized by its permittivity, conductivity, and relaxation processes, which can be explored using BDS across a wide frequency range. A self-healing polymer sample is exposed to an electric field generated by a broadband frequency generator, causing polarization and reorientation of dipoles. The dielectric properties, including permittivity and conductivity, are measured as a function of frequency. The resulting dielectric spectrum provides information about the material's relaxation processes,



molecular dynamics, and response to the electric field across a wide range of frequencies. Probes or electrodes are used to detect and measure the electrical response.

BDS (Body Dynamics) is a method for analyzing motional processes in polymers using a dynamic frequency range of  $10^{-2}$  to  $10^{-9}$ . The molecular mobility of groups, segments, or entire polymer chains is what drives this process. BDS can characterize mobility as a function of polymer architecture, making it useful for evaluating polymer healing processes. Hernández et al. investigated the potential of this method by observing the self-healing rubber's healing procedure under carefully controlled circumstances at a constant temperature. They discovered that the dielectric signal, which indicates healing, varies according to the presence of (nanoscopic) heterogeneities at the healed contact (Hernandez M et al., 2015).



**Figure 4.10** Normalized dielectric loss  $\epsilon''$  versus frequency for pristine and healed rubber samples at  $40\text{ }^{\circ}\text{C}$  (Hernandez M et al., 2015).

## 4.4 SCATTERING TECHNIQUES

X-ray scattering is a powerful analytical technique used to study the structural properties of materials, including self-healing polymers. This technique utilizes X-rays to probe the arrangement of atoms and molecules in a sample, providing insights into its molecular structure and organization. X-ray scattering is based on the principle that X-rays can interact with the electrons in the atoms of a material, causing them to scatter. The scattering pattern contains information about the spatial arrangement and organization of atoms and molecules in the sample. X-rays are generated using an X-ray source to produce high-energy photons. A sample is placed on a sample holder for controlled positioning. Detectors capture and record scattered X-rays, creating diffraction patterns that reveal the sample's structure. X-rays interact with atoms and molecules in the sample, scattering in different directions. The diffraction pattern is analyzed to reveal crystal structure, crystallographic orientation, and atomic arrangement.

Self-healing polymers have been widely studied using small and wide-angle X-ray scattering (SAXS and WAXS), which has shown the presence of ordered structures. Due to the significant polarity difference between ionomers, these structures are connected to the self-healing process. The limited mobility of these clusters is advantageous for mechanical properties but negative for self-healing. Ionic aggregates may still be present in the melt even when a phase transition takes place during heating, defying the presumption that cluster behavior and healing capacity are related. Other examples are cross-linked self-healing metallopolymer and hydrogen bonding polymers. The molecular arrangement changes in self-healing polymers have been better understood as a result of these studies, but their inherent capacity for self-healing has not yet been satisfactorily explained.

## 4.5 THERMAL AND RHEOLOGICAL CHARACTERIZATION

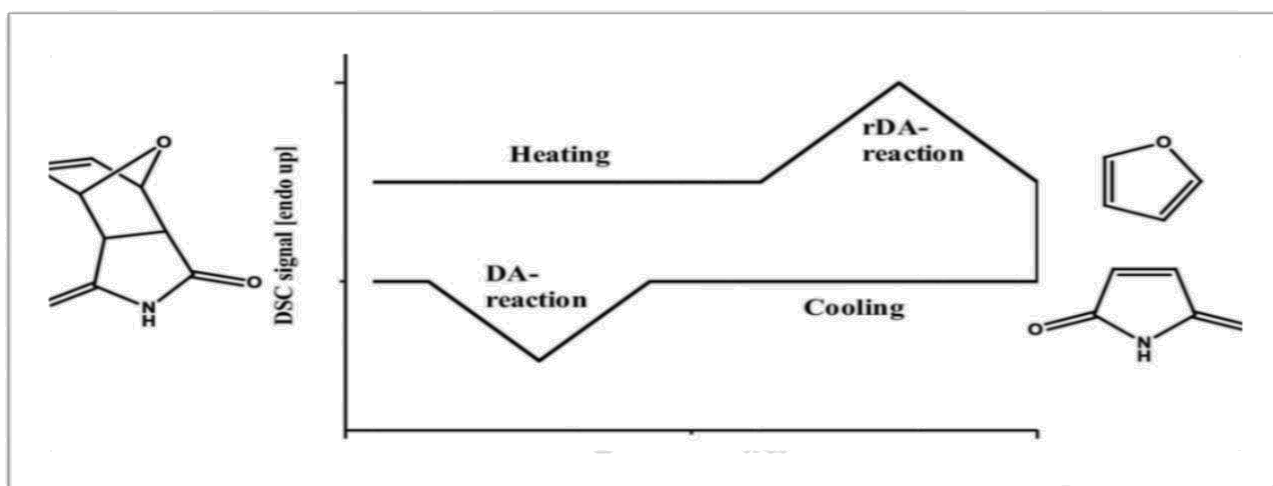
Rheology is a fundamental analytical technique used to study the flow and deformation behavior of materials, including self-healing polymers. This technique focuses on understanding how materials respond to applied stress, providing insights into their mechanical properties and behavior. The principle of rheology lies in analyzing how materials deform, flow, or respond to stress when subjected to external forces. Rheological measurements help in understanding the viscoelastic properties, such as viscosity, elasticity, and flow behavior of a material, and how these properties evolve over time and under various conditions. A rheometer is a crucial instrument for rheological measurements, consisting of a rotor and a stator. It uses sensors like torque and displacement sensors to measure stress, strain, and deformation of the sample. A computer controls the rheometer, records measurements, and analyzes the data. The sample is loaded onto the rheometer's geometry, and the sensors record the sample's response, including torque and displacement.

The study of self-healing polymers and their temperature dependence through rheology is a powerful tool for understanding dynamic processes. The recovery of  $G'$  (storage modulus) is an indicator of self-healing behavior and can be used to quantify it. Rheology measurements can also be used to follow dynamic processes for non-covalent systems, such as poly(n-butyl acrylate)-co-(acrylic acids)ionomers (Bose RK et al., 2015). The self-healing ability correlates with the bond lifetime, which depends on the amount of ionic groups, the nature of the cation, and the temperature. The activation energy of the healing process can be determined using this approach. The study of self-healing system networks revealed that relaxation occurred on the time scale of tens or hundreds of seconds, depending on the strength of transient polymer building-block association and the metal-to-terpyridine stoichiometric ratio. The study of

disulfide-based thermos responsive elastomers revealed a correlation between its rheological and fracture measurements, highlighting the direct link between rheology and crack healing.

Differential Scanning Calorimetry (DSC) is an analytical technique used to study the thermal behavior of materials, including self-healing polymers. DSC measures the heat flow (heat capacity) associated with thermal transitions in a sample as a function of temperature, providing valuable information about phase transitions, enthalpies, and thermal stability. DSC is based on the principle that when a material undergoes a thermal transition (e.g., melting, crystallization), it either absorbs or releases heat. This heat flow is detected and measured to analyze the thermal properties and phase changes in the material. The DSC instrument uses a sample holder, furnace, reference material, and thermocouples to measure temperature and data. The sample is placed in a holder, and the furnace provides controlled heating or cooling. A reference material is used to compare heat flow and calibrate the system. Thermocouples measure the temperature difference between the sample and reference material, enabling precise temperature control and data acquisition. The DSC produces a thermogram plotting heat flow versus temperature, providing information about phase transitions and enthalpic changes.

DSC measurements can show how reversible bonds can be opened, which requires energy. Research has examined the thermal behavior of ionomers, observed DA systems, and tracked the endothermic rDA reaction, which needs energy to break the reversible covalent bond. DSC can be used to calculate the rDA temperature, which coincides with the self-healing ability's temperature dependence. DSC can be used to demonstrate the reaction's reversibility and the inherent nature of the polymer's healing behavior.



**Figure 4.11** Reversible opening of furan–maleimide Diels–Alder system during DSC measurements

## **CHAPTER 5**

### **BENEFITS AND APPLICATIONS OF SHP**

Self-healing polymers represent a cutting-edge advancement in material science, demonstrating remarkable potential in various applications. Their intrinsic ability to autonomously repair damage offers a host of benefits, including significantly extending the lifespan and durability of materials, thereby reducing maintenance costs and environmental impact. Applications span diverse industries, from aerospace and automotive sectors, where they enhance safety and longevity, to consumer electronics and textiles, where they improve aesthetics and usability. The transformative potential of self-healing polymers lies in their capability to redefine the standards of material resilience and contribute to a sustainable and economically efficient future.

#### **5.1 BENEFITS OF SHP**

Self-healing polymers offer several advantages, including extended lifespan and durability, reduced maintenance costs, environmental impact, improved safety, flexibility, and adaptability. They can repair small cracks and damages, increasing the material's overall lifespan. They also contribute to sustainability by minimizing the need for material replacement or disposal. Self-healing properties enhance structural integrity, making structures and materials safer. These polymers can adapt to various types of damage, making them versatile for various applications. Additionally, they enhance the reliability and performance of the material by maintaining its structural integrity even after damage.

#### **5.2 APPLICATIONS OF SHP**

Self-healing polymers have various applications in various industries, including the aerospace industry, automotive industry, consumer electronics, biomedical devices, infrastructure and construction, and textiles and clothing. They can be used in aircraft components to repair minor damage, maintain aesthetic appeal, repair scratches or damages on screens or casings, improve longevity of medical implants, enhance the durability of concrete and other structural materials, and

create fabrics that repair minor tears or punctures, increasing the lifespan of clothing. Overall, self-healing polymers offer numerous benefits and benefits.

In conclusion, self-healing polymers represent a cutting-edge innovation with remarkable potential benefits and diverse applications. These polymers offer extended material lifespan and durability by autonomously repairing minor damages, thus reducing maintenance costs and minimizing environmental impact through prolonged product use. Industries ranging from aerospace and automotive to consumer electronics and biomedical devices can leverage self-healing polymers to enhance safety, decrease maintenance expenses, and introduce sustainable solutions. As research advances, we can anticipate an exciting future with even more versatile and multifunctional self-healing polymers, shaping a resilient and sustainable material landscape for various applications.

## **CHAPTER 6**

### **CHALLENGES AND FUTURE SCOPE OF SHP**

Self-healing polymers, with their innate ability to autonomously repair damage, present a promising avenue for revolutionizing material science and engineering. However, advancing this field is not without its challenges. The complexity of designing polymers with effective and reliable self-healing mechanisms, while addressing scalability, cost, and integration into existing systems, remains a substantial hurdle. Overcoming these obstacles holds the key to a bright future for self-healing polymers. The potential applications span a wide spectrum, from aerospace and automotive industries to consumer electronics and healthcare. As research continues, we foresee self-healing polymers evolving towards enhanced healing capacities, multifunctional properties, and sustainable, biomimetic designs. Integration with emerging technologies like nanotechnology and 3D printing will further amplify their impact, leading to self-repairing materials that redefine durability and sustainability in various domains. Achieving these milestones promises a transformative shift towards resilient and self-sustaining materials, shaping the future of engineering and technology.

#### **6.1 CHALLENGES OF SELF HEALING POLYMERS**

The development of self-healing polymers faces multifaceted challenges. Designing polymers that effectively self-repair without compromising mechanical properties or introducing toxic components is a delicate balance. Achieving scalable production methods while keeping costs reasonable remains a significant hurdle. Furthermore, understanding the long-term stability, efficiency, and applicability across different environments is crucial for widespread adoption. Addressing these challenges requires collaborative efforts from multidisciplinary teams encompassing chemistry, material science, engineering, and nanotechnology.



## **6.2 FUTURE SCOPES OF SELF HEALING POLYMERS**

The future of self-healing polymers is promising and transformative. Advancements in nanotechnology will enable precise integration of healing agents at the molecular level, enhancing the efficiency and speed of repair. Multifunctional self-healing polymers will emerge, offering combined properties such as strength, conductivity, and resilience. Additionally, as sustainability gains traction, self-healing polymers made from renewable and eco-friendly sources will contribute to a more environmentally conscious approach. The integration of self-healing capabilities into everyday products and critical infrastructure will redefine material durability, reducing maintenance costs, and positively impacting industries such as aerospace, automotive, healthcare, and consumer goods.

## **CHAPTER 7**

### **CONCLUSIONS**

In the realm of materials science and engineering, self-healing polymers represent a groundbreaking advancement with immense potential to revolutionize various industries. The ingenious mechanism behind self-healing polymers, inspired by natural healing processes, has opened new doors for developing materials that can autonomously repair damage at the molecular level. The intrinsic ability of these polymers to mend and recover from mechanical, thermal, or chemical damage significantly enhances their durability and longevity.

Characterization techniques like atomic force microscopy, spectroscopic analyses, rheological studies, and imaging technologies provide invaluable insights into the healing mechanisms and performance of self-healing polymers. These techniques aid researchers and engineers in fine-tuning the composition and structure of polymers to achieve optimal healing properties.

The advantages of self-healing polymers are compelling, including an extended lifespan, reduced maintenance costs, enhanced safety, and a positive environmental impact. Applications span diverse industries such as aerospace, automotive, consumer electronics, healthcare, and construction, where self-healing polymers offer enhanced resilience and longevity, leading to improved product performance and safety.

However, challenges such as complex chemistry, scalability, cost-effectiveness, and long-term stability need to be addressed for wider adoption. Future scopes in this field are promising, including enhanced healing capabilities, multifunctional properties, sustainable and eco-friendly designs, and integration with emerging technologies like nanotechnology. As research and

technology advance, self-healing polymers are poised to play a pivotal role in shaping a sustainable and resilient future for material technologies.

In conclusion, the field of self-healing polymers holds immense promise, and ongoing research and development are essential to unlock the full potential of these extraordinary materials, paving the way for a transformative paradigm shift in material science and engineering.

## REFERENCES

1. Azevedo do Nascimento, A. (2022). Self-Healing Polymers and Composite Materials. IntechOpen. doi: 10.5772/intechopen.100908
2. B. Jony, M. Thapa, S. B. Mulani, S. Roy, Smart Mater. Struct. (2019), 28, 025037.
3. Bekas DG, Tsirka K, Baltzis D, Paipetis AS. Self-healing materials: A review of advances in materials, evaluation, characterization and monitoring techniques. Composites Part B Engineering. (2016);87:92-119. DOI: 10.1016/j.compositesb.2015.09.057
4. Blaiszik BJ, Kramer SLB, Olugebefola SC, Moore JS, Sottos NR, White SR. Self-healing polymers and composites. Annual Review of Materials Research. (2010);40:179-211. DOI: 10.1146/annurev-matsci-070909-104532
5. Bode S, Bose RK, Matthes S, Ehrhardt M, Seifert A, Schacher FH, Paulus RM, Stumpf S, Sandmann B, Vitz J, Winter A, Hoepfner S, Garcia SJ, Spange S, van der Zwaag S, Hager MD, Schubert US (2013) Polym Chem 4:4966–4973
6. Bode, S., Enke, M., Hernandez, M., Bose, R. K., Schubert, U. S., García, S. J., & Hager, M. D. (2015). Characterization of Self-Healing Polymers: From Macroscopic Healing Tests to the Molecular Mechanism. Springer International Publishing Switzerland.  
[https://doi.org/10.1007/12\\_2015\\_341](https://doi.org/10.1007/12_2015_341)
7. Bose RK, Hohlbein N, Garcia SJ, Schmidt AM, van der Zwaag S (2015) Phys Chem Chem Phys 17:1697–1704
8. Brown EN (2011) J Strain Anal Eng Des 46:167–186
9. C. M. Dry, N. R. Sottos, Proc. SPIE ,Passive smart self-repair in polymer matrix composite materials,Proc. SPIE 1916, Smart Structures and Materials 1993: Smart Materials, (23 July 1993); <https://doi.org/10.1117/12.148501>

10. Chen S, Mahmood N, Beiner M, Binder WH (2015) *Angew Chem Int Ed* 54:10188–10192
11. Dhanasekaran, R.; Reddy, S.S.; Kumar, A.S. Application of Self-Healing Polymers to Overcome Impact, Fatigue and Erosion Damages. *Mater. Today Proc.* 2018, 5, 21373–21377. [[Google Scholar](#)] [[CrossRef](#)]
12. El Choufi, N., Mustapha, S., Tehrani B., A., & Grady, B. P. (2022). An Overview of Self-Healable Polymers and Recent Advances in the Field. *Macromolecular Rapid Communications*, 43(17), [2200164]. <https://doi.org/10.1002/marc.202200164>
13. Grande AM, Garcia SJ, van der Zwaag S (2015) *Polymer* 56:435–442
14. Guadagno L, Raimondo M, Naddeo C, Longo P, Mariconda A, Binder WH (2014) *SmartMater Struct* 23:045001
15. Hernandez M, Garcia SJ, van der Zwaag S (2015) In: Proceedings of the fifth international conference on self-healing materials ICSHM, Durham, NC, USA, p 85
16. J. Nji, G. Li, *Polymer* 2010, 51, 6021
17. Kalista SJ, Ward TC, Oyetunji Z (2007) *Mech Adv Mater Struct* 14:391–397
18. Kessler MR, Sottos NR, White SR (2003) *Compos Part A* 34:743–75325.
19. Kupfer S, Zedler L, Guthmuller J, Bode S, Hager MD, Schubert US, Popp J, Grafe S, Dietzek B (2014) *Phys Chem Chem Phys* 16:12422–12432
20. L. Huang, N. Yi, Y. Wu, Y. Zhang, Q. Zhang, Y. Huang, Y. Ma, Y. Chen, *Adv. Mater.* 2013, 25, 2224.
21. M. Hu, S. Peil, Y. Xing, D. Döhler, L. Caire Da Silva, W. H. Binder, M. Kappl, M. B. Bannwarth, *Mater. Horiz.* 2018, 5, 51.
22. M. Yamaguchi, S. Ono, K. Okamoto, *Mater. Sci. Eng., B* 2009, 162, 189.
23. Madara SR, Srath Raj NS, Selvan CP. Review of research and developments in self-healing composite materials. *IOP Conference Series: Materials Science and Engineering*.

2018;346:012011. DOI: 10.1088/1757-899X/346/1/012011

24. Md. Wasikur Rahman, Nawrin Rahman Shefa, "Minireview on Self-Healing Polymers: Versatility, Application, and Prospects", *Advances in Polymer Technology*, vol. 2021, Article ID 7848088, 12 pages, 2021. <https://doi.org/10.1155/2021/7848088>
25. Mohammadi MA, Eslami-Farsani R, Ebrahimnezhad-Khaljiri H. Experimental investigation of the healing properties of the microvascular channels-based self-healing glass fibers/epoxy composites containing the three-part healant. *Polymer Testing*. 2020;91:106862. Available from: <https://doi.org/10.1016/j.polymertesting.2020.106862>
26. R. Gupta, D. Huo, M. White, V. Jha, G. B. G. Stenning, K. Pancholi, *Compos. Commun.* 2019, 16, 67.
27. Radovic I, Stajcic A, Radisavljevic A, Veljkovic F, Cebela M, Mitic V V., et al. Solvent effects on structural changes in self-healing epoxy composites. *Materials Chemistry and Physics*. 2020;256:123761. Available from: <https://doi.org/10.1016/j.matchemphys.2020.123761>
28. S. A. Hayes, F. R. Jones, K. Marshiya, W. Zhang, *Composites, Part A* 2007, 38, 1116.
29. S. An, M. W. Lee, A. L. Yarin, and S. S. Yoon, "A review on corrosion-protective extrinsic self-healing: Comparison of microcapsule-based systems and those based on core-shell vascular networks," *Chemical Engineering Journal*, vol. 344, pp. 206–220, 2018.
30. S. J. Garcia, H. R. Fischer, *Smart Polymers and Their Applications* (Eds: M. Aguilar, J. San Román), Woodhead Publishing, Cambridge 2014. <https://doi.org/10.1533/9780857097026.1.271>
31. S. J. Kalista, T. C. Ward, Z. Oyetunji, *Mech. Adv. Mater. Struct.* 2007, 14, 391.
32. S. Prager, M. Tirrell, *J. Chem. Phys.* 1981, 75, 5194.
33. S. R. White, N. R. Sottos, P. H. Geubelle, J. S. Moore, M. R. Kessler, S. R. Sriram, E. N.

- Brown, S. Viswanathan, Nature 2001, 409, 794.
34. T. F. A. de Greef, M. M. J. Smulders, M. Wolffs, A. P. H. J. Schenning, R. P. Sijbesma, E. W. Meijer, Chem. Rev. 2009, 109, 5687.
  35. Varley RJ, van der Zwaag S (2008) Polym Test 27:11–19
  36. Vega JM, Grande AM, van der Zwaag S, Garcia SJ (2014) Eur Polym J 57:121–126
  - A. W. Bosman, R. P. Sijbesma, E. W. Meijer, Mater. Today 2004, 7, 34.
  37. White SR, Sottos NR, Geubelle PH, Moore JS, Kessler MR, Sriram SR, et al. Autonomic healing of polymer composites. Nature. 2001;409:794-817.
  38. Williams GJ, Bond IP, Trask RS. Compression after impact assessment of self-healing CFRP. Composites Part A: Applied Science and Manufacturing. 2009;40:1399-1406.  
Available from: <http://dx.doi.org/10.1016/j.compositesa.2008.05.021>
  39. X. Chen, M. A. Dam, K. Ono, A. Mal, H. Shen, S. R. Nutt, K. Sheran, F. Wudl, Science 2002, 295, 1698.
  40. X. Lu, G. Fei, H. Xia, Y. Zhao, J. Mater. Chem. A 2014, 2, 16051.
  41. Y. Huang, M. Zhong, Y. Huang, M. Zhu, Z. Pei, Z. Wang, Q. Xue, X. Xie, C. Zhi, Nat. Commun. 2015, 6, 10310..