Developing High Strength Adhesives for Metal-Polymer Bonding in Industrial and Strategic Applications

MS Thesis

By

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COMSATS University Islamabad

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Developing High Strength Adhesives for Metal-Polymer Bonding in Industrial and Strategic Applications

A Thesis submitted to
COMSATS University Islamabad, Lahore Campus

In partial fulfillment
of the requirements for the degree of

Master of Science in
Chemistry

by

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Dedication

Dedicated to my whole Family, especially to my respected father **Muhammad Mansha** and my loving and caring mother **Rukhsana Asad** and my beloved brother **Shahroz Asad Advocate** to whom I owe my existence and their unwavering support, sacrifices, motivation and boundless love have been a constant source of guidance and support, enabling my progress toward academic achievement.

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“In the name of ALLAH, the most beneficent, the merciful, the only Creator”

First and foremost, I Thank **Allah Almighty**, who always blessed me with everything best! And granted me the ability to make another little involvement in the vast world of research and also to the teacher of the universe **Hazrat Muhammad (PBUH)** who is the ocean of knowledge and candle for every researcher!

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Abstract

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By

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An adhesive is a non-metallic compound that has a wide range of applications as compared to traditional methods. Silicones, acrylics, polyurethanes and epoxy are some major structural adhesives that are widely used in structural applications. Metal rubber bonding is important in many industrial sectors to achieve hybrid strength, durability and for damping. It provides elasticity and resistance to temperature and chemicals. But due to surface energy mismatch, manufacturing and inappropriate adhesive selection M-R bonding face challenges in high strength. To overcome this challenge epoxy is selected as an adhesive that has high strength, durability, high chemical and thermal resistance and having tunable properties via curing agents, fillers, coupling agents and modifiers. However, brittleness and restricted pot life limits its applications. So, by adding appropriate fillers, proper surface treatment, adding modifiers and coupling agents adhesion strength and toughness of epoxy enhanced. By incorporating filler content 3%, 5% and 7% with APTES and PEG diff content in epoxy resin and hardener adhesive is formulated. Mechanical and chemical surface treatment applied to steel metal plates, rubber and adhesive layer applied on steel plates and then placed in compression molding for bonding. By performing various characterization techniques Lap shear test, FTIR, XRD and SEM epoxy adhesive is characterized and from these techniques it observed that 5% filler content is optimal value and it gives 53MPa adhesion strength that is 85% highest then neat epoxy adhesive.

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PU	Polyurethane Adhesives
EP	Epoxy
SEM	Scanning electron microscopy
XRD	X-ray diffraction
FTIR	Fourier transform infrared spectroscopy
M-R	Metal-Rubber
NR	Natural Rubber
NBR	Nitrile Butadiene Rubber
HNBR	Hydrogenated Nitrile Butadiene Rubber
PEG	Polyethylene glycol
APTES	3-aminopropyltriethoxy silane

Chapter 1

Introduction

1.1 Introduction to Adhesives:

An adhesive is a non-metallic compound that is able to connect various other materials by adhesion to the surface and it must be able to provide sufficient internal cohesion. Without altering their shape, similar and dissimilar adherend materials are joined using the adhesive bonding process. The high-tech sectors including electronics, automotive, and aerospace are just a few that have used the multipurpose bonding technique[1]. Plastic, ceramics, metal, cork, rubber, and other materials may all be joined together using adhesives. They can also be used to combine diverse materials and conductive materials[2]. Automotive, aerospace, leather, shoes, electronics, composites, foams, glass, furniture, wood, and packaging are just a few of the numerous industries where adhesives used for adhesion[3].

1.2 Role of Adhesives in modern Engineering Systems:

There are many adhesive connection based benefits such as to improve including fabrication process, design freedom, light in weight, a quick and simple even load distribution throughout the bonded area, and they would also have the ability to combine disparate materials in a more efficient way[4].

Aerospace applications, such as aircraft, spacecraft, and missiles, usually use structural adhesives, which are anticipated to have high toughness, long-term serviceability at high temperatures, good resistance to crack initiation and propagation, superior fatigue resistance, and excellent resistance to organic fluids and moisture[5].

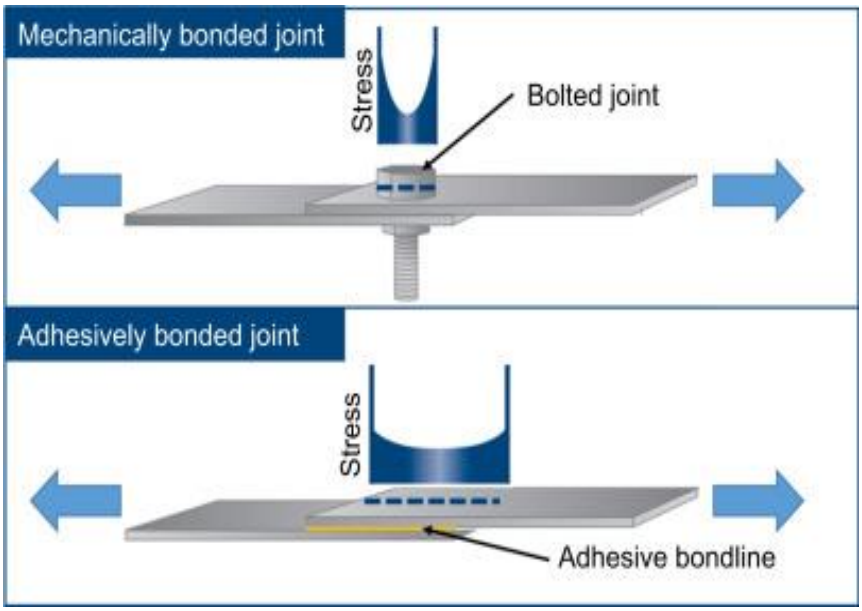
1.3 Adhesives over mechanical fasteners:

Polymeric adhesives have numerous benefits over more conventional structural joining techniques like bolting, brazing, welding, and mechanical fastening[6]. Since adhesives are

lightweight polymers that can take the place of bulky welded joints and mechanical fasteners, one of the primary technical benefits is the possibility to lower the vessel's overall weight[7].

Because they distribute stress more evenly and may take use of adhesives' ductility to reduce stress concentrations, adhesive joints are structurally more efficient than mechanical fasteners. Mechanically connected connections, on the other hand, frequently result in localized high-stress zones and wasteful material consumption[8]. The building's lifetime and dependability are enhanced by this uniform stress distribution, which lessens the need for frequent maintenance and repairs. Compared to welded joints mechanical fasteners and, adhesively bonded surfaces are smoother, which may reduce drag and increase hydrodynamic efficiency, both of which could result in lower emissions and fuel consumption. The seal created by the adhesive bond stops impurities from penetrating[9].

By allowing for weight reduction, more design freedom, improved corrosion resistance, and higher fatigue performance, adhesive bonding provides a number of benefits over mechanical fasteners, making it a more dependable and effective option for contemporary engineering applications. Under extremely high or low temperatures, certain fastener materials can become particularly durable[10]. In complicated technical devices utilized in automotive, telecommunications, photonic devices, aerospace, and sustainable power production and storage, structural adhesives are particularly useful for joining disparate materials. Their stability, strength, and ease of use greatly aid in the device's production and maintenance[11].



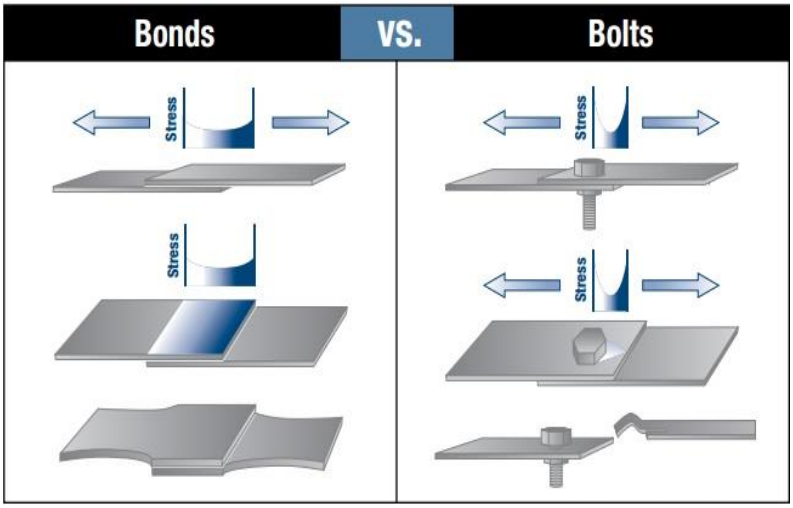


Figure.1.1 Adhesive Bonding Vs Mechanical Bonding [12]

By providing a number of benefits over conventional joining techniques like welding and mechanical fasteners, the adoption of adhesive bonding technology in shipbuilding can dramatically lower greenhouse gas emissions through a number of ways[13].

The market for adhesives is expected to experienced golden days due to the continuous improvements in the sector. Due to its improved qualities, simplicity of use in a variety of applications, and global availability, adhesive's market value is rising quickly[14].

1.4 Metal-Rubber Bonding

When two materials are attracted to one another on a molecular level, metal-rubber bonding occurs. Forces such as van der Waals, covalent, or ionic interactions helps in the formation of this bond. The strength of bond depends on the surface tension of the rubber and the surface energy of the metal. A stronger and more stable connection results from reduced interfacial tension[15].

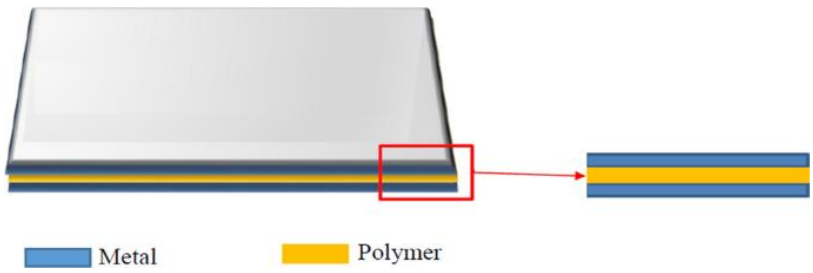


Figure.1.2 M-R bonding[16]

1.4.1 Importance of Metal-Rubber bonding:

The metal-rubber bonding exhibits high structural stiffness, damping, and elasticity. Its qualities include sound insulation, sealing, heat preservation, and vibration reduction. Additionally, the bonding joints are lightweight and inexpensive[17].

Bonded Rubber to Metal composites were used to prevent oil and other fluid leaks, reduce the deleterious effects of vibration, and provide shock protection. The non-aeronautical vehicles of war, rail and rapid transit rolling stock, track beds, and rail crossings all require Rubber-to-Metal assemblies for above mentioned purposes[18].

Metal Rubber is a conductive, flexible nano-composite that may be utilized for real-time strain sensing in metal-rubber bonded structures and maintain electrical performance at high strain (>200%). Because its resistance varies with deformation, it is perfect for military and aerospace applications where conventional strain gauges are ineffective. In harsh conditions, it facilitates the creation of intelligent, multipurpose adhesive interfaces[19]. Since several synthetic rubbers were developed in the 20th century, rubber is now a necessary component of many home and industrial goods, particularly tires for automobiles. But because rubber is a rather weak material, it is strengthened before usage. Metals, inorganic compounds, polymers, and fiber are examples of effective reinforcements[20].

Figure.1.3 Metal-Rubber Bonded Products

Rubber-metal bonding is crucial for applications in the automotive industry, such as engine mounts and suspension units, and civil engineering, such as bridge bearings Rubber lining of metals protects against corrosion, with strong adhesion essential for extending the lifespan of equipment like gas scrubbers, valves, and chemical storage tanks.[21]. In industries like medical, and appliances where fundamental processes like fluid control, energy conversion, sealing, vibration isolation, and/or combinations of these are needed, rubber to metal adhesion is necessary[22].

The leading edges of helicopter rotor blades are bonded with stainless steel to increase durability, and in high-temperature military systems, ablative compounds are affixed to steel surfaces to provide thermal protection. The gluing of rubber to steel is also essential for sonar systems[23].

1.5 Characteristics Of Rubber:

Rubber is used in many different industries, such as agriculture, aircraft, medicine, and automobiles. Rubber can be reinforced with steel wire, fabric, and textile cords to increase its strength, and it can be acquired at varying hardness levels to offer diverse qualities[24].

Although they differ depending on the type, rubbers generally offer benefits like light weight, flexibility, elasticity, extremely low glass-transition temperatures, the capacity to regain their original dimensions after an applied stress is released, resistance to abrasion, impact resistance, effective heat dispersion, corrosion resistance, and high damping capacity[25].

1.5.1 Natural Rubber (NR):

Natural rubber (NR) is a key component of tires, road construction, gloves, buildings and other NR products because of its exceptional tensile strength and elongation qualities. NR is tapped from trees and utilized as a biopolymer to alter bitumen. The studies on the modification of bitumen with NR were mostly carried in the United Kingdom during the 1950-1960s. Between 2001 and 2017, the amount of NR produced worldwide increased from roughly 6.9 to 13 million metric tons (MMT)[26].

1.5.2 Styrene Butadiene Rubber (SBR):

The primary elastomer in vehicle tire tread composition is styrene butadiene rubber (SBR), which is used as the main elastomer in the car tire treads (30-70 wt). The tire experiences a variety of physico-chemical stresses while being used on the road, including mechanical shear stress, which causes the tire to deteriorate and release SBR into the environment as tire and road wear particles (TRWP). Once created, then these particles are carried to different environmental compartments (air, soil, runoff, estuaries, sediments)[27].

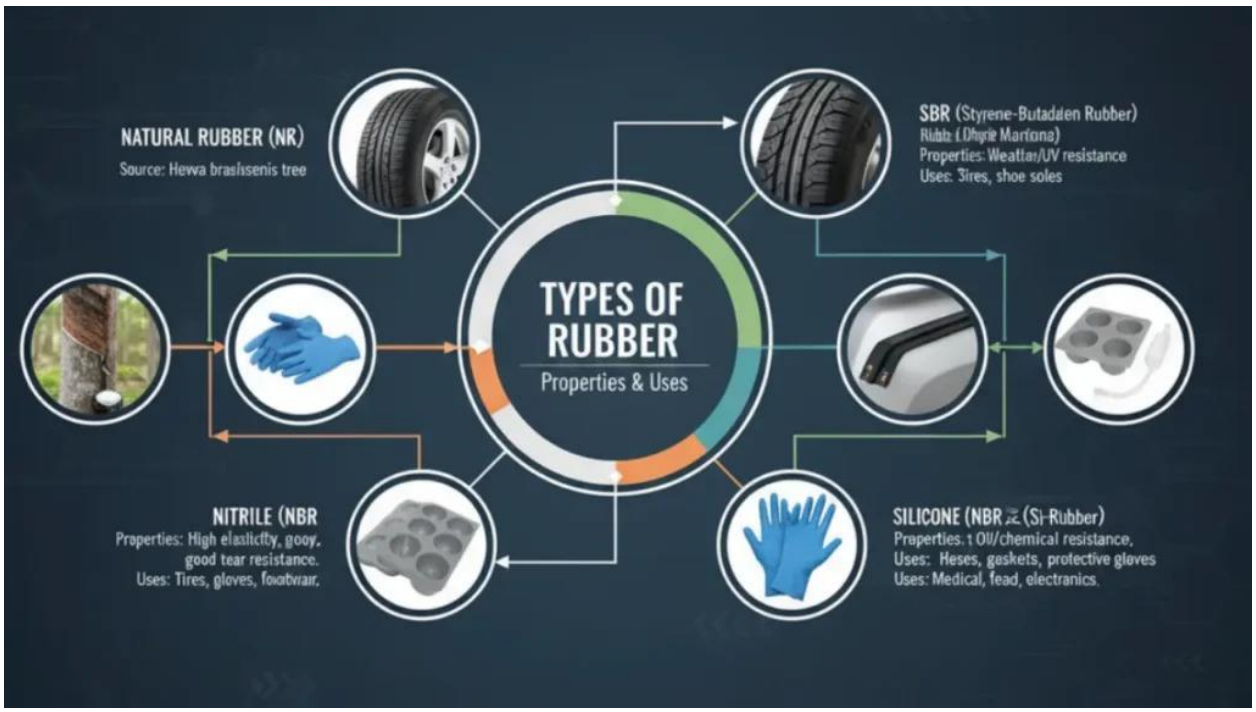


Figure.1.4 Types and Applications of Rubber

1.5.3 EPDM Rubber:

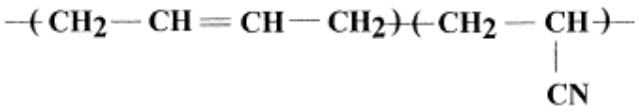
Ethylene and propylene are polymerized with a non-conjugated diene monomer to create EPDM, a synthetic rubber that is vulcanized at a high temperature to permit the production of sulfur bridges. The most widely used rubber compounds on an industrial scale are EPDM rubber compounds, which are often produced by combining EPDM rubber with accelerants, fillers (like carbon black), activators, antioxidants, and vulcanizing agents (like sulfur). They are typically distinguished by their excellent mechanical qualities and strong resistance to weathering, ozone,

UV, and aging. Gaskets, O-rings, window profiles, belts, cable electrical insulation, and waterproofing membranes are all made with EPDM foams[28].

1.5.4 Nitrile-butadiene rubber (NBR):

For over fifty years, acrylonitrile–butadiene rubber (NBR), also known as nitrile rubber, has been produced commercially. Because of its reasonable cost, outstanding resistance to oils, fuels, and greases, ease of processing, and strong resistance to swelling by aliphatic hydrocarbons, NBR has a lot of industrial demand. NBR possesses Excellent adhesion to metal and rigid materials. Approximately 80% of NBR is utilized in the automotive and manufacturing industries[29].

The Chemical structure of NBR is as shown:



1.5.5 Limitations Of Diff Types Of Rubber:

The limitations of different types of rubber can be listed as:

- Natural rubbers NR: low air-permeability, weak electrical insulating properties, low solvent, low oil resistance, low tensile strength, low-resistance to crack-initiation.
- SBR rubbers: poor curing-rate, low strength, high flammability, poor oxidation and ozone-resistance[30].
- EPDM rubbers: poor oil-resistance, poor burning resistance, poor adhesion of raw-blends, poor thermal-stability, poor solvent-resistance
- Using additives to recipes, vulcanization techniques, modification, or bonding with various substrates like metals, plastics, glass, and other polymers, attempts are made to address the drawbacks found in rubbers[31].

1.6 Metal Rubber Bonding Challenges:

The bonding between metals and rubbers is a special problem due to the high polarity, elasticity, surface energy dissimilarity, different physical and mechanical properties and different chemical structure between metal and rubber. It is difficult to create a strong link between these two radically dissimilar materials (metal and rubber). Because rubbers are soft and have low surface energy, whereas metals are hard and have high surface energy[32]. There are notable variations in the surface physical and chemical characteristics of steel and rubber as adhesive substrates, and there is a growing need for direct rubber-to-steel bonding. For this reason, specific surface treatments, coupling agents, and modified adhesive formulations are needed to guarantee robust and durable adherence[33].

1.7 History of Adhesives:

With the history of bonded assemblies, the development of adhesives and sealants has also been developed over time. The first known adhesive-like materials were used in the ancient mythology, like the story of Daedalus bonding feathers with wax more than 3000 years ago. Although it was described in symbols at an early age, it was not until much later that the scientific explanation of adhesion started. Galileo in the seventeenth and eighteenth centuries proposed that there were natural substances, which could bind materials, and Newton proposed that powerful forces of attraction between particles could hold bodies together as the early molecular theories of adhesion[34].

The earliest known mention of a commercially produced glue is found in a patent in the UK in 1754, although mass manufacturer of adhesives was not discovered until the early twentieth century. Empirical techniques, like the 1922 "finger test" where an engineer tested the brittle nature, the flexibility and the fracture properties of a sample of glue by breaking it between fingers, were common during this time to test the glues. The initial testing was done in the form of a comparison instead of a quantitative performance[35].

Most structural adhesives are natural until the beginning of the twentieth century. Another significant innovation was the popularity of phenol-formaldehyde resins in the mid-1910s - the first entirely synthetic polymer adhesive - and then other syntactic systems over the following decades. Historical evolution of commercial structural adhesives urea-formaldehyde (1930)

nitrile-phenolic and acrylic adhesive (1940) epoxies and cyanoacrylates (1950) high-temperature polymers, e.g. polyimides (1960), and second generation acrylics (1970)[36].

Because of these advancements, structural adhesives have gradually shifted to load-bearing and non-critical applications (such as sealing and attaching lightweight components). Because of its exceptional strength, chemical resistance, adaptability, and ability to join disparate materials, epoxy resin-based adhesives were extensively used in the aerospace, automotive, construction, electronics, and wood manufacturing industries. Synthetic adhesive advancements have thus marked a turning point in modern materials engineering, enabling high-performance bonded structures in numerous industrial areas[37].

1.8 Bonding Phenomenon:

Rubber can be joined to metal using adhesive bonding technology, or vulcanized rubber products can be bonded to the metal. The adhesive's purpose is to fuse rubber and metal together by creating molecular interfacial contact through wetting and physical and/or chemical bonds[38].

The three primary adhesion mechanisms are the mechanical coupling, chemical bonding, and thermodynamic adhesion. The physical attraction of one material's surface to another is known as adhesion. These physical forces are the same ones that are typically connected to descriptions of the states of matter. In mechanisms of polymeric materials, adhesion are significantly influenced by van der Waals forces. The interface cohesion would be created by the adhesives like chemicals and adhesion between two or more materials would also be very essential in synthesis of polymers[39].

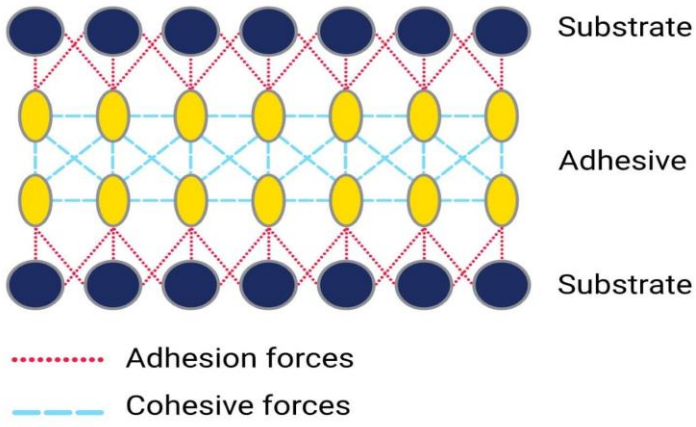


Figure.1.5 Adhesive Bonding[40]

It was suggested that a variety of physical and chemical processes, such as adsorption and the creation of strong interfacial forces at the metal-adhesive interface, chemical crosslinking within the adhesive, interdiffusion, and cross-bridging at the rubber-adhesive interface, combine to form strong metal-adhesive-rubber joints. Since most rubbers are apolar polymers, their adhesive qualities are poor. Direct adhesion between rubbers and metals can occasionally be seen or improved by adding additives to the rubber compound or by modification the rubber[41].

Adhesion refers to the bonding contact between the adhesive and the adherend material, whereas cohesiveness indicates the internal bonding inside the adhesive substance. Adhesion mechanisms are the subject of numerous theories that work in concert to promote sticky attachment. The primary bonding theories now in use for rubber/metal bonding mechanisms include co-crosslinking theory, electromagnetic theory, adsorption theory, and others[42].

These theories are categorized according on the scale at which they operate:

- Atomic scale, which is defined by **Chemical bonding**
- Molecular size, which includes **Diffusion**
- Wettability, weak boundary layer, and acid-base interactions; microscopic scale, which includes **Mechanical Interlocking**
- Macroscopic scale, which includes **Electrostatic Interactions**[43].

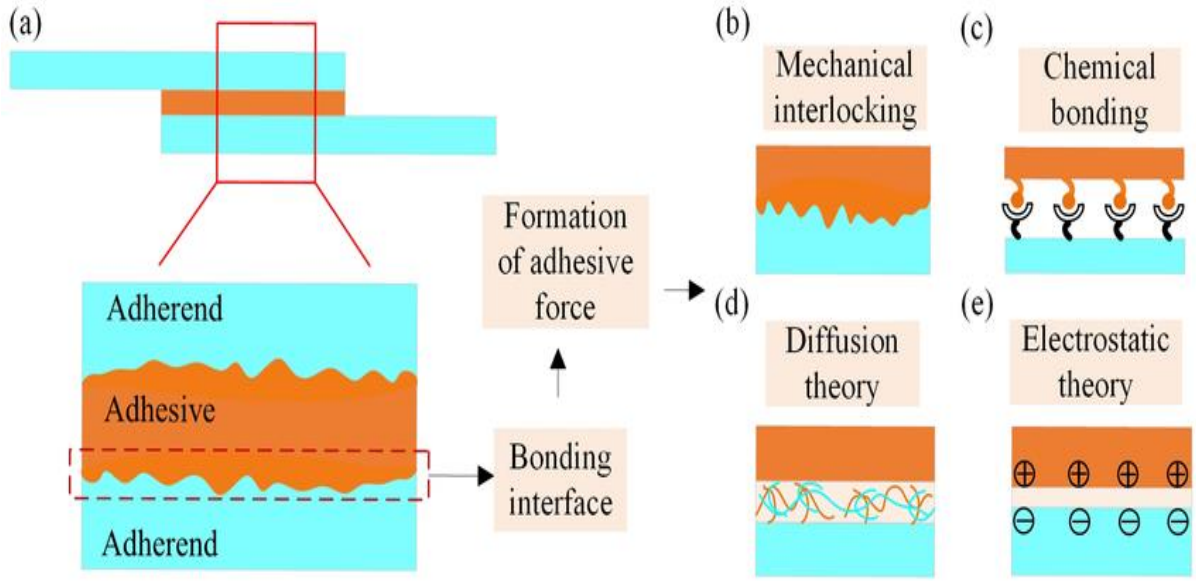


Figure.1.6 Adhesive Bonding Theories[42]

1.9 Industrial and Strategic Applications of Adhesives in Metal-Rubber Bonding:

The science of adhesive bonding between rubber and metal is essential for various strategic and industrial applications. In this kind of bonding the flexibility and vibration resistance of rubber are combined with the strength and rigidity of metals. It is frequently utilized when parts need to manage both severe loads and movement or vibration[44].

Rubber-metal bonding is frequently utilized in industry to create bushings, vibration isolators, shock absorbers, engine mounts, and seals. Automobiles, building systems, machinery, and oil and gas equipment all contain these parts. Compared to mechanical attachment or welding, adhesive bonding is preferable because it distributes stress uniformly, lowers the structure's weight, and eliminates the need for potentially brittle rivets or screws. Moreover, it offers good gas and liquid sealing[45].

Performance requirements are greater in strategic applications including defense, aerospace, and marine systems. Adhesives used here must withstand constant vibration or impact, harsh temperatures, high humidity, fuel, and chemicals. For example, rubber–metal bonding are utilized in sealing components and vibration isolation systems in defense vehicles and airplanes that need to function dependably in challenging environmental circumstances. Rubber-metal adhesive bonding also helpful in absorbing noise and vibration while preserving structural integrity in missiles and submarines[46].

The excellent strength, chemical resistance, and thermal stability of epoxy-based adhesives make them one of the most popular methods for metal-rubber bonding.

Adhesives are essential, in order to improve the functionality, dependability, and safety of industrial and strategic rubber and metal components. Critical engineering applications benefit from lighter, more effective, and more lasting designs made possible by the development of modern adhesive systems[47].

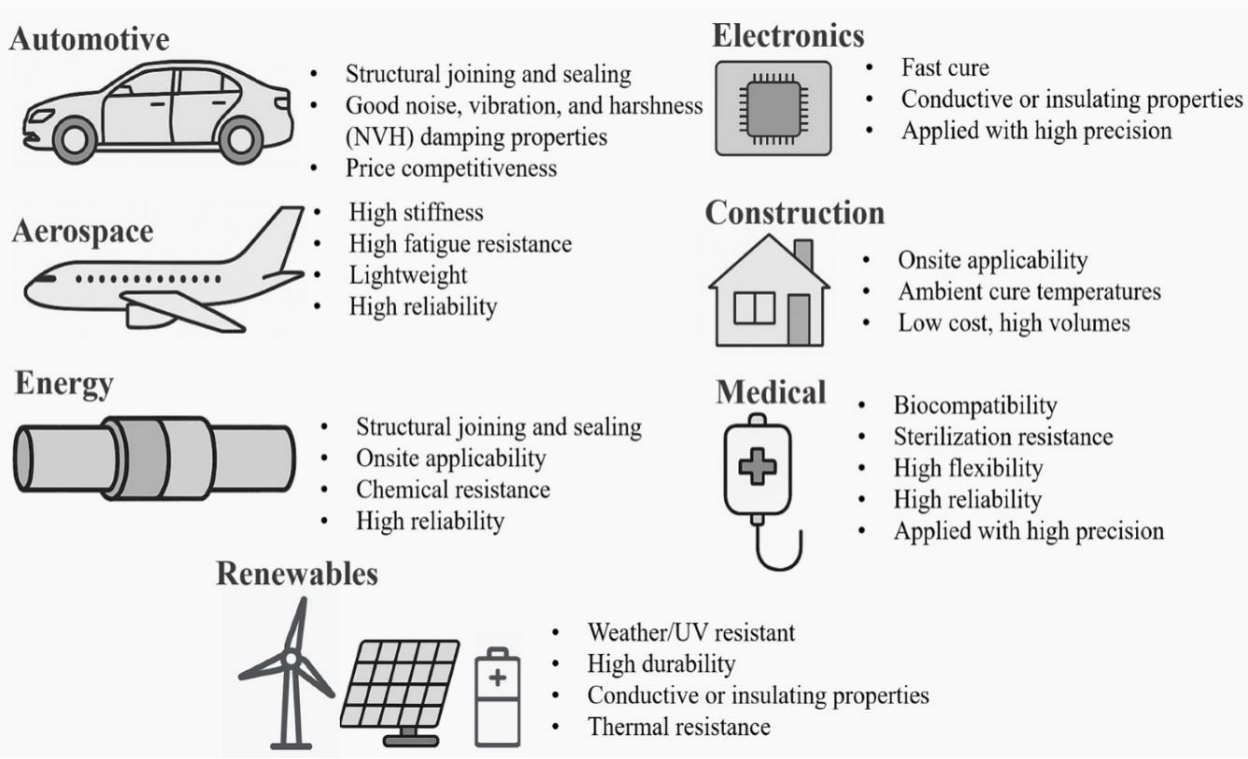


Figure.1.7 Applications of Adhesive Bonding [48]

1.10 Classification of Adhesives:

Adhesives can be categorized depending on their areas of use, the type of material that needs to be bonded, or their physical state at the time of application. Adhesives are generally divided into two categories according to their origin: synthetic adhesives (man-made polymers created for certain performance needs) and natural adhesives (derived from plant or animal sources), each of which has a distinctive function in bonding applications[49]. Because of their affordability, accessibility, and other advantageous qualities, natural materials are frequently selected. However, because of their superior bonding powers, ease of manufacture, resistance to heat and chemicals, increased mechanical strength, and resistance to moisture and grease, synthetic materials have dominated the adhesive market[50].

1.10.1 Natural Adhesives:

Similar to conventional adhesives, bio-adhesives and animal derived adhesives are desired for their capacity to create strong bonds by filling in gaps and joining disparate materials with high shear and tensile strength.

Animal-Based Adhesives	**Advantages**	**Disadvantages**
Tissue and bones	Cheap, non-toxic, sets quickly, has a high shear strength, and doesn't discolour wood	Has low water and damp resistance and does not produce distinct adhesive lines
Albumin and blood	Rapid heat setting, excellent dry shear strength, microorganism resistance, and does not discolour wood	Suitable to glue thin sheets
Casein	Resistance to water, damp conditions, elevated temperature, high shear strength	May discolour woods, dissolves only at high pH, expensive, not suitable for exterior use
Plant-Based Adhesives	**Advantages**	**Disadvantages**
Soybean	Non-toxic, has strong dry strength, and is moderately resistant to heat, wet, and damp environments.	Denaturation of proteins in alkaline solution which is caustic and discolour wood, sensitive to microbial degradation, and not suitable for exterior applications
Peanut	Non-toxic, hygroscopic, superiority of colour	Low shear strength, small bubble-like voids, and peanut allergies limit its applications

Gluten	Non-toxic, sustainable source of protein	Costly

Table1.1 Classification of Natural Adhesives[51]

On the basis of their chemical composition adhesives are classified into four categories: thermoplastic, thermosetting, elastomeric and hybrid[52]. Due to their exceptional qualities, thermoplastics such as vinyl polymers, cyanoacrylate, acrylate polymers, acetate, methyl cellulose, ethyl cellulose, and carboxymethyl cellulose are utilized in a variety of applications[53]. Thermosetting adhesives are highly resistant to humidity, solvents and heat with minimal elastic deformation under the action of loads due to their highly cross-linked polymer structure[54]. Thermoset polymer resins were typically recognized for their low fracture toughness and brittleness[55].

Because of their non-crosslinked linear nature, thermoplastic adhesives have limited resistance to heat, moisture and solvents. They can withstand shear stresses at moderate temperatures, but their chains slide easily and therefore creep and have lower dimensional stability than thermosetting adhesives. For that reason, majority of the structural adhesives are thermosetting by nature[56].

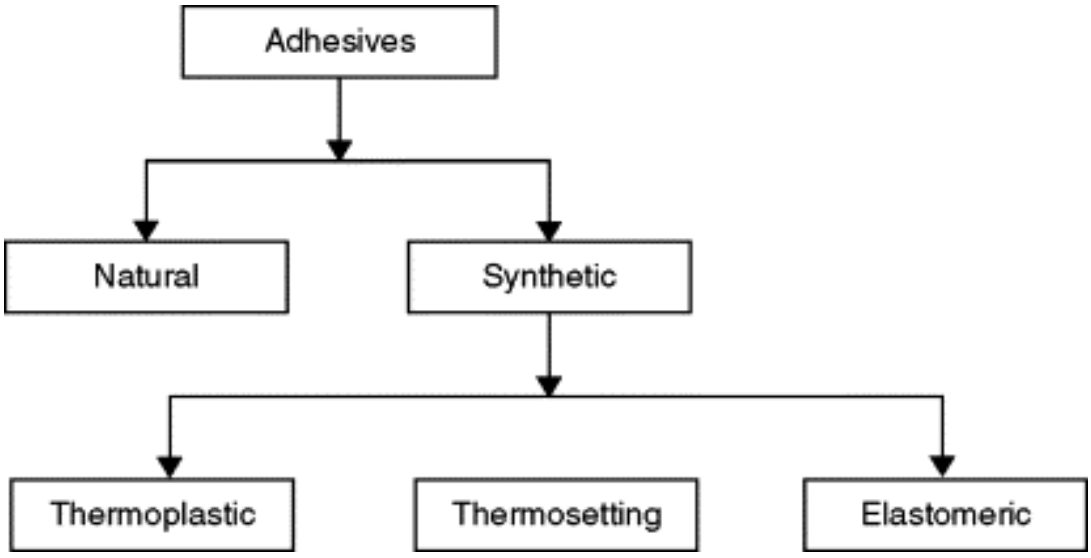


Figure.1.8 Classification of adhesives [57]

1.10.2 Structural Adhesives:

Structural adhesive generally known as a high strength glue, which joins parts together within a load bearing structure. Structural adhesives offer a number of benefits, including strong bonding, production efficiency, and design flexibility. Structural adhesives find extensive application in aircraft in order to bond metal-metal, metal-composite and composite-composite components[57].

1.11 Characteristics Of Structural Adhesives:

Structural adhesives are highly preferred for binding rigid constructions since they are materials with high strength that can handle large loads. They can be cured at both high temperatures and at room temperatures. Under service conditions, joints bonded with structural adhesives can be stressed to a high percentage of the maximum failure load[58]. They are extensively used for construction of structures found in automotive, semiconductor, aerospace and electronic applications. These adhesives are frequently utilized in the building sector for a variety of purposes, including restoring, strengthen, and reinforcing pre-existing constructions[59].

1.12 Classification of Structural Adhesives:

Most frequently used structural adhesives are:

Figure.1.9 Structural Adhesives Classification

Each family of adhesive has specific advantages and drawbacks[60].

The most significant adhesives for engineering applications are Polyurethanes, which offer a high degree of flexibility at low temperatures, Silicones, that have a high degree of resistance to heat and Epoxies, which are known for their high strength and resistance to high temperature. Adhesives based on cyanoacrylates can provide fast bindings, but they can be harsh when combined with PC resins, particularly if the parts have a lot of applied or molded-in tensions[61].

Compared to mechanical techniques, adhesive assembly is frequently far quicker and less expensive. Regarding the ultimate use, the adhesive selection is essential, and several characteristics must be taken into account, including tensile shear strength, rate of cure, impact resistance, load-bearing capacity, resistance to hot or cold conditions and durability[62].

The choice of the right kind of adhesive, the optimal surface preparation of the bonded materials and the appropriate bonding technology are all the factors that effect how effective will be the bonding process.

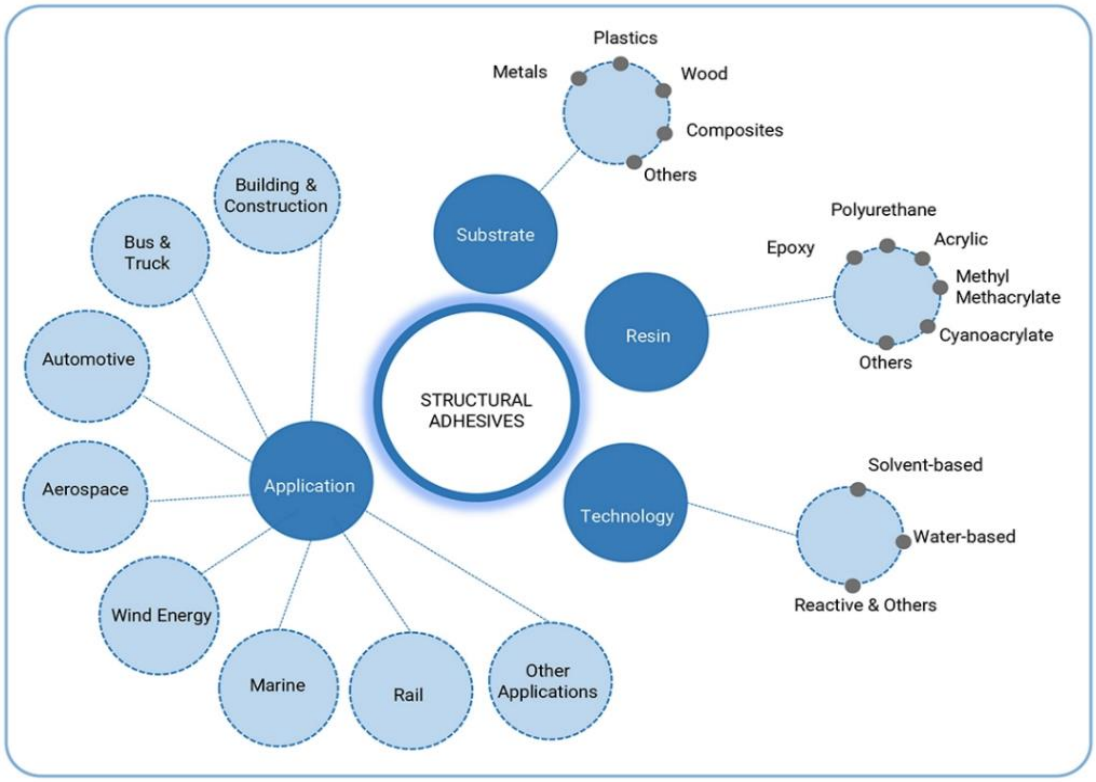


Figure.1.10 Structural Adhesives[63]

1.13 Parameters for Selections of Adhesive Type:

Scientific factors must be taken into account when choosing an adhesive for a particular structural requirement[64]. The choice of adhesive is usually assessed experimentally, and it should be able to tolerate temperatures comparable to those experienced during the vulcanization process. the choice of the adhesive is made depending on the amount of strength needed, the nature of stress (peel or shear, statical or dynamic) and the environment of operation[65].

The adhesive choice criteria rely on the performance of the parameters of a given use. It is beneficial for the user to be completely aware of all these factors. These parameters include:

- The substrate
- Environmental factors
- The joint design
- Service Life
- Application Technique
- The types of material being bonded (dissimilar or similar)
- Process control
- Cost competitive with other joining techniques

The process of adhesive selection is not easy since a single adhesive cannot address all the applications. Practically, compromises have to be made, and the user is expected to give the properties that are most crucial to the desired application priority[66, 67].

1.14 Polyurethane Adhesives:

Polyurethanes Adhesives (PU), single-part or two-part adhesive, are high-performance and highly versatile, and apposes a diverse set of properties, such as the ability to adhere to a diverse set of substrates. They are flexible and have high impact and abrasion resistance.[68]. Excellent mechanical properties at low temperatures (i.e. high elongation capacity, high energy absorption capacity, high resistance in harsh environment, thermal stability and chemical resistance) are included as excellent properties of polyurethane adhesives[69].

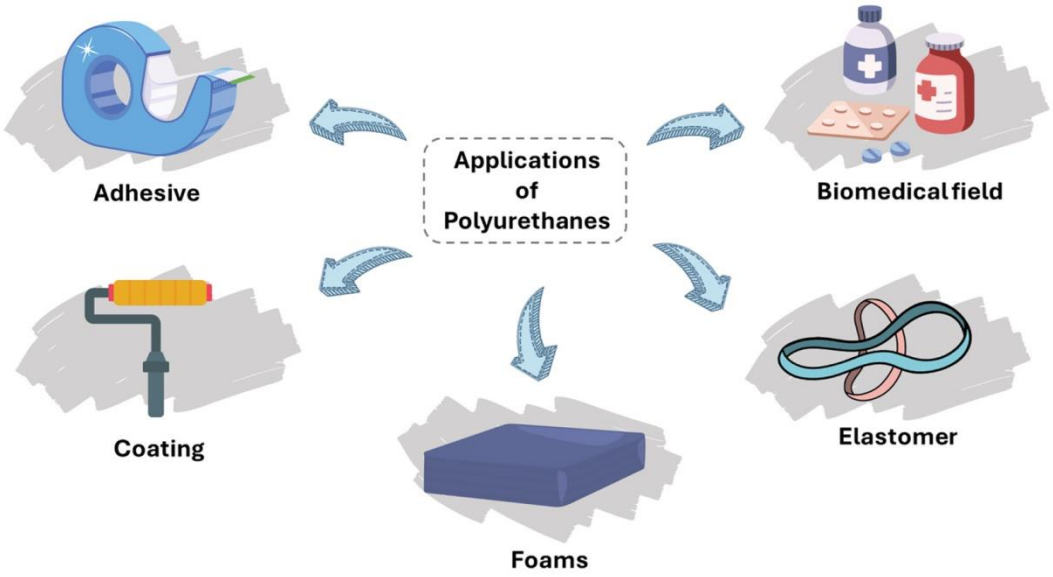


Figure.1.11 Applications of Polyurethanes

A wide range of substrates, including rubber, plastics, metals, wood, glass, and ceramics, may be bonded by using polyurethanes. Automotive parts, furniture assembly, packaging, and footwear are some of its uses[70]. The Tg of polyurethanes, in general, exceeds that of silicones, but is less than from highly cross-linked and structural epoxy resin adhesives[71].

The adhesive qualities of PUAs are greatly influenced by their composition, which is made up of hard (related with the diisocyanate) and soft (associated with the polyol) segments in their polymeric structure. The soft portions offer the capacity to wet, while the hard segments supply the required mechanical and physical strength[72].

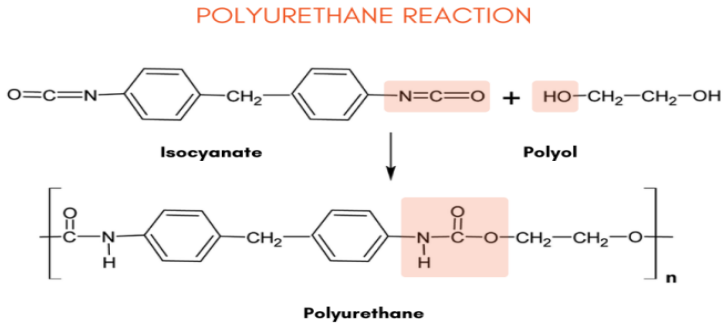


Figure.1.12 Structure Of Polyurethane[73]

1.14.1 Limitation of Polyurethane Adhesives:

However, because of their poor performance at higher temperatures, their application as

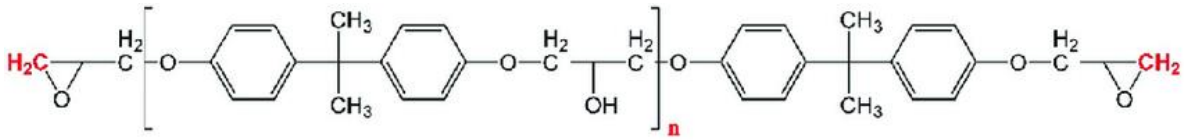
structural adhesives has been restricted[74].

1.15 Epoxy Adhesives:

Epoxy resin, a thermosetting polymer is characterized by its strength, durability, and temperature. It has been widely used as paints and coatings in the construction, automotive, and aerospace industries[75]. The structure of epoxy resin is made up of two or more ring-like epoxy groups, and they have very desirable qualities that may be adjusted based on the use.

Epoxy adhesives are thermosetting resins that soften but do not dissolve when heated. They solidify through polymerization. High shear strengths are provided by epoxy, which can be adapted to suit a range of bonding requirements. Epoxy bonds are typically stiff, filling up tiny spaces well and exhibiting minimal shrinking[76].

Because of its many uses, epoxy resins—which are mostly made from chemicals derived from petroleum—are employed in various applications. Diglycidyl ether bisphenol A (DGEBA), which has superior mechanical and chemical qualities, is one of the most popular kinds of epoxy resin. By curing epoxy resin at various temperatures with various hardeners, such as polyamines, polyamides, anhydrides, and mercaptans, this resin creates a crosslinked network.



a) Diglycidyl ether bisphenol A (DGEBA)

Figure.1.13 Chemical Structure Of DGEBA

1.15.1 Applications of EP:

Epoxy resins are utilized in many different applications as adhesives, coatings, electronic device encapsulants, and matrices for composite materials because of their superior mechanical and insulating qualities, as well as their resilience to heat and chemicals[77]. Epoxies are an essential industrial product and a vital component of industry due to their strength, adaptability, and superior adhesion to a range of surfaces like concrete, wood, glass, ceramics, metals, and many more materials can be bonded together with epoxy[78].

High modulus and failure strength, low creep, and, with careful formulation, good performance

at high temperatures are just a few of the beneficial properties.

1.15.2 Factors Influence the Properties of EP:

The basic component of epoxy adhesives is an epoxy resin that cures, or hardens, to produce a thermosetting polymer. Epoxy resin is frequently based on di-glycidyl ether of bisphenol A[6].

Epoxy structure consists of two or more ring-like epoxy groups and has highly desirable qualities that can be adjusted based on the application. Therefore, the final qualities of ERs will be influenced by the type of:

- ❖ Prepolymer
- ❖ Hardeners
- ❖ Modifiers
- ❖ Fillers

That are utilized in their development[79]. Moreover, applying different curing chemicals allows to regulate the rate of curing of epoxy resins[80].

Figure.1.14 Applications of Epoxy[81]

1.15.3 Advantages of EP:

The advantages of epoxy resin systems include minimal curing shrinkage, strong bonding strength, superior material compatibility, a highly amorphous and cross-linked microstructure, and good resistance to corrosion[82]. Epoxies have a wide range of chemical structures,

mechanical qualities, and physical attributes. They are and will remain one of the most widely used plastic materials for applications[83].

Hardeners cause the epoxies to become cross-linked; the degree of cross-linking raises the modulus and glass transition temperature, decreases creep, and enhances performance at high temperatures[84].

Because of their great strength, tolerance to temperature changes, low cost, and ease of processing, ERs are suitable materials for structural applications[85].

1.15.4 Drawbacks of EP:

- Although epoxy adhesives are very strong for metal bonding, they have a number of inherent disadvantages, including brittleness and localized stress concentration because of limited molecular mobility and the absence of plastic deformation caused by a thick network structure in three dimensions[86].
- Because of their high cross-linked structure, pure epoxy resins are frequently brittle that leads to poor resistance to crack initiation and propagation[87].
- Since epoxy resins are stiff and brittle, they have poor impact qualities, it also effect its further applications[88].

1.16 Steps To Improve Strength of Ep:

Some steps should be done to reduce the brittleness and to improve the toughening of EP curing goods in order to guarantee impact resistance and lower the stress during curing[89].

By altering the adhesive composition, it is possible to improve not only the adhesive bond strength but also other characteristics, such as resistance to certain hazardous use circumstances. One kind of modification is physical modification, which involves adding appropriate substances, such as fillers, modifiers, or modifying agents[90].

- Fillers are added during curing to enhance mechanical characteristics and boost thermal conductivity, which aids in heat dissipation and guards against localized overheating or possible explosion in energetic systems.
- Reactive or non-reactive diluents are added after a room-temperature curing agent has been prepared to lower the viscosity of the epoxy system, improving its processability

and application performance.

- To improve dispersion and overall composite performance, coupling agents are used to increase the interfacial adhesion between the epoxy matrix and filler[91].
- To make them more flexible and processable, plasticizers and nano particles are added to their composition[92].

1.17 Effect Of Fillers:

Solid or fibrous materials that are chemically inert are called fillers. By adding fillers, properties including adhesion, heat resistance, chemical resistance, rheological, optical, and weather resistance can be obtained[93].

One of the most common parts of ER systems are fillers, and the type of filler, its quantity, the mixing circumstances, and the type of basic resin and curing agent all affect how much the addition of fillers will affect the final epoxy system's characteristics. Among the most significant benefits of fillers are their capacity to improve mechanical strength characteristics, corrosion resistance, thermal stability, abrasion resistance, and dimensional stability[94].

Although pure polymers can offer certain beneficial qualities but they typically require additional assistance to function more effectively. Fillers are added to the polymer to accomplish this. Fillers enhance a material's strength, resilience, or pliability. These fillers can be rubber particles, fibers (such carbon, glass, or aramid), or inorganic powders[95].

When fillers are added to epoxide resins, certain of the cured material's qualities improve. In certain situations, it also makes processing the material easier, which extends the life of the composition. It reduces the exothermic effect of the crosslinking reaction, and frequently lowers the costs[96].

The brittleness and fracture energy of epoxies have been improved during the past few decades by combining them with rigid nanofillers including silica, alumina, and carbon nanotubes (CNTs) and soft rubber particles[97].

1.17.1 Rubber Particles as Filler:

Reactive rubbers, waste tire powder, core shell particles (CSPs), are some of the fillers that have

been suggested to overcome these limitations and increase the toughness and strength of epoxy resins[98].

By following 15–20% of liquid rubber toughening, the EP bending and impact resistance have greatly increased, fracture toughness also significantly improved but the strength, modulus ,stiffness and heat resistance performance are diminished because of the reduced strength and modulus of rubber[99]. A significant drop in the modified epoxy resin's glass transition temperature (Tg) and Young's modulus may result due to the poor compatibility between epoxies and liquid rubbers[100].

Epoxy is typically toughened by adding reactive and non-reactive elastomers, but it has been noted that doing so causes stiffness and a reduction in thermal characteristics[101].

Numerous tougheners, both reactive and nonreactive, have been created over time. While some technologies are well-established in several industrial applications, others were created only for specialized uses. Fillers such as clay, fumed silica, or short-cut glass fibers are known to boost toughness[102].

Two novel material types have been reported to toughen epoxy with minimal modulus loss or without it. One employs nanoparticles, including nanotubes, nanoclay, nanorubber, and nanosilica. An inorganic nanoparticle content of 5–10 weight percent considerably raises the Young's modulus[103]. In another, fragile polymers are effectively toughened using block copolymers with minimal loss of stiffness rather than pure rubber[104].

1.17.2 Effect Of Inorganic Nanoparticles Fillers:

Inorganic fillers have been used extensively to increase epoxy resins' resistance to cracking[105]. Because nanoparticles have a very high specific surface area, they interact with the polymer matrix through interfacial interactions, which primarily regulate the materials' new properties[106]. Adhesives used in aircraft applications need to be able to withstand both high temperatures and mechanical strains. Researchers have added micro- or nano-sized fillers to epoxy adhesives to increase their heat resistance[98].

The common epoxide resin fillers include powdered and granulated copper, aluminum, aluminum silicate, chalk, silica, graphite, quartz, metal fibers, carbon nanotubes, and carbon black[107].

Nanoparticles' homogeneous dispersion and small size have made them widely used in a variety of fields[108].

Nanoparticles can withstand the beginning of microcracks because of their high surface activity, which makes them easier to create chemically or physically combination with the polymer.

Utilizing nanoparticles, especially silica nanoparticles, has drawn a lot of attention as a viable substitute for increasing the fracture toughness of adhesives and polymers[109].

Because of its appropriate mechanical, thermal, and adhesive capabilities, silica nanoparticles have been extensively studied[110].

1.17.3 Effect of Silica Nanoparticles as a Filler:

A novel technique for improving the mechanical characteristics of these thermosetting polymers has emerged in recent years. This is accomplished by adding a nanophase structure, like tiny silica particles, to the polymer. The modulus, yield strength, and fracture toughness of the polymer can all be significantly improved by these materials[111]. Utilizing silica nanoparticles as a toughening agent has the potential to improve polymer fracture toughness without the negative consequences of rubber and thermoplastic polymer particles' lower glass transition temperature[112].

The most significant characteristics of silica nanoparticles are their large surface area, tiny size, and uniform size distribution. Additionally, the silica surface contains hydroxyl groups that can facilitate strong chemical interactions with the polymer[113].

It has been demonstrated that these nanoparticle-modified epoxies not only further boost the epoxy polymer's toughness but also prevent a noticeable increase in the viscosity of the epoxy monomer because of the tiny size of the silica particles[114]. Toughness is increased by adding rubber particles, but not at high temperatures. On the other hand, at high temperatures, nanoparticles of silica can improve fracture toughness without lowering stiffness or strength[115].

Nano silica is used to increase the adhesion, hardness, modulus, wear resistance, tear strength, fatigue endurance, and self-heating properties of rubber. According to certain theories, silanol groups on the surface of silica improve compatibility with metal oxides[116].

For nanofillers to be used effectively, the most crucial factors are shape, size, volume fraction, aspect ratio, surface modification, dispersion of nanofiller, Tg, and crosslink density. Numerous investigations have been conducted to examine how these criteria affect EPs' fracture toughness[117].

The inclusion of fillers to adhesive formulations increases their strength and bonding' durability by 25–30%. Wrong filler choice can also influence the adhesion to various substrates as a result of filler particles that may accumulate at the surface leading to loss in the adhesion surface area[118].

1.18 Effect Of Modifiers:

Effectively selecting the right diluents and their ideal concentration will enable the resin to readily achieve a certain flexibility and, as a result, well-defined mechanical properties[119]. Research has been done on toughening EP with semi-crystalline or amorphous thermoplastics to increase its toughness without significantly lowering its fundamental mechanical and thermal characteristics, including as Tg, UTS, and Young's modulus[120].

Thermoplastics are thought to be an excellent option for epoxy toughening. Without compromising other essential mechanical properties, thermoplastics such as polyethylene glycol (PEG), polyethylene imide (PEI), polyethersulfones, polyetherketone, etc., can be added to epoxy resin to boost its fracture toughness[121]. Because thermoplastics melt at high temperatures and cure at low temperatures, they can form a stable, homogeneous phase after being blended with epoxy resin and allowed to cure[122].

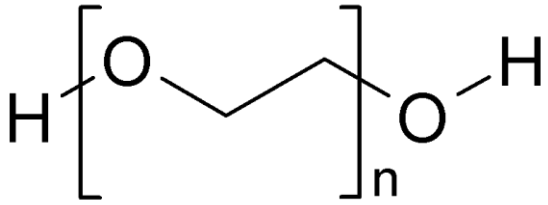


Figure.1.15 PEG Structure

Polyethylene glycol (PEG), one of the thermoplastics, is used as an efficient filler in epoxy. Zavareh et al. describe the toughening impact of PEG in epoxy and found an improvement of roughly 5.7%. Additionally, they reported that the addition of PEG improved the tensile

characteristics of epoxy[123]. Recent observations have shown that PEG 600 modified epoxy resin can exhibit increased toughness, and that PEG-1000 aids in achieving increased strength and toughness at cryogenic temperature (CT). PEG is gaining increased interest in epoxy modification[124].

1.19 Effect Of Silane Coupling Agent:

Silane coupling agents' special capacity to join polymers with disparate substances, like inorganic oxides, such as silica and alumina, makes them useful in a variety of applications. The failure of the composite due to polymer rupture indicates that the bond thus created has exceptional initial strength, and even after significant environmental aging, the bond shows remarkable strength retention[125].

Silane coupling agents improve overall strength and tear resistance by increasing cross-link density. In addition, it improves damping behavior, lowers compression set, and heat buildup, which increases the material's stability and durability under stress[126].

Through the formation of strong covalent bonds at the interface, silane coupling agents aid in improving the binding between rubber and metal. As water replaces the epoxy at the surface, the initial adhesion, which frequently depends on weak hydrogen bonds, may degrade in humid environments. Because silanes strengthen bonding and act as a moisture barrier, they lessen this issue. As a result, epoxy adhesive in metal-rubber couplings performs better and is more durable[127]. The silane can be introduced to the resin where it migrates to the substrate via standard mixing and application processes, or it can be applied to the substrate as a pretreatment in many systems[128].

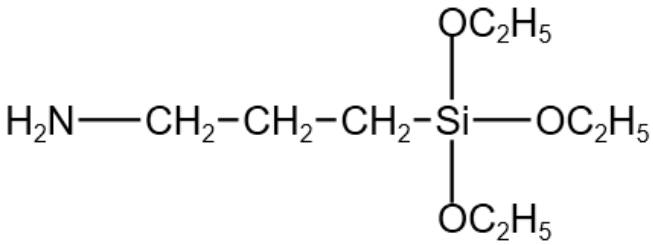


Figure.1.16 Structure of APTES

Common silane coupling agents to enhance surface characteristics are KH-550 (3-aminopropyltriethoxysilane) and KH-560 (3-glycidoxypropyltrimethoxysilane). By minimizing clumping, they serve as bridges between the epoxy matrix and the filler particles, aid in particle

dispersion. The epoxy group in KH-560/GPTMS and the amino group in KH-550 form a strong bond with the epoxy matrix[129].

However, in KH-550 H2N(CH2)3Si(OC2H5)3, the amine group functions as a catalyst for epoxy curing, allowing the silane coating to properly attach to the epoxy matrix and offering a superior interface compared to KH-560 and GPTMS[130].

1.20 Effect Of Curing Agent:

A material added to an adhesive that promotes the curing reaction is known as a Curing Agent or Hardener. Curing agents are compounds that can solidify or harden a composition by reacting with other ingredients. Through their chemical combination with the base resin and incorporation into the final polymer molecule, these influence the curing reaction. They are selected particularly to react with a specific resin. Curing agents will significantly impact the adhesive system's basic characteristics and curing qualities[131].

Curing agents are made up of molecules that contain reactive cross-agents, ionic and cationic inhibitors, and active hydrogen and its derivatives. These molecules are usually of equal weight[132]. Epoxy adhesives typically consists of two components: a curing agent and epoxy resin. It is important to remember that the appropriate ratio of epoxy resin to curing agent is essential since an incorrect ratio might cause unreacted groups to form in the network, which diminishes the resin's ultimate qualities[133].

Reaction rate, curing cycle, and final product properties are all significantly influenced by the curing agents[132].

When the epoxy resin reacts with the proper curing agent during the curing process, the oxirane groups at the edges of its polymer chains experience a ring-opening reaction. The resin is changed into an insoluble and flexible thermosetting polymer by this process, which creates a strongly cross-linked, three-dimensional network[134].

Numerous curing techniques have been developed to boost the epoxy system's hardness, including wet coating, formwork curing, membrane curing, curing by absorbing heat, hot mixing method, infrared curing, and others[135].

The benefits of room temperature curing (curing temperature 15–40 °C) over other curing techniques are low toxicity, low internal stress, low energy usage, and minimal shrinkage due to the thermal expansion difference[136].

1.20.1 Polyamide Curing Agent:

Common room-temperature curing agents for epoxy resins include aliphatic amines, modified aliphatic amines, and low molecular weight polyamines. The most commonly utilized of them are phenolic amines and low molecular weight polyamines[137].

Most "all-purpose" epoxy adhesives contain polyamide curing agents. They cure at room temperature and adhere effectively to a variety of surfaces, such as glass, metals, plastics, and elastomers. Additionally, the polyamide-cured epoxy offers a reasonably flexible adhesive with fair peel strength, moisture resistance, and heat cycling characteristics[138].

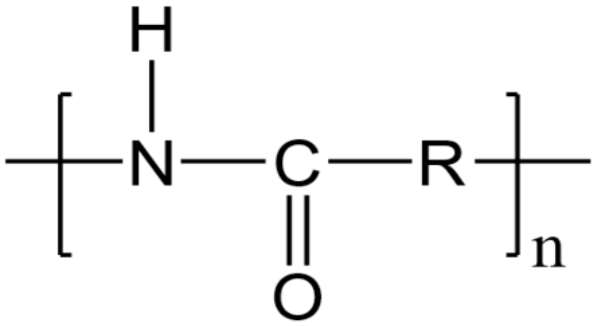


Figure.1.17 Structure of Polyamide

The polycondensation of dimer acids and polyamines yields low molecular weight polyamide curing agents. The advantages of low molecular weight polyamide over conventional curing agents include greater adhesion, improved flexibility, and less toxicity[139].

1.21 Surface Treatment Method:

Machining oil, protective greases, and other impurities left behind from production and shaping frequently cover metal surfaces. As a result, the metal's surface energy decreases (a comparison of different "pre-treatments" for stainless steel revealed that the metal's surface energy increased as the thickness of the contamination layer decreased).

To possess a good interfacial strength and a long lasting joint, abrasion, or chemical treatments,

mechanical surface cleaning or solvent cleaning should be done carefully. The choice of the right kind of adhesive, the optimal surface preparation of the bonded materials and the appropriate bonding technology are all the factors that effect how effective will be the bonding process[140].

A contaminated adherend surface has a significantly lower adhesion strength than a clean surface, which may lead to the formation of a weak interface layer. As a result, sufficient surface preparation of the adherend is necessary to:

(1) Clean the surface and eliminate contaminants from the adherend surfaces

(2) Improve the roughness of the adherend surface

(3) Decrease the apparent contact angle and expand its area of contact with the adhesive

(4) Activate the adherend surface, providing a more strong bond[141].

1.21.1 General Process For Surface Treatment:

The general procedure for surface treatment is as follows:

- Firstly, the acetone is used to clean the adherend surface of impurities.
- In order to improve the bonding strength of the interface, the adherend surface might be processed using physical and/or chemical means to increase its surface roughness.
- Third, distilled water and acetone are used to clean the adherend in order to further eliminate the minute particles that were left behind by the earlier processes.
- Lastly, the surface is dried to guarantee that all of the moisture has been eliminated.

Keep in mind that the goal of the so-called macroscopic and/or microscopic surface treatments is to provide the ideal bonding conditions.

Surface treatment modifies a steel surface's chemical and physical characteristics, which can modify the bonded joint's strength and mechanism of failure[142].

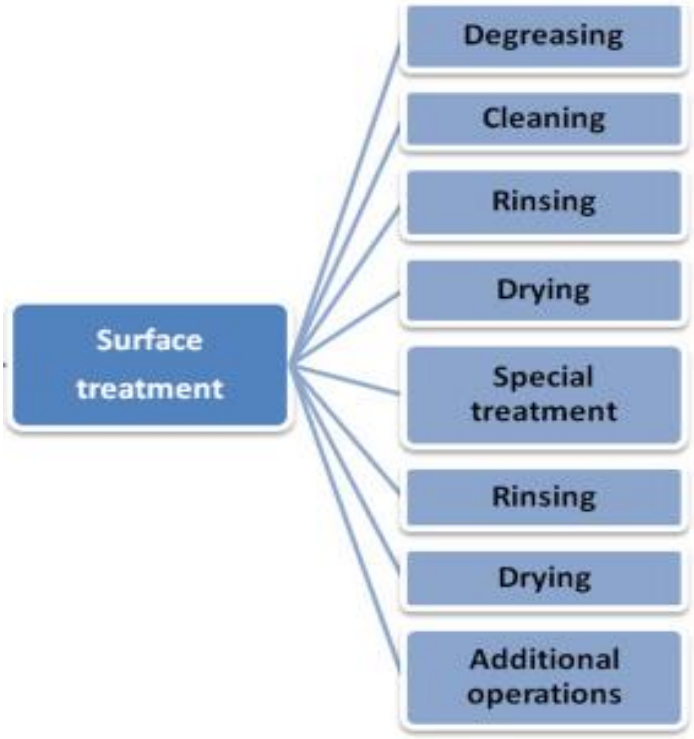


Figure.1.18 General Process Of Surface Treatment

1.21.2 Mechanical Treatment:

The main purposes of mechanical treatments are to remove some of the current oxide layer and create a clean, macroscopically rough surface. The initial dry strength of the adhesive/adherend contact is enhanced by the combination of a fresh, clean adherend surface with notable macro-roughness. The common techniques of increasing the surface roughness and surface energy include abrasion and sand-blasting of a solid. Wire brushing, rubbing with sand, emery sheets, or abrasive pads, and grit blasting with steel, silica, or corundum grits are examples of mechanical

pre-treatments. These techniques entail abrasion of the metal surface, increasing the possible bonding area and producing a rough surface[143].

Cleaning of a surface which was previously subjected to mechanical treatment is usually done by using an appropriate liquid. The liquid should be neutral to the substrate and capable of dissolving impurities like grease, dust etc. Low boiling liquids like acetone, alcohols and chloroform are generally used in this case. In general, it is believed that mechanical methods like grit-blasting or abrasion provide better bonding surfaces than degreasing alone[144].

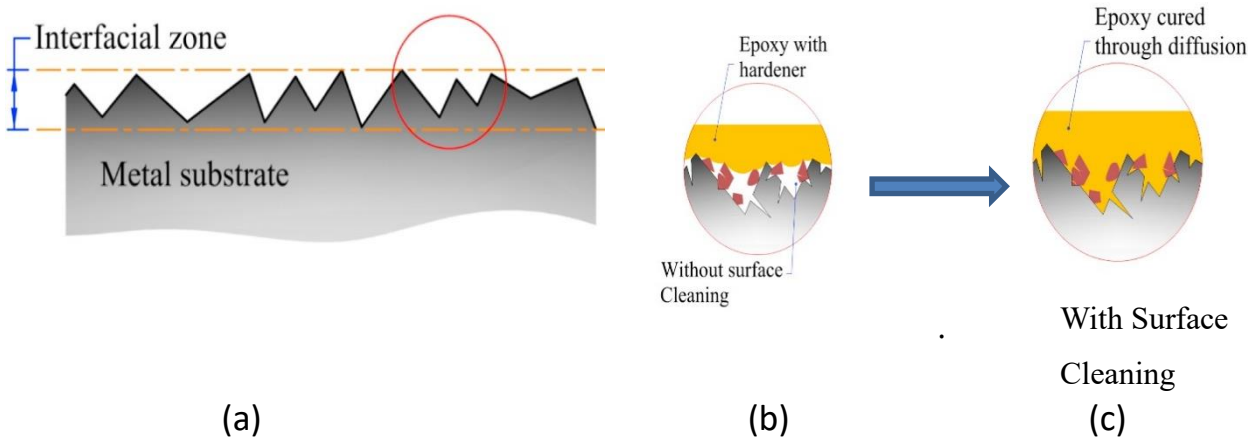


Figure.1.19 Effect of Surface Treatment on Bonding[145]

Alkaline clean or chemical pretreatment for stainless steel followed by immersion in a solution consisting of 20-25% nitric acid(by weight) and 75-80% distilled water(by weight) at 50 to 55 °C for 20-30 minutes. Care must be taken to preserve it after optimum surface condition has been obtained before adhesive has been applied[146].

Chapter 2

Literature Review

2.1 Industrial Use and Development of Modern Adhesives:

Adhesive bonding is characterized as a very efficient means of joining in aircraft repair and manufacturing, which is better than mechanical fastening in terms of the reduction of weight and enhancement of fatigue characteristics and allows transferring the load effectively. It is highlighted in the paper that to attain credible structural bonds, adhesive chemistry needs to be controlled, and the adherends surface prepared appropriately. Elimination of poor boundary layers, avoidance of contamination, and regular activation of the surface is found to be vital to long-lasting performance. Surfaces cleanliness, the state of oxide and interfaces interactions are found to be crucial in joint strength, environmental resistance, and long-lasting stability. It is also observed in the study that the use of bonding in metal-composite hybrid structures is increasing and the need to use more sophisticated inspection methods and long durability histories is necessary to justify high-end aerospace applications[147].

Modern adhesives are extensively used in industry to bond a variety of materials and are made using a variety of formulation techniques. While natural alternatives like starch or dextrin only give quick bonding, permanent solutions like epoxies and polyurethanes offer excellent shear strength. Although the content in this work is primarily descriptive and lacks specific performance data, synthetic adhesives are preferred due to their strength, durability, and adaptability. For current engineering applications, further research is required to create adhesive compositions that are more robust, durable, and ecologically friendly[148].

Hybrid joining involves the integration of two or more methods of joining, that is, mechanical fastening, welding, and adhesive bonding, to obtain better joint performance than either of the methods. Initial studies revolved around the choice of adhesives and characterization of joints, epoxy adhesives are most commonly applied because of their high strength and convenience, whereas polyurethanes and polyimides have a high degree of flexibility and thermal resistance.

The existing literature has indicated a better load sharing, stiffness, fatigue resistance, and corrosion protection of the hybrid joints, particularly, the weld-bonded or fastened-bonded joints. There are still difficulties in simulation of processes, in the knowledge of the environmental impacts and optimization of adhesives in particular hybrid methods. The method is becoming more applicable in lightweight, multi-material structures in the automotive, aerospace, and industrial applications[149].

Bitumen, birch tar, and collagen-based glues have been displaced by novel synthetic polymers such as phenol-formaldehyde, epoxy, polyurethane, acrylics, and high-temperature adhesives. Applications in electronics, healthcare, construction, automotive, and aerospace have benefited from this research. There is little quantitative data, mechanical analysis, or discussion of durability and environmental impact, despite the fact that the historical overview and uses are thoroughly discussed. The utilization of eco-friendly and renewable adhesives, enhanced analytical methodologies, and sophisticated bonding methods for innovative composite materials are some of the future directions[150].

Renewable based biopolymers are being introduced as substitutes to the petroleum-based adhesives, gums, emulsions, and binders. Starch, proteins, lignin, and plant oils are some of the important materials that can be chemically or physically altered to improve its properties such as water resistance and bonding strength to be utilized in wood composites, packaging, pharmaceuticals and construction. The market of these environmentally friendly products is growing due to the increasing environmentally conscious attitude and the technological development. Regardless of the difficulty in expense and performance, modern innovation will bring them to a more profitable point and less reliance on fossil fuels, which is the key to a more sustainable future of industrial materials[151].

Functionally graded adhesives (FGAs) improve joint performance by promoting uniform stress distribution throughout the bond line through continuously changing composition and characteristics. Joint strength, toughness, and failure load are increased by manufacturing techniques such graded curing, varied adhesive mixing, and the deliberate use of micro- or nanoparticles. Considering these advantages, there are still issues with particle agglomeration, production complexity, repeatability, and preserving the graded structure under operating

circumstances. Although FGAs provide a great deal of design flexibility for aerospace and automotive applications, further study is required so that they can be widely used in industry[152].

Adhesive materials, joint design, production, and modeling techniques have all seen major advances in adhesive bonding technology. Together with non-structural alternatives like pressure-sensitive and bio-based adhesives, structural adhesives like polyurethanes, acrylics, and toughened epoxies been developed. Functionally graded, hybrid, and self-dismantling joints are examples of innovative joint design techniques that are complimented by new additive manufacturing applications. Cohesive zone models, hyper elasticity, and viscoelasticity are examples of advanced numerical modeling approaches that make it possible to accurately anticipate joint performance, failure, and longevity under a variety of scenarios. All things considered, adhesive bonding is still a flexible and developing technology that is essential for lightweight, multi-material constructions used in the electronics, automotive, and aerospace sectors[153].

Hybrid epoxy-polyhydroxyurethane networks were fabricated and defined as products of epoxy and cyclic carbonate monomers with amine hardener. The crosslink density was decreased with the addition of cyclic carbonate, whereas the hydrogen bonding was increased, which increased the toughness of the material. These polymers were outstanding aluminum substrate adhesives with 50/50 epoxy-polyhydroxyurethane ratio offering the best balance of features and high adhesive capability than standard epoxy. In this way, the possibility of designing polymer network chemistry to meet its high-performance and greener adhesives is emphasized[154].

Adhesive bonding is described as a flexible and multipurpose joining technique based on important phenomena such chemical bonding, wetting, mechanical interlocking, molecular diffusion, and electrostatic attraction. The selection of a variety of adhesive systems, such as thermoplastic, thermosetting, solvent-based, water-based, hot-melt, and reactive formulations, is influenced by the characteristics of the substrate, the need for curing, and the service conditions. It is demonstrated that the quality of adhesion is highly dependent on the energy of the surfaces, contamination, surface preparation, and mechanical behavior of bonded materials. Adhesive bonding allows the joining of dissimilar or heat-sensitive materials compared to mechanical or

thermal joining, offers an efficient distribution of stress and may serve to provide sealing or insulating properties, but the process needs to be carefully controlled to provide durability, reliability and repeatable performance[155].

Understanding the adhesive behavior in extreme conditions has traditionally been a research topic on the effect of temperature and loading rate on mechanical performance. Previous experiments had demonstrated that adhesives tend to become stronger with an increase in strain rate and weaken at a low temperature. The present work builds on this knowledge by studying an epoxy adhesive at room and lower temperatures, where the strength is only enhanced with strain rate at moderate temperatures whereas stiffness and failure strain does not follow systematic trends as temperature decreases. The results indicate the multifaceted nature of the contribution of localized heating and thermal mismatch. The research, however, is restricted to a single type of adhesive and indicates that further research should be conducted on a wide range of different formulations and conditions[156].

The past five decades have been characterized by a lot of research on issues of adhesive bonding at extreme temperatures because polymeric adhesives are degraded as opposed to metals or composite materials. Initial investigations had identified the influence of adhesive shrinkage and thermal expansion with the result that shrinkage has minimal effect on joint strength but may induce undesirable deformations, whereas differential thermal expansion produces very high stresses in rigid adhesive joints, which may cause premature failure. Recent efforts have been made to enhance adhesive formulations to enhance temperature performance, as well as the geometry of joints such as dual and graded joints, with the assistance of more advanced simulation and design tools. A combination of material, design and modeling technologies offers a full picture of joint behavior that allows strong, reliable and durable adhesive bonds in high-tech application having high thermal loads and the current research work is furthering the existing strategies[157].

2.2 Epoxy Adhesives:

The increased interest in high-technology adhesives has prompted a lot of research on nanoparticle-modified epoxy systems, with previous investigations showing that nanoscale fillers

can affect the strength, toughness and thermal stability however were usually poorly dispersed and were not reliable to provide consistent performance increases. The article summarizes recent achievements in application of nanoparticles of various shapes, sizes and functionalities to optimize mechanical, thermal and fracture properties of epoxy adhesives, and how their dispersion and interaction with the curing network dictates ultimate behaviour. Although the paper provides useful comparisons of clays, graphene, MWCNTs, HNTs and other fillers, the discussion is limited by inconsistency in the reported methods and lack of long-term data. Recent developments in the research focus on hybrid and core-shell nanoparticles, but the control of predictable multifunctional functions is still a major issue[158].

The use of epoxy resins is popular due to the ability to customize their chemistry and processing, and the fact that the majority of applications involve the necessity to meet high-fire-safety criteria. Previous studies determined the effect of resin type, curing agent, and curing conditions on flammability, and much previous practice had been done on halogenated, phosphorus based, silicon based flame retardants, and nanoparticle flame retardants, but several older systems had a flaw of brittle nature, toxicity and low recycles. The article summarizes the representative progress in the field of modified and synthesized flame-retardant systems and their comparative performance of efficiency, and processability and applicability to various applications. One of the main limitations is the selective coverage because the big amount of existing studies prevents a full assessment especially in terms of long-term sustainability and environmental effects. The discussion outlines existing challenges of safeguarding, multi-purpose, recyclable and bio-based flame-retardant designs in the following generation epoxy adhesives[159].

Epoxy adhesives are commonly employed in the process of bonding metals, glass, concrete, ceramics, wood and plastics because they have a powerful, hard cross-linked structure and minimal curing contraction. Initial progress was concerned with traditional room-temperature and thermal-cure systems, which were very strong yet took a long time to cure, and could not be used with flexible substrates. The recent studies have overcome such shortcomings by developing low-temperature thermal cure, thermal snap-cure hybrid, UV-cationic and UV-thermal dual-cure hybrid, and toughened epoxy formulations to enhance the impact resistance and mechanical performance. These inventions have increased the use in general industry, construction, electronics, automotive, aerospace and defense industries. The future work is

focused on sustainable epoxy adhesives to fulfill environmental requirements, minimize the ecological effect, and fulfill customer needs without compromising or lowering mechanical, thermal, and adhesive performance, and as such, a move towards sustainably high-performance bonding solution is evident[160].

Structural strengthening Cold-curing epoxy adhesives are common and their performance may vary with curing conditions. Previous literature had observed that the temperature during curing has an influence on mechanical properties and this paper makes a comparison between room temperature curing and accelerated curing at 80-90 deg C. It was found that at high temperature, the rate of strength development is accelerated but the result is a large porosity that results in low tensile strength and stiffness despite the correction of lost cross-section. Analysis through images assisted in measuring porosity and the influence of porosity on strength. According to the study, major shortcomings of accelerated curing include increased porosity, and long-term durability problems due to moisture or chemical intrusion through pores need to be studied[161].

Epoxy adhesives are known to have high strength and stiffness though they are inherently brittle and hence cannot be used in most structural applications. To counter this, epoxy matrix can be supplemented with small particles of rubber like carboxyl-terminated butadiene acrylonitrile (CTBN). These particles form a multiphase microstructure, in which the rubber constituent serves to absorb energy and inhibit the spread of the cracks. Under the stress of the epoxy, the rubber particles cause the plastic deformation and create minute cavities in the surrounding matrix, which dissipates the energy and toughen the material. This mechanism can greatly enhance the fracture energy and impact resistance of the adhesive, an order of magnitude, and has little effect on other useful properties, such as stiffness, modulus or thermal stability. This strategy has been extensively thought to work in enhancing toughness in epoxy without affecting its other engineering performance properties. But this slightly reduce its other properties like stiffness, modulus and thermal stability[162].

Epoxy adhesives are frequently employed in structural applications because of their great strength and thermal stability. However, in order to obtain balanced performance, their inherent brittleness frequently needs to be modified. Combining hard fillers like alumina microparticles with flexible toughening agents like recycled rubber particles and thermally stable additives like

phenolic resins is one efficient method. Research has demonstrated that these multiphase formulations can improve thermal degradation resistance and greatly increase lap shear strength, sometimes by almost 80%. Mechanisms like crack deflection, energy absorption around stiff particles, and better stress distribution within the adhesive matrix are frequently cited as the causes of these improvements. While this approach offers useful information about the toughening behavior of hybrid-modified epoxies, factors like the unpredictability of recycled materials and the limitations of micron-scale fillers show the significance that controlled formulation development is needed to producing reliable, high-performing epoxy adhesive systems[163].

Existing literature revealed that adhesives do not act similarly at low temperatures, as well as at high loading rates, but the tensile behavior of such adhesive has not been completely comprehended. Recent studies in epoxy systems indicate that strain rate has a strong influence on strength and ductility at moderate temperatures with extremely low temperatures hinder these advances and slow strain softening because of the limited movement of molecules. Such comparison with other families of adhesives, like polyurethane, would imply that epoxy materials could be more stable in cold, high-speed loading conditions. Nevertheless, the research is currently confined to several formulations and test conditions, which means that wider research is required on various adhesives, geometries of joints, and severe environmental conditions[164].

Traditional epoxy paints have been known to have difficulties in mechanical strength, adhesion and corrosion resistance especially in severe conditions like marines. Initial efforts were made on enhancing these properties by modifying polymers and by incorporation of fillers although there were still constraints in the high crosslink density and interfacial bond strength. Recent studies have created an epoxy/epoxidized eucommiaulmoides gum (EP/EEUG) coating with 5 wt% KH792-modified nano-silica which creates a network of doubled crosslinking. The nano-silica reacts with polymer structure and metal surface, and it improves adhesion, mechanical stability, and resistance to corrosion. The coating was optimized resulting in 54-56 percent improvement in adhesion, 19 percent improvement in tensile strength, 80 percent enhancement in elongation and retention of high impedance after 15 days in 3.5 percent NaCl. The shortcomings are an assessment of a single type of filler and concentration, and the synergies of various types of

nanofillers have not been studied. Future research might involve the use of multi-nanofiller systems, self-healing surfaces and long term durability[165].

Nanocomposites made of epoxy are also common as adhesive because they have enhanced mechanical characteristics and resilience of joints. The nano-fillers that improve adhesion are diverse with carbon nanotubes (CNTs), graphene nanoplatelets (GNPs), nanoclays, nano-silica and nano-alumina when uniformly dispersed and bonded to epoxy matrix. Good dispersion techniques are mechanical mixing, ultrasonication and surface modification of nano- fillers. Adequate filler content enhances the strength of cohesion and minimizes stresses left behind whilst excessive levels may cause agglomeration and increased viscosity, which influence bonding. Nanoparticles in the form of plates like nanoclays prove to be the best in the complete inhibition of moisture diffusion whereas the spherical nanoparticles absorb more moisture[166].

The goal of recent developments in epoxy-based thermally conductive adhesives (TCAs) is to create lead-free substitutes for conventional solder used in electronics. To enhance heat transmission while preserving electrical insulation, these systems employ a variety of conductive fillers, including metals like silver and copper, ceramic fillers like BN and AlN, and carbon materials like CNTs and graphene. In order to overcome epoxy's inherently low thermal conductivity, research additionally looks into conduction mechanisms, hybrid filler combinations, and filler surface treatment. The main difficulty is that a significant volume of filler is required to ensure that the glue conducts heat effectively. However, the glue may weaken and lose part of its mechanical strength if too much filler is used. Although the majority of the research is limited to epoxy systems, the studies often provide useful information about how to develop these materials. There is little information on how these adhesives function over extended periods of time, and there is little comparison with other kinds of polymers[167].

Recent studies have focused on employing nanofillers to improve epoxy adhesives. The combined impact of nanoclay (C30B) and multi-walled carbon nanotubes (MWCNTs) on epoxy adhesives was examined in this work. Ep/1.0 C30B demonstrated the maximum strength in lap shear testing, outperforming pure epoxy by 52%. While XRD verified nanoclay exfoliation, SEM and TEM investigations showed clear fracture characteristics and excellent nanofiller dispersion. According to DSC and TGA analyses, nanofillers improved heat stability by raising

curing and degradation activation energies. The study shows that the kind, shape, and distribution of nanofiller have a significant impact on mechanical, morphological, and thermal performance; nevertheless, in order to prevent phase separation, synergistic effects must be carefully controlled[168].

Epoxy resins (ERs) are commonly employed to coating metals such as steel and aluminum against corrosion since their polar functional groups enable a high rate of attachment to the surface to create a protective coating. Simple organic compounds offer short-term corrosion inhibition and surface coverage, whereas both pure and cured ERs are superior to organic compounds because of the superior coverage on the surface and long-term protection. It can also be further improved by adding organic or inorganic fillers to prevent penetration of corrosive elements in the coating by blocking the small pores. ERs are not very soluble in water and therefore are typically coated and not used in solutions[169].

The enhancement of the mechanical properties of adhesives and adhesive joints has been an important area of research, with the preliminary studies on geometry of substrates, microparticles, nanoparticles and fiber reinforcements. This review explains the effect of reinforcements of various scale in determining the strength, stiffness, and fracture toughness of polymeric adhesives. Micro- and macro-fibers increase strength and stiffness and are constrained by the direction of the load, whereas nanoparticles, as a result of high surface area, improve mechanical characteristics and can serve as moisture barriers, improving durability. The effectiveness is determined by the type of reinforcement, its content and the method of manufacturing. The paper emphasizes the necessity of selective use of reinforcements, depending on their application, and how difficult it is to standardize its effect on the adhesive performance[170].

The mechanical performance of epoxy adhesives used for structural bonding frequently varies significantly based on the type of resin and the ratio of curing agent, and current research offers a thorough analysis of these impacts. With a focus on the compressive behavior and shear strength of steel single-lap joints, the study assesses bisphenol-A-based epoxy systems cured with polyamide hardeners at various stoichiometric and over-stoichiometric ratios. The findings demonstrate that, especially for changed resins, compositions cured within the suggested

stoichiometric range provide greater compressive and shear strength than those containing extra hardener. Additionally, the adhesives showed somewhat ductile failure as opposed to completely brittle failure. Previous studies have also shown how cure chemistry affects epoxy performance. The article's limited testing scope, which excludes long-term performance evaluation and environmental durability, is a major drawback[171].

Previous research indicated that epoxy bonding materials were very good with metals but failed when exposed to wet or hot environments, and the traditional surface treatments are expensive and not simple. This paper explores a more basic method of incorporating nano-Al2O3 to epoxy to make it bond to steel. It demonstrates that even small doses of nanoparticles, in particular, 2 wt, have a significant positive effect on the adhesion strength and change the failure mode to mixed. Better bonding is associated with the formation of new chemical groups in the interface. Nevertheless, it is limited to a single type of nanoparticles and curing conditions. Future studies would involve the investigation of alternative nanofillers, long-term sustainability, and reinforcement schemes[172].

Numerous studies on rubber adhesion have established basic mechanisms like diffusion, mechanical interlocking, thermodynamic wetting, and acid-base interactions. Previous research has also shown how fillers, compatibilizers, and surface treatments can improve bonding with metals, plastics, fibers, and blended elastomers. Building on these fundamentals, the discussion incorporates important factors that affect interfacial strength, such as compatibility, reactivity, surface energy modification, and crosslink density. It also describes useful industrial techniques to improve adhesion efficiency, such as chemical oxidation, plasma treatment, anodization, flame treatment, and aqueous primer systems. The compilation provides extensive theoretical and application-based understanding, but it is still restricted by the lack of quantitative comparison of adhesion values, the limited assessment of long-term durability, and the insufficient coverage of new nanocomposite-based adhesive technologies required for recently developed structural applications[173].

Rubber-to-metal bonding adhesives that are waterborne have been used since the 1990s, although there are few studies on formulation in detail because of proprietary considerations. The study examined the polychloroprene latex-based adhesives through statistical experimental

design, such as fractional factorial and response surface designs, on the impact of components on adhesion. Twenty-six formulations were put through viscosity, wettability, non-volatile solid and mechanical strength tests such as lap- shear test and pull-out tests. It was established that tackifier resin, silicon dioxide and latex type had the most significant effect on the adhesive and cohesive properties. The best adhesion was obtained when vulcanization was done at 150 ^{o}C at 15 min pressure. The research gives an understanding of the importance of formulation variables in the bonding of rubber to metal[174].

Nitrile rubber (NBR) and hydrogenated nitrile rubber (HNBR) are engineered synthetic elastomers that have been created to answer the challenging industry needs. NBR is made through the copolymerization of acrylonitrile and butadiene in which the ratio of acrylonitrile determines the resistance to oil, fuel, and solvents. HNBR is a product of suitable hydrogenation of NBR which contributes immensely to thermal stability, ozone resistance, and mechanical strength. The two types of rubbers are highly resistant to oils, fuels and chemicals and can therefore be used in seals, hoses, gasket and as automotive and aerospace components. They include formulation optimization, controlled crosslinking, and filler reinforcement to provide better durability and service life. The high heat and aging properties of HNBR enable it to be used in harsh environments where other elastomers cannot perform, and make it reliably work in high engineering[175].

Rubber-metal composites are very popular because of their lasting nature particularly in the sea. Early investigations indicated that there are difficulties in long-term adhesion because of corrosion on metal surfaces. Cathodic discharge takes place on the metal in marine environments making hydroxyl groups (-OH) which breaks the bond between rubber and metal in the long run. This paper is aimed at the knowledge of the nature of these surface modifications that are caused by corrosion, and how these modifications support the weakening of adhesives with respect to metal surface chemistry in joint failure. Although the results help to understand the adhesion degradation mechanism, the study was constrained to a set of environmental conditions, and the methods of avoiding long-term adhesion degradation or enhancing durability were not studied widely[176].

Although rubber-to-metal bonded parts are often utilized, it can be challenging to assess the quality of the bond. Previous techniques were inaccurate or damaging. In this investigation, faults in rubber bonded to steel under vacuum and heat were found using an optical technique called shearography. The rubber surface's deformation is expected by a numerical simulation, and the outcomes agreed with the experiments. Shearography was able to identify regions with unequal adhesive thickness and microscopic debonds as thin as 4 mm. Although it was only tested on particular materials and situations, this technique offers a practical, non-destructive means to assess bonding quality. This study has discussed the use of a thick coating of adhesive to connect steel and rubber[177].

Traditionally rubber-metal bonding has relied on brass finishes, cobalt-based adhesion promoters, solvent-based primers which have drawbacks connected to corrosion-resistance, environmental effects, and durability. Silane-based bonding systems have also become an alternative of attaining high and long lasting bonding between sulfur-vulcanized rubber as well as metallic substrates like steel, brass and galvanized metals. The silane coating on metal surfaces and chemical reaction between silane and rubber in vulcanization process has a role to play in interfacial bonding and cohesive failure. These systems exhibit a better heat, humidity and corrosive environment resistance, showing potential to have numerous applications of environmentally-friendly and corrosion-resistant rubber-metal bonding[178].

2.3 Role Of Surface Treatment In Adhesion Strength:

Structural adhesives are represented as high-performance thermosetting structures that create permanent, load bearing joints of rigid, high-strength substrates like metals, ceramics, and reinforced composites. Their evolution rose to early phenolic formulations to the present day epoxy, urethane and modified acrylic systems that were introduced to enhance toughness, durability and environmental resistance. These adhesives offer consistent strength over broad temperature environments and avoid creep over extended loads, adhesion integrity under moisture, thermal and chemical environments. Their application has grown beyond aerospace and military applications to automotive, electronic, and general manufacturing since they can be used to bond dissimilar materials and eliminate weight, vibration and concentrations of

mechanical stresses. However, proper surface preparation, joint design, and curing management are critical to their performance[179].

Early advancements in adhesive bonding made synthetic polymers lightweight alternates for mechanical fastening, allowing for enhanced corrosion protection, large-area load transmission, and fatigue resistance in aircraft and aerospace structures. Over time, research has shed light on adhesion mechanisms, structural polymer behavior, and the critical function of metal surface pretreatment for steels, titanium, and aluminum. The current developments support high-performance assemblies such airplane skins, honeycomb structures, and spacecraft components while enhancing environmental durability under moisture, heat cycling, and chemical exposure. Simplifying surface preparation, enhancing chemical interaction at the interface, expanding long-term durability data for advanced metal–polymer systems, increasing adhesive capacity to higher temperatures, and enabling dependable room-temperature curing films are all areas of ongoing improvement[180].

The adhesive bonding between metals has gone a long way back since its initial uses with phenolic and epoxy based systems, and has become a fundamental part of the current lightweight technology in the aerospace and automotive industry. The existing research and development is largely concerned with the improvement of the joint durability with more sophisticated surface treatment, such as the chromium-free anodizing and sol-gel, as well as the development of tough structural adhesives. This technology has proven to be mature as evidenced by the successful applications of new material systems (like Fibre Metal Laminates (FMLs) like GLARE(r)) in the Airbus A380, which have much better fatigue and damage tolerance. In the future, the direction of the field is environmentally friendly operations, i.e., the absence of chromates, the creation of high-toughness and nano-structured adhesives that can be out-of-autoclave cured. Moreover, the combination of advanced modelling technology and the development of higher-quality optical measurement systems will allow making the next-generation structures more reliable in their predictive design and strong joint performance[181].

Debonding may take place in fiber-reinforced polymer (FRP) strengthened steel structures through either adhesion failure in the steel/adhesive or FRP / adhesive interface, cohesion failure in the adhesive, or both. A failure in cohesion is desirable since it makes it possible to develop

design theories that depend on adhesive properties but adhesion failures must be excluded. This paper was an organized effort to test the combinations of surface-adhesive on steel in order to halt failure of adhesion at the steel surface/adhesive interface. Different steel surface preparation procedures such as solvent cleaning, hand grinding, and grit blasting were tested with some of the frequently used adhesives. Surface energy, chemical composition, and roughness/topography were used to measure surface characteristics. The findings showed that effective grit blasting with appropriate adhesive can be used to avoid adhesion failure and the treated surface on steel can be well-described with the help of the three most important surface parameters[182].

Chapter 3

Materials and Methodology

3.1 Materials:

Nano-silica filler was purchased from sigma Aldric, Epoxy resin Bisphenol A diglycidal Ether (DGEBA), Polyethylene glycol (PEG) diluent, KH-550 (3-aminopropyltriethoxy silane) coupling agent was purchased from sigma Aldric, Polyamide curing agent (PA), Acetone, Nitric Acid (69%) was purchased from sigma Aldric, HNBR (Hydrogenated Nitrile Butadiene Rubber), Steel metal plates

3.2 Methodology:

In this study, different factors nano-silica filler, APTES coupling agent, PEG diluent and curing agent with different content ratios were selected for epoxy adhesive formulation and later it was used for metal rubber bonding. These factors enhances the adhesion strength and toughness of epoxy system.

3.3 Epoxy Adhesive Formulation:

Firstly, the nano-silica powder is dried out at 80^{o}C in an oven for 8h to remove all moisture content from nano-silica powder. At room temperature epoxy resin was then mixed with 3, 5 and 7% by weight of dried nano-silica powder. The mixing was continued for 1h by mechanical stirring at stirring speed of 1000rpm. After that homogenizing process ultrasonication performed with alternative 30s cycles by using 20kHz ultrasonic waves.

At room temperature PEG and APTES with 3, 5 and 7% by weight mixed in epoxy and nano-silica solution by mechanical stirring. Stirring was continued until proper mixing achieved. Degassing of mixture was performed for 10-15 min before adding hardener to remove air bubbles that formed during stirring.

Finally, hardener was added in the mixture by resin to hardener ratio of 2:1 and then mixed it for 5-10 min.

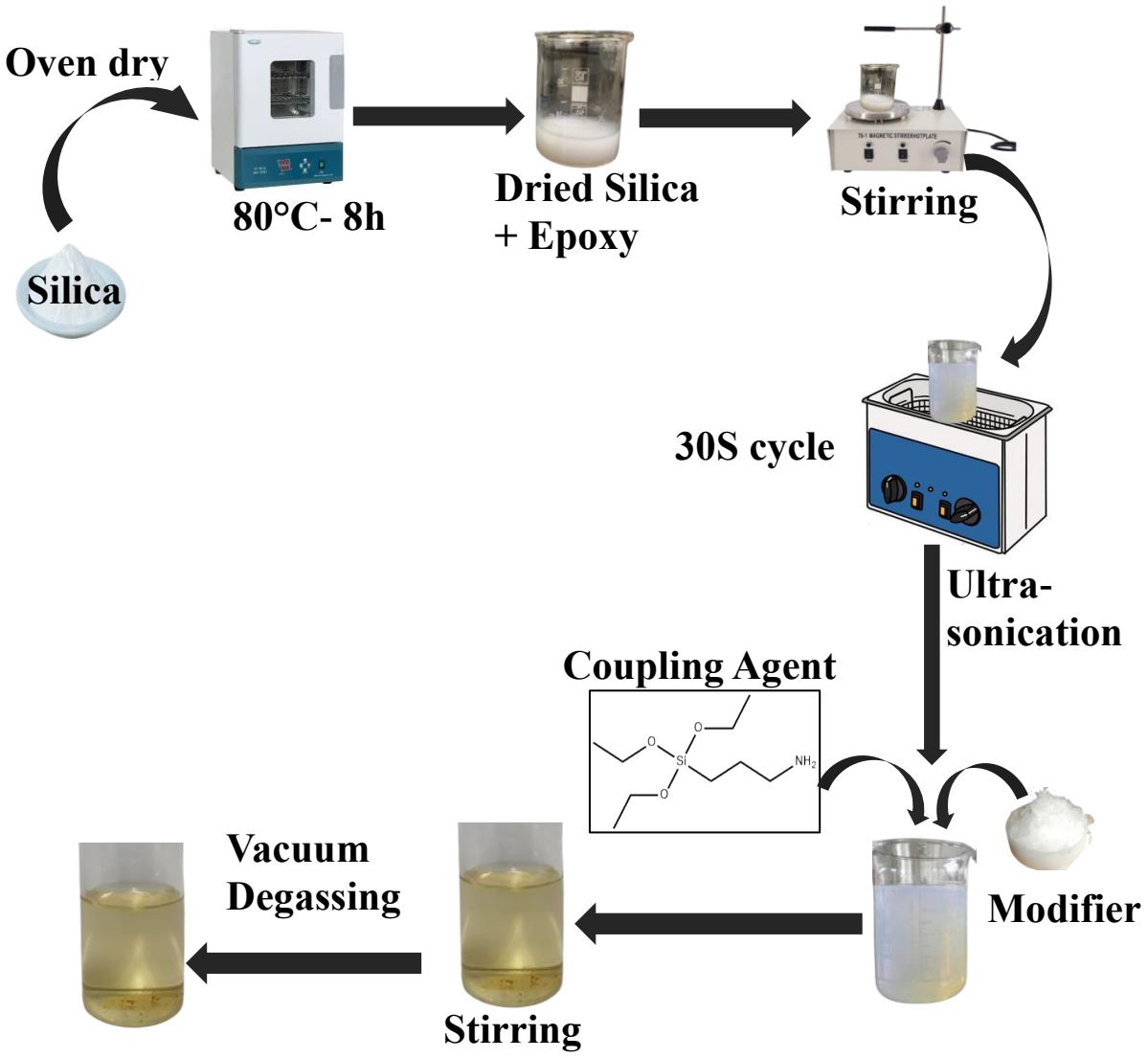


Figure.3.1 Methodology

When hardener was added to mixture and stirred air bubbles formed during stirring due to the reaction between hardener and resin and it could largely effect the final properties of the product. So, that to avoid this effect the mixture was again placed in vacuum oven and degassing was performed for 10-15 min to remove all air bubbles[183].

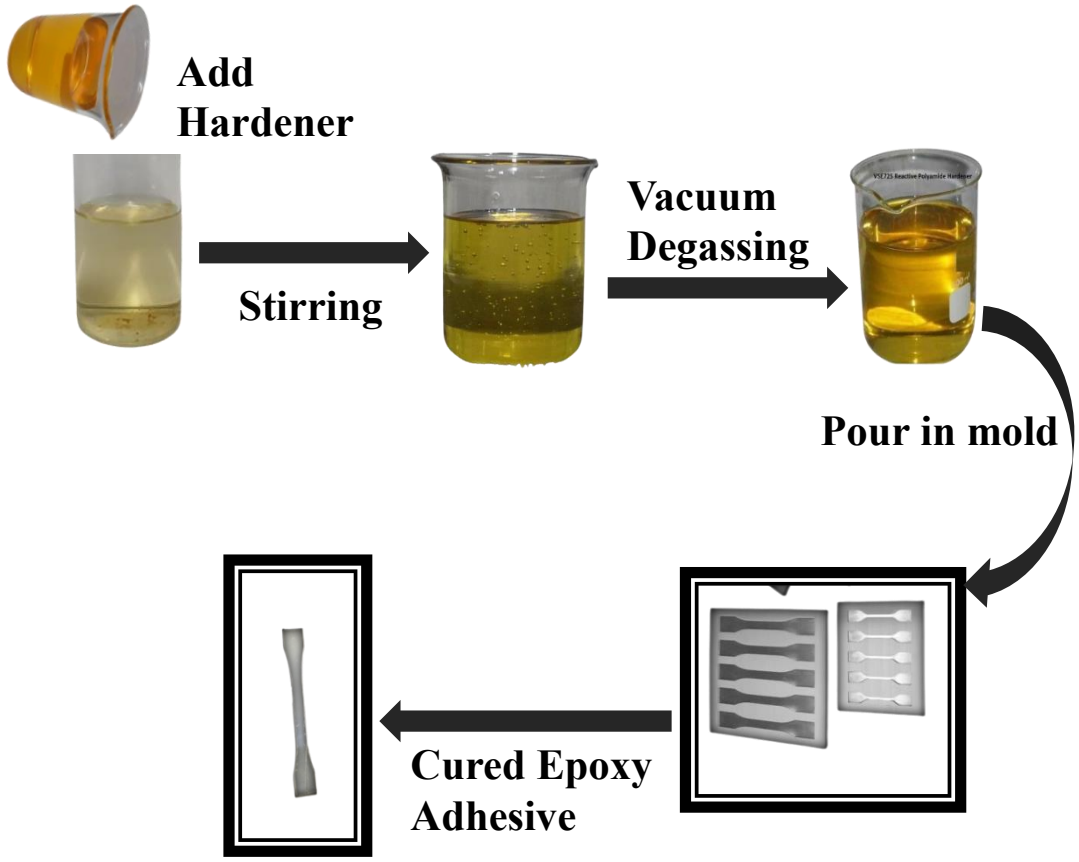


Figure.3.2 Epoxy Adhesive Formulation

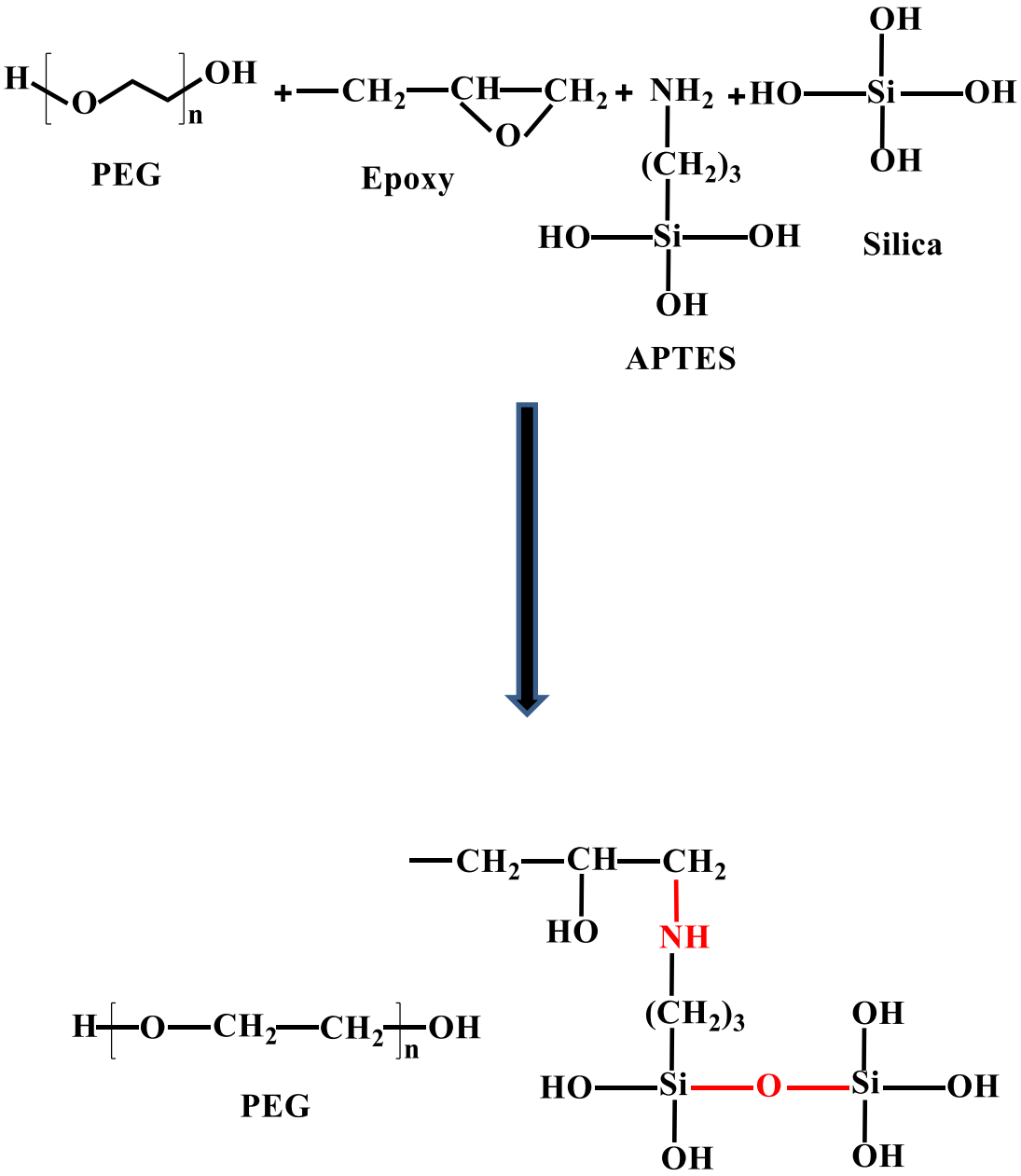
Four samples were prepared with different content of nano-silica, PEG and APTES and all these four different samples applied on metal for metal rubber bonding.

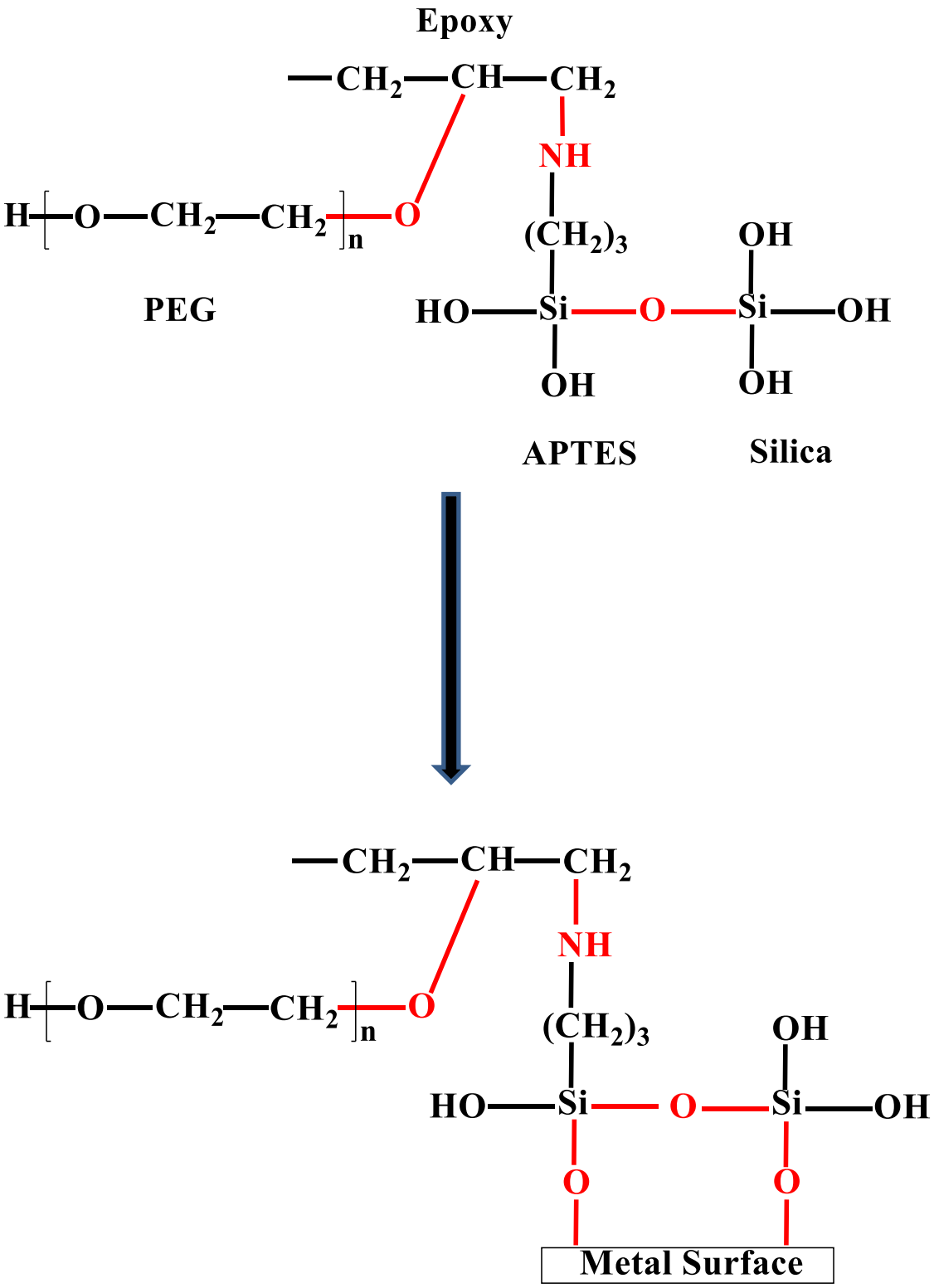
Sr. No	Sample Name	Epoxy Resin wt%	Hardener wt%	Filler wt%	Modifier wt%	Coupling Agent wt%
01	S0	100	50	0	0	0
02	S3	100	50	3	3	3
03	S5	100	50	5	5	5
04	S7	100	50	7	7	7

Table.3.1 Epoxy Adhesive Recipe

The prepared samples of epoxy adhesive was poured into mold and the adhesives was cured at 80^{o}C for 1h. After the adhesive cured removed the mold and characterizations was performed on that cured adhesive sample.

3.4 Chemistry of Adhesive Formulation:



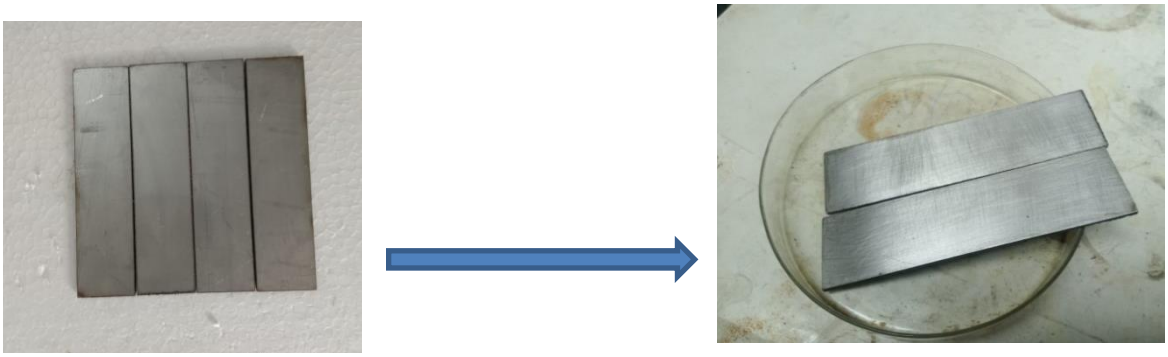

Epoxy
CH2 CH CH2
NH
H O CH2 CH2 n O
(CH2)3
OH
HO Si O Si OH
OH
OH
PEG
APTES
Silica
CH2 CH CH2
NH
H O CH2 CH2 n O
(CH2)3
OH
HO Si O Si OH
O
O
Metal Surface

3.5 Surface Treatment of Metal:

Metal plates was degreased with solvent (acetone/toluene/xylene) to remove contamination from metal surface. Manual abrasive blasting was then performed with the help of emery cloth to rough the surface of metal that enhance adhesion.

3.5.1 Chemical Surface Treatment:

Chemical surface treatment of metal was done with (69%) nitric acid and distilled water solution with 20 : 80% ratio respectively, in which metal plates was immersed at room temp for almost



Before Surface Treatment After Surface Treatment

Figure.3.3 Before and after surface treatment

30-35 min. After that the metal plates was rinsed with tap water followed by DI water, and the plates were dried in oven at 60^{o}C for 30 min to remove residual moisture and solvents.

3.6 Metal-Rubber Bonding:

The steel surface was prepared and epoxy adhesive formulated then metal rubber bonding was done. HNBR cut into small pieces to placed between metal plates and observe its adhesion with metal plates.

3.6.1 Sample Preparation For M-R bonding:

On the one edge of metal plate epoxy adhesive was applied with the help of brush or spetula. According to standards the adhesive layer thickness should be 1.0mm-1.5mm, below and above this range the strength decreases. After a layer of epoxy adhesive applied on the one metal plate the same procedure was done with second metal plate. Rubber pieces was placed on surface of metal plate and the second metal plate put on it.

Figure.3.4 Sample Preparation For M-R bonding

3.6.2 Curing Process For M-R Bonding:

The prepared samples were placed in compression molding machine for 30 min at 140^{o}C temperature. In order to establish consistent and dependable metal–rubber bonding, this stage made sure that the heat transfer was homogeneous, the connection was sufficiently bonded, and the adhesive layer and rubber was fully crosslinked and vulcanized.

Figure.3.5 Metal-Rubber Bonding

3.7 Characterization:

Epoxy adhesive after formulation is characterized by using different characterization techniques included Shear Strength, FTIR, XRD and SEM.

3.7.1 Lap Shear Analysis:

Lap shear test is used to determine the bonding performance of adhesives during shear loading, which is closely comparable to the real service conditions in structural and aerospace joints. It is applied to investigate the effect of surface preparation, and compare the various adhesive systems. Failure modes are also identified by the test which gives an insight on the quality of adhesion, the effectiveness of the curing, and the long time durability of adhesive joints.[184].

3.7.2 FTIR Spectroscopy:

FTIR is an effective method for using atomic vibrations to analyze molecular structure, especially in organic materials and polymers. Chemical bonds and functional groups can be identified using FTIR spectra, which operate as molecular fingerprints. Chemical functional groups in samples ranging from gases to liquids and solids can be identified using FTIR spectroscopy, which works by first obtaining an interferogram of a sample signal using an interferometer and then conducting a Fourier Transform to produce the infrared spectrum[185].

3.7.3 XRD Analysis:

The X-ray diffraction (XRD) technique is employed to determine the crystalline phases and structural properties of materials by studying the diffraction patterns of materials. XRD assists in determining the phase composition, crystallinity and structural changes that take place during the processing or modification of the material. It gives critical data on the crystal structure, phase purity and degree of order, and is not achievable through spectroscopic methods alone, and is thus an essential tool in correlating structure with material properties[186].

3.7.4 SEM (Scanning Electron Microscope):

Scanning Electron Microscopy (SEM) is applicable in the analysis of micro- and nanoscale structures, which reveals the high-resolution images of topography and material composition of a surface. Together with Energy-Dispersive X-ray Spectroscopy (EDS), SEM allows the qualitative and quantitative analysis of the elements. The selection of the right sample with polishing and drying is also important in ensuring proper imaging. Types of SEM applied include conventional, environmental and low-vacuum enabling the analysis of a wide range of materials, including metals, polymers and concrete[187].

Chapter 4

Results and Discussion

4.1 FTIR Analysis:

The FTIR analysis of the epoxy adhesive with 0, 3, 5 and 7% filler with APTES and PEG demonstrated characteristic peaks in the epoxy network.

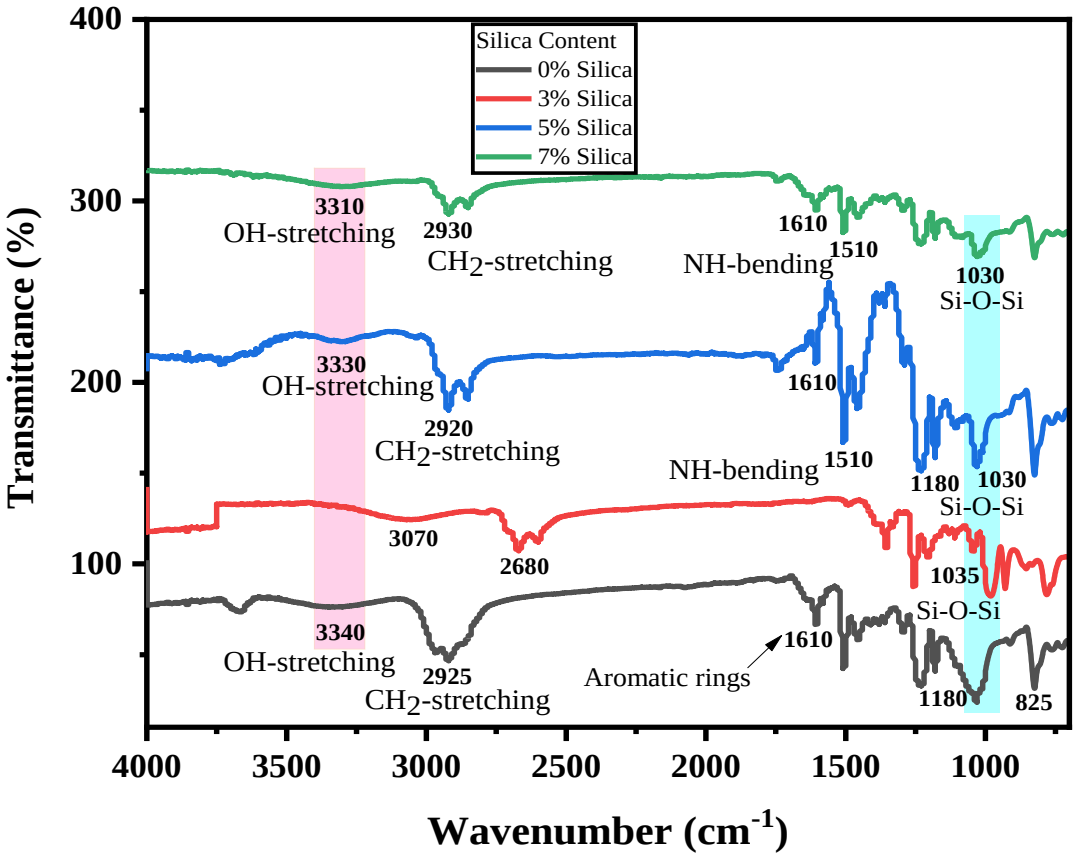


Figure.4.1 FTIR Analysis of Epoxy Adhesive

The FTIR spectrum of epoxy without any modification shows the typical absorptions of an epoxy system. The oxirane ring vibration is observed at ~810-915cm^{-1}, which is a clear indication of the remaining epoxide groups. The intense C-O-C vibrations are observed in 1100-1200cm^{-1} range and aromatic vibrations are observed at 1610cm^{-1} and 1510cm^{-1}. Aliphatic CH_2

bands are observed at a frequency of ∼2925-2870cm^{-1} and a broad hydroxyl band observed at around 3400cm^{-1}, which proves the presence of epoxy functional groups and the partial ring opening in the course of curing.

In the case of APTES and PEG modified 3% nano-silica, the -OH band is significantly decreased and band shifts, the Si-O-Si peak also decreased, which is an indication of inferior siloxane network formation.

The incorporation of APTES and PEG modified 5% nano-silica is observed by the Si-O-Si sharp band at ∼1030-1090cm^{-1} and a strong -OH band at ∼3400cm^{-1} due to silanol grops. Additive integration is further confirmed by PEG sharp peaks (CH_2 at 2850-2950cm^{-1} , C-O-C near 1180cm^{-1}) and APTES (N-H at 3300-3400cm^{-1} , NH bending at ~1500-1600cm^{-1}). APTES related NH bending sharp peak at ~1510cm^{-1} indicates high strength, improved dispersion and reinforcement efficiency.

In the case of APTES and PEG modified 7% nano-silica, the -OH band is significantly decreased and the Si-O-Si peak also decreased, which is an indication of inferior siloxane network formation. PEG broad peaks and APTES related NH_2 bending broad peak of 7% nano-silica indicates lower strength and poor dispersion.

Overall, 0% to 7% dried nano-silica content transitions confirm that an optimal content of filler, coupling agent and reactive diluent is necessary to achieve good transfer of stress whereas less or more content can decrease the performance because of in optimal dispersion or stress concentration.

4.2 XRD Analysis:

The X-ray diffraction pattern of epoxy adhesive with 0, 3, 5and 7% filler content and PEG and APTES tells the nature of adhesive. As opposed to crystalline material, the S0 have broad and diffused peaks, which are typical of amorphous structures. The diffraction pattern does not show any sharp diffraction peaks, which proves the amorphous nature of the epoxy resin.

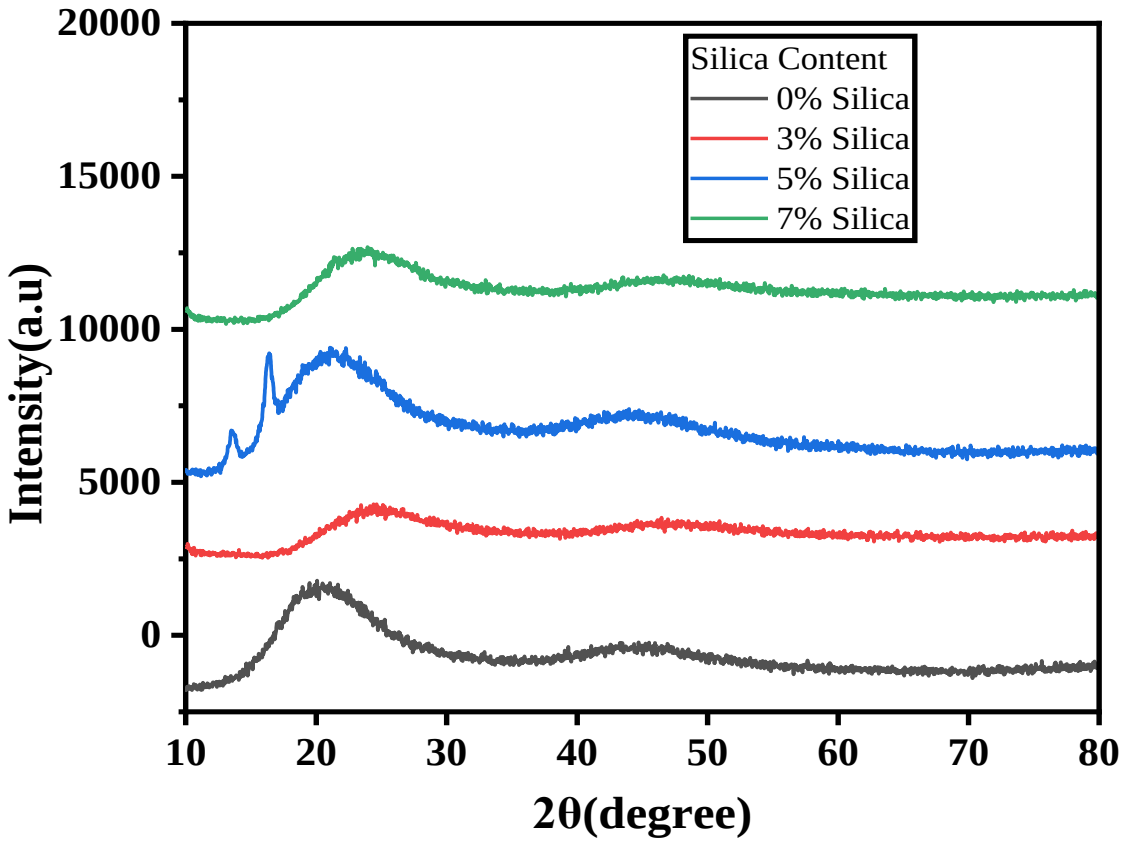


Figure.4.2 XRD Analysis of Epoxy Adhesive

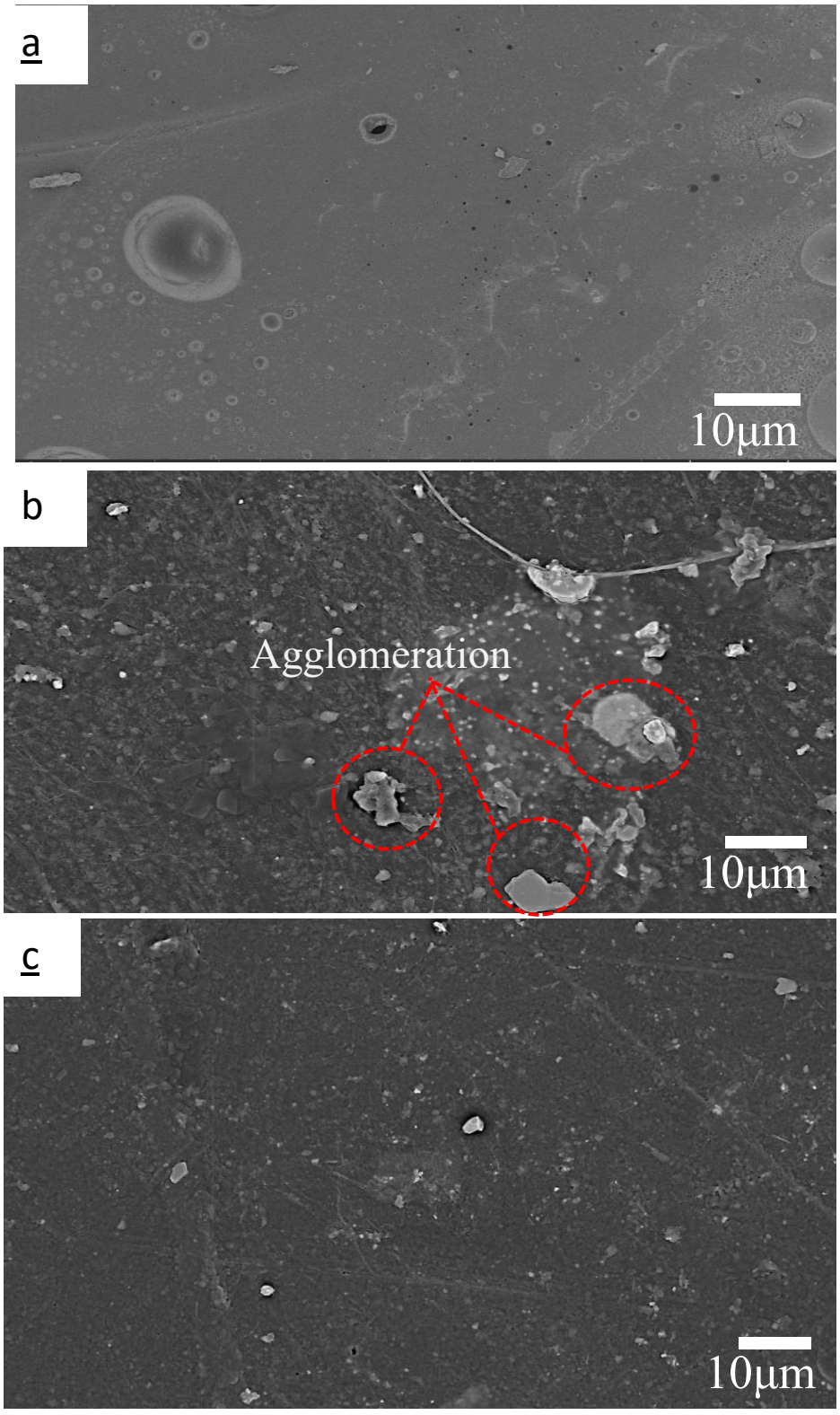
For S0 sample of epoxy adhesive a broad hump is observed at $2\theta \approx 20\text{-}25^0$. This indicates highly disorder structure of epoxy resin. In S3 the hump get more broad poor dispersion of silica and other additives.

While in S5 a broad hump is clearly observed at $2\theta \approx 20\text{-}25^0$ with two small sharp peaks at $2\theta \approx 15\text{-}17^0$ these sharp peaks strongly indicated the crystalline nature of silica. These semi-crystalline peaks provide strong indication for dispersion of silica in epoxy.

But in S7 it observed that again sharp peaks absent that indicates poor dispersion of silica in epoxy the broad hump indicates the amorphous structure of epoxy resin.

Overall the XRD analysis confirms the semi-crystalline nature of epoxy adhesive. These structural features are significant because they affect adhesive, mechanical, and thermal properties, especially for polymeric and composite materials.

4.3 SEM For Epoxy Adhesive:



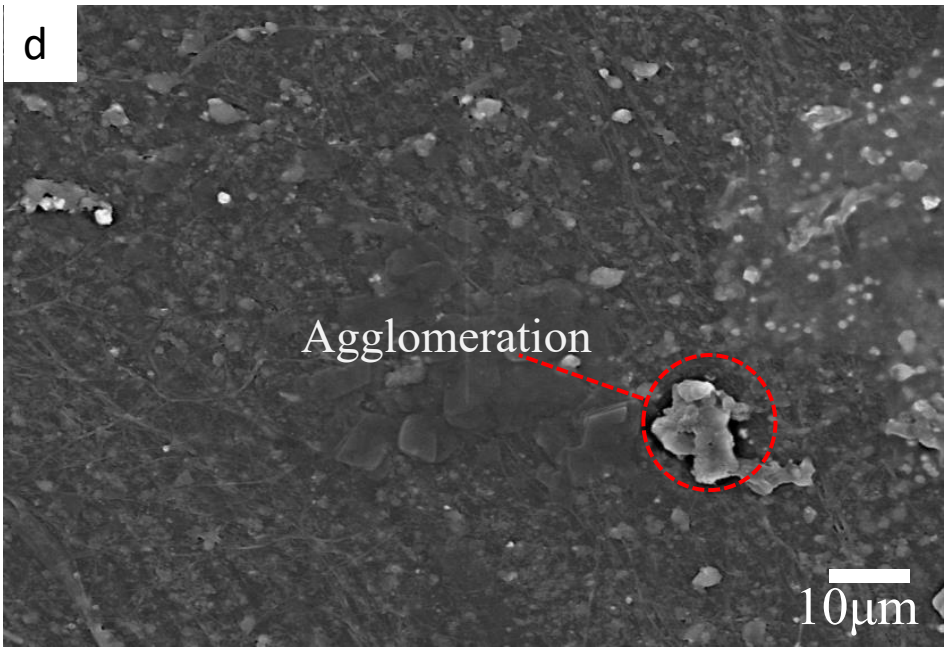


Figure.4.3 SEM of Epoxy Adhesive

The SEM analysis of epoxy adhesive shows the dispersion of silica that highly effect the adhesion strength of metal rubber bonding. The image (b) with 3% silica content shows the agglomeration of silica particles within epoxy adhesive that weaken the adhesion strength, while in image (c) there is clear dispersion with 5% silica content that is effective for strong bonding.

But as filler content increases from 5% to 7% the agglomeration starts that weaken's the strength. So, these SEM results confirm that an optimal content of filler, coupling agent and reactive diluent is necessary to achieve good transfer of stress whereas less or more content can decrease the performance because of in optimal dispersion or stress concentration.

4.4 Lap Shear Analysis:

In this graph, the neat epoxy adhesive was taken as baseline for the measure of improvement of shear strength. Approximately 30-35% shear strength increased by incorporation of APTES and PEG modified 7% nano-silica. However, by incorporating APTES and PEG modified 5% nano-silica approximately 80-85% strength improved as compared to neat epoxy and around 30-35% improvement seen as compared to 7% nanosilica.

The order of performance was S5 > S7 > S0 > S3.

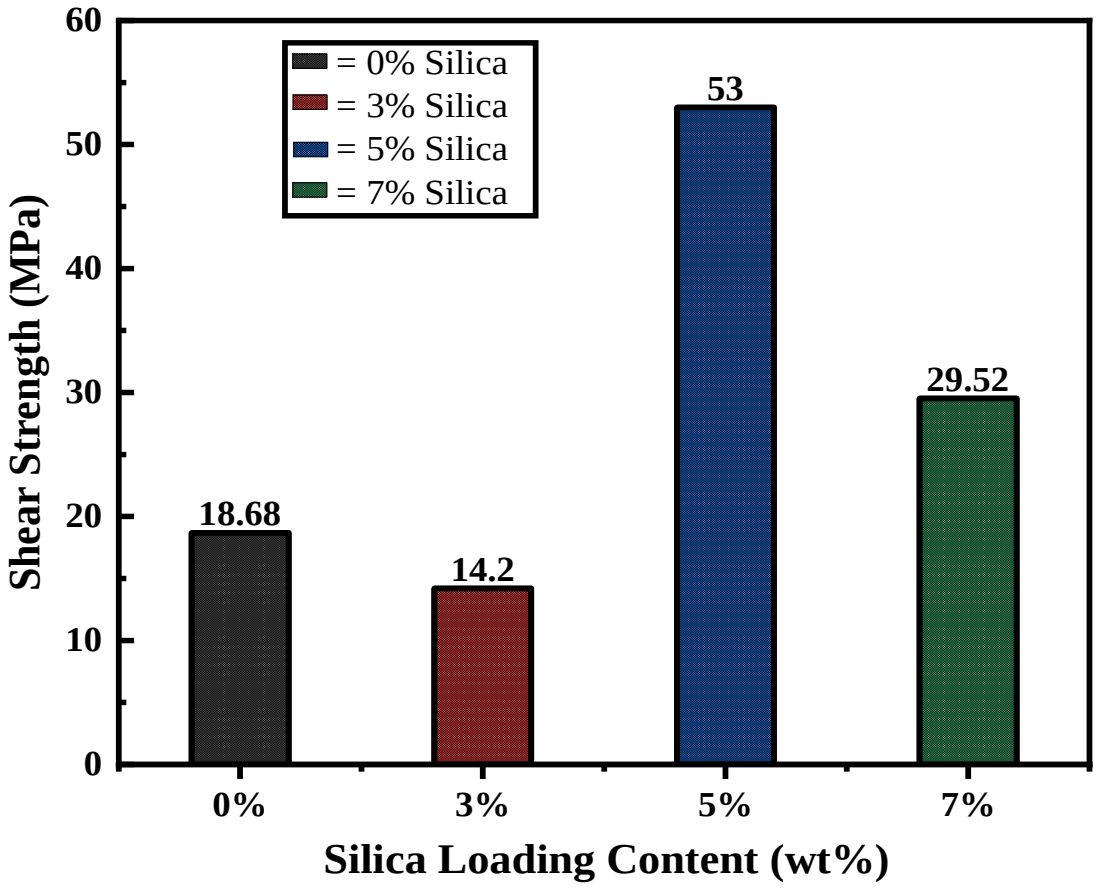


Figure.4.4 Lap Shear Analysis

The outcomes show how silica strengthens the epoxy adhesive. The approximately 30–35% increase in interfacial strength for 7% nano-silica(S5) over neat epoxy(S0) demonstrates that APTES and PEG modified nano-silica improve interfacial strength by limiting the mobility of polymer chains and more efficiently spreading applied stress evenly throughout the matrix.

Furthermore, the APTES and PEG modified 5% nano-silica sample's shear strength significantly increased around about 80–85% when compared to raw epoxy, indicating the importance of drying treatment of nano-silica. The presence of moisture on untreated silica surfaces may reduce stress distribution by weakening filler dispersion, introducing interfacial gaps, and disrupting silanol–epoxy interactions. Moisture remover from surface of nano-silica by drying, increases the surface activity of silica, facilitating a stronger chemical connection and enhances its compatibility with the epoxy matrix.

With 7% filler loading the strength enhanced as compared to 0% and 3 % loading but lower than 5% loading. This implies that too much filler can result in aggregation or uneven distribution of stress making the reinforcement less efficient even after chemical modification.

These improvements highlight the importance of surface pre-treatment and filler concentration in optimizing the mechanical performance of epoxy adhesives, with 5% dried, surface-modified silica offering the optimum mechanical reinforcement.

Chapter 5

Conclusion

In this research modified epoxy adhesive were successfully formulated and characterized to evaluate the influence of silica filler, PEG and APTES. This modification shows strong metal-rubber adhesion in industrial applications.

APTES modification in epoxy shows the strong dispersion of filler and prevent agglomeration that enhanced adhesion strength. PEG modification enhances the toughness, tensile strength and curing process by participating in the reaction via its –OH groups. Shear strength analysis confirms the strong M-R adhesion, morphological and spectroscopic analysis (FTIR, SEM, XRD) confirmed the interaction and incorporation of the components.

Future investigations should focus on the pot life of epoxy adhesive, sustainable and bio-based epoxy resin and hardener and optimization of surface modification techniques.

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