CHAPTER 1

INTRODUCTION

1.1 ADHESIVES-AN OVERVIEW

An adhesive is any substance that, when applied to the surfaces of materials, binds the surfaces together and resists separation (Kinloch 1987), can be liquid or semi-liquid. Adhesives come from both natural and synthetic sources. The types of materials that can be bonded are many but adhesives are especially useful for bonding thin materials. Adhesives can be cured by either evaporating a solvent or by chemical reactions that occur between two or more constituents. Adhesives are useful for joining thin or dissimilar materials, minimizing weight, and providing a vibration-damping joint (Onusseit et al 2010). One of the disadvantages of most adhesives is that most do not form an instantaneous joint, unlike many other joining processes, because the adhesive needs time to cure (Cooper 2012).

The ancient Greeks developed adhesives for use in carpentry, and prepared glues that included the following items as ingredients: egg whites, blood, bones, milk, cheese, vegetables and grains. Tar and beeswax were used by the Romans for glue. Around 1750 the first glue or adhesive patent was issued in Britain. The glue was made from fish. From then patents were rapidly issued for adhesives using natural rubber, animal bones, fish, starch, milk protein or casein (Nicholson et al 1991).
1.2 MODERN TYPES OF ADHESIVES

Modern adhesives are classified either by the way they are used or by their chemical type (Hussey & Wilson 1996). The strongest adhesives solidify by a chemical reaction. Less strong types harden by some physical change. Key types in today’s industrial applications are as follows.

Anaerobics

Anaerobic adhesives harden when in contact with metal and air is excluded, e.g. when a screw is tight in a thread. Often known as ‘locking compounds’ or ‘sealants’, they are used to secure, seal and retain turned, threaded, or similarly close-fitting parts. They are based on synthetic resins known as acrylcs. Due to the curing process, anaerobic adhesives do not have gap-filling capability but have advantage of relatively rapid curing.

Cyanoacrylates

A special type of acrylic, cyanoacrylate adhesives cure through reaction with moisture held on the surfaces to be bonded. They need close-fitting joints. Usually they solidify in seconds and are suited to small plastic parts and to rubber. Cyanoacrylate adhesives have relatively little gap-filling capability but can be obtained in liquid and thixotropic (non-flowing) versions.

Toughened Acrylics / Methacrylics

A modified type of acrylic, these adhesives are fast-curing and offer high strength and toughness. Supplied as two parts (resin and catalyst), they are usually mixed prior to application, but specialized types are available
which are applied by separate application: resin to one bond surface, catalyst to the other. They tolerate minimal surface preparation and bond well to a wide range of materials. The products are available in a wide range of cure speed and as liquids or pastes which will gap-fill up to 5mm.

**UV curable adhesives**

Specially modified acrylic and epoxy adhesives, can be cured very rapidly by exposure to UV radiation. Acrylic UV adhesives cure extremely rapidly on exposure to UV, but require one substrate to be UV transparent. The UV initiated epoxy adhesives can be irradiated before closing the bondline, and cured in a few hours at ambient temperature or may be cured at elevated temperature.

**Polyurethanes**

Polyurethane adhesives are commonly one part moisture curing or two-part. They provide strong resilient joints, which are resistant to impacts. They are useful for bonding GRP (glassfibre-reinforced plastics) and certain thermoplastic materials and can be made with a range of curing speeds and supplied as liquids or with gap-filling capability of up to 25 mm.

**Modified Phenolics**

The first adhesives for metals, modified phenolics now have a long history of successful use for making high strength metal-to-metal and metal-to-wood joints, and for bonding metal to brake-lining materials. Modified phenolic adhesives require heat pressure for the curing process.
Hot Melts

Related to one of the oldest forms of adhesive, sealing wax, today’s industrial hot melts are based on modern polymers. Hot melts are used for the fast assembly of structures designed to be only lightly loaded.

Plastisols

Plastisol adhesives are modified PVC dispersions which require heat to harden. The resultant joints are often resilient and tough.

Rubber adhesives

Based on solutions of latexes, rubber adhesives solidify through loss of solvent or water. They are not suitable for sustained loading.

Polyvinyl Acetates (PVAs)

Vinyl acetate is the principal constituent of the PVA emulsion adhesives. They are suited to the bonding of porous materials, such as paper or wood, and general packaging work.

Epoxy adhesives

Epoxy adhesives consist of an epoxy resin plus a hardener. They allow great versatility in formulation since there are many resins and many different hardeners. They form extremely strong durable bonds with most materials. Epoxy adhesives are available in one-part or two-part form and can be supplied as flowable liquids, as highly thixotropic products with gap-filling capability of up to 25 mm, or as films. Epoxy or epoxide resins are a group of
reactive compounds that are characterized by the presence of the epoxy group, which is the simplest epoxy compound have structure of ethylene oxide, oxirane group. They are capable of reacting with suitable hardeners to form cross-linked matrices of great strength and with excellent adhesion to a wide range of substrates. This makes them ideally suited to adhesive applications in which high strength under adverse condition is prerequisite. Epoxy adhesives offer following advantages (Hussey & Wilson 1996):

- Good adhesion to many surfaces
- A range of mechanical properties, depending on formulation and curing
- A wide range of cure characteristics (from RT to 180°C)
- Low shrinkage
- No by-products evolved during curing
- Range of available adhesive forms (film, paste, one or two component)

### 1.3 PRESSURE-SENSITIVE ADHESIVES

Pressure-Sensitive Adhesives are very well suited to apply on tapes and labels, but they do not solidify and are often able to withstand adverse environments. They are not suitable for sustained loading. The properties which are useful in characterizing a PSA are tack, peel strength (adhesion) and shear strength (cohesion). The main advantage of pressure sensitive adhesives compared with other types of adhesive are those of ease and convenience of use. No storage is required, no mixing or activation necessary, no waiting is involved. Most often the bond is readily reversible. They adhere by simply applying pressure to a huge variety of materials. Pressure sensitive adhesives find wide uses in clinical applications such as self adhesive
bioelectrodes. Nowadays it has become that the important requirements for these applications are the essential characteristics of PSA coupled with biodegradability and anti bacterial property.

Pressure-sensitive adhesives (PSAs) are an interesting class of products that offers the potential to produce a novel generation of self-adhesive products with a number of excellent properties such as water-solubility, removability and repositionability, or photoreactivity. The term “pressure-sensitive” implies that adhesives which in the “dry” form are permanently tacky at room temperature and firmly adhere to a variety of widely different surfaces upon mere contact without the need for more than finger or hand pressure (Benedek 2006, Benedek & Heymans 1997, Satas 1989, Houwink & Salomon 1982, Greenman & Montgomery 1969).

The first commercial PSA was derived from natural rubber, which is still one of the principal polymeric constituents. Shortly after World War II co-polymers of the higher alkyl acrylates (acrylics) were introduced into the PSA adhesives and these grew in subsequent decades and became second in volume only to rubber-based PSAs. Since their introduction half a century ago, acrylic PSAs have been successfully applied in many fields. They are used in self-adhesive tapes, labels and protective films, as well as in dermal dosage systems for pharmaceutical applications, in biomedical electrodes, and in the assembly of automotive parts, toys, electronic circuits and keyboards (Czech 2004).

Among the other types of PSAs in use today like silicones, polyurethanes, polyesters and polyethers, the acrylic PSAs are more popular within this group. Acrylic self-adhesive polymers are synthesized from a wide selection of acrylic and methacrylic ester monomers having pendant functional groups. The three basic types of acrylics which are commonly used
today are solvent-based, water-borne and solvent-free acrylic PSAs (Czech 2004). David et al (2009) explains that the Pressure Sensitive Adhesives (PSA) present an interesting class of products that offers a potential to produce a novel generation of self-adhesives with a great number of excellent properties.

1.3.1 Adhesion through Chemical Bonding

Molecules of the adherent material may form chemical bonds with the molecules of the adhesive across the interface.

The chemical bonds may be either ionic or covalent.

- **Ionic bond** is formed when an atom donates its electron to another atom. As a result of the electron transition two ions form: positively charged cation and negatively charged anion. The force of electrostatic attraction between the two ions forms ionic bond. Ionic bond may be formed between two materials with different electronegativities (the difference is greater than 1.7).

- **Covalent bond** is a chemical bond, in which two atoms share one or more pairs of electrons. Covalent bond may be formed between two materials with similar electronegativities (the difference is lower than 1.7).

- **Intermolecular bonding** Intermolecular bonds are result of relatively weak attraction forces between the neighbouring molecules.
- **Hydrogen bonding** is an intermolecular bonding formed between a hydrogen atom chemically bonded to an electronegative atom and other electronegative atom of a neighbouring molecule.

- **Van der Waals forces** are the result of electrostatic attraction between neighbouring molecules having permanent or instant transient dipole groups.

### 1.3.2 Types of Forces Applied over Adhesive Joints

Two adherents (substrate) may be bonded by different ways shown in the picture Figure 1.1. Adhesive layer thickness should be minimal and uniform. Lap and strap joints provide the maximal bonding strength. A lap joint is a technique of joining two pieces of material together by overlapping them. A joint design that combines the butt joint and lap joint is called as strap joint. Butt joint is the weakest joint type. A butt joint is a joinery technique in which two members are joined by simply butting them together. The butt joint is the simplest joint to make since it merely involves cutting the members to the appropriate length and butting them together.

**Failure mechanisms of adhesive bonding**

During the testing of adhesive joints three types of failure can be absorbed. Cohesive failure, adhesive failure and structural failure. Cohesive failure happens within the molecules of adhesives, Adhesive failure results due to week interaction of adhesive with substrate and structural adhesive failure can be observed when the substrate teared off while testing of adhesives (Figure 1.2).
Figure 1.1 Types of forces applied over adhesive joints

Figure 1.2 Failure mechanisms of adhesive bonding
1.4 THE ROLE ACRYLATES AND METHACRYLATES IN ADHESIVES AND COATING SCIENCE

Acrylic adhesives based on acrylate and methacrylate monomers and have been commercially used for more than 50 years. These products are supplied as two separate components that can be mixed prior to application or each component as such can be applied to separate surfaces. Among acrylates and methacrylates, methacrylates are preferred over acrylates primarily due to odour of the acrylates. The ever-changing high-performance acrylic and methacrylic PSA market continues to expand and present new challenges. To date, the industry has seen a strong growth in traditional applications, as well as the emergence of new applications. Chemistry of the polymers with self-adhesive properties has taken on an added dimension with the introduction of various new raw materials, polymerization techniques and cross-linking methods. This expansion of the technology ensures that the future performance and environmental requirements will be met.

Emulsions and solutions of polymethylmethacrylate or its copolymers are used as caulking materials and sealants. They have moderate movement capability and excellent weatherability. Acrylics tend to have a strong odour and are usually applied outdoors. Acrylic resins (polymethyl methacrylate) have exceptional optical clarity and good weather resistance, strength, electrical properties, and chemical resistance. They have low water absorption characteristics. However, acrylics are attacked by strong solvents, gasoline, acetone, and similar organic fluids.

Most pressure sensitive adhesives are made from formulations based on elastomers (natural, butyl, and nitrile and styrene butadiene thermoplastic), acrylate, or silicone resins. Some adhesive systems can cure by exposure to radiation. They can be cured by ultraviolet light, visible light,
or electron beam radiation. Radiation cured adhesives are limited to applications where the bondline is relatively thin and the substrates are transparent to the energy source. Thus, coating applications are more common than adhesive applications. Radiation cured adhesives commonly use acrylate or unsaturated polyester base resins. Acrylic structural adhesives use the same types of chemical components in their formulation as the original anaerobic adhesive. Modern formulations are based on crosslinked polymethyl methacrylate. Low viscosity methacrylate resins were less hazardous than polyesters; low temperature or room temperature cure cast grafted to vinyl terminated nitrile rubber.

Large-scale commercial uses of methacrylates include poly (methyl methacrylate) (PMMA)-based Plexiglas and other thermoplastic resins. Acrylic polymers are used in pressure-sensitive adhesives and hydrogels. Acrylic and methacrylic polymer families are also used extensively in academic and industrial research. These monomers are being used to synthesize a number of polymers due to the versatility of the synthetic routes for these monomers.

Acrylic and methacrylic monomers can be tailor-made for specific applications. By changing the side chain, acrylic and methacrylic polymer polarity can be tuned to the polarity nature from hydrophilic to hydrophobic. While poly (acrylic acid) (PAA) is hydrophilic, poly (ethylene glycol) grafted onto a methacrylate-backbone (Chen & Shull 1999) is significantly more hydrophobic. Most acrylic and methacrylic polymers possessing intermediate side chain polarities are amphiphilic. As a result, they were used expansively (Mumby et al 1986) in the formation of Langmuir-Blodgett films and micelles (Flanigan et al 1999, Kriz et al 2000). While the impact of crosslinking on adhesives was known for many decades, improving adhesive performance via the operation of non-crosslinkable branched (Hagan et al 1979) topologies is
a newer field of study. Polymer branching was utilized in the design of polymers with more or less adhesion than the linear counterparts, depending on the desired use of the material. Topologies including star (Harlan et al 2001, Ryntz 1989), graft (Brookhart et al 1999) and branched polymers were used previously to improve the performance of adhesives and coatings.

The basic acrylic monomers or oligomers contain unsaturated double bonds (vinyl groups), and consequently cured by addition polymerization involving free-radical reaction. Free-radical producing compounds such as peroxides, peracetic acids, and sulfones are added to acrylic resins to instigate polymerization. Free-radical polymerization of acrylics may also be induced by UV or visible light. These UV-curing adhesives, most of which are based on acrylic or modified acrylic resins are of increasing profitable importance today for the rapid bonding of electronic devices, fiber optics etc. Reactive methacrylate monomers include methylmethacrylate, diethyleneglycol dimethacrylate and butyl methacrylate (Hussey & Wilson 1996).

Major features of acrylic adhesives include

- Adhesion to a variety of substrates
- Water resistance
- Durability
- Flexibility when modified
- Good low temperature properties
- Excellent optical properties
- Low toxicity.
1.5 POLYMERS WITH ANTIBACTERIAL PROPERTY

The development of synthetic antimicrobial agents is a promising need due to antibiotic resistance of bacteria causing fatal infectious diseases, which significantly threaten the public health in global regions. The resistance of bacteria was found initially in hospitals, however, the drug-resistant strains rapidly spread to other public places as well as communities across countries (Levy & Marshall 2004). Kurod et al (2009) investigated the optimal balance of hydrophobic and cationic side chains for the antimicrobial and hemolytic activities of amphiphilic polymethacrylate copolymers. The polymers vary systematically in the nature of their hydrophobic groups, composition, and length. The results revealed that the hydrophobic groups and high molecular weight of polymers increases the antibacterial activity and haemolytic activity.

Bacterial infection is still a seriously important issue in a variety of areas, such as medical devices, health care products, water purification systems, hospitals, dental office equipment, food storage or household sanitation (Kenawy et al 2007). Bacteria adherence and growth causes several health problems as a result of surgical incisions, ventilation, cure of prostheses, urinary and intravascular catheters, among others. Especially, where non-natural materials such as synthetic polymers or metals are used (Breathnach et al 2005). Medical devices such as catheters, prostheses, ventilation tubes, heart valves are applied directly in contact with a body. Therefore, when the bacterium adheres on them they become potential sources of bacterial infection. Infection occurrence depends on living bacteria in planktonic state adhesion to medical device material surface. When they are attached, they grow to bacterial microcolonies with ability to secrete extracellular matrix, a product with risk potential to the human body.
Bacteria form a biofilm on the surface and they are much more protected against environmental changes even against antibiotics (Ziebuhr et al 2006, Pavithra & Doble 2008, Hoiby et al 2010 and Coenye & Nelis 2010). Moreover, as a final step of bacterial colonization, bacteria cells start to release to surrounding and cause infection immediately, there is growing interest in using low-temperature plasma to modify the surface of various materials (Elersic et al 2011, Cvelbar et al 2011& Lehocky et al 2009). This interest has developed for two reasons. First, plasma can produce a unique topological structure and modification, and, second, the extent of modification can be easily controlled by treatment conditions (Cvelbar et al 2011, Lehocky et al 2007, Lehocky et al 2006; Adamczyk et al 2004, Lehocky et al 2009, Jaganjac et al 2012 & Mracek et al 2010). Moreover, plasma treatment method is a non-polluting technique, which is not negligible for industrial fabrication, and requires only short reaction times (Junkar et al 2011, Vesel & Mozedic 2012 & Mozetic 2012). Using plasma activation, the surface functionalities and characteristics can suitably be tailored on a nanometer scale without losing desirable mechanical characteristics of bulk polymer.

The antibacterial polymers can be used in paints on hospital room walls and every day objects such as door knobs, children’s toys, computer accessories, and telephones. This provides them antiseptic and thus prevents the spreading of bacterial infections. They are used in the textile industry to form antimicrobial (Tashiro 2001 & Ikeda et al 1984) fibers and as disinfectants and preservatives in pharmaceuticals (Tebbs & Elliott 1993). Other likely uses of these polymers are as cleaning solutions for contact lenses (Jarvis & Martone 1992) as well as coatings and chemically bound components of biomaterials (Borman 2002).

In polymeric biocides, there are many factors, which can be expected to affect their antibacterial activity such as molecular weight and its
distribution, configuration and conformation, hydrophilic–lipophilic balance (HLB), and spacer length between active groups in the polymer molecule that will result in a change in both conformation and charge density of the polymer, thus affecting the mode of interaction with cytoplasmic membranes and leading finally to different antimicrobial activities (Ikeda et al, 1986).

1.6 TYPE OF POLYMERIZATION

Carothers, Mark and Flory classified the polymers into two categories based on the mechanism of polymerization.

a) Condensation polymerization (or) step growth polymerization.

b) Addition polymerization (or) chain growth polymerization.

1.6.1 Condensation Polymerization

Condensation polymers are any kind of polymers formed through a condensation reaction, releasing small molecules as byproducts such as water or methanol, as opposed to addition polymers which involve the reaction of unsaturated monomers. Eg: polyamides, polyacetals, polyesters, etc.

Polycondensation is brought about by monomers containing two or more reactive functional group (such as hydroxyl, carboxyl and amino) condensing with each other. Basic reactions here are the same as between various functional groups in low molecular weight organic compound. For example, the reaction between a hydroxyl group and carboxylic group gives an ester and a water molecule.

\[ \text{CH}_3\text{OH} \rightarrow \text{CH}_3\text{COOH} \rightarrow \text{CH}_3\text{COOCH}_3^+ \text{ H}_2\text{O} \]
During ester formation, the reactive functional groups are consumed, giving an unreactive functional group. There is no more reactive functional group left with the product and hence, it cannot react further with any other reactant molecule in order to form a different product.

The polycondensation polymerisation should have the following requirements,

- The monomer should have two reactive functional groups for polymerization to proceed.
- The polymerization proceeds by step-wise reaction reactive functional group.
- Only one type of reaction (i.e. condensation reaction in this case) between two functional groups is involved in polymer formation.

The polymer formed still contains both the reactive functional groups at its chain end and hence is active and not dead as in chain polymerization.

1.6.2 Addition Polymerization

Addition polymers are formed by the combination of monomers without the elimination of some byproduct molecules. Alkene, Alkadienes and their derivatives are used as monomer in the formation of addition polymers. Addition polymerization can take place through the formation of either free radical (or) ions such as carbanions (or) carbocations. Addition
polymerization reaction is very rapid and takes place in 3 steps (a) chain initiation (b) chain propagation (c) chain termination.

Addition polymerization is brought about by the migration of atoms from one monomer molecule to another or the intermediate product. Vinyl monomers as well as monomers pair with reactive functional group can undergo addition polymerization. Styrene for example, can be polymerized in the presence of perchloric acid by this method. The process involves the following mechanism.

Polyurethane polymer is formed from a diisocyanate and a diol by a polyaddition reaction in which the hydrogen from the hydroxyl group of the diol migrates and adds on to the nitrogen of the isocyanate group.

In addition polymerization, molecules built is not high; molecular weight goes on increase in time.
Addition polymerization is divided into 2 types.

1) Ionic polymerization
2) Free radical polymerization.

1.6.3 Ionic Polymerization

The addition polymerization that takes place due to ionic intermediate is called ionic addition polymerization. Based on the nature of ions used for the initiation process, ionic polymerization is classified into 2 types,

i) Cationic polymerization
ii) Anionic polymerization

i) Cationic polymerization: Cationic polymerization is initiated by using catalysts such as BF\(_3\), AlCl\(_3\), FeCl\(_3\), SnCl\(_4\), H\(_2\)SO\(_4\), and HF in presence of small amount of H\(_2\)O.
Eg: Isobutylene – butyl rubber, polystyrene, polyvinyl ether

ii) Anionic polymerization: Anionic polymerization is initiated by anion (may be base (or) nucleophiles such as n-butyl lithium (or) Potassium amide) Monomer, containing e\(^-\) withdrawing groups like phenyl (–C\(_6\)H\(_5\)). Nitrile (–CN) etc. undergo anionic addition polymerization.
Eg: polystyrene, polyacrylonitrile
1.6.4 Free Radical Polymerization

The polymer chain growth is brought about by free radicals produced by the decomposition of compound called initiator. The term chain growth represent a process involving a continuous and very rapid addition of the monomer units to form polymer molecule or polymer chain. As more and more monomer units are added, the length of the polymer chain increase continuously and the chain grows rapidly.

Initiators

Initiators are thermally unstable compounds and decompose into product called free radicals. If R-R is an initiator, and the pair of electron forming the bond between the two R’s, can be represented by dots, the initiator can be written as

\[ R \cdot R \]

When energy is supplied to this compound, in the form of heat, the molecule is split into two symmetrical compounds. Each compound carries with it an electron pair. This type of decomposition, where the molecule is split into two identical fragment, is called ‘homolytic decomposition’ The two fragment, each carrying one unpaired electron with it, are called free-radicals, i.e.,

\[ R-----R \rightarrow R' \]

The decomposition of the initiator to form free radicals can be induced by heat energy, light energy or catalysts.
A host of low molecular weight compounds comprising mainly azo compounds, peroxide; hydro peroxides, peracids and peresters are useful as initiators. For examples, benzoylperoxide (BPO) and azobisisobutyronitrile (AIBN);

Free-radical frontier Polymerisation (FP) is the one most commonly studied (Pojman & Miyata 2010 & Bidali et al 2003) method of polymerization. Free-radical polymerization is polymerization that uses radicals to grow polymer chains. This is a type of chain growth polymerization. There are three steps involved in a chain growth polymerization: initiation, propagation, and termination. Initiation involves using an initiator to generate a radical that attaches to the monomer and creates a monomer radical. Propagation is the process which continues to grow the polymer chain by having the radical on the chain reaction with more monomers. Termination occurs when two radicals meet and form a stable bond.
Another area where FP’s speed gives an advantage is in adhesives. Adhesives are substances that are applied to join two or more objects together (Petrie 2007). The idea of using adhesives to join materials in the place of nuts and bolts has gained popularity because adhesives reduce the weight, improve the stress distribution, and are more visually pleasing due to no visible sign of bonding (Pizzi & Mittal 2003). Curing is the process of the adhesives “drying”. This occurs by having the adhesive’s solvent evaporate and bind whatever is connected to the adhesive or by having the adhesive react chemically with the object that it contacts, with the adhesive itself, or both.

1.7 COPOLYMERIZATION

In Copolymerization two or more monomers / monomer pairs are polymerized simultaneously and hence, the polymer is composed of more than one repeat unit. For example, styrene – butadiene rubber (SBR) the first commercially made synthetic rubber is a copolymer obtained by the free radical polymerization of two monomers, styrene and butadiene. It is composed of both styrene as well as butadiene repeat units.

In general, copolymerization can be represented as


The copolymer formed is composed of both the monomeric units A and B arranged at random. The A: B ratio and the degree of randomness depend on composition of monomers.
1.8 ADVANTAGES AND DISADVANTAGES OF GLYCIDYL METHACRYLATE (GMA)

Glycidyl Methacrylate (GMA) is a functional monomer with outstanding chemical resistance, versatility and weatherability. GMA can be tailored to meet a wide variety of demanding specifications. GMA, which is a high purity, dual functionality monomer ideally suited for coating and resin applications. Primary applications for GMA include automotive and powder coatings, radiation curable coatings, waterborne resins, industrial and protective finishes, appliance and hardware finishes, adhesives, electrical laminates, as well as plastic modifiers. Poly (glycidyl methacrylate) is a highly versatile polymeric building block for post-polymerization modifications. The treatment of poly (glycidyl methacrylate) with nucleophilic agents yielded new linear homo/co-polymers. The materials obtained have different physicochemical properties depending upon the nucleophiles used (Benaglia et al 2013). Ideal characteristic of GMA is its dual functionality - due to the methacrylic and epoxy groups. This gives to it the possibility to combine the chemical properties of acrylates, reacting with styrene, by acrylates or by ethylene, and epoxies.

Glycidyl methacrylate was readily biodegradable (OECD 301C: 100 % after 28d) and readily hydrolyzed (T = 2.83, 3.66 and 2.22 day at pH 4.7 and 9, respectively). GMA is mutagenic when interacted with bacteria. Direct photodegradation of GMA is not expected because glycidyl methacrylate has not absorption band in UV and Visible region. Glycidyl methacrylate is low bioaccumulative based on Log Pow (0.96 at 25°C). There is no data which shows that GMA is carcinogenic in nature (Cover page SIDS initial assessment report-GMA 2000).
Over the past three decades the functional polymers have attracted the researchers to explore their interest in developing many new polymers with new functional groups. They are not only synthesized now and also being studied for their macromolecular properties and the properties involving the functional groups. These studies provide an approach to consequent modification of the polymer for specific end application. Those modified polymers used in various fields as adhesives, additives, coatings, processing aids. Functionalized polymers plays an essential role as biocides in neural networks (Liz et al 2001), photoresist material (Oyama et al 2001) Smart gels, These functional polymers also act a part of cosmetics, in printing inks, in paints, as flocculants in waste water treatment in ceramic processing etc.,

Ernest and Lamb (2005) reported that Poly (methyl methacrylate), PMMA, and poly (2-hydroxyethyl methacrylate), PHEMA, are the most common monomers of the methacrylic acid ester polymers. Due to its good optical (high transparency and clarity) and mechanical properties, PMMA has been used in a extensive range of fields such as biomaterials, optoelectronics and optic fibers. Vijayanand et al (2007) carried out the synthesis and characterization of monomer reactivity ratios and thermal properties of homopolymer and copolymer of 4-nitro-3-methyl phenyl methacrylate with GMA. Elizalde-Pen et al (2007) synthesised and characterized the polymers of chitosan-g-GMA with MMA.

Adil Denizli et al (2005) carried out synthesis and characterization of poly (hydroxyl ethyl methacrylate-N-methacryloyl-(l)-glutamic acid) copolymer beads for removal of lead ions. Liany Feng et al (2007) studied preparation and properties of poly (N-methacryloyl L-Leucine methyl ester). Francis & Ajayaghosh (1995) carried out the synthesis and characterization of copolymer of S-Methacryloyl O-ethyl xanthate. Patil et al (2010) investigated on synthesis and antibacterial activity of carvacryl ethers. Park et al (2001) reported an article on vinyl monomers with benzoic acid and phenolic moiety pendant groups. The results showed that even though the antimicrobial activity of the polymers is lower than the corresponding monomers they could be used in adhesives and coating technology. The concentration of antimicrobial agent used on the surface of polymers for coating technology could be higher than that on the polymeric material with low molecular weight which showed better antibacterial activity.


Elena Canellas et al (2010) reported the partition and diffusion of volatile compounds from acrylic adhesives used for food packaging multilayers manufacturing. They studied the behaviour of the compounds found on the acrylic adhesives in four different real laminates. Partition coefficients between several types of acrylic adhesives and substrate materials (polyethylene, polypropylene, couche paper and kraft paper) were experimentally calculated. From the diffusion and migration coefficient they were calculated the toxicity of the chemicals used.

Martin Schulz et al (2010) studied drug release and adhesive properties of crospovidone-containing matrix patches based on polyisobutene and acrylic adhesives. The adhesive properties of polyisobutene patches were investigated in vitro and in vivo. The area under the curve of force–distance curves recorded with the texture analyzer correlated well with the in vivo skin adhesion. The elongation at detachment showed the same trend as the in vivo matrix creep. Crospovidone contents ≤ 30% had no detrimental effect on the adhesive properties of the patches. Zbigniew Czech & Robert Pelech (2009) studied on the thermal degradation of acrylic pressure-sensitive adhesives based on butyl acrylate and acrylic acid. The thermal degradation of acrylic pressure-sensitive adhesives at 250°C was investigated using pyrolysis-gas chromatography. Unsaturated monomers including butyl acrylate and butyl methacrylate were formed during thermal degradation of butyl acrylate–acrylic acid copolymers. As a result of side chain reactions in the thermal destruction of the butyl acrylate–acrylic acid-based self-adhesives, a remarkable amount of butyl alcohol was produced. The unsaturated monomers formed as a result of thermal degradation could potentially be used in a new polymerization process.
Panchaxari et al (2013) reported on the design and characterization of diclofenac diethylamine transdermal patch using silicone and acrylic adhesives combination. The results indicated the high percent drug permeation (% Cumulative Drug Permeated (CDP)-23.582) and low solubility nature (1%) of Silicone adhesive and high solubility (20%) and low% CDP (10.72%) of acrylic adhesive. The combination of adhesives showed desirable characteristics for DDEA permeation with adequate % CDP and sufficient solubility. Release profiles were found to be dependent on proportion of polymer and type of permeation enhancer. The acute skin irritancy studies advocated the non-irritant nature of the adhesives used.

Tokumura et al (2010) studied, the potential dermal irritating effect of residual (meth)acrylic monomers in pressure sensitive adhesive tapes. They studied seven acrylic monomers, Acrylic Acid (AA), Methyl Acrylate (MA), ethyl acrylate (EA), n-butyl acrylate (n-BA), n-hexyl acrylate (n-HA), 2-ethylhexyl acrylate (2-EHA) and 2-hydroxyethyl acrylate (HEA), as well as three methacrylic monomers, methacrylic acid (MAA), methyl methacrylate (MMA) and 2-hydroxyethyl methacrylate (2-HEMA). They first examined their cytotoxic effect on a cultured dermis model using the MTT method to determine their EC\textsubscript{50} and then performed a primary irritation test in rabbits using the monomers at three different concentrations (i.e., EC\textsubscript{50}, one-tenth EC\textsubscript{50} and 10 times EC\textsubscript{50}). Their results showed that residual unpolymerized (meth) acrylic monomers in adhesive tapes are unlikely to induce skin irritation except for HEA.

Zbigniew Czech et al (2012) studied the influence of selected photoinitiators type II on tack, peel adhesion, and shear strength of UV-crosslinked solvent-borne acrylic pressure-sensitive adhesives used for medical applications. They synthesized solvent-borne acrylic PSA containing different unsaturated photoinitiators and investigated their relevant and...
significant properties such as tack, peel adhesion, and shear strength after UV exposure. Cengiz Soykan et al (2000) published an article entitled copolymers of phenacyl methacrylate with glycidyl methacrylate: synthesis, characterization and monomer reactivity ratios. They explained the synthesis, spectroscopic and thermal characterization, and determination of reactivity ratios for copolymers of phenacyl methacrylate with glycidyl methacrylate.

Thamizharasi & Reddy (2000) reported on the synthesis and characterization of thermally stable naphthyl acrylate polymers. They studied property of naphthalene moiety incorporated polymers, since it imparts high mechanical property and good thermal stability for applications as coating materials in Leather Industry. Sutapa Ghosh & Krishnamurti (2000) studied and reported the use of glycidyl methacrylate monomers for developing crosslinkable pressure sensitive adhesives. They explored the use of acrylic copolymer emulsions containing epoxy groups as cross-linkable PSAs.


Rivas et al (2003) reported that the advantage of polymers used as biocides was justified in the minimization of environmental problems due to less toxicity compared to low molecular weight compounds that are usually liquids or gases. Kesenci et al (2002) studied on the removal of heavy metal

Guo & Severtson (2008) studied on effect of amphiphilic additives on the behavior of water-based acrylic pressure-sensitive adhesives during paper recycling fragmentation behavior. The findings presented explained the guidelines for the synthesis and formulation of recycling-compatible acrylic water-based PSAs. Zhenping Cheng et al (2005) reported that the polymer microspheres with permanent antibacterial surface from surface-initiated atom transfer radical polymerization. They demonstrated the permanence of the bactericidal activity through the repeated applications of the surface-modified poly (4-vinylbenzyl chloride) microspheres without any significant loss of their surface activity or functionality.

Copolymerization of vinyl monomers can be carried out in bulk, solution, suspension and emulsion polymerization techniques using free radical initiators. Among these the free radical initiated copolymerization in solution has been investigated by a number of researchers. Copolymerization is the most successful method adopted for the preparation of materials with tailor made properties. Soykan et al (2008) investigated on the synthesis, characterization, monomer reactivity ratios and thermal properties of copolymer of N-(4-bromophenyl)-2-methacrylamide with glycidyl methacrylate. Patel et al (2006) studied the

Godwin et al (2004) studied the properties of homopolymer of 4-propanoylphenyl methacrylate and its copolymer with glycidyl methacrylate: synthesis, characterization, reactivity ratios and application as adhesive. Synthesis of copolymers of acrylic or methacrylic monomers MMA or GMA and determination of monomer reactivity ratios using $^1$H-NMR analysis have been reported by some of the researchers. Leena et al (2000) reported an article on comparative in vitro cytotoxicity of ethyl acrylate and tripropylene glycoldiacrylate to normal human skin and Lung Cells. Nicholson (1991) studied the glass-ionomer cements as adhesives. Boesel et al (2006) analysed about the incorporation of $\alpha$-amylase enzyme and bioactive filler into hydrophilic, partially degradable, and bioactive cements (HDBCs) as a new approach to tailor simultaneously their degradation and bioactive behaviour.


Vijayaraghavan & Reddy (1999) investigated on the Influence of the “comonomers (styrene and methyl acrylate) on the rate of

Vijayanand et al (2002) reported on the copolymers of 3, 5-dimethyl phenyl methacrylate and methyl methacrylate: synthesis, characterization and determination of reactivity ratios. Pitchumani et al (1982) reported on the reactivity ratios of ethyl acrylate-n-butyl methacrylate copolymer system by $^1$H NMR analysis. Bankova et al (1996) prepared the homopolymers of 5-chloro-8-quinolinyl acrylate and 5-chloro-8-quinolinyl methacrylate and their copolymers with acrylic and methacrylic acid. Elif Vargun et al (2010) reported that the synthesis and characterization of 2-hydroxyethylmethacrylate (HEMA) and methylmethacrylate (MMA) copolymer used as biomaterial. A series of poly (methylmethacrylate-co-2-hydroxyethylmethacrylate) (PMMA-co-PHEMA) copolymers were synthesized by emulsion polymerization technique. Copolymer compositions were determined by FT-IR and $^1$H-NMR spectroscopy.

Bankova et al (1996) synthesized and studied the antibacterial activity of copolymers containing acrylic moiety and vinyl moiety and reported that the acrylic acid content increases the antibacterial property of
copolymers with increase in their composition. Moon et al (2003) reported the syntheise of vinyl monomers and polymers with azole moieties and observed that the polymers are more effective antibacterial agent than monomers. Copolymers of glycidyl methacrylate and a divinylbenzene bearing phosphonium group were reported by Nonaka et al (1995).

Lama et al (2012) studied the Survival and Growth of Bacillus cereus, Pseudomonas aeruginosa and Staphylococcus aureus in extreme environments present during the early stages of a conventional leather making process. Pseudomonas aeruginosa ATCC10145 and Staphylococcus aureus ATCC25923 were inoculated over leather and the survival was monitored following a conventional pre-tanning and chromium-tanning process. The studies showed the presence of inoculated bacteria in effluent and on skins. A higher bacterial growth was observed during the pre-soaking process, followed by a significant reduction during the main-soaking, unhairing and reliming processes.

1.10 SCOPE AND OBJECTIVES OF THE PRESENT WORK

Antibacterial polymers have attracted the polymer researchers due to their applications in adhesives and coating technology.

The present investigation deals with the synthesis of new monomers and their polymers and copolymers with aromatic and phenolic moiety which may contribute the adhesive and coating science to make better adhesive with antibacterial property. The adhesive property of polymers and copolymers were tested on leather. Leather has been used as a testing material because it is more prompted to microbial growth rapidly. The antibacterial studies may help to produce bacteria free leather products. The lap shear strength gives maximum bonding strength of the polymer adhesives, tested
over leather following British Standard SATRA TM123, which has been widely used by leather testing research institute. The research work comprises with the following objectives.

- To prepare acid chlorides such as acryloyl chloride and methacryloyl chloride by reacting acrylic acid and methacrylic acid respectively with benzoyl chloride.
- To synthesize monomers, 4-benzyloxyphenylacrylate [M1] and 4-benzyloxyphenylmethacrylate [M2] by reacting 4-benzyloxy phenol with acryloyl chloride and methacryloyl chloride, respectively in the presence of triethylamine.
- To synthesize monomers, 3[(s)-1(s)-phenylethylaminoethyl]phenyl acrylate [M3] and 3[(s)-1(s)-phenylethylaminoethyl]phenyl methacrylate [M4] by reacting 3[(s)-1(s)-phenylethylaminoethyl] phenol with acryloyl chloride and methacryloyl chloride respectively in the presence of triethylamine.
- To synthesize monomers, 4-(2-methoxycarbonyl)-2-(t-butoxymethyl amino) ethylphenylacrylate [M5] and 4-(2-methoxycarbonyl)-2-(t-butoxymethylamino) ethyl phenyl methacrylate [M6] by reacting 4-(2-methoxycarbonyl)-2-(t-butoxymethylamino) ethyl phenol with acryloyl chloride and methacryloyl chloride respectively in the presence of triethylamine.
- To prepare the following homopolymers [P1-P6] from synthesized monomers [M1-M6] by free radical solution polymerization technique.
  - Poly (4-benzyloxyphenyl acrylate) (4-BOPA) [P1]
- Poly (4-benzylxyphenyl methacrylate) (4-BOPMA), [P2]
- Poly (3(s)-1(s)-phenyl ethyl amino ethyl) phenyl acrylate) (PEAEPA), [P3]
- Poly (3(s)-1(s)-phenyl ethyl amino ethyl) phenyl methacrylate, (PEAEPMA), [P4]
- Poly (4-(2-methoxycarbonyl)-2- (tert-butoxymethylamino) ethyl phenyl acrylate) (MCTBMAEPA), [P5]
- Poly (4-(2-methoxycarbonyl)-2- (tert-butoxymethylamino) ethyl phenyl methacrylate) (MCTBMAEPMA), [P6]

- To prepare the following copolymers [P7-P12] from monomers with GMA by free radical solution polymerization technique.
  - Poly(4-BOPA-co-GMA), [P7]
  - Poly(4-BOPMA-co-GMA), [P8]
  - Poly(PEAEPA-co-GMA), [P9]
  - Poly(PEAEPMA-co-GMA), [P10]
  - Poly(MCTBMAEPA-co-GMA), [P11]
  - Poly(MCTBMAEPMA-co-GMA), [P12]

- To characterize the monomer, homopolymer and copolymers by UV, FT-IR, \(^1\)H-NMR and \(^{13}\)C-NMR spectroscopic techniques.

- To test the solubility of homopolymer and copolymers in various solvents at 30\(^0\)C.

- To find out the thermal behaviour of homopolymer and copolymers by Thermogravimetric analysis (TGA) and
Glass transition temperature ($T_g ^\circ C$) by differential scanning calorimetric analysis (DSC).

- To study the antibacterial activity of synthesized monomers, polymers and copolymers by well diffusion and N–broth dilution methods

- To determine the lap shear strength to evaluate the adhesive property of homopolymers and copolymers.

- To evaluate the cytotoxicity of synthesized homopolymers by MTT assay.

- To study the water absorption property of polymers.