STUDIES ON ELECTRICALLY CONDUCTIVE ADHESIVES

A Major Project Submitted in fulfilment for the award of the

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BY

TANYARADZWA MUZATA

(2K13/PTE/14)

UNDER THE GUIDANCE OF

Prof. D.KUMAR

DEPARTMENT OF APPLIED CHEMISTRY AND POLYMER TECHNOLOGY

DELHI TECHNOLOGICAL UNIVERSITY, DELHI-11042

CERTIFICATE

This is to certify that Mr **Muzata Tanyaradzwa,** M.Tech (2K13/PTE/14) student has completed satisfactorily the project entitled **Studies on Electrically Conductive Adhesives** in the partial fulfillment for the award of the degree of Master of Technology in Polymer Technology of Delhi Technological University, Delhi during the academic session 2014-2015.

To the best of my knowledge and belief, this work has not been submitted to any other University or Institutions for the award of any degree or diploma.

Prof. D.KUMAR

Project Supervisor

Head, Department of Applied Chemistry & Polymer Technology

DTU, Delhi

DECLARATION

I declare that the work presented in this thesis titled **Studies on Electrically Conductive Adhesive**s, submitted to the Department of Applied Chemistry and Polymer Technology, is an authentic record of my work carried under the supervision of **Prof. D.Kumar,** Head of the Department of Applied Chemistry and Polymer Technology, Delhi Technological University Delhi during the academic session 2014-2015.

I have not submitted the matter embodied in this major project as a whole or in part to any other institute or university for the award of any degree or diploma.

Date   Signature of Candidate

Place: DTU, Delhi

.

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Tanyaradzwa S.Muzata

2K13/PTE/14

M.Tech. (Polymer Technology)

Dept. of Applied Chemistry & Polymer Technology

DTU, Delhi-110042

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ABSTRACT

Electrically conductive adhesives made up of silver nano-particles as the main filler and polyaniline co-filler were synthesised and then characterized for their electrical and mechanical properties. Silver is a metallic substance which has the highest electrical conductivity among metals and also it has the ability to conduct electricity in its metallic and oxide form. Also, polyaniline (PANI) is a conducting polymer which possesses moderate conductivity that lies in between the silver and epoxy resin. Incorporation of polyaniline and silver in epoxy facilitates the electrical conduction. Polyaniline (PANI) also prevents the aggregation of silver filler particles caused by the localization of charge carriers. Polyaniline (PANI) enabled the bridging effect in which it enhanced the tunnelling of electrons above the silver-nano particles. Investigations on the silver-polyaniline reinforcements based epoxy as a promising alternative to lead/tin solders was exhibited in the project due to enhanced tuning of the mechanical and electrical properties of silver-polyaniline epoxy composite and silver-epoxy system in cured state. A comparison of the three composites, silver-polyaniline-epoxy, polyaniline-epoxy and silver-epoxy and also different polyaniline concentrations in the conductive adhesives was done and silver-polyaniline epoxy showed the highest conductivity (1.184 S/cm) and the composite with 10% polyaniline concentration showed the highest conductivity (10.62×10^{-6} S/cm) among all concentrations studied in the present report. Silver-polyaniline-epoxy composite showed the highest shear strength of 28 MPa at 1% polyaniline. The motivation behind combining the two reinforcements was to eliminate the use of lead tin solders. In this project report, the optical, mechanical, morphological and electrical properties of ICAs have been reported.

CHAPTER 1
INTRODUCTION

1.1 Introduction

Electrically conductive adhesives are one of the most important adhesives used in the electronic industry. They are used as interconnecting bridges in integrating different electronic components on the whole device system board. The electrically conductive adhesives must be made in such a way that they act as a medium to distribute electric current to the specific electronic components; act as thermal management material and most importantly must be able to attach the electronic component to the whole electronic system. The main aim of the electrically conductive adhesive is to ensure optimum functioning whilst making sure that there is no performance hindrance. The lead/tin (Pb/Sn) containing solders were one of the mostly used adhesive materials in the previous decades but due to their numerous disadvantages they are now not frequently used. The lead/tin containing solders have lost the niche in the adhesive market because they are not friendly both to the environment and human beings due to the lead metal which has detrimental effects. Electrically conductive adhesives are considered to be better than lead containing materials because they are favourable to human health and the environment.

The electrically conductive adhesives are made up of a polymeric matrix and conductive filler. Electronic products which use ECAs are most regarded due to their environmental and human friendliness, they do not contain the harmful lead metal, they are easy to manufacture and their processing conditions are favourable. For the ECAs to be considered perfect in their specific purposes they should possess two important characteristics which are electrical conductivity and adhesion. ECAs should have high electrical conductivity and mechanical strength, hence to address this issue the use of silver nano-particles as the main filler material and polyaniline as the co-filler and epoxy as the main resin material. It should be noted that increase in silver nano-particles does not guarantee an increase in conductivity. High cost of silver prevents its excessive use in ECAs, and also physical properties such as impact strength, adhesion and modulus can also suffer due to over-loading of silver. A minimum volume of the silver nano-particles required to impart electrical conductivity in the ECAs is termed as the percolation threshold. To balance the electrical conductivity and other physical

properties such as shear strength addition of conducting polymer co-filler such as polyaniline serves as a better option. Polyaniline (PANI) is a conducting polymer which (PANI) possesses less conductivity as compared to silver, its incorporation into the epoxy system will result in less detrimental effects on the physical properties of the composite and also aids the silver nano-particles by preventing their migration problem.
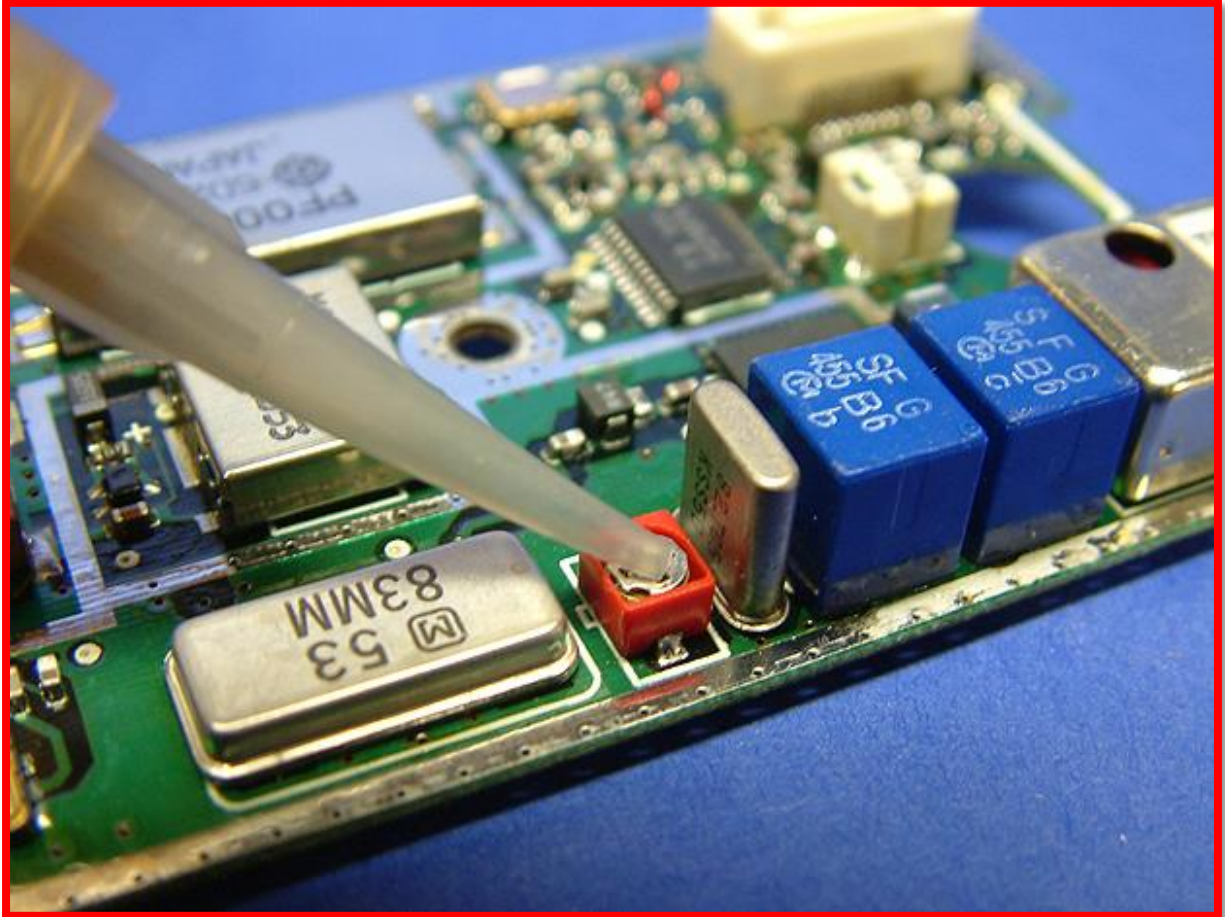
Fig 1.1 Electrically conductive adhesive application

During the 20th century, thermoset (matrix) polymers filled with metal fillers were internationally accepted as electrically conductive adhesives. In this time, ECAs are now used in the electronic hardware industry and are of paramount importance in the manufacturing of electronic board systems. Electrically conductive adhesives are used mainly as pastes as shown in fig 1.1 or as solid films. Because of their multiplicity of advantages such as low manufacturing costs and also being lead free hence friendly to the environment, the electrically conductive adhesives have substituted a multiplicity of commonly used interconnections. The table below shows the advantages and disadvantages of electrically conductive adhesives over solders.

ELECTRICALLY CONDUCTIVE ADHESIVES

Table 1.1 Advantages and disadvantages of traditional soldering and conducting adhesive

Interconnection method	Advantages	Limitations
Conductive adhesives	- Easy rework - Low cost - Low VOCs - Low processing temperatures - Easy process control - Excellent adhesion - Varying curing time - Ability to relieve stress - Directional conductivity possible	- Silver migration - Limited thermal stability, thermal resistance is very high - Absorption of water - Low mechanical strength
Traditional soldering	- Good electrical connections - Easy rework - Batch process - Mature process	- Need reflux - Corrosion - Contains toxic lead - Limited wetting - It experience stress cracking

1.2 Applications of ECAs

1. They are used as interconnections in printed circuit boards.
2. Used to connect temperature sensitive components.
3. They prevent electromagnetic radiation.
4. They prevent electrostatic charging's in scanning electron microscope.
5. Die attachments

ECA's can be used as solder replacement, interconnection, sealing, electrical shielding, various electronic components bonding, fastening and brazing [1-2].

1.3 Isotropic conductive adhesives

Isotropic conductive adhesives are composites made up of various conductive fillers such as copper, silver or polyaniline and a polymeric matrix. Isotropic conductive adhesives have a multiplicity of advantages such as being lead free and offer low processing cost as compared to solders. Many different polymers are used as matrices for ICAs that include polyesters, urethanes, polyamides, epoxies, acrylics and phenolics. Epoxies dominate and are likely to maintain the role because of their balance of functional properties, availability, relative safe use and moderate cost. ICAs are typically filled with 1-20μm silver nanoparticles and may have a filler volume up to 30% or more of total volume. The conductive fillers are responsible for conductivity throughout the whole adhesive system. ICAs perform dual functions which are: electrical connection and mechanical bond. Specifically, electrical connections are facilitated by conductive fillers and mechanical bonding is provided by polymer matrix, mostly epoxy. Excessive filler loading might compromise the shear strength of the adhesive, hence the main focus is to fabricate an adhesive with optimum electrical conductivity whilst the maintaining good mechanical properties. Electrical conductivity of ICAs increases when it has fully cured due to shrinkage higher shrinkage of the matrix will result in low bulk resistance henceforth resulting in better conductivity. ICAs with higher shrinkage results show lower bulk resistance or better conductivity [3]. However, like all other lead-free materials. It should be noted that the high working ability of ICAs is mainly due to the type and amount of filler present. In recognition of the importance and challenges of ICAs, worldwide efforts have been dedicated too much study on these ICAs.

1.4 Anisotropic conductive adhesive

Due to their low loading of conductive fillers which is usually below 20% by volume [4], anisotropic conductive adhesives provide electrical conductivity in the Z-axis direction. Conductivity in the X-Y plane is difficult due to low volume of the conductive fillers. ACAs provide new material system for solder replacement besides ICAs.
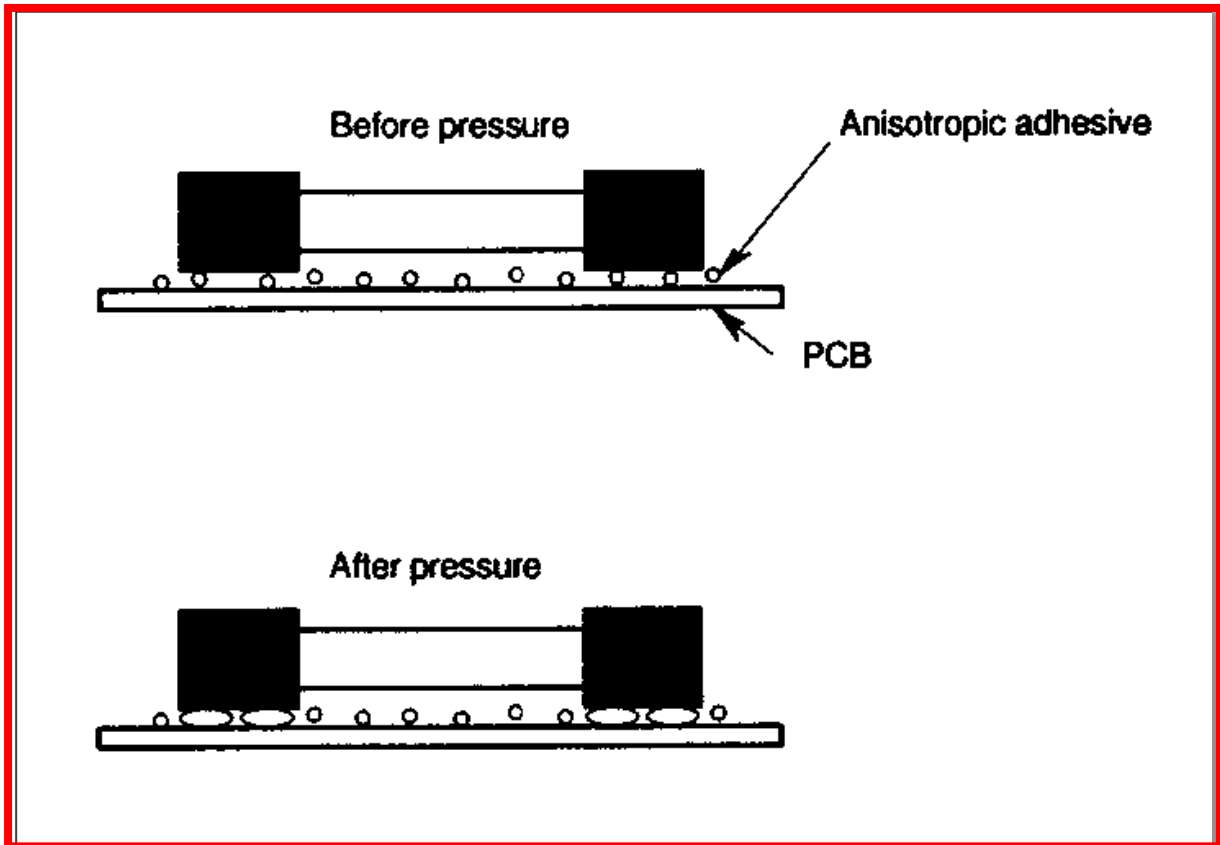
Fig 1.2 Anisotropic mechanism

The anisotropic nature of these materials makes them perfect candidates for very fine pitch components [5], where particle density in adhesive and its dispersion consistency is extremely important to prevent open or short-circuit events [4]. The requirement of complicated process and specific bonding are the main disadvantages of these materials compared to solders and ICAs. Anisotropic adhesives can be found in liquid or solid form.

1.5 Materials for electrically conductive adhesives

Table 1.2 Comparison of adhesive matrices for electronic application

Materials	Advantages	Disadvantages
Epoxies	High temperature	Longer cure cycles
	High purity	Degassing required for two component systems
	Low outglassing	Exotherms in large quantities when using aniline curing agents
Polyurethanes	Highly flexibility only at low temperature, stress absorbing high versatile chemistry	Low thermal stability and service temperature than epoxies
Silicons	Prevent formation of stress	Surface energy is low
	High and low temperature stability	Swelled by non-polar solvents
	High Purity	Degassing required
Polyimides	High temperatures stability compared to epoxies	Trapped solvent can produce voids
	High purity	High stress materials
	Reduced bleed out	Multi-step curing required to volatize solvent

1.6 Thermoplastic adhesives

Thermoplastics are plastics which can be melted and remelted again and again. Thermoplastics are usually available in solid or paste form. Thermoplastics and thermosets are the frequently used material in developing ECAs [6]. Since thermoplastic matrices are already in their polymerized form, they are not frequently used as compared to thermoset matrix. Thermoplastic adhesives first have to be melted or dissolved in a suitable solvent and then different conductive fillers can be added. However, due to high viscosity of the melted thermoplastic it is very difficult to mix the filler material into them. Certain solvents are capable of reducing the viscosity and facilitate higher loading of the filler. Not all thermoplastics can dissolve in widely used solvents this result in a processing which has

limited applicability in adhesive application due to bubble formation after solvent vaporization. It should also be noted that thermoplastics melting and remelting capability make them difficult in using them in high temperature conditions, this thermoplastic disadvantage gives an edge to thermosets as perfect material for polymer matrix. Some of the commercially available thermoplastic adhesives can be used for joining of component assembly but their properties are not competitive to those of thermosets [4]. ACAs mainly use thermoplastic conductive adhesives because they do not require specific application. Therefore, thermoplastic adhesives are employed with the use of heat and pressure where it softens and bonds to adherents.

1.7 Thermoset adhesives

Thermosets are three dimensioned polymers which cannot melted again after processing as compared to thermoplastics. Thermoset adhesives properties are permanently changed upon curing. Thermoset systems are mainly used in ICAs. Epoxy is a typical thermoset polymer used to synthesize the ICAs. Epoxies have been widely used due to their favourable mechanical properties such as good excellent adhesion to different materials and also chemical properties such as good corrosion resistance. Epoxies can be tailored to survive thermal cycling and also conditions which are humid. Low molecular weight, viscous epoxy is used as the primary component with co-reacting hardener. Typical epoxy cross-linking materials are anhydrides, amines, and dicyanodiamides. Amines and anhydrides are frequently used as curing agent to cross-link epoxy matrix. The main epoxies are diglycidyl ether of bisphenol-A (DGEBA), synthesized by reacting epichlorohydrin and bisphenol-A, are the common materials for liquid adhesives. In case of ECAs, before the epoxy is blended under shear force with the conductive filler it is first processed. The curing process facilitates the polymerization process which results in a thermoset system. Heat treatment upon mixing causes components to react chemically and forms high molecular weight, cross-linked epoxy. Three-dimensional network of cross-links prevent movement of polymeric chains in thermosets. Addition of additives at low concentrations can enhance certain properties such as impact crack resistance, adhesion and modification of rheology [7]. Single component ECA system is preferred but it has a limited storage life unless refrigerated. Two-component system faces a serious concern of entrapment of air during the mixing process.

1.8 Epoxies

Since, ECAs are made up of the conductive fillers and a polymeric matrix, therefore we discuss about epoxies as matrix and its corresponding composites in this section. Epoxy resins are made up of an oxirane group. Epoxy adhesives comprise as a liquid containing epoxide groups, and a curing agent containing the functional groups with which the epoxide groups combine to form a cross-linked polymer. This cross-linked matrix good adhesion and excellent strength. These important characteristics results in them being used in a multiplicity of functions which offer adverse conditions. This conversion of resin into hard, three dimensional network in which the resin is cross-linked by strong covalent bonds is called curing or hardening. When the reaction between resin and curing agent is capable of taking place at room temperature the two components are mixed immediately before use, but if the mixture is inactive under ordinary storage conditions the components are mixed together and marketed as single package.

The time taken for the epoxy system to be cured and deemed unusable when the epoxy resin is mixed with the hardener is known as the pot of life of the system. This time is therefore the practical working life of the mix, during which the material must be applied to the job concerned. The pot of life can vary from a few seconds to several weeks depending on the epoxy resin formulations. The curing that takes place when the resin and hardener are brought into intimate contact is an irreversible reaction that results in a thermoset resin.

The development of epoxy resins has been directed towards many different fields of applications, one important application being adhesive bonding. Epoxy resin based adhesives are most used to bond metallic materials, wood and plastic materials. Despite the fact that the work on epoxy resins started in the 20th century, the epoxy resins have now established a reputation as the most widely used adhesive on a multiplicity of materials such as steel due to their high shear bonding strength.

1.8.1Significance of epoxy resins

Due to their excellent adhesion and high strength, epoxy resin adhesives have been widely accepted as a good adhesive material by different adhesive producers. They have helped immensely in the joining and fastening technology.

1. **Adhesion**: Because of their polar groups, epoxies have high adhesion on materials such as wood, glass, ceramics and metals. Epoxies can be made to have low viscosity which is very important in the ability to adhere to this materials.

2. **Cohesion**: The strength of cohesion in the glue line is very strong, and adhesion of the epoxy to other materials is very good, failure under stress only occurs in one of the adherents rather than the epoxy.

3. **Solids**: Unlike the phenolics and some other resinous adhesives, epoxies cure without releasing water.

4. **Low shrinkage**: Less strain is there in the glue line when there is less shrinkage. The shrinkage can be reduced by incorporation of silica, aluminium or other inorganic fillers.

5. **Low creep**: Cured epoxies have the ability to maintain their shape under prolonged stress as compared to thermoplastics such as polyvinyl acetate, nitrocellulose, and polyvinyl butyral.

6. **Resistance to solvents and moisture:** Unlike proteins, starch, dextrins, gums, and polyvinyl alcohol, the epoxies are insensitive to moisture.

7. **Can be modified**: Epoxy adhesives properties can be changed by (a) alloying the epoxy with another resin, (b) selection of base resin and curing agent or (c) compounding with fillers.

8. **Cured at ambient temperatures**: Epoxy resin adhesives can be cured at room or lower temperature by selection of proper curing agents. It has particular advantage and the application window of these resins has increased enormously because of the possibility of low temperature curing.

9. **Temperature stability:** Epoxies show great temperature stability and hence find application in a wide range of service temperatures. Epoxies can be used high temperature environments.

1.8.2 Disadvantages

1.   Toxicity: Some epoxies and diluents are known to cause dermatitis. Some amine curing agents are toxic. Good housekeeping is the best preventative measure. The cure epoxies are not deleterious to health.

2.   Low shelf life: Some films and tape adhesives should be kept at very low temperatures so that they cannot be affected offsetting their advantages of convenience and reliability.

3.   Moderate to high cost: Epoxies are expensive, if compared to their immediate competitors, but this hardly has any appreciable effect on the overall cost factor of the assembled product.

1.9 Chemistry of epoxy

Glycidyl ether of bisphenol F (DGEBF) is the most widely used in thermosetting ICA formulations due to their excellent adhesion and excellent mechanical properties. Most epoxy resins can be cured with either hardeners such as carboxylic anhydrides (such as 4-methylhexahydrophthalic anhydride (MHHPA), cycloaliphatic or aromatic amines, polyphenols, dicyandiamides, and isocyanates at a curing temperature of beyond 120°C or hardeners such as primary or thiols secondary aliphatic amines or polyaminoamides at a temperature between room temperature and 120°C. Carboxylic acid anhydrides hardeners show perfect properties such as less moisture absorption and shrinkage during curing process [8]. Anhydride-cured epoxy main disadvantage is that they need curing high temperatures to initiate the curing reactions to achieve desired mechanical properties and thermal stabilities.
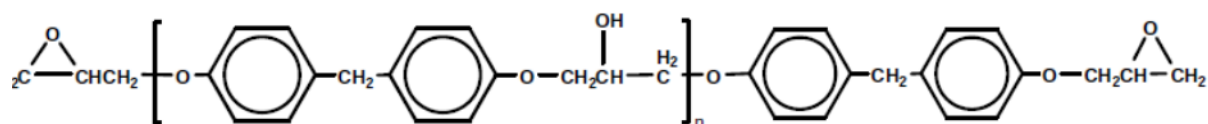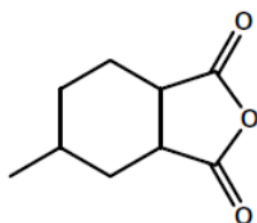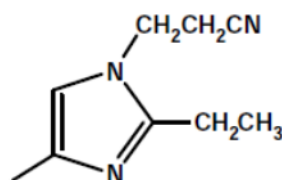
(a) DGEBF

(b) MHHPA   (c) 2E4MZCN

Figure 1.3 Chemical structures of DGEBF, MHHPA and 2E4MZCN

The curing mechanism of epoxy-anhydride systems remains unclear due to several competing reactions which can occur due to tertiary amine catalyst. In the absence of tertiary amines, the uncatalyzed reaction mechanism is shown in figure above, as proposed by Fisch et al. [8-9]. The OH group present in the backbone of an epoxy resin gives away its proton and hence opening the anhydride ring, resulting in an ester group and a carboxylic acid group. The carboxylic acid group then chemically combines with an epoxy resin to form di-ester-alcohol, which can continue the polymerization until termination occurs through condensation reaction of one carboxylic acid end and alcohol to an ester linkage. As a result of the occurrence of etherification reaction, only 0.85 equivalents of anhydride, instead of one equivalent of anhydride in stoichiometry are needed to provide maximum cross-link densities and the required properties.
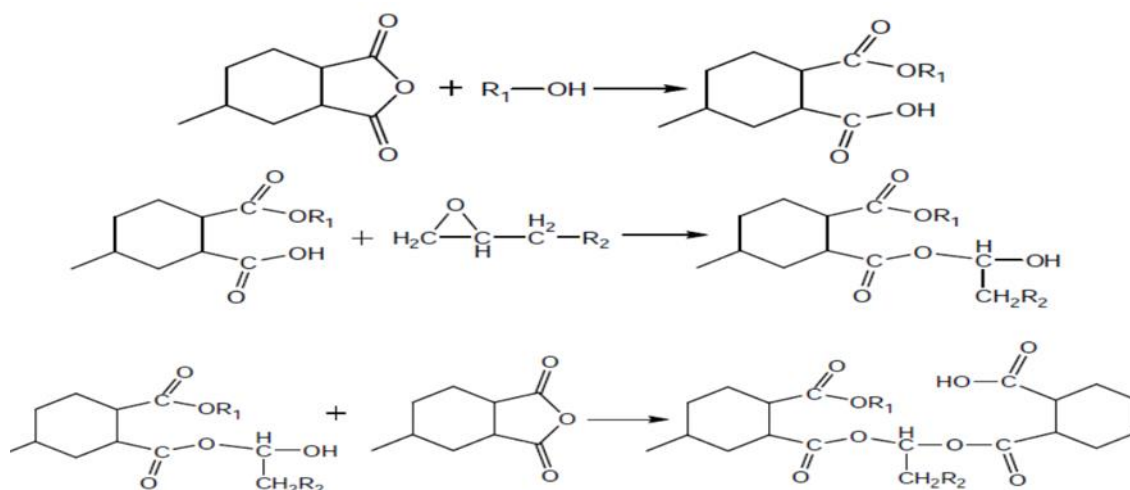
Figure 1.4 Schematic representation of uncatalyzed anhydride-epoxy curing

To accelerate the curing process, strong Lewis bases, such as tertiary amines are usually incorporated into a formulation. In the presence of catalyst, such as (2E4MZ-CN), several possible initiation mechanisms have been proposed, as shown in Figures 1.1 and 1.2. In the above figure, curing reaction involves the formation of a zwitterion tertiary when the tertiary amine reacts with an epoxy resin. A carboxylate anion is formed when an alkoxide anion reacts reacts with an anhydride group. An epoxy group then reacts with the carboxyalte anion yielding a new alkoxide anion. Etherification between an epoxy resin and an alkoxide anion is a competing reaction resulting in an ether linkage. Fisch suggested a mechanism which is being recommended[9]. In this mechanism, a nucleophilic attack opens the Lewis bases anhydride rings and form internal salts containing a quaternary nitrogen atom and a carboxylate anion. An alkoxide ester is then yeilded when the carboxylate anion reacts with epoxide groups, which react with anhydride to form new carboxylate anion esters. These carboxylate anion esters can further react with epoxide groups and this alternating reaction continues until the termination reaction occurs through the combination of two living

polymers.
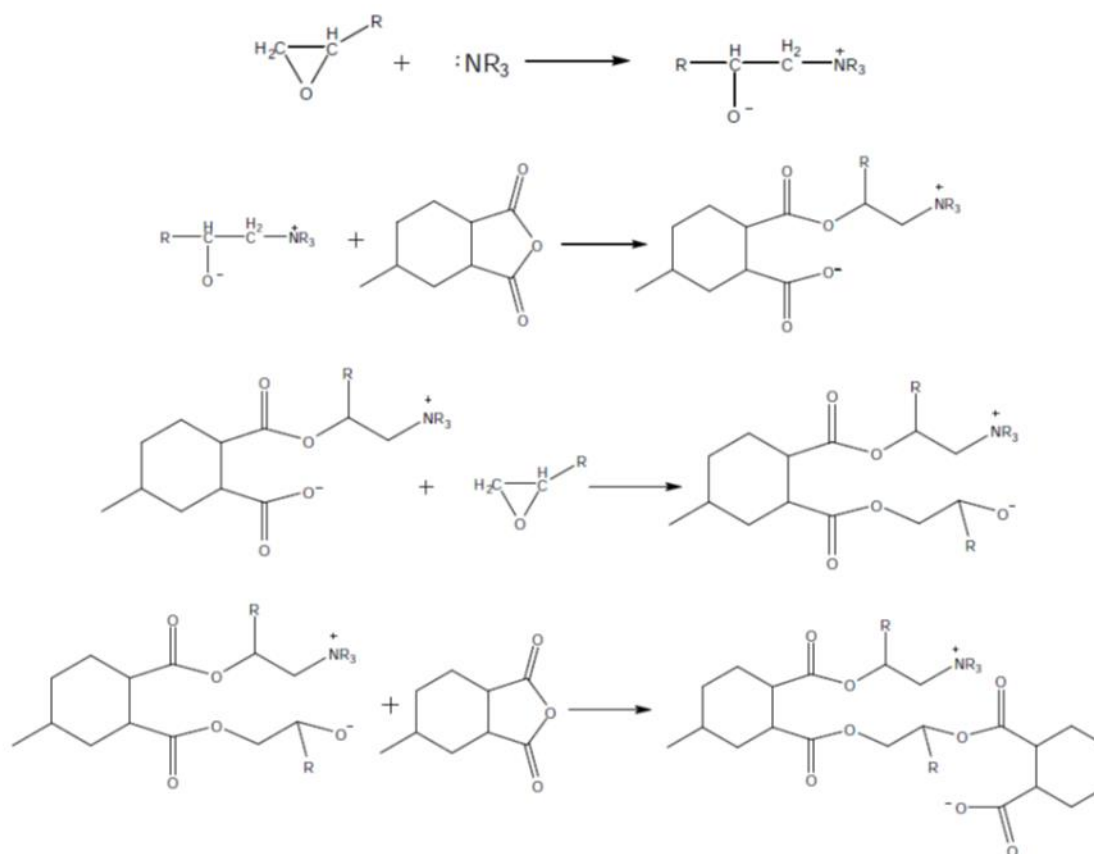
Figure 1.5 Anhydride-epoxy reaction catalyzed by tertiary amines

Curing of an epoxy resin with an anhydride results to a linear polymer chain growth which then branches resulting in cross linking. During the reaction, the polymer chains are linked to each other to form an infinite polymer network. The polymer chain network is produced when there is a change from the viscous liquid state to an elastic gel state. The point where the gel is formed is defined as the time or temperature at which the formation of infinite polymer network occurs. The gel formation usually occurs at 55-80% conversion. The curing reaction then proceeds. Vitrification is another important phenomenon that occurs during the curing reaction. Transformation from the viscous liquid occurs when the glass transition temperature reaches the curing temperature. The vitrification point is defined as the point at which further curing reaction is prohibited due to the formation of a rigid glass.

1.10 Curing agents

The simple conversion of the epoxy resins from their liquid state to highly cross-linked state is called curing or hardening of the resin. The chemical substances that bring about the

change are called hardeners or curing agents. These substances are responsible for imparting epoxy resins the unique adhesive property and mechanical strength. The overall property of the epoxy adhesives are an outcome of careful selection of various curing agents.

1.   **Aliphatic primary amines**: They allow curing at room temperature; their only disadvantage is poor heat deflection temperature and inconvenient mix ratio.

2.   **Aromatic primary amines:** They have good chemical resistance and also they have the ability to provide heat, their main disadvantage is that they have poor color stability and they needed to be converted to a more convenient physical state for use since they come in solid form.

3.   **Amine adducts**: Both aliphatic and aromatic amines can be adducted with small amounts of mono- or diglycidyl epoxies to produce amine adducts of medium to high viscosity that have decreased volatility and irritancy, more convenient mix ratios and often, better reactivity.

4.   **Mercaptans**: They are unreactive on their own.

5.   **Tertiary amines**: They are very efficient curing agents because they can cure at room temperature.

1.11 Electrically conductive fillers

Conductive fillers are usually incorporated into the adhesive matrix so as to facilitate movement of electric charge. Currently silver is the most used conductive filler because of a multiplicity of factors such as high chemical stability and high electrical conductivity and are cheap as compared to gold [10]. Although gold, copper, nickel and carbon are usually used, carbon has low electrical conductivity hence its use is very minimal as compared to other conductive fillers. Silver is considered as unique filler because its metallic and metal oxide form is both electrically conductive. On the other hand, oxides of copper and nickel are poor conductors; their conductivity decreases with aging [4]. This effect is most significant with nano-sized particles. ECA properties are not only affected the individual phases and filler loading, but also the filler geometric shape, its size, how it is distributed in the matrix, and orientation, adhesion between conductive filler and matrix and also the amount of particle agglomeration mainly in silver nano-particles. Many commercial ECAs utilize silver with flake geometry as filler due to their surface area which high enhancing the efficient flow of

electric charge and also lowing the viscosity. ECA fillers have a generally size ranging from 1 to 20 μm. High electrical conductivity is mainly as a result of large particles which also lower the viscosity hence making silver flakes favourable. Silver-filled epoxies have shown improved conductivity after thermal treatment, mainly due to the shrinkage of epoxy matrix which brings silver particles together to establish electrically conductive pathway. Therefore, conductivity is found to increase after thermal treatment.

The main problem which comes by using silver as conducting filler is the electro-migration problem which is the movement of ions throughout the matrix resulting in low electrical conductivity. To curb this problem polyaniline has to be incorporated into the epoxy adhesive so as to obtain maximum conductivity.

1.12 Polyaniline: As a co-filler

Addition of conductive metallic fillers to different polymeric matrix has been widely used and was once regarded as a good way to produce electrically conductive adhesives, but the main problem of adding metallic conductive fillers only such as silver, copper and carbon was the processing cost, reduced mechanical properties, corrosion and incompatibility between the metallic filler and the matrix. Hence a need to eliminate such problems resulted in the advent of polyaniline as an alternative or as a co-filler to the metallic fillers. Inherently conducting polymers such as polyaniline, polypyrrole, polythiophene, and polyacetylene can be a potential replacement for conventional filler-polymer systems.

Polyaniline has been regarded as the most promising conducting polymer among other conducting polymers such as polypyrrole, polyacetylene and polythiophene. Polyaniline conducts electricity based on the movement of electrons along its polymer chain. Due to its electrical, optical and magnetic properties which are most similar to metals and semiconductors, polyaniline is regarded as a synthetic metal. Metallic characteristics can be seen in polyaniline because of the polyaniline backbone which is conjugated [11-12]. Polyaniline exists in 4 different types of oxidation states: leucoemeraldine base which is the oxidized state, penigraniline base is the reduced state and emeraldine base is made up of both the pernigraniline and leucoemeraldine base and then the conductive emeraldine salt. Conductivity in the emeraldine salt that is the emeraldine base being doped with an acid such as HCl. Protonation occurs when the polyaniline is oxidized with dopants such as HCl [13-14]. Due to the closeness of positive charges, there is a rearrangement which takes place [15]. Hence, continuous electron transfer takes place. When charge carriers are introduced into the

valence band, conductivity increases drastically. Conductivity levels of polyaniline measured by various researchers are comparatively lower than those of pure metals. Polyaniline has exhibited some potential in possible implementations as an electrical contact and conductivity enhancement. Nano-printing of PMMA containing polyaniline was demonstrated for adhesion applications [16]. Polymer composites which are conductive and blends can be produced by bringing together a copolymer of polyaniline with an insulating polymer. The conductivity of the blend can be adjusted by increasing the concentration of polyaniline. Researchers studied the electrical properties of polyaniline based composite adhesive. They found that 30% volume of polyaniline is necessary to initiate the conduction in insulating adhesive matrix. On the other hand, they indicated that emeraldine salt of polyaniline may catalyze the oxidation of substrates resulting in formation of insulating metal oxide layer such as aluminium oxide. In this work, we have tried to develop the flexible and electrically conductive coating of polyaniline which can be used in various applications but mainly as a interconnect material.

1.13 Adhesion of electrically conductive adhesives

There are five theories which explain how ECAs adhere to particular components. Adhesion of ECAs is due to mechanical interlocking, mutual diffusion, chemical bonding, electrostatic forces and adsorption. Among the five adhesion theory adsorption theory is believed to be the one which is responsible for effective bonding between two substrates. ECAs which consist of an epoxy resin have superior adhesion capability because of the good adhesive properties possessed by the epoxy resin. When different fillers are added into the matrix so as to increase both the electrical and mechanical properties they also bring their own filler properties. Additions of these fillers into the polymer matrix usually alter their adhesion properties. Random distribution of silver particles in the matrix imparts good adhesion strength to the composite. The random orientation was also effective in preventing crack propagation. The joint strength was improved by having large amounts of resin at the interface, instead of filler particles. Entrapment of gases (air, solvent vapours) in ECAs can badly affect the adhesive strength of the matrix. Two methodologies can be used to address this problem [4]. When ECAs are exposed to vacuum, majority of non-bonded gases can readily escape from an adhesive matrix resulting in enhancement of adhesion. Pre-curing at low temperature can also help to eliminate the gases from ECAs. Researchers have shown that exposure of the adhesive material to vacuum and pre-curing has some positive effects on the adhesive strength [17-18]. Polymer adhesion can also be improved by using coupling

agents. Filler particle performance in the composite can be improved by enhancing the chemical bonds of the adhesion material so that they can combine easily with the surfaces of the fillers. Researchers have shown that the use of organo-silanes as coupling agents improves the adhesive strength and also prevent corrosion in certain metals such as aluminium [19]. It has been also observed that silane and titanate coupling agents can improve electrical as well as mechanical properties of the epoxy based conductive adhesives [20]. In recent years, combined use of thermoplastic binders with epoxy thermoset has shown significant improvement in adhesion strength and re-workability [21]. Increasing the filler load in the matrix is one of the major problems which alter the adhesion strength of the composite in a negative way, henceforth much research has to be dedicated so as to improve the adhesion strength whilst also increasing the electrical conductivity of the overall adhesion system.

1.14 How ECAs conduct electricity

When a certain amount of conductive fillers is embedded into the insulating matrix, to form a continuous linkage of filler particles, the composite transforms from being an insulator into an electric conductor from being an insulator. When the volume fraction of the conductive filler increases, continuity probability as a result also increases until a critical volume fraction, this is when electrical conductivity becomes higher and only increases at a slight rate with increasing volume fraction. Particle size distribution, particle shape, and pre-treatment of particle are one of the factors which are known to affect the volume fraction threshold magnitude [22]. Interestingly, ECA pastes have high bulk resistance but it should be noted that the resistance decreases sharply when the matrix is cured. It is regarded that before curing, the silver particles should be in contact each other so as to form a continuous electrical path. There are two mechanisms explains how conductivity occurs in ECAs mainly after curing.
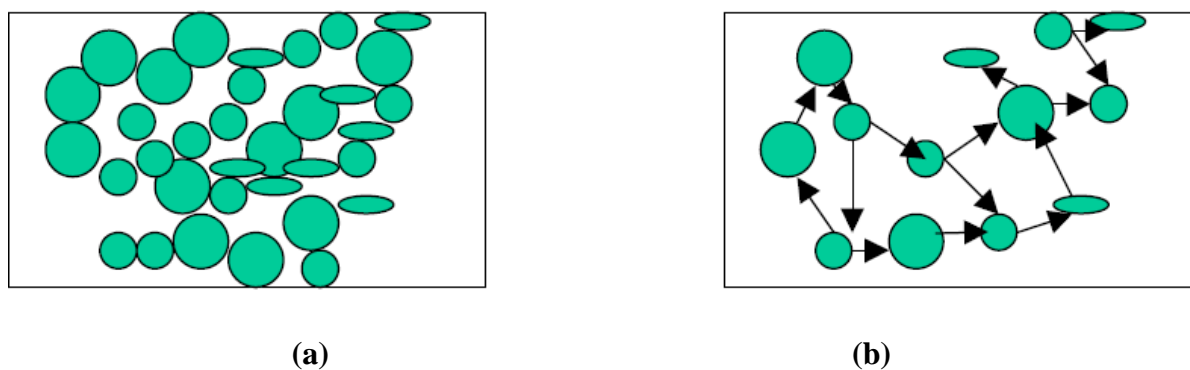
(a)   **(b)**

Fig 1.6 Shows the two types of conductive mechanisms

The first mechanism states that conduction development is because of the close proximity of the silver nano-partilces inside the matrix which is as a result of curing shrinkage and effects of silver particle lubricant [23-24]. It is observed that, silver nano-particles without external pressure applied become electrically conductive when the lubricants decompose. It was also observed that the silver particles agglomerated after heating. The second mechanism is due to the tunnelling effect of the silver nano-particles the polyaniline particles in the polymer matrix. Researchers have studied the correlation between the macroscopic conductivity and interface conductivity of the adhesive [25] and they conducted optical and electrical spectroscopic analysis on the conductive adhesive which contained silver flakes whilst monitoring the dynamics of sample conductivity and silver surface chemistry. The results revealed carboxylate species decomposition and the amorphous carbon layer formation on the silver surface. Carbon in amorphous state is very conductive as compared to the saturated organic hydrocarbons, this implies an important increase in the conductivity during thermal cure in other literature, and compressive force contribution towards conductivity is also discussed [26]. During the cure of the ECAs, the epoxy resin shrinks. Cure shrinkage is calculated as follows

$$\% \text{ Cure} = (1/d_1) \div (1/ds_1 d_1)$$

Where d_1 and ds are the densities before and after cure of the liquid systems respectively. When resins cure, they exert some compressive forces, this forces make the silver nano-particles embedded in the resin to come close together, the coming together of the silver nano-particles will make them to form a conductive pathway resulting in improved electrical conductivity. The interrelated variables such as cure shrinkage, crosslinking density and volume change results in the pressure of the conductive particles in the cured state. Resin cure shrinkage contributes to a vital role during conductivity establishment of a conductive

adhesive but it should be noted that the removal of lubricant layer on the silver particles can't be eliminated.

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CHAPTER 2
EXPERIMENTAL TECHNIQUES

2.1 Synthesis of silver nano-particles

2.1.2 Chemical approach

The most commonly used method producing silver nano-particles is by the chemical approach which can be termed as the chemical reduction method. Usually organic and inorganic reducing agents are employed so as to synthesise the silver nano-particles. A multiplicity of different reducing agents such as ascorbate, sodium citrate, sodium borohydride ($NaBH_4$), tollens reagent, polyol process polyethylene glycol-block copolymers and, N-dimethylformamide (DMF), these reducing agents reduce the silver ions in either aqueous or non-aqueous solutions. The silver ions are reduced and form metallic silver. The clusters formed after agglomeration lead to the formation of metallic colloidal silver particles.

Fig 2.1 Colour pattern of silver nano-particles

.**2.3 Chemical synthesis of silver nano-particles**

Table 2.1 Specifications of materials along with their sources

Material	Source
Silver sulphate	Central Drug House, New Delhi
Trisodium citrate	Central Drug House, New Delhi

2.3.1Chemical synthesis of silver nano-particles by Turkevich method

1. Boil 60mL of silver nitrate 1M solution, on a hot plate.

2. Stir solution with a magnetic stir bar.

3. Once boiling, add 6mL of 10mM trisodium citrate drop wise, about 1 drop per sec.

4. Wait for solution to change to a light golden colour.

5. Carefully remove beaker from hot plate and let solution cool.

Fig 2.2 Formation of silver nanoparticles under heat whilst stirring

2.4 Preparation of polyaniline

2.4.1 Materials Used

Table 2.2 Specifications of materials along with their sources

Material	Acronym	Source
Aniline	PANI	RFCL Limited, New Delhi
Hydrochloric acid	HCl	N/A
Ammonium persulphate	APS	RFCL Limited , New Delhi

2.4.2 Synthesis of polyaniline

I. 20ml of HCL (1M) is poured into a 100ml beaker and 4mmol of aniline is added and then stirred with a magnetic stirrer for 1hr.

II. 5g of APS is weighed and then added to 20mL of HCl. The solution is stirred by a magnetic stirrer for 1hr.

III. The ammonium persulphate solution is added dropwise to the aniline solution and the then left for 24hr at room temperature.

IV. A green precipitate is finally produced which is then filtered and washed several times by acetone so as to remove impurities. The filtered polyaniline is then dried at 80°C in an oven until it dries.

2.4.3 Polymer growth mechanism

The polymer growth mechanism of polyaniline occurs in the following stages

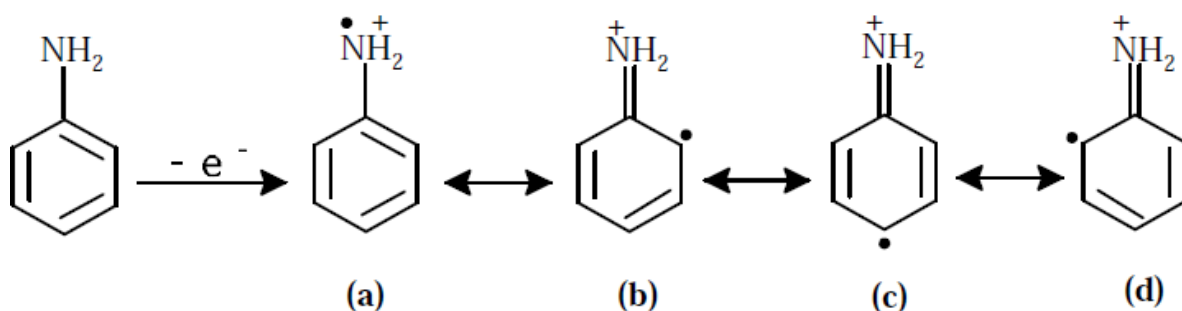I. Formation of radical cation by electron transfer from the 2Ss energy level as shown below

.

Figure 2.3 Radical cation formation

II. The second step comprises of the formation of the dimer in the "head-to tail" reaction between the radical cation and its resonant form. The dimer is then oxidized to produce a radical cation dimer, as shown in figure below.
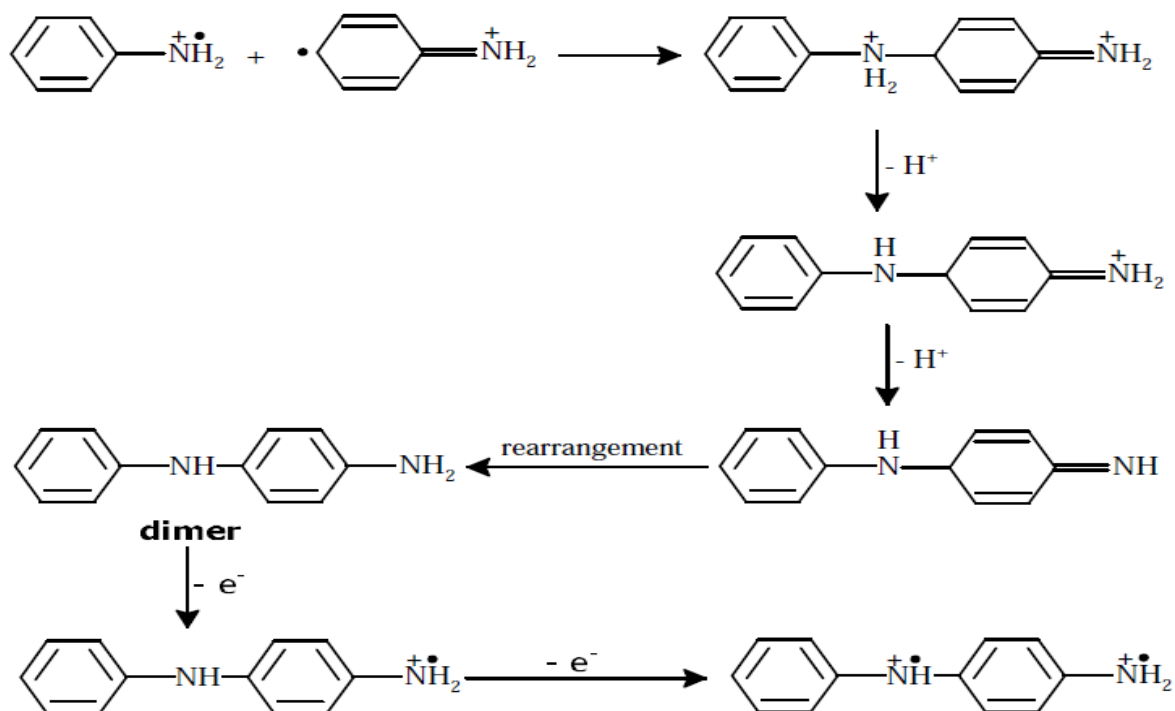
Figure 2.4 Dimer formation

III.   The radical produced then reacts with radical cation monomer to produce a trimer or a tetramer. Continuation of the polymerization results in the polyaniline shown below
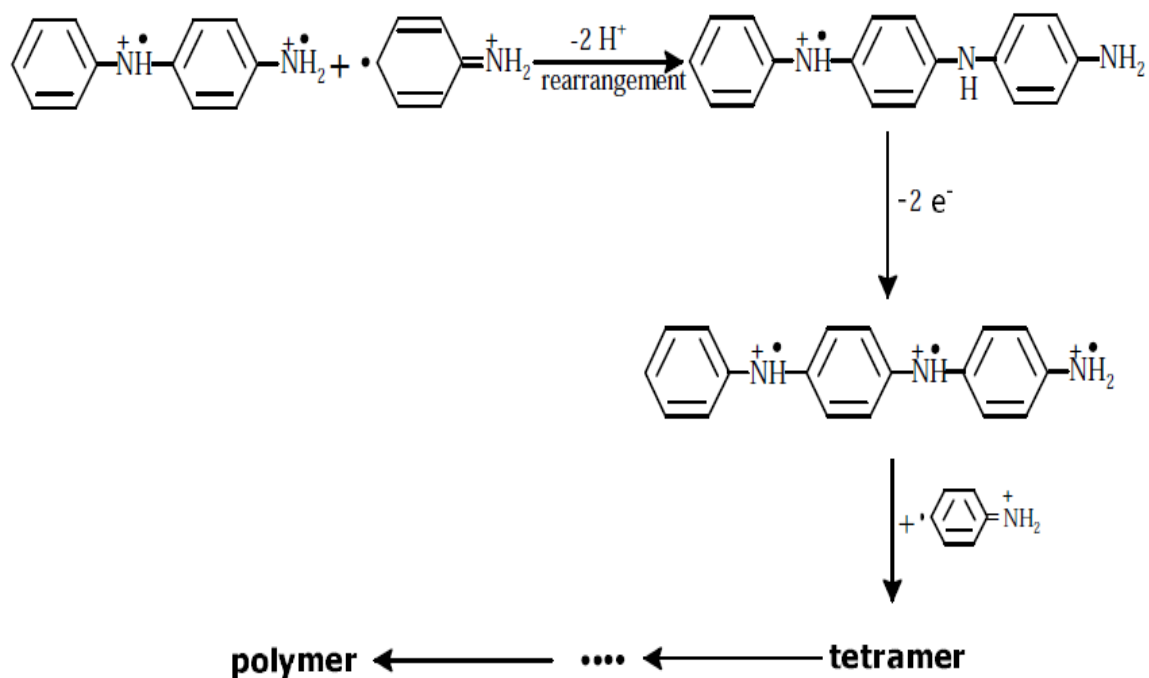

Figure 2.5 Alternative routes for PANI polymer formation

Some side reactions were also produced, which are shown below

- ❖ coupling of aniline and its oligomers in "ortho" position;
- ❖ formation of benzidine groups ("tail to tail" coupling);
- ❖ chlorine substitution in aromatic ring (in systems with HCl and LiCl or NaCl);
- ❖ formation of N=N bonds which are azo groups
- ❖ polymer hydrolysis of the (=O and -OH groups).

All those reactions introduce undesirable elements to the structure of PANI and are considered to be chain defects
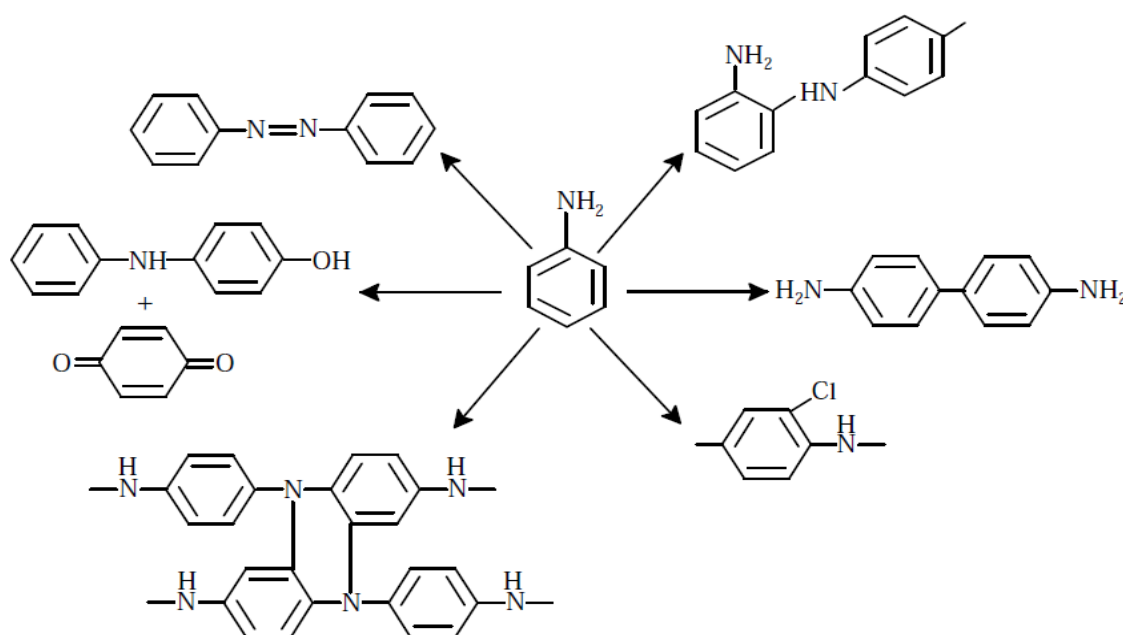

Figure 2.6 Side reactions occurring during polyaniline synthesis.

2.5 Formulation of the composite

The composite was produced from three diferent materials which are polyaniline, silver nano-particles, epoxy resin and a curing agent as per following procedure

I.   The epoxy resin was mixed with the with the two fillers silver nano-particles and polyaniline at different concentrations and then mechanically stirred using a stirring rod. The curing agent was added at a ratio of 100 parts of epoxy and 13 parts of curing agent.

II. The mixture was stirred until a homogenous mixture was obtained.

III.   The mixture was then placed in a petri dish and allowed to cure for 24hrs.

2.5.1 Preparation of ICA

Different fillers (silver-polyaniline , silver and polyaniline) were added to known amounts of the procured resin mixture and mixed thoroughly using a glass rod to obtain ICAs mixtures which were then cured at room temperature for a day and also different PANI concentrations were added with 1,3,5,10, 15 ,20% PANI concentrations. The conductive filler concentration is described as weight percentage.

2.6 Characterization

Characterization of a product formed after synthesis is an important parameter, because it is very important in giving useful parameters which determine the important properties of product. Chemical characterization involves the determination of oxidation states. Thermal analysis involves (Thermo Gravimetric Analysis) and Differential scanning calorimeter, whereas physical characterization consists of spectroscopic analysis using UV-visible spectrometer and Fourier Transform Infra-Red (FT-IR). Redox behaviour of conducting polymers is determined by this technique. The characterization of most chemically synthesized material includes electro-chemical, spectroscopic and thermo gravimetric characterization of polyaniline and the polyaniline epoxy adhesive. The characterization methods used for the characterization of polyaniline synthesised is described in following sections.

2.7 Spectroscopic characterization

Spectroscopic characterization of the polymer polyaniline is carried out by both Ultraviolet-visible and Fourier Transform Infrared techniques. UV spectroscopy gives the bands of energy gap and defective states, FTIR points and proves the chemical structure and also the presence of different linkages in polymers.

2.7.1 Ultraviolet-Visible absorption spectroscopy

UV absorption spectroscopy characterization method is the measure of the reduction in strength of a signal of the light beam after it goes through a sample or in case after reflection from a surface of the sample. UV-Vis consist of transmittance, absorption and reflection measurements in visible and near Infrared region. Absorption of UV radiation by organic molecules in the visible and ultraviolet region consists of the promotion of electrons. Higher energy states are revealed by orbitals that are not in the ground state and are called anti-bonding orbitals. The electronic transition that happens in the visible and UV regions are of different types. Transitions to anti-bonding orbitals are associated with unsaturated centres in the molecule. Molecules which contain isolated double bond absorb in the range between 162 to190 nm, while conjugated molecules absorb usually above 210 nm. Extension of the conjugated systems intensifies the absorption peaks and shifts it further to wavelengths which are higher, towards the visible spectrum. The UV technique does not only provide data about

the different bonding but also is a perfect tool for the determination of the band energy, which is a vital parameter used in investigating on how the conduction process occurs.
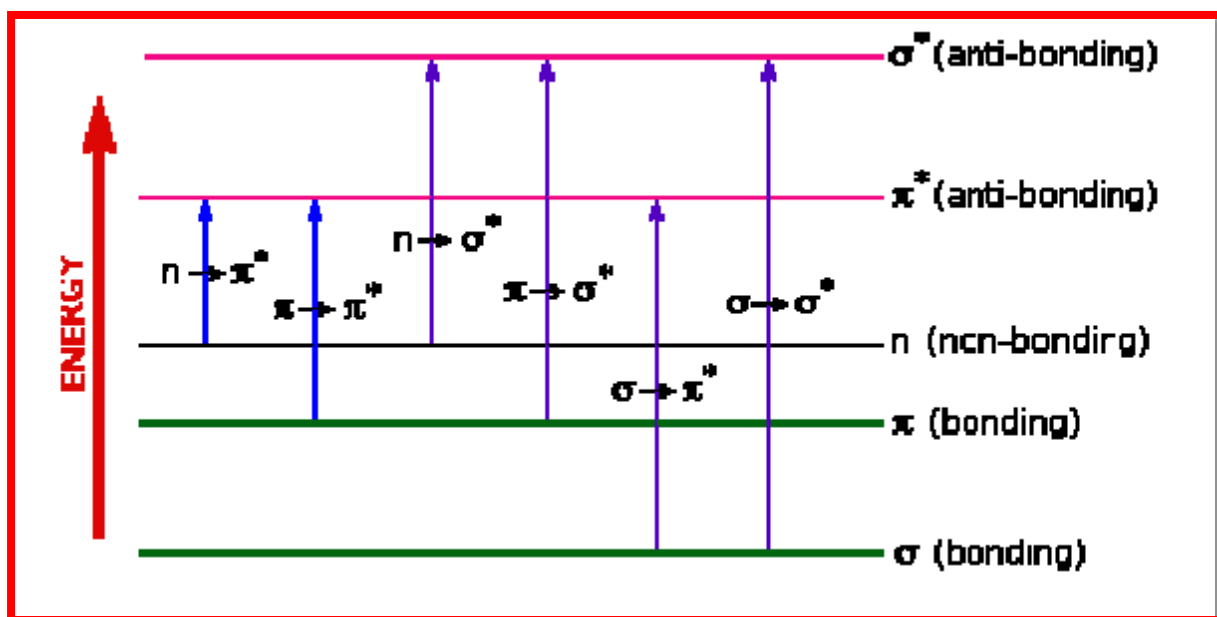

Fig 2.7 Energy Level Diagram

The energies noted in the energy level diagram are sufficient to excite a molecular electron to a high energy orbital. The absorption spectroscopy in this region is sometimes termed as the electronic spectroscopy. As the norm, energetically favoured promotion of the electron will most likely to be from the highest molecular orbital. When molecules posesses an energy which is equivalent to the electron transition are exposed to light, a certain amount of energy is absorbed when electron promotion occurs. The wavelength at which absorption occurs is measured by the optical spectrometer, also with the amount of absorption on each exact wavelength. The corrected value of absorption is termed as the "molar absorptivity ", it is important in when comparing spectras of various molecules.
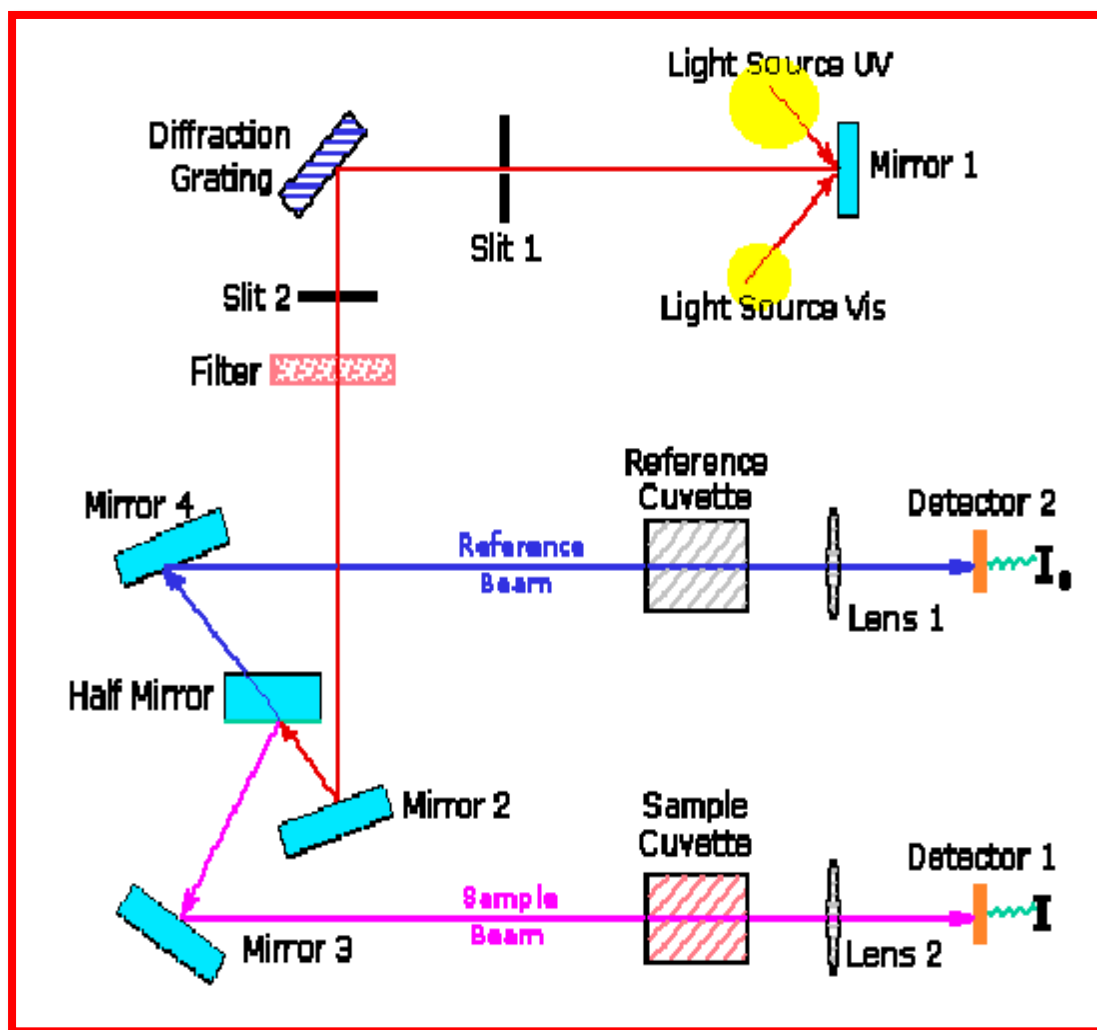
Fig 2.8 Block Diagram of Ultraviolet-Visible Spectrometer.

2.7.2 Fourier transform infrared (FT-IR) spectroscopy

An FTIR spectrum of the synthesised polyaniline has been taken by the spectrometer using the KBr pallets technique. The molecule absorbs radiation when the vibration of natural frequency of some part of molecule is equal to the frequency of the incident radiation. When the accurate wavelength of radiation is absorbed, the molecule then vibrates at increased amplitude. Fourier transform infrared (FT-IR) spectroscopy provides useful and correct information concerning the chemical structures of the molecules, without much tire-some evaluation method. FT-IR provides a very fast way of identifying chemical structures especially the organic ones. FT-IR spectroscopy employs an interferometer in place of monochromatic, this device is responsible for producing the spectra. This has an advantage of providing much higher radiation source throughout.

2.8 Lap shear test

The lap shear test is a standard test which is used to determine the ability of adhesive material to remain bonded to two substrates without breaking under shear forces. This particular test is also used to determine the environmental durability. Two substrates with similar dimensions were used to determine the shear strength of the adhesive.
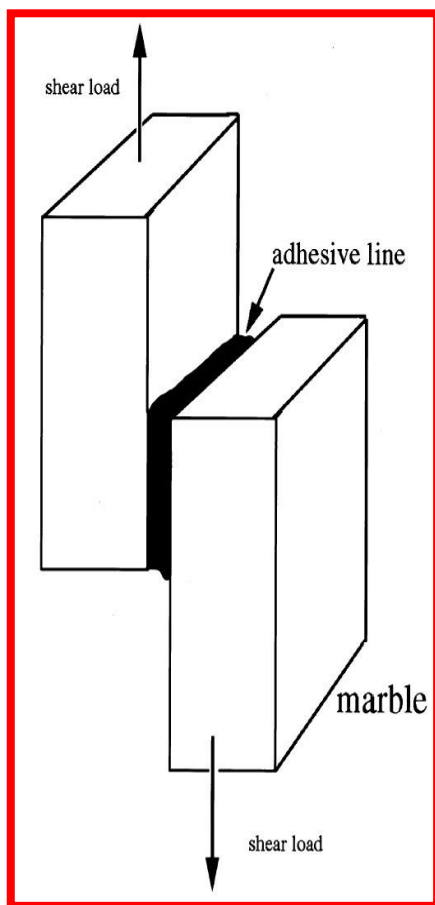
Fig 2.9 Lap Shear Test illustration

The prepared adhesives with different polyaniline filler loading were applied on the marked surfaces of the substrates and were left for 24hrs to adhere. After the stipulated time frame the substrates were then placed on a Universal tensile machine so as to determine the shear strength of the adhesives by pulling them at a uniform rate.
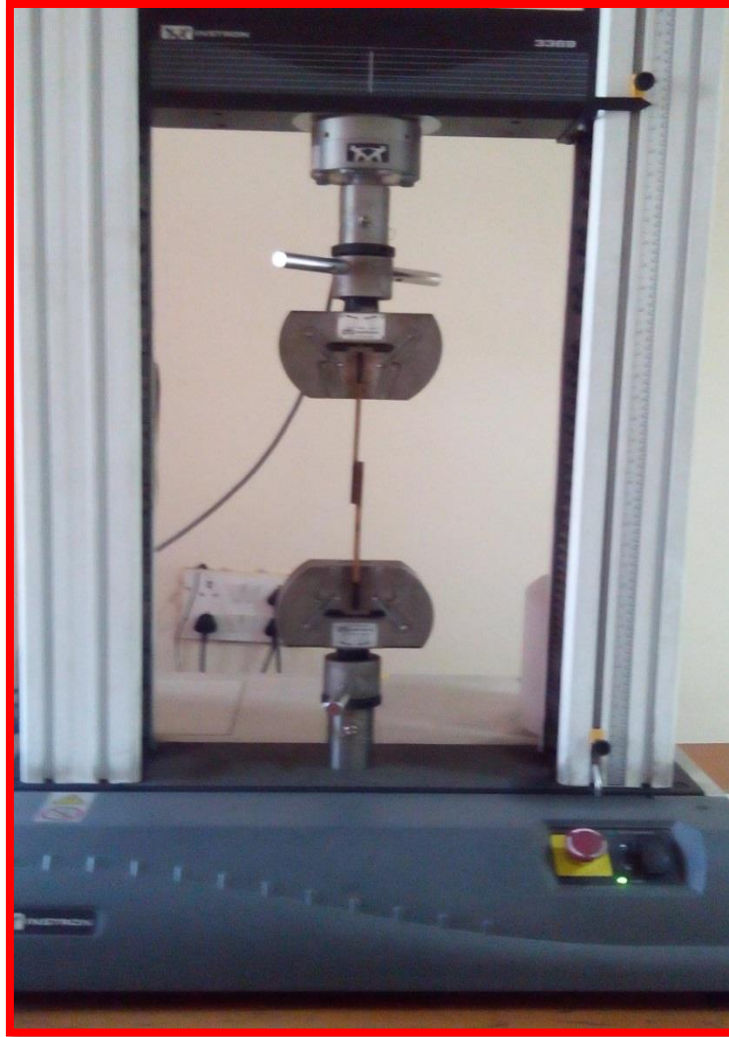
Fig 2.10 Pictorial view of UTM

2.9 Measurement of electrical conductivity

Conductivity of the composite thin films was measured by four probe technique. The four probe point is a simple apparatus for measuring resistivity of semiconductor samples. Convectional four point probes are millimetre sized devices comprising of electrodes made up of tungsten carbide material which is a hard material. The four probe metallic tips are automatic which move up and down when taking measurements. The measurements are performed by four different electrical connections to a thin film, and allowing an electrical current to pass through two connections whilst checking the corresponding voltage at the two other connections. The four electrodes are aligned in a row and a current is passed via the outer electrodes, whilst voltage drops across the inner electrodes V is measured using an

electrometer. Due to the high impedance of the electrometer, the current passing through the sample. As a result, the measured four point resistance is noted down.

Fig 2.11 Pictorial view of four probe apparatus

The four point method is usually used for resistivity measurements on semi-conductors, where the contact resistance can be considerable. Using the voltage and current readings from the probe, resistivity can be calculated, from the resistivity values, the conductivity is calculated for the area parameters.

CHAPTER 3
RESULTS AND DISCUSSION

3.1 Structural and optical characteristics

3.1.2 Morphology of Polyaniline

The polyaniline samples have been prepared by interfacial polymerization. In this polymerization process, by-products (oligomers and inorganic salts) of the reaction were separated by an organo/aqueous system which is immiscible. Fig 3.1 given below shows the polyaniline micrographs. It clearly shows that the particles are slightly uniform and with an even surface.
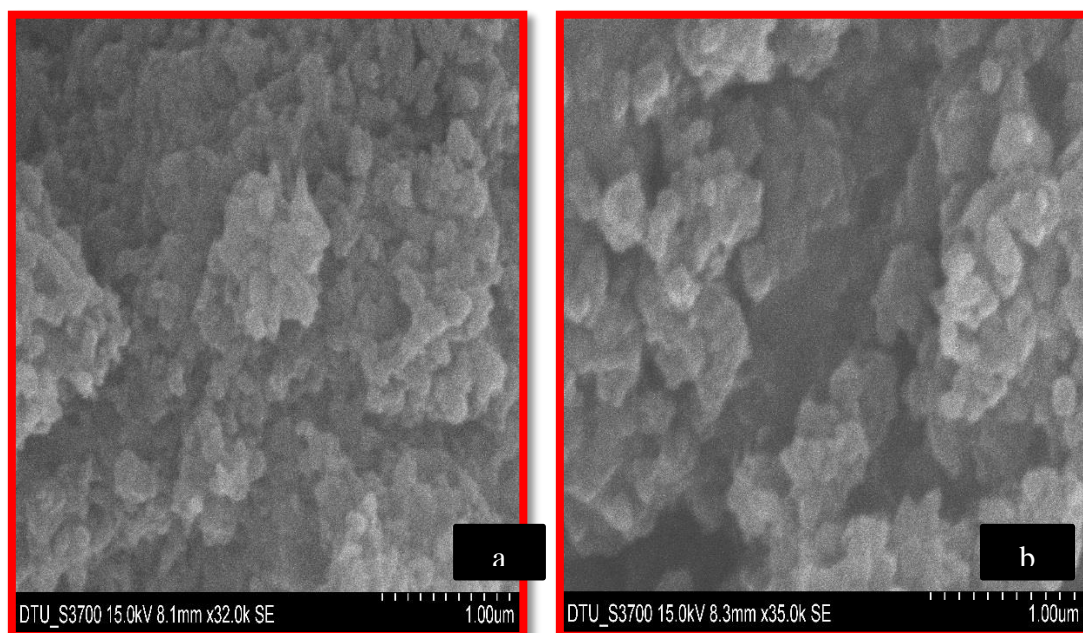

Fig 3.1 Micrographs (a) polyaniline nanofibers (b) agglomerated polyaniline

During the interfacial polymerization, the green PANI appears at the interface, moving into the water phase and finally diffusing into the whole water layer. As the reaction continues, the colour becomes darker of the organic phase and eventually stops changing, showing that the reaction has completed. Generally, three stages are proposed for polyaniline production: (1) nucleation; (2) initial growth; (3) secondary growth. The conventional method only results in agglomerated polyaniline as shown in fig 3.1 (b). Nanofibers are produced during the nucleation stage. Further growth of the nanofibers will enhance the polymerization

process resulting in secondary growth. Agglomerated polyaniline particles are as a result of secondary growth.

Fig 3.2 below shows the surface of the conductive adhesive containing 1% PANI concentration at a magnification of 5 micro meters and of silver-epoxy composite.
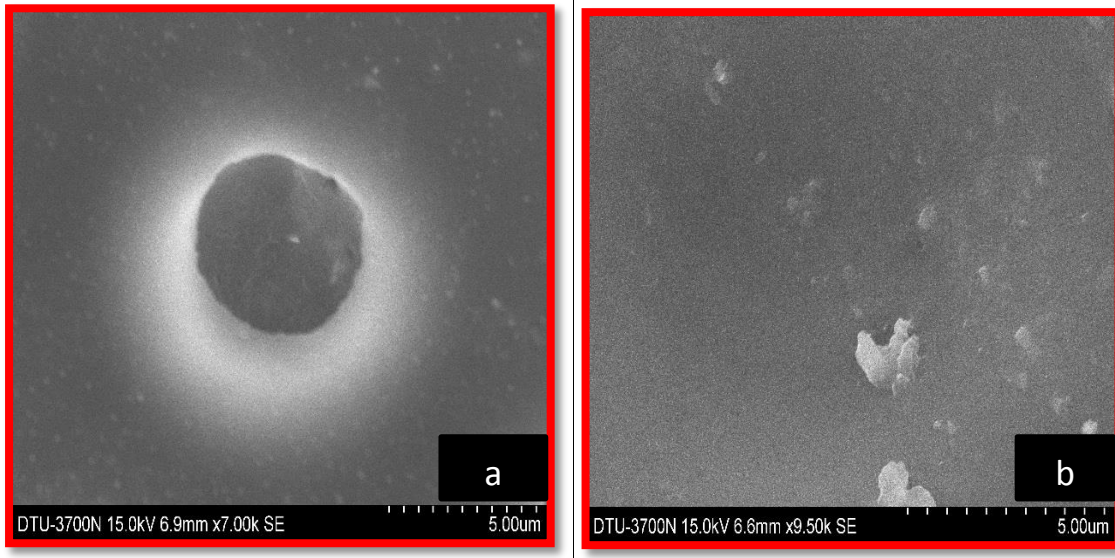

Fig 3.2 (a) Silver-polyaniline-epoxy (b) silver-epoxy composite micrographs

This micrograph shows that at a low concentration, the PANI particles are not fully dispersed, henceforth the concentration has to be increased so as to increase the dispersion of PANI throughout the matrix. This is significant in the improvement of conductivity of the adhesive.

3.1.3 Morphology of silver nano-particles

Scanning electron microscope shows the formation of silver nano-particles. The nano-particles were formed by using the chemical reduction method. Silver sulphate was reduced by sodium tricitrate to produce the silver nano-particles below.
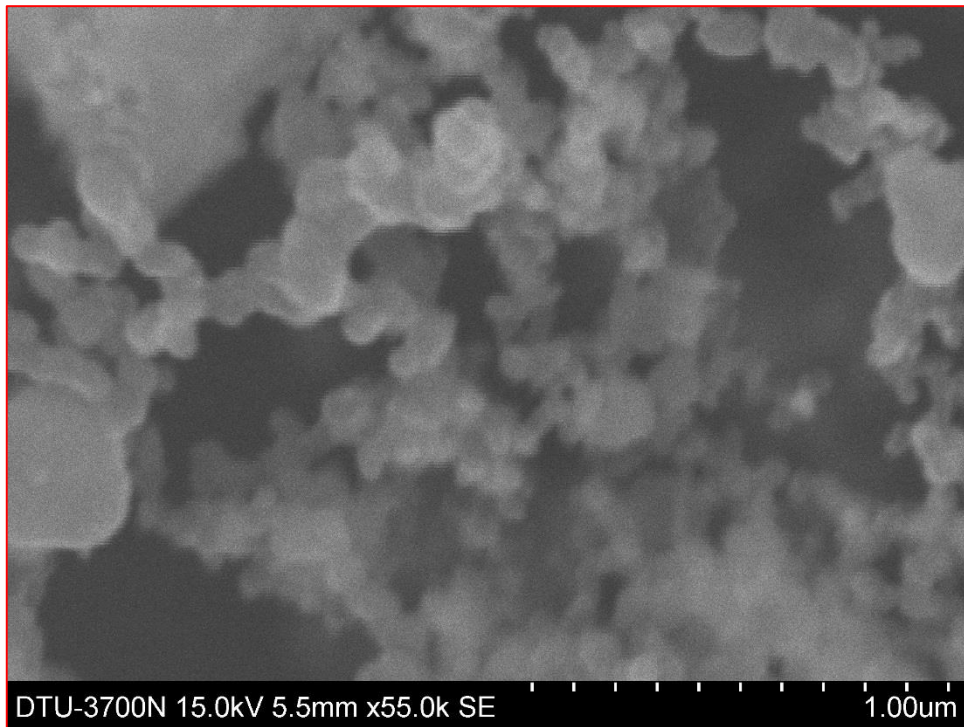
Fig 3.3 Micrograph of silver nano-particles

3.2 UV spectroscopy studies

3.2.1 Polyaniline UV spectra

UV-Visible spectroscopy shows a change in optical spectra accompanying doping which are significant. These spectral changes play an important role and clearly showing the doping spectrum of polymer in the emeraldine base state in DMSO solvent as shown below in Fig 3.4. The spectra show two electronic transitions at 325 and 635 nm.
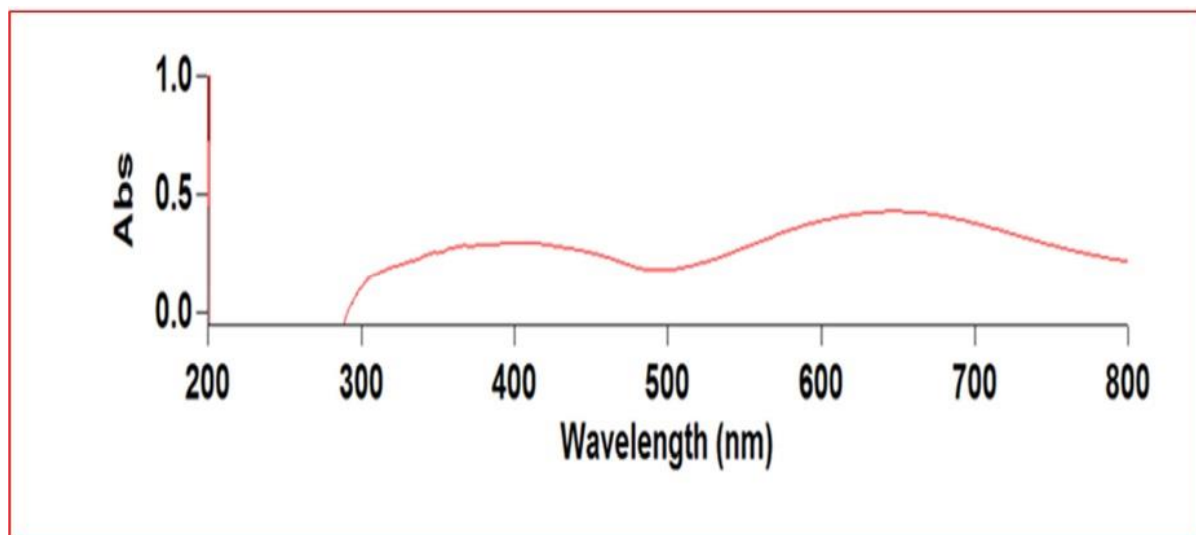
Fig 3.4 Polyaniline UV-visible spectra

The UV visible spectrum of emeradine in base form suggests that the benzenoid amine groups might have caused the 325 nm absorption. The absorption peak at 635nm has been thought to be arising from the excitation occurring from quinoid ring and the two surrounding imine group. Absorption peak at 325 nm has been attributed to both π to π^* transition of the benzenoid ring and orbitals which would be lying low.

3.3.2 Silver nano-particles

UV-visible spectroscopy is the most widely used method for silver nano-particles structural characterization. The UV-visible spectra exhibits a 420nm surface plasmon absorption band showing that spherical silver nano-particles are present. As shown in Fig 3.5, there were no notable obvious changes in peak position for three weeks, only for the increase in absorbance.
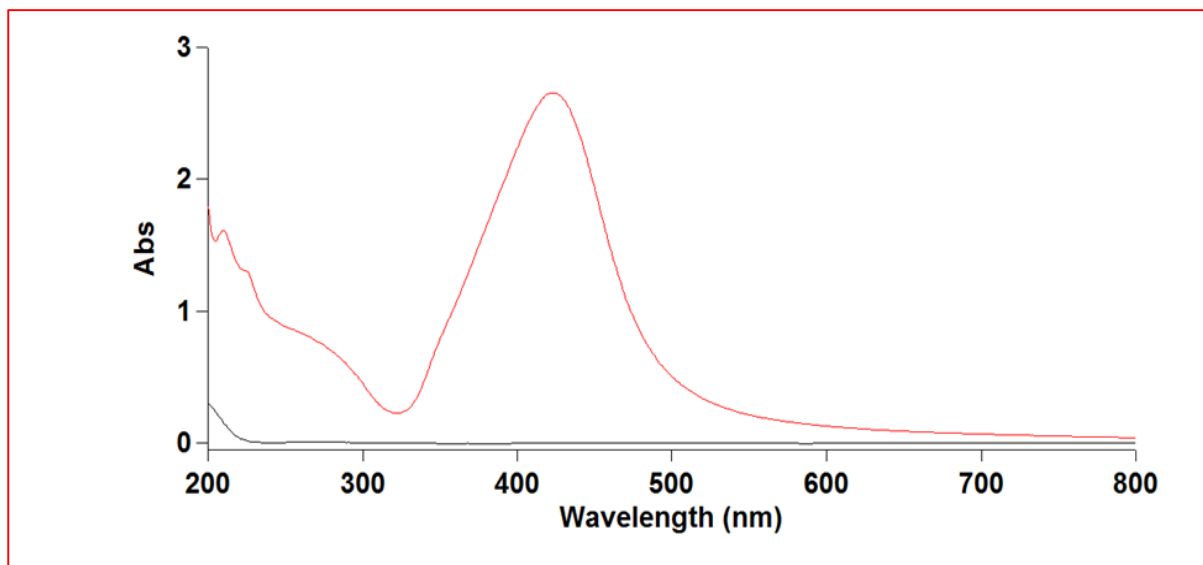
Fig 3.5 UV-Visible spectra for silver nano-particles

Electrostatic repulsion between the nanoparticles takes place as each silver particle is surrounded by molecules of citrate and becomes negatively charged. The absorption peak of the silver particles shifted from 421 to 425 nm after 1 month because of the aggregation of the nanoparticles with time and macro particles require lesser energy and hence longer wavelength.

3.4 FTIR studies

3.4.1 FTIR studies of polyaniline doped with HCl

The presence of the two bands in the vicinity of 1500 and 1600 cm^{-1} are assigned to the non-symmetrical C6 ring stretching modes.
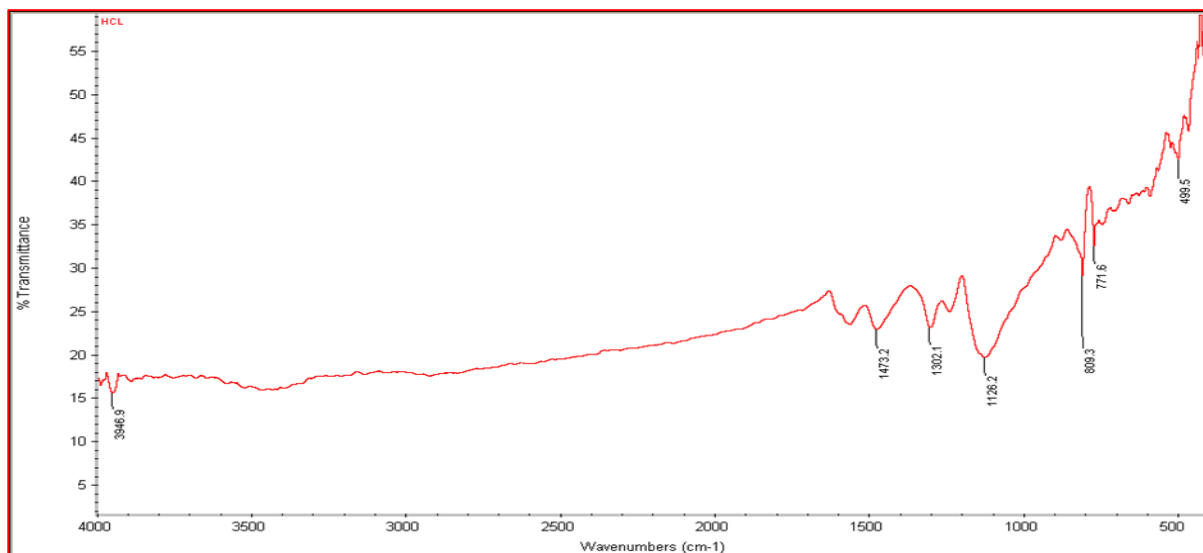
Fig 3.6 FTIR spectra of polyaniline

The frequency vibration which occurs at 1600 cm^{-1} is as a result from the quinoid rings while the 1500 cm^{-1} shows the presence of benzenoid ring units. The amine and imine units presence are shown by the two bands.

3.5 Lap shear test results of polyaniline-epoxy conducting adhesive

One of the main functions of ECAs is to mechanically attach specific components onto a substrate during the construction phase specific electronic device. The adhesion strength should be able to withstand thermal shocks, impact, thermal cyclings and vibration tests as specified for various applications. To achieve maximum adhesion, the adhesive must completely wet the surface and minimize voids at the interface. The effect of the fillers was fully investigated as shown from the diagrams below.
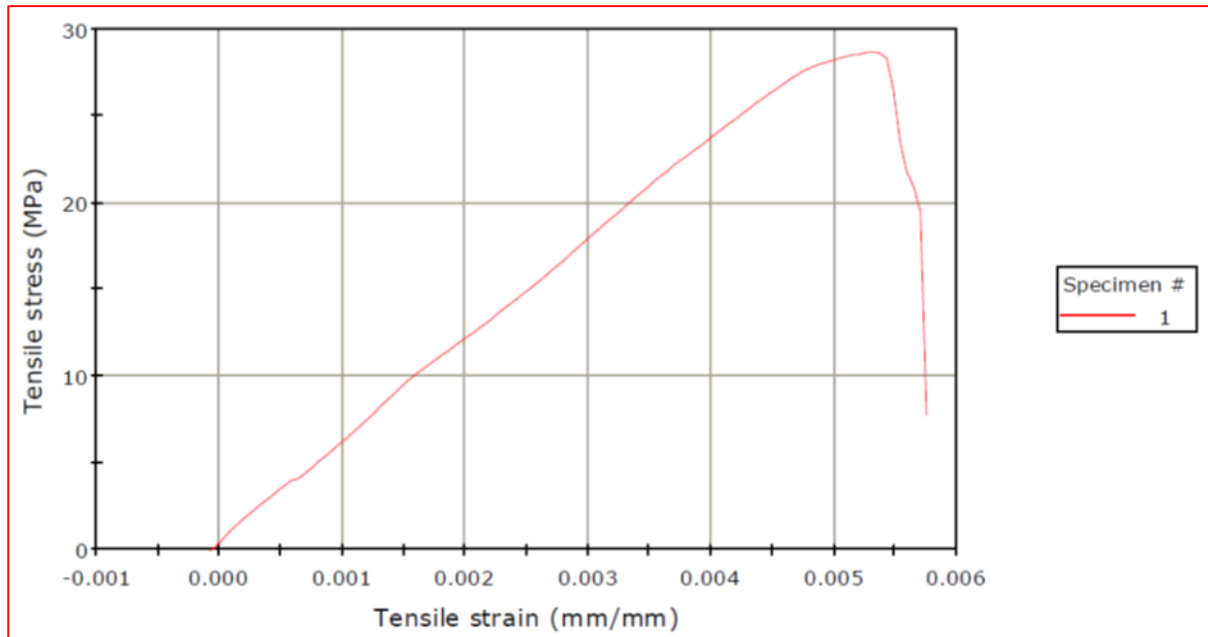
Fig 3.7 Shear strength of silver-polyaniline-epoxy composite at 1%

The UTM result of the composite at 1% showed shear strength of 28MPa. The high strength is attributed to the fact that low filler loading does not affect much the adhesive properties of the epoxy matrix.
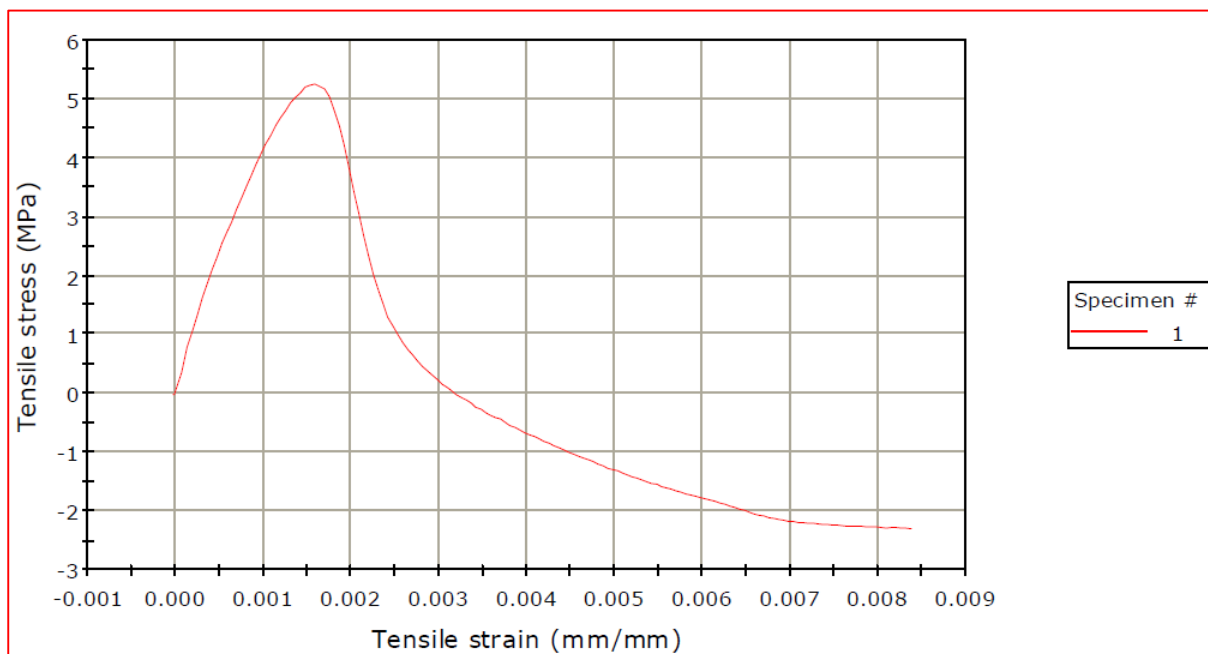

Fig 3.8 Shear strength of silver-polyaniline-epoxy at 3%

Gradual increase in the filler loading also results in gradual decrease of the adhesive strength of the matrix.
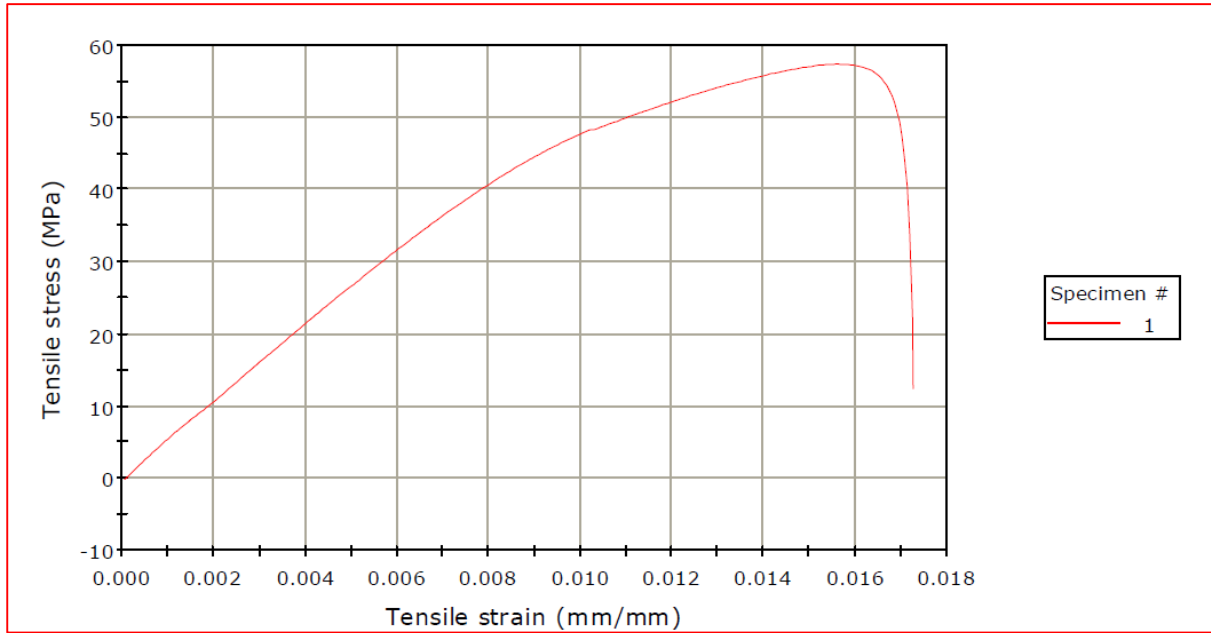
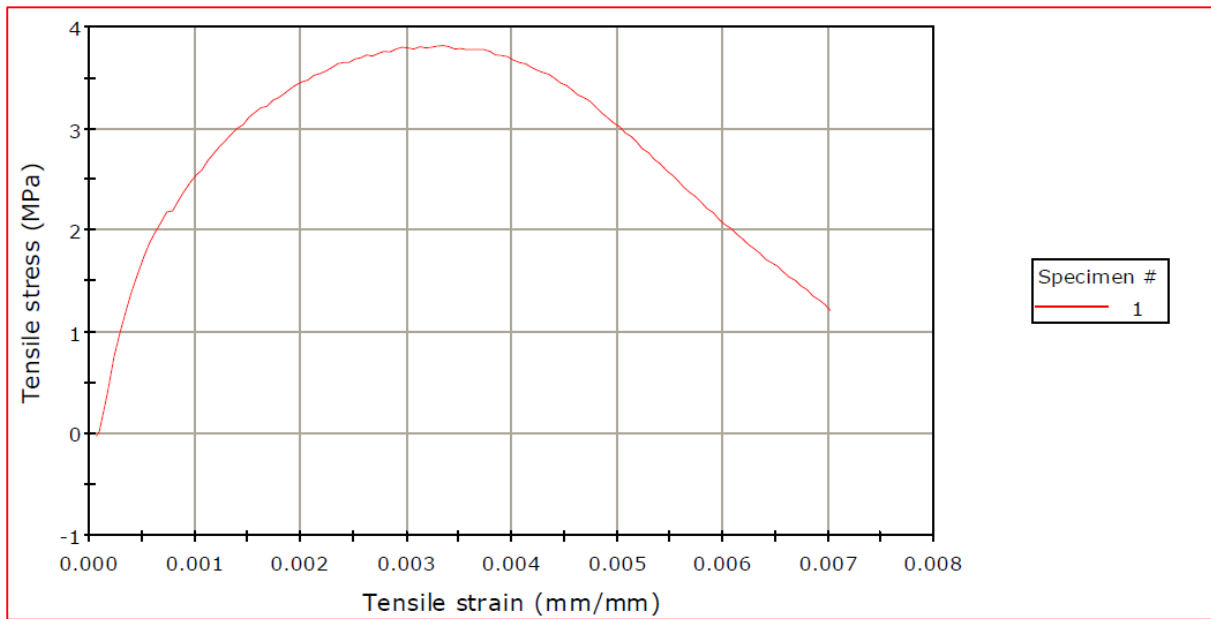*Fig 3.9 Shear strength of silver-polyaniline-epoxy at 5%*

Fig 3.10 Shear strength of silver-polyaniline-epoxy at 7%

The strength of the matrix further decreases as the filler loading is increased to 7%.
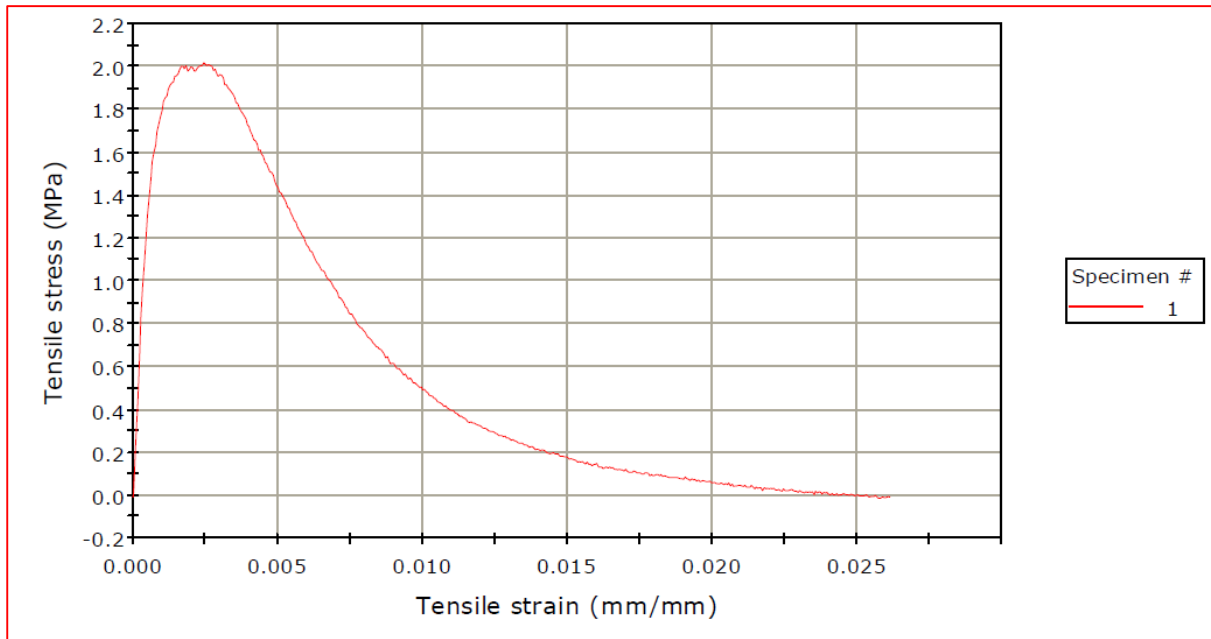
Fig 3.11 Shear strength results of silver-polyaniline-epoxy at 10%

At a filler loading of 10% there is significant decrease of the adhesive strength, this is due to the high amount of filler which affects the adhesive properties of the epoxy matrix and also the filler increases the viscosity of the adhesive hence the adhesion becomes poor.
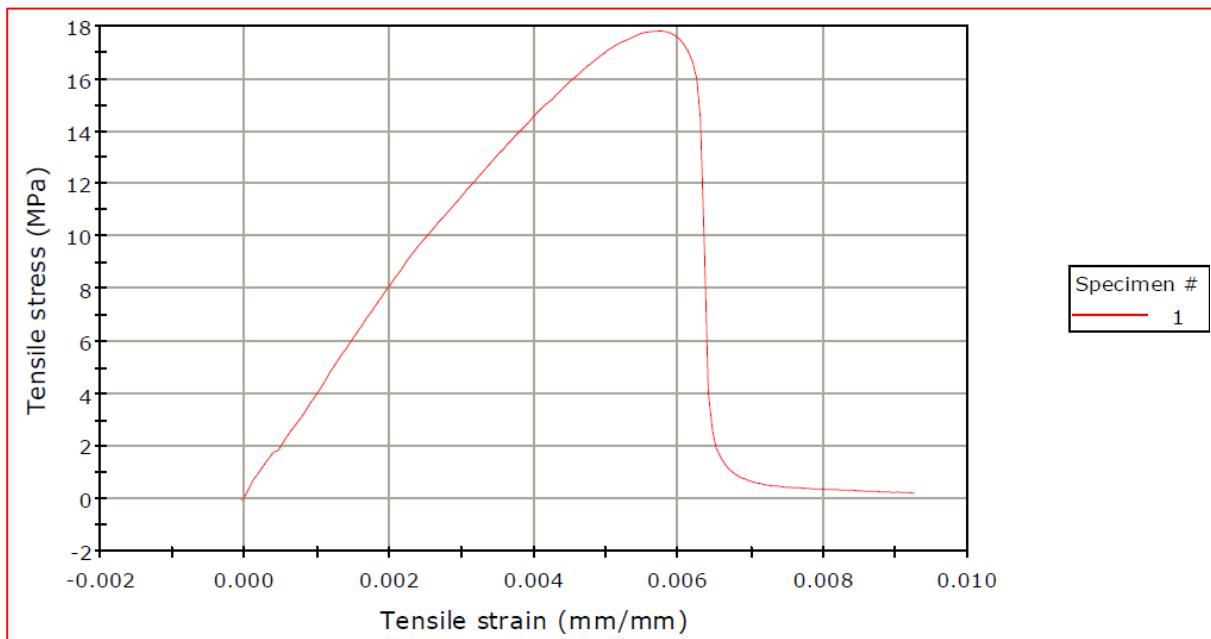

Fig 3.12 Shear strength results of silver-epoxy composite

Six samples of ICAs were studied, as shown from the previous figures, the lap shear forces decreases with increase in the polyaniline filler loading, this is because the filler particles disturb the reactive surfaces of the epoxies which are responsible for adhesion.

Fig3.13 Relationship between the strength of the adhesive and filler loading

The higher concentrations of polymer filler disallow the effective formation of matrix network. Although, an epoxy matrix is not affected by moisture, filler particles may absorb water and detach causing voids and cracks under impact. From the graph above it can be clearly shown low filler loading results in high shear strength hence a balance between conductivity and adhesion must be created.
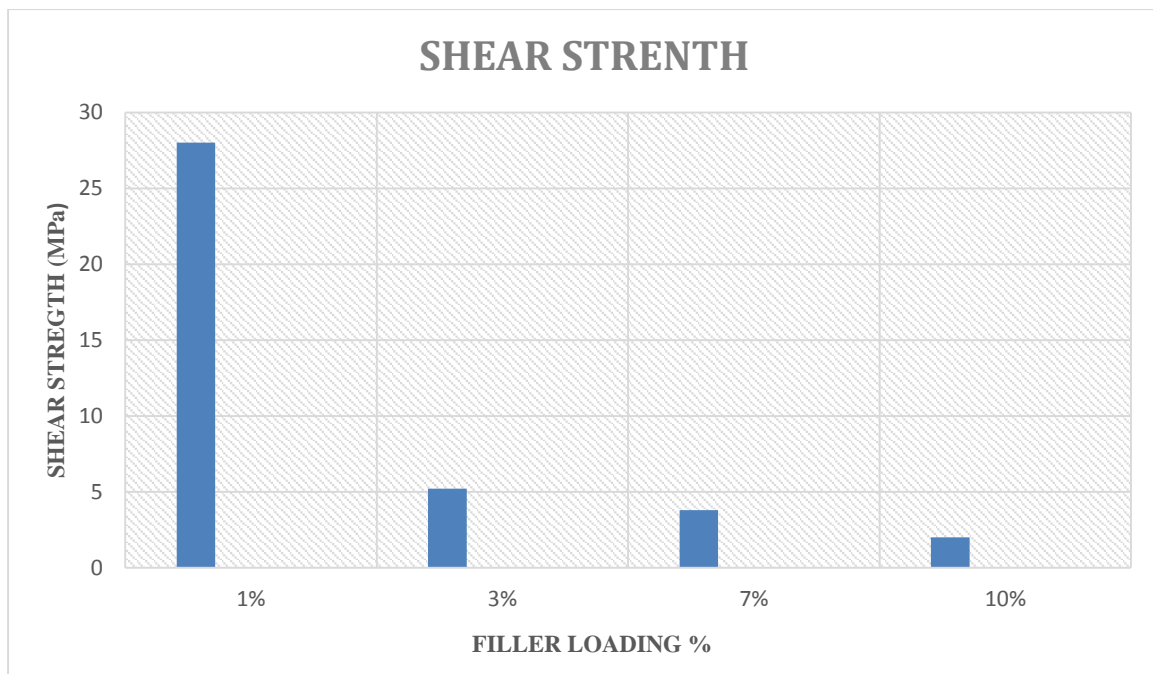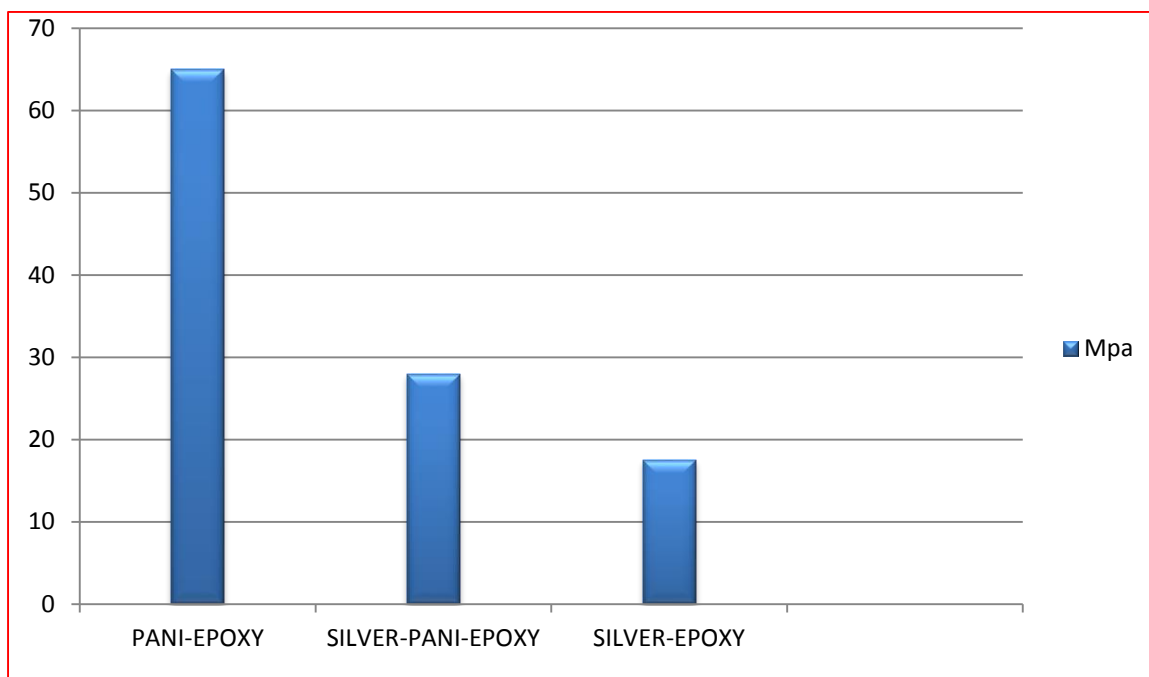

SHEAR STRENTH

Fig3.14 Shear strength of three different ECAs

From the graph above it can be clearly seen that between the three different conductive adhesives, PANI-EPOXY showed a favourable strength 65 MPa, followed by silver-polyaniline-epoxy which showed shear strength 28 MPa, which further decreasing in case of silver-epoxy as 17.5 MPa. The low value of silver-epoxy-polyaniline composite can be attributed to the fact that the two fillers reduced the adhesion strength of the epoxy matrix due to interaction with the chemical bonds of the matrix.

3.6 Electrical conductivity

Electrical conductivity variations in the type of filler was carefully analysed using the four probe technique.

Table 3.1 Current and voltage data of silver-polyaniline-epoxy Composite (1%)

Current	Voltage	Voltage/Current
0.10	0.118	1.180
0.250	0.294	1.176
0.50	0.590	1.180
1	1.2	1.200
		Mean=1.184

Resistivity = 1.184

Thickness = 0.1 cm

Correction factor =2.76

Resistivity =1.184/2.76

=0.5388

Conductivity = 1/0.5388

=1.855 $\times 10^{-6}$ S/cm

Table 3.2 Current and voltage data of silver-polyaniline-epoxy composite (5%)

Current	Voltage	Voltage/current
0.100	0.05	0.5
0.200	0.12	0.6
0.300	0.17	0.5667
0.400	0.27	0.675
		0.585

Resistivity $=0.585/2.76$

$= 3.759 \times 10^{-6}$

Conductivity $=1/3.759 \times 10^{-6}$

$\underline{=3.759\times10^{-6} \text{ S/cm}}$

Table 3.3 Current and voltage data of silver-polyaniline-epoxy composite (10%)

Current	Voltage	Voltage/Current
0.500	0.13	0.26
		0.26

Resistivity $= 0.26 /2.76$

$=0.0942\times10^{-6}$

Conductivity $=1/0.0942\times10^{-6}$

$\underline{=10.62\times10^{-6} \text{ S/cm}}$

Table 3.4 Current and voltage data of silver-epoxy composite

Current	Voltage	Voltage /Current
0.010	0.05	5
0.020	0.09	4.5
		Mean =4.75

Resistivity $= 4.75$

$= 4.75/2.76$

$=1.72 \times10^{-6}$

Conductivity $=\underline{0.58 \times10^{-6}\text{S/cm}}$

Polyaniline-epoxy composites did not show any conductivity values when using the four probe technique; this can be due to low concentration, the polyaniline was not able to initiate any meaningful conductivity.
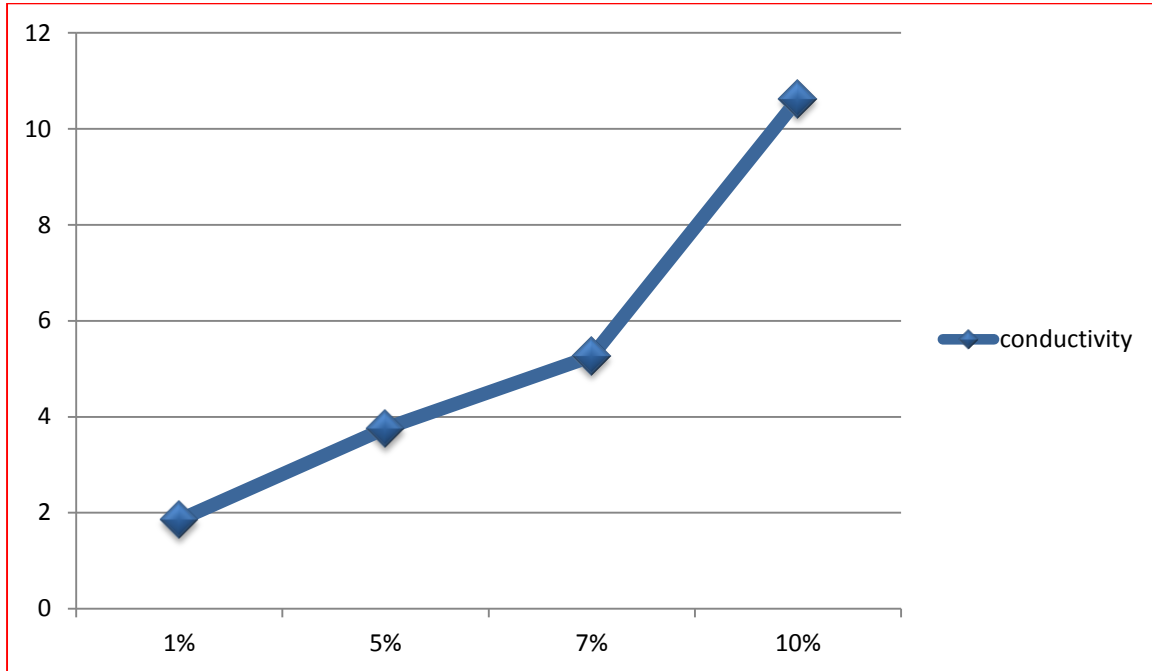

Figure 3.15 Conductivity of the ECAs at different concentrations

It can be seen from Figure 3.16 that an increase in concentration of polyaniline in the composite increases the conductivity of the composite; this is due to the fact that the polyaniline particles forms interconnects which allow movement of electric charge in the composite.
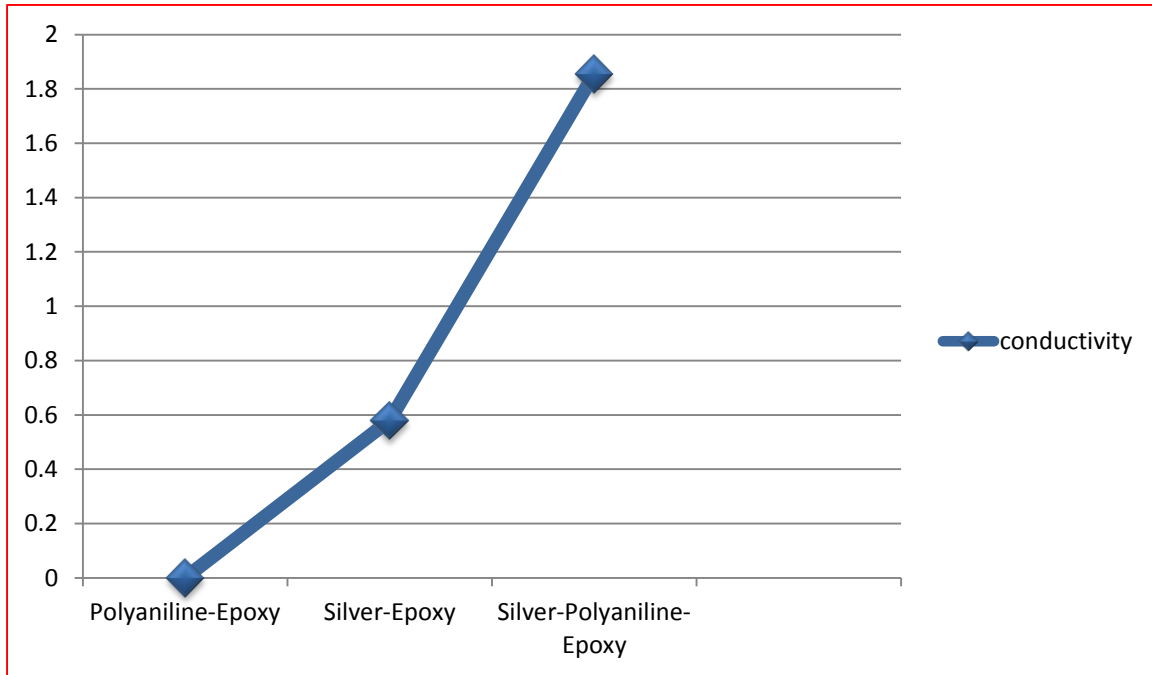
Fig 3.16 Conductivity of three different ECAs

Figure 3.17 shows that the silver-polyaniline epoxy composite showed the highest conductivity among the all three composites due to the fact that silver nano-particles have high conductivity as compared to polyaniline and also the polyaniline particles aided in the bridging effect to make interconnects so as to allow the efficient movement of electrons throughout the system. Silver-epoxy composite showed the conductivity value of 1.855×10^{-6} S/cm, the low conductivity values may be due to the fact that silver particles may have suffered some migration effect hence resulting in a lesser conductivity as compared to silver-polyaniline-epoxy composite. Polyaniline-epoxy didn't show much conductivity, due to the lack of silver nano-particles which have high conductivity and also at such lower concentration polyaniline is unable to give interconnects and therefore unable to conduct electrical charge.

CHAPTER 4

CONCLUSION AND FUTURE RESEARCH

The research has fully explored the use of silver nano-particles as the main filler and conducting polyaniline polymer as the co-filler for the preparation of conductive adhesive composite. The electrical conductivity of polyaniline is less than that of silver metal, but we found that the less volume of the total filler is needed to initiate the conduction of the composite because at 1% polyaniline concentration 1.855×10^{-6} S/cm was recorded. The bridging effect of the polyaniline helped to facilitate conductivity in the composite and also stabilise the electrical contact resistance of the electrically conductive adhesive.

We aimed the propensity of polyaniline as alternative filler for ECAs. We demonstrated the chemical synthesis of polyaniline using HCl as a suitable and effective dopant. Increase in the doping level of polyaniline increases the electrical conductivity as dopant molecules induce the protonation effect which subsequently results in delocalization of π-electrons

This project report resulted in several interesting and exciting aspects which need to be further investigated for a better understanding and to enrich further the current knowledge base and also futuristic applications.

Electrical contact between the fillers and matrix is important so as to establish a profound conduction mechanism, though indirect techniques can help to provide data about the physical contact between fillers, direct measurement between the fillers of the contact area and its relation with contact resistance. The SEM characterization was found to be supplementary to study the microstructure of the ECAs. Quantitative information concerning such as the size of the filler, contact dimensions and dispensation are of paramount importance to understand the effectiveness of the parameters.

Another problem which cannot be ignored is the non-uniform dispersion of fillers, which limits the fine pitch capability of the ECAs. Aggregation of the filler can increase the viscosity and affect the rheology which is also important for processability.

Electrically conducting polyaniline can be considered as a perfect co-filler in ECAs. Since the conductivity of polyaniline does not approach that of silver, that's when the silver nano-

particles come into play. Optimization of polyaniline polymerization can be done to attain high conductivity. Silver-polyaniline combination into the epoxy boosts the necessary conductivity for specific applications which needs high conductivity.