Synthesis and Studies of Polyurethane based Conducting Adhesives with Zinc and Nickel nano-Particles as fillers

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Certificate

This is to certify that **Mr. OM PRAKASH PARIDA**, M. Tech student in the Department of Applied Chemistry And Polymer Technology has submitted this project report on "Synthesis and Studies of "**Synthesis and Studies of Polyurethane based Conducting Adhesives with Zinc and Nickel nano-Particles as fillers**" in partial fulfillment of the requirement for award of degree of Master of Technology in Polymer Technology, Delhi Technological University (formerly Delhi College of Engineering), Delhi, during the academic year 2015-16. It is a record of the student's research work carried out under my supervision and guidance. It is an authentic record of the work carried out by the student himself and has not been submitted for the award of any other degree to the best of our knowledge.

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Abstract

The present work has been carried out with an objective to synthesize a PU based electrically conductive adhesive (ECA) using metallic fillers such as Zinc and Nickel. For the better dispersion of fillers in polymeric matrix, the filler used in the present studies were of nano-range. The solder that has dominated the present day electronic industry has many inherent demerits and drawbacks. It is associated with health hazards and bad environmental impacts due to presence of lead in it. To overcome these health hazards, the researchers have been exploring the field of ECAs to find a suitable replacement. The future of present day electronics industry depends upon the research and development work done in the field of conducting adhesive. Commonly used ECA is epoxy and filler based conducing adhesive. But the strength of epoxy substrate is less. Hence, we have tried to enhance the conductivity of polyurethane based adhesive. We have used metallic filler to enhance the conductivity of the PU based adhesives to develop ECA. Along with conductivity it is desirable to have good mechanical strength of the sample should be good. Thus, conductivity along with good mechanical strength of ECA that can have potential for the replacement of solder technology in future. In the present studies, we have used with zinc and nickel nano-particle as fillers with the polyurethane adhesive. The comparison of conductivity and mechanical strength of the adhesives using different fillers was done. It was observed that the conductivity of PU was enhanced with addition of metallic filler.

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Chapter-1

Introduction

1.1-INTRODUCTION

The electronic interconnections, dominated by lead/tin solders, have to undergo sea change before being replaced completely by 'Electrically Conductive Adhesive'-ECA. The present day electronic industry is dominated by lead/tin solders. However, as the environmental awareness of the increased toxicity of the lead has received global attention there is need to replace the Sn/Pb based by a non-toxic adhesive[5]. The negative effects of lead/tin solder are on brain, kidney and nervous system of the human body. Along with that it affects the biosphere due to the major frequent use and unregulated dumping of the electronic appliances and printed circuit boards where lead is used[6]. Hence, time has come to think for the alternative of lead/tin solder.

Electrically conductive adhesives (ECA) have been identified as a potential alternative to Sn/Pb solders in electronic interconnection applications[6]. All electrically conductive adhesives conduct electric current and they also provide a strong, durable bond between different substrates including metals. High performance conductive adhesives were designed by combining the thermosetting resin and the efficient electrically conductive fillers. One of the most effective techniques used to improve the electrical conductivity of polymers is the incorporation of conductive fillers in the polymer matrix[9].

Over the past decades, the use of electrically conductive adhesive (ECA's) has expanded rapidly in the microelectronics industry. The major applications for ECA's are die attachment, liquid crystal display (LCD), and surface-mounted assembly of packaged components on printed wiring board (PWB's). ECA's can be used as solder replacement, interconnection, sealing, electrical shielding, various electronic components bonding, fastening and brazing[5,6].

Unlike other types of adhesives, electrically conductive adhesives perform two primary functions. First, conductive adhesives form joints with sufficient strength so that they can bond two surfaces. Secondly, they form an electrical interconnection is formed between the two bonded surfaces[7]. This dual functionality is usually achieved in composite form by dispersion of particles in an insulating adhesive matrix. The commonly used conductive fillers include carbon black, graphite flakes, and micron or nano-sized metal particles such as silver, nickel, copper or aluminium[19]. Typical polymer matrices are epoxy, silicone, polyamide or polyurethane. The primary properties of these adhesives are high and stable electrical conductivity. Typically, these adhesives have an electrical resistivity of 10^4 (Ohm-

cm), which is about two orders of magnitude higher than the best metallic conductors[25]. The metal fillers, which are added to the epoxy resin usually improve its other properties such as strength, thermal conductivity *etc.*, and therefore, can also be used to impart specific composite properties such as thermal expansion, thermal conductivity, shrinkage and heat resistance.

Compared to traditional tin/lead (Sn/Pb) soldering technology, conductive adhesive joining technology offers many advantages, such as:

(i) Lower sensitivity to thermo-mechanical stresses, due to higher flexibility than solder.
(ii) Lower cure temperature enabling the use of heat sensitive or non-solder able materials.
(iii) High resolution capability for fine-pitch interconnections due to smaller particle size than solder pastes.
(iv) Simple processing and thereby lower cost.
(v) Environmental compatibility.

The conductive adhesive joining technology still has some problems[7,8]. The major ones being conductivity lower than solder, sensitivity to type and quality of component and board metallization, longer curing times, and the question of durability in various climatic environments. The processing parameters, such as temperature, pressure, cure time, pot and shelf life are critical to the success of making reliable electrical and mechanical interconnections. A conductive adhesive joint may fail in many different ways. These include thermal stresses caused by the coefficient of thermal expansion mismatch between the substrate and component, and by mismatch between the adhesive and adherend during temperature cycling, oxidation of the bonding surfaces and of the filler, and degradation by UV-light or corrosive gases. A better understanding of the design, reliability, material, and manufacturing characteristics of various conductive adhesive is to be improved to make the conducting adhesive as replacement for future lead/tin based solder technology.

MAIN ISSUES OF ECA APPLICATIONS

Although electrically conductive adhesives have potential usage[10] and various advantages over solder for SMT and microelectronics applications, issues and problems still remain to be solved in order to successfully implement ECAs for solder replacement in electronics

assemblies. SMT requires short process times, high yield, high component availability, reliable joints for different components, visual inspection of joints, and capability of repair. ECAs will not be a drop-in replacement for solder in the existing surface mount production lines. First, it will not be cost effective to do so. Special component lead plating and board conduction pad metallizations need to be optimized for conductive adhesives. Standard materials, components and assembly equipment for specific applications need to be developed combining the material vendors', research organizations', and application companies' efforts together. Mechanical bonding strength and electrical conductivity cannot be compromised for the new material development. Fine pitch and thinner lead trends have improved both the pick and placement machine accuracy and the stencil printing process (the laser etched or electroplated stencils and precise stencil printing machine). ECAs have more rigid process requirements for positioning due to their non selective wetting and lack of self-alignment. Currently major concerns for using ECAs for SMT are the limited availability of components and substrates designed for adhesives, and the lack of methods to predict life-time reliabilities and their relationship to the accelerated life time tests performed as solder joints. Different electrical and mechanical failure mechanisms require one to monitor these properties separately during life-time tests. There are difficulties to inspect the adhesive joints and judge the quality of the joints from visual and x-ray inspection methods, which work for solder joints perfectly. Repairability and reworkability of adhesive joints need to be investigated and improved. Adhesion strength between the component leads, adhesives, and board terminal metallizations is one of the most critical properties for high volume SMT applications.

Electrical conductance of the adhesive joints degrades under humidity exposure. Interfacial and contact resistance increases especially on non-noble lead and board pad finishes under accelerated life time tests. Assembly and cure processes of ECAs are also critical for a reliable adhesive joint.

How to enhance the reliability of ECA adhesive

Another critical reliability issue of conductive adhesive is the lower adhesion strength[10,11]. High adhesion strength is a critical parameter in fine pitch interconnection that is fragile to shocks encountered during assembly, handling and lifetime. There are two types of adhesion mechanisms, physical bonding and chemical bonding, which contribute to the overall adhesion strength of polymer on a surface. Chemical bonding involves the formation of covalent or ionic bonds to link between the polymer and the substrate. In other words, a

chemical reaction must take place for the formation of chemical bonds. Physical bonding involves mechanical interlocking or physical adsorption between the polymer and surface of substrate. In cases where the molecules of the polymer are highly compatible with the molecules of the substrate, they interact to form an inter-diffusion layer. In mechanical interlocking, polymer and substrate interact on a more macroscopic level, where the polymer flows into the crevices and the pores of substrate surface to establish adhesion. Therefore, a polymer is expected to have better adhesion on a rougher surface because there is more surface area and ‘‘anchors’’ to allow for interlocking between the polymer and the substrate. This section summarizes the efforts on the adhesion improvement of conductive adhesives.

Plasma cleaning and vacuum process

Plasma cleaning of surfaces has been considered as one of the effective approaches to enhance the adhesion strength of conductive adhesives[11]. During the plasma etching process, the plasma radicals react with the contaminants and those long chains organic molecules can be broken down into small gaseous ones (mostly gaseous water and carbon-oxide conjunctions). These particles can be evacuated from the system by the vacuum pump. After the surface is cleaned of oxide, a layer of atoms available in the chamber will deposit on the clean surface, protecting the metal from new oxidation. Furthermore, the plasma can also etch the surface to enhance the mechanical interlocking mechanism for adhesion improvement. With plasma treatment, the adhesion strength of conductive adhesives could be improved. However, the improvement also requires a high vacuum process due to the possible corrosion on the highly cleaned surface caused by the moisture in ECAs. After vacuum process, the surface was changed by removal of air and water and the contraction of adhesives.

Application of coupling agents in ECA

Another approach to improve adhesion is by using coupling agents[12]. Coupling agents are organo functional compounds based on silicon, titanium, or zirconium. For example, R–X–$(O–R0)_3$, where, X = Si, Ti or Zr, R = organic chain that interacts with the polymer, and R0 = organic chain that interacts with the substrate. A coupling agent consists of two parts and acts as intermediary to ‘‘couple’’ the inorganic substrate and polymer. There are a few theories about how coupling agents can enhance bonding. The first is the chemical bonding theory, where the R0 groups of the coupling agent can form hydrogen bonds to the surface, and then condense to form covalent bonds to the surface. Then, the R group of the coupling agent would react with the polymer during the curing reaction. Another theory is based on how

coupling agents affect the wetting capability of the surface and its surface energy. Good wetting is necessary for good adhesion, and for a liquid or a polymer to wet a surface, its surface tension must be lower than that of the substrate. Generally, inorganic surfaces have high surface tension, while organic liquids have surface tension less than 100 dyne/cm^2(i.e. 10 N/m^2). However, inorganic surfaces can be hydrophilic and a layer of water may accumulate on it, thus causing the surface tension of the surface to decrease. Polymers with some polar characteristics can displace water molecules on the surface, and good wetting can still take place. In the case of non-polar polymers, coupling agents may help to reduce surface tension of the polymer. Silane coupling agents have been commonly used to improve the adhesion performance. For example, chemically etched 304 stainless steel can react with g-aminopropyltrimethoxysilane. The methoxy groups of the silane coupling agent can first hydrolyze to hydroxyl groups which are quite reactive and can react with the metal surface metal hydroxyl groups, forming a metal oxygen silane chemical bond. The other organo-reactive group (amine end of the coupling agent) can react with polyamic acid, a precursor of the polyimide polymer, to form a better and strong metal–polymer interfacial bonding. As such, it produces mechanically stronger polyimide/stainless steel interfaces. Other approaches use the formation of a thick metal-oxide layer prior to application of the silane coupling-agent to improve adhesion to organic films. Silane coupling agents have also been shown to reduce the rate of hydration of aluminum surfaces and improve adhesion to organic films. In conductive adhesives, application of specific silane coupling agents with appropriate concentration can increase the adhesion strength on different metal surfaces. As an example of effect of coupling agents on adhesion strength of ECAs shows the adhesion data of polyarylene ether derivative (PAE-2E) with a coupling agent (CA-4), and the obvious increase in adhesion strength on NiAu and Sn surfaces was observed.

Although silane coupling agents are mostly used, some other coupling agents with various functional groups, such as thiol, carboxylate coupling agents, are also used. It has been reported that surface roughness affects the adhesion strength of conductive adhesives. Surface with larger roughness typically shows higher adhesion strength. Roughening of surfaces, for example by sand blasting, chemical etching, plasma treatment, or anodization to specific morphologies has been employed to enhance the adhesion strength and provide structural durability in humid or corrosion environments.

Optimization of elastic modulus

In order to enhance the adhesion, another approach is to lower the elastic modulus of adhesive resins. By using low elastic modulus resins, the thermal stress at the adhesion interface can be reduced and, thus, the improved the adhesion strength. The adhesion strength increases with lowering the elastic modulus. However, too low modulus value deteriorates the cohesive force and thus, decreases the adhesion strength. Therefore, the elastic modulus needs to be optimized to improve the adhesion properties[6].

In addition to the methods listed above, some other factors such as curing conditions and structures of IC packaging may also affect the adhesion strength of conductive adhesives.

Improvement of reliability in thermo-mechanical cycling test

The poor thermal cycling (TC) performance of the ECA joints has been another reliability issue for board level interconnects. It has been found rather difficult to control the TC failures of the ECA joints[6]. Generally, the failure of the electrical interconnection during the TC test could be caused by many factors such as coefficient of the thermal expansion (CTE) mismatch between the IC component chip/the interconnection materials/the substrates, elastic moduli difference of these components, adhesion strength of the interconnect materials on the IC chip and the substrate, the mechanical properties of the IC chips, the glass transition or the softening point of the ECA materials, moisture uptake in the interface and the bulk ECAs, the surface or interface property change and so forth. Especially, the thermal stress in the ECA joints generated by a huge temperature difference during the TC and the interfacial delamination due to the adhesion degradation could be the critical reasons. In this aspect, a feasible solution to the TC failure problem is to introduce flexible molecules into the epoxy resin matrix. By releasing the thermal stress with the flexible molecules, the thermomechanical stresses could be dramatically reduced and the ECA/component joint interfaces could keep intact through the thermal cycling test. In addition, application of low CTE adhesives by using high loading of fillers has been proved to induce lower shear strain induced by CTE mismatch between chip and board under temperature cycling[4,6].

Commercially available materials

When designing materials to achieve fine pitch interconnections, several important variables must be considered and are application dependent. These variables include adhesive characteristics as well as particle types[4,5]. Two basic types of adhesives are available:

thermosetting and thermoplastic materials. Thermoplastic adhesives are rigid materials at temperatures below the glass transition temperature (Tg) of a polymer. Above the Tg, polymers exhibit flow characteristics. When using this type of material, assembly temperatures must exceed the Tg to achieve good adhesion. The principal advantage of the thermoplastic adhesives is the relative ease with which the interconnection can be disassembled for repair operations. Thermosetting adhesives, such as epoxies and silicones, form a three-dimensional cross-linked structure when cured under specific conditions. Curing techniques include: heat, UV light, and added catalyst. As a result of this irreversible cure reaction, the initial uncross-linked material is transformed into a rigid solid. The curing reaction is not reversible. This fact may hinder disassembly and interconnection repair. The ability to maintain strength at high temperature and the deformation of robust adhesive bonds are the principal advantages of these materials. For the selection of the adhesive, the robust bonds should be formed to all surfaces involved in the interconnection. Numerous materials surfaces can be found in the interconnection region including: SiO_2, Si_3N_4 polyester, polyimide, FR-4, glass, gold, copper, and aluminum. Adhesion to these surfaces must be preserved after standard tests such as temperature–humidity-bias aging and temperature cycling. Some surfaces may require chemical treatment to achieve good adhesion. In addition, the adhesive must not contain ionic impurities that would degrade electrical performance of the interconnections.

The materials used in this are carefully chosen. The adhesive substrate used is polyurethane and the filler used are the nano- particles of nickel and zinc.

Polyurethane

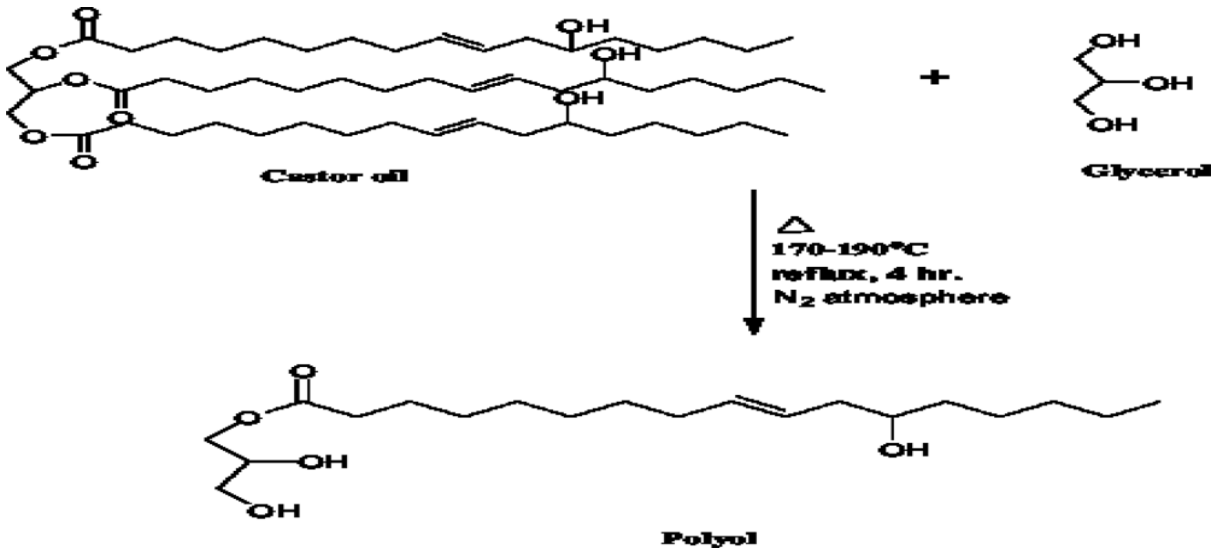
Polyurethane (PUR and PU) is a polymer composed of organic units joined by carbamate (urethane) links. While most polyurethanes are thermosetting polymer that do not melt when heated, thermoplastic polymers are also available.

Polyurethane polymers are traditionally and most commonly formed by reacting a di- or polyisocyanate with a polyol. Both the isocyanates and polyols used to make polyurethanes contain on average two or more functional groups per molecule.

Some noteworthy recent efforts have been dedicated to minimizing the use of isocyanates to synthesize polyurethanes, because the isocyanates raise severe toxicity issues. Non-isocyanate based polyurethanes (NIPUs) have recently been developed as a new class of polyurethane polymers to mitigate health and environmental concerns.

Polyurethane products often are simply called “urethanes”, but should not be confused with ethyl carbamate, which is also called urethane. Polyurethanes neither contain nor are produced from ethyl carbamate.

Polyurethane adhesives can be prepared from castor oil or soya oil. Polyols are prepared from these oils. Commonly used oil is castor oil which contains ricinoleic acid. This is treated with glycerol in presence of nitrogen atmosphere at 170^0c- 190^0c.



(Fig-1- Preparation of polyol)

1.2- Objective of the Project

The research work provided in this thesis is mainly focused on the synthesis polyurethane based conducting adhesive with different kind of metal fillers like Nickel and Zinc nano particle. Normally, the polyurethane is not a conductor of electricity and hence cannot be used as adhesive at the place of metal joints. Hence, it is required to increase the strength of the conductivity of the Polyurethane. This can be achieved by adding metallic fillers in the nano range. With the gradual increase in the concentration the conductivity of the resulting adhesive increases. But the mechanical strength of the adhesive joints tends to decrease. Thus, an optimization is required to between strength and conductivity of the adhesive.

Normally, epoxy is used as the polymer matrix in which filler are added. But we chose polyurethane instead of epoxy because of its better mechanical property. Metal filler like iron and copper have greater conductivity but they are prone to oxidation, blooming. Iron and copper get converted to their respective oxides and hence reduce the life span of the resulting adhesive joint. Similarly,use of silver nano-particle makes the ECA costly although it has good conducting property. Hence, we have planned to use cheaper materials like zinc and nickel.

The aim of the present project is to synthesis and study of polyurethane based conducting adhesives with zinc and nickel nano-particles as fillers. The studies has been conducted with the following objectives:

(1) Synthesis of Zinc and Nickel nano-particles.
(2) Preparation of polyols from castor oil.
(3) Preparation of zine and nickel based PU adhesives.
(4) Characterization of resulted adhesives.

Chapter-2

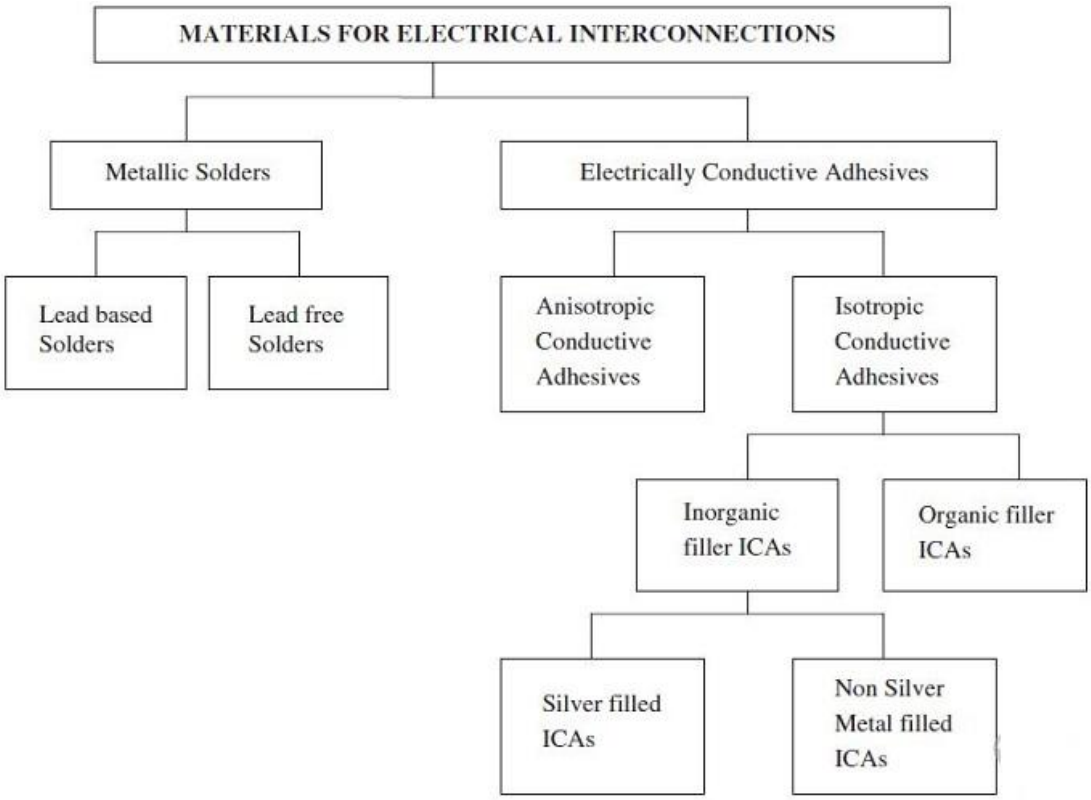
Literature Review

Literature Review

The objective this thesis is to study the study various kinds of electrically conductive adhesive and their application and develop an electrically conductive adhesive (ECA) made up of polymer matrix of polyurethane and particulate fillers of metal. To understand the details of conducting conductive adhesive we have gone through following literature review.

2.1- Conducting Adhesive

Conducting adhesive has two things to perform. One is to provide a conductive path for the flow of electricity and the other task is to provide mechanical strength to the interconnections[1,2]. Electrically conductive adhesives are composites consisting of solid conducting filler dispersed in non-conducting matrix. The polymer provides mechanical strength where as fillers provide electrical path. Different kinds of metal inter-connections are classified as follows:



(Fig-2- Classification of different kinds of interconnections [3])

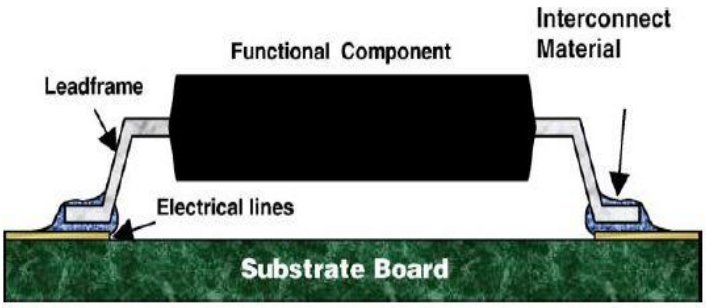
2.1.1-Metallic solders-

Metallic solders are the commonly used materials for inter-connections[1,2,3]. They are mainly of two types-

(a) Lead based solder
(b) Lead free solder

Among these two most frequently used solder is lead based solder. Although lead free solder is an alternative for lead free soldier but it didn't got popularity due to rough surface provided by lead free solder as compared to lead solder. Thus, despite all the hazardous effects and bad environmental factor the lead solder is still used in almost all electrical interconnection applications.

(Fig-3- Lead and Lead solder)



(Fig-4- Interconnect of substrate and metal contact by solder)

2.1.2-Electrically Conductive Adhesive (ECA)

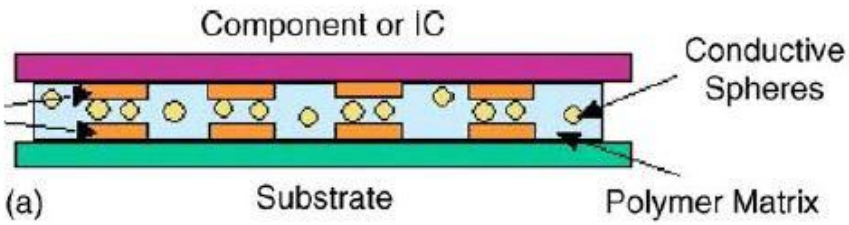
To avoid the health problems and environmental issues associated with the lead/tin type metallic solders scientists are trying to develop alternative type of conducting adhesive[2]. They are mainly of two types-

(a) Anisotropic conducting adhesive (ACA)
(b) Isotropic conducting adhesive (ICA)

2.1.2.1- Anisotropic conducting adhesive

Anisotropic ECAs have a property of allowing current to flow uni-directionally, i.e., along only one axis. This property is achieved by using concentration of conductive filler below

isotropicity, i.e., the concentration of conductive particles is limited to allow electricity to travel along the z-axis only, and not on the x-y plane. ACAs are currently available in two forms, i.e., single component, heat curable liquids and pastes, and heat curable thermosetting or thermoplastic films. ACAs in the form of film or paste are interposed between the substrate surfaces to be connected and heat and pressure are



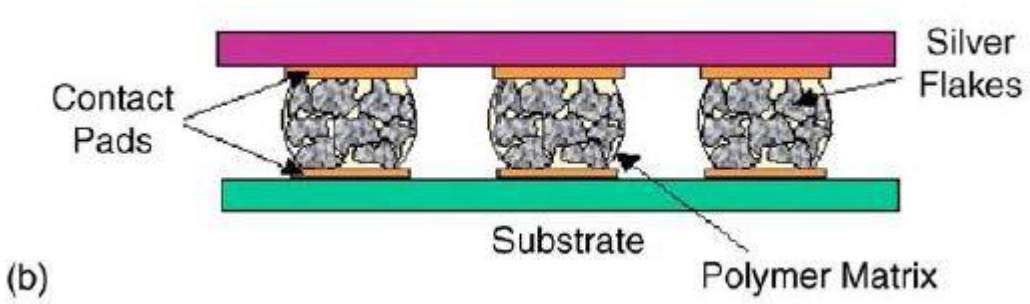
(Fig-5- schematic representation of ACA)

simultaneously applied to this assembly until the particles bridge the two adherents. Once the electrical continuity is produced, the polymer binder is hardened by thermal curing in the case of thermosets or by cooling in the case of thermoplastics[2]. ACAs can be used to provide structural strength without an electrical connection on other areas of the device. In the global marketplace, 90% of all ACAs are currently sold as films used for flat panel displays. Other applications include flip-chip-on-glass, smart cards and flip-chip-board, where soldering cannot be applied because of thermal sensitivity of the substrate. Currently available ACA products offer a random distribution of conductive particles, i.e., the particles are not distributed in an organized manner and may come in contact with one another or may be absent in areas where they are required. This creates voids or open circuits thus limiting their use in the high-end electronic applications. Also, the need for application of heat and pressure simultaneously while the matrix is hardened restricts its use.

2.1.2.b- Isotropic conductive adhesives (ICAs)

ICAs offer non-directional or all-directional conductivity by incorporating higher filler concentrations[2,3]. At such high concentrations, the materials achieve percolation threshold and are electrically conductive in all directions after the materials are cured. ICAs can be

utilized on the materials that require a ground path. ICAs can be used as heat or room temperature curing, single or two-component formulations. Epoxies are the most prompt polymer binders due to their ability of low temperature curing while silver is the most popular filler used because of its moderate cost and high conductivity. ICAs are often called 'polymer solders'. These can be used as an electrical interconnect on non-solderable substrates such as ceramics, plastics, or to replace solder on thermally sensitive components. ICAs have been proposed as an alternative to tin/lead solders in surface mount technology (SMT) applications.



(Fig-6- Schematic of ICA)

The main advantage of ICA over lead/tin solder is as follows:

(a) ICA offer environmental friendly alternative for lead solder.
(b) No flux is used in ICA and hence no use of environment polluting choloflorocarbon for cleaning purpose.
(c) ICA involves low processing temperature as compared to metallic solder.
(d) ICA has low thermo-mechanical fatigue.
(e) They can be used in wide range of surfaces including glass, ceramics etc
(f) They can be used in finer pitch application.
(g) They involve lower processing steps and lesser processing time.
(h) They are of low cost as the volume of material used is less.

Now-a-days, there has been a lot of research going on throughout the globe to produce ICAs with desirable overall properties and to overcome the limitations hindering their success as complete replacement for tin/lead solders[1,2,3]. The main focus of these studies is on reliability properties like resistance stability and adhesion shear tests, humidity effects and other thermal properties, usually with comparison to solder properties and environment friendly manufacturing process. These efforts to modify designs and formulations have

culminated into ICAs with improved electrical conductivity, contact resistance stability and better impact strength.

ICAs are comprised of polymeric binders (which provide mechanical strength) and conductive fillers (which act as channel for charge transport). The characteristics of an ICA are essentially the result of its two components[6]. The insulating matrix may be either thermoplastic or thermosetting depending upon the final application of the assembly. Although, thermoplastic systems have some advantages like re-workability and assembly speed but they are not normally chosen as matrices for ICAs. Robust thermosetting systems are the more common choice offering resistance to heat, moisture and mechanical stress. ICA formulations usually include epoxy resin as the polymeric matrix. Epoxy based materials have been widely used in engineering components because of their outstanding mechanical and thermal properties as well as processability[2,3]. The use of epoxies has been the state-of the art for a long time. Epoxies have many beneficial properties like low shrinkage, good adhesion, resistance to thermal and mechanical shocks, low dielectric constant. They also have good resistance to moisture, solvents and chemical attacks. The desirable properties may further be improved with suitable choice of solvents, fillers, colorants, flame-retardants, plasticizers and curing agents and accelerators. Lu and Wong described the development of novel conductive adhesives for surface mount applications[23,24]. An epoxy based electrically conductive adhesive system was developed that had improved compatibility with tin/lead finished components, much lower moisture absorption, faster cure, comparable bulk resistivity, comparable adhesion strength, and higher glass transition temperature.

The most popular filler material for ICAs is silver, (Ag) which is cheaper than Au, and has superior conductivity and chemical stability[6,7]. Also, it is easy to precipitate into a wide range of controllable sizes and shapes, and silver oxides show high conductivity. Filler particles may come in the form of spheres, fibres, flakes or granules, but the optimum geometry is that which provides minimum critical filler concentration for low resistance, the best contact between neighbouring metallic particles, and strongest adhesion to the polymer, i.e., flakes due to their higher aspect ratio. Small particles are better than large particles, providing more particle-to-particle contact, greater conductivity and consistency of product. A spherical silver powder was used as conductive filler. Recently, other metals are used as filler in place of silver. These metals are mainly copper, aluminium, iron etc.

Despite all these positive points ICA has a lot of negative aspect that needs to be rectified before it fully replace the solder technology in future completely. The major disadvantages of this technology are as follows:

(a) Lower level of conductivity of ICA as compared to metallic solder.
(b) Unstable contact resistance with non-metal parts.
(c) Poor impact performance.

2.1.2.1-Various applications ICA are given below

(a) <u>Chip on board can be fixed by ICA</u>

The principal function of die attach[3,4] adhesives is to mechanically attach the integrated chip (IC) to the substrates in a highly reliable manner. Die attach can be accomplished using one of several materials. A good die attach material must have attributes fitted to the desired functionality which is often governed by mechanical, thermal, and electrical properties. Sufficient adhesion is required to ensure that the die remains fixed in place when it is subjected to assembly processing or during actual device service[21]. Thermally, it shall impart the least stress during expansion and effectively accommodate transfer of heat generated in the die to the package. Until recently, hermetic die attach was accomplished using inorganic adhesives such as silver filled glass, gold/tin or gold/silicon eutectic. Eutectic die attach is a low throughput, manual method that cannot be easily adapted for high speed automation. Although silver/glass die attach has provided some processability improvements over the eutectic process, it still requires a lengthy and precise temperature profile in order to remove the organic vehicle at a controlled rate. As die sizes become larger, silver glass firing process becomes difficult to control. In hermetic packages, the high temperature eutectic and silver filled glass die attach raise concern on mechanical, thermal, and diffusional stresses that greatly affect device performance, thereby prompting the use of a polymeric substitute processed at low temperatures. Good dispensability is certainly a process concern, which is necessary to minimize non-uniform die attach especially in large die. Non-uniform die attach can enhance die stresses (causing the die cracks), thus becoming a reliability issue. Polymer adhesives are used extensively in the attachment of IC to a variety of electronic packages. The polymer-based adhesives offer many advantages such as lower stresses on IC die due to low material moduli (both the storage and loss moduli) and curing temperature, ease of use in a manufacturing environment, and low cost compared to inorganic adhesives. For certain

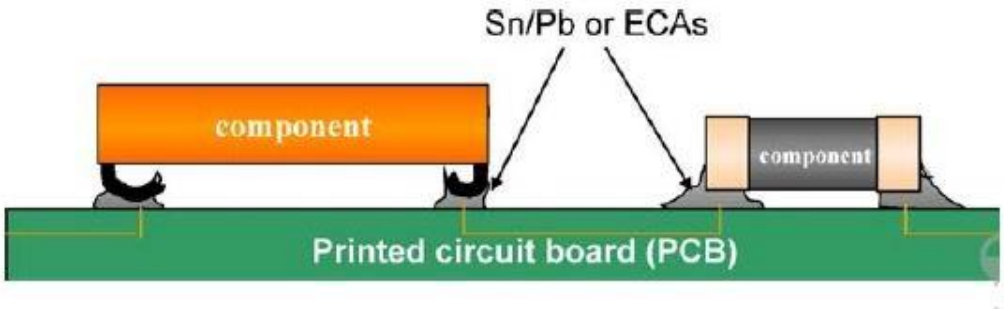
cases, the attachment of some bare IC die also requires electrical contact to the backside of the die.

(b) <u>Flip–chip bonding using ICAs</u>.

Isotropic conductive adhesive materials use much higher loading than ACAs to give electrical conduction isotropically or in all directions throughout the material. In order for these materials to be used for flip–chip applications, it is necessary to apply them selectively onto those areas which are to be electrically interconnected, and to ensure that spreading of the materials does not occur during placement or curing which would cause electrical shorts between the separate pathways[2,3]. ICAs are generally supplied in paste form. To precisely deposit the ICA paste, screen or stencil printing is most commonly used. However, to do this to the scale and accuracy required for flip–chip bonding would require very accurate pattern alignment. To overcome this requirement, the transfer method may be used. For this technique, raised studs or pillars are required on either the die or the substrate. The ICA is then selectively transferred to the raised area by contacting the face of the die or the substrate to a flat thin film of the ICA paste which adheres to the prominent surfaces. This thin film may be produced by screen printing and the transfer thickness may be controlled by changing the printed film thickness. This method confines the paste to the area of the contact surfaces and the quantity may be adequately controlled so as to prevent spreading between pathways when the die is placed. Pressure during bonding is not required for this technique which gives the option of oven curing the assembly.

(c) <u>Surface-mount electronic component applications</u>

Surface-mount technology (SMT) is the main technique for interconnecting chip components to substrate by packing and placing the components on the printed circuit board and using the reflow furnace to melt the solder alloy for the electronic system interconnection[1,2]. Fig. 6 shows a scheme of several different components interconnected by surface-mount technology. Tin–lead (Sn–Pb) solder has been exclusively used as the interconnection material in surface-mount technology, because current commercial ECAs, in spite of the numerous advantages, cannot be used as drop-in replacements for solder in all applications due to some challenging issues.



(Fig-7- schematic structure of surface mount interconnection)

As mentioned, due to the extreme toxicity of lead and legislations for lead-free electronics, worldwide efforts have been put in the study of ECAs. Significant progress has been made to address different materials properties and reliability issues for the development of high performance conductive adhesives as a potential replacement of lead-containing solders in SMT application as well[1].

With the advent of nanotechnology, many research groups have used the advantages of this technology in ICAs. Nano-sized metal particles have been used in ICAs to improve electrical conduction and mechanical strength[5]. With nano-sized particles, agglomerates are formed due to surface tension effect. ICA filled with aggregates of nano-size Ag particles as highly porous conductive filler. The approach was to decrease the metal loading to improve the mechanical performance for specified electrical properties. In another study two classes of metal fillers were studied (i.e., nanoscale and micro-scaled particles) to decrease the total metal loading while retaining the good electrical conductivity using a bimodal filler distribution.

2.1.2.2-Mechanism of electrical conductivity in ECA

The addition of a conductor to an insulator affects the electrical properties of the composite according to the degree of filling and proximity of conductive particles to other conductive particles. Three situations are possible: no contact between conductive particles, close proximity, and physical contact[6]. When the conductive particles are isolated, the conductivity of the composite is changed only slightly. The composite remains an insulator, although its dielectric properties may change significantly. When the conductive particles are in close proximity, electrons can penetrate the thin gap (<10 nm) between the particles. The process of electron transport across an insulator gap is referred to as tunneling.

The metal-insulator-metal structure in the metal filler contact area is our main interest. Considerable work has been done on comparable electrical contact behaviour[6,7]. The tunneling effect is extremely sensitive to the gap width (thickness of the film) and height of the potential barrier to be penetrated, and these quantities are never exactly known, so the calculations are typically and necessarily made with approximations and simplifying assumptions about the applied voltage, the temperature (zero or finite), and the shape of the potential barrier between the conductors. The exponential dependence of the tunnelling resistance on the gap width and the insulator potential barrier height shows the importance of maintaining close proximity between adjacent conductive particles, and of the insulator film type between the metal fillers.

Another condition is that the metal fillers physically contact each other to form a continuous network throughout the composite. The composite conducts through the particle network by the conduction mechanism of the metal particles (band-type conduction). Band and tunneling conduction can be differentiated by the AC and DC behavior of the composites. A composite which conducts by a tunneling mechanism will exhibit a higher AC conductivity than DC conductivity. In highly loaded composites actual touching does occur, where the current-voltage characteristics of such composites are linear (ohmic). The non-ohmic behavior observed in other composites is due to the electron tunneling mechanism. However, claims refuting the above statement show that even composites with resistivities as high as 107 Ω-cm exhibit linear voltage-current characteristics except at the electrodes[7,8]. The total non-ohmic behavior of composites is claimed to be caused by extended space charge distributions near the electrodes. These space charge distributions are generated by local polarization of the matrix material.

Actual physical metallic contacts or tunneling conduction between metal particles possibly coexist in the metal-filled polymer system, depending on filler loading, processing conditions, polymer-metal wettability, and temperature[6]. An organic lubrication layer (fatty acids) is usually applied to the silver surface during manufacture of the silver flakes to avoid flake aggregation when milling. Residual acid layers might still remain on the silver flakes in the conductive adhesives. Possible chemi-sorbed oxide or sulfide layers and polymer layers wetted on the metal particles may also exist. These film layers will contribute to the tunneling conduction especially before the cure of the adhesive matrix. Isotropically conductive adhesives (ICAs) are typically formed by loading silver flakes into an adhesive matrix such that the percolation threshold is exceeded[6]. Electrical connection is provided by the continuous network of metal particles. The discontinuous electrical property change of the

composite is normally explained in terms of the metal filler concentrations by percolation theory. The point where the electrical resistivity decreases dramatically is called the percolation threshold. Above the percolation threshold concentration, networks of chains of conductive particles are formed throughout the composite, although this network does not necessarily imply physical contact between adjacent particles. The percolation model is normally analyzed statistically by Monte Carlo techniques. This approach has not been completely successful in predicting the performance of real composites.

There are various theories that define the mechanism of conduction in the electrically conductive adhesive-

Percolation theory

When a sufficient amount of conductive filler is loaded into an insulating polymer matrix, the composite transforms from an insulator to a conductor, the result of continuous linkages of filler particles[6,7]. Assuming a random dispersion of the conductive filler, as its concentration increases, no significant change occurs until a critical concentration (volume fraction) Vc is reached. This point where the electrical resistivity decreases dramatically, called the *percolation threshold*, has been attributed to the formation of a network of chains of conductive particles that span the composite.

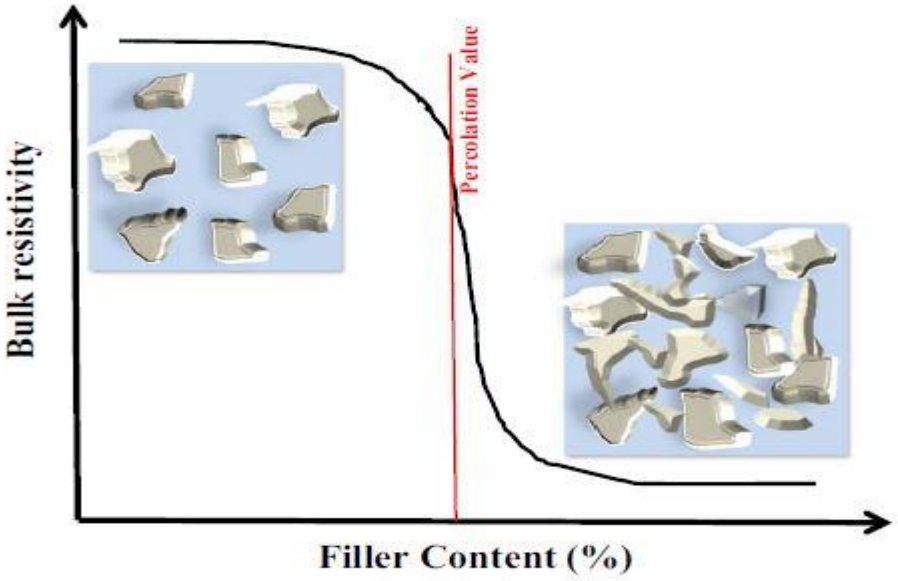
The probability of a continuous network being formed by filler particles in a matrix is related to the statistical average number of contacts each particle makes with neighboring particles and the maximum number of contacts per particle that are possible[8]. At the critical point of network formation, the critical number of contacts per particle is given by

$$Cp = PcZ$$

where, Pc is the critical probability of network formation, and Z is the maximum number of possible contacts, or coordination number. Experimentally it is showed that the value of Cp for a random dispersion of spheres in a matrix is 1.5. For spherical particles, Cp is apparently a constant.

For the random sphere case as above, Pc is 0.305, which also represents the critical concentration (volume fraction), Vc, for the filler particles. This represents the point at which

network formation begins and the sharp drop in resistivity starts. These equations do not adequately account for preparation technique, particle size distribution, or particle-particle interaction effects.



(Fig-8- Typical percolation curve of ECA)

Network formation theories for flakes, fibers, and other irregular shapes are even less well developed. For irregular fillers with a completely random distribution, the critical value of Pc is assumed to be the same as that for spherical fillers.

The percolation modeling literature commonly includes finite intra-particle resistivities, but inter-particle resistances are seen less often. This is partly because the most common systems of interest would assume electron tunneling between particles, and the exponential dependence of the tunnelling probability on separation introduces a strong parametric dependence on a poorly characterized. Percolation models of the electrical resistance of ICA systems have included both intra-particle and inter-particle resistances, but so far with only gross approximations, e.g. with the simplifying assumption of uniform tunneling thickness.
The percolation value depends on different parameters such as size, shape, nature, and the dispersion state of conductive fillers. Each parameter influences the quality of conductive filler linkage in electrical network differently. The size of conductive fillers and their size distribution are important parameters on percolation threshold concentration. The percolation concentration also depends on the morphology of conductive fillers. Lower percolation threshold can be obtained using a high aspect-ratio filler because they can provide more

connected pathways at lower filler content. The dispersion state of conductive fillers also has a significant effect on the percolation value. Presence of agglomerations in some level can be useful to form a percolated network at lower filler contents.

(2) **Inter-particle conduction**

Inter particle conduction is generally assumed to take place directly from metal to metal, or by tunneling through an insulating layer, whether of intervening polymer or of surface contaminants, or by conduction through a surface oxide film, which for Ag would be a conductive degenerate semiconductor[6,7,8].

There is a range of tools available to characterize conduction mechanisms, including frequency effects, non-ohmic high field behavior, temperature dependencies, etc., and the absence of any observation of negative temperature coefficient of resistance (TCR) or non-ohmic behavior is sufficient to eliminate most other conduction mechanisms from contention. Silver is typically tarnished, and presumably would oxidize within the polymer, even if initially "clean," but it is not clear what effect the surface lubricants identified on flake surfaces would have on this process[7].

No matter which of the mechanisms apply at the gap itself, the contact area is accepted as being typicallysmall, of diameter, d=10 nm or less. Clearly there will be some constriction of current flow between particles at the contact, and the Holm theory specifies this contact resistance to be $\rho/2d$.

The internal pressure exerted by the curing process must be quantified for further progress to be made. Returning to the differences between the contact conduction mechanisms, the TCR will be zero (or slightly negative) for tunneling and positive for the oxide. Unfortunately, it is difficult to find data on the exact electrical properties of the oxide, which are subject to local formation conditions, so it is not known whether the TCR would be less or greater than the metal particle TCR. It would appear from the formula that the constriction resistance would have the same TCR as the metal particles', but the derivation does not include the mean free path reduction which will be associated with contact dimensions less than the bulk value in the particles; this extension to the theory is necessary[8,9].

The inter-particle conduction mechanism remains undetermined, and the points made above, which reflect those in the literature, are very general. What is needed is a comprehensive

basic study of the metal polymer interface, to investigate charge transfer and band effects in the polymer(s), time and temperature effects, and how the process proceeds during curing. In addition, actual contact points need to be located and isolated, and the potential distribution plotted across the boundary from one particle to the other.

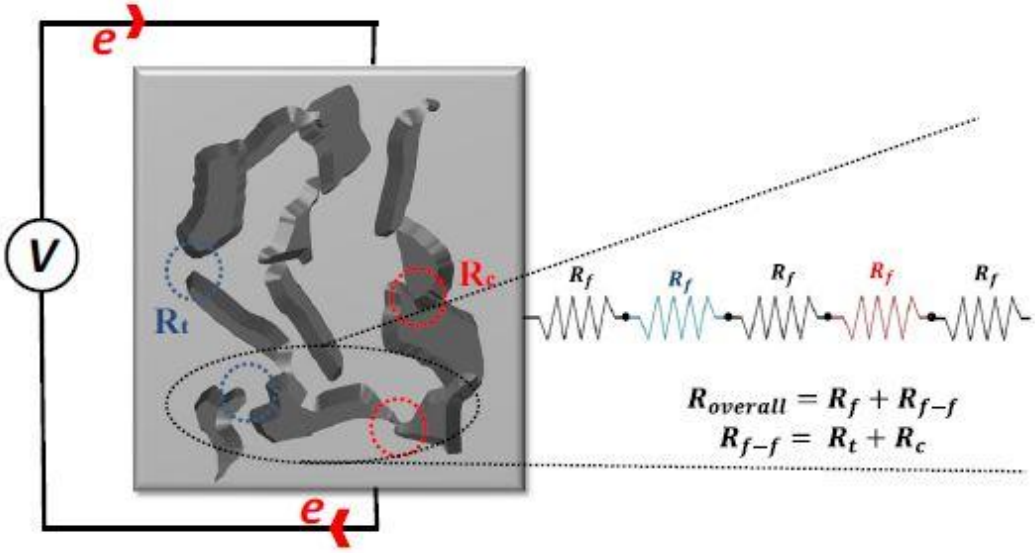
Surface lubricant, and has achieved reduction of overall resistance by replacing the traditional stearic acid with shorter chain alternatives. On the other hand, it has been seen that the lubricant breaks down during cure, and leaves a carbon residue on the flake surface, which is expected to control the inter-particle resistance[9].

Frequency dependencies are easily determined and can be definitive in the identification of some conduction mechanisms. In the ICA case, ac measurements were expected to short circuit the tunnel gaps between particles, with the corner frequencies providing the means to separate out the particle resistance from the inter-particle gap contribution. The method was validated by ac measurements before cure[10].

Resistivities below the percolation threshold decreased with frequency to limiting values similar to those above it. (This experiment suggests the use of impedance spectroscopy as a manufacturing quality test for ICAs, as for solder paste.) When applied to cured ICAs, however, no such effect was observed, so either there is no tunneling gap (i.e. conducting oxide or metal-metal contact) or the tunnel resistance is just much less than the particle resistance.

(3) *Intra-particle resistance*

Intra- particle resistance accounts for a substantial proportion of the measured ICA resistance, and in some cases essentially all of it. This conclusion is based on TCR measurements on a variety of commercial ICAs, where the TCR values range downwards from the bulk metallic value, but are always positive. Within the limits of experimental accuracy, the data are consistent with a model of the intra-particle metallic resistance in series with a zero TCR contact resistance, but cannot be totally conclusive. Thermal testing needs to be extended to much lower temperatures to resolve this point. For ten micron diameter flakes one micron thick, and micron-sized smaller particles, the electron mean free path is not going to be reduced significantly from the bulk value, and no accounting is needed for size effects in the particles. But the nature of the surface (i.e. rough or smooth for diffuse or specular scattering) could be important for the assessment of mean free path limitation for constriction resistance.



(Fig-9 – Different kinds of particle resistance)

The ac measurements mentioned above were run on the same ICA materials which gave TCRs identical to the bulk value for Ag, and so it is not surprising that the ac characteristics were in total accordance with the predictions of skin effect resistance and inductance for Ag. These experiments should be duplicated for materials with greater inter-particle resistances. At frequencies where skin effect is dominant, the lower resistance advantage enjoyed by solder disappears, as the effective cross-sectional area shrinks with the skin depth for solder and ICA alike.

(4) *Contact resistance*

The resistivity of the filled adhesives containing spherical particles can be[7,8] expressed by:

$$\rho = C^2 \pi D R_s / m\Phi$$

where, D is the diameter of the spherical filler, Rs is the contact resistance, and m is the average contact number, which is a function of the particle volume fraction. Using computer simulation, determined the following functional relation between m and Φ

$$m = 0.1625 + 5.7323\,\Phi - 5.171\,\Phi^2 \quad (1.5 < m < 2.0)$$

The contact resistance Rs can be determined by using the relation,

$$Rs = Rc + Rt$$

The constriction resistance is given by

$$Rc = (\dot{\rho}_1 + \dot{\rho}_2)/4a$$

where, $\dot{\rho}_1$, and $\dot{\rho}_2$ are resistivities of the two particles in contact, and a is the contact area.

The tunnel resistance, Rt is given by,

$$Rt = \dot{\rho}_0 / \pi a^2$$

where, $\dot{\rho}$ 0 (Ω m2) defines the tunnel resistivity.

Gap in the literature

From the study of above literature we found out that ECA needs a lot of change if it is going to replace the present day lead/tin based solder technology. Major works has been done in the field of epoxy based conducting adhesive as reported in literature[1,2,3,4]. This is because adding of filler in epoxy is easy and it gets dispersed easily. But the mechanical strength of the resulting adhesive is not quite good. In this context work is needed to find an alternative adhesive that can be made electrically conducting adhesive. In this regard polyurethane is a good adhesive having better adhesion properties. So, our work here is to make polyurethane based adhesive with good conducting property.

In literature [6,7] there is the use of silver particle, flakes as fillers along with polymer matrix. The problem with silver is that it is very costly despite its good conducting property. Thus, it makes the electrically conducting adhesive less viable economically. Similarly, use of iron and copper fillers have their own set of problems as described in Li, G. I, WONG [21]. They are prone to oxidation due to environmental conatct. This will lead to blooming and resulting the weakening of the joint. Thus, we can search for some alternative filler. Particle size also matter. Maximum work has been done regarding particulate filler of micro range but nano range particles have good properties of conductivity that needs to be studied.

Quantity of fillers used when they are of large size is very high. More and more volume fraction is required when particle size is bigger. The smaller the particle size better is the conductivity property and mechanical strength. This relationship of particle size with that of various properties of resulting adhesive needs to be studied.

Zinc and nickel nano-particles along with PU may have not been frequently studied previously in any of the studied literature. Thus, we have tried to find out their mechanical strength along with conductivity varying their concentration in adhesive.

Chapter-3

Experimental Studies

3.1-Experimental Studies

The objective of the experiment is to prepare the conducing adhesive of polyurethane and test the mechanical strength and conductivity. For this purpose polyurethane is used as polymer matrix and nano-particles of nickel and zinc are used as fillers. The primary task was to prepare the nano particles of Ni and Zn and do their characterization.

3.1.1-Preparation of Nano-particles of Nickel

Nickel nano-particles are prepared using the sol-gel method. The list of materials used in the preparation is given below in table-1.

Table-1- materials for nickel nano-particle

Materials used	Name of the company
Hydrazine	Arrow Fine Chemicals Ltd, India
Nickel Nitrate	A.B. enterprise Mumbai
PEG	Arrow Fine Chemicals Ltd, India
NaOH	Advanced chemical sales corporation,India
Distilled water	Reaseacch Lab-1 DTU

Experimental Procedure

(1) 0.4 M solution of Nickel nitrate in 100ml distilled water was pepared.

(2) 1ml of hydrazine was added to it.

(3) 2ml of PEG was added to it.

(4) The resulting solution was stirred for 12hours at 75^0C in magnetic stirrer continuously.

(5) NaOH was added drop wise till the P^H was set at 12.

(6) This was washed with distilled water and the impurities and NaOH were removed.

(7) It was at 60^0C for 8 hours.

(8) It was centrifuged to obtain high gel.

(9) Then the resulting samples were put at 700^0c for 4hours for calcination.

The particles obtained are subjected to various characterization process like SEM, EDX and XRD for the determination of size and shape and material present in it.

3.1.2- Preparation of Zinc Nano-particle

Zinc nano-particles are prepared by sol-gel method in the lab. The materials used in this are given in the table-2 below.

(Table-2- materials for zinc nano-particle)

Materials required	Name of the company
Hydrazine	Arrow Fine Chemicals Ltd, India
Zinc Acetate	Advanced inorganic Ltd, Delhi.
PEG	Arrow Fine Chemicals Ltd, India
NaOH	Advanced chemical sales corporation,India
Distilled water	Research Lab-1,DTU

Procedures for the preparation zinc nano-particle

(1) 0.4 M solution of Zinc Acetate in 100ml distilled water was prepared.

(2) 1ml of hydrazine was added to it.

(3) 2ml of PEG was added to it.

(4) The resulting solution was stirred for 12hours at 75^0C in magnetic stirrer continuously.

(5) NaOH was added drop wise till the P^H was set at 12.

(6) This was washed with distilled water and the impurities and NaOH were removed.

(7) It was stirred at 60^0C for 8 hours.

(8) It was centrifuged to obtain high gel.

(9) Resulting gel was calcinations at 700^0c for 4hours.

The particles obtained are subjected to various characterization process like SEM, EDX and XRD for the determination of size and shape and material present in it

3.1.3- Preparation of Polyurethane Adhesive

The preparation of PU adhesive is done following the procedure given in the literature [7,15]. First of polyol is prepared with hydroxyl value 300. The materials used are given in table-3

Table-3- materials for adhesive preparation

Material Name	Name of the company
Castor oil- hydroxyl value=160	CDH, India
Methylene diphenyl diisocyanate (MDI)	Sigma-Aldrich
Catalyst- Dibutylene Dilaurate(DBTDL)	HMEDA, India.
Methyl Ethyl Ketone (MEK)	CDH, India
Nano particles of Zinc and Nickel	Prepared in lab

Procedure for Preparation of Polyol

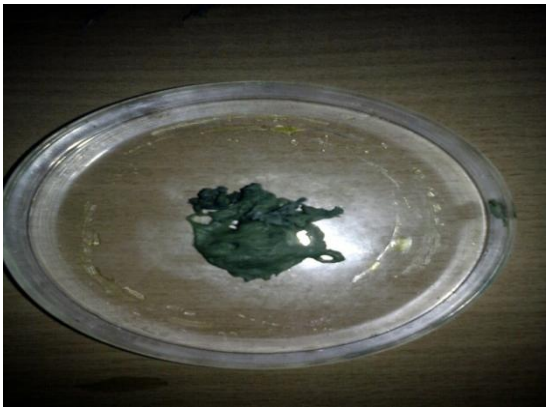
The modification of castor oil was carried out under the inert atmosphere i.e in the presence of nitrogen. The setup consisted of a four necked glass reactor of 500 mL capacity with 180 mm height and 90 mm diameter equipped with a mechanical stirrer. The stirrer was mounted on an overhung shaft, i.e. shaft supported from above, along the axis of the reactor, with a clearance from the bottom equal to one third of the diameter of the reactor. The shaft was driven by a 1/8 H P motor which was controlled through a dimmerstat. Heating was carried out by means of an oil bath. Reactor was supported on a circular copper plate with in the oil bath. Nitrogen was supplied at a constant flow rate to avoid any oxidation reaction within the reactor. One of the necks of the reactor was equipped with a reflux condenser, to minimize the carry over losses. The reaction kettle was charged with castor oil. Glycerol 10% (w/w) was added to it. The reacting contents were heated to a temperature of 220±100C. The stirring speed is kept constant at 1000 rpm. The progress of condensation reaction and its

stability were confirmed by checking its hydroxyl value. For this purpose, the samples at regular intervals were taken out and checked for hydroxyl value, acid value, viscosity and water content. The heating was carried out till a hydroxyl value of 390-410 mg KOH/g is achieved. The time required to complete the reaction was 3-4 hrs. The resulted polyol was stored in dark bottles away from direct sun light.

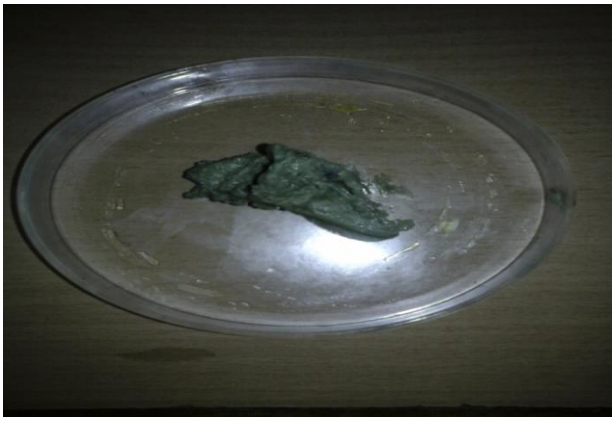
Preparation adhesive

Polyol and MDI are added in calculated amount and stirred continuously for 30min in nitrogen atmosphere at room temperature. Methyl Ethyl Ketone is added to adjust the adequate flow of the solution. In another flask mixture of polyol and requisite amount of nano particle of Zn and Ni are added along with DBTDL. Both the solutions are mixed properly and stirred to form the resulting adhesive.

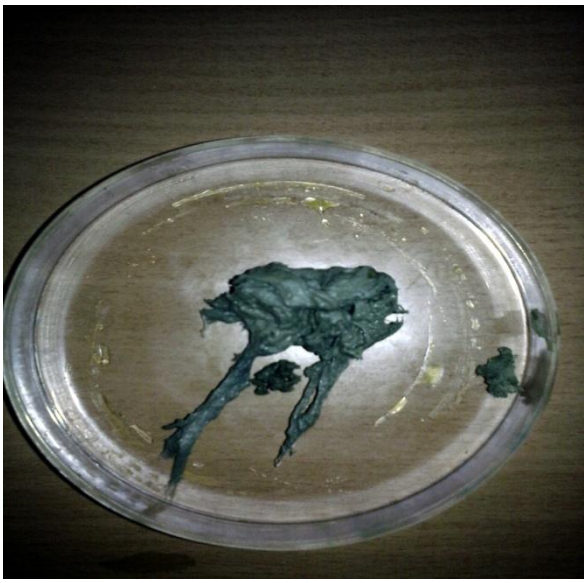
PU adhesive



Pu+2% Zn

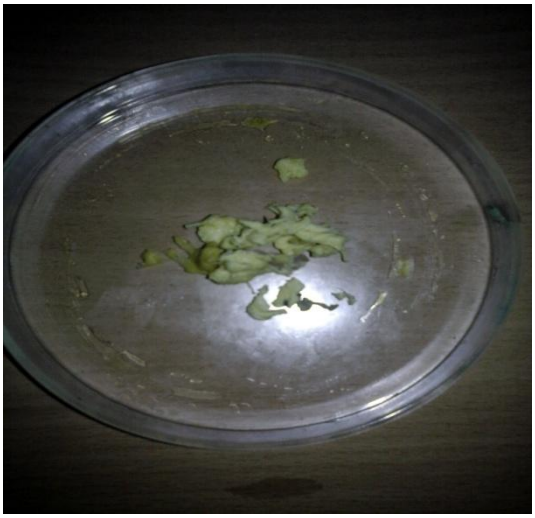


Pu+4% Zn



Pu+6% Zn

Pu+8% Zn



Pu+2% Ni

Pu+4% Ni

Pu+6% Ni

Pu+8% Ni

(Fig-10- Different kinds of adhesive)

3.1.3- Preparation sample for lap shear test

Aluminium strips are taken and they are cleaned properly through sand paper. The dimension of the joint is 60mm x 10mm x 2mm. The adhesive is applied on it through glass rod and spread uniformly. Then they are fixed properly and dried for 2-3 days. The joint is subjected for tensile test in the tensile testing with a force of 5KN using universal testing machine of Instron-4301. Mechanical strengths of different samples are measured.

(Fig-11- Sample for tensile test)

3.1.4- Conductivity test in four probe meter

The adhesive is made in pallet form and is put between the probes of the four probe conductivity meter. The sample should be properly fixed between the probes. The voltage is set at zero. Gradually the current is increased and the corresponding voltage is noted down. The value of resistivity is calculated and from that corresponding value of conductivity is measured.

Chapter-4

Characterization Technique

4-Characterization Technique

These are the characterization techniques use for studying the properties of the samples.

4.1-Scanning electron microscopy (SEM)

A scanning microscope (SEM) is one type of electron microscope which produces images of the samples by scanning it using a focused beam of electrons. The electrons are interacts with the atoms in the sample and produces various signals that contain information regarding the sample's surface topography and composition. The electron beam is usually scanned in an exceedingly formation scan pattern and therefore the beam's position is combined with the detected signal to provide a picture. SEM can be able to do resolution higher than 1 nanometer. Specimens will be observed in high vacuum, in low vacuum, in wet conditions and at a wide range of cryogenic or elevated temperatures.

Fig-13-SEM HITACHI, model no. S-3700N with EDX with X-ray at DTU, Delhi

4.2- X-ray diffraction (XRD)

Fig-13- X-ray diffraction machine in DTU

X-ray powder diffraction (XRD) is a high-speed analytical technique mostly used for phase determination of a crystalline material and can also be used to get information about unit cell dimensions. The analyzed material is finely ground, homogenized, and average bulk composition is calculated. X-ray diffraction is based on constructive interference of monochromatic X-rays with a crystalline sample. These X-rays are produced by a cathode ray tube, which is then filtered to generate monochromatic radiation, collimated to condense, and directed to the sample. The interaction of the incident rays with the sample cause constructive interference and a diffracted ray is produced, when conditions satisfy Bragg's Law ($n\lambda=2d \sin \theta$).

4.3-Fourier transform infrared spectroscopy (FTIR)

FTIR reckons on the fact that most of the molecules absorb light in the infra-red range of the electromagnetic spectrum. This absorption corresponds particularly to the bonds of the molecule. The frequency range is calculated as wave numbers over the range of 4000 – 600 cm^{-1}.

The background emission spectrum of the Infra-Red source is recorded, followed by the emission spectrum of the Infra-Red source with the sample in place. The ratio of the sample emission spectrum to the background emission spectrum is directly related to the sample's absorption spectrum. The resultant absorption spectrum due to the bond natural vibrational frequencies shows the presence of different chemical bonds and functional groups in the sample. FTIR is specifically useful for identification of organic molecular groups and compounds because of functional groups, side chains and cross-links involve will have characteristic vibrational frequencies in the infra-red range.

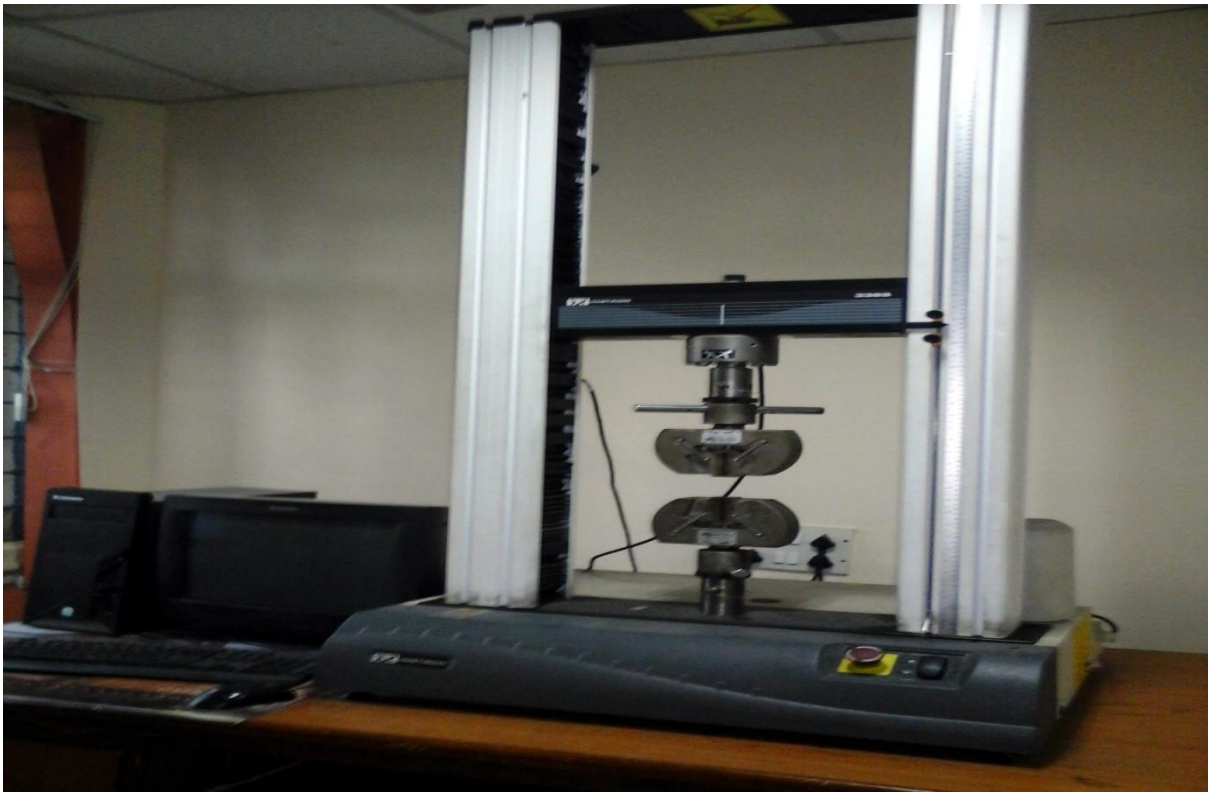
Fig-14: FTIR machine in DTU

3.4- Universal Testing Machine

A universal testing machine (UTM), also known as a universal tester, materials testing machine or materials test frame, is used to test the tensile strength and compressive strength of materials. The "universal" part of the name reflects that it can perform many standard tensile and compression tests on materials, components, and structures.

The specimen is placed in the machine between the grips and an extensometer if required can automatically record the change in gauge length during the test. If an extensometer is not fitted, the machine itself can record the displacement between its cross heads on which the specimen is held. However, this method not only records the change in length of the specimen but also all other extending / elastic components of the testing machine and its drive systems including any slipping of the specimen in the grips.

Once the machine is started it begins to apply an increasing load on specimen. Throughout the tests the control system and its associated software record the load and extension or compression of the specimen.



(Fig-16- UTM (Instron) at DTU)

3.5- Four Probe conductivity meter

The Four Probe Method is one of the standard and most widely used method for the measurement of resistivity. In its useful form, the four probes are collinear. The error due to contact resistance, which is significant in the electrical measurement on semiconductors, is avoided by the use of two extra contacts (probes) between the current contacts. In this arrangement the contact resistance may all be high compare to the sample resistance, but as long as the resistance of the sample and contact resistance's are small compared with the effective resistance of the voltage measuring device (potentiometer, electrometer or electronic voltmeter), the measured value will remain unaffected. Because of pressure contacts, the arrangement is also specially useful for quick measurement on different samples or sampling different parts of the sample.

(Fig-18- Four Probe meter)

Probes Arrangement

It has four individually spring loaded probes. The probes are collinear and equally spaced. The probes are mounted in a teflon bush, which ensure a good electrical insulation between the probes. A Teflon spacer near the tips is also provided to keep the probes at equal distance. The probe arrangement is mounted in a suitable stand, which also holds the sample plate and RTD sensor. This stand also serves as the lid of PID Controlled Oven. Proper leads are provided for the current and voltage measurement.

PID Controlled Oven

This is high quality temperature controlled oven suitable for Four Probe Set-up. The oven has been designed for fast heating and cooling rates, which enhances the effectiveness of the controller. While the basic design of the controller is around the PID configuration for its obvious advantages, wastage

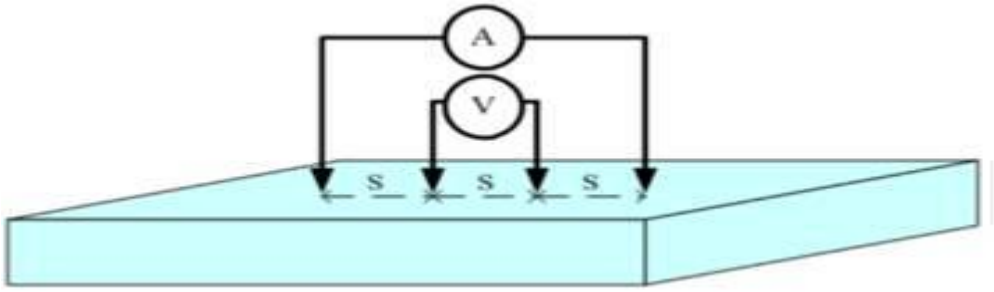
of power is avoided by using a Pulse Width Modulated (PMW) switch. This combination has the advantages of both on-off controller and linear PID controller. The result is a good stable and accurate temperature control. Platinum RTD has been used for sensing the temperature. A wheatstone bridge and an instrumentation amplifier are used for signal conditioning. Feedback circuit ensures offset and linearity trimming to a great degree of accuracy. The set and measured temperature are displayed on 3½ digits DPM through selector switch.

Low Current Source, Model :

(for high resistivity samples)

Low Constant Current Sources are needed, when the sample resistance, is large. As in the case of silicon wafers or high resistivity film deposits. Large resistance makes the measurement prone to pickups from the mains. This problem is reduced to very low level by using the battery instead of mains. Since the current requirement is very small, the batteries should have a reasonably long life. An internal voltage reference of 2.5 volt ensures reliable operation even when the batter voltage falls. A ten turn potentiometer makes the current adjustment very easy.

Measurement of resistivity



(Fig-17- Arrangements in conductivity measurement)

Distance between probes(S)= 2.0mm

Thickness of the sample= S mm

$\dot{\rho}_0 = \frac{V}{I} \times 2\Pi S$

Resistivity ($\dot{\rho}$) is given by

$\dot{\rho} = \frac{\acute{\rho}0}{G7(W/S)}$

where the value of $G7(W/S)$ is given by

$G_7(W/S) = (2S/W)\log_e 2$

Chapter -5

Results

and

Discussion

Characterization of Nano Particle

The characterization of nano particle is important in property study of the material. Here we have used SEM, EDX and XRD to characterize the nano-particle.

5.1- Characterization Nickel Nano Particle

Nickel nano particles are characterized by the SEM micrograph, EDX and XRD analysis. Their size of the particles and crystallinity is judged.

5.1.1- Scanning Electron Microscopy of Ni Nano Particle

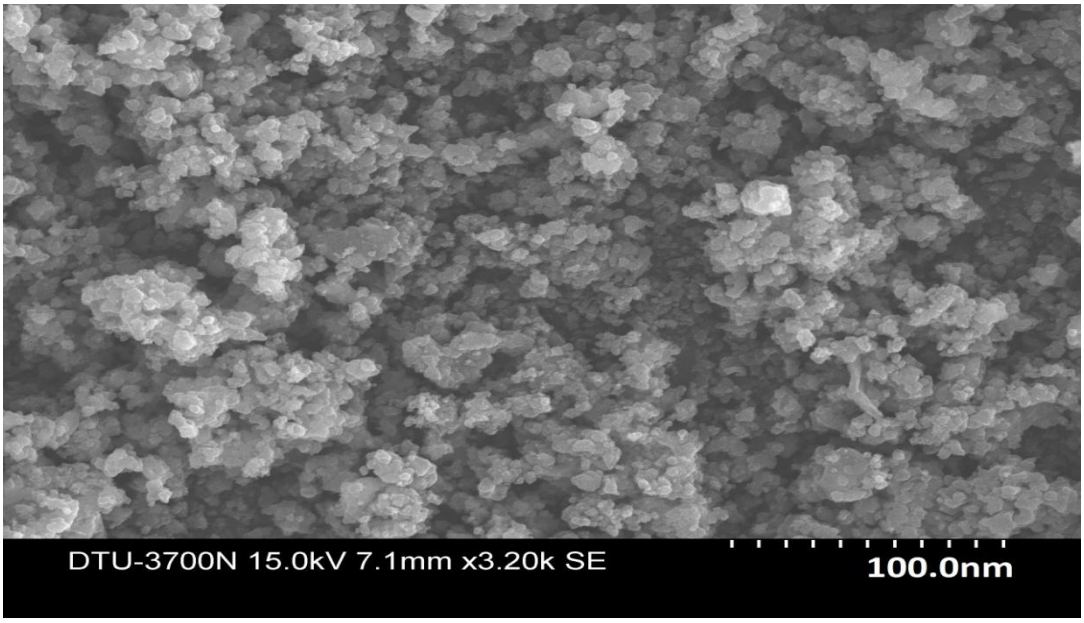


Fig-18- SEM image of Ni nano particle

From the above result it is clear that particles of nano range have synthesized. The result are studied under 15.0kV and particles are found in nano range.

5.1.2- EDX Report of Nickel Nano-Particle

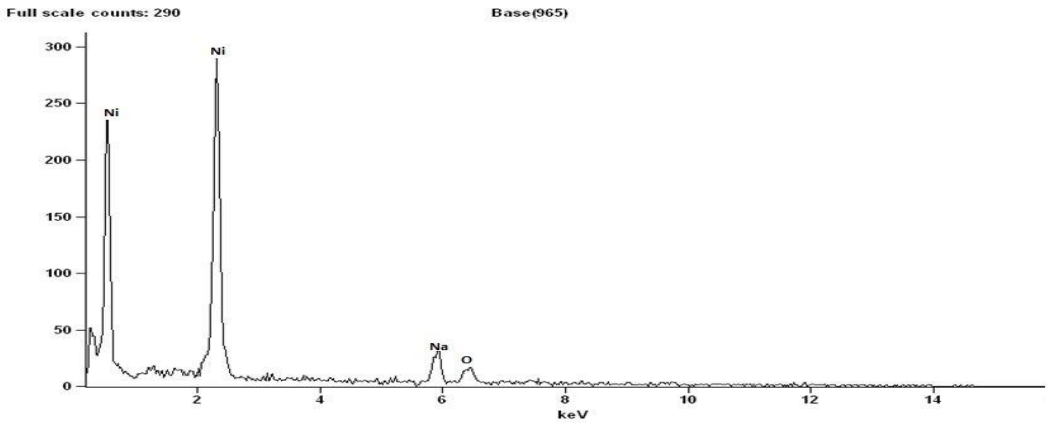


Fig-19- EDX qualitative diagram

From the above result it is clear that nano-particles prepared are more pure and don't contain much impurities as the percentage of Na and oxygen present is negligibly small.

5.1.3- XRD graph of Nickel Nano-Particle

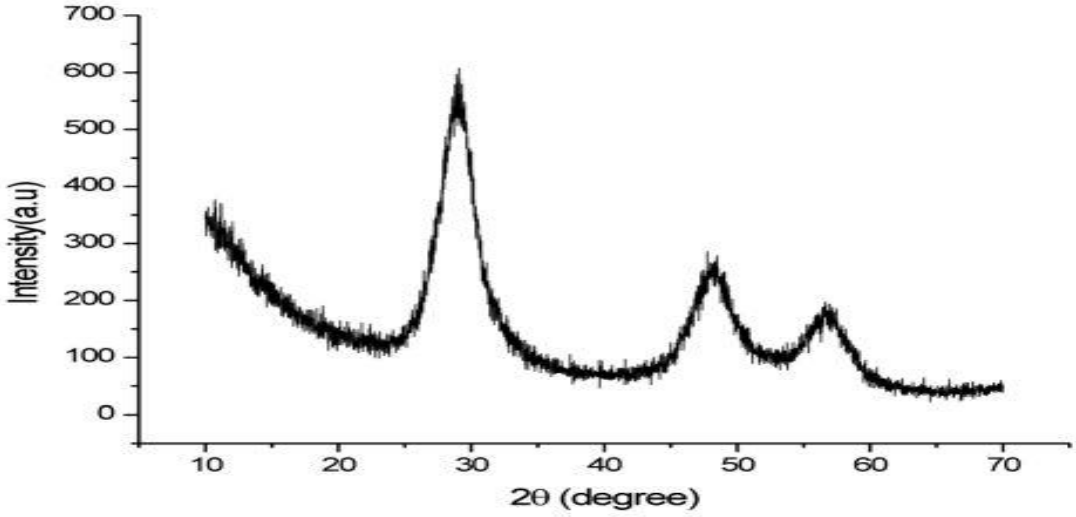


Fig-20 XRD result of Nickel Nano Particle

Plotting the XRD curve we that there are 3 peaks approximately at 30^0, 49^0 and 58^0. They are marked by corresponding miller indices of (111) , (200), (222). This shows the crystallanity of the FCC nickel nano parictle. The crystalline size is calculated by the major diffraction peak of (111) using Scherrer formula.

5.2- Characterization Zinc Nano Particle

Nickel nano particles are characterized by the SEM micrograph, EDX and XRD analysis. Their size of the particles and crystallinity is judged.

5.2.1- Scanning Electron Microscopy of Zn Nano Particle

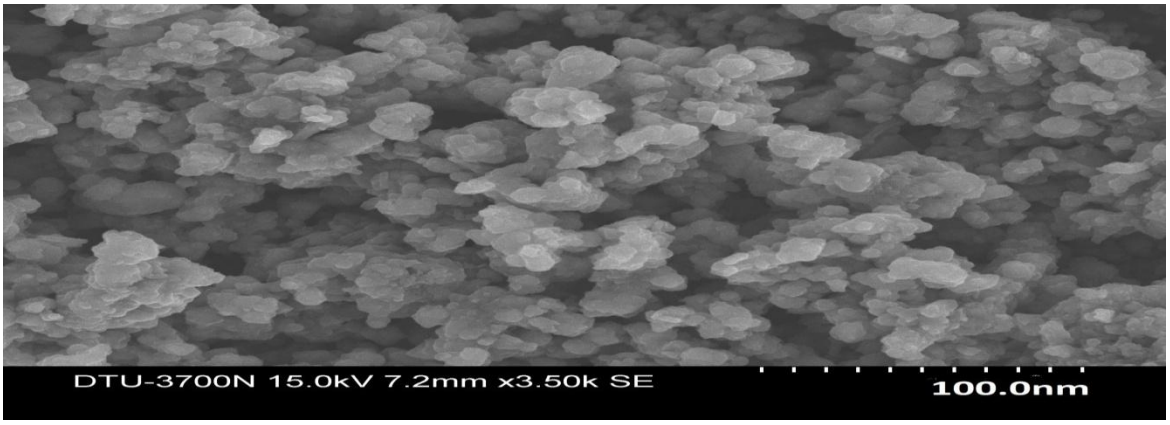


Fig-21- SEM image of Zinc nano particle

From the above result it is clear that particles of nano range have synthesized. The result is observed in 15kv and the particles are found in nano range.

5.2.2- EDX Report of Zinc Nano Particle

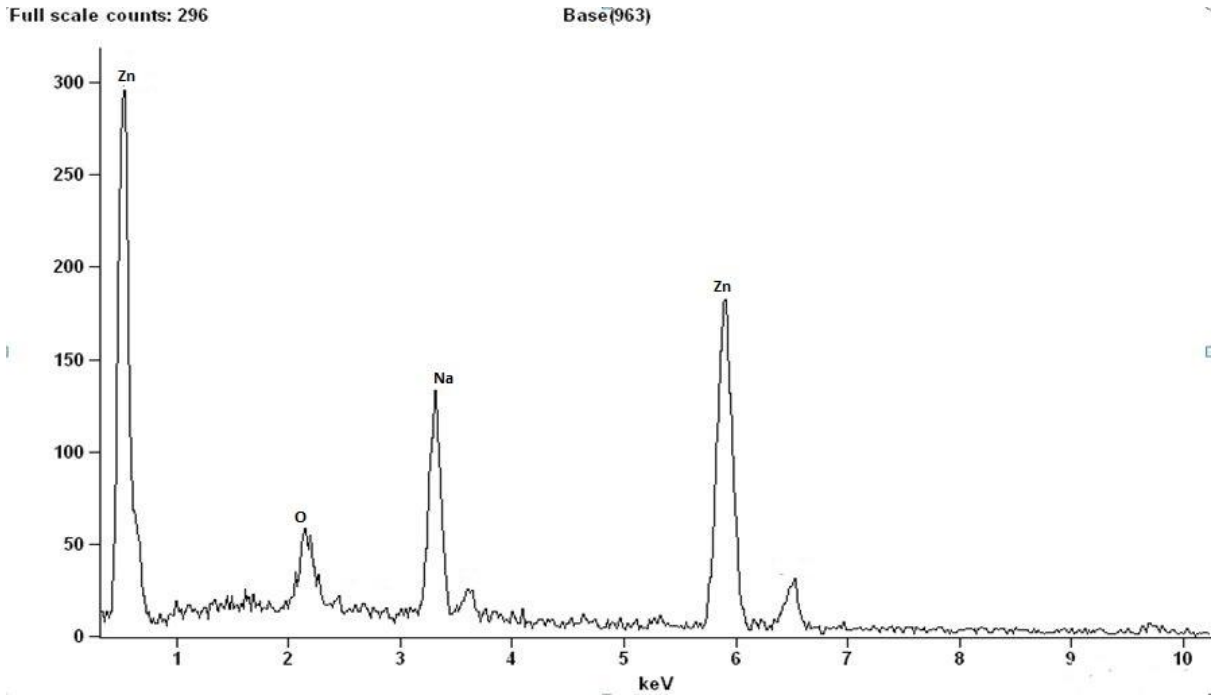


Fig-22- EDX result of Zinc nanoparticle

The qualitative result of EDX of zinc nano-particle shows that it conatins some impurities like Na, oxygen in small quantity. Thus the sample is pure with less quantity of impurities in it.

5.2.3- XRD Result of Zinc Nano-particle

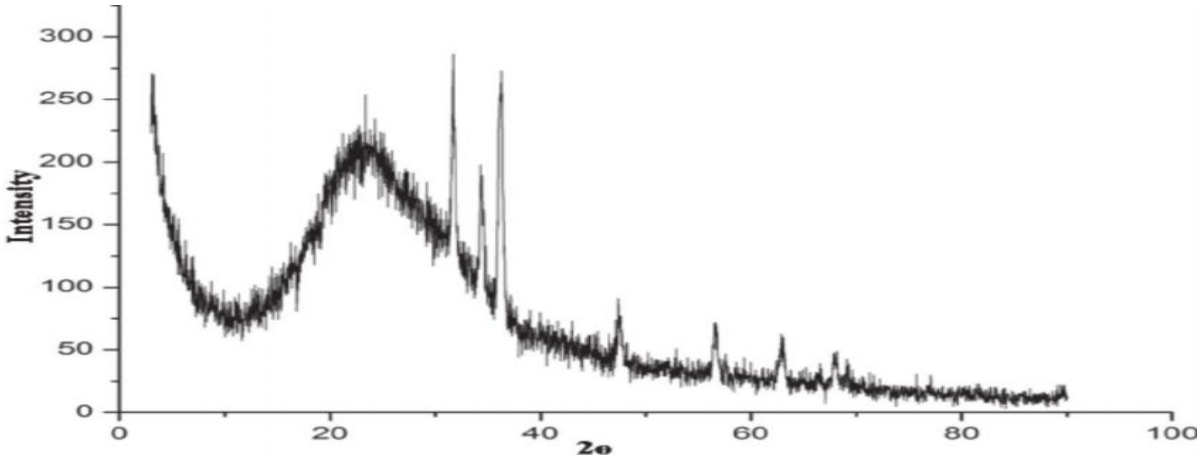


Fig-23 XRD result of Zinc Nano Particle

There are more than one peak which shows that the structure is crystalline. The peak obtained between 30^0- 40^0. Comparing this with theoretical data we calculated particle size to be $38A^0$.

5.3-Lap shear strength adhesive joint measurement using UTM

5.3.1- Lap Shear Strength of PU and Nickel Nanoparticle Adhesive

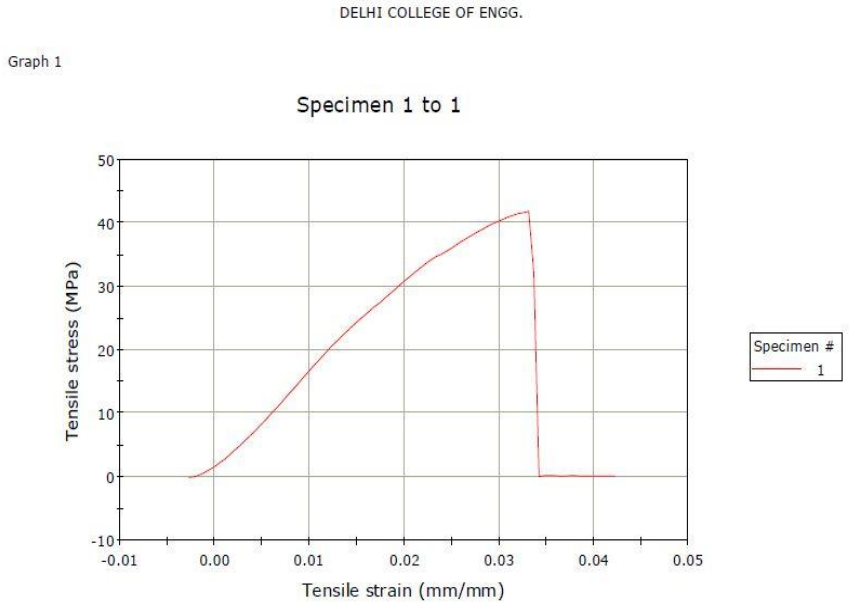


Fig-24-UTM result of Pure PU adhesive joint

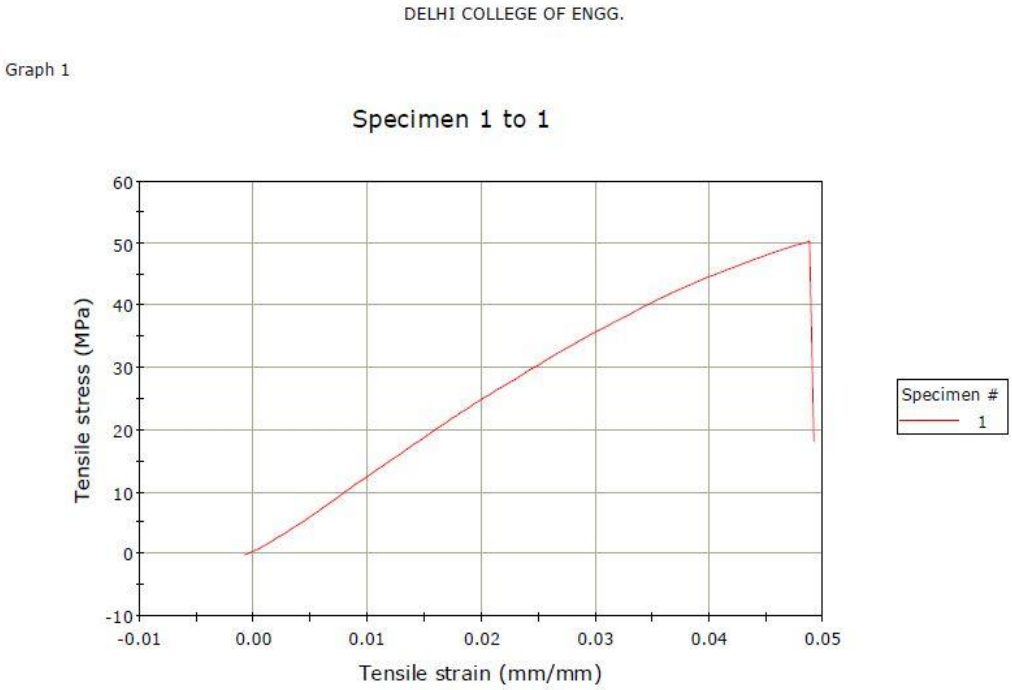


Fig-25- UTM results of PU+ 2% nickel nanoparticle

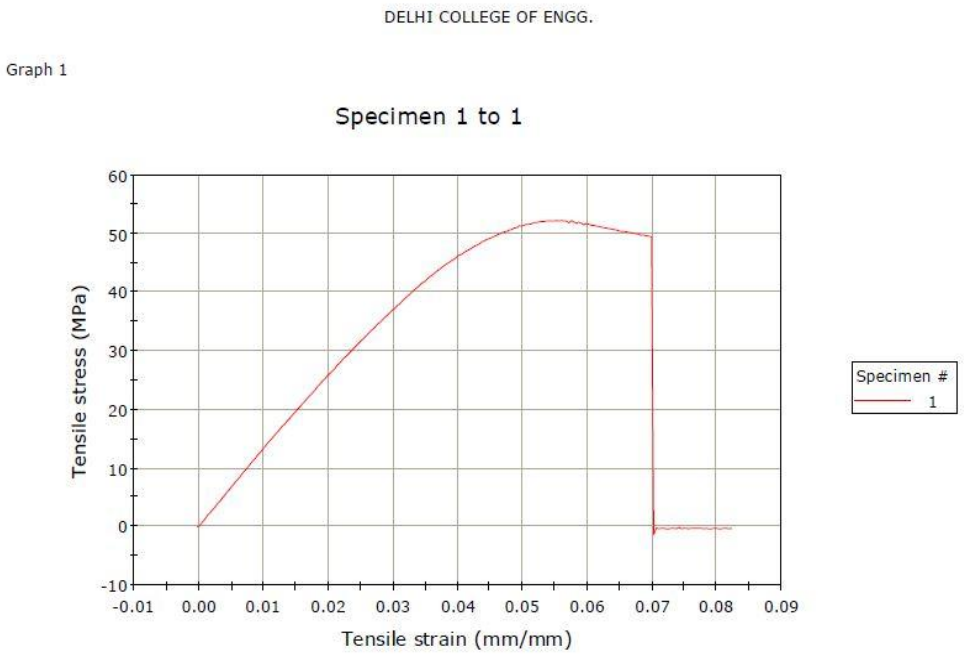


Fig-26- UTM results of PU+ 4% nickel nanoparticle

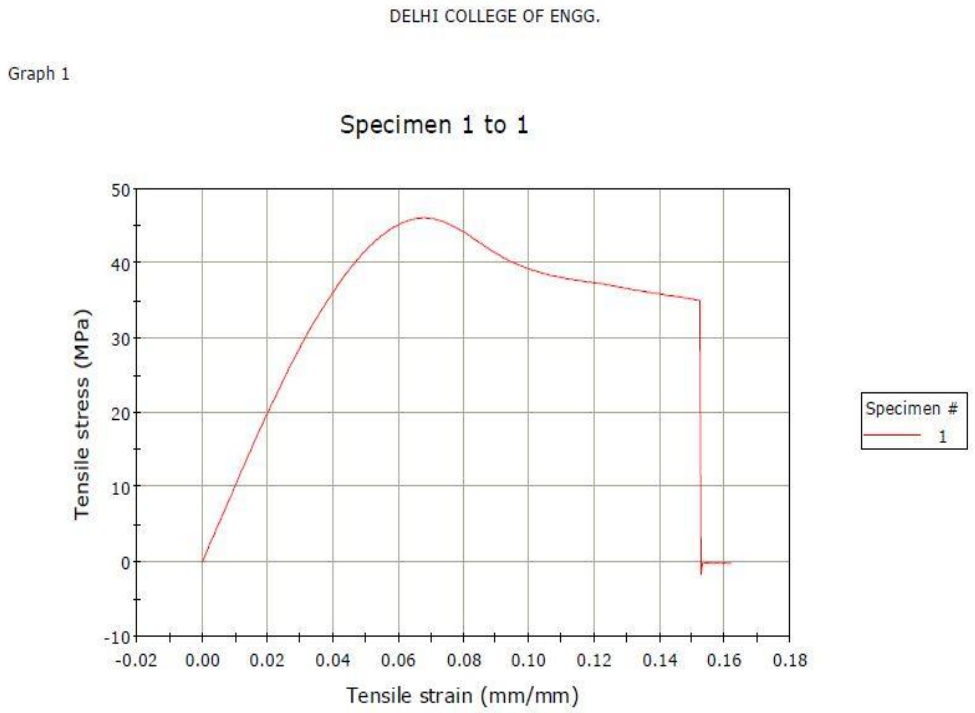


Fig-27- UTM results of PU+ 6% nickel nanoparticle

Fig-28- UTM results of PU+ 8% nickel nanoparticle

The prepared samples are subjected to tensile test using universal testing machine (UTM) and the value of lap shear strength is given in the table below.

Table-4 – Average lap shear strength of different sample

PU+%age of filler	Average Lap shear strength(MPa)
Pure PU	38
PU+2% Ni	43
PU+4% Ni	45
PU+6% Ni	46
PU+8% Ni	39

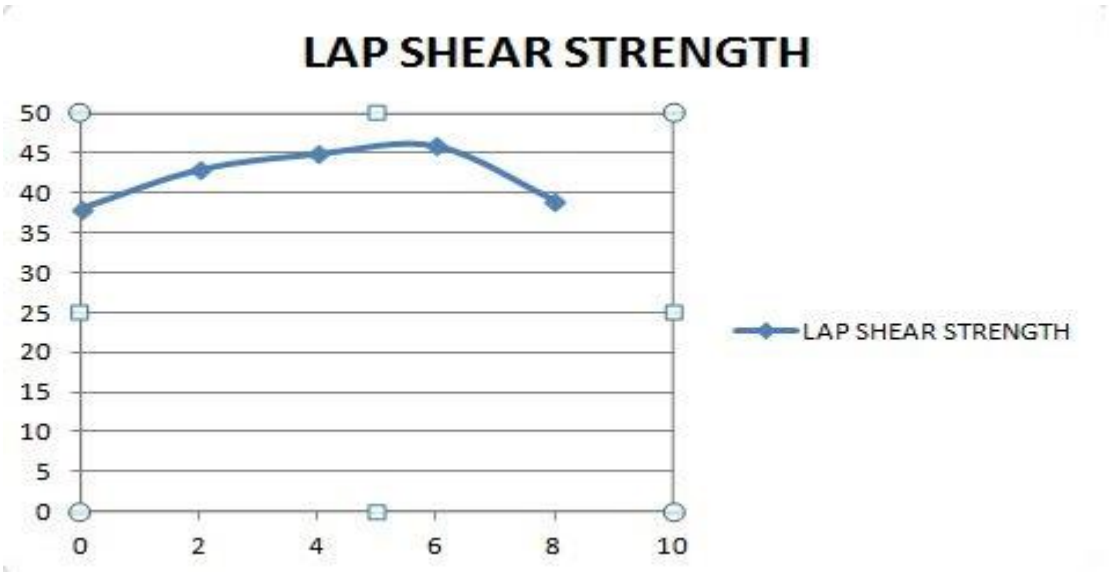


Fig-29- Average lap shear strength of adhesive

From the above it is clear that the lap shear strength has increased with increase in filler concentration from 38 MPa to 46MPa by increasing the filler concentration from 2% to 6%. With further increase to 8% the value of lap shear strength has decreased by a considerable amount. So, the optimum value of mechanical strength is obtained a 6% of filler concentration.

5.3.2 Lap Shear Strength of PU and Zinc Nano-particle filler

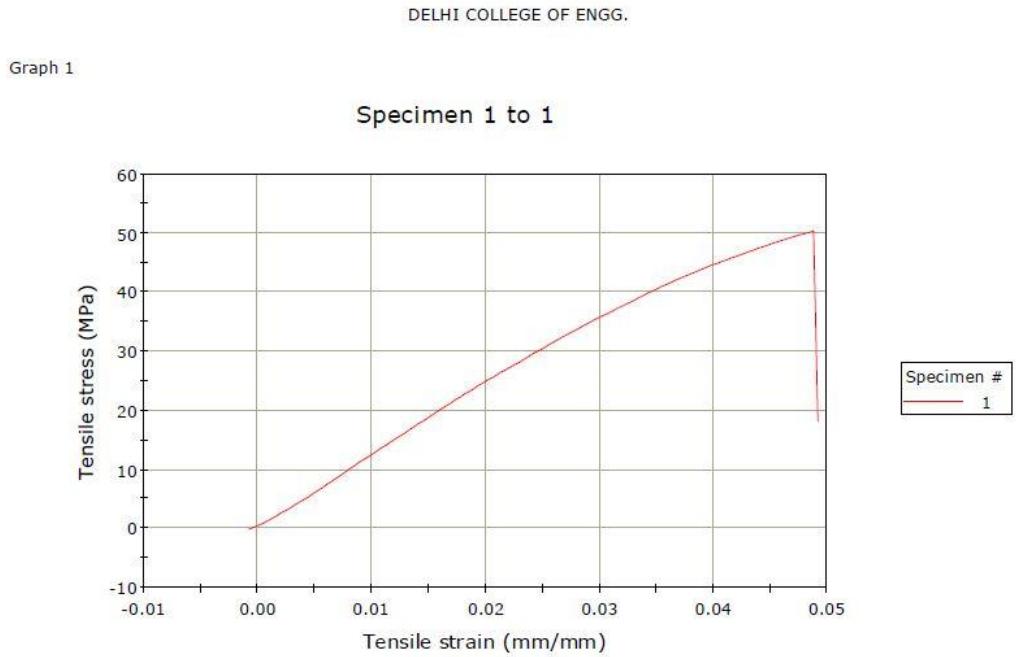


Fig-30- PU+ 2% zinc

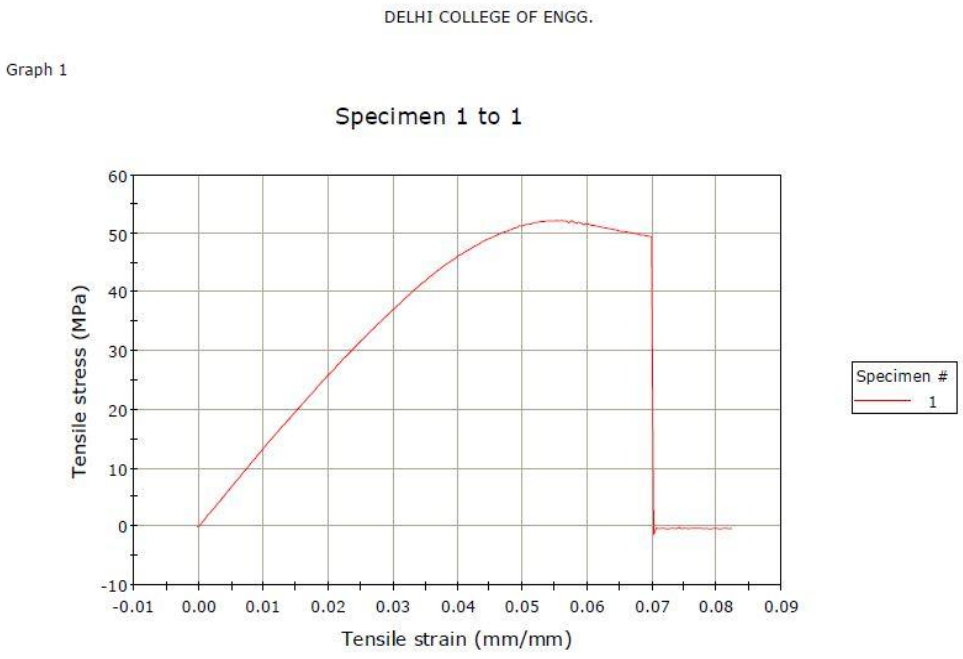


Fig-31- PU+ 4% zinc

Fig-32 -PU+ 6% zinc

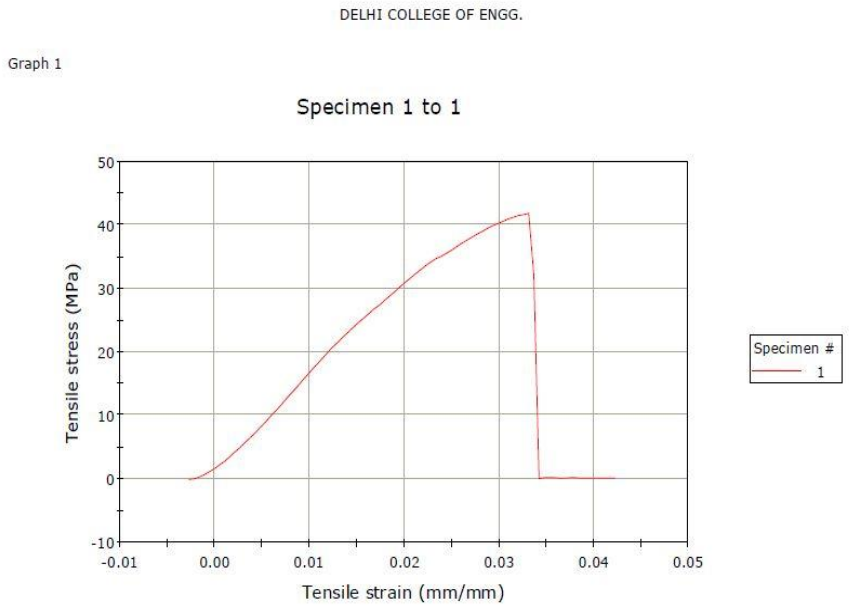


Fig-33- PU+ 8% zinc

The samples of PU and zinc nano-particles are subjected to tensile testing using universal testing machine. The values of tensile results are given in the table below .

Table-5- Average lap shear strength of different sample

PU+%age of filler	Average Lap shear strength(MPa)
Pure PU	38
PU+2% Zn	45
PU+4% Zn	48
PU+6% Zn	52
PU+8% Zn	41

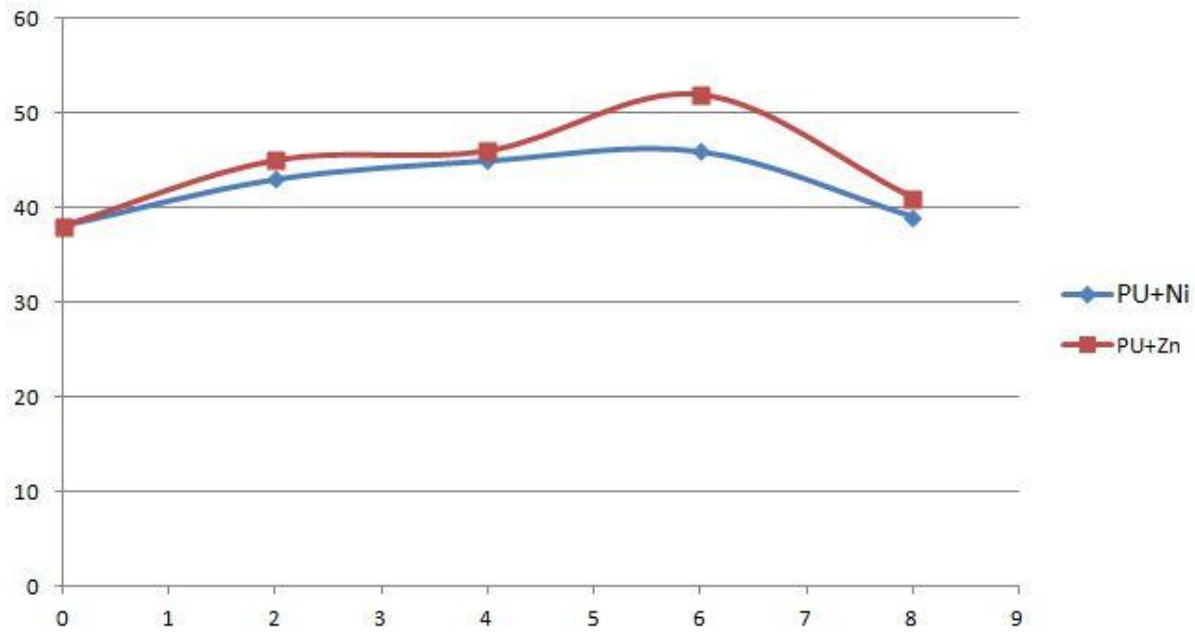


Fig-33- comparative analysis of lap shear strength

The comparative analysis of the above figure gives us that the lap shear strength of the Zn and PU adhesive increases with increase in filler concentration. The more the filler concentration the better is the strength. But after a certain value of filler concentration the strength of the resulting sample decreases. In spite of that lap shear strength of the Zinc filled PU conducting adhesive is better than that of the nickel filled PU adhesive. The decrease in value of strength after a certain filler concentration is because the more concentration obstructs the chain movement of the making the sample more rigid.

5.3.3-FTIR Result

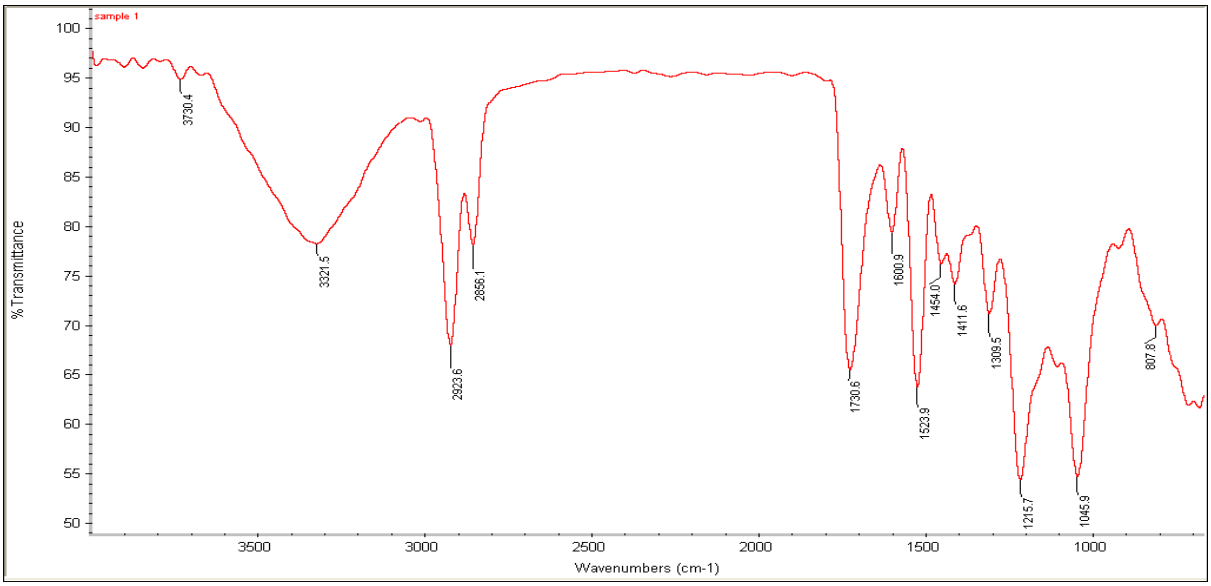


Fig-34-FTIR graph of PU

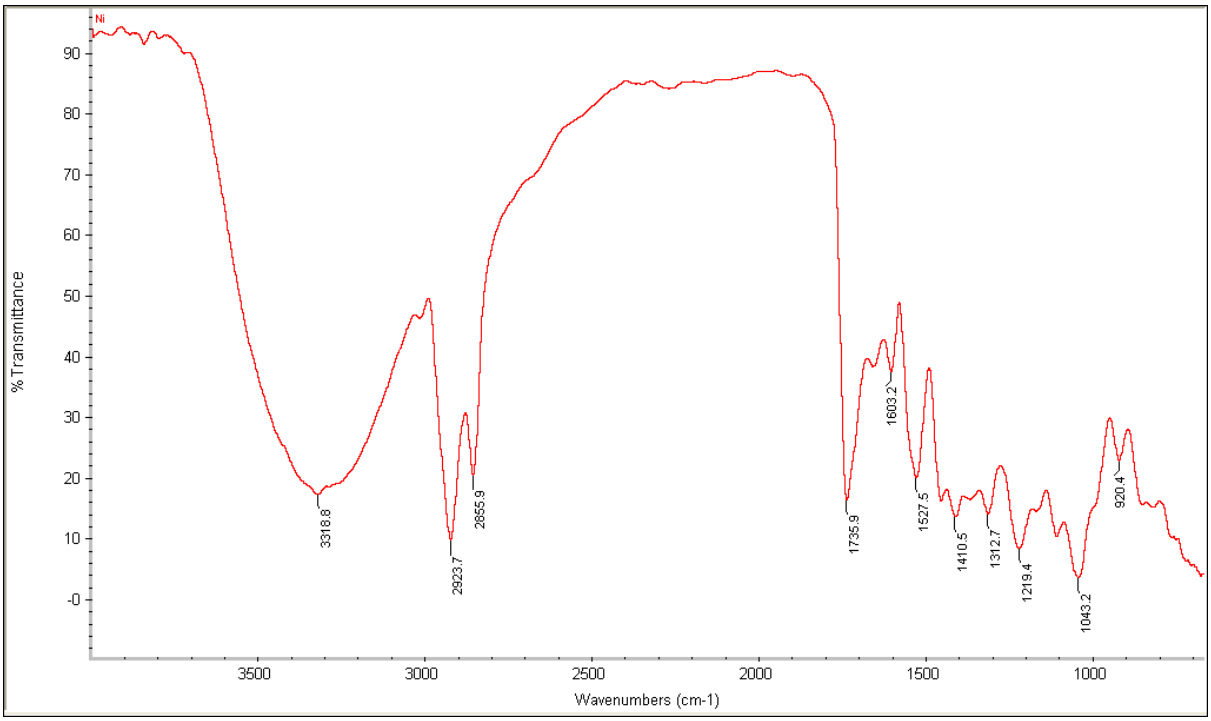


Fig-35- PU+Ni nano-particle

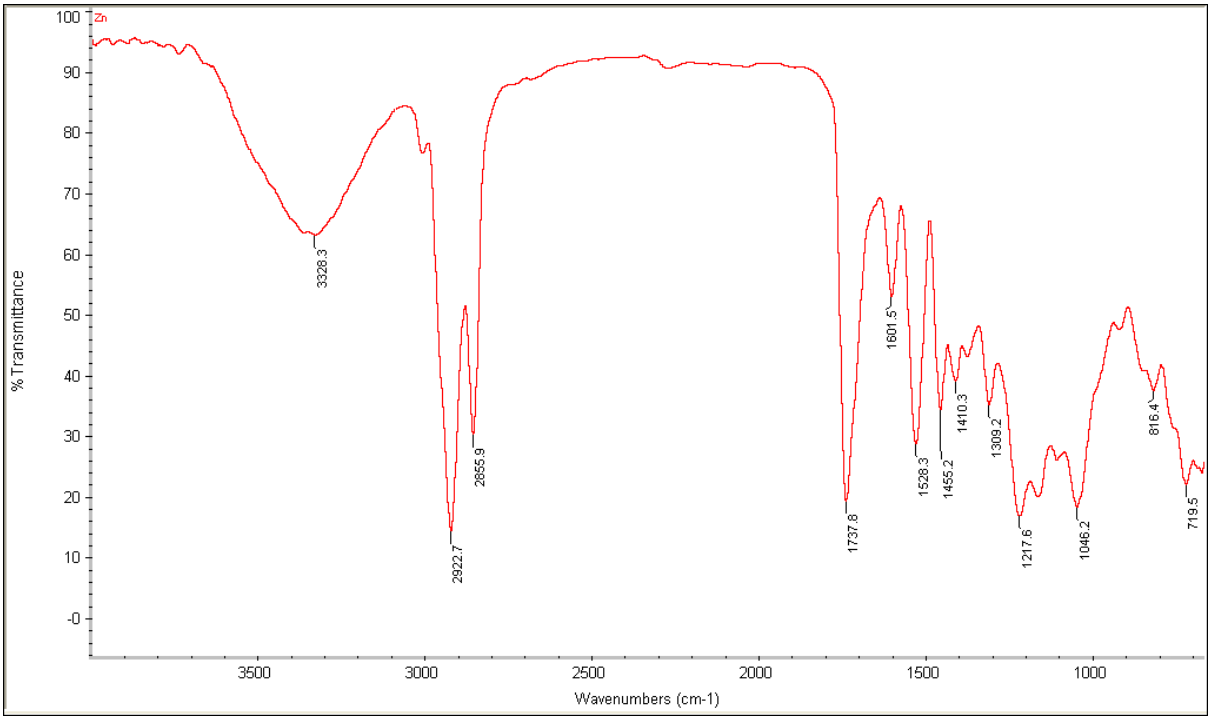


Fig-36-PU+ Zn nano particle.

IR spectra of the castor oil–based polyol and PU samples showed a broad band at 3321 cm−1 due to the OH group. IR bands at 2923.6 and 2861cm−1 are due to alkyl C-H stretching of aliphatic segment of fatty chain as discussed in previous studie. It was observed that the reaction was not taking place spontaneously after the addition of isocyanate and catalyst, but some significant changes were observed. The intensity of this signal decreased with time, but some amount of NCO remained unreacted, even after a reaction with polyol was completed (asMDI was taken in excess), which is desirable for a reaction with the hydroxyl group of substrate.

5.4.Conductivity Result

Resistivity of PU adhesive is very high= $4x10^{13}$

Conductivity of PU adhesive=$2.5x10^{-14}$

Calculation for conductivity of PU+2% nickel

V=35v I=0.001µA

V/I=$3.52x10^{10}\Omega$

$\rho_{0=}$(v/I)x2x3.14xS

S=0.2 cm

$\rho_{0 =}$ ρx(2s/w)xln2

$\rho_{0=}4.42x10^{10}$

Resistivity (ρ)= 1/ σ =$8x10^{9}\Omega$cm

Conductivity(σ)= $1.25x10^{-10}$S cm^{-1}

Calculation for conductivity of PU+4% nickel

V=19.77v I=1mA

V/I=19779Ω

$\rho_{0=}$(v/I)x2x3.14xS

S=0.2 cm w=0.05cm

$\rho_{0 =}$ ρx(2s/w)xln2

$\rho_{0=}$24843 Ωcm

Resistivity (ρ)= 1/ σ =4484Ωcm

Conductivity(σ)= $2.23x10^{-4}$S cm^{-1}

Calculation for conductivity of PU+6% nickel

V=24.2mv I=0.1A

V/I=0.2427Ω

$\rho_{0=}$(v/I)x2x3.14xS

S=0.2 cm w=0.05cm

$\rho_{0 =}$ ρx(2s/w)xln2

ρ_0=0.3034 Ωcm

Resistivity (ρ)= 1/ σ =0.0434Ωcm

Conductivity(σ)= 23S cm^{-1}

Calculation for conductivity of PU+8% nickel

V=18.16v I=1A

V/I=0.01818Ω

ρ_0=(v/I)x2x3.14xS

S=0.2 cm w=0.05cm

ρ_0 = ρx(2s/w)xln2

ρ_0=0.0228 Ωcm

Resistivity (ρ)= 1/ σ =4.132x10^{-3} Ωcm

Conductivity(σ)= 242S cm^{-1}

Tables-6- Conductivity of different Sample of nickel

Name of the Sample	Conductivity in S cm^{-1}	Character
PU	2.54x10^{-14}	Insulator
PU+ 2% Ni	1.25x10^{-10}	Insulator
PU+4% Ni	2.23x10^{-4}	Semi-conductor
PU+6% Ni	17	Conductor
PU+8% Ni	242	Conductor

Calculation for conductivity of PU+2% zinc

V=104.7v I=0.0001 µA

V/I=1.04x10^{12} Ω

ρ_0=(v/I)x2x3.14xS

S=0.2 cm w=0.05cm

ρ_0 = ρx(2s/w)xln2

ρ_0=1.31x10^{12} Ωcm

Resistivity (ρ)= 1/ σ =2.38x10^{11} Ωcm

Conductivity(σ)= 4.2x10^{-12} S cm^{-1}

Calculation for conductivity of PU+4% zinc

V=77v I=0.001 µA

V/I= 77002196 Ω

ρ_0=(v/I)x2x3.14xS

S=0.2 cm w=0.05cm

ρ_0 = ρx(2s/w)xln2

ρ_0=97022767 Ωcm

Resistivity (ρ)= 1/ σ =17513134 Ωcm

Conductivity(σ)= 5.71x10^{-8} S cm^{-1}

Calculation for conductivity of PU+6% zinc

V=2.48v I=1mA

V/I= 2484 Ω

ρ_0=(v/I)x2x3.14xS

S=0.2 cm w=0.05cm

ρ_0 = ρx(2s/w)xln2

ρ_0=3129 Ωcm

Resistivity (ρ)= 1/ σ =564.97 Ωcm

Conductivity(σ)= 1.77x10^{-3} S cm^{-1}

Calculation for conductivity of PU+8% zinc

V=0.494v I=0.1A

V/I= 4.94 Ω

ρ_0=(v/I)x2x3.14xS

S=0.2 cm w=0.05cm

ρ_0 = ρx(2s/w)xln2

ρ_0=6.22 Ωcm

Resistivity (ρ)= 1/ σ =1.123 Ωcm

Conductivity(σ)= 0.89 S cm^{-1}

Tables-7- Conductivity of different Sample of Zinc

Name of the Sample	Conductivity in S cm^{-1}	Character
PU+2%Zn	$4.2x10^{-12}$	Insulator
PU+ 4% Zn	$5.71x10^{-8}$	Insulator
PU+6% Zn	$1.77x10^{-3}$	Semi-conductor
PU+8% Zn	0.89	Conductor

From the above calculation we got the value of conductivity of various samples of nickel and zinc nano particle along with PU adhesive. The above result shows that the conductivity of nickel has enhanced considerably with increase in filler concentration. Increase in filler concentration has increased the conductivity in case of zinc but not up to the level of nickel. This proves that nickel nano particles can be used for preparation electrically conductive adhesive than that of zinc. The increase in conductivity is due to the formation of conducting path inside the non-conducting polymer matrix due to the presence of metallic nano-particle fillers. This path formed acts as the medium for flow of current making it as conductor. Reslts show that this tendency is better in case of nickel as compared to zinc. This is the reason for varied conductivity between zinc and nickel in PU adhesive.

Chapter-6

Conclusion

Conclusion

This experiment was conducted for developing a electrically conductive adhesive (ECA) using polyurethane and metallic filler of Zinc and Nickel. It is seen that the conductivity of PU was enhanced with addition of metallic filler. With the addition of nickel nano-particle filler the conductivity of resulting adhesive was enhanced considerably and it showed the property of conductor with conductivity at 8% filler concentration reaching up to 242Scm^{-1}. Where as in case of zinc nano particle filler the conductivity was not enhanced to great extent and reached to a maximum of 0.89Scm^{-1} at same 8% filler concentration. This shows that nickel nano particle is a good filler as compared to zinc nano particle. But the mechanical property data is somewhat reverse. With increase in filler concentration the mechanical property of the resulting adhesive enhanced but after filler concentration of 6% the lap shear strength of the sample started decreasing. This decrease is due to the formation of localised stress points with increase in concentration. Overall the mechanical property of Zinc sample was better than nickel samples. Considering the good conductivity property of nickel it can said that PU along with nickel is befitting to be used as electrically conductive adhesive. Its mechanical property is better than epoxy based ECA. It is also cost effective as compared to silver based ECA. Hence, nickel can be used as a viable alternative in the preparation of conducting adhesive.

Future Scope of Research

ECA is the future of coming day's electronic industry. It has the potential to replace the present day lead/tin based solder technology. But before that these ECAs need to undergo a process of rapid change. The major problem in the implementation ECA is the low conductivity as compared to solders. Thus, increasing the conductivity will be the major scope of future research in this field. Along with that its weathering property is very bad because mechanical strength decreases with presence of moisture. So, this may be the area of further research.

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