DEVELOPMENT OF CONDUCTIVE ADHESIVES: A PROSPECTIVE ALTERNATIVE FOR Sn/Pb SOLDERING

Thesis submitted to the

FACULTY OF TECHNOLOGY
UNIVERSITY OF DELHI

for the award of the degree of the

DOCTOR OF PHILOSOPHY

in

APPLIED CHEMISTRY

by

IRFAN AHMAD MIR

under the supervision of

DR. D. KUMAR
Department of Applied Chemistry,
DELHI COLLEGE OF ENGINEERING,
University of Delhi,
BAWANA ROAD, DELHI-110042

CERTIFICATE

This is to certify that the thesis titled **“Development of Conductive Adhesives: A Prospective Alternative for Sn/Pb Soldering”** submitted to the Faculty of Technology, University of Delhi, Delhi, in fulfilment of the requirements for the award of the degree of Doctor of Philosophy in Applied Chemistry embodies the original research work carried out by Mr. Irfan Ahmad Mir under my supervision and this work has not been submitted in part or full for any degree or diploma of this or any other University. It is further certified that the scholar has devoted more than two years, the minimum stipulated period, for the completion of this work.

(PROF. A. TRIVEDI)
Head,
Deptt. of Applied Sciences & Humanities,
Dean, Faculty of Technology,
University of Delhi,
Delhi

(DR. D. KUMAR)
Supervisor,
Department of Applied Chemistry,
Delhi College of Engineering,
Delhi Technological University,
Bawana Road, Delhi-110042.

بسم الله الرحمن الرحيم

Dedicated
To
the
loving Memory
of my dear mother
who couldn’t
live enough to see her
dream come
true

ACKNOWLEDGEMENT

The path towards this thesis spans several years of work and many people have been involved and contributed directly or indirectly, to only few of them it is possible to give a mention here. The author acknowledges his debt to those who have helped along the way and influenced the formation of the understanding and the approach for the research presented in this thesis.

This endeavour was accomplished only by the kind help, unparallel support and extreme patience of my supervisor Dr. D. Kumar. His good advice, unsurpassed knowledge, continued encouragement and invaluable suggestions were the guiding realms for this work. I feel honoured in expressing my gratitude to Prof. P. B. Sharma, Vice chancellor, Delhi Technological University for inspiring and facilitating this work. I must acknowledge the help of Prof. G. L. Verma, head of Applied Chemistry department, faculty members of the department, in particular Dr. Archana Rani, office and laboratory staff of the department and all the dear students who shared a special bond all through my years in the department. I owe my gratefulness to the Dean, Faculty of Technology, University of Delhi for co-operation. Thanks are also due to accounts, academic and technical staff of DCE for their help. The financial assistance of DCE and senior research fellowship of CSIR is deeply acknowledged.

From my first days in Delhi College of Engineering many people have shared so many special moments, contributing to a common story whose colourful pages now lead me towards a new chapter. I am deeply indebted to all my colleagues for providing the proper environment for research. Dr. Neetika Gupta, Dr. Shalini Sharma, Dr. Vidya Gupta, Sudha and Reetu to name a few. Amongst them all, the contribution of Tarushee Ahuja and Sapna Jain was invaluable for helping me get through the difficult times, and for all the emotional support, camaraderie, entertainment, and care they provided.

For pursuing this dream, I had the blessings of my kith and kin. My grandparents Late Haji Mohd. Qasim Mir and Late Mrs. Zoona, my parents, Mr. Mohd. Yaqoob Mir and Late Mrs. Syeda Hameeda, my sisters, Arifa and Nadiya and my brother Syed Abbas have given me their unequivocal support throughout, as always, for which my mere expression of thanks likewise does not suffice. I wish to thank my entire extended family for their wishes and support. My uncle Mr. G. M. Mir, my aunts Mrs. Maryam,Mrs. Masarat my cousins Mr. Liyaqat Ali, Ubaid and Jasiya, my niece Amma Zainab for their love, faith and belief in me. All along the way I was very fortunate to have the company of some truly worth friends. Dr. M. Irfan Beig, Zahoor Shah, Rashid Beig, Deepak Aggrawal, Rachna Chabra, Dr. S. Tafazul, Syed Nabiz and Priyanka Sareen deserve a special mention.

IRFAN AHMAD MIR

CONTENTS

Page no.

LIST OF TABLES

Page no.

LIST OF FIGURES

Page no.

Page no.

PREFACE

Electronic interconnections have been dominated by tin/lead solders since decades and they are widely used even today. However, as the environmental awareness increased the toxicity of lead has received universal attention and its overall adverse effect on human health is being closely monitored. Even small quantities of Pb can lead to damage of brain, nervous system, liver and kidneys when ingested. Disposal of electronic waste especially printed circuit boards containing lead is a major concern globally, because lead accumulation in water sources due to continued dumping of this waste is severely affecting the biosphere.

Hence, world attention has been brought towards eliminating or minimizing the use of lead in electronic interconnections. Legislation and policies have been proposed in Europe and United States to ban or limit the use of lead in solders. In July 2006, the use of several chemicals and agents was restricted in the European Union according to the RoHS (Restriction of hazardous substances) directive. Lead that is commonly used in solders was among these substances. However, such efforts haven’t yet been effective due to lack of a suitable alternative for lead based solders. Therefore, great efforts are being made to develop lead free and environmentally sound interconnect bonding technology as an alternative to tin/lead solders.

The first alternative developed is lead-free solders, which are essentially low melting temperature metals and metal alloys. In Japan & European Union, commercial industry has already acceded to lead-free solders. However, there are some marked limitations associated with this technology, which have not allowed it to flourish in the global market. The other alternative is electrically conductive adhesives (ECA’s). ECAs provide an environment friendly solution for interconnections in electronic applications. Another major reason for the interest in conductive adhesives is the requirement of increasing miniaturization and integration, which leads to smaller passive components and more complex IC components. Continuing improvement in adhesive technology has enabled ECAs to replace solder in many electronic assembly applications. ECAs offer several potential advantages over conventional solder interconnection technology including finer pitch printing, lower temperature processing and more flexible and simpler processing. Also, ECAs have greater flexibility, creep resistance and energy damping as compared to lead free solders, which can reduce the possibility of failures that occur in lead-free solder interconnections. Therefore, ECAs and among them isotropically conductive adhesives (ICA) are perceived as next generation interconnect materials for electronic packaging. However, compared to mature soldering technology, conducting adhesive technology is still in its infancy and some limitations and drawbacks do exist. Main limitations of current ICAs like limited impact resistance, unstable contact resistance and poor mechanical strength in various climatic and environmental conditions are major obstacles preventing ICAs from becoming a general replacement for solders in electronic applications. A better understanding of the properties like impact failure and loss of conductivity due to corrosion has been attributed to presence of metallic fillers in ICAs. So, there is an immediate need for replacement of these metallic fillers with some more reliable filler materials. This need has to be addressed by identifying or developing the proper materials suitable for application as fillers in ICAs.

This study identifies the already established non-metallic conductive materials as probable fillers for developing ICAs which may be used as prospective alternative to tin/lead soldering. The main objective of this dissertation is to incorporate organic conjugated conducting polymers and carbon nanotubes as fillers in an anhydride cured epoxy matrix and study the composites so formed for their use as ICAs. The optimization of filler concentration and its effect on overall properties forms the core of this research work. Incorporation of a filler phase inside the matrix decreases its impact performance. Hence proper filler loadings have to be used so that the resulting impact performance of these materials is suitable enough for them to bind the electronic components to the substrates. Currently available ICAs use metals especially silver as filler. Presence of this metallic phase inside the matrix polymeric phase leads to phase separation and hence adhesion at filler-epoxy interface is weak. This is responsible for poor impact properties of metal filled ICAs. Moreover, the filler loading in these ICAs is very high (up to 80%). Only a small portion of shear strength of polymer matrix can be retained. This study also attempts to address this limitation by incorporating organic conducting polymers inside the matrix. Since, there is an improved compatibility between the two phases, better adhesion with filler is expected. Although, CNTs show comparatively lesser compatibility, yet their effect on impact performance is substituted by their high electrical conductivity because of which very small filler loadings are needed for effective conductivity establishment. Also, metal filled ICA bound interconnections are susceptible to oxidation or corrosion due to the presence of dissimilar metals at the interface. It leads to decrease in conductivity of the joints when exposed to moist service conditions. By replacing metals with highly stable conducting polymers and CNTs, environmentally stable conductive adhesives are formed.

The overall properties of the ICAs developed are a direct function of the effective diffusion of filler particles within the matrix. If fillers are properly distributed, conductivity is established smoothly due to the formation of infinite conductive channels. Also, it leads to uniform distribution of stress under impact.

PANI synthesized by conventional chemical polymerization when used as filler and it shows difficulty in mixing due to large particle dimensions. But in case of PPy synthesized by suspension polymerization, the particle size is uniform and small. Hence, lower filler loadings produce good conductivity and the ICAs developed have better impact properties. Similarly, when nanofibres of PANI are used, conductivity improves and impact strength is enhanced. Due to good dimensional stability and small size, CNTs when used as fillers impart good conductivity and improved impact performance to ICAs. Hence, it is established that dimensions and uniformity of filler particles has an appreciable impact on the overall performance of ICAs.

CHAPTER 1

INTRODUCTION

The research work presented in this thesis is mainly focussed on the synthesis of epoxy based composites. These composites were prepared by using conducting polymers and carbon nanotubes as fillers in the epoxy matrix and explored for their utility in electronics industry as conductive adhesive. To understand their better suitability, we are presenting an introduction to the conducting polymers, epoxy and composites in the following sections of this chapter. First section gives a detailed description of organic conducting polymers.

1.1 Conducting Polymers

Conducting Polymers (CP) represent a relatively new class of materials with promising properties. This special class of polymers often referred to as '**Synthetic metals**' possess the unique electronic, electrical, magnetic & optical properties of a metal along with known advantages of conventional polymers like light weight, easy processibility, resistance to corrosion and low cost. As a result of these properties, CPs have literally taken charge as conductors with a wide range of applications, either in their innate state or in combination with other polymers as hybrid or composite materials.

A brief history

Much like the history of other complex chemicals, organic conducting polymers had their origin many years before their true identification was accomplished. Their history represents a fascinating sequence of discovery and rediscovery crowned by the 2000 Nobel Prize in chemistry. It was the year 1862, when H. Letheby from the college of London Hospital published the first report on the synthesis of a CP. He had found that oxidation of aniline in sulphuric acid resulted in the formation of a product named as '**Aniline black**' which was partially conductive. But the remarkable conducting nature of this product remained dormant for more than a century as its main use was restricted for dyeing and printing purposes. Although, a slow progress in analysis of chemical nature of CPs was going on, an appreciable breakthrough which established this field and rendered it a significant importance came only after the revolutionary discovery in 1975. It was discovered that poly (sulphur nitride) an inorganic polymeric explosive exhibited interesting electrical properties. This material not only possessed good electrical conductivity but also showed superconducting behaviour at very low temperature (0.3K). The paradigm shift began soon after when Shirakawa, MacDiarmid and Heeger in 1977 reported that polyacetylene which is the simplest polyconjugated system, can be rendered conductive by reaction with iodine or bromine vapours [1]. They achieved a remarkable enhancement in conductivity of polyacetylene by several orders, i.e., 10^5 Scm^{-1} by simple doping with oxidizing agents like I_2, A_6S_5, $NOPF_6$ (p-doping) or reducing agents (n-doping) such as sodium napthalide. Later spectroscopic studies established that this reaction is redox in nature and consists of the transformation of neutral polymer into polycarbocations by the simultaneous insertion of corresponding number of Br_3^- or I_3^- anions between the polymer chains in order to neutralize the positive charge developed on the polymer chain as a result of doping reaction [2]. This discovery triggered an extensive world-wide research devoted to effective understanding of the chemistry, physics & engineering of these conducting polymers in their neutral (undoped) and charged (doped) states. The structure and properties of many previously known polymers were reinterpreted and rediscovered. The structures of various CP families along with their conductivities are shown in **Fig. 1.1**. Also, new members of the extensive family of

CPs were synthesized. Although, the early studies in CPs focused mainly on their synthesis, characterization and transport properties, as well as on theoretical studies related to their conducting properties, but soon it became evident that this new family had a series of other very interesting properties, like those related to semiconducting nature or electrochemical behaviour.

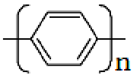
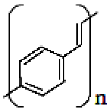
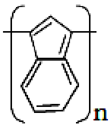
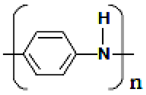
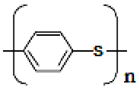
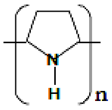
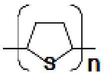
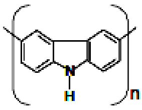
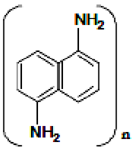
Conducting Polymer	Structure	Conductivity (S/cm)
Polyacetylene		~ 1000
Polyparaphenylene		100~ 500
Polyparaphenylene vinylene		~ 3
Polyazulene		~ 0.1
Polyaniline		1~ 100
Polyparaphenylene sulfide		1~ 100
Polypyrrole		40~ 100
Polythiophene		10 ~ 100
Polycarbazole		10 ~ 100
Polydiaminonaphthalene		10^{-3}

Figure 1.1: Structures, and conductivities of some common conducting polymers

Conduction mechanism

Since, CPs show enhanced electrical conductivity by several orders of magnitude on doping, the mechanism of conduction in such polymers is very complex. The basic conduction properties of CPs at room temperature and dependence of electrical conductivity on temperature are explained in terms of the band theory of solids. The band gap of a polymer is a measure of its ability to show intrinsic conductivity and hence band gap essentially determines, whether a thermal excitation can lead to electrical conductivity. The fraction of electrons excited across the band gap at any temperature is roughly equal to $e^{-Egap/2KT}$ (KT=0.025 eV at room temperature) [3]. Organic polymers are generally insulators because the band gap is too large. However, like semiconductors with impurities, when organic polymers are partially oxidized (p-doping) or reduced (n-doping) by means of chemical redox agents (dopants), charge carrier density increases [1]. The carrier is thermally excited from a fermi level and shifted by impurities to a conduction or valence band. But for CP with an aggregation of disordered molecules, the band structure is different and is characterized by a mobility gap, which is defined by the energy at a boundary where electrons or holes are not moving rapidly. So, the carriers in the mobility gap can only move by hopping because of strong interference by molecules. In a simple case, the carrier moves to nearby molecule and hopping increases at elevated temperatures. But at lower temperatures, the carriers cannot hop easily and they jump to a far-distant site. This is called variable range hopping [VRH].

Electronic conduction of CPs can occur by hopping or metallic conduction. The temperature dependence of electrical conductivity in poly (acetylene) with small dopant concentration complies with normal band theory and is explained by hopping and VRH. While, in poly (acetylene) with 0.1M AsF_5, conductivity decreases with increase of absolute temperature, characteristic of metallic conduction. This occurs when charge density increases by doping and the mean free path of carriers becomes larger than the mean lattice space due to expansion of the localized state.

Electronic structure of CPs

It is convenient to discuss electronic structure of poly(acetylene) (PA) to understand the electronic properties of CPs, because PA is simplest conjugated polymer and secondly, the understanding of electrical properties of CPs was triggered by the discovery of doping of PA. In its undoped form, PA possesses a semiconducting behaviour. This is attributed to the so-called peierl's distortion, wherein C-C bonds are unequal, i.e, they are alternatively shorter or longer. This non-equivalence of bonds has an important effect on electronic properties of PA as it opens a gap between the fully occupied π band (valence band) and empty π^* band (conduction band). Thus, PA can be treated as intrinsically semi-conducting with a band gap of 1.5 eV.

It has been assessed that for a polymer to support electronic conduction mere possession of charge carriers may not be enough. It should have an overlapping set of orbitals to provide reasonable carrier mobility along the polymer chain. Also, a polymer with a relatively small band gap, small ionization potential, large electron affinity and large band width, shall be relatively a better conductor.

The concept of solitons, polarons and bipolarons has been used to explain the electronic phenomenon in CPs [4]. Any irregularity in the alternation of bonds in trans-poly (acetylene) chains results in the formation of a radical which can freely move amongst the polymer chains. It is called a neutral soliton. A charged soliton can also be produced by charge injection due to the doping or optical excitation. If the electron is removed from the radical, positively charged soliton is formed. While as a negatively charged soliton gets formed if an electron is added to the radical. For these aromatic and heterocyclic polymers two types of chemical structures are depicted namely, benzenoid and quinoid, but because the quinoid structure requires a higher energy level, benzenoid structure prevails. However, when suitably doped the quinoid structure is preferred with the formation of radical ion that is called polaron.

Also, when the dopant increases and two polarons are formed on a polymer chain, they combine to form a dication, called as bipolaron as shown in **Fig. 1. 2**. A further increase in the dopant leads to the formation of a bipolaron band which finally overlaps with a valence band and a conduction band to form a degenerate band, at which point metallic conduction appears because the conduction band is partly filled, e.g., the authentic energy gap of poly (thiophene), 2.0 to 2.2 eV becomes only 0.14 eV at the nominal 100% doping. The concept of polaron and bipolarons explains how the electric charge is injected by chemical or electrochemical doping into the electroconductive polymers [1, 5].

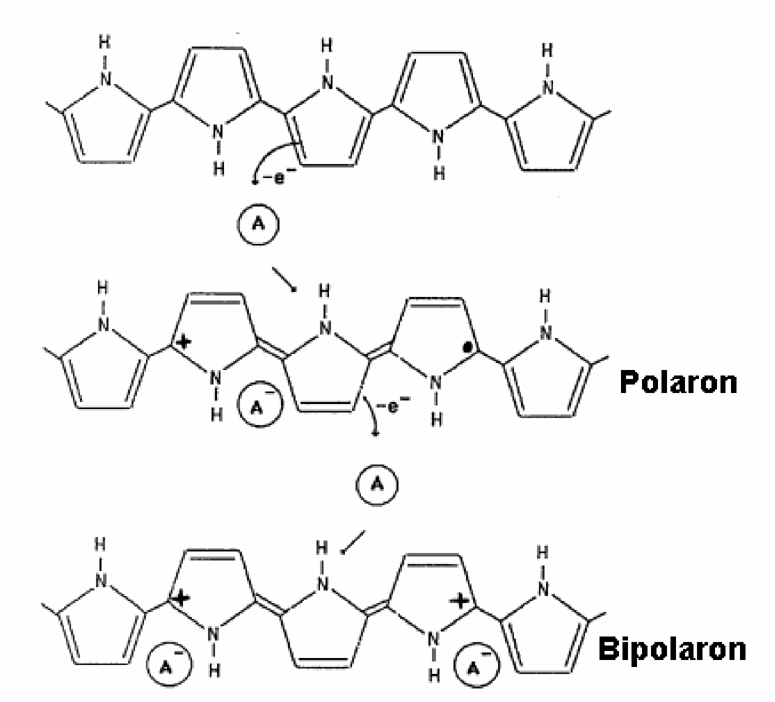


Figure 1.2. Polaron and bipolaron formation Concept of doping

CPs in their natural forms are essentially semiconducting and do not show characteristic metallic conductivity. But after the discovery that polyacetylene can be rendered highly conducting due to charge injection into molecular chains, the applications of CPs have enormously grown and the substances that accomplish this charge injection are dopants. This charge injection in CPs is referred to as doping. Doping symbolizes a very unique phenomenon associated with CPs which not only defines the main characteristic underlying their specialty but also provides CPs their unique distinct identity. Dopants or doping agents can be electron acceptors causing partial reduction (n-doping) or electron donors causing partial oxidation (p-doping) of polymer backbone. The process of doping involves the transition of an organic polymer either semi-conducting or insulator having conductivity in the range of 10^{-10} to 10^{-5} Scm^{-1} into a metal like material with conductivity of 1 to 10^{4} Scm^{-1}. This transition from an insulator or semi-conductor to metallic state has a definite reason. During n-doping, acceptor catches the electrons located on any level of valence band and as the doping progresses there is a partial void of electrons at the upper portion of a valence band. This contributes to electronic conduction as the charge carrier, and it distorts the distance between the carbon and carbon atoms of the main chain of the polymer to form a positively charged polaron. On the other hand during p-doping, electrons get injected into the lower part of the conduction band from the donor. This distorts the position of carbon atoms of the main chain of polymer and a negatively charged polaron is formed which contributes to electronic conduction. As the doping progresses, both positive and negative charged polarons may be formed giving rise to a bi-polaron. Further, progression of doping creates a state wherein these polaron states overlap each other to form a new band that shows metallic property [6].

Although, doping is accomplished by many methods, like vapour phase doping, liquid phase doping, electrochemical doping, self doping, photo-doping and ion-exchange doping etc. Among these only two, chemical and electrochemical methods are mostly used. Chemical doping involves the direct exposure of polymers to dopants either oxidants or reductants. Oxidation or reduction with proper electron donors or acceptors occurs by charge transfer mechanism. This can be illustrated by following chemical reactions [7].

p-type doping: $(\pi\text{-polymer})_n + {}^3/_2\,ny\,(I_2) \longrightarrow [(\pi\text{-polymer})^{+y}\,(I_3^-)_y]_n$

n-type doping: $(\pi\text{-polymer})_n + [\,Na^+\,(C_{10}H_8)^-\,]_y \longrightarrow [(Na^+)_y\,(\pi\text{- polymer})^{-y}]_n + (C_{10}H_8)^0$

Chemical doping is an efficient and straight forward process, wherein complete doping to achieve high charge concentrations yields reasonably high quality materials. However, it is difficult to control the degree of doping and attempts to obtain intermediate doping levels often results in inhomogeneous materials. Conductivity of several conducting polymers achieved by doping is presented in **Table 1.1**.

Table 1.1. Maximum conductivity and type of doping of some important CPs

Conducting polymer	**Maximum conductivity (Scm^{-1})**	**Type of doping**
Polyacetylene (PA)	200-1000	n, p
Polyparaphenylene (PPP)	500	n, p
Polyparaphenylene sulphide (PPS)	3-300	p
Polyparavinylene (PPV)	1-1000	p
Polypyrrole (PPy)	40-200	p
Polythiophene (PTh)	10-100	p
Polyisothionapthene (PITN)	1-50	P
Polyaniline (PANI)	5	p

Electrochemical doping on the other hand solves the problems of intermediate doping effectively. In this process, electrodes supply the charges to polymer via electron transfer reactions, whereby ions diffuse into (or out of) the polymer matrix from the nearby electrolyte to compensate the electronic charge introduced. Doping is conducted in an electrolytic cell by inserting a polymeric specimen as working electrode and a counter electrode into an electrolyte made by dissolving the dopant as ions in a suitable solvent and applying a suitable voltage between the electrodes. During doping by an acceptor, voltage is applied so that the polymer specimen has a positive electric potential. While, during doping in case of a donor, voltage is applied so that it has a negative electric potential. These reactive processes are reversible and the polymer can be de-doped by applying a reverse voltage [6]. The voltage between the polymer film and the counter electrode determines the doping level. Electrochemical doping can be illustrated by following reactions.

p-type doping: $(\pi\text{-polymer})_n + ny^{\cdot}\ [Li^+(BF_4^-)]_{soln.} \longrightarrow [(\pi\text{-polymer})^{+y}\ (BF_4^-)_y]_n - nye^-$

n-type doping: $[(\pi\text{-polymer})_n + ny^{\cdot}\ (Li^-(BF_4^-)]_{soln.} + nye^- \longrightarrow [(Li^+)_y(\pi\text{-polymer})^-]_n$

The biggest advantage of this process is centered on the property that conductivity ranging between undoped (semiconducting or insulating) and that of the polymer can be obtained simply by adjusting the level of doping [7]. Electrochemical doping of polyaniline is shown in **Fig. 1.3**.

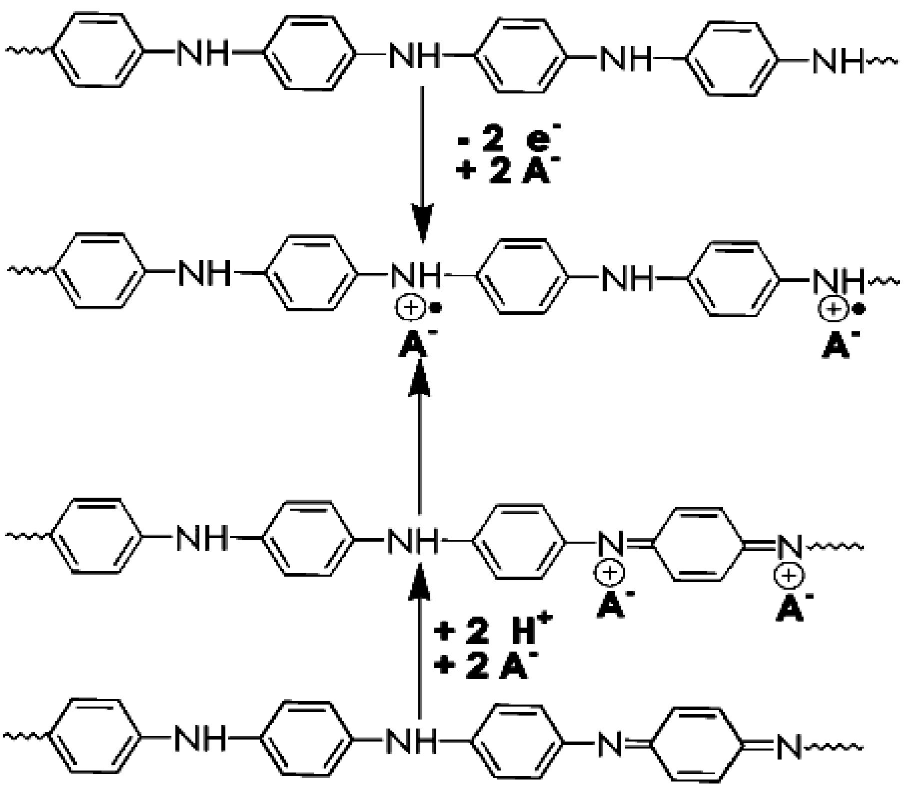


Figure 1.3. Doping of polyaniline

Synthesis of CPs

Like the enormous diversity of CPs, their modes of synthesis too show a large versatility. Their synthesis may involve typical chemical procedures like condensation and addition, oxidative coupling, co-ordination polymerization or electrochemical methods etc. The foremost essentiality although is that polymerization involves the incorporation of extended π electron conjugation. Polymerization must preserve the basic bond constitution of monomers and the scheme of conjugation must be invoked either instantly or in successive steps. Thus, a number of processes have evolved which although different by nature show a characteristic feature of transforming simple monomers into conducting polymers. The exact procedure may include typical general routes like condensation and addition polymerization, organo-metallic coupling polymerization, oxidative coupling or some specific routes like electrochemical polymerization, photochemical polymerization, metathesis polymerization, precursor route polymerization, solid state polymerization, plasma polymerization, ring opening polymerization and Langmuir-Blodgett film deposition etc. A general description of these procedures can be best explained by considering the polymerization of individual representatives or types, thereof separately and envisaging the strength of each procedure separately.

Oxidative coupling is widely used to synthesize large amounts of polymers. This process involves oxidation of monomers to cation radical and their coupling to form di-cation and their successive repetitions generates a polymer. Almost all CPs can be synthesized by this method. It is the most commonly used synthetic route for polyphenylenes, wherein oxidation of substituted and unsubstituted benzenes occurs by treatment with a lewis acid catalyst/oxidant system. Poly(p-phenylene) has been synthesized by stirring benzene, anhydrous $AlCl_3$ and anhydrous $CuCl_2$ for 2 h at temperatures ranging from 25 to 35°C [8]. It is believed that reaction involves an initial one-electron oxidation of benzene to its radical cation, followed by reaction of radical cation with several benzene molecules to give an oligomeric radical cation [9]. A second one electron oxidation followed by loss of two protons aromatizes the terminal rings, and oxidative rearomatization of the dihydro structures by $CuCl_2$ yields the polymer [10].

Similarly, polythiophenes can be obtained by oxidative coupling of thiophene (**Fig. 1.4**) or 2,2' bithiophenes with arsenic pentafluoride (AsF_5). Iron trichloride ($FeCl_3$) has been used as oxidizing agent with chloroform as solvent under anhydrous conditions for a very convenient method of polymerization of thiophene or bis-thiophene monomers [11]. The oxidative coupling of thiophenes provides materials with higher molecular weights.

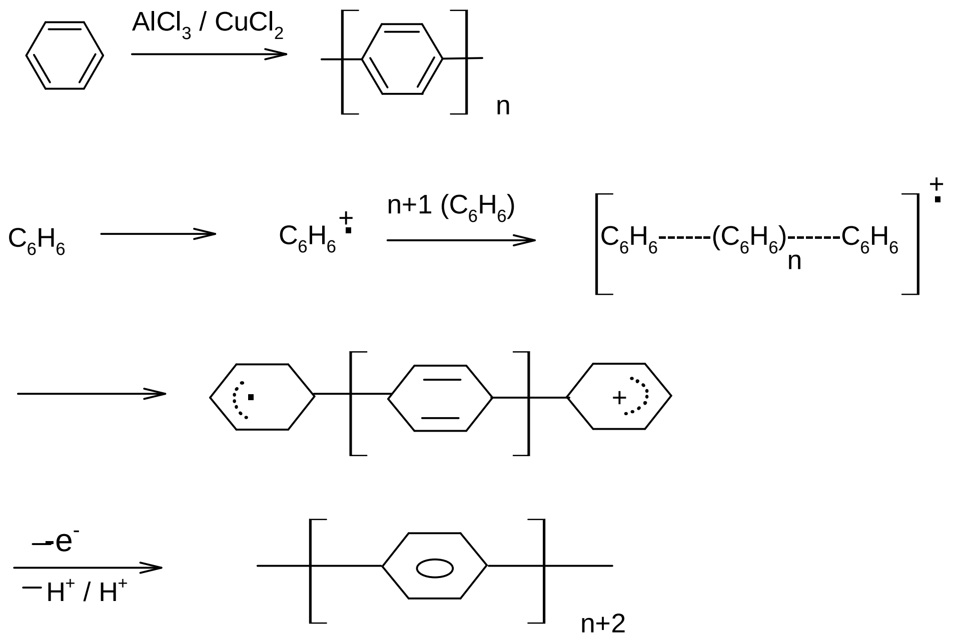


Figure 1.4. Proposed oxidative coupling mechanism to polyphenylenes

Another important technique for synthesis of CPs involves metallic or organometallic mediation. The simplest and earliest approach is the formation of polyacetylene. Polyacetylene which represents the simplest polyconjugated organic polymer was first synthesized in hexane by Natta et al as a linear, high molecular weight, polyconjugated polymer of high crystallinity and regular structure in 1958, using $Al(Et)_3/Ti(OPr)_4$ as the initiator system [12]. However, the applicational potential of this polymer was exploited only after Shirakawa and co-workers in 1970's developed a simplified approach to synthesize film samples of the polymer, which on treatment with oxidizing agents, such as halogens or AsF_5, exhibited significant conductivity [13-16]. This procedure continues to be of prime importance even today, although, precursor route reported in 1980's is gaining significant importance as well. This method reported by Edwards and Feast [17] employed an entirely different approach to the synthesis of polyacetylene by preparing a soluble, relatively stable and well characterized precursor polymer which could be converted to polyacetylene where and when required.

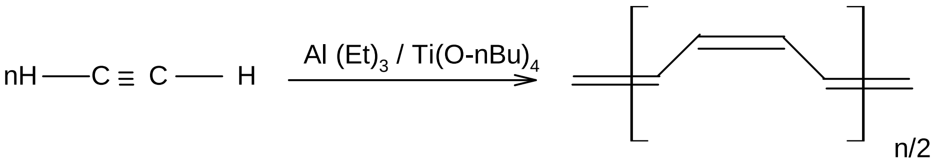


Figure 1.5. Shirakawa's route to polyacetylene synthesis

These approaches led to the formation of polymer with different morphology and relative order. Generally, polymer obtained by Shirakawa's route (**Fig. 1.5**) has a fibrillar morphology with low bulk density and variable crystallinity whereas the precursor polymer route gives continuous solid films which can be essentially amorphous, semi-crystalline or highly crystalline with an added advantage that they can be oriented by stretching during or prior to conversion.

A number of CPs have been polymerized using different organometallic compounds. Organomagnesium derivatives are most widely used in polythiophene synthesis. The reaction of 2,5-dibromo thiophene with magnesium and subsequent polymerization using a nickel catalyst was reported in 1980. The reported yield was 40-60% [18,19]. An improved yield of up to 93% was obtained by using 2,5-diiodothiophene and Ni (dppp) Cl_2 as catalyst [20]. The preparation of polyphenylenes via coupling by Grignard's reagent has been reported enormously. Grignard coupling of di-halobenzene in the presence of organometallic or organic promoters has been used for the synthesis of a range of para and meta substituted polyphenylenes [21-23].

One process that is becoming most preferred general method for synthesis of CPs is electrochemical polymerization. It comes with an advantage of being simple and has a good level of reproducibility. Added to it the process can be used to form films of different sizes depending on the size of the electrode. This procedure evolved with the preliminary attempts by Dall'olio and co-workers who prepared pyrrole black by polymerization of pyrrole monomer in aqueous sulphuric acid on a platinum electrode [24]. The setup used for electrochemical polymerization essentially has a single or dual compartment cell having a standard three electrode configuration in a typical electrochemical bath consisting of a monomer and a supporting electrolyte both dissolved in an appropriate solvent. The process can be carried out galvanostatically, i.e., at constant current, potentiostatically, i.e., at constant voltage and potential scanning/cycling or sweeping methods in a three electrode system consisting of a working electrode, counter electrode and reference electrode. The working electrode acts as a substrate for electrodeposition of polymers and has inert electrodes like Pt, Au, SnO_2, Indium Tin Oxide coated glass substrates. A counter electrode which is a foil of Pt, Au and Ni is used sometimes. Electrodeposition is performed against a reference electrode like saturated calomel electrode (SCE), Ag/AgCl electrode etc [25]. Generally, potentiostatic conditions are recommended to obtain thin films while galvanostatic conditions are recommended to obtain thick films [26]. Electrochemical synthesis can be used to prepare free standing homogenous and self doped films. Polyazulene, polythiophene, polyaniline, polycarbazole and many other polymers have been synthesized electrochemically. Electrochemical synthesis of polythiophenes has been widely used. Although, the mechanism is not fully understood, yet a general outlay proposed proceeds via coupling of two radical cations, formed by the oxidation of monomer. Aromatization of the bithiophene intermediate is the driving force for the transformation of the dihydrodimer. The dimer, having a lower oxidation potential than the monomer is readily oxidized and undergoes further coupling. The polymer is deposited in its oxidized conducting form onto the electrode, allowing the polymerization to proceed [10]. Similarly, electrochemical synthesis of PANI occurs through formation of aniline cation radical $C_6H_5NH_2^+$ through the transfer of electron from 2s energy level of nitrogen atom to the electrode. These radicals may then combine to form polyaniline.

Using this novel technique, a variety of other CPs like polypyrrole, polyphenylene oxide etc. have been synthesized. The most salient feature of this technique is that polymerization, doping and processing take place simultaneously while in conventional polymerization techniques polymer synthesis, doping and processing occur separately.

Applications of conducting polymers

The unique properties of CPs have led to a variety of applications of these materials, such as in light emitting diodes (LED), electrochromic materials, batteries, anticorrosion coatings, chemical and biosensors etc.

Ever since the first discovery of electroluminescence (EL) in semiconducting conjugated polymers, interest has grown rapidly and many polymers have been successfully used in LEDs. The polymer based LEDs are especially attractive for use in display technology. The great interest in such polymer based devices is understandable in terms of significant advantages that these systems have in possessing better mechanical properties and geometry possibilities as compared to conventional semiconductors. Another favourable aspect of the polymer LED is that it is possible to cover the spectral range from blue to near infrared, even within a single family of conductive polymers such as polythiophene. The recent demonstrations of voltage-controlled electroluminescence colours from polymer blends in LEDs as well as the possibility of obtaining polarised light from oriented polymers in LED devices, extend the possibilities of fabricating ‘exotic’ polymer devices. The conducting film consisting of ordered PEDOT ultrathin layers was investigated as a hole injection layer for organic light-emitting diodes (OLEDs). The results reported showed that, compared to conventional spin-coating PEDOT film and electrostatic self-assembly (ESA) film, the improved performance of OLEDs was obtained after using ordered PEDOT LB film as hole injection layer. It is also seen that well-ordered structure of hole injection layer was attributed to the improvement of OLED performance, leading to the increase of charged carrier mobility in hole injection layer and the recombination rate of electrons and holes in the electroluminescent layer [27].

Another important application of CPs gaining good ground these days is FET. A field effect transistor (FET) is defined as a transistor that operates by its ability to control, by use of a varying electric field the electric current flowing into a semiconductor. The electric field is varied by adjusting the electric voltage imposed on a gate electrode adjacent to the semiconductor. As a semiconductor material, p-doped poly (thiophene) produced by electrolytic polymerization, was first used for this purpose. In the poly (thiophene) FET, the poly (thiophene) membrane works as a channel layer containing positive carriers and the source drain currents, I_S, change from 100 to 1000-fold with the application of the gate voltages, V_G. However, it is not suitable for practical applications since its carrier mobility is as small as about 10^{-5} cm^2/V_S, which is five orders of magnitude smaller than that of a practically used amorphous Si thin film transistor, $100–10^{-1}$ cm^2/V_S. In order to obtain a large I_S value with a small V_G value, it is absolutely necessary to develop a semiconductor material with large carrier mobility. Research is now being undertaken to look for better electroconductive polymer materials with higher carrier mobility in order to make the switching frequency of a polymer transistor higher. Nano-conducting polymers are emerging as suitable materials for such applications [28].

The use of conducting polymers as active materials in laboratory lithium cells is more recent and begun precisely after the realization of the reversible electrochemistry of these polymers. Their lightweight and mixed conducting nature provided an opportunity to improve upon cells based on oxides and opened the possibility to develop plastic batteries. However, conducting polymers were not problem-free. Their intrinsic capacity to store charge turned out to be relatively low and some of their characteristic properties could even represent a handicap in certain cases. For instance, the insertion mechanism for p-doped conducting polymers, the most common and promising for this type of application is radically different from that of inorganic active materials. Conducting polymers are formed by oxidative polymerization and their hole doping (p) takes place with the incorporation of anions to their structure. But reduction of these materials during battery discharge takes place with the simultaneous deintercalation of those anions [29]. Flexible, aligned carbon nanotubes/CP electrodes are now used in lithium ion batteries [30]. Bilayered nanofilm electrodes made of polypyrrole (PPy) and poly-2, 5-dimercapto-1, 3, 4-thiadiazole (poly-DMcT) were produced by electrochemical means onto a carbon-fiber substrate, with the goal of preventing the loss of the electroactive mass of the disulfide and improving the electrode stability during the charge/discharge cycling process. The growth charge/mass ratio for the bilayered polymeric electrode was optimized, leading to a high electrochemical performance cathode with a stable specific capacity of about 320 mA h g^{-1} after 100 cycles [31].

Supercapacitors represent a different (and complementary) approach to the storage of charge, based on interfacial processes, and allow for higher power density but lower energy density than batteries. Originally supercapacitors harnessed double-layer charge storage on the interface between microporous carbon materials and suitable electrolytes in a purely electrophysical capacitive mechanism, but over time a new type of devices known as electrochemical supercapacitors are leading the way towards higher specific energy systems. These are based on redox active materials able to cycle repeatedly between two oxidation states and therefore represent an approximation between traditional supercapacitors and batteries. Conducting organic polymers have also been proposed and studied as active materials for electrochemical supercapacitors. Polythiophene and polyparafluorophenylthiophene PFPT have been chemically synthesized for use as active materials in supercapacitor electrodes [32]. Three types of electrically conducting polymers (ECPs), i.e., polyaniline (PANI), polypyrrole (PPy) and poly (3, 4-ethylenedioxythiophene) (PEDOT) have been tested as supercapacitor electrode materials in the form of composites with multiwalled carbon nanotubes (CNTs). The energy storage in such a type of composite combines an electrostatic attraction as well as quick faradaic processes called pseudo-capacitance [33]. Calcium carbide (CaC_2)-derived carbon (CCDC)/polyaniline composite materials were prepared by in situ chemical oxidation polymerization of an aniline solution containing well-dispersed CCDC. The results show that the CCDC/PANI composite electrodes have higher specific capacitances than the as grown CCDC electrodes and higher stability than the conducting polymers. Besides, the capacitance retention of coin supercapacitor remained 80.1% after 1000 cycles [34]. An electrosynthesis of hydrophilic polyaniline nanofiber electrode for electrochemical supercapacitor has been described. The supercapacitive performance of nanofibrous polyaniline film tested in 1 M H_2SO_4 electrolyte showed highest specific capacitance of 861 F g^{-1} at the voltage scan rate of 10 mV/s [35]. Composites of carbon nanotubes and conducting polymers have been prepared via chemical synthesis, electrochemical deposition on preformed carbon nanotube electrodes, and by electrochemical co-deposition. The composites combine the large pseudocapacitance of the conducting polymers with the fast charging/discharging double-layer capacitance and excellent mechanical properties of the carbon nanotubes. As a result they exhibit excellent electrochemical charge storage properties and fast charge/discharge switching, making them promising electrode materials for high power supercapacitors [36].

All conducting polymers are potentially electrochromic, redox switching giving rise to new optical absorption bands with simultaneous transport of electronic charge and counter ions in the polymer matrix and structural changes along the polymer backbone. Electrochromic behaviour in polymers such as polypyrrole, polyaniline or polythiophene and their derivatives has been studied deeply [37]. Polypyrrole has been extensively utilised as an electrochromic material and can be easily synthesised chemically or electrochemically with a varying range of optoelectronic properties available through alkyl and alkoxy substitution. Thin films of neat polypyrrole are yellow in the undoped insulating state and black in the doped conductive state. Polyaniline films are electrochromic materials which exhibit switching among yellow–green–dark blue and black colours, although the better cyclability and stability has been observed between yellow and green. The mechanism responsible for the colour changes involve protonation/deprotonation and/or anion ingress/egress processes. Thin films of neat polythiophene are blue in the doped (oxidised) state and red in the undoped form. A great deal of research has been focused on the synthesis of 3-alkylthiophene derivatives which exhibit a lower oxidation potential than the parent polythiophene. However, the main breakthrough in the development of electrochromic conducting polymers was the synthesis of poly(3,4-ethylenedioxythiophene) (PEDOT) due to superior stability and cyclability. PEDOT exhibits a dark-blue colouration in its neutral state and a sky-blue colour in its doped state giving a high optical contrast which has attracted much attention in the field of electrochromism as an active material for electrochromic devices [38]. *N*-ethyl substituted poly(3,4-ethylenedioxypyrrole), a new electrochromic polymer, has been produced and its spectroelectrochemical properties have been investigated. This material displays multicolour electrochromism, switching between green, violet, and grey. Three different electrochromic devices have been laminated and evaluated using the electrochromic polymer, an ion-conducting polymer electrolyte, and one of the following counter electrodes: tungsten oxide, polyaniline, or poly-di-methyl-(3,4-propylenedioxythiophene) [39]. Terepthalic acid bis-(2-thiophen-3-yl-ethyl) ester (TATE) was achieved via esterification reaction of 2-thiophen-3-yl-ethanol and terepthaloyl chloride. Electropolymerisation of TATE and its copolymer with thiophene were prepared and studied for their electrochromic properties by Yelda et al [40].

Corrosion is deterioration of essential properties in a material due to reactions with its environment. Electrochemically-active polymer coatings, such as those formed by polyaniline, enable certain active-passive metals to become more resistant to oxidation, apparently by enhancing their native passivity. Polyaniline applied in the emeraldine state is reduced by substrate metal to leucoemeraldine state; reaction of leucoemeraldine with air restores the polymer's emeraldine oxidation state. Oxidation-reduction chemistry between substrate metal and polyaniline results in a nobler, better passivated metal surface [41]. Numerous reports are now available that describe the positive effect of conducting polymer coatings on the corrosion resistance of stainless steel, mild steel and aluminium [42-48]. A recent study of chaudhari et al offers an electrochemical polymerization recipe to synthesize strongly adherent poly (o-anisidine) coating on copper from aqueous media for possible use in corrosion protection application [49]. A ter-polymer film of pyrrole, *o*-anisidine and *o*-toluidine has been electrochemically synthesized on low carbon steel. This highly stable and extremely thin (0.80 μm) film can find application for various purposes where the stability of polypyrrole like films constitutes a drawback [50]. Kaushik et al reported coatings of polythiophene on mild steel as corrosion protection materials [51]. Polyaniline coating doped with dodecylbenzesulfonate anions was electrodeposited galvanostatically on type 304 stainless steel used as bipolar plates of proton-exchange membrane fuel cell. The studies show polyaniline coating increases the free corrosion potential of the steel by more than 300 mV and 450 mV, respectively, with a corrosion rate more than two orders of magnitude lower than that of the uncoated steel [52]. Application of polythiophene derivatives as anticorrosive additive in paints has also been reported [53, 54].

In recent years there has been a surge of interest for use of CPs for sensing applications. CPs have a unique property of efficiently transferring charge produced by biochemical reactions to electric circuits. In addition to that they can be easily deposited over defined areas of electrode. These advantages have made them the most interesting entrapment materials for biosensors. There are numerous reports reviewing their extensive use in biosensors [2, 55-62]. The progress in this field has been sharp and current focus is towards identifying new analytes, enhancing sensing properties, improving usability and decreasing costs. Nowadays, functionalized conducting polymer nanomaterials have received great attention in nanoscience and nanotechnology because of their large surface area [57, 63-66]. An ascorbic acid sensor was fabricated via the drop-casting of dodecylbenzene sulphonic acid (DBSA)-

doped polyaniline nanoparticles onto a screen-printed carbon-paste electrode. The sensor showed good selectivity and sensitivity in that it did not respond to a range of common interferents such as dopamine, acetaminophen, uric acid and citric acid, but was capable of the detection of ascorbic acid at a sensitivity of 0.76 μA mM^{-1} or 10.75 μA mM^{-1} cm^{-2} across a range from 0.5 to 8 mM ($r^2 = 0.996$, $n = 6$), and a limit of detection of 8.3 μM (S/N = 3). The sensor was compared to a range of other conducting polymer-based ascorbate sensors and found to be comparable or superior in terms of analytical performance [67]. A rapid and efficient strategy to detect novel heat shock protein 90 (Hsp90) inhibitors as anti-cancer agents has been recently developed with field-effect transistor (FET) sensor based on carboxylated polypyrrole nanotubes (CPNTs). The CPNTs were covalently immobilized onto the microelectrode substrate to maintain stable electrical contact between the CPNTs and the microelectrodes in the liquid phase. Subsequently, Hsp90 was attached to the CPNTs surface through condensation reactions between the terminal amino groups in Hsp90 amino acid residues and the carboxyl groups on the CPNTs. The Hsp90-conjugated CPNT FET sensor provided a convenient and sensitive method to observe the affinity between Hsp90 to Hsp90 inhibitors in real-time. This result suggests that the FET sensor will open up the potential application for new anti-cancer drug discovery (Hsp90 inhibitors) after a judicious optimization [68].

There are numerous other applications reported like that in fuel cells [69, 70], heavy metal removal from aqueous solutions [71, 72], biomedical application [73, 74], film industry [75], controlled dye release [76], controlled drug release [77], and more importantly conductive adhesive etc.

1.2. Conductive Adhesives

New interconnect materials are always necessary as a result of evolving packaging technologies and increasing performance and environmental demands on electronic systems. In particular, conductive adhesives have gained popularity as a potential replacement for solder interconnects. The interest in using conductive adhesives instead of solder, comes partly from the fact that interconnects can be formed at low temperatures, and partly from the interest in eliminating lead from electronic interconnections.

Electrically conductive adhesives (ECAs) are composite materials consisting of solid conductive fillers dispersed in a non-conductive matrix. The polymer matrix provides the mechanical adhesion while the conductive fillers provides for electrical conduction by forming a network connecting to each other in the polymer matrix. ECAs are gaining a lot of interest as potential soldering replacement materials. Packaging of electronic circuits has been dominated by lead based soldering technology since decades and even nowadays, a large majority of integrated circuits are mounted on circuit boards using Sn-Pb soldering. A schematic illustration of bonding between the component and the substrate material is given below in **Fig. 1.6**.

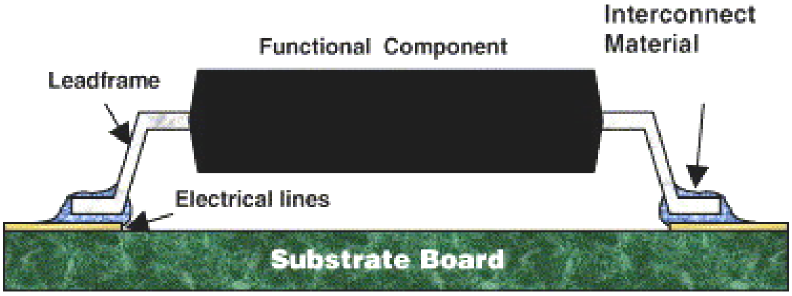


Figure 1.6. Schematic illustration of side view of bonding between the component and the substrate via interconnect material

However, as the environmental awareness increased, the toxicity of lead has received universal attention and its overall adverse effect on human health is being closely monitored. Even small quantities of lead can lead to damage of brain, nervous system, liver and kidneys when ingested [78]. Disposal of printed circuit boards (PCB's) containing lead leads to lead accumulation in water sources and can affect the biosphere.

Hence, the pressure to eliminate or minimize the use of lead in electronic interconnections is growing. Legislation and policies have been proposed in Europe to ban or limit the use of lead in solders, and the United States is likely to follow the trend [79, 80]. Therefore, great efforts have been made to develop lead free and environmentally sound interconnect bonding technology as an alternative to Sn/Pb solders. The first alternative was the use of lead free low melting temperature metals and metal alloys for soldering. It was effective in some applications but some limitations still exist in lead free solder technology, including the relatively high cost or limited availability of some candidate metals, and the requirement for relatively high soldering temperature for some metals and metal alloys. Also, joint embrittlement and fatigue are serious concerns when compared with Sn/Pb soldering. Solder joints by lead free solders have been found to become brittle after reflow and temperature cycling induces fatigue cracks which causes solder joint failure [81, 82].

The other alternative is ECA. As compared to traditional Sn/Pb soldering, ECAs possess certain distinct advantages as:

- They offer an environment friendly alternative to solders as these are lead-free
- Since no flux is used in ICAs, therefore the environment polluting chlorofluorocarbon solvents used to clean the flux are eliminated

- They involve low processing temperature as compared to conventional soldering which involves high temperature (>200ºC)
- They have a low thermo-mechanical fatigue
- They can be used on a wide range of surfaces (including ceramics, glass and other non-solderable surfaces).
- They can be utilized for finer pitch applications like screen printing of PCBs etc
- ICAs have the benefit for shorter and quicker assembly times, since it involves fewer processing steps
- ICAs are essentially low cost as the volume of material used is greatly reduced

A schematic representation showing comparison in using soldering and ECA for surface mount application is shown in **Fig. 1.7**, while the comparison between characteristics of the two interconnect technologies is presented in **Table 1.2**.

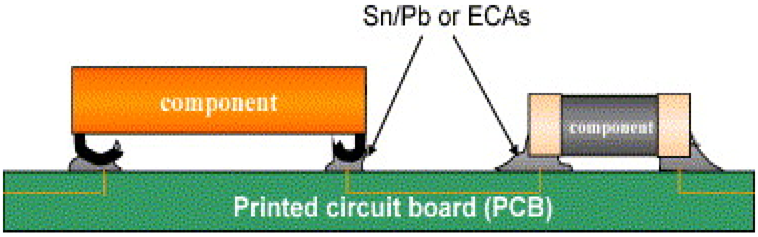


Figure 1.7. A Schematic structure of surface mount interconnection.

Table 1.2. Comparative characteristics of Sn/Pb solder and ECA.

Characteristics	**Sn/Pb solder**	**ECA**
Volume resistivity (Ω cm)	0.000015	0.00035
Typical junction R (mW)	10–15	<25
Thermal conductivity (W/m K)	30	3.5
Shear strength (psi)	2200	2000
Finest pitch (mil)	12	<6–8
Minimum processing temperature (°C)	215	150–170
Environmental impact	Negative	Very minor
Thermal fatigue	Yes	Minimal

In addition, compared to lead free solders, conductive adhesive systems exhibit greater flexibility, creep resistance and energy damping, which can reduce the possibility of failures that occur in lead free solder interconnections [83].

Despite all these advantages, ECAs are believed not to be a complete drop-in replacement for soldering, at least in the near future. This being a relatively new technology comes with some limitations and shortcomings. Lower electrical conductivity than solders, poor impact resistance, and long term electrical and mechanical stability are some critical concerns that have limited wider applications of electrically conductive adhesive technology. Numerous studies are conducted worldwide to have a better understanding of the mechanism underlying these problems and to improve the performance of ECAs for electronic applications.

Types of electrically conductive adhesives

ECAs have been mainly divided into two groups depending on the direction of conduction, i.e., anisotropic and isotropic ECAs. Anisotropically conductive adhesives (ACAs) have a property of allowing current to flow uni-directionally, i.e., along one axis only. 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 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 with heat and pressure simultaneously applied to this assembly until the particles bridge the two adherends. Once the electrical continuity is produced, the polymer binder is hardened by thermal curing in case of thermosets or by cooling in case of thermoplastics [84]. 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 [85].

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.

Isotropically conductive adhesives (ICAs) offer non-directional or all-directional conductivity by incorporating higher filler concentrations. 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 found 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. Some of the applications of ICAs in electronic interconnection are shown in **Fig. 1.8.**

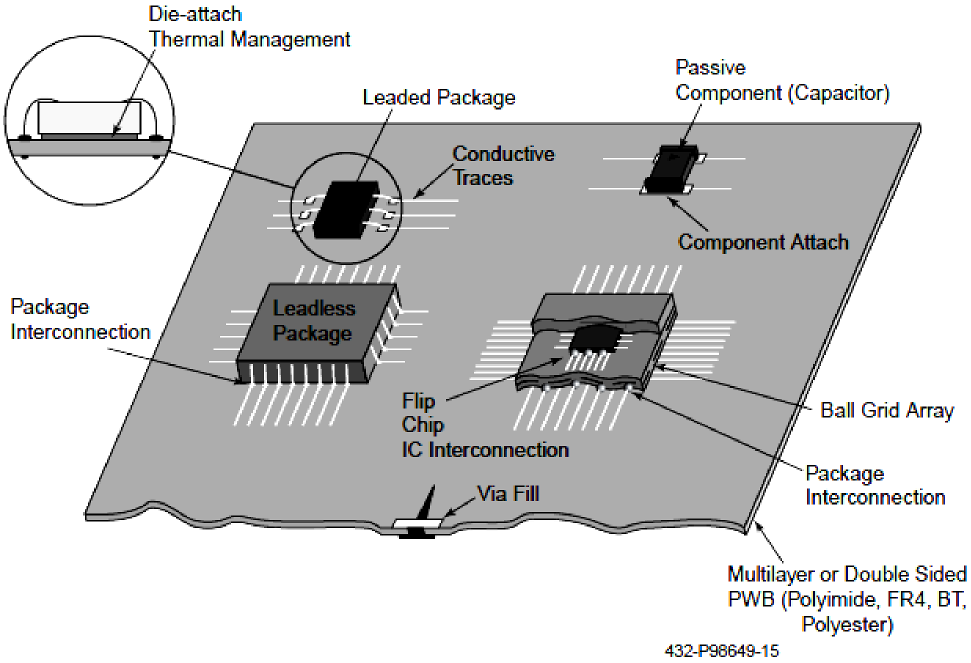


Figure 1.8. Applications of ICAs in electronic interconnections

ICAs are often called '**polymer solders**' [86]. 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 Sn/Pb solders in surface mount technology (SMT) applications [87-89]. Many papers in literature have reported the ICA development, discussed the benefits and drawbacks of ICAs, compared them to traditional Sn/Pb solders [90-92] and highlighted the main technological applications of ICAs. As an alternative to solder technology, ICA technology has to overcome the limitations it poses. In recent years, there has been a lot of research going 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. The main focus of these studies is on reliability properties like resistance stability and adhesion shear tests [93], humidity effects [94] and other thermal properties [88, 95], usually with comparison to solder properties and environmental friendly manufacturing process [96]. These efforts to modify designs and formulations have culminated into ICAs with improved electrical conductivity, contact resistance stability and better impact strength. Different aspects of ICAs have been presented in depth in the following sections.

Matrix and filler materials in ICAs

Matrix polymers

ICAs are essentially composites containing a polymer binder that provides for the mechanical strength and conductive fillers which offer conduction. Matrix polymers can be either thermoplastics, which can be moulded or softened by application of heat, or thermosets that cannot be melted or re-shaped once cured. Thermoplastic matrix based adhesives have the important advantage that they can be processed rapidly and are easy to rework. No chemical reaction takes place during application process and heat applied is used to cause physical change typically the transition from solid state to flowable phase. These materials have good reworkability and offer short bonding process. Since these materials soften due to temperature and tend to flow during application of force, they have limited applications. Thermosetting matrix essentially undergoes chemical reaction and takes a definite time to process. However, these materials resist deformation even under high temperature and have much more mechanical strength as compared to thermoplastics. Robust thermosets are the preferred choice for matrix material worldwide and show a lot of resistance to heat, moisture, and mechanical stress. Many thermosets require little or no solvent which is preferred from an environmental point of view and also prevents formation of solvent bubbles and voids during curing.

Thermosetting epoxy resins have been used as the polymeric matrix since the early 1950’s and are by far the most common adhesive binders. Epoxy based materials have been widely used in engineering components because of their outstanding mechanical and thermal properties as well as processability. 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 [97-100]. They also have good resistance to moisture, solvents and chemical attacks [101]. Their desirable properties may further be improved with suitable choice of solvents, fillers, colorants, flame retardants, plasticizers, curing agents and accelerators [102].

D. Lu et al [103] described the development of novel conductive adhesives for surface mount applications. 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. Michael Lantzsch [104] studied different epoxy adhesives with soldering properties and listed the advantages of using epoxy tacky flux. Similarly, O. Figovsky et al [105] reported the development of novel one part fast-curing epoxy adhesives. The influence of various amine hardeners on gelation time, heat resistance and shelf life at room temperature was investigated.

Generally, ICA formulations include epoxy resin as the polymeric matrix. S. Liong et al recently reported a thermoplastic ICA matrix called polyarylene ether which has low moisture absorption [106]. More recently, a new class of conductive adhesives which is based on epoxide-terminated polyurethane (ETPU) has been developed [107]. This class of conductive adhesives has the properties of polyurethane materials such as high toughness and good adhesion. Yang et al presented their study on a new kind of flexible ICA material which is suitable for printing RFID tag antennas. It is a polyurethane (PU) based ICA for printing RFID tag antennas. Due to the well known excellent mechanical performance of the PU based dispersant, this PU based ICAs exhibited much better flexibility [108]. Haiyung Li et al [109] published a paper about a liquid diepoxide re-workable epoxy resin for ICAs. This material had good mechanical properties, low moisture uptake, and a low decomposition temperature which allows the components to be detached without damaging the board and its surroundings. Similarly, a multifunctional epoxy resin was used as matrix for producing heat resistant ICAs [110].

Fillers

ICAs are currently available as metal filled composites. The most important criteria for selection of filler are conductivity and stability while retaining the mechanical properties of the matrix polymers. Some of the commonly used fillers in ICAs include silver, nickel etc. A schematic representation of ICA joint showing conductive filler is given in **Fig. 1.9** below.

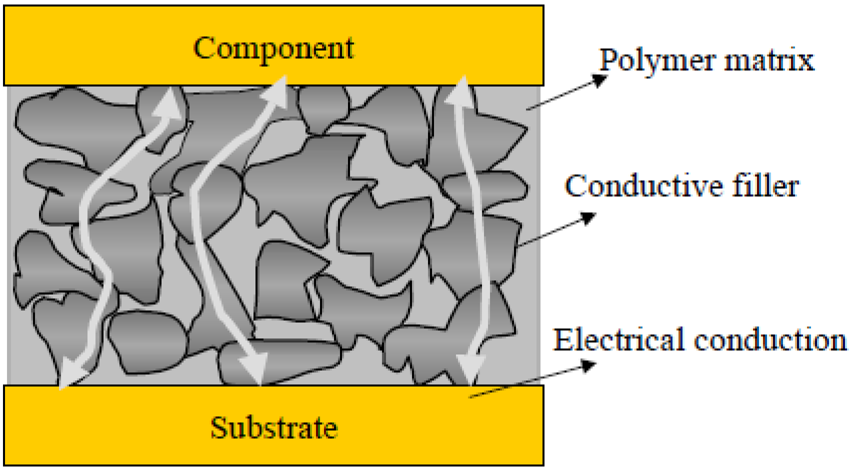


Figure 1.9. A schematic representation of ICA showing conductive filler

Silver is the most commonly used conductive filler for isotropic conductive adhesives because of its high electrical conductivity, chemical stability, and lower cost compared to gold. While most other metals used as fillers like copper form non-conductive oxides, after exposure to heat and humidity, silver oxides also show high conductivity. Also, silver can be easily precipitated into a wide range of controllable sizes and shapes [102]. The silver fillers are typically fabricated into flakes and pre-treated with organic lubricants to ensure the proper rheology of the ICAs [111]. The organic lubricant on the surface of silver flakes can greatly affect the performance of ICAs, including the dispersity of the Ag flakes in the ICA [112], rheology, and electrical conductivity of the ECA [111]. A mixture of silver flakes and particles with broad size distribution can offer improved conductance over narrow size distribution [113]. Flakes can provide improved conductivity by allowing the flake-like particles to overlap one another. On the other hand, the voids caused by the overlapping can be filled with the small particles. Many such systems containing silver as filler were developed to improve the performances of silver-based conductive adhesives. Use of highly porous Ag powder as filler material has been reported by Kottaus, et al [114]. It was observed that the thermo-mechanical properties of the adhesives using porous Ag were improved because of the infiltration of the resin into the pores. However, such systems show poor electric properties. A spherical silver powder was used as conductive filler by L. Fan et al [115]. Kim et al [116] developed a new low-temperature assembly process using a new class of ICAs with fusible filler particles for flip-chip interconnection technology. The two different types of conductive paths (necking type and bump type) in the ICA formulations, corresponding to the resin materials, were formed by the wetting and coalescence behaviors of the fillers. The reduction capability of the base resin material was effective in achieving a good metallurgical interconnection between the fillers and metallization. Such a good metallurgical interconnection exhibited lower resistance. Similarly, an ICA filled with low-melting point alloy fillers was developed by D. Liu and C.P.Wong [117]. The results showed that good metallurgical connections were formed between the silver flakes inside the ICA and between the ICA and the nickel substrate. Due to the metallurgical connections, the ICA showed low contact resistance on nickel as well as stable contact resistance on nickel surfaces during elevated temperature and humidity aging.

A novel flexible electrically conductive adhesive (FECA) has been designed for electronic interconnect applications that require high flexibility on the flexible substrates and connectors using silver flakes as filler. A high performance FECA with tunable modulus, flowability, glass transition temperature, electrical conductivity and adhesion strength was developed for the next-generation large scale flexible flat panel displays and printed electronics applications. Additionally, high transparency and flexibility ECAs have been achieved [110].

Unlike silver, nickel has a unique ability to resist oxidation and hence makes it suitable to be used as stable conductive filler. But its main disadvantage lies in the fact that it is hard and cannot be easily fabricated into optimized geometries. Generally, isotropic nickel adhesives show both higher filler resistance and contact resistance than silver based ICAs [113]. In addition to direct use of metals, metal-plated conductive particles have been used mostly in anisotropic conductive adhesives. Although, the original intent of using plated particles was to reduce cost, various types of plated particles have been specially designed for specific characteristics and end uses. Low-melting point metals have also been used as the coating material of the filler particles, which provide metallurgical bonds among the conducting particles as well as to the substrate and thus lead to the enhanced electrical and mechanical properties of the joints [118]. Transient liquid phase sintering has been used to establish metallurgical connections between particles in ICAs [119]. Silver, nickel and gold plating on non-metals such as glass and plastic are among the most common types of filler products [120].

In addition to above mentioned conductive fillers, other fillers such as gold and carbon particles are also used in special applications. Due to the high cost, gold filler is mainly used for highly demanding military and space applications [121]. Because of their poor conductivity, carbon-based adhesives are only used for low conductivity applications such as keyboards or shielding [102]. Marshall [122] reported use of copper as conductive filler, but Cu has a limited success due to its tendency to form a non-conductive oxide surface layer. ECAs using surface-modified copper fillers have recently been developed. In particular, to overcome the problem associated with the oxidation of copper, copper nanoparticles were coated with organic substance from when nanoparticles were made. The organic-coated copper was tested as a filler metal. A very low resistivity was reported with such ICAs [123]. In order to overcome the problem associated with the oxidation of copper, the silver was coated with copper filler, and the silver-coated copper was tested as a filler metal. As a result, it was found that the electrical resistance of ICA with silver-coated copper filler was clearly lower and more stable than that of ICA with copper filler after curing and after reliability tests. Also, H.Takezawa et al [124] used non-noble metals like Al, Ni & Zn as conductive filler. It was found that the addition of Zn filler demonstrated significant improvement in stability of contact resistance. Researchers at Helsinki University and IBM have developed solder filler conductive adhesives. The basic idea was to form metallurgical joint using adhesive as a mechanical support and to some extent as a fluxing agent. The results show that good metallurgical joint can be achieved when metallization of bonding surfaces are compatible with solder filler [125].

An ICA based on conductive polyaniline filler was developed recently. The ICA was prepared using commercial DBSA doped polyaniline as filler in an insulating matrix of methacrylate/acrylate monomers involving UV curing. Conductivity level of 1

Scm^{-1} was reached with PANI/DBSA content of 15-20 wt%. The samples had a stable resistance although, the tensile strength of the adhesive decreased. But such an adhesive can find a lot of applications in OLEDs because of its transparent nature [126]. Similarly, development of low temperature processing thermoplastic intrinsically conductive polymer which can be used as filler in ICA was reported by Linda et al [127].

With the advent of nanotechnology, many research groups have used the advantages of this technology in ICAs [128]. Nano-sized metal particles have been used in ICAs to improve electrical conduction and mechanical strength [129]. With nano-sized particles, agglomerates are formed due to surface tension effect. Kottaus et al [130] reported an 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., nano-scale and micro-scaled particles) to decrease the total metal loading while retaining the good electrical conductivity using a bimodal filler distribution [131]. The TEM images of ICA filled with nano and micro-scaled particles showing the bridging effect are presented in **Fig. 1.10**. Moon et al [132] studied the thermal behavior of silver nano-particles with respect to the sintering reaction. Surface changes of the particles during sintering and crystal structure variation have been discussed as well. A novel kind of isotropical conductive adhesives was made by using silver (Ag) nanowires and nanosized silver particles as conductive fillers. ICA filled Ag nanowires exhibited higher conductivity,

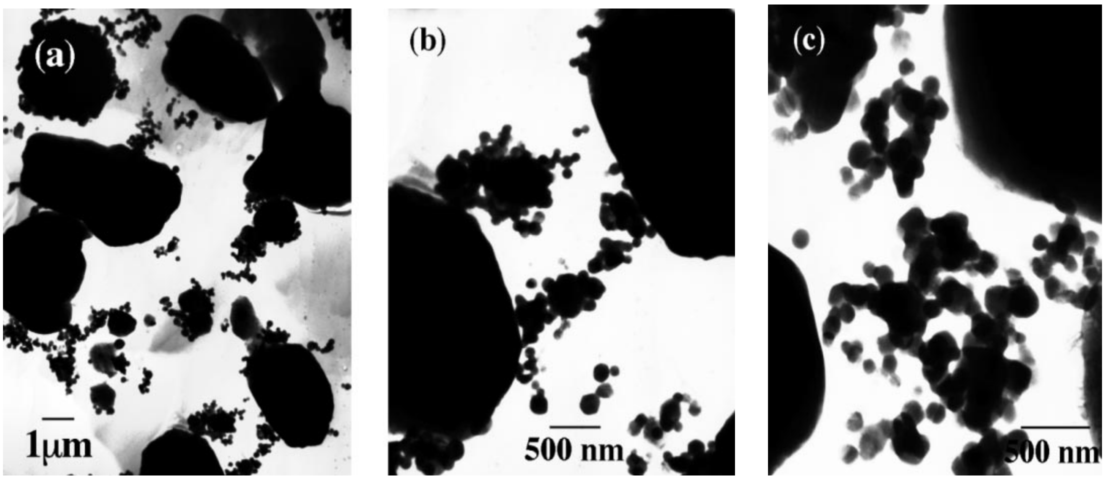


Figure 1.10. TEM images of ICAs showing nano-particles bridging the gap between micro-scaled particles

higher shear strength and low percolation threshold value than traditional ICA [133]. Different polymer pastes filled with nanoparticles were investigated by Telychkina et al in their study, and the possibility of obtaining of the improved electrical characteristics of materials using silver nanoparticles as conductive filler was shown [134]. However, for nano isotropic conductive adhesives, the dispersion of Ag nanoparticles in epoxy compared to micron sized silver flakes is much more difficult because of higher viscosity induced by high surface area of nanoparticles. A recent report for the nano ICAs demonstrated decent dispersion of nanoparticles in polymers and low resistivity via nanoparticle sintering by nanoparticle surface functionalization. In the study, both silver flakes and surface functionalized silver nanoparticles were incorporated into a polymer matrix and their electrical properties were evaluated and an ultra low resistivity conductive adhesive was achieved. The morphology studies showed that the decreased resistivity resulted from the sintering of silver nanoparticles among silver flakes. The sintered particles are believed to fill the gap between the flakes and enhance the interface properties. In a similar study, the silver nanowires with a slenderness ratio of 50~60 were successfully synthesized through a polyol process and modified on the surface by aliphatic acids. The modified silver nanowires began to sinter at 200°C and became shorter and thicker gradually, and eventually formed large chunks at higher temperature. The electrically conductive adhesives filled with silver nanowires were formulated and characterized. The sintering of nano-size silver in ICAs reduced the number of contact points between fillers and increased the conductivity of ICAs [135]. In a recent study, Mach et al claimed that adhesives modified with nanoparticles have lower sensitivity to combined climatic ageing in comparison with adhesives without nanoparticles. The reason is that the contact areas between nanoparticles are substantially smaller in comparison with the contact areas between flakes. Therefore the contact pressure between nanoparticles is higher than between flakes and the contact is more resistive to external climatic load [136]. A 70 nm sized silver particle filler has been used to study the effect to electrical conductivity of ICA after surface treatment. Upon surface treatment of silver with silane-based coupling agent, the treated silver filled epoxy system demonstrated incredible improvement in electrical properties. The current conductivity (DC) for treated filler was ≈ 4 Scm^{-1} compared with untreated filler with 4.54×10^{-3} Scm^{-1} for 5 % w filler loading [137]. ICAs with ultra-low electrical resistivity (≈ 5×10^{-6} Ω.cm) were successfully created by using the combination of micron sized silver flakes and nanoparticles where a diacidic surfactant was employed. The morphology studies revealed that this low resistivity was accomplished by dramatic reduction of interfaces between conductive fillers due to low temperature sintering of silver nanoparticles. In addition, the thermal analysis showed that the surfactant aided the sintering process by means of maintaining a clean oxide free nanoparticle surfaces in the polymer resin [138].

Conductivity in ICAs

The conductivity in ICAs is a result of conduction between conductive filler particles. Several studies have been undertaken to understand the fundamental procedure for development of conductivity inside the insulating polymer matrix. A general understanding is that electronic conduction through the two-phase metal-polymer matrix takes place by percolation along chains of filler particles, but there is no universal conclusion with regard to the conduction mechanism between particles [90, 91, 139]. In case of ICAs, as the conductive filler loading is progressively increased, the electrical conductivity does not significantly increase until the filler loading reaches a critical value. This point where the electrical resistance decreases abruptly is called percolation threshold (P_c). At this point, the filler particles have established a continuous conductive path. A schematic representation of evolution of conductivity in ICAs with respect to filler concentration is given in **Fig. 1.11**. Practically, ICAs are made with filler loadings greater than percolation threshold. Although, percolation theory predicts that insulators containing about 20 % or higher volume loadings of dispersed metallic particles should be electrically conductive, ICA pastes filled with 25-30 % of filler are not conductive unless subjected to curing. Studies carried out by D. Lu et al [140, 141] indicated that the establishment of electrical conductivity resulted primarily from more intimate contact by curing shrinkage of the polymer matrix during the processing of ICAs and there is a strong correlation between the polymerization shrinkage of epoxy curing and the electrical conductivity finally established with the material.

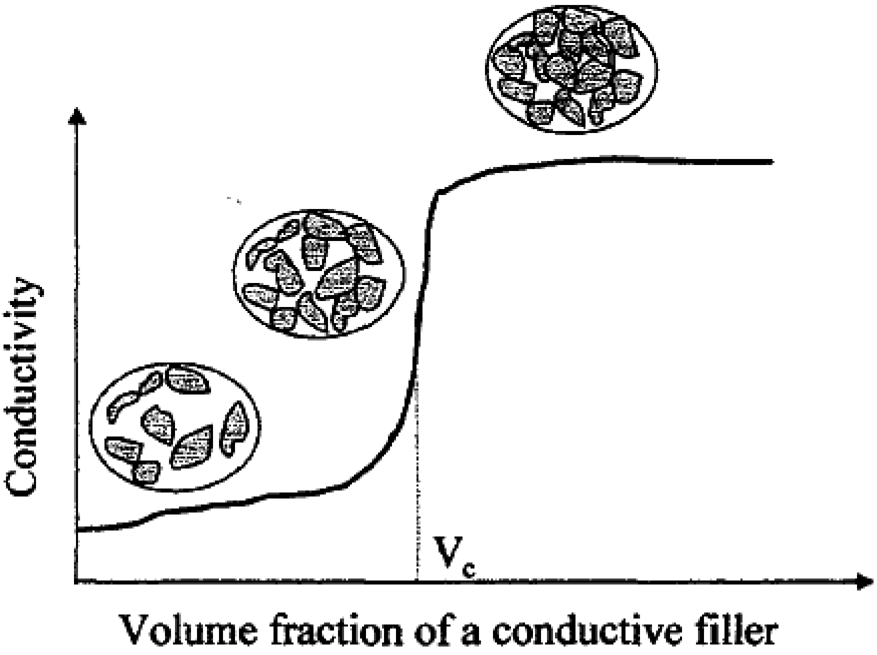


Figure 1.11. A schematic representation of evolution of conductivty in ICAs with increase in filler content

ICAs and there is a strong correlation between the polymerization shrinkage of epoxy curing and the electrical conductivity finally established with the material. ICAs with higher shrinkage showed lower resistance or better conductivity. Klosterman et al [142] measured the resistivity of ICAs during cure and related it to the cure kinetics of the epoxy matrix. Based on the observation that the resistivity decreased dramatically around a specific temperature with ramp cure and over a narrow time range (<10 s) with isothermal cure, they suggested the conduction development was accompanied by breakage and decomposition of the tarnish, organic thin layers which cover the silver flake surface, and by the enlargement of the contact area between silver flakes by thermal stress and shrinkage during the epoxy cure. In thermoplastic ICA, drying (solvent evaporation) is found to be the step in which the conductive paths are established [106]. Electrical conductivity of ICAs is inferior to that of solders, although, the conductivity is adequate for most applications, yet it needs to be improved [143]. Conduction mechanism of ICAs, i.e., particle to particle conduction and electron tunneling is shown in **Fig. 1.12**.

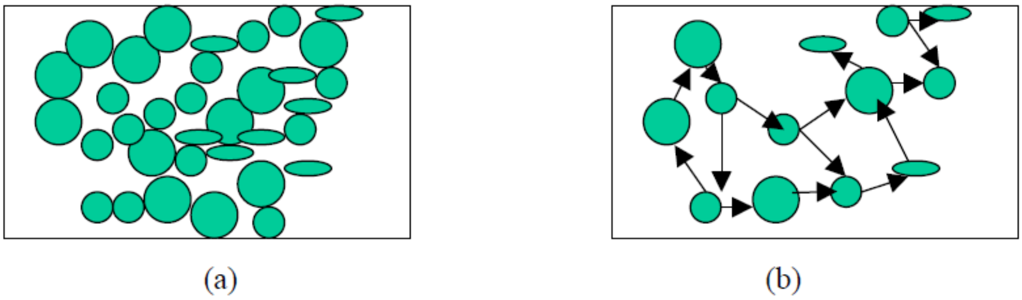

(a) (b)

Figure 1.12. Conduction mechanism in ICAs (a) Particle-to-particle (b) Electron tunnelling

Although, the mechanism for producing high electrical conductance in particle filled adhesives has been the basis of numerous experimental and theoretical investigations, the specific details regarding conduction between nearest neighboring particles are not fully understood [141, 144-147]. For this purpose a model of an ICA joint was developed to consider the particle alignment and distribution as well as the voltage and current distribution inside the adhesive. In this way, the influence of parameters like filler content, particle arrangement, and particle size on the joint resistance becomes evident. The influence of the particle orientation and the particle aspect ratio on the probability of interconnection was discussed using the developed simulation [148]. Silver flakes with surfactant stearic acid, are widely used as the conductive fillers in most ICA formulations [103]. This layer of organic lubricants can affect the viscosity of conductive adhesive paste and prevent agglomeration of silver flakes. Studies have showed that this layer is actually a silver salt formed between the silver surface and the lubricant which typically is a fatty acid [111, 149]. To improve conductivity, the organic layer needs to be partially or fully removed. Three short-chain di-carboxylic acids, malonic acid, adipic acid and terepthalic acid were used as lubricant removers by Yi Li et al [150]. Such acids can partially remove or can completely replace the C-18 stearic acid, thus making it easier for the electrons to tunnel/transport between silver flakes. Malonic acid and adipic acid, which have single bond short chain in between the di-carboxylic groups, increase the conductivity of conductive adhesives greatly. Terepthalic acid, however, deteriorates the conductivity due to the rigid benzene functional group in the molecule. Thus, significant improvement of electrical properties of ICAs was achieved without adversely affecting the physical and mechanical properties of ICAs.

Joseph Miragliotta et al [151] investigated the degree of correlation between the chemical nature of the silver interface, i.e., interface conductivity, and the development of macroscopic conductivity in a metal-filled adhesive sample. They performed both electrical and optical spectroscopic analysis of a silver-filled conductive adhesive, which simultaneously monitored the dynamics of sample conductivity and silver surface chemistry respectively using Surface enhanced Raman scattering (SERS). The results showed a partial decomposition of the carboxylate species and the formation of an amorphous carbon layer at the silver surface. Since amorphous carbon is highly conductive in comparison to a saturated organic hydrocarbon, this result implies a significant increase in the adlayer conductance during thermal cure.

It has been observed that ICA paste has low conductivity before curing while conductivity increases dramatically after curing. It was also observed that intimate contact between conductive fillers caused by resin cure shrinkage is the main mechanism for establishment of conductivity of ICAs. An ICA with higher cure shrinkage generally shows better conductivity [78, 140]. D. Liu and C.P.Wong [141] investigated the changes in properties, especially, cure shrinkage of an ICA during cure and correlated them with establishment of conductivity. An ICA was cured isothermally by a temperature increase from 30 to 250ºC, and its heat flow, storage modulus, dimensional change, and electrical conductivity were studied using a DSC, rheometer, TMA and electrical multimeter respectively. They observed that during non-isothermal heating, the curing and shrinkage of an ICA occurred over a small range of temperature. Similarly, during an isothermal cure, the ICA cured and shrank over a small time interval; in this interval, the conductive particles were packed more closely, thus decreasing resistance and establishing the conductivity. ICAs achieved high conductivity only when enough cure shrinkage occurred and ICA with higher cure shrinkage showed higher conductivity. Several epoxy based curing systems were used as the matrices for the ICA's by L. Fan et al [115] and the effect of curing process upon the resultant bulk resistivity of ICAs was studied. With silver particles as the conductive phase, the experimental results indicated a strong correlation between bulk resistivity and curing temperature or cure kinetics, which could be explained by the mechanism of competition between the packing of silver spheres and the clearing of the insulating layer out of the interparticle space. For epoxy based ICAs, a small amount of a multifunctional epoxy resin can be added into an ICA formulation to increase crosslink density, shrinkage and thus increase conductivity [140]. Similarly, appreciable improvement in conductivity was observed in a thermoplastic ICA when its glass transition temperature (T_g) was adjusted using a plasticizer to maximum effectiveness of its dryness [152].

Reliability of ICAs

Ever since their inception into the world of electronic interconnections, ICAs have been studied extensively for their suitability and reliability. The main concerns are their poor electrical and mechanical stability upon exposure to environmental aging conditions as well as their poor impact properties. The main factors that affect the reliability of ICAs include adhesive type, filler ratio, size and shape, degree of curing of the matrix and damping properties.

Deterioration of electrical conductivity and adhesion failure in circuits connected by ICAs has been studied extensively [93, 153-155]. The mechanical and electrical performance of conductive adhesive joints is found to be dependent on the metal finish of the substrates. The influence of the component and board metallization on the durability of ICAs was studied by Jagt et al [82]. In their research work, electrical and mechanical behaviour of conductive adhesives was discussed for bonding R 1026 resistors with Sn/Pb or Ag/Pd terminations on bare copper, Sn/Pb or Au plated boards before and after climate testing. They concluded that with the noble Ag/Pd termination, the increase in electric resistance of the resistors in the climate was significantly less, compared with Sn/Pb terminations. They believed that the deterioration of contact resistance on Sn/Pb was due to a significant extent to surface oxidation and adhesion failure. Similarly, failure mechanism and reliability of ICA joints on Sn37Pb, Cu, Au plated surfaces upon exposure to the 85°C/85%RH environment has been studied. It was observed that the mechanical strength and electrical performance were both reduced with increasing aging time in the Sn37Pb and Cu systems. They attributed these phenomena to the formation of Cu_2O on the copper metallization and the formation of PbO on the Sn37Pb surface, as both Cu_2O and Sn37Pb are both poor conductors and may form weak boundary layers at the interface. On the other hand, the gold metallization system exhibited stable electrical performance after the hot/wet humidity test. The mechanical performance of the gold metallization system after environmental aging, however, was not presented in their study [154]. It was observed in many such studies that galvanic corrosion rather than simple oxidation at the interface between ICA and the non-noble metal was the main mechanism for the shift in contact resistance. The non-noble metal acts as an anode, is reduced by losing electrons, and turns into metal ions ($M - ne^- = M^{n+}$). The noble metal acts as cathode and its reaction generally is $2H_2O + O_2 + 4e^- = 4OH^-$. Then the M^{n+} combines with OH^- to form a metal hydroxide and then metal oxide. After corrosion, a layer of metal hydroxide or metal oxide is formed at the interface. Since, this layer is electrically insulating, the contact resistance increases dramatically. Many efforts have been made to prevent or minimize contact resistance shift by galvanic corrosion. As the process needs wet conditions, so that an electrolyte gets formed at the interface which induces galvanic corrosion, ICAs with low moisture absorption are devised to minimize unstable contact resistance [141, 155]. Also, it has been found that impurities of the polymer binder lead to the formation of electrolyte, hence high purity of polymer binder is ensured [156]. Another method of preventing galvanic corrosion is by introducing some organic corrosion inhibitors into the ICA formulations [157, 158], which acts as a barrier film between metal and environment by adsorbing over the metal surface [159-162]. D.Lu and C.P.Wong [163] developed ICAs with stable contact resistance and studied the effect of purity of the resins and moisture absorption on contact resistance. Several different additives (oxygen scavengers and corrosion inhibitors) for contact resistance stability under elevated temperature and humidity ageing have been studied. They observed that ICA formulated with resins of higher purity show more stable contact resistance. Also, conductive adhesives with low moisture absorption tend to have more stable contact resistance. Both oxygen scavengers and corrosion inhibitors can somewhat delay the increase of contact resistance of ICAs on non-noble metals. However, the corrosion inhibitors are more effective than the oxygen scavengers in terms of stabilizing contact resistance. They also described the contact resistance behavior of a class of conductive adhesives, which is based on anhydride cured epoxy systems. This class of ICAs show low moisture absorption. Contact resistance of these conductive adhesives decreased initially and then increased slowly as the metal oxide formation on metal surface started. Further, one of the corrosion inhibitor showed its best effectiveness in stabilizing contact resistance [164]. D. Durand et al [165] presented a concept of poly-solder with good contact resistance stability with standard surface mount devices on both solder-coated and bare circuit boards in a US patent. They incorporated some electrically conductive particles that have sharp edges into the ICA formulations. The particles called as ‘oxide penetrating filler’, need to be driven through oxide layer and held against adhered materials. This is accomplished by employing polymer binders with high shrinkage on curing. Many studies have been reported to improve contact resistance stability of ICAs like by using sacrificial anode material, using low melting point alloy fillers or developing transient liquid phase sintering conductive adhesives [117, 124, 131]. In microelectronic applications, silver migration between electrodes has been a major concern. A novel approach to reduce silver migration and enhance the long term reliability of conductive adhesives was discovered by using self-assembled monolayer molecular wires. The approach enhances the long-term reliability and durability of conductive adhesives and enables it for high voltage applications. In addition, the self-assembled molecular wires help the dispersion of conductive fillers (in particular, nanosized, i.e., <100 nm conductive fillers in the polymer matrix and enhance the electrical conductivity of conductive adhesives. Formation of surface complex between the carboxylate anion and a surface silver ion reduces the solubility and diffusitivity of the silver metallization which reduces silver migration of the components and therefore leads to effective migration control in nano silver conductive adhesives [166]. A schematic picture of degradation of silver filled ICA/Sn interface is shown in **Fig. 1.13**.

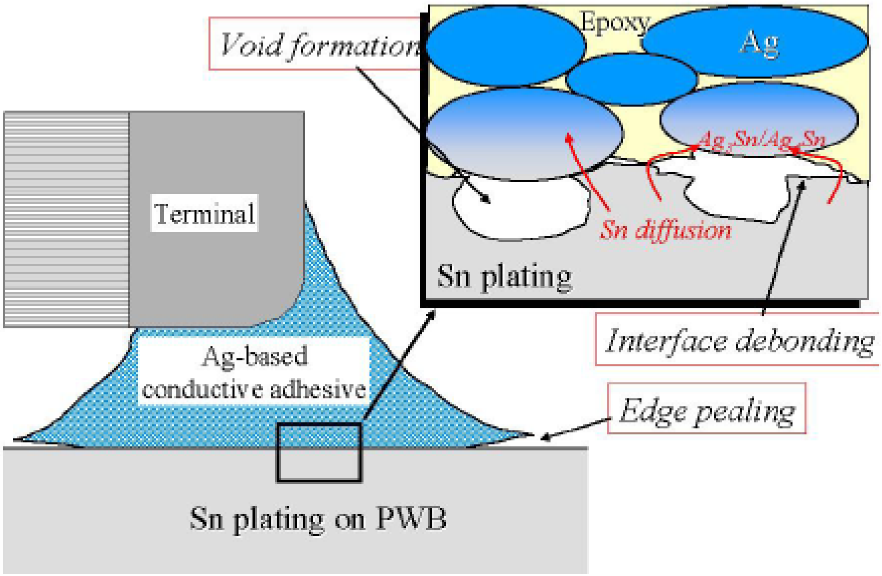


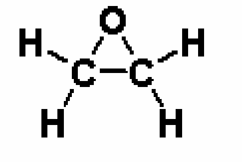
Figure 1. 13. A schematic representation of degradation of silver filled ICA/Sn interface

Probably due to loading of filler into polymer matrix, the impact performance of ICAs is one of the most important properties. The results obtained by Shuangyan Xu et al [167] showed that the falling wedge test is able to discriminate between the impact performance of adhesives and the technique is capable of screening conductive adhesives for bonding purposes. ICAs available currently are not able to show great impact performance, so efforts are going on to develop ICAs with better impact strength which will pass the standard drop test. Yang Rao et al [168] studied the impact performance of different ICAs. They used Finite Elemental Analysis (FEA) technique to conduct the modal analysis of the packages and to estimate their natural vibration frequencies. Constrained layer damping theory was used to explain the results of drop tests. It was found that conductive adhesive formulations that have very high loss factor in the frequency range estimated by FEA passed the drop test and showed high impact performance. This suggests that the loss factor of an ICA plays a very important role in determining the drop test results and impact performance. Different approaches have been employed to improve impact strength of ICAs. S.Macathy [169] suggested decrease in filler loading to improve the impact strength. However, such an effort can lead to decrease in electrical properties of an ICA. Vona and Tong [170] reported the development of ICAs using resins with low modulus so that this class of conductive adhesives may be able to absorb the impact energy developed during the drop. Similarly, conformal coating of surface mount devices was used to improve mechanical strength. It was demonstrated that conformal coating could improve the impact strength of conductive adhesive joints [171, 172]. M. Keil et al [173] reported a simple method of enhancing impact strength of ICAs. They used micron-sized carbon fibers to produce more efficient distribution of mechanical forces within the joint. A mechanical shear test investigation demonstrates that a significant internal strength improvement can be achieved with the addition of low weight percentages of carbon fibers into a commercially available conductive adhesive. On a close examination of the drop test survival data, it is found that the success rate correlates with the (imaginary) dissipation modulus rather than with adhesive strength [167, 174]. One way to design materials with high dissipation modulus is to select polymers with glass transition temperature (T_g) below the operating range, i.e., below room temperature in general [175]. Recently, D.Lu and C.P.Wong [107] reported the development of a new class of ICAs which is based on epoxide-terminated polyurethane (ETPU). This class of ICAs incorporates the properties of polyurethane materials such as high toughness and good adhesion. However, the modulus of such adhesive can be adjusted by incorporating some epoxy resins such as bisphenol-F type epoxy resins. These ICAs showed a broad loss factor (tan δ) peak with temperature and a high tan δ value of a material is a good indication of the damping property and impact performance of the material. This class of ICAs showed superior impact performance and substantial stable contact resistance with non-noble metal surfaces such as Sn/Pb, Sn and Cu.

ICAs may be subjected to various environmental conditions during their service period. Moisture is commonly encountered in the service environment, and must be considered a critical factor in determining the long-term reliability of adhesively bonded joints. Water can affect both mechanical adhesion and electrical conduction in ICAs. Water can degrade adhesive properties by either depression in glass transition temperature, acting as plasticizer in the system or give rise to voids. This leads to degradation of mechanical properties. Various effects of moisture on reliability of ICAs have been extensively studied by various groups and many theories have been suggested. There is a dramatic increase in electrical resistance and decrease in shear strength after ICA joints are exposed to moisture [176]. After soaking the ICA joints in deionized water for 24 hours, fatigue tests were performed by Gomatam et al. It was observed that the fatigue life is decreased at higher humidity conditions as compared to normal test conditions [177]. Dudek et al subjected the ICA joints to 85°C/85%RH conditioning and found that bulk resistance of the joints increased substantially. They used a simplified finite element model to calculate the contact pressure between conductive fillers. They also found that due to small dimensions of the joint, moisture diffuses rapidly to the inside of the adhesive joint. The moisture swelling effects can then decrease the contact pressure between conductive fillers. Since, the contact pressure at the particle to particle interfaces prevents chemical degradation, the process of lowering contact pressure seems to make the adhesive even more sensitive to chemical degradation [178]. Nature of the surface of component plays an important part in moisture stability of ICA joints. This is probably due to resistance to oxidation of different plating materials. Gaynes et al measured the contact resistance of conductive adhesive joints subjected to 85°C/85%RH conditioning and observed that a palladium alloy surface provided an electrically superior joint compared to gold, tin or nickel [179]. The mechanical behavior of conductive adhesive joints exposed to elevated temperature and relative humidity conditions has been investigated, and failure mechanisms of conductive adhesive joints have been determined by Xu et al [180]. They studied silver filled epoxy based adhesive systems in conjunction with printed circuit board substrates with metallization of Au/Ni/Cu and Cu. This study revealed that both conductive adhesives as well as substrate metallization play important roles in the durability of conductive adhesive joints. Moisture attack on the adhesive joint was divided into three phases: displacement of adhesive from the substrate, oxidation of metal surface and weakening of metal oxides.

1.3. Epoxies

Since, conductive adhesives are comprised of polymer matrix and fillers, therefore we discuss about epoxies as matrix and its corresponding composites in the following sections of this thesis.Epoxy or epoxide resins are group of reactive compounds that are characterized by the presence of the oxirane group.



Epoxy adhesives comprise a liquid or a fusible solid containing epoxide groups, and a curing agent containing functional groups with which the epoxide groups combine to form a crosslinked polymer. This cross-linked matrix is of great strength and has excellent adhesion to a wide range of substrates. This makes them ideally suitable to adhesive applications in which high strength under adverse conditions is a prerequisite. This conversion of resin into hard, infusible three-dimensional network in which the resin molecules are crosslinked together by means of strong covalent bonds is called **curing** or **hardening** of the resin. When the reaction between resin and hardener is capable of taking place at room temperature the two components are mixed immediately before use, but if the mixture is relatively inactive under ordinary storage conditions the components are mixed together and marketed as “single package” adhesive. In some cases, the adhesive system although “single component” contains resin and hardener reacted to an intermediate but fusible stage. Such adhesive systems are generally called “B-stage”.

The time taken from the initial mixing of the resin and curing agent to the point when the viscosity of the mixture has become so high as to render the mix unusable is called the “pot 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 life can vary from a few seconds to several weeks; such is the wide range of possibilities with epoxy resin formulations.

The curing that takes place when the resin and hardener are brought into intimate contact, for example by melting the solid under appropriate conditions, is an irreversible reaction that results in a thermoset resin. The reaction does not involve condensation polymerization and therefore no low-molecular weight substance such as water is split off. For this reason the shrinkage that takes place during cure is negligible. Their unique characteristics in addition to negligible shrinkage during cure include an open time equal to the usable life, excellent chemical resistance, ability to bond non-porous substrates and great versatility. Although, they were hailed as wonder products when first introduced, it became evident later that they cannot do everything. They have, however, clearly established niches, especially in high-technology applications, and have shown a steady growth.

The development of epoxy resins has been directed towards many different fields of applications, one important application being adhesive bonding. Adhesives based on epoxy resins are widely used for bonding metals, concrete and a whole range of non-porous materials. Although, work on epoxy resins started in the mid-1920's, they established their reputation as adhesives for bonding metals in 1950's by virtue of their ease of application and the very high strengths of the bond that they form. Since then, epoxy resin production and sales have steadily increased, and in the last decade the world market of epoxy resins has grown on an average by about 15 %. At least, 95 % of the epoxy resins sold is of the one basic type, i.e., the diglycidyl ethers of diphenylolpropane (also known as bisphenol A) usually referred as DGEBA resins. One of the important reasons for their popularity is that bisphenol A is probably the cheapest suitable aromatic dihydroxy compound available. Among them most widely used epoxy resins are the family of products produced by the reaction between epichlorohydrin and bisphenol A. The remaining 5 % of epoxy resins sold includes the cycloaliphatics, glycidyl esters and amines, epoxidised olefins and the specialized glycidyl ether resins such as brominated types and the epoxy novolacs. A general trend of the end-user applications shows that surface coatings industry still dominates the market as a major consumer of the resins. Electrical and electronics applications also form a major user industry. Other uses individually remain a small proportion, although they play a major role in overall earnings picture of the resins.

Significance of epoxy resins

Because of their strength, versatility, and excellent adhesion to a variety of surfaces, epoxy resin adhesives have gained wide acceptance by diverse users. They have revolutionized joining and fastening technology. Some of the commercially available epoxy resins along with their important properties are listed in **Table 1.3**. The wide scale popularity of epoxies is a consequence of these important characteristics:

1. ***Adhesion****:* Because of their epoxide, hydroxyl, amine and other polar groups, the epoxies have high specific adhesion to metals, glass, and ceramics. They can be formulated to give mixes of low viscosity with improved wetting, spreading, and penetrating action. The variety of functional groups also provides good affinity between metals and plastics. For example, epoxies are in use for the bonding of copper to phenolic laminate in printed circuits.
2. ***Cohesion****:* When the resin is properly cured, the cohesive strength within the glue line is so great, and adhesion of the epoxy to other materials so good, that failure under stress often occurs in one of the adherends rather than in the epoxy or at the interface. This happens with glass and aluminum as well as with weaker adherends such as concrete and wood.
3. ***Solids:*** Unlike the phenolics and some other resinous adhesives, the epoxies cure without releasing water or other condensation by-products. This makes it possible to bond the epoxies at only contact pressures or with no pressure at all. Also, since there is no water to remove (as with rubber lattices) and no volatile solvents (as with nitrocellulose cements), the epoxies are convenient for the assembly-line bonding of impervious surfaces such as metals and glass.

4. ***Low shrinkage:*** The epoxies cure with only a fraction of the shrinkage of vinyl-type adhesives such as polyesters and acrylics; consequently less strain is built into the glue line, and the bond is stronger. Also, the epoxies do not pull away from glass fibers as polyesters. The shrinkage can be reduced to a fraction of 1% by incorporation of silica, aluminum, and other inorganic fillers.

5. ***Low creep:*** The cured epoxies, like other thermoset resins, maintain their shape under prolonged stress better than thermoplastics such as polyvinyl acetate, nitrocellulose, and polyvinyl butyral.

6. ***Resistance to moisture and solvents:*** Unlike proteins, starches, dextrins, gums, and polyvinyl alcohol, the epoxies are insensitive to moisture. Their resistance to solvents is also outstanding and accounts for their rapid advance in the coatings field. They are effective barriers to heat and electric current.

7. ***Can be modified:*** The properties of epoxy adhesives can be changed by (a) selection of base resin and curing agent, (b) alloying the epoxy with another resin, 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 a 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 formulated for use in cryogenic applications or for continuous service in high temperature environments.

Table 1.3 Some common epoxy resins with their properties

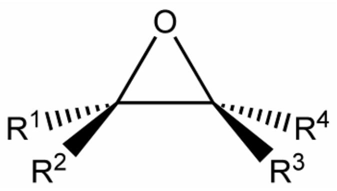
Resin	Chemical type	Epoxide equivalent weight	Viscosity (cP at 25°C)	Supplier
Low viscosity				
Araldite DY026	1:4butanediol diglycidyl ether	110-115	10	CIBA GEIGY
DER 732	Propylene glycol diglycidyl ether	305-335	55-100	Dow
DER 736	Propylene glycol diglycidyl ether	175-205	30-60	Dow
Epikote 812	Glycerol triglycidyl ether	140-160	100-170	Shell
Epikote 871	Linoleic acid diglycidyl ether	390-470	400-900	Shell
Medium viscosity				
Araldite GY260	DGEBA	185-196	12000-16000	CIBA GEIGY
DER 331	DGEBA	182-192	11000-14000	Dow
Epikote 880	DGEBA	185-192	10000-16000	Shell
Beckopox EP 140	DGEBA	180-192	9000-12000	Hoechst
High viscosity				
Epikote 834	DGEBA	230-280	(Softens at 35-40°C)	Shell
DER 337	DGEBA	230-250	Not given	Dow
Beckpox EP151	DGEBA	400-500	20000-30000	Hoechst
Araldite EPN 1139	Epoxy novolac	170-180	50000	CIBA GEIGY
Epikote 154	Epoxy novolac	176-181	35000-7000 at 52°C	Shell
DEN 438	Epoxy novolac	176-181	20000-50000 at 52°C	Dow
Monofunctional				
Allyl Glycidyl Ether	Allyl glycidyl ether	114	1	Shell
Dow BGE	Butyl glycidyl ether	143	3	Dow
Cardura E	Versatic acid glycidyl ether	240-250	7-8	Shell
Beckopox EP 080	2-Ethylhexyl glycidyl ether	190-205	2-3	Hoechst

Despite such important advantages, epoxies have some disadvantages as well,

1. ***Toxicity:*** Some epoxies and diluents are known to cause dermatitis. Some amine curing agents are toxic. Good housekeeping is the best preventive measure. The cured epoxies are not deleterious to health.
2. ***Low pot and shelf-life:*** Mostly, two component adhesive formulations must be mixed shortly before use. Some films and tape adhesives must be stored at low temperature for extended life, partially 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.

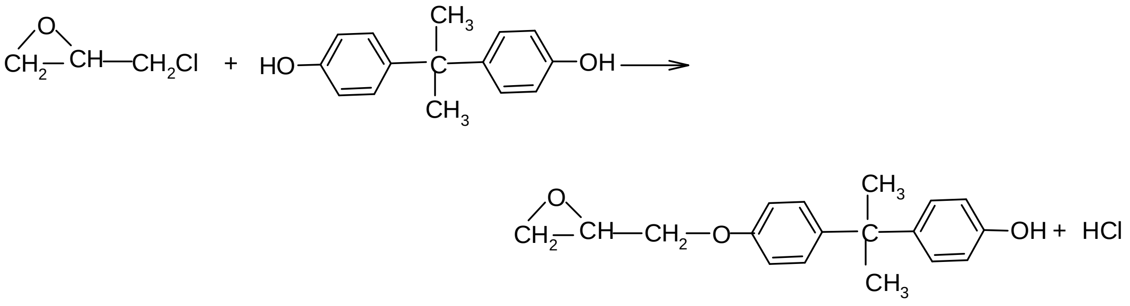
Chemistry of epoxies

In the anhardened state the chemical structure of an epoxy resin (less well-known as ethoxyline resin) is characterized by the epoxide group.

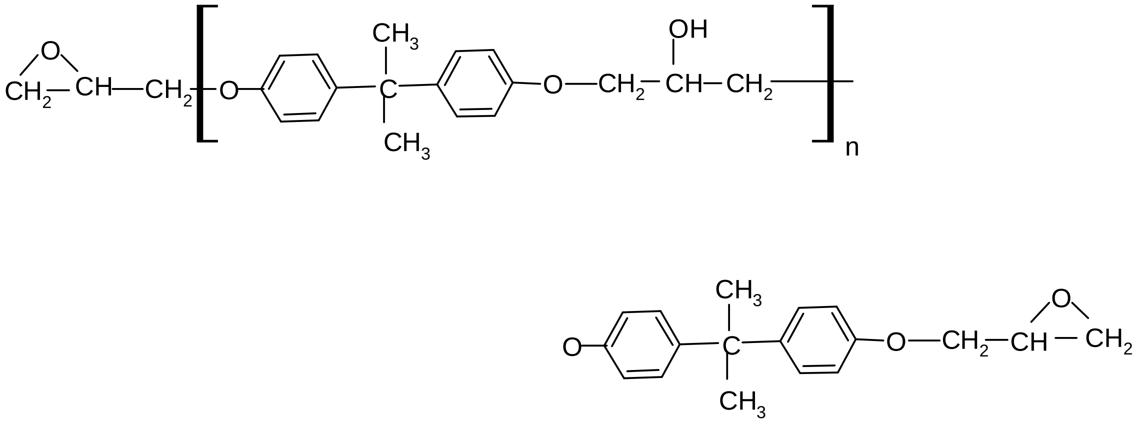


The epoxy, epoxide, oxirane, or ethoxyline group is a three membered ring consisting of an oxygen atom attached to two connected carbon atoms. The term “epoxy resin” usually refers to an intermediate molecule which contains at least two reactive epoxy groups. Such resins are categorized as “thermosetting,” since they are capable of “curing” to form crosslinked networks. The rings can be opened by either acidic or basic materials, functioning either as catalysts for homopolymerization or as reactive hardeners.

The most widely used epoxy resins are the family of products produced by the reaction between epichlorohydrin and bisphenol A. Credit for the first synthesis of bisphenol-A based epoxy resins is shared by Dr. Pierre Castan of Switzerland and Dr. S.O. Greenlee of the United States who accomplished the feat in 1936. Epichlorohydrin is capable of reacting with hydroxyl groups, with the elimination of hydrochloric acid in the following manner.



It reacts with additional epichlorhydrin to produce a macromolecule of general structure as given below:



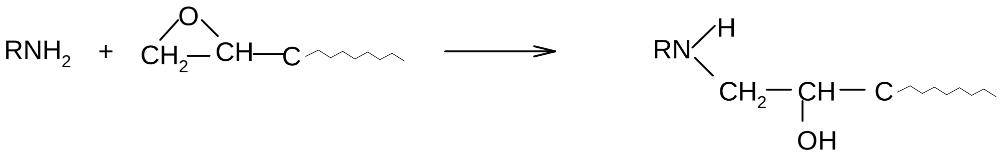
Commercially useful grades are relatively low molecular weight products in which *n* ranges from 0 to about 4. When *n* is between 0 and 1, the product is liquid, and this is the most useful product for adhesive applications. As *n* increases, the product moves towards a brittle solid. Solid grades find application principally in paints. Regardless of molecular weight, the resulting resin has two epoxy groups per molecule. Resins of greater functionality can be produced from polyols having more than two hydroxyl groups per molecule. Thus, phenol novolac resins can be reacted with epichlorhydrin to produce epoxy novolac resins. These products may have much greater functionality, although stearic considerations limit the useful size of the molecule. Because of their functionality, epoxy novolacs have greater cross-link density, generally yielding better temperature resistance at the expense of increased brittleness. They are thus seldom used on their own, but make useful modifiers of the properties of DGEBA resins.

Other products that may be epoxidized in this way include dihydric and trihydric phenols, aliphatic polyols such as glycerol, and simple alcohols such as butanol or allyl alcohol. These products, especially the monofunctional glycidal ethers, are used at relatively low percentages to modify properties of DGEBA resins, particularly to achieve lower viscosities.

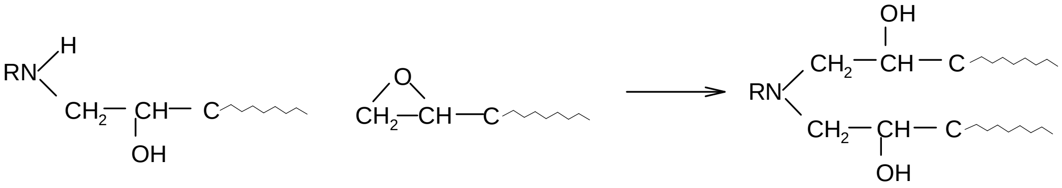
Epoxy groups may also be produced by oxidation of olefinic unsaturation within animal and vegetable oils. The resulting products have too low a functionality for use as resin in their own right, but are added to DGEBA resins to introduce a measure of flexibility.

The resulting epoxy resin is capable of reacting with various products, or itself, to form a solid, infusible product of considerable strength. The fact that these reactions generally occur without the production of low molecular weight by-products means that shrinkage during cure is negligible. This reduces stresses in cured structure, contributing to the strength of the cross linked matrix and eliminating the need for sophisticated clamping techniques.

The two cross linking reactions are external, by reaction of the oxirane group with active hydrogen, and internal, by homopolymerization through the oxirane oxygen. The former is typical of cross-linking by hardeners and the latter of catalyzed cross-linking. Both hardners and catalysts are referred to as curing agents. The classic epoxy curing mechanism is illustrated by the reaction between a primary amine and an epoxy group:

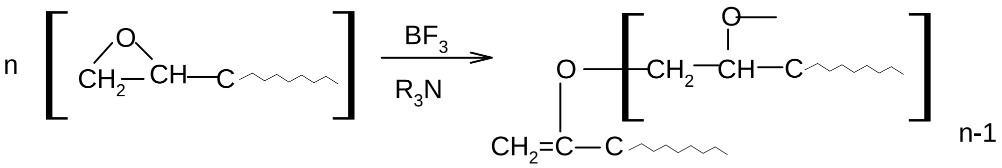


The product can react with an additional epoxy group to continue the cross-linking process as given below:



The reaction is characteristic of hardeners having active hydrogens available, including amines, amides, and mercaptans. The reaction is catalyzed by hydroxyl groups, especially phenolic hydroxyls and tertiary amines. Because of the bulk of the substituent groups involved, steric factors have a major influence on the reaction rate. Thus low-molecular weight hardeners tend to react more vigorously and produce more cross-linked structures, while hardeners of high molecular weight tend to react more sluggishly. Hardeners may thus be selected to produce highly exothermic reactions. Similarly, DGEBA resins having both epoxy groups at the ends of the molecule will react more readily with hardeners than will epoxy novolacs or other types of epoxies in which one or more of the functional groups may be hindered by the rest of the molecule.

Homopolymerization occurs readily in the presence of catalysts, especially at elevated temperatures.



Again this reaction is accelerated by hydroxyl groups or tertiary amines. This is also the predominant reaction with anhydrides. In fact, reactions with resin and hardener or catalyst are very much more complex than these idealized reactions, and both reactions as well as a number of side reactions probably occur to varying extents in any cross-linking mechanism.

Epoxy resins react with hardeners in stochiometric quantities. Thus, knowledge of the number of reactive sites is needed in order to calculate correct ratios. For the resin, this is given by the epoxide equivalent weight (EEW), which is the quantity of resin required to yield one epoxy group. For a DGEBA type in which $n = 0$, the molecular weight is 340. Since, there are two epoxy groups per molecule, the EEW is thus 170. Typically, the pure liquid DGEBA resins commercially available for adhesive applications have epoxide equivalent weight in the range of 180 to 310, usually 190 to 210, while for paints or special applications, EEW may reach 2000 or more. The epoxy novolacs usually have EEW in the range of 150 to 250, usually around 180.

The viscosity of the DGEBA resin is dependent primarily on molecular weight. Even at low molecular weight, viscosity is typically in excess of 6000 cP, while at EEW 190 viscosity is usually around 12000 cP. For applications requiring low viscosity, it is thus necessary to include other types of epoxy resin or to use reactive or nonreactive diluents to achieve the desired viscosity.

Curing agents

The simple conversion of the epoxy resins from their liquid state to highly crosslinked state is called **curing** or **hardening** of the resin. The chemical substances that bring about this 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 a careful selection of various curing agents. Several classes of curing agents each having distinctive characteristics may be used.

1. ***Aliphatic primary amines:*** Common examples include diethylene triamine (DETA), tetraethylene pentamine (TEPA), *n*-aminoethyl piperazine, and isophorone diamine. They give good cure at room-temperature stochiometric ratios but have poor heat deflection temperature, inconvenient mix ratios, high peak exotherm, and are strongly irritant. Isophorone diamine produces very light colored mixes with good color stability.

2. ***Aromatic primary amines:*** These offer improved heat and chemical resistance and longer pot life with reduced exotherm, but poor color stability and sluggish cure. They are generally solids and require some formulating to produce easily handle able products. Reactions proceed best at elevated temperatures, where their irritancy can be a problem. For room-temperature cures, they should be used with catalysts of which phenols, BF_3 complexes, and anhydrides are the best. *m*-phenylene diamine (MPDA) and methylene dianiline (MDA) are the best examples.

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. ***Tertiary amines:*** Although their primary use is as catalysts with other hardeners, tris (dimethylaminomethyl) phenol (DMP 30) is an effective curing agent on its own, at both room and elevated temperatures.

5. ***Amides:*** Although amides on their own are too unreactive, reaction products of polyamines with fatty acids to produce amidopolyamines provide the largest group of commercial hardeners for adhesive applications. Reduced volatility and irritancy and a convenient mix ratio offer the compounder ease of handling. The mix ratio is relatively noncritical; increasing hardener levels yield increased flexibility and adhesion but reduced heat deflection temperature and chemical resistance. Initially, amidoamines have poor compatibility and an induction period is necessary to allow the reaction to start. Pot lives are relatively long and exotherms low, but low-temperature cure is poor. Small quantities of imadazoline improve adhesion to metals. Dicyandiamide is a special example of an amide that can be used on its own. Its low reactivity yields a usable life in excess of 6 months, but at elevated temperature, it reacts quickly.

6. ***Mercaptans:*** Most mercaptans on their own are unreactive, but with catalysts produce flexible cures. Certain mercaptans in conjunction with DMP 30 provide extremely rapid cure, with low exotherm, making them ideally suited to retail applications.

7. ***Acids and anhydrides:*** This group of curing agents provides the best performance at high temperature. Boron trifluoride monoethylamine, oxalic

acid, and maleic and pthalic anhydride are used for electrical or high temperature application, often with catalysts such as benzyldimethyl amine (BDMA) or DMP 30.

The properties and characteristics of various curing agents are presented in **Table 1.4.**

Modifiers

The simple resin-curing agent combination alone seldom provides a material with all the properties required for use in a given application, and other materials must be added so as to modify the properties of the cured resin or to make it cheaper. The correct choice of the types and amounts of the different components of an epoxy formulation is a fairly precise, difficult and important task because of the final properties and eventual performance of the system depend upon it. The various classes of materials that can be added to the resin and curing agent combination are:

1. ***Diluents:*** These are used primarily to reduce the viscosity of the epoxy resin systems. Diluents can be reactive or non-reactive. The reactive site in the former may be an epoxide or other functional groups. About 12 phr of butyl glycidyl ether reduces the viscosity of the standard resin from 10,000 cP down to 500-700 cP at 25°C. Some of the commercial medium viscosity (2000 to 4000 cP) epoxy resins contain dibutyl phthalate as nonreactive diluents. Before using any diluents, its compatibility with the total formulation should be checked. Solvents should be evaporated after the formulated adhesive has been applied to the substrate, but before the bonding surfaces are brought together.
2. ***Flexibilizers:*** Cured epoxy resins are usually hard but brittle solids. If a tougher, more flexible material is required, which is better able to withstand mechanical stresses or thermal shock, the epoxy system is modified by addition of

flexibilizers. They enter the reaction with epoxy group and increase the distance between the crosslinks, thereby making the product flexible. Besides using amidoamine type curing agents, flexibility can be imparted by incorporating into formulation, polysulfides, or flexible epoxy resins. The latter are derived from aliphatic polyols or long chain acids.

3. ***Fire retardants:*** Techniques employed to improve the fire-retardant properties of the cured resins mostly involve the incorporation of bromine or chlorine atoms into the system, usually by utilizing halogenated epoxy resins or chlorinated curing agents. Certain fillers and diluents are also available in this respect.

4. ***Polymeric modifiers:*** Various thermoplastic as well as thermosetting polymers including elastomers have been used to modify the properties of the cured epoxy resin products. Combination of epoxies with nylon, phenolics, and nitrile rubber is of major significance in case of film or tape adhesives. Nylon-epoxy films are blends containing 30 to 50% by weight of epoxies. Alloying with nylon results in high tensile shear strength as well as peel strength. Epoxy-phenolics are generally sold as tapes and are used in the aerospace applications requiring high shear strength at high temperatures. Nitrile-epoxy systems are composed of solid epoxy resin modified with carboxy-terminated butadiene-nitrile co-polymer. The modification provides toughness and elasticity to the cured bond line. The film adhesives based on the nitrile-epoxy combination are widely used in construction of commercial jet-liners. Thermoplastic polyurethane modified epoxy systems have been developed and are shown to possess good peel strength and flexibility. Such systems have been used in electrically conductive adhesives recently.

Table 1.4. Properties and characteristics of various curing agents

Curing agent	Usage	Uncatalyzed cure (°C)	HDT (°C)	Applications
Aliphatic primary amines				
Diethylene triamine	10-12	Ambient	80-100	Short pot life
Tetraethylene pentamine	13-15	Ambient		Ambient curing systems
Diethylamine propylamine	5-8	40-80		
n- Aminoethyl piperazine	22-25	Ambient		
Aromatic primary amines				
m – Phenylene diamine Methylene dianiline	12-15 25-28	60-100 60-100	150-180	Longer pot life General purpose epoxies
Tertiary amines				
Benzyl dimenthylamine Tris (dimethyl aminomethyl) phenol	6-10 3-6	60-100 20-60	80-100	Catalysts, especially with Polysulfide
Amides				
Dicyandiamide	3-5	120-160	120	Latent catalysts for one pack epoxies
Acids				
Boron trifluoride monoethyamine	2-4	120-15-	175	Heat resistant epoxies
Oxalic acid	5-10	120-160	60-120	Catalyst for anhydrides
Anhydrides				
Phthalic anhydride	60-80	120-140	120-150	Encapsulation
Maleic anhydride	50-80	80-120		

5. ***Cure accelerators:*** Certain simple substances can increase the rate of reaction between the epoxy resins and some curing agents, and wide variations in the rate of cure can be achieved by the addition of small amounts of catalyst. For example, phenol causes the rate of reaction between an epoxy resin and simple aliphatic amine to increase by several orders of magnitude.

6. ***Fillers and reinforcements:*** These are often incorporated in epoxy adhesives to obtain one or more of the following advantages: low cost, less shrinkage, lower coefficient of thermal expansion, greater heat resistance, better thermal conductivity, and electrical properties etc. Fillers have a variety of functions but are chiefly used to make the system cheaper and to modify the physical and mechanical properties. Addition levels may be 50 to 300 phr. Although, most filler will increase the density of the cured product, certain lightweight fillers will decrease density. Viscosity increases depend on surface area, oil absorption and filler type. Chemical resistance may be improved or made worse, depending on fillers selected. Highly alkaline fillers should be avoided, especially with acid-cured systems, as they may retard setting. Settlement of fillers during storage depends primarily on the particle size of the filler and its density, and the viscosity of the formulated product. Fine particle fillers with relatively low specific gravity in high-viscosity products will settle much less, especially if the product is at all thixotropic. Where coarse fillers must be used, an approach towards a fully filled void-less system where the volume of liquid is such as just to fill the voids will solve the problem. Incorporation of fine fillers, use of pigment-dispersing aid, and where application permits, use of thixotroping agent will help to reduce or eliminate settlement. Depending on addition levels, fillers will generally increase the usable life and extend the cure time of the mix.

> Tensile and compressive strength usually increase maximally then decrease on further additions. Most fillers have relatively little effect on heat deflection temperature. Chemical resistance will vary from filler to filler. Shrinkage is usually reduced.

Reinforcements are inert, fibrous materials whose prime purpose is to increase the strength of the system. Glass and metal fibres are widely used, the glass being in fibrillar form or woven into a cloth or mat and the metal fibres being used as discrete fibres or whiskers. Carbon fibres are also now becoming important. The whole subject of polymeric composite materials is based on the combination of a resin matrix with a fibrous reinforcement, and epoxy resins play an important role in this particular technology.

It can be seen, therefore, that what is generally referred to as an epoxy resin is more properly a carefully formulated mixture of ingredients. The correct formulation of these ingredients is a skilled task and much of epoxy resin technology consists in the successful development of formulations ‘tailor made’ for a particular application.

1.4. Composites

Mixtures of materials can be homogenous or heterogeneous. In the case of polymers, the homogenous mixtures are classified by plastic technologists as blends and heterogeneous mixtures as composites [181]. The basic principle underlying the development of the technology of composites is that the combination of two dissimilar materials results in a product with properties different from those of the starting materials. For example, glass fibres have a Young’s modulus of about 69 GN/m^2, an ultimate tensile strength of about 1400 MN/m^2 and a linear stress/strain relationship to failure with no yield. Unreinforced epoxy resins, in comparison, have ultimate tensile strengths of 1.4-3.5 GN/m^2 and a non-linear stress/strain relationship.

By combining the two materials into composite, a new material is formed, with an ultimate tensile strength of about 420 MN/m^2 and a Young's modulus of 28 GN/m^2.

The properties of a composite depend upon a number of factors such as:

1. The nature of the separate constituents and the adhesion between them. The fibrous reinforcement carries the major part of the applied stress in a composite, whereas the resin matrix transmits the stress to each fibre. The adhesion between the resin and fibre is therefore the critical point, and if the adhesion is poor, rapid failure of the composite may occur when it is stressed.
2. The relative amounts of resin and fillers present in the composite. In general, an increase in resin content leads to a decrease in strength, but an increase in resistance to weathering and chemical attack. A decrease in resin content imparts higher flexural and tensile strengths and Young's moduli. The electrical properties of epoxy-glass composites are hardly affected by the glass content except for the permittivity, which increases with increasing fibre content. Fibre contents depend upon the method used to fabricate the composite and in general, filament wound and compression moulded pre-peg materials have a fibre volume fraction between 0.5 and 0.8, whereas hand layup items have a lower fibre fraction (about 0.4).
3. The orientation of the reinforcing material like fibres. They can be oriented in a unidirectional, bidirectional or random manner, and the properties of the composite will depend upon this orientation. Reinforced plastics do not show the same properties in all directions, i.e. they are anisotropic.

Matrix materials for composites are not restricted to synthetic organic polymers. Successful composites have been fabricated from inorganic matrix materials such as phosphate bonded oxides, ceramic-metal combinations (cermets) and metals themselves. The main factors that usually need to be taken into consideration when choosing a matrix resin are:

a) The mechanical strength required from the composite. This strength also depends upon the type of reinforcement and its arrangement within the matrix.

b) The specified performance of the composite in its working environment. The matrix must be able to maintain its properties under service conditions.

c) The fabrication process to be used. The resin should be easy to use in the process.

d) The cost of the resulting composite in conjunction with the use to which it will be put.

Five resins are currently used for the production of composites i.e. epoxies, polyesters, phenolics, silicones and polyimides. Out of these five, polyesters are the most widely used, followed by phenolics. Epoxy resins probably rank third in terms of amounts used, followed by silicones and then polyimides. Polyesters are much inferior in mechanical properties although they are lower in cost than epoxy resins. Silicones are expensive low-strength resins and are chosen only when their long-term heat resistance and electrical properties are needed. Phenolics offer good short-term performance at high temperature and are low in price. The more recently developed polyimides are used almost exclusively for their short and long term thermal resistance properties. Generally, epoxy matrices are used for continuous exposure to temperature of 175°C, and polyimides for 175-310°C. For short-term exposure, epoxy resins are acceptable up to 230°C, whereas polyimides can be used up to 370°C, but imides are difficult to process as they require a high curing temperature and release volatile compounds during cure.

Epoxy resin composites have gained a lot of attention due to their excellent properties. Some of the properties that lead them to be selected for high performance applications of composites are:

a) Easy handling and processability,
b) Low shrinkage and absence of volatile compounds during cure,
c) Good adhesion to glass and other reinforcing materials,
d) High level of thermal resistance,
e) Excellent chemical and moisture resistance,
f) Good thermal and electrical insulation properties.

Epoxy composites contain glass, carbon, boron fibres as reinforcements. These composites have a very high level of mechanical properties, fatigue resistance, chemical and thermal resistance. The technology of plastics reinforced with glass-fibre is well established, and such composites have a wide variety of applications. They have been used in rocket motor cases for the Minuteman, Polaris and Poseidon missiles, and for many secondary structural components of aircraft such as radomes and fairings. Epoxy-glass is superior to metals in strength/weight characteristics, but offers no advantages in stiffness/weight. The cost of using an epoxy composite rather than a more traditional material is of great importance, and must be set against the likely benefits and disadvantages that will accrue. Composites of epoxy resins with carbon or boron fibres possess properties that are not commonly found in engineering materials. They have high strength, low density, high Young’s modulus and good elasticity, showing only 0.5 – 1 % elongation at break. Steel, in contrast, shows a 20 % elongation at failure. An important factor possessed by composites is their ease of fabrication into complex shapes.

Epoxy resin based composites are used where their superior properties are needed and the extra cost involved in using them is offset by the benefits obtained. The transport, storage and processing of oil and oil products requires tanks and pipes that can withstand the corrosive attack of these substances. A similar requirement exists in the chemical, food, gas and water industries, all of which have a need for chemically resistant tanks and pipes. Extensive use of epoxy-glass filament wound pipe is now made in the US and Europe not only for services such as water, natural gas and petroleum, but also for gas gathering, brine lines and waste disposal. Epoxy-glass composites are most sought after in electronics industry for their mechanical strength and electrical resistance. Slot liners made of these composites are used in certain large electrical generators. Because of their low weight, many epoxy composite materials are used in different components of space vehicles. Several US missiles had their performance improved by substituting of an epoxy composite for a metal component. Similarly, epoxy composites find many applications in aircraft like in propeller spinners, anti-icing pads, wing spars etc. It has been estimated that if all gangways and underseat panels in a Boeing 747 were replaced with carbon fibre reinforced epoxy panels (CFRP), an extra seven passengers could be carried. Such composites have also been used in manufacture of sports equipment like skis, squash rackets, racing oars, kayaks, canoes and cricket bat springs etc. An area where epoxy-carbon fibre composites have great potential is in the fabrication of small reciprocating machine parts such as shuttles and other parts of weaving machines, the revolving parts of centrifuge and parts of internal combustion engines.

Inevitably, epoxy resin composites have become an important part of construction industry and engineering fields as replacement for many metals. This trend has been accelerating with the improvement in fabrication techniques of such composites as well as change in raw materials. Epoxy resin composites are being used for all such applications and show a lot of prospect in being utilized for more specialized uses in almost every sphere of high performance engineering applications.

Epoxy resin composites with CPs and carbon nanotubes as filler have been studied in detail throughout this Ph.D programme and compiled in this thesis. Infact, it all signifies a new area of research where these composites are being exploited as an alternative to Sn/Pb soldering technology.

1.5 Aim

The primary focus of our research work is to develop ICAs with improved properties by replacing the metallic fillers with intrinsically conducting polymers and carbon nanotubes. It is aimed that the limitations associated with metallic fillers mainly limited impact resistance can significantly be substantiated by using non-metallic fillers. The nature and dispersion of conductive fillers is of prime importance in deciding the final properties associated with such ICAs. So, we have used different conductive fillers with varied morphologies to improve the overall properties of these conductive adhesives. Moreover, the significance of the work lies in the fact that desired properties are achieved with relatively low filler loadings.

1.6 Plan of work

This work involved development of ICAs which are essentially epoxy based composites and was accomplished through following steps,

a) Conductive fillers, i.e, polyaniline and polypyrrole were synthesized,

b) Composites of polyaniline, polypyrrole and CNTs were prepared with epoxy matrix,

c) These composites were cured and studied for their thermal behaviour, conductivity, impact properties and surface morphology,

d) Technological utility of these conductive adhesives was studied by drop test and environmental aging studies.

1.7 References

1. Pron A, Rannou P. Prog Polym Sci 2002;27:135.
2. Lefrant S, Lichtman LS, Temkin M, Fichten DC, Miller DC, Whitwell GE, Burlich JM. Solid State Commun 1979;29:191.
3. Bakshi AK. Bull Mater Sci 1995;18:469.
4. Heeger AJ. In: Skotheim TA, editor, Handbook of conducting polymers, vol. 2. New York: Marcel Dekker 1986. p. 729.
5. MacDiarmid AG. Angew Chem Int Ed 2001;40:2581.
6. Yasufuku S. IEEE Electrical Insulation Magazine 2001;17:14.
7. Park SM, Lee HJ. Bull Korean Chem Soc 2005;26:697.
8. Kovacic P, Jones MB. Chem Rev 1987;87:357.
9. Milosevich S, Saichek K, Hincehey L, England WB, Kovacic P. J Am Chem Soc 1983;105:1088.
10. Feast WJ, Tsibouklis J, Pouwer KL, Groenendaal L, Meijer EW. Polymer 1996;37:5017.
11. Sugimoto R, Takeda S, Gu HB, Yoshino K. Chem Express 1986;1:635.
12. Natta G, Mazzanti G, Corradini P, Atti Acad. Naz. Lincei, Cl. Sci. Fis. Mat Nature 1958;25:3.
13. Shirakawa H, Ikeda S. Polymer J 1971;2:231.
14. Ito T, Shirakawa H, Ikeda S. J Polym Sci Polym Chem Ed 1974;12:11.
15. Shirakawa H, Louis EJ, MacDiarmid AG, Chiang CK, Heeger AJ. J Chem Soc Chem Commun 1977;16:578.

16. Chiang CK, Fincher CR, Park YW, Heeger AJ, Shirakawa H, Louis EJ, Gau SC, MacDiarmid AG. Phys Rev Lett 1977;39:1098.

17. Edwards JH, Feast WJ. Polymer 1980;21:595.

18. Yamamoto T, Sanechika K, Yamamoto A. J Polym Sci Polym Lett Ed 1980;18:9.

19. Lin J, Dudek LP. J Polym Sci Polym Lett Ed 1980;18:2869.

20. Kobayashi M, Chen J, Chung TC, Moraes F, Heeger AJ, Wudl F. Synth Met 1984;9:77.

21. Ibuki E, Ozaka S, Fujioka Y, Okada M, Yanagihara Y. Chem Pharm Bull 1982;30:2369.

22. Ibuki E, Ozaka S, Fujioka Y, Okada M, Yanagihara Y. Chem Pharm Bull 1982;30:802.

23. Toshima N, Asakura T. Bull Chem Soc Jpn 1993;66:948.

24. Dall'olio A, Dascola Y, Varacca V, Bocctti V. Compt Rend C 1968;267:433.

25. Gurunathan K, Vadivel Murugan A, Marimuthu R, Mulik UP, Amalnerkar DP. Mat Chem Phys 1999;61:173.

26. Diaz AF, Kanazawa KK. Extended linear chain compounds, J.S.Miller Ed. Plenum publishing corporation, Vol 3.1982;p. 417.

27. Xu J, Yang Y, Yu J, Jiang Y. App Surf Sci 2009;255:4329.

28. Joo J, Kim BH, Park DH, Kim HS, Seo DS, Shim JH, Lee SJ, Ryu KS, Kim K, Jin JI, Lee TJ, Lee CJ. Synth Met 2005;153:313.

29. Golodnitsky D. Encycl Electrochem Pow Sour 2009;112.

30. Chen J, Liu Y, Minett AI, Lynam C, Wang J, Wallace GG. Chem Mater 2007;19:3595.

31. Davoglio RA, Biaggio SR, Rocha-Filho RC, Bocchi N. J Power Sour 2010;195:2924.

32. Laforgue A, Simon P, Sarrazin C, Fauvarque JF. J Pow Sour 1999;80:142.

33. Frackowiak E, Khomenko V, Jurewicz K, Lota K, B´eguin F. J Power Sour 2006;153413.

34. Zheng L, Wang Y, Wang X, Li N, An H, Chen H, Guo J. J Power Sour 2010;195:1747.

35. Dhawale DS, Salunkhe RR, Jamadade VS, Dubal DP, Pawar SM, Lokhande CD. Current Appl Phys 2010;10:904.

36. Peng C, Zhang S, Jewell D, Chen GZ. Prog Natur Sci 2008;18:777.

37. Chandrasekhar P, Zay BJ, McQueeney T, Birur GC, Sitaram V, Menon R, Coviello M, Elsenbaumer RL. Syn Met 2005;155:623.

38. Mortimer RJ, Dyer AL, Reynolds JR. Displays 2006;27:2.

39. Kraft A, Rottmann M, Gilsing H, Faltz H. Electrochim Acta 2007;52:5856.

40. Coskun Y, Cirpan A, Toppare L. Polymer 2004;45:4989.

41. Tallman DE, Spinks G, Dominis A, Wallace GG. J Solid State Electrochem 2002;6: 73.

42. McAndrew TP. Trends Polym Sci 1997;5:7.

43. Sitaram SP, Stoffer JO, Okeefe TJ. J Coat Technol 1997;69:65.

44. Yagova IV, Ivanov SS, Bykov IV, Yagov VV. Protection Met 1998;34:132.

45. Zarras P, Stenger-Smith JD, Ostrom GS, Miles MH. ACS Symp Ser 1999;735:280.

46. Biallozor S, Kupniewska A. Synth Met 2005;155:443.

47. Rohwerder M, Duc LM, Michalik A. Electrochim Acta 2009;54:6075.

48. Armelin E, Oliver R, Liesa F, Iribarren JI, Estrany F, Alemán C. Prog Organ Coat 2007;59:46.

49. Chaudhari S, Mandale AB, Patil KR, Sainkar SR, Patil PP. Surf Coat Technol 2006;200:5557.

50. Yalçınkaya S, Tüken T, Yazıcı B, Erbil M. Current Appl Phys 2010;10:783.

51. Kousik G, Pitchumani S, Renganathan NG. Prog Org Coat 2001;43:286.

52. Ren YJ, Chen J, Zeng CL. J Power Sour 2010;195:1914.

53. Ocampoa C, Armelin E, Liesa F, Alem´an C, Ramis X, Iribarren JI. Prog Org Coat 2005;53:217.

54. Liesa F, Ocampo C, Alema´n C, Armelin E, Oliver R, Estrany F. J App Polym Sci 2006;102:1592.

55. Ahuja T, Mir IA, Kumar D, Rajesh. Biomater 2007;28:791.

56. Rahman MA, Kumar P, Park D, Shim Y. Sensors 2008;8:118.

57. Rajesh, Ahuja T, Kumar D. Sens Actuat B: Chem 2009;136:275.

58. Guimard NK, Gomez N, Schmidt CE. Prog Polym Sci 2007;32:876.

59. Lange U, Roznyatovskaya NV, Mirsky VM. Anal Chim Acta 2008;614:1.

60. Peng H, Zhang L, Soeller C, Travas-Sejdic J. Biomater 2009;30:2132.

61. Malhotra BD, Chaubey A, Singh SP. Anal Chim Acta 2006;578:59.

62. Teles FRR, Fonseca LP. Mater Sci Engineer: C 2008;28:1530.

63. Xia L, Wei Z, Wan M. J Col Inter Sci 2010;341:1.

64. Bajpai V, He P, Goettler L, Dong JH, Dai L. Syn Met 2006;156:466.

65. Shamsipur M, Kazemi SH, Mousavi MF. Biosen Bioelectron 2008;24:104.

66. Bai H, Zhao L, Lu C, Li C, Shi G. Polymer 2009;50:3292.

67. Ambrosi A, Morrin A, Smyth MR, Killard AJ. Anal Chim Acta 2008;609:37.

68. Kwon OS, Hong T, Kim SK, Jeong J, Hahn J, Jang J. Biosens Bioelectron 2010;25:1307.

69. Huang S, Ganesan P, Popov BN. Appl Catal B: Environ 2009;93:75.

70. Inamuddin, Shin KM, Kim SI, So I, Kim SJ. Electrochim Acta 2009;54:3979.

71. Zhang Y, Li Q, Sun Li, Tang R, Zhai J. J Hazard Mater 2010;175:404.

72. Ansari R, Feizy J, Delavar AF. E- J Chem 2008;5:853.

73. Green RA, Lovell NH, Wallace GG, Poole-Warren LA. Biomater 2008;29:3393.

74. Abidian MR, Martin DC. Biomater 2008;29:1273.

75. Min G. Synth Met 1999;102:1163.

76. Winther-Jensen B, Clark NB. React Funct Polym 2008;68:742.

77. Lira LM, Co´rdoba de Torresi SI. Electrochem Commun 2005;7:717.

78. Wong CP, Daoqiang Lu. In: Proc. Fourth International Conference on Adhesive Joining and Coating Technology in Electronics Manufacturing. New York, 2000.p.121.

79. Tremble B. IEEE Spectrum 1998;35(5):55.

80. Alpert BT, Schoenberg AJ. Electron Packag & Prod. Nov 1991;130.

81. Suraski D, Seelig K. IEEE Trans Electron Packag Manuf 2001;24:244.

82. Jagt JC, Beris PJM, Lijten GFCM. IEEE Trans Components Packag Manuf Technol, B 1995;18(2):292.

83. Wong CP, Lu D, Tong QK. In: Proc. Third International Conference on Adhesive Joining & Coating Technology in Electronics Manufacturing, Binghamton, New York, 1998.p.28.

84. Gilleo K. Soldering & Surface Mount Technology 1995;19:12.

85. Yim MJ, Paik KW. Int J Adhesion & Adhesives 2006;26:304.

86. Corbett S, Domiano MJ. Surface Mount Technology 1997;48.

87. Greaves J. In: Proc. Nepcon West Technical Programme, 1993.p.1479.

88. Gaynes MA, Lewis RH, Saraf RF, Roldan JM. IEEE Trans Components Packag Manuf Technol, B 1995;18(2):299.

89. Nguyen G, Williams J, Gibson F, Winster T. In: Proc. International Electronic Packaging Conference, Binghampton, New York, 1993.p.479.

90. Li L, Morris JE. Int J Microelectron Packag 1988;1(3):159.

91. Liu J, Morris JE. In: Proc. Workshop on Polymeric Materials in Microelectronics & Photonics (POLY'99), Paris, 1999.p. 259.

92. Morris JE, Liu J. Electrically Conductive Adhesives. Ed. Suhir E, Lee YC, Wong CP. Springer Verlag, 2006.

93. Liu J, Ljungkrona L, Lai Z. IEEE Trans Components Packag Manuf Technol, B 1995;18(2):313.

94. Rorgen R, Liu J. IEEE Trans Components Packag Manuf Technol, B 1995;18(2):305.

95. Rusanon O, Lenkkeri J. IEEE Trans Components Packag Manuf Technol, B 1995;18(2):320.

96. Hvims H. IEEE Trans Components Packag Manuf Technol, B 1995;18(2):284.

97. Tummala RR, Rymaszewski EJ, Klopfenstein A. Microelectronic Packaging Handbook, Part III. New York: Chapman & Hall, 1997.

98. Lau JH. Chip on Board Technologies for Multichip Modules. New York: Van Nostrand Reinhold, 1994.

99. Wong CP. Polymers for Electronic and Photonic Applications. San Diego, California: Academic Press, 1993.

100. Bauer RS. Polymers for Electronic and Photonic Applications. Ed. Wong CP. San Diego, California: Academic Press, 1993.

101. Tan F, Qiao X, Chen J, Wang H. Int J Adhesion & Adhesives 2006;26:406.

102. Liu J. Conductive Adhesives for Electronics Packaging. UK: Electrochemical Publications Ltd, 1999.

103. Lu D, Wong CP. J Appl Polym Sci 1999;74:399.

104. Lantzsch M. In: Proc. Fourth International Conference on Adhesive Joining & Coating Technology in Electronics Manufacturing, Espoo, Finland, 2000.p. 168.

105. Figovsky O, Sklyarsky L, Sklyarsky O. In: Proc. Fourth International Conference on Adhesive Joining & Coating Technology in Electronics Manufacturing, Espoo, Finland, 2000.p. 107.

106. Liong S, Wong CP, Burgoyne WF Jr. IEEE Trans Components Packag Technol 2005;28(2):377.

107. Lu D, Wong CP. IEEE Trans Electron Packag Manuf 1999;22(4):324.

108. Yang C, Yuen MMF, Gao B, Ma Y. In: Proc. Fifty ninth Electronic Components and Technology Conference, ECTC 2009.p.1337.

109. Li H, Wong CP. IEEE Transactions on Advanced Packaging 2004;27(1):165.

110. Inoue M, Liu J. Second Electronics System integration Technology Conference, ESTC 2008.p.1147.

111. Lu D, Tong QK, Wong CP. IEEE Trans Components Packag Manuf Technol, A 1999;22(3):365.

112. Markley DL, Tong QK, Magliocca DJ, Hahn TD. IN: Proc. International Symposium on Advanced Packaging Materials, Processes, Properties and Interfaces, 16-20, 1999.

113. Shimada Y, Lu D, Wong CP. In: Proc. Sixth International Symposium on Advanced Packaging Materials, Braselton, Georgia, 2000. p. 336.

114. Kottaus S, Guenther BH, Haug R, Scheafer H. IEEE Trans Components Packag Manuf Technol, A 1997;20(1):15.

115. Fan L, Tison C, Wong CP. In: Proc. Eighth International Symposium on Advanced Packaging Materials. Georgia, 2002.p. 184.

116. Kim JM, Yasuda K, Fujimoto K. J Electron Mater 2004;33(11):1331.

117. Lu D, Wong CP. In: Proc. International Symposium on Advanced Packaging Materials, Braselton, Georgia, 2000. p. 7.

118. Kang SK, Purushothaman S. Journal of Electronic Materials 1999; 28(11):1314.

119. Gallagher C, Matijasevic G, Maguire JF. In: Proc. Forty seventh Electronic Component and Technology Conference. Sanjose, California, 1997. p. 554.

120. Jagt JC. IEEE Trans Components Packag Manuf Technol, A 1998;21(2):215.

121. Kooring CWL, Riphagen, D. Electrocomponent Science and Technology 1980;**7:**69.

122. Marshall DW. J Adhesion 2000;74(1-4):301.

123. Ho L, Nishikawa H, Takemoto T, Kashiwagi Y, Yamamoto M, Nakamoto M. In: Proc. European Microelectronics and Packaging Conference, EMPC 2009.p.1.

124. Takezawa H, Mitani T, Kitae T, Sogo H, Kobayashi S, Bessho Y. In: Proc. Eighth International Symposium on Advanced Packaging Materials, Goergia, 2002.p. 139.

125. Kivilahti J, Savolaien P. Conductive Adhesives for Electronics Packaging. Ed. Liu J. UK: Electrochemical Publications Ltd, 1999.

126. Pietila M, Makela T, Levon K, Kivilahti J, Isolato H. In: Proc. Fourth International Conference on Adhesive and Coating Technology in Electronics Manufacturing, Espoo, Finland 2000.p. 118.

127. Chow LLW, Li J, Yuen MMF. In: Proc. Eighth International Symposium on Advanced Packaging Materials, Georgia, 2002.p.127.

128. Morris JE. In: Proc. Conference on High Density Microsystem Design and Packaging and Component Failure Analysis, 2006.p.199.

129. Mach P, Radev R, Pietrikova A. In: Proc. Second Electronics System integration Technology Conference, ESTC 2008.p.1141.

130. Kottaus S, Haug R, Scheafer H, Henneman OD. First IEEE International Symposium on Polymeric Electronics Packaging, Norrkoping, Sweden, 1997.p.64.

131. Fu Y, Liu J, Willander M. Int J Adhesion & Adhesives 1999;19(4):281.

132. Moon KS, Dong H, Maric R, Pothukuchi S, Hunt A, Li Y, Wong CP. J Electron Mater 2005;34(2):168.

133. Tao Y, Xia Y, Wang H, Gong F, Wu H, Tao G. IEEE Transac Advanc Packag 2009;32(3):589.

134. Telychkina O, Boehme B, Heimann M, Morris JE, Wolter K. In: Proc. Thirty second International Spring Seminar on Electronics Technology, ISSE 2009.p.1.

135. Zhang Z, Chen X, Yang H, Fu H, Xiao F. In: Proc. International Conference on Electronic Packaging Technology & High Density Packaging (ICEPT-HDP), 2009.p.834.

136. Mach P, Richter L, Pietriková A. In: Proc. Thirty first International Spring Seminar on Electronics Technology, ISSE 2009.p.228.

137. Kornain Z, Amin N, Jalar A, Ang Ye C, Ahmad I. In: Proc. IEEE International Conference on Semiconductor Electronics, ICSE 2008.p.549.

138. Jiang H, Moon K, Li Y, Wong CP. In: Proc. Fifty Sixth Electronic Components and Technology Conference, 2006.p.6.

139. Morris JE. In: Proc. Third Microelectronic Materials Conference, Berlin, 2000.p. 181.

140. Lu D, Tong QK, Wong CP. In: Proc. International Symposium and Exhibition on Advanced Packaging Materials, Process, Properties and Interfaces, Braselton, Georgia, 1999.p.2.

141. Lu D, Wong CP. Int J Adhesion & Adhesives 2000;20:189.

142. Klosterman D, L Li, Morris JE. IEEE Trans Components Packag Manuf Technol, A 1998;21(1):23.

143. Vargo LS. Electron Packag Prod 1986;48.

144. Ruschau GR, Yoshikawa S, Newnahm RE. J Appl Phys 1992;72:953.

145. Wei Y, Sancaktar E. J Adhesion Sci Technol 1996;10:1199.

146. Sancaktar E, Dilsiz N. J Adhesion Sci Technol 1999;13:679.

147. Mikrajuddin A, Shi FG, Chungiboonpatana S, Okuyama K, Davidson C, Adams JM. Mater Sci Semicond Process 1999;2:309.

148. Mündlein M, Nicolics J. IEEE Transac Comp Packag Technol 2005;28:765.

149. Lu D, Tong QK, Wong CP. In: Proc. Eighth International Symposium on Advanced Packaging Materials, Braselton, Georgia, 1998.p.256.

150. Li Y, Moon KS, Li H, Wong CP. In: Proc. Ninth International Symposium on Advanced Packaging Materials. Atlanta, Georgia, 2004.p.1.

151. Miragliotta J, Benson RC, Philips TE. In: Proc. Eighth International Symposium on Advanced Packaging Materials. Georgia, 2002.p.132.

152. Liong S, Wong CP, Burgoyne WF Jr. In: Proc. Electronic Component and Technology Conference, California, 2002.p.1140.

153. Perichaud MG, Deletage JY, Fremont H, Danto Y, Faure C. Microelectron Relability 2000;40:1227.

154. Liu J, Gustafsson K, Lai Z, Li C. In: Proc. Second International Conference on Adhesive Joining and Coating Technology in Electronics Manufacturing, Stockholm, Sweden, 1996.p.141.

155. Klosterman D, Li L. Journal of Electronics Manufacturing, 1996;5(4):277.

156. Lu D, Wong CP. In: Proc. Fourth International Symposium and Exhibition on Advanced Packaging Materials, Processes, Properties and Interfaces, Braselton, Georgia, 1999.p.288.

157. Lu D, Wong CP. In: Proc. Fourth International Conference on Adhesive Joining & Coating Technology in Electronics Manufacturing, Espoo, Finland, 2000.p.1.

158. Tong QK, Fredrickson G, Kuder R, Lu D. In: Proc. Forty ninth Electronic Components and Technology Conference, California, 1999.p.347.

159. Leidheiser H Jr. J Coatings Technol 1981;53(678):29.

160. Trabanelli G, Carassiti V. Advanced Corrosion Science and Technology. Ed. Fontana MG, Stachle RW, vol. 1. New York: Plenum Press,1970.

161. Trabanelli G. Corrosion Mechanisms. Ed. Mansfeld F. New York: Marcel Dekker,1987.

162. Riggs OL Jr. Theoretical Aspects of Corrosion and Corrosion Inhibition. Ed. Nathan CC. Houston USA: NACE International,1973.

163. Lu D, Wong CP. IEEE Trans Components Packag Technol 2000;23(4):620.

164. Lu D, Wong CP. IEEE Trans Components Packag Technol 2000;23(3):440.

165. Durand D, Vieau D, Chu AL, Weiu TS. US Patent 5180523, Nov. 1989.

166. Li Y, Moon Y, Whitman A, Wong CP. IEEE Transac Comp Packag Technol 2006;29:758.

167. Xue S, Dillard D. IEEE Trans Components Packag Technol 2003;26(3):554.

168. Rao Y, Lu D, Wong CP. Int J Adhesion & Adhesives 2004;24:449.

169. Macathy S. In: Proc. Surface Mount International, Sanjose, 1995.p. 562.

170. Vona SA, Tong QK Jr, Kuder R, Shenfield D. In: Proc. Fourth International Symposium and Exhibition on Advanced Packaging Materials, Processes, Properties and Interfaces, Braselton, Georgia, 1998.p. 261.

171. Liu J, Lai Z, et al. In: Proc. Third International Conference on Adhesive Joining and Coating Technology in Electronics Manufacturing. Binghampton, New York, 1998.p.1.

172. Liu J, Weman B. In: Proc. Second International Symposium on Electronics Packaging Technology, Shanghai, China 1996.p.313.

173. Keil M, Bjarnason B, Wickstrom B, Olsson L. Advanced Packaging 2001;10(9).

174. Tong Q, Vona S, Kuder R, Shenfiled D. In: Proc. Third International Conference on Adhesive Joining & Coating Technology in Electronics Manufacturing, Binghampton, New York, 1998.p.272.

175. Luo S, Wong CP. In: Proc. Eighth International Symposium on Advanced Packaging Materials, Braselton, Georgia, 2002.p.226.

176. Li L, Morris JE, Liu J, Lai Z, Ljungkrona L, Li C. In: Proc. Forty fifth Electronic Component & Technology Conference, Las Vegas, North Virginia, 1995.p.114.

177. Gomatam R, Sancaktar. E, Boismier D, Schue D, Malik I. In: Proc. International Symposium on Advanced Packaging Materials: Processes, Properties and Interfaces, Braselton USA, 2001.p.6.

178. Dudek R, Berek H, Fritsch T, Michel B. IEEE Trans Comp Packag Technol 2000;23:462.

179. Gaynes MA, Lewis RH, Saraf RF, Roldan JM. IEEE Trans Comp Packag Manuf Technol Part B: Advanced Packaging 1995;18:299.

180. Xu S, Dillard DA, Dillard JG. Int J Adhesion & Adhesives 2003;23:235.

181. De Paoli MA. Handbook of organic conductive molecules and polymers: vol. 2. Conductive polymers: synthesis and electrical properties. Edited by H. S. Nalwa 1997. John Wiley & Sons Ltd.p.773.

CHAPTER 2

ISOTROPICALLY CONDUCTIVE ADHESIVE WITH POLYANILINE POWDER AS FILLER

In this chapter, we present a novel application of conducting polymer, polyaniline (PANI) as conductive filler for the development of isotropically conductive adhesives (ICAs). ICAs are an environment and user friendly alternative to traditional lead bearing solders. Metallic fillers present in currently used ICAs have certain limitations due to unstable contact resistance and poor impact properties. Therefore, we have developed ICAs using protonic acid doped polyaniline as the conducting filler in an anhydride cured epoxy system (EP). Fundamental material characterization like DSC, TGA and SEM of the ICAs was conducted to study their properties. Conductivity of these materials was measured by four probe method while impact properties were studied by lap shear and drop tests. Samples were aged at 85°C/~100% RH for more than 500 h and the effects of aging were studied. Conductivity of ICA was 10^{-3} S cm^{-1} measured at 25% PANI filler concentration. These results demonstrate the potential of these polyaniline filled systems to function as ICA. The research presented in this chapter has been published in Journal of Polymeric Materials [1].

2.1 Polyaniline

Polyaniline (PANI) is one of the most intensively investigated polymers during the last decade. Due to its ease of synthesis and processing, environmental stability, relatively high conductivity and cost economics, polyaniline is probably the most industrially important conducting polymer today [2-3]. Polyaniline is a typical phenylene based polymer having a chemically flexible -NH- group in the polymer chain flanked by phenyl ring on either side. Polyaniline represents a class of macromolecules whose electrical conductivity can be varied from an insulator to a conductor by the redox process. This polymer can achieve its highly conductive state either through the protonation of the imine nitrogens or through the oxidation of amine nitrogens. For example, the conducting state of PANI can be obtained in its 50% oxidized emeraldine state in aqueous protonic acids like HCl and the resulting material is a p-type semiconductor [4-6]. With the extent of doping, polyaniline can have four different oxidation states [7, 8] like leucomeraldine base (LEB), emeraldine (EB), emeraldine salt (ES) and pernigraniline (PNB) as shown schematically in **Fig. 2.1**.

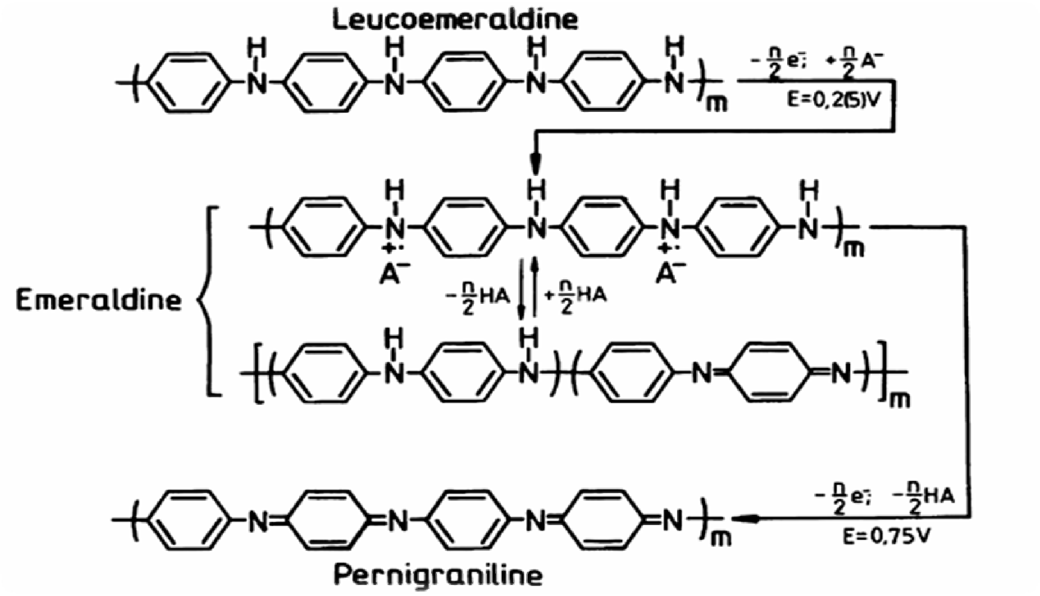


Figure 2.1. Various oxidation states of Polyaniline

Starting from the electrically insulating leucoemeraldine, electrically conducting emeraldine can be obtained by standard chemical or electrochemical oxidation. But, upon further oxidation a second redox process occurs, which yields a new insulating material, pernigraniline. In addition to this unusual behavior, a decrease of conductivity by 10 orders of magnitude is obtained just by treatment of the conducting emeraldine in neutral or alkaline media. Protonation induces an insulator-to-conductor transition, while the number of p-orbital electrons in the chain remains constant. A lot of work has been devoted to understand the mechanism of this unusual transition. Oxidative doping of the leucomeraldine base or protonic acid doping of the emeraldine base material produces the conducting emeraldine salt whose conductivity varies between 0.5 to 400 S cm^{-1} depending on the means of preparation. Extensive studies of ES material have shown that the metallic state is governed by inhomogeneous disorder. In the conducting state, there are regions that are three-dimensionally ordered in which the conducting electrons are three-dimensionally delocalized and regions where the polymer is strongly disordered, in which conduction electrons diffuse through one-dimensional polymer chains that are nearly electrochemically isolated. One dimensional localization in these nearly isolated chains lead to decrease in conductivity with decrease in temperature.

Chemical Synthesis

Polyaniline can be synthesized mainly by chemical or electrochemical oxidation of aniline under acidic conditions. The method of synthesis depends on the intended application of the polymer. For bulk production chemical method, where as for thin films and better patterns electrochemical method is preferred.

The conventional method of emeraldine salt synthesis is the bulk or chemical polymerization of aniline monomer in aqueous media in presence of a protonic acid like HCl [3, 9-12]. An oxidant like ammonium per sulphate or potassium dichromate can be used to initiate the reaction [13-15]. The ideal molar ratio of monomer to acid to oxidizing agent is proved to be 1: 1: 1 [16, 17]. The aniline monomer in the protonic acid medium is mixed with aqueous solution of ammonium per sulphate with a continuous stirring for 4 h to obtain a green precipitate. The green precipitate so obtained is then filtered and washed with distilled water so as to obtain oligomer free emeraldine salt. The factors affecting the polymerization process include the pH of the solution, type of acids used, its concentration, effective size, solvation and electronegativity of the conjugate base associated with a given acid. Various attempts have been made to synthesize PANI by chemical polymerization and to understand the effect of different dopants and reaction conditions. In one such study, PANI powder prepared in HCl (2M) using $(NH_4)_2S_2O_8$, KIO_3 and $K_2Cr_2O_7$ as oxidizing agents showed that the maximum conductivity and electroactivity similar to that of PANI prepared electrochemically indicating that type of oxidizing agent has little effect on the conductivity and electroactivity [18].

Electrochemical polymerization

The electrochemical polymerization of aniline provides films exhibiting a well defined morphology. This process has an advantage of being very simple and has high level of reproducibility. This morphology strongly depends on preparation conditions such as the type of electrolyte, the electrode and the electrochemical procedures used. It is a radical combination reaction and can be precisely controlled. It results in the formation of ordered films for specific end uses. The process can be accomplished galvanostatically (constant current), potentiostatically (constant voltage) or by cyclic voltammetry. Electrochemical polymerization is carried out usually in a conventional three electrode electrochemical assembly containing protonic acid solution as an electrolyte and monomer. The first step in polymerization involves oxidation of aniline and formation of radical cation. After that radical formation, a coupling takes place predominantly by 1,4 coupling of monomer units and ultimately polymer is synthesised in the form of a film on working electrode. PANI films have been deposited enormously by this technique for various applications. The specific advantage of this method is that PANI coated electrode system can be tailor made for particular end use.

Composites of PANI

PANI has assumed tremendous importance due to the large number of applications. However, the main limitation associated with most of the CPs is that they cannot be processed by conventional methods of processing. However, PANI has been used due to its ease of synthesis and relative stability. But in its doped state, PANI is not easily soluble in most solvents and its thermal stability is also low. This limitation has been focus of numerous studies and many attempts have been made to overcome this problem. Most important way out was by formation of blends and composites of PANI with processible polymers. Composites of PANI have found a number of industrial applications like corrosion protection, EMI shielding, conductive adhesives etc. Therefore, we focus on the preparation of composite materials based on PANI for conductive adhesives.

The processing methods adopted for preparation of PANI composites are essential in determining the properties of such composites. Known methods of producing PANI composites can broadly be divided into two types, i.e., synthesis based on aniline polymerization in the presence of or inside a matrix polymer, and blending method to mix a previously prepared polyaniline with a matrix polymer.

The main feature of these methods is the in-situ dispersion of PANI particles inside the matrix of other polymers by synthesizing PANI inside the solution or dispersion of the matrix polymer. Many variations to this general phenomenon are possible. One method involves polymerization of aniline at lower temperatures using an appropriate oxidant in presence of water soluble polymers or tailor-made reactive copolymers like poly(2-vinylpyridine-co-p-aminostyrene), PVA, poly(N-vinylpyrrolidone) etc. This technique results in sterically stabilized colloidal dispersions of PANI particles of different size and morphology. These colloids can be further mixed with film-forming latex particles or with stable matrix polymer dispersions to produce conducting composites. Ruckenstein et al [21] reported a method to produce PANI/PMMA and PANI/PS composites via oxidative aniline polymerization carried out by adding an aqueous solution of ammonium per sulfate and HCl dopant to a concentrated emulsion containing an aqueous solution of the ionic surfactant (sodium dodecylsulfate) as the continuous phase and an organic (benzene) solution of the host polymer and aniline as the dispersed phase. The corresponding composites were obtained by co-precipitation of the host polymer and PANI, with a percolation threshold of ≈ 2 – 10 volume percent PANI. Similarly, Pan et al [22] reported a composite of PANI with polyacrylonitrile. PANI was synthesized by emulsion polymerization using dodecyl benzene sulphonic acid (DBSA) as surfactant and protonating agent. The composite films were obtained by casting the mixed solution of PANI-DBSA dissolved in chloroform and polyacrylonitrile in DMSO. Another most widely approach involves doping of PANI with long alkyl chain organic acids like camphor sulphonic acid (CSA), DBSA etc. The bulk non-polar tail renders the PANI in conducting form to be soluble in some ordinary organic solvents such as *m*-cresol, chloroform, xylene etc. Therefore, such doped PANI can be solution processed with common insulating polymers in a proper solvent. Many such composites involving solution belnding of PANI doped by CSA and matrix polymers like PMMA [23], PA [24], and PANI doped by DBSA with PS [25], EPDM [26], PVC [27, 28], Epoxy resin [29], Nylon 6,6 [30] have been reported. Recently, Dai et al have reported a polyacrylamide (PAM)/PANI composite hydrogel by interfacial polymerization. Composites were prepared by swelling of PAM hydrogels in a solution containing APS dissolved in 1M HCl. The swollen hydrogels were introduced in aniline solution in hexane and polymerization occurred inside the PAM network [31].

The electrochemical polymerization of aniline on a matrix is another way of preparation of PANI composites. Although this method is not practical in large scale technologies, but it is very useful in small geometries like in biosensors, microelectronics, batteries etc. This process has some advantages like precise control of PANI properties and possibility of avoiding by-products etc. This method has already been used to produce composites of PANI with PMMA, PU, PC etc.

A typical method to obtain PANI composites is probably the grafting of some polymers to a PANI surface. Chen et al [32] demonstrated chemical modification of EB via its UV-induced surface graft polymerization with methoxy–poly(ethylene glycol) monomethacrylate macromonomer in aqueous media. These modified PANI films doped with $HClO_4$ were effective in reducing protein adsorption and platelet adhesion, and were claimed to have potential application as biomaterials and blood compatible materials. Thermally initiated graft copolymerization was also used in the case of EB and acrylic acid [33]. This grafting method can be used effectively where the adhesion properties are important.

In industrial context and for bulk production, dry blending method is more useful and economical. It involves direct mixing of PANI in various geometrical forms inside a procured matrix or matrix solutions. The composite is obtained either by curing or solvent evaporation. A patent by Laasko et al [34] was directed to a method of producing electrically conductive thermosetting composites. According to their invention, different thermosets, e.g., phenol-formaldehyde resin, melamine formaldehyde resin or polyester resin could be converted into electrically conductive materials by using a conductive component polyaniline. The later was protonated by a protonic acid containing at least one hydroxyl group. Protonated polyaniline with such acids was able to act in the thermoset composition not only as conductive component, but also as curing agent. Particularly, phenol-4-sulphonic acid protonated PANI was easily dissolved in the resin, resulting in homogeneous and uniform thermosetting compositions. Similar, thermosetting conductive composites have been prepared by direct mixing of PANI protonated with different acids. Jia et al [35] studied the effect of DBSA on dispersion of PANI inside epoxy matrix. It was reported that excess of DBSA results in lowering of percolation threshold and hence improved dispersion of PANI in the composites. The effect of PANI-DBSA on the curing parameters of an epoxy resin cured with an amine based hardener has been reported. It was observed that in presence of more reactive aliphatic amine, PANI-DBSA also participated in the curing process [36]. Effect of morphology of HCl doped PANI on electrical conductivity of PANI-epoxy composites was investigated. It revealed that composites containing PANI wires had the lowest percolation threshold as compared to PANI particles or fibres [37]. In an alternative approach, oligomeric polyaniline in emeraldine base form was blended with epoxy resin and the composite was cured with aliphatic amine to form interpenetrating network. A perfect network of PANI salts in these composites was formed and the percolation threshold was very low. The interpenetrating network could be doped with protonic acids to give conductive compositions [38]. An overview of such composites shows that they exhibit a great opportunity to be used for specific applications. Already some have been used as antistatic or EMI shielding coatings. Keeping in view the above reported literature, the present work deals with such composites and explores their application as isotropically conductive adhesives. This work presents a major leap in the development of novel ICAs with organic polymer filler for electronic applications.

2.2. Experimental

2.2.1. Materials used

The matrix polymer used was an epoxy named Epon-862 which is based on diglycidyl ether of bisphenol-F (DGEBF), manufactured by Hexion speciality chemicals, USA and was purchased from Miller Stephenson chemical company, USA. The epoxy equivalent weight of the Epon-862 is approximately 170 g/equivalent. Anhydride curing agent, hexahydropthalic anhydride (HHPA) and the catalyst, 2-ethyl-4-methylimidazole (2E4MZ) were obtained from Sigma Aldrich chemicals Pvt. Ltd. Aniline and HCl were supplied by CDH chemicals India, while ammonium persulphate (APS) was purchased from Merck Specialities Pvt. Ltd. India. All chemicals except aniline were used as received. Aniline monomer was double distilled before use.

Table 2.1. Specifications of material and chemicals along with their sources.

Material	Acronym	Source
Epon 862	DGEBF	Hexion speciality chemicals, Inc. Houston, Texas, USA
Hexahydropthalic anhydride	HHPA	Sigma Aldrich chemicals Pvt. Ltd. Bangalore, India
2-ethyl-4-methylimidazole	2E4MZ	Sigma Aldrich chemicals Pvt. Ltd. Bangalore, India
Aniline A.R	ANI	Central Drug House, New Delhi, India
Hydrochloric acid A.R	HCl	Central Drug House, New Delhi, India
Ammonium persulfate, A.R	APS	Merck specialities Pvt. Ltd. Mumbai, India

2.2.2. Synthesis of polyaniline

Polyaniline was synthesized via a conventional route in aqueous medium using protonic acid like HCl as dopant and oxidizing agent such as ammonium persulfate, $(NH_4)_2S_2O_8$, as initiator [39]. An appropriate quantity of hydrochloric acid was added in measured quantity of deionized water from Millipore Synergy 185 assembly to prepare 1 M HCl solution. Freshly distilled aniline monomer (0.2M) was added to this solution and stirred to get aniline acid solution and kept in an ice-bath to attain the reaction temperature 0-4°C. In another beaker an aqueous solution of APS (0.2 M) in deionized water was prepared and kept at freezing temperature till it attains the reaction temperature. This solution was added drop wise to the aniline-HCl solution under constant stirring. The mixture was stirred for 4-5 h for the completion of reaction. A dark green precipitate is obtained to mark the formation of PANI. The precipitate was filtered under vacuum, washed thoroughly with deionized water several times to remove excess salts and then the precipitate was dried in an oven to make it moisture free. The dried mass was ground into fine powder.

2.2.3. Formulation of resin

The resins for the ICAs were formulated as per the following procedure

a) Curing agent (HHPA) which is solid at room temperature was heated slightly to melt it. An appropriate quantity of epoxy resin and hardener was added in a ratio of 1:0.85.

b) The mixture was stirred by a glass rod with heat, if necessary, until a homogenous mixture was formed.

c) After the mixture cooled down to room temperature, a certain amount of 2E4MZ, i.e., 0.1 parts per hundred parts of epoxy resin was added and mixed thoroughly. The mixture was left undisturbed for some time to remove air bubbles before further use.

2.2.4. Preparation of ICA

Different amounts of PANI powder were added to known amounts of the precured resin mixtures and mixed thoroughly using a glass rod to obtain ICAs with 5, 10, 15, 20, and 25% PANI concentrations. The conductive filler concentration is described as weight percent (wt %).

2.3. Characterization

2.3.1. Differential Scanning Calorimetry

Differential scanning calorimetry (DSC) is a thermoanalytical technique in which the difference in the amount of heat required to increase the temperature of a sample and reference are measured as a function of temperature. Both the sample and reference are maintained at nearly the same temperature throughout the experiment. Generally, the temperature program for a DSC analysis is designed such that the sample holder temperature increases linearly as a function of time. The reference sample should have a well-defined heat capacity over the range of temperatures to be scanned.

The main application of DSC is in studying phase transitions, such as melting, glass transitions, or exothermic decompositions. These transitions involve energy changes or heat capacity changes that can be detected by DSC with great sensitivity.

The technique was developed by E.S. Watson and M.J. O'Neill in 1960, and introduced commercially at the 1963 Pittsburgh Conference on Analytical Chemistry and Applied Spectroscopy [40]. The term DSC was coined to describe this instrument which measures energy directly and allows precise measurements of heat capacity [41].

The basic principle underlying this technique is that, when the sample undergoes a physical transformation such as phase transitions, more or less heat will need to flow to it than the reference to maintain both at the same temperature. Whether less or more heat must flow to the sample depends on whether the process is exothermic or endothermic. For example, as a solid sample melts to a liquid it will require more heat flowing to the sample to increase its temperature at the same rate as the reference. This is due to the absorption of heat by the sample as it undergoes the endothermic phase transition from solid to liquid. Likewise, as the sample undergoes exothermic processes (such as crystallization) less heat is required to raise the sample temperature. By observing the difference in heat flow between the sample and reference, differential scanning calorimeters are able to measure the amount of heat absorbed or released during such transitions. DSC may also be used to observe more subtle phase changes, such as glass transitions. It is widely used in industrial settings as a quality control instrument due to its applicability in evaluating sample purity and for studying polymer curing.

The result of a DSC experiment is a curve of heat flux versus temperature or time. There are two different conventions: exothermic reactions in the sample shown with a positive or negative peak, i.e., it depends on the different kind of technology used by the instrumentation to make the experiment. This curve can be used to calculate enthalpies of transitions. This is done by integrating the peak corresponding to a given transition. It can be shown that the enthalpy of transition can be expressed using the following equation:

$$\Delta H = KA$$

where ΔH is the enthalpy of transition, K is the calorimetric constant, and A is the area under the curve. The calorimetric constant will vary from instrument to instrument, and can be determined by analyzing a well-characterized sample with known enthalpies of transition.

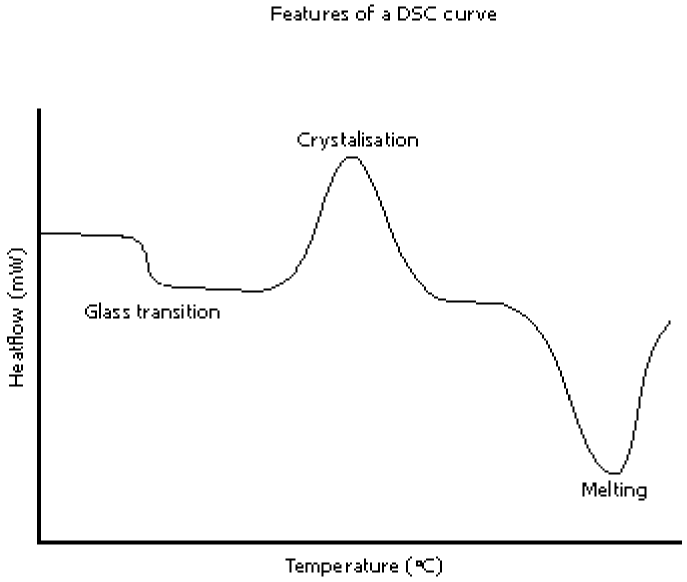


Figure 2.2. A schematic DSC curve demonstrating the appearance of common features

Differential scanning calorimetry can be used to measure a number of characteristic properties of a sample. Using this technique, it is possible to observe fusion and crystallization events as well as glass transition temperatures (T_g). DSC can also be used to study oxidation, as well as other chemical reactions. Glass transitions may occur as the temperature of an amorphous solid is increased. These transitions appear as a step in the baseline of the recorded DSC signal. This is due to the sample undergoing a change in heat capacity; no formal phase change occurs. As the temperature increases, an amorphous solid will become less viscous. At some point, the molecules may obtain enough freedom of motion to spontaneously arrange themselves into a crystalline form. This is known as the crystallization temperature (T_c). This transition from amorphous solid to crystalline solid is an exothermic process, and results in a peak in the DSC signal. As the temperature increases the sample eventually reaches its melting temperature (T_m). The melting process results in an endothermic peak in the DSC curve. The ability to determine transition temperatures and enthalpies makes DSC an invaluable tool in producing phase diagrams for various chemical systems.

Figure 2.3. A pictoral view of DSC instrument (Model Q20)

DSC is used widely for examining polymers to check their composition. Melting points and glass transition temperatures for most of the polymers are available from standard compilations, and the method can show up possible polymer degradation by the lowering of the expected melting point, T_m, for example. T_m depends on the molecular weight of the polymer, so lower grades will have lower melting points than expected. The percentage crystallinity of a polymer can also be found using DSC. It can be found from the crystallisation peak from the DSC thermogram since the heat of fusion can be calculated from the area under an absorption peak. Impurities in polymers can be determined by examining thermograms for anomalous peaks, and plasticisers can be detected at their characteristic boiling points.

For the current study, curing profiles of the composite samples were studied by using a differential scanning calorimeter (model Q20) from TA Instruments, New Castle, Delaware, USA. A pictoral view of DSC is shown in **Fig. 2.3**. The system utilizes software universal analysis V4.5A for control and analysis of results. Dynamic scans were run on samples of about 10 mg, at a heating rate of 5°C/min from room temperature to 250°C. Freshly mixed samples were placed in an aluminium hermetic DSC pan and heated under a nitrogen purge. After the dynamic scan, samples were cooled to room temperature and scanned again at the same rate. Glass transition temperature (T_g) of the samples was derived from the curve of reversible heat flow Vs temperature.

2.3.2. Thermogravimetric Analysis

Thermogravimetric analysis or (TGA) is a type of testing that is performed on samples to determine changes in weight with respect to change in temperature or time. Such analysis relies on a high degree of precision in three measurements: weight, temperature, and temperature change. As many weight loss curves look similar, the weight loss curve may require transformation before results may be interpreted. A derivative weight loss curve can be used to tell the point at which weight loss is most apparent. Again, interpretation is limited without further modifications and deconvolution of the overlapping peaks may be required.

TGA is commonly employed in research and testing to determine characteristics of materials such as polymers, to determine degradation temperatures, absorbed moisture content of materials, the level of inorganic and organic components in materials, decomposition points of explosives, and solvent residues. It is also often used to estimate the corrosion kinetics in high temperature oxidation.

Figure 2.4. A pictoral view of TGA (Model Q50)

Simultaneous TGA-DTA/DSC measures both heat flow and weight changes (TGA) in a material as a function of temperature or time in a controlled atmosphere. Simultaneous measurement of these two material properties not only improves productivity but also simplifies interpretation of the results. The complementary information obtained allows differentiation between endothermic and exothermic events which have no associated weight loss (e.g., melting and crystallization) and those which involve a weight loss (e.g., degradation).

The analyzer usually consists of a high-precision balance with a pan (generally platinum) loaded with the sample. The pan is placed in a small electrically heated oven with a thermocouple to accurately measure the temperature. The atmosphere may be purged with an inert gas to prevent oxidation or other undesired reactions. A computer is used to control the instrument.

Analysis is carried out by raising the temperature gradually and plotting weight against temperature. The temperature in many testing methods routinely reaches 1000°C or more, but the oven is so greatly insulated that an operator would not be aware of any change in temperature even if standing directly in front of the device. After the data is obtained, curve smoothing and other operations may be done to find the exact points of inflection.

A method known as hi-res TGA is often employed to obtain greater accuracy in areas where the derivative curve shows peaks. In this method, temperature increase slows as weight loss increases. This is done so that the exact temperature at which a peak occurs can be more accurately identified. Several modern TGA devices can vent burn off to a fourier-transform infrared spectrophotometer to analyze composition.

For the current work, TGA thermograms of the composites were recorded using TGA instrument (model Q50) of TA instruments, New castle, Delaware, USA, under nitrogen environment up to 600°C at a heating rate of 10°C/min. A pictoral view of TGA is given in **Fig. 2.4**. The instrument uses software universal analysis V4.5A for control and result analysis.

2.3.3. Conductivity measurement

Conductivity was measured by four point probe technique on cured films of the ICAs. The four point probe is a simple apparatus for measuring the resistivity of semiconductor samples. It is a well known tool for performing reliable measurements of electronic transport properties in semiconductors. Conventional four point probes are millimetre sized devices with spring loaded electrodes of tungsten carbide or similar hard materials. The four metal tips are part of an auto-mechanical stage which travels up and down during measurements. The measurements are performed by four separate electrical connections to a sample, and driving an electrical current through two of these connections while monitoring the corresponding electrical potential at the two other connections. The four electrodes are aligned in a row (as shown in **Fig. 2.5**), and a current (I) is driven through the outer electrodes, while the voltage drop across the inner electrodes V is measured using an electrometer. Since, the input impedence of the electrometer is very high, the current running through the electrometer electrodes is negligible compared to the current running through the sample (originating from the outer current source electrodes). As a consequence, the measured four point resistance V/I does not contain any significant contribution from the contact resistance between the four electrodes and the sample. The four point method is often used for resistivity measurements on semiconductors, where the contact resistance can be considerable.

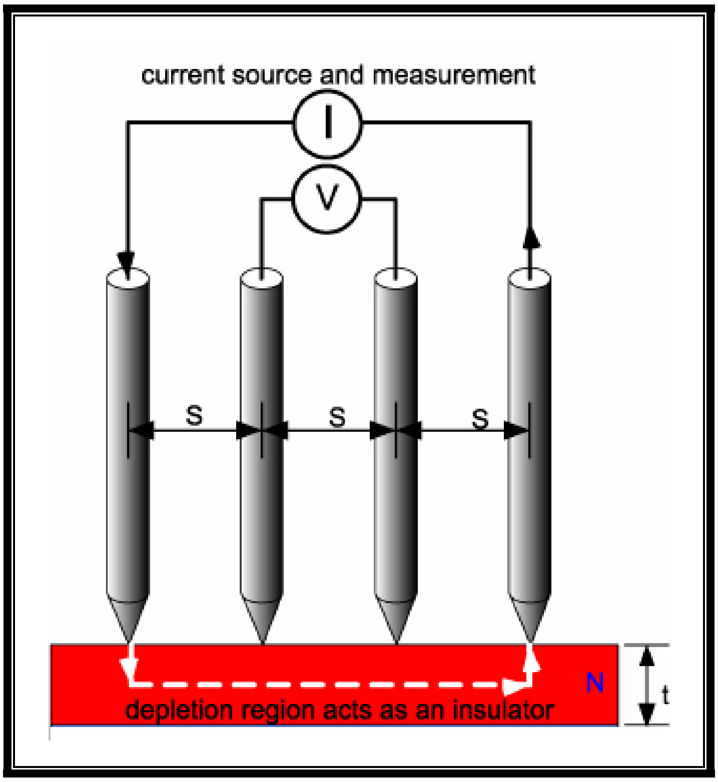


Figure 2.5. Four point probe alignment

Using the voltage and current readings from the probe, the resistivity can be calculated using the equation

$$\rho = \frac{\pi t}{ln2}\left(\frac{V}{I}\right)$$

From these resistivity values, conductivity is calculated for the area parameters.

The procedure for laying films of the ICAs on a substrate is described as below. Two parallel strips of tape 5 mm apart were placed along the length of a clean standard glass slide. A small amount of test ICA was placed in the space between the tape strips (**Fig. 2.6**).

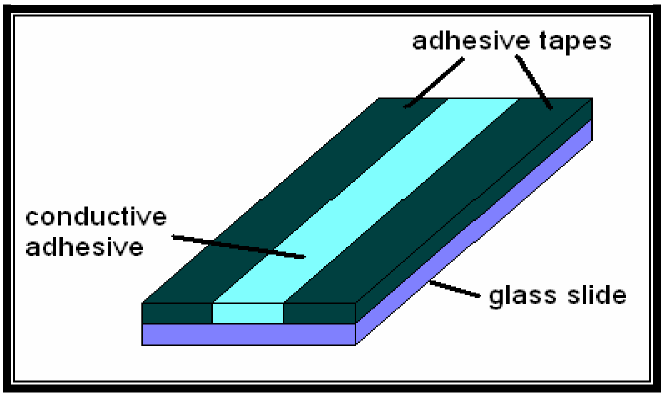


Figure 2.6. Scheme for laying composite films for conductivity measurement

Using a square glass cover slip held at 45° angle, the adhesive was squeezed into the space. The cover slip rides on the tape and provides a uniform film of the adhesive of about 3 μ thickness. The tape was removed and the glass slides were placed in a 150°C pre-heated oven for 1 h. After cure, the samples were dipped in acetone for 2-3 h till solvent swelling occurs and peeled off the glass slide as thin films using a doctor’s blade. The films were dried in oven and kept for one day before the conductivity test.

Conductivity was measured by means of the standard in line four probe method using semiconductor characterization system of Keithley instruments Inc. Cleveland, Ohio, USA (Model 4200). **Fig. 2.7** shows a pictoral view of Keithley 4200 resistivity measurement assembly. Both surfaces of the films were scratched using flint paper before measurements to ensure proper contact. An average of 12 measurements was taken for each sample.

Figure 2.7 Keithley 4200 resistivity measurement assembly

2.3.4. Lap shear test

Lap shear determines the shear strength of adhesives for bonding materials. The test method is primarily comparative. The test is applicable for determining adhesive strengths, surface preparation parameters, and adhesive environmental durability. Lap shear test was performed as per ASTM D3163 specifications. Two specimens with polyimide material on one side and copper surface on the other and dimensions 1 x 4″are bonded together with adhesive so that the overlap area is 1 x 1″ as shown in **Fig. 2.8**.

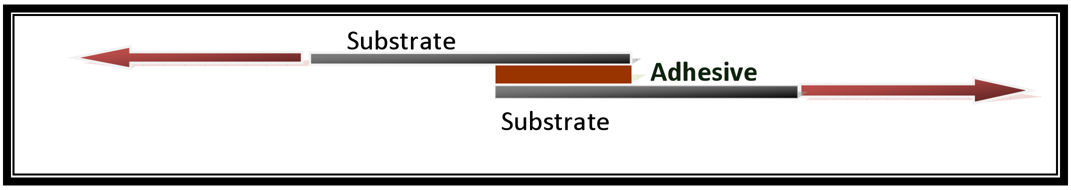


Figure 2.8. Lap shear overlap assembly

The overlap area was etched by flint paper prior to bonding with the adhesive to be tested. The adhesive was applied between etched panels and clamped in place. The thickness was maintained using end strands of a lead wire of diameter 0.1 mm. After curing, the cooled specimens were pulled apart by an Electronic Universal Testing Machine (UTM model 3369) of Instron, UK at a pull rate of 0.05 in/min and peak stress was determined. This instrument is depicted in **Fig. 2.9**. Two groups of specimens were prepared. In each group, five samples were prepared for every kind of ICA. One group was tested after cure, second was tested after conditioning for 200 h at 85°C/~100% RH.

2.3.5. Drop test

Drop tests were based on the standard established by National Center of Manufacturing Sciences (NCMS). Forty-four input/output (I/O) plastic leaded chip carriers (PLCC) are used in drop test to evaluate the impact performance of ICA samples. Two strips of tape, 150 µm thick, are placed on a piece of printed circuit board, 75 mm long and 38 mm wide, coated either with tin/lead or copper. The distance between the two is approximately 20 mm.

Figure 2.9 Electronic Universal Testing Machine (UTM model 3369) of Instron, UK

A conductive adhesive paste is dispensed onto the board between the strips of tape with a doctor's blade, so that the thickness of the adhesive layer before cure is the thickness of the tape. Then the PLCC is placed on the adhesive layer carefully with tweezers and is gently pressed onto the patch of adhesive. The tape strips are removed and the assembled specimen is cured. Almost 72 h after cure, each specimen is dropped repeatedly from a height of 60″ (1.5 m approx.) onto a vinyl coated concrete floor. The number of drops required to detach the PLCC from the substrate is recorded. An in house drop test channel was made to conduct the measurements and the sample assemblies were allowed to drop from the requisite height of 60″. For an ICA to be used for solder replacement, it has to survive 6 drops without the test assembly being detached. Drop test were performed by dropping the test assembly through the channel on to concrete floor ensuring that it falls vertically. A schematic of drop test set up is shown in **Fig. 2.10**.

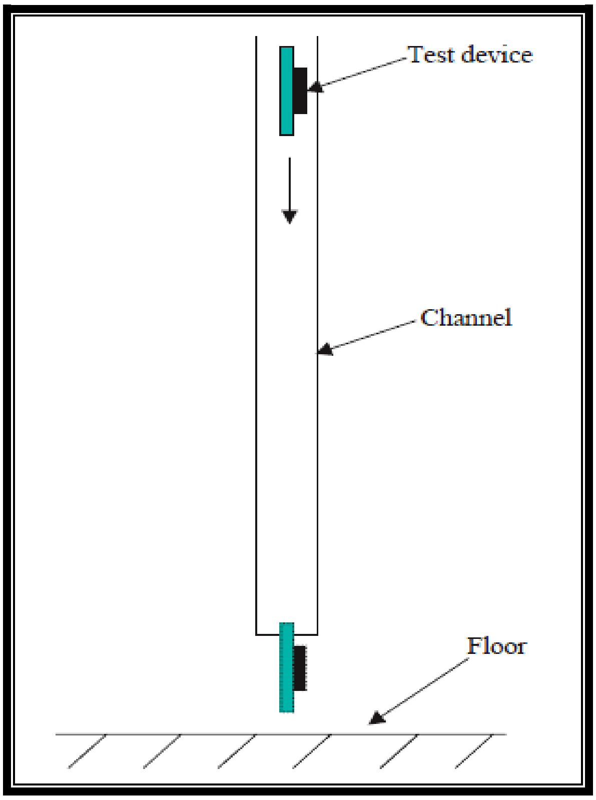


Figure 2.10. A schematic of Drop test setup

The surface of the adhesive joints was examined by a simple microscope to identify the cracks. The cause of detachment, i.e., whether the detachment occurred at PLCC surface or by cracking of adhesive material was examined. An average of five tests was taken for each sample.

2.3.6. Moisture absorption test

Moisture absorption tests were performed on bulk samples by conditioning at 85°C/~100% RH until 500 h. Five samples of each adhesive were laid on a standard glass cover slip and cured for 1 h at 150°C in a preheated oven. The cured samples were weighed on a Mettler instruments, Greifensee, Switzerland balance (AE-240) and placed on a plastic mesh above the water level in a temperature controlled water bath. Selected samples were periodically removed and weighed at ageing times. The water bath was maintained at 85°C and tightly closed except when samples were removed for testing so that the relative humidity in the water bath chamber was nearly 100%. Unfortunately, no attempt was made to determine whether moisture equilibrium was achieved [42].

2.3.7. Scanning electron microscopy

The scanning electron microscope (SEM) is a type of electron microscope that images the sample surface by scanning it with a high-energy beam of electrons in a raster scan pattern. The electrons interact with the atoms that make up the sample producing signals that contain information about the sample's surface topography and composition etc.

The types of signals produced by SEM include secondary electrons, back-scattered electrons (BSE), characteristic X-rays, light (cathodoluminescence), specimen current and transmitted electrons. Secondary electron detectors are common in all SEMs, but it is rare that a single machine would have detectors for all possible signals. The signals result from interactions of the electron beam with atoms at or near the surface of the sample. In the most common or standard detection mode, secondary electron imaging, or SEI, the SEM can produce very high-resolution images of a sample surface, revealing details about < 1 to 5 nm in size. Due to very narrow electron beam, SEM micrographs have a large depth of field yielding a characteristic three-dimensional appearance useful for understanding the surface structure of a sample. A wide range of magnifications is possible, from about 10 times (about equivalent to that of a powerful hand-lens) to more than 500,000 times, about 250 times the magnification limit of the best light microscopes. Back-scattered electrons (BSE) are beam electrons that are reflected from the sample by elastic scattering. BSE are often used in analytical SEM along with the spectra made from the characteristic X-rays. Characteristic X-rays are emitted when the electron beam removes an inner shell electron from the sample, causing a higher energy electron to fill the shell and release energy. These characteristic X-rays are used to identify the composition and measure the abundance of elements in the sample.

The first SEM image was obtained by Max Knoll, who in 1935 obtained an image of silicon steel showing electron channeling contrast. Further pioneering work on the physical principles of the SEM and beam specimen interactions was performed by Manfred von Ardenne in 1937, who produced a British patent but never made a practical instrument. The SEM was further developed by Professor Sir Charles Oatley and his postgraduate student Gary Stewart and marketed first in 1965 by the Cambridge Instrument Company as the "Stereoscan". The first instrument was delivered to DuPont.

In a typical SEM, an electron beam is thermionically emitted from an electron gun fitted with a tungsten filament cathode. Tungsten is normally used in thermionic electron guns because it has the highest melting point and lowest vapour pressure of all metals, thereby allowing it to be heated for electron emission, and because of its low cost. Other types of electron emitters include lanthanum hexaboride (LaB_6) cathodes, which can be used in a standard tungsten filament SEM if the vacuum system is upgraded and field emission guns (FEG), which may be of the cold-cathode type using tungsten single crystal emitters or the thermally-assisted Schottky type, using emitters of zirconium oxide. The electron beam, which typically has an energy ranging from a few hundred eV to 40 k eV, is focused by one or two condenser lenses to a spot about 0.4 to 5 nm in diameter. The beam passes through pairs of scanning coils or pairs of deflector plates in the electron column, typically in the final lens, which deflect the beam in the x and y axes so that it scans in a raster fashion over a rectangular area of the sample surface. When the primary electron beam interacts with the sample, the electrons lose energy by repeated random scattering and absorption within a teardrop-shaped volume of the specimen known as the interaction volume, which extends from less than 100 nm to around 5 µm into the surface. The size of the interaction volume depends on the electron's landing energy, the atomic number of the specimen and the specimen's density. The energy exchange between the electron beam and the sample results in the reflection of high-energy electrons by elastic scattering, emission of secondary electrons by inelastic scattering and the emission of electromagnetic radiation, each of which can be detected by specialized detectors. The beam current absorbed by the specimen can also be detected and used to create images of the distribution of specimen current. Electronic amplifiers of various types are used to amplify the signals which are displayed as variations in brightness on a cathode ray tube. The raster scanning of the CRT display is synchronised with that of the beam on the specimen in the microscope, and the resulting image is therefore a distribution map of the intensity of the signal being emitted from the scanned area of the specimen. The image may be captured by photography from a high resolution cathode ray tube, but in modern machines is digitally captured and displayed on a computer monitor and saved to a computer's hard disc. Magnification in a SEM can be controlled over a range of up to 6 orders of magnitude from about 10 to 500,000 times. Provided the electron gun can generate a beam with sufficiently small diameter, a SEM could in principle work entirely without condenser or objective lenses, although it might not be very versatile or achieve very high resolution. In a SEM, as in scanning probe microscopy, magnification results from the ratio of the dimensions of the raster on the specimen and the raster on the display device. Assuming that the display screen has a fixed size, higher magnification results from reducing the size of the raster on the specimen, and vice versa. Magnification is therefore controlled by the current supplied to the x, y scanning coils, or the voltage supplied to the x, y deflector plates, and not by objective lens power. All samples must also be of an appropriate size to fit in the specimen chamber and are generally mounted rigidly on a specimen holder called a specimen stub. Several models of SEM can examine any part of a 15 cm semiconductor wafer, and some can tilt an object of that size to 45°.

For conventional imaging in the SEM, specimens must be electrically conductive, at least at the surface, and electrically grounded to prevent the accumulation of electrostatic charge at the surface. Metal objects require little special preparation for SEM except for cleaning and mounting on a specimen stub. Nonconductive specimens tend to charge when scanned by the electron beam, and especially in secondary electron imaging mode, this causes scanning faults and other image artifacts. They are therefore usually coated with an ultrathin coating of electrically-conducting material, commonly gold, deposited on the sample either by low vacuum sputter coating or by high vacuum evaporation. Conductive materials in current use for specimen coating include gold, gold/palladium alloy, platinum, osmium, iridium, tungsten, chromium and graphite. Coating prevents the accumulation of static charge on the specimen during electron irradiation. Two reasons for coating, even when there is enough specimen conductivity to prevent charging, are to increase signal and surface resolution, especially with samples of low atomic number (Z). The improvement in resolution arises because backscattering and secondary electron emission near the surface are enhanced and thus an image of the surface is formed.

For the present work, scanning electron micrographs (SEM) were obtained with a ZEISS EVO series scanning electron microscope (Model EVO50) Carl Zeiss SMT Ltd. Cambridge, UK at an acceleration voltage of 10 kV. A pictoral view of SEM is shown in **Fig. 2.11**. All samples were plasma coated with a thin layer of gold to provide electrical conduction and reduce surface charging.

Figure 2.11. A pictoral view of SEM instrument (EVO50)

2.4. Results & Discussion

2.4.1. Curing behaviour

DSC is a useful tool to investigate the curing profile of epoxy resin, both neat and after adding filler. **Fig. 2.12** shows the typical DSC thermograms of neat epoxy/anhydride system and that of ICAs with different concentrations of PANI filler.

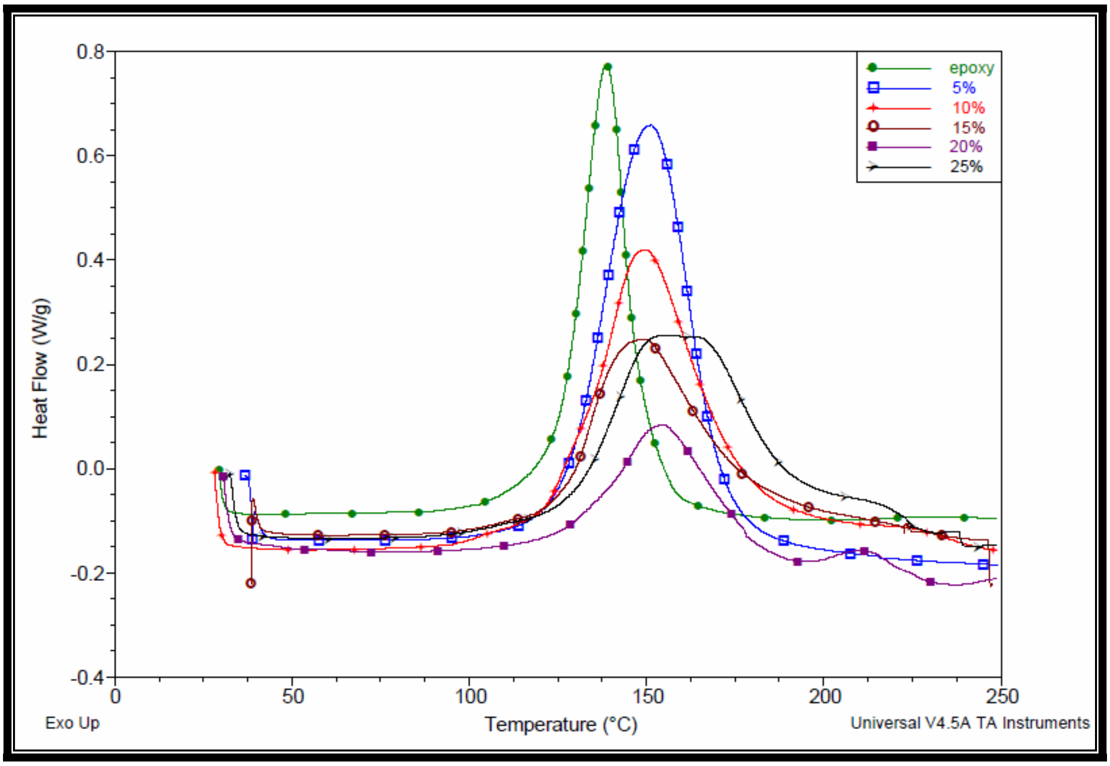


Figure 2.12. DSC thermograms of epoxy resin and epoxy/PANI composites

The exothermic peak of epoxy/anhydride system appears at 138°C, depicting the complete cross linking reaction of the epoxy system. A single exothermic peak is observed for different concentrations of PANI in epoxy matrix indicating that the basic curing profile of the epoxy system is not affected by the addition of PANI. It is observed that with the increase in concentration of PANI in the ICAs, the peak maximum is slightly shifted to higher temperature and also curing time is increased as indicated by widening of the peak. Also, ΔH decreases with increase in PANI conc. These changes may be attributed to the fact that with the increase in PANI conc, epoxy conc decreases proportionately, i.e., percentage of cured component is decreased. It is obvious that PANI particles have a significant influence on the curing process of the epoxy system as the cured component is decreased. These results are in accordance with observations reported in literature [29]. ICA with PANI concentration of 25% shows a flattening of peak and higher ΔH value. This conc was difficult to mix as there was a drastic increase in viscosity while mixing this conc with epoxy resin and the mixture became dry. It may be concluded that the percentage of cured component falls beyond an optimum level and influence of PANI over the curing process becomes too significant for an efficient cure.

Glass transition behaviour for the ICAs was determined by cooling the samples after DSC measurement to room temperature and then re-heating the cured samples up to 250°C at the same rate. The T_g value of neat epoxy system is around 115°C. Interestingly, even a 5% PANI conc has a visible effect on glass transition characteristics as depicted in **Fig. 2.13**.

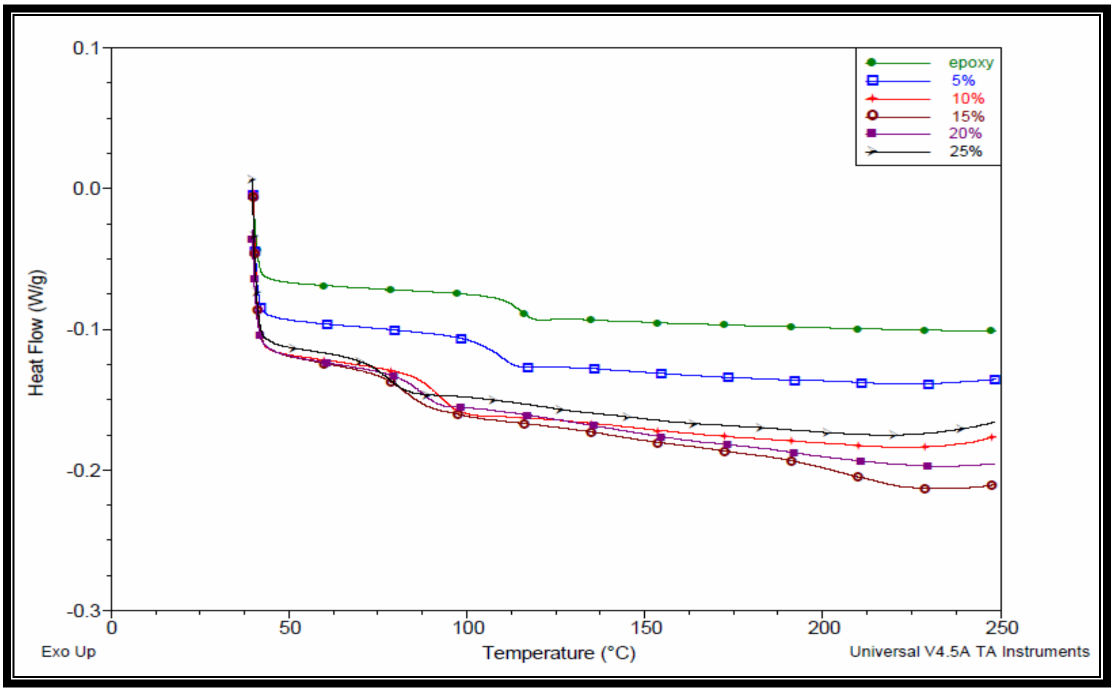


Figure 2.13. Variation of glass transition temperature with increase in PANI content

Similarly, incorporation of higher amount of PANI in epoxy matrix leads to a significant shift of T_g range, indicating that the quality of cross-linked network is substantially influenced. It can be observed from the overall cure behaviour of the ICAs that they cure at a very low temperature compared to Sn/Pb solder reflow temperature. It makes them suitable for attaching heat sensitive components and substrates. Also, they were cured rapidly, which can save the time and lower the cost.

2.4.2. Thermogravimetric analysis

TGA thermograms of ICAs with different PANI concentrations are shown in **Fig. 2.14**.

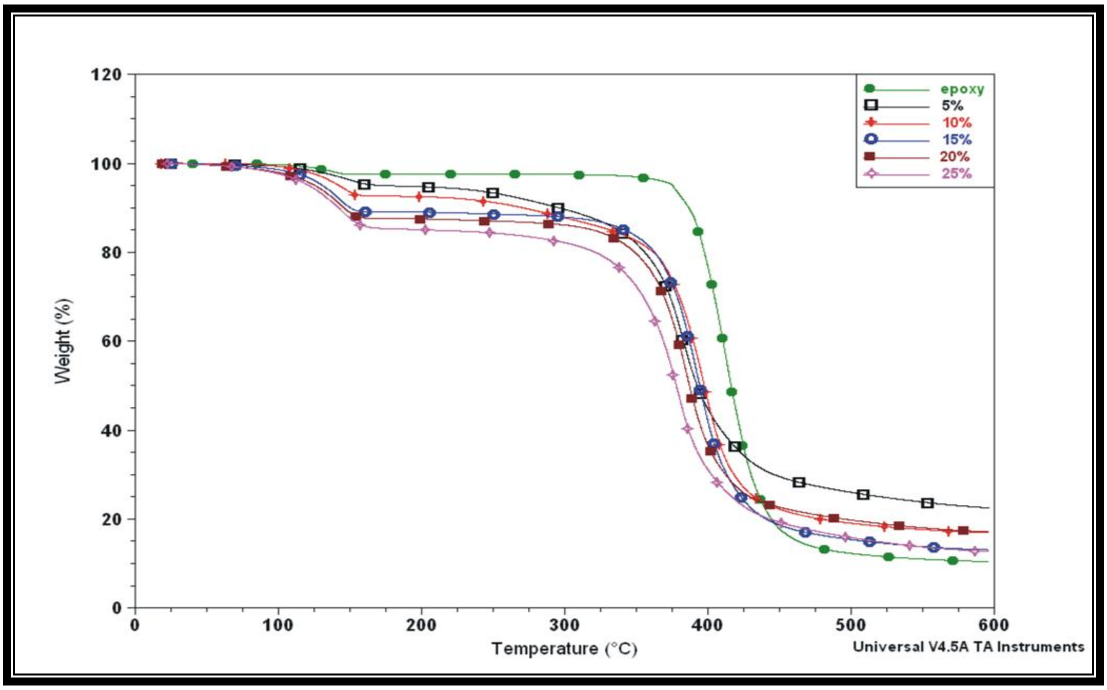


Figure 2.14. TGA thermograms of epoxy resin and epoxy/PANI composites

Neat epoxy shows a small weight loss before 150°C which may be due to loss of volatiles and then undergoes a complete degradation around 600°C. TGA thermograms show that as the PANI is incorporated, there appears a weight loss around 150°C which increases as the conc. of PANI increases. This may be attributed to loss of moisture and oligomers and is characteristics of PANI phase. All the samples showed stability upto 350°C and there is a steep weight loss till 450°C which is the general feature of epoxy system. Hence, it revealed that cured ICAs with different concentrations of PANI tend to maintain the stability of the epoxy matrix at higher temperatures.

2.4.3. Electrical Conductivity

Variation of electrical conductivity with the increase in PANI conc in ICAs is shown in **Fig. 2.15**. The conductivity of the ICAs increases with the increase in PANI conc from their typical insulating value of 10^{-14} to ~ 10^{-3} Scm^{-1} for 25% PANI conc.

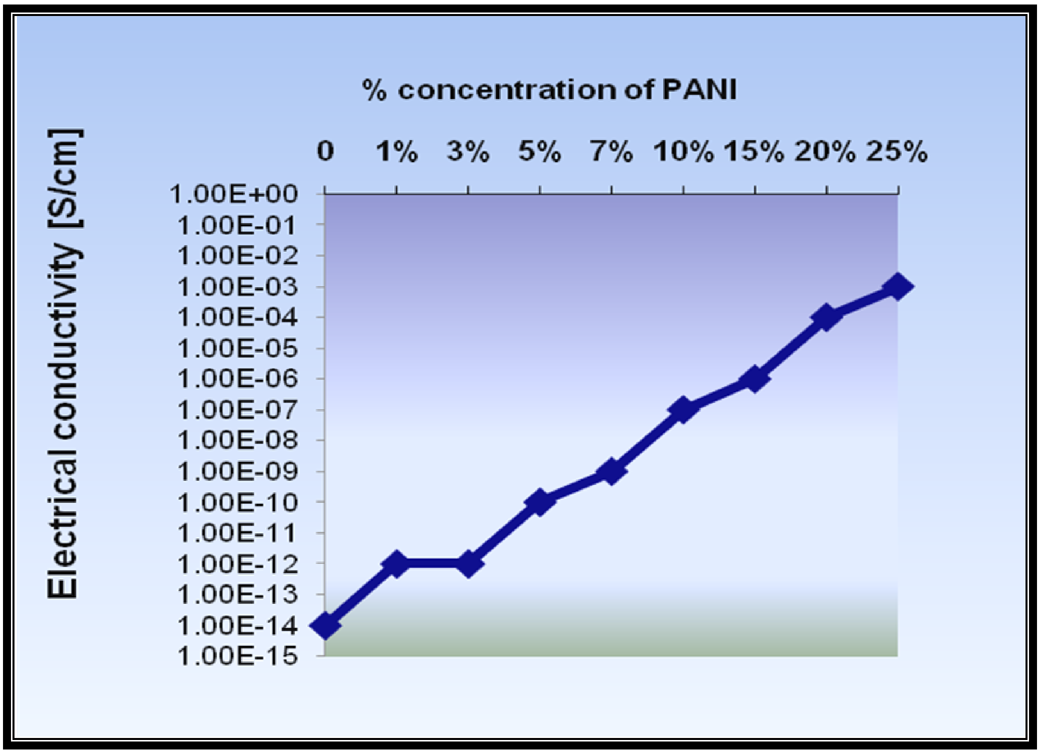


Figure 2.15. Electrical conductivity as a function of PANI conc.

It occurs due to the formation of conducting channels by the distribution of PANI particles inside the epoxy matrix. The percolation threshold (taken at 10^{-6} Scm^{-1}) i.e., the minimum amount of PANI which has to be added so that an infinite cluster of particles is formed throughout the sample which can produce conductivity, is achieved by adding about 10% of PANI. For smaller concentrations of PANI, the conductivity remains low, but even 1% PANI increases the conductivity of the insulating matrix appreciably. This can occur due to encapsulation of the dispersed PANI from the epoxy matrix or by the formation of non continuous conductive paths because of low filler conc [29].

2.4.4. Moisture absorption

ICAs may be exposed to various environmental conditions during their service life. Moisture is commonly present in service environment, and is one of the critical factors for determining the long-term reliability of adhesive bonded joints. Polymer systems are susceptible to warm; moist environments and can considerably alter the performance of the adhesives. Moisture absorbed in a polymer matrix can lead to a wide range of effects, both reversible and irreversible, including plasticization by weakening the intermolecular interactions among the functional groups of the chains. ICA samples were subjected to highly humid conditions and the observations with respect to weight change are given in **Fig. 2.16**.

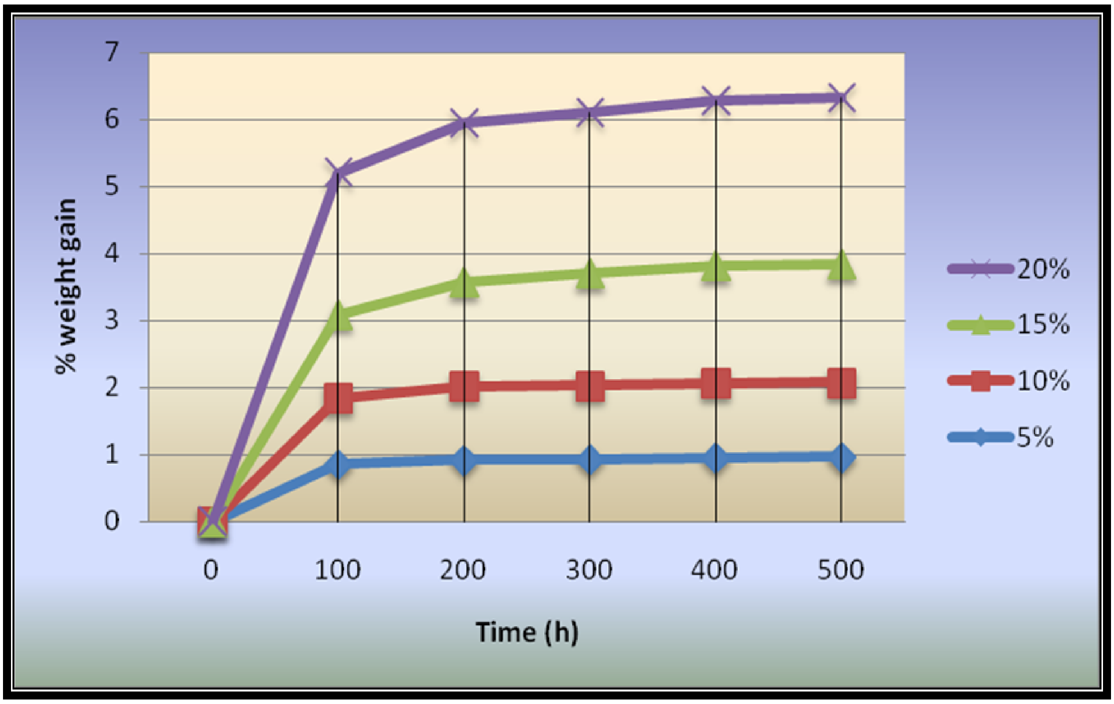


Figure 2.16. Moisture absorption behaviour with increasing PANI content

It is observed from the figure that all the samples exhibit rapid moisture uptake during first 100 h. This rapid gain may be due to binding of water by the filler particles which are not strongly adhered to matrix network. These results are further complimented by the fact that weight gain increases with the increase in filler conc as proportion of uncured part increases. Similar results for HHPA cured materials are reported earlier [43] which further supports our work.

2.4.5. Drop test

As per NCMS guidelines, an adhesive on a test assembly must pass 6 drops from a height of 60″. The samples were studied for drop performance by recording the number of drops required to detach the chip from drop assembly. An average of five samples was taken for each adhesive sample and results are shown in **Fig. 2.17**.

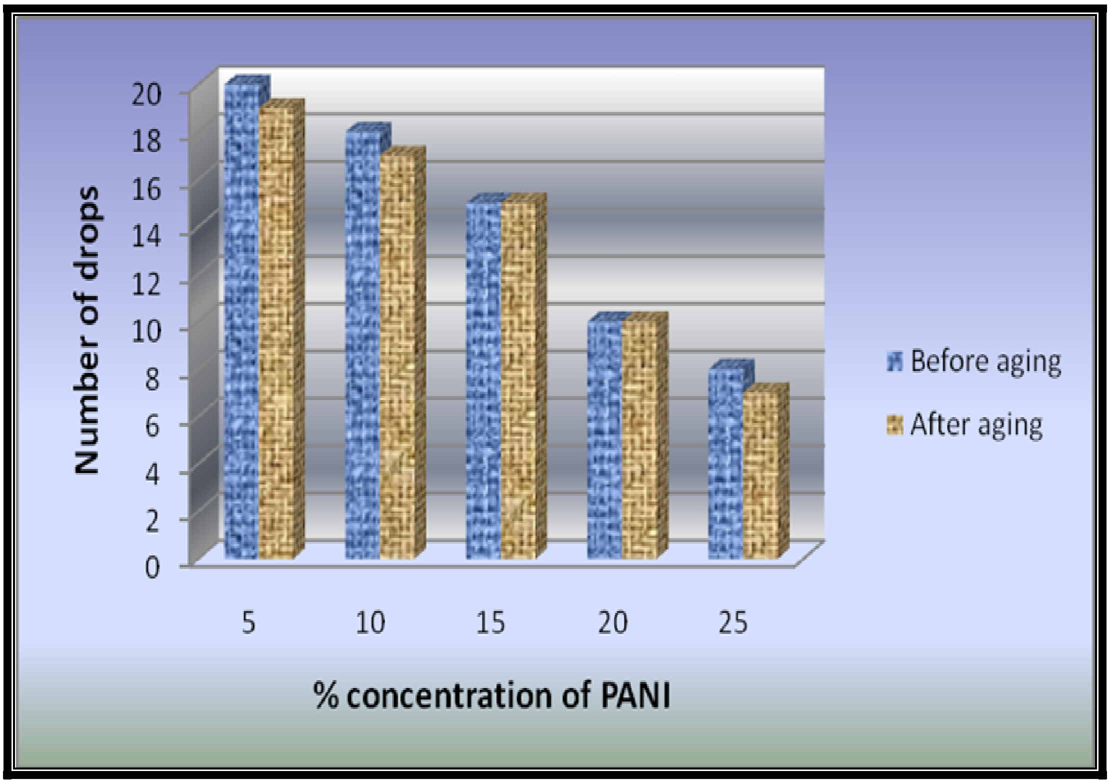


Figure 2.17. Drop test performance of ICAs

All the samples except 25% PANI containing ICA showed no signs of fracture after 6 drops even when observed under a simple microscope. The ICA with 25% PANI showed fractures at the ends after 5th drop and detached completely after 8 drops. The surface of the joint appeared very rough after curing for this adhesive. This may be due to the less proportion of curable epoxy system in this adhesive which imparts the impact strength. Also, the agglomeration of large particles may have prevented the epoxy network to crosslink properly due to physical hinderance. Impact distribution during fall will be seriously affected in such conditions. The abundant matrix phase cannot absorb the impact stress and hence the adhesive property of this sample was poor. It was also observed that the detachment started from the ends of the PLCC and there were cracks in the sample which shows that it not only has poor adhesion but cohesion within the material was also low. Samples were studied for drop performance after environmental aging at 85°C/~100%RH until 500 h. The results indicate that there was no significant effect on the drop performance of the samples after aging.

2.4.6. Lap shear strength

Lap shear strength is another critical parameter for impact performance of ICAs. Five specimen of each ICA sample were studied. As shown in **Fig. 2.18**, lap shear of adhesives decreases with increase in PANI conc. This is due to hindrance caused by filler particles in adhesion of matrix network and decrease in transmission of mechanical energy from the matrix to the filler. But the bond between the matrix and filler particles is strong enough to impart the desired impact strength to ICAs. Test coupons with ICA having PANI conc 25% broke while being fitted in the grips of UTM even before they could be pulled apart. Hence, the results of the same were not reported. It seems that at such a high conc of PANI, filler particles disallow the effective formation of matrix network. The fracture surface of the test coupons clearly showed that the test coupons broke by withering of the lap coupons rather than by breaking of adhesive material. The etched copper surface does not undergo effective wetting hence the adhesion at that surface is lesser. No surface cracking was observed on the adhesive material and toughness of the ICA was intact. After aging at 85°C/~100%RH until 500 h, samples show a small decrease in lap shear strength, thus these adhesives do not show a significant damping of adhesive strength under harsh environmental conditions. Although, epoxy matrix is not affected by moisture, filler particles loosely adhered to matrix network may absorb water and detach causing voids and crack propagation under impact. The effect of aging on lap shear also shows an increasing trend with increase in PANI concentration. Hence, proper formulation and dispersing of filler particles is important for good environmental stability of ICAs.

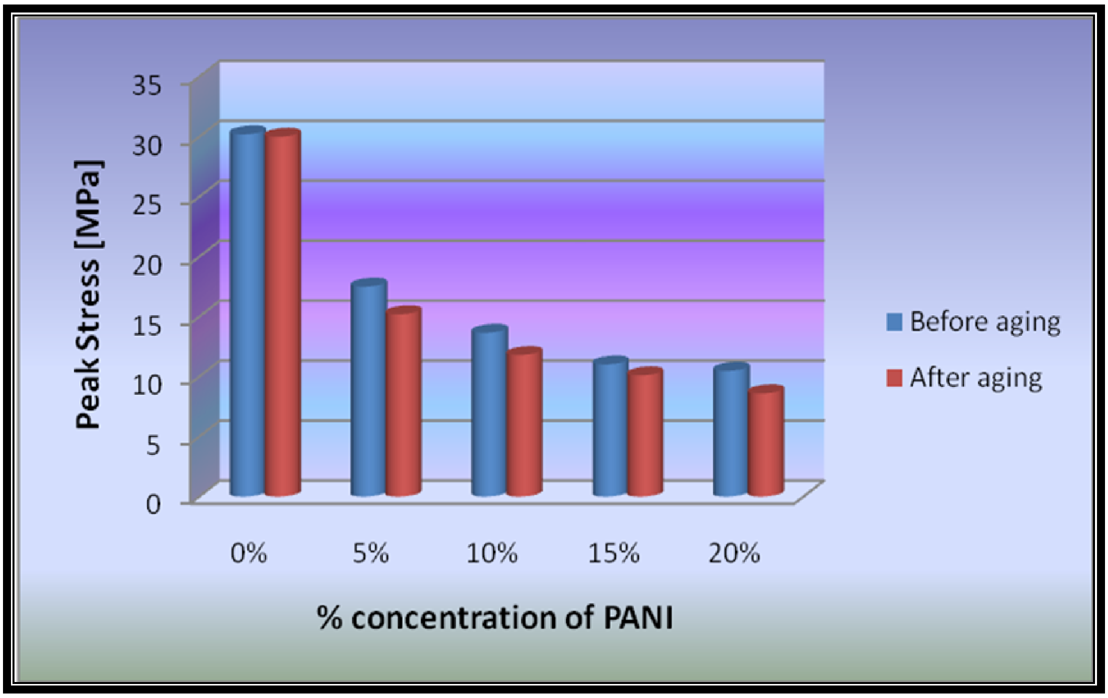


Figure 2.18. Lap shear strength of ICAs with different concentrations of PANI

2.4.7. Scanning electron microscopy

The surface morphology of ICAs along with the neat epoxy was studied using scanning electron microscopy. **Fig. 2.19** shows a SEM micrograph of the neat epoxy matrix with smooth contour-less surface. This sample was transparent with characteristic sheen on surface.

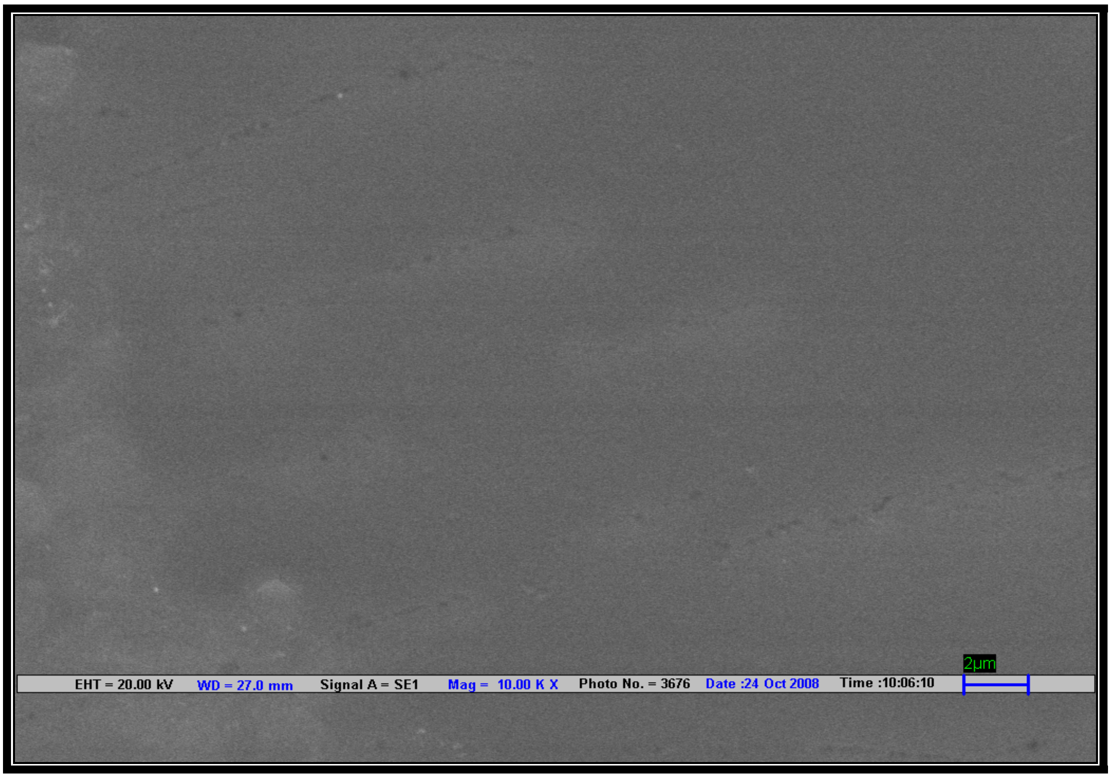


Figure 2.19. SEM micrograph of neat epoxy matrix

Fig. 2.20 is the micrograph of the PANI powder synthesized by chemical polymerization using HCl as dopant. It is clearly depicted that the particles are non uniform in shape and size with uneven surface. Large agglomeration is also evident. **Fig. 2.21** shows the fractured surface of conductive adhesive containing 20% PANI conc. It can be observed that PANI particles are dispersed within the epoxy matrix, yielding a conducting composite. There is no proper phase boundary between PANI particles and the epoxy matrix. This implies that the PANI particles are well distributed within the matrix and there is a strong interaction between the matrix and the filler. These observations show that the conductive filler was smoothly incorporated inside the matrix using the hand dispensing method employed in this work. The strong interaction between the two phases explains the improved conductivity characteristic and the good impact properties of the ICAs produced.

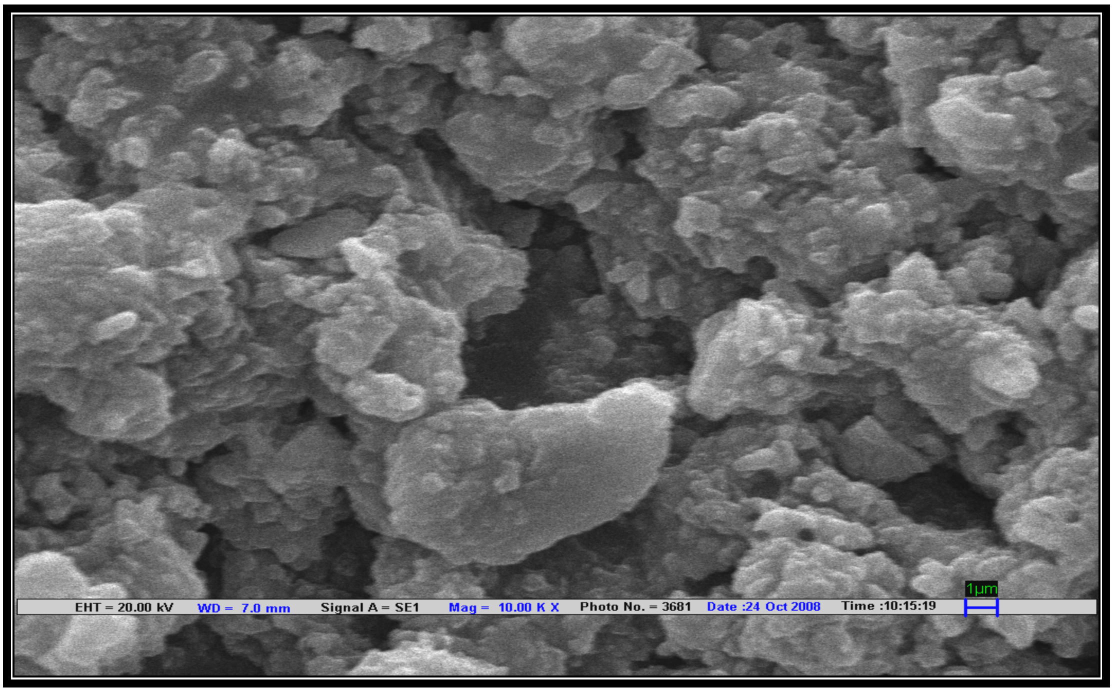


Figure 2.20. SEM micrograph of PANI

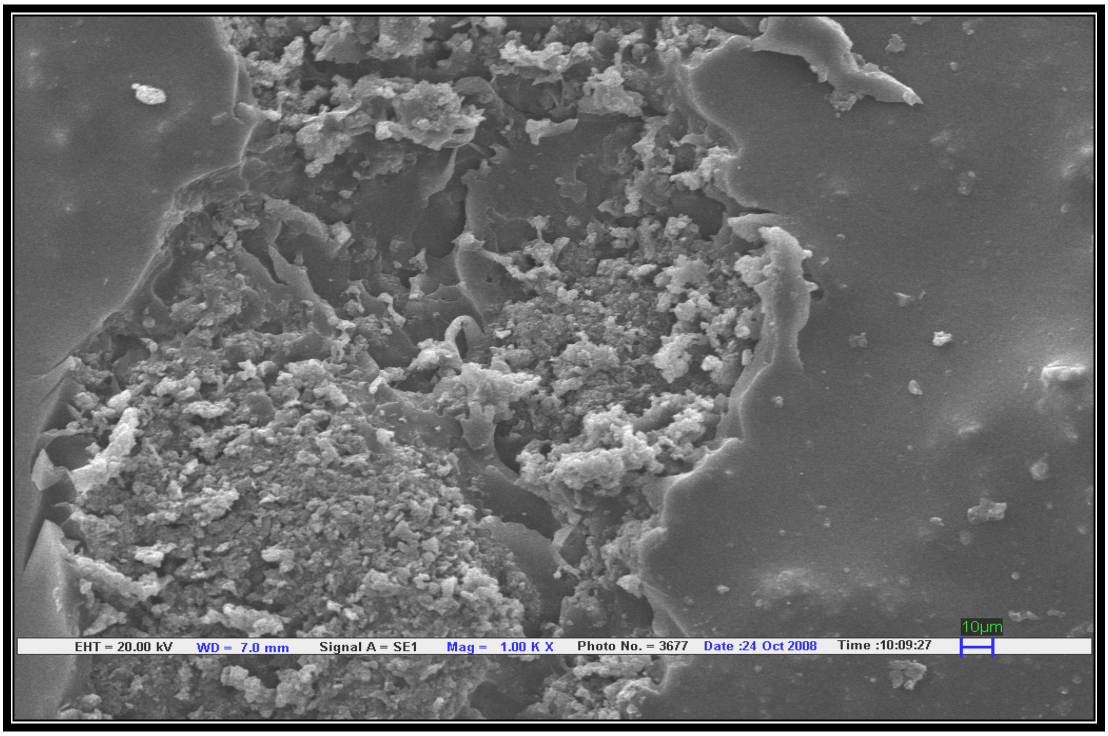


Figure 2.21. SEM micrograph of composite with 20% PANI

2.5. Conclusion

Composite samples with different concentrations of PANI in epoxy/anhydride matrix were studied for their prospective use as isotropically conductive adhesive. Thermal properties of the cured ICAs were studied using DSC and TGA techniques. It was observed from thermal studies that on adding PANI to resin, the T_g range of the samples shifts towards lower temperature which indicates that the presence of PANI affected the cross-linking of epoxy matrix. The TGA thermograms were very close to that of neat epoxy system. The impact properties although affected by the PANI conc, were substantially good as compared to ICAs with metal fillers. These improved impact properties are a direct consequence of using organic conducting polymer fillers instead of metallic filler due to reduction in phase barrier. Electrical conductivity showed an increasing trend with the increase of PANI conc. Although, a conductivity of 10^{-3} S cm^{-1} was obtained at 25% PANI filler concentration but this ICA shows poor impact properties. From the interpretation of the results presented in this chapter, we can conclude here that it is possible to produce isotropically conducting adhesives with improved impact properties by incorporating PANI in an epoxy matrix. Low conductivity can be a constraint which needs to be improved. Since, composites were prepared by manual mixing of PANI powder with epoxy resin, there is a possibility of uneven distribution of filler particles to some extent. In order to get better impact properties and conductivity, PANI particles need to be finely dispersed in the matrix.

2.6. References

1. Mir IA, Kumar D. Int J Poly Mater 2010;59:994.
2. Shimano JY, MacDiarmid AG. Synth Met 2001;123:251.
3. Cao Y, Andretta A, Heeger AJ, Smith P. Polymer 1989;30:2305.
4. Chiang JC, MacDiarmid AG. Synth Met 1986;13:193.
5. Cadenas JL, Hu H. Solar Energy Mate Sol Cells 1998;55:105.
6. MacDiarmid AG, Chiang JC, Richter AF. Synth Met 1987;18:317.
7. Green AG, Woodhead AE. J Chem Soc 1912;101:1117.
8. Green AG, Woodhead AE. J Chem Soc 1910;97:2388.
9. Cao Y, Andretta A, Heeger AJ. Polymer 1998;67:1863.
10. Kricheldorf HR. Handbook of Polymer Synthesis, Marcel Dekker, New York, 1992.p.1390.
11. Xie HQ, Xiang Q. Euro Polym J 2000;36:507.
12. Mau I, Ziong M, Sebenik A. Synth Met 1999;101:717.
13. MacDiarmid AG, Chiang JC, Halpern M, Huang WS, Mu SL, Somasiri NL, Wu W, Yangier SI. Mole Cryst Liqu Cryst 1985;121:173.
14. Austrias GE, MacDiarmid AG, Epstein AJ. Synth Met 1989;29:E157.
15. Armes SP, Miller JF. Synth Met 1985;12:85.
16. Vijayan M, Trivedi DC. Synth Met 1999;107:57.
17. Kang ET, Neoh KG, Tan KL. Synth Met 1995;68:142.
18. Rodrigues MA, De Paoli MA. Synth Met 1991;41:2957.

19. Abe M, Ohtani A, Umemoto Y, Akizuki S, Ezoe M, Higuchi J, Nakamoto K, Okuno A, Noda Y. J Chem Soc Chem Commun 1989;22:1736.
20. Yasuda A, Shimidzu T. Polym J 1993;25:329.
21. Ruckenstein E, Yang S. Synth Met 1993;53:283.
22. Pan W, Yang SL, Li G, Jiang JM. Eur Polym J 2005;41:2127.
23. Araujo PLB, Aquino KAS, Araujo ES. Inter J Low Rad 2007;4:149.
24. Zhang L, Long Y, Chen Z. Adv Func Mater 2004;14:693.
25. Segal E, Haba Y, Narkis M. J Polym Sci Part B: Polym Phys 2001;39:611.
26. Roselena F, Robert HS, Marco AD. Eur Polym J 2002;38:2459.
27. Paul RK, Pillai CK. Eur Polym J 2001;80:1354.
28. Afzal AB, Akhtar MJ, Nadeem M, Hassan MM. Curr App Phys 2010;10:601.
29. Tsotra T, Friedrich K. Synth Met 2004;143:237.
30. Khalid M, Mohammad F. Synth Met 2009;159:119.
31. Dai T, Qing X, Wang J, Shen C, Lu Y. Comp Sci Tech 2009; In press.
32. Chen Y, Kang ET, Neoh KG, Wang P, Tan KL. Synth Met 2000;110:47.
33. Chen Y, Kang ET, Neoh KG, Tan KL. Eur Polym J 2000;36:2095.
34. Laasko J, Osterholm JE, Jarvinen H. US Patent 5662833:1997.
35. Jia W, Tchoudakov R, Segal E, Joseph R, Narkis M, Seigmann A. Synth Met 2003;132:269.
36. Moreira VX, Garcia FG, Soares BG. J App Polym Sci 2006;100:4059.
37. Jia QM, Li JB, Wang LF, Zhu JW, Zheng M. Mat Sci Eng A 2007;448:356.
38. Yang X, Zhao T, Yu Y, Wei Y. Synth Met 2004;142:57.

39. Kumar D. and Chandra R. Ind J Eng Mat Sci 2001;8:209.

40. Watson, O'neill E, Michael J. U.S. Patent 3,263,484:1966.

41. Wunderlich B. Thermal Analysis. Academic Press. New York 1990.p.137.

42. Xu S, Dillard DA, Dillard JG. Int J Adhes Adhes 2003;23:235.

43. Tan F, Qiao X, Chen J, Wang H. Int J Adhes Adhes 2006;26:406.

CHAPTER 3

NANOCOMPOSITES OF POLYANILINE/EPOXY AS ISOTROPICALLY CONDUCTIVE ADHESIVES

In the previous chapter, polyaniline (PANI) as powder was used as filler for ICAs, but the coarse nature of the PANI powder made it difficult to incorporate this filler inside the matrix efficiently. It is an established fact that the size and geometry have a great influence on the overall characteristic of the composites. In view of this trouble, nano-fibres of PANI are introduced as filler into epoxy/anhydride matrix to produce isotropically conductive adhesives with improved properties. PANI nano-fibres synthesized by interfacial polymerization technique show smooth dispersion in the matrix. Uniformity and smaller size of nano-fibres help in formation of strong epoxy network with least hindrance from filler phase. It results in better impact performance of the ICAs and percolation threshold is comparatively low. SEM observations have established that there is an improved diffusion of nano PANI within epoxy matrix. Overall the properties obtained with PANI nano-filler show a significant improvement when compared to PANI of macroscopic dimensions reported in previous chapter. The findings from the research presented in this paper are already accepted for publication in Journal of Adhesion Sciences & Technology [1].

3.1. Introduction to Nanocomposites

Reinforcing of fillers in polymers is a typical process in materials science to generate novel composites, with properties that are a synergistic combination of the polymeric matrix and the organic or inorganic filler particles. Typical examples are the addition of carbon black to natural rubber and to some synthetic elastomers, and the addition of silica to various polymers, particularly polysiloxanes. In recent years, the focus has been on such composites where at least one of the phases has dimensions in nanoscale. By having their two phases interacting at almost the molecular level, such nanocomposites can exhibit properties (mechanical, thermal, optical, electronic, magnetic etc) that are not obtainable from traditional macro-composites. Since, having very large interfacial areas may also be of critical importance, a homogeneous dispersion of the nanoparticles in the polymer matrix becomes important. The techniques used to prepare such nanocomposites include simple mechanical blending, in-situ polymerization, polymer intercalation and exfoliation, and in-situ sol–gel processing.

Apparently, the term '**nanocomposites**' was proposed for the first time by Theng in 1970 [2]. The definition of nanocomposite materials has broadened significantly to encompass a large variety of systems such as one, two, three-dimensional and amorphous materials, made of distinctly dissimilar components and mixed at the nano scale. Nanocomposite materials not only represent a creative alternative to design new materials and compounds for academic research, but also their improved or unusual features allow the development of innovative industrial applications. There is no doubt that these new generations of hybrid materials, have opened a new world of promising applications in many areas like in optics, electronics, ionics, mechanics, energy, environment, biology and medicine etc. Membranes and separation devices, functional smart coatings, fuel and solar cells, catalysts, sensors, etc. are few such examples.

Nanostructured materials are understood to be new entrants in the field of classical molecular structured entities. Introduction of nanoparticles into a polymer matrix ensures significant property improvements with very small loading levels. Traditional micro-particle additives require much higher filler concentration to achieve similar results. There are three basic reasons for changes in properties of materials when their dimension is reduced to the nanometer level:

(1) *Quantum confinement*, where the energy levels of the atom, electron, or nucleus change as the size of the confined region changes; the well- known particle in a box situation. Since the quantized energy levels (En) vary inversely with the size of the box *(L)*, small changes in *L* when that size is small amounts to very large changes in the energy levels. Small changes in *L* when *L* is large do not result in large shifts in the energy levels. Therefore, any property which depends on the value of the energy level, or the spacing between energy levels, will likely change when you have a material structure which will confine those particles, like electrons and atoms.

(2) *High interface area*, where the number of atoms at an interface becomes very large. For a polycrystalline material, when the diameter of the crystals (e. g., grains) is of the order of microns, the fraction of atoms at the interface is only of the order of 0.5 %. As the dimension of the grain is reduced, the fraction of atoms at the interface increases quickly.

(3) *Closeness of the material lengths to the critical length scale of the property*. Every property has a critical length scale associated with that property (e. g., the mean free path in electrical and thermal conductivity, diffusion length in atomic transport, wavelength in scattering behavior, penetration depth in absorption, and half-life in radioactive decay processes), and material behavior will typically change when a material length scale becomes comparable with that property length scale.

The main advantages associated with nanomaterials are a result of nano dimensions of the fillers incorporated. Since, nanoparticles show better adhesion to polymer matrix, it results in the enhanced strength of nanocomposites relative to conventional composite. Also, small size of nanoparticles ensures small size of pores in the case of exfoliation of a matrix from filler particles. It results in the strength increase too. Introduction of small amount of nanoparticles to polymer significantly enhance the adhesion of polymer to different substrates as well. Although, there are some limitations like high cost, tendency to aggregate and increasing viscosity due to high surface area to volume ratio.

Polymer matrix nanocomposite (PMNCs) is a novel composite material comprising dispersed metal, ceramic or polymer nanoparticles in the matrix of polymer. In the area of nanotechnology, PMNCs have generated a significant amount of attention in the recent literature [3, 4]. It is known that well dispersed nanoparticles in PMNCs can significantly improve the mechanical and optoelectronic properties of PMNCs. Fabricating high quality nanocomposites becomes a challenge due to the difficulty in producing uniformly dispersed nanoparticles in polymer matrix, significant viscosity increases, the poor interaction between nanoparticles and matrix, etc. Poor dispersion and the weak bonding between nanoparticles and matrix result in a deleterious effect on the mechanical properties of the nanocomposite. The incorporation of the nanofillers has been carried out in two ways: a) by physical blending with the matrix phase (post-synthesis), b) by direct incorporation of the filler during the synthesis process of matrix which allows a higher filler content and a more homogeneous distribution in the composite. Since, this chapter involves nanocomposites of polyaniline, in the following sections different aspects related to these novel materials will be discussed.

PANI nanocomposites

Intrinsically conducting polymers, including polyacetylene, polyaniline, polypyrrole, polythiophene, poly(*p*-phenylene-vinylene), etc. which possess the electrical, electronic, magnetic, and optical properties of a metal while retaining the mechanical property, processability etc. commonly associated with a conventional polymer are more commonly known as "**synthetic metals**" [5]. Among these polymers, polyaniline (PANI) has elicited the most interest since its electrical conductivity was found by MacDiarmid et al. [6] in 1985, due to its wide range of conductivity from insulating to metallic regime, unique redox tunability, good environmental stability, low cost, ease of synthesis, and promising applications in various fields, such as metallic corrosion protection [7,8], electromagnetic interference shielding [9], electrostatic discharge [10], sensors [11], actuators [12], to mention just a few. However, two major limitations of conducting polyaniline are an inability to process it by conventional methods and its poor mechanical properties. These limitations can be overcome by preparing conducting polyaniline blends and composites which possess the mechanical properties of the insulating host matrix and the electrical properties of the conducting polyaniline guest. When the host is a polymer, the resulting system is termed as organic polyaniline blend or composite, but when the host is a non-polymer material (e.g., metal oxides, silica) it is invariably referred to as a composite.

Conducting polyaniline composites are a novel class of materials for which the threshold for the onset of electrical conductivity can be reduced to volume fractions well below that required for classical percolation, which is 16% by volume for a conducting material dispersed in an insulating matrix in three dimensions. Due to a low percolation threshold and a continuous increase in conductivity, for volume fractions above the threshold, conducting polyaniline composites can be reproducibly fabricated with controlled levels of electrical conductivity while retaining the desired mechanical properties of the polymer matrix. Dispersing the PANI in conventional polymers forms the most crucial part in designing such materials from both the scientific and technological point of view. Accordingly, synthesis of nano-structured PANI, on one hand, is the key step in preparing highly dispersed blend of PANI with other processable polymers, and thus to improve the processability of PANI. On the other hand, some special physical and chemical properties differing from the bulk material will be achieved on nano-structured PANI and will render it for new applications [13], such as chemical sensors, energy conversion and storage, light-emitting display devices, microelectronics, optical storage, and so on. The earliest approach used PANI nanoparticles, mainly synthesized by dispersion technique and electrochemical method [14]. But with the advent of nanotechnology, one dimensional nano-structured PANI, including nanofibers, nanowires, nanorods, nanotubes, nanofibrils, nanobelts and nanoribbons, presents several advantages in fabricating nano-devices and in preparing nanoscale electrical connections in highly conducting polymer composites, etc. PANI composites have attracted a lot of attention because of various, often novel, potential applications of these relatively new materials. Applications for such composites are wide spread. These materials are used for interconnections, printed circuit boards, encapsulations, die attach, heat sinks, conductive adhesives, electromagnetic interference (EMI) shielding, electrostatic discharge (ESD), and aerospace engineering [15].

Conventional PANI synthesis is known to produce particulate products with irregular shapes. Therefore, many methods have been developed to make PANI nanostructures (with diameters less than 100 nm) [16]. These methods have been broadly divided into template synthesis and template free synthesis depending whether a template is used or not [17]. The former is further divided into hard (physical) template or soft (chemical) template approach according to solubility of the template in the reacting media, while the latter is sub divided into sonochemical synthesis, radiolytic synthesis, rapid mixing reaction method and interfacial polymerization. Other approaches like seeding polymerization and combined soft and hard template synthesis have also been reported.

a) ***Hard template synthesis:*** The hard template synthesis method, which is proposed by Martin et al [18–22], involves synthesizing the intrinsically conducting polymers like PANI, polypyrrole, as well as other materials including metals [23,24], carbons [25,26], in the pores, channels of hard templates such as membranes [20–22], zeolites [27], anodic aluminum oxide (AAO) [28–30], and so on. For example, PANI filaments with diameters of 3 nm have been achieved in the hexagonal channels of mesoporous aluminosilicate [27]. However, the disadvantage of the method is that, firstly, a rather tedious post-synthesis process is required in order to remove the templates [31]; secondly, the nano-structured polymers may be destroyed [32] or form undesirable aggregated structures after being released from the templates [33].

b) ***Soft template synthesis:*** The soft template synthesis method, always called the template-free method [34–37] or self-assembly method [38] in the literature is that in which no hard template is used, and involves synthesizing the PANI, as well as polypyrrole [35,39], in the presence of structure-directing molecules such as surfactants [40,41], deoxyribonucleic acid (DNA) [42,43], polyelectrolytes [44], thiolated cyclodextrins [45], sulfonated porphyrin [46], liquid crystalline [47], and ethanol [48,49], which act as templates for production of the one-dimensional nanomaterials. The surfactants are often complex acids with bulky side groups, such as the naphthalenesulfonic acid (NSA) [50,51], camphorsulfonic acid (CSA) [52–55], azobenzenesulfonic acid (ABSA) [56], chiral 2-pyrrolidone-5-carboxylic acid (PCA) [57], 2-acrylamido-2-methyl-1-propanesulfonic acid (AMPSA) [58] etc. The polyelectrolytes include poly(acrylic acid), poly(styrenesulphonic acid), etc. [59]. The method is simple and cheap in comparison with the hard template method because it omits the use of the hard templates and therefore the wearisome post synthesis processing.

c) ***Radiolytic synthesis:*** In this method, the aqueous solution of aniline and ammonium per sulphate (APS) in HCl was irradiated with gamma rays without any template [60]. In case of parent solutions with typical concentration of 0.1M aniline, 0.3M HCl, and 0.002–0.1M APS, the morphology of the final product was predominantly nanofibers with diameters of 50–100 nm and length of 1–3 µm, though less than 5–vol.% of globular structures were still presented. While with APS concentrations in the range of 0.05–0.1M in the parent solution, rodlike structures with diameters of 250–500 nm and lengths of 5–10 µm were observed, which represent 5 vol.% of the total PANI.

d) ***Rapid mixing reaction:*** With the solution of APS mixed rapidly with that of aniline, rather than the conventional slow addition of the solution of APS to that of aniline, PANI nanofibers with comparable shapes and sizes to those of interfacial polymerization [61,62] method were obtained, rendering this method the simplest one in producing PANI nanofibers [63]. Owing to the even distribution of aniline and APS molecules in the solution, all the initiator molecules were consumed rapidly after the start of the polymerization and the secondary growth of PANI was suppressed, resulting exclusive nanofibers in the product. The growth of PANI nanofibers was related with the polarity of the solvents. For example, in aqueous systems, pure nano-fibers were produced, while in ethanol and isopropanol, mixture of short nanofibers attached with irregular particles and agglomerates of 100–300 nm particulates were obtained, respectively.

e) ***Sonochemical synthesis:*** By dropwise addition of an acidic APS solution to an acidic aniline solution, just like the conventional PANI synthesis procedure, with the aid of ultrasonic irradiation, PANI nanofibres with higher polymer yields were successfully prepared by Jing et al [64,65]. It was stated that three possible competitions exist in the reaction system, if more aniline and APS are present following the formation of the primary PANI nanofibers, i.e., (1) the continuing formation of primary PANI nanofibers, (2) the growth of the primary nanofibers into unevenly surfaced thicker fibers, and (3) the growth and agglomeration of the thicker fibers into irregular particles.

f) ***Electrochemical approach:*** Aside from the above-mentioned chemical template-free approaches, one-dimensional nano-structured PANI was also synthesized by electrochemical template-free approaches [66–68]. PANI nanofibrils, as well as microfibrils or rods, have been found by Langer et al [69–73] in electrochemically synthesizing PANI from an aqueous medium at pH ~1 without any template. The nanofibrils doped with fullerene derivatives exhibited diameters of 10–100 nm and lengths of 500–2000 nm [73]. Both single nanofibrils and their networks were obtained with controlled charge flows [72]. Large arrays of uniform and oriented nanowires of PANI with diameters less than 100 nm were synthesized by Liang et al [74] and Liu et al [75] on a variety of substrates by a three-step electrochemical deposition procedure, also without using any templates.

g) ***Interfacial polymerization:*** Initially, PANI or its composite films were produced via interfacial polymerization approach in which aniline was co-dissolved with the surfactant [76] or polymers [77] in the organic phase, while APS in aqueous acidic phase, giving rise to the films at the interface of the two immiscible liquids. However, both nanofibers [78,79] and nano-particles [80] of the polymer were produced recently, rendering the approach one of the general and facile among a variety to synthesize one-dimensional nano-structured PANI. In a typical reaction [78,79,81-83], aniline was dissolved in the organic phase, which can either be one with density lower than water such as hexane, benzene, toluene, etc. or be one with higher density, such as carbon tetrachloride, methylene chloride, etc., with different concentrations. Meanwhile, APS was dissolved in an aqueous acid solution, covering a great variety of acids such as HCl, sulfuric acid, CSA, toluene sulfonic acid, among others. Now these two solutions were gently transferred to a reaction vessel such as a beaker or a vial, generating an interface between the two layers. Green PANI was formed firstly at the interface as the reaction proceeds and migrated gradually into the aqueous phase until the whole aqueous phase is filled homogeneously with dark-green PANI at last. Finally, the aqueous phase was collected after sufficient time of reaction by dialysis or filtration to remove the impurities like excess dopants, etc., yielding PANI nanofibers in the form of a water dispersion or powder. De-doped PANI nanofibers can be obtained by further washing or treating with ammonia. In consideration of the formation mechanisms, it was revealed that interfacial polymerization suppressed effectively the secondary growth of PANI, which occurred naturally in the conventional synthesis of PANI, leading thus to the exclusive formation of nanofibers [63]. The monomer and oxidant, separated in two phases, met only at the interface and reacted there then, forming PANI nanofibers. The nanofibers formed moved away rapidly from the interface and diffused into the water phase due to their hydrophilicity. As such, the nanofibers were continuously withdrawn from the interface, allowing formation of new nanofibres at the interface. As far as the synthesizing parameters (such as the solvents, polymerization temperature, and monomer concentration) are concerned, it was demonstrated that all aqueous/organic systems produce similar PANI nanofibers, whose morphology was unaffected in the subsequent de-doping process [78,82]. However, both the diameters and the quality/uniformity of the nanofibres were affected by the acids and their concentrations. For example, the average diameters of the fibers synthesized in HCl, CSA, perchloric acid, and other acids (such as sulfuric acid, nitric acid and 4-toluenesulfonic acid) are 30, 50, 120, and 30–50 nm, respectively [82]. In case of strong acids like HCl and CSA, lower the concentration of the acid, the lower is the fraction of nanofibers in the final product. While in case of medium or weak acids like tartaric acid or pyrrolidone-5-carboxylic acid, the products were mixtures of nanofibers and particles even at high concentrations. It was therefore stated that high concentrations of strong acids favored the formation of PANI nanofibers. The diameters of the nanofibers prepared by interfacial polymerization can be controlled by using surface active dopants like AMPSA or CSA, and surfactants in the aqueous phase [84].

h) ***Combined soft and hard template synthesis:*** In order to fabricate highly oriented PANI nanostructures, a novel method combining the soft and hard template synthesizing technique was employed [85]. Typically, aniline and the surfactant, e.g., C_3-ABSA, was dissolved in deionized water to form a homogenous emulsion and ultrasonicated for a while. The hard template, e.g., a porous, hydrophilic Al_2O_3, was immersed in the emulsion and ultrasonicated for some time. Afterwards, the APS solution was added rapidly to initiate the polymerization. With different reacting time, the oriented PANI nanotubes and nanofibers were produced within the pores of the hard template.

i) ***Seeding polymerization:*** By adding a small amount of various nanofibers like the PANI nanofibers in diameter of~50 nm, the single-walled carbon nanotubes bundles in diameter of ~20 nm, nanofibrous hexapeptide in diameter of ~12 nm, and the V2O5 nanofibers in diameter of ~15 nm, into the reacting solution of aniline and APS, Zhang et al [86] invented the so-called “nanofiber seeding” method for preparation of PANI nanofibers. Typically, about 1–4 mg of these seeding nanofibers were added firstly into a stirred solution of aniline (0.14 M) in hydrochloric acid (1.0 M), and a solution of 0.04 M APS was added then to the mixture to initiate the polymerization. The resulting dark-green precipitate of PANI was isolated after 1.5 h and dried under dynamic vacuum. The morphology of all the seeded PANI products was fibrillar with fiber diameters in the range of 20–60 nm.

For the current work PANI nanofibres were obtained by interfacial polymerization technique. This technique provides a very simple approach of producing nanofibres in bulk without the use of any specific template or surfactant.

3.2. Experimental

3.2.1. Materials

Table 3.1. Specifications of material and chemicals and their sources.

Material	Acronym	Source
Epon 862	DGEBF	Hexion speciality chemicals, Inc. Houston, Texas, USA
Hexahydropthalic anhydride	HHPA	Sigma Aldrich chemicals Pvt. Ltd. Bangalore, India
2-ethyl-4-methylimidazole	2E4MZ	Sigma Aldrich chemicals Pvt. Ltd. Bangalore, India
Aniline A.R	ANI	Central Drug House, New Delhi, India
Hydrochloric acid A.R	HCl	Central Drug House, New Delhi, India
Ammonium persulfate, A.R	APS	Merck specialities Pvt. Ltd. Mumbai, India
Xylene	Xy	Merck specialities Pvt. Ltd. Mumbai, India

The details of chemicals except xylene being used in the present work are reported in the experimental section of the previous chapter, i.e., chapter 2. Xylene was purchased from Merck India and used as received.

3.2.2. Synthesis

PANI particles were prepared in a single step oxidative polymerisation. The detailed procedure of PANI synthesis is already reported in the literature [87] and also given in the section 2.3.2 of chapter 2 of this thesis. PANI nano-fibres were synthesized using interfacial polymerisation by the process reported by Huang et al [68]. 3.2 mM aniline was dissolved in 10 ml of xylene while ammonium persulphate (0.8 mM) was dissolved in 10 ml of 1.0 M hydrochloric acid solution. Both the solutions were kept at low temperature (~4 °C). The aniline solution was transferred to a 50 ml glass vial and then APS solution was carefully poured to obtain an interface between the two layers. The polymerisation reaction was allowed to proceed for 24 h at room temperature. PANI obtained was filtered and washed several times with deionised water followed by ethanol.

3.2.3. Preparation of composites

The anhydride curing agent is solid at room temperature, was heated slightly, and mixed with epoxy resin in proper ratio. The mixture was cooled and then appropriate amount of accelerator was added and mixed properly using a glass rod. Different amounts of PANI powder and PANI nano-fibres were added and thoroughly mixed by glass rod to obtain different filler content composites. The conductive filler concentration was kept at 5, 10, 15, 20, and 25% by weight. During mixing, it was observed that PANI fibres are easy to mix. Samples were cured for 1 h in a preheated oven at 150 °C.

3.3. Characterization

Various characterization techniques used for the above samples have already been discussed in detail in chapter 2 of this thesis under section 2.3. These techniques have been used in a similar manner here too.

3.4. Results and Discussion

3.4.1. Electrical conductivity

The electrical conductivity of ICA samples relates to the volume fraction of filler particles and their particle size. Conductive behaviour depends on the creation of conducting contacts between filler particles when dispersed in the insulating matrix. Conductivity of the cured films of samples was studied by four probe method using the procedure already mentioned in section 2.3.3. The variation of electrical conductivity of epoxy/PANI powder and epoxy/PANI nanofibres is shown in **Fig. 3.1**.

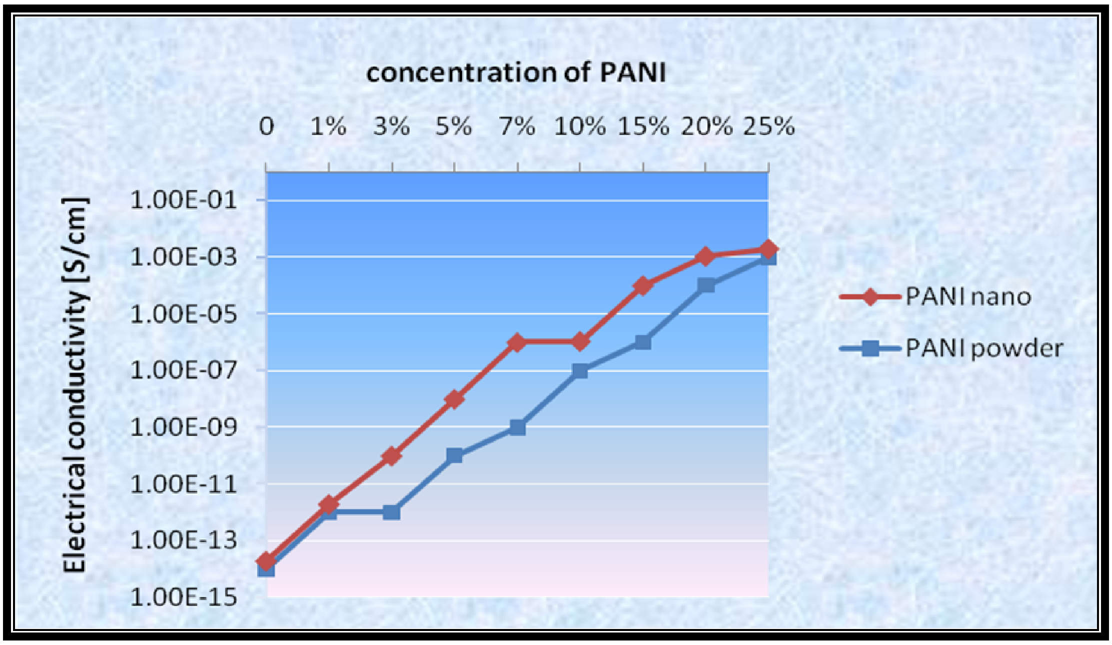


Figure 3.1. Electrical conductivity of ICAs as a function of the PANI conc.

It is observed that the maximum conductivity obtained in both cases remains the same, i.e., 10^{-3} Scm^{-1}. However, the percolation threshold with the PANI nanofibres is low, which indicates that the percolation threshold depends on the morphology of filler particles. Since, PANI nano-fibres have nano dimensions and high aspect ratio, the reinforcement is obtained at very low filler content, contrary to high PANI powder required to achieve similar conductivity. Also, the optimum value of conductivity is obtained with higher filler concentrations in case of PANI powder. For PANI powder, a coarse dispersion level is obtained and particles form large agglomerates, while in case of PANI nano-fibres the dispersion is smooth because the fibres are easily dispersed in the matrix forming effective conducting channels. It was observed while mixing the nano-fibres in the matrix, that these fibres are easily mixed and show a uniform diffusion. The uniformity in shape and small size helps the fibres to establish themselves easily within epoxy matrix and form paths for conduction at almost molecular chain level. Decreasing the percolation threshold is very important for conductive composites not only because it reduces the cost but also because it minimises the influence of filler on the mechanical and thermal properties.

3.4.2. Moisture resistance

Conductive adhesives are exposed to different conditions of humidity and temperature during their service life, so they must show a significant resistance towards moisture. Moisture has been known to affect the polymeric system and alter the mechanical properties by weakening the intermolecular interaction between functional groups of the polymeric chains. Moisture may affect the interface between filler and matrix in composites. Samples of ICAs with PANI nano-fibres and powder were subjected to elevated conditions of humidity and temperature as per the procedure mentioned in section 2.3.6 and the observations were recorded as weight change for different periods of time which is shown in **Fig. 3.2**. It is observed that although the ICA samples show a strong resistance towards humidity, yet a small weight gain is seen in all cases. The comparative studies between PANI powder and PANI nano-fibre filled

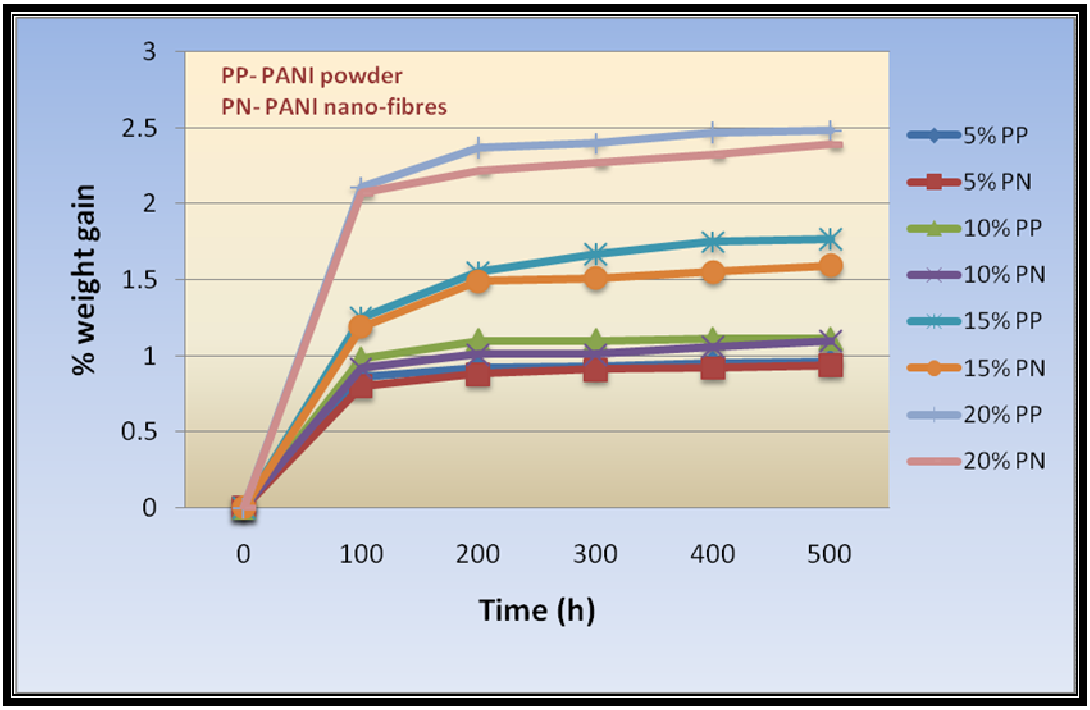


Figure 3.2. Weight gain of ICAs with respect to time of exposure to moisture

ICAs reveal that moisture absorption is irrespective of morphology. Most of the weight gain occurs till 100 h, thereafter the effect of moisture is almost over. This weight gain may be due to the binding of water molecules to filler particles which are loosely adhered to the matrix network. Again, it is clearly evident that percentage of weight gain increases with increase of filler content, which points to the strong possibility that the moisture effect may be ascribed to increase in uncured filler phase whatever the morphology may be.

3.4.3. Drop test performance

For an effective interconnection, the impact strength of adhesives should be high by virtue of which it is able to withstand the mechanical shocks it encounters during handling, processing and transportation. As per National Centre of Manufacturing sciences (NCMS), USA guidelines, an ICA can be effectively used for interconnections if it passes the drop test, i.e., a sample assembly bonded by it must not detach even after 6 drops from a height of 60 in. Drop test performance of the ICA samples was obtained in a similar manner as reported in section 2.3.5. The results as shown in **Fig. 3.3** envisage the fact that drop performance of ICAs containing PANI nano-fibres is far superior to the ICAs with PANI powder as filler.

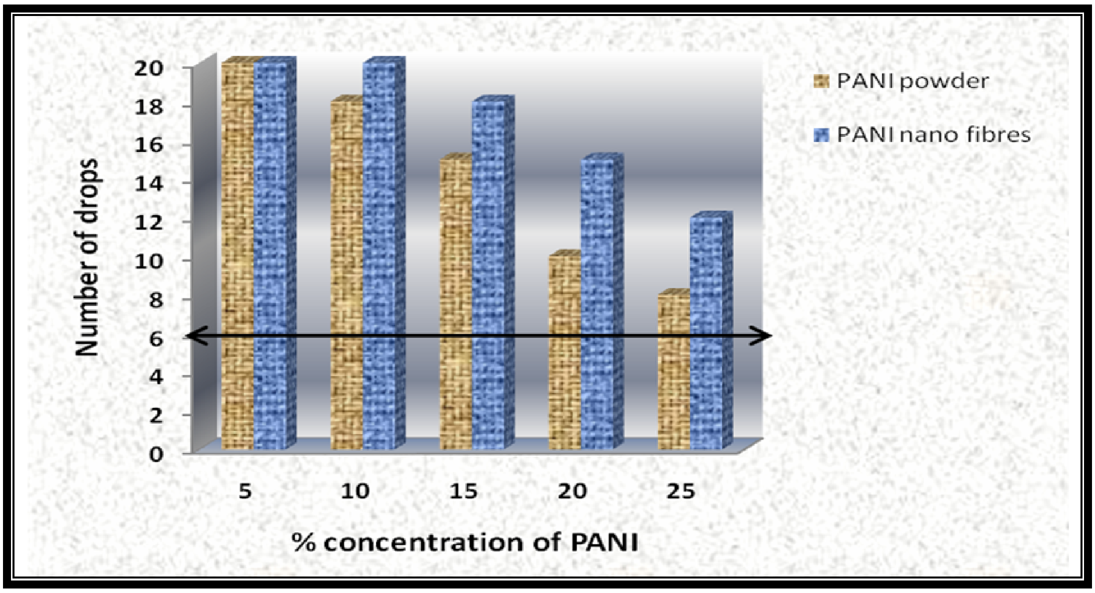


Figure 3.3 Drop test performance of ICAs

ICA with 25% PANI powder fails the drop test and the assembly shows wearing at the ends even in the 5th drop. It was also observed that the surface of the sample was very rough after curing while ICA containing same concentration of PANI nano-fibres has a smooth surface, showing relatively good impact strength and is stable far beyond the minimum requirement. The observations simply point to the fact that the uniformity in size and nano dimensions of these fibres enables them to effectively penetrate the matrix network and hence the damping property, i.e., the capacity to dissipate energy increases.

3.4.4. Lap shear test

In order to estimate the adhesive strength of the ICA samples, they were subjected to a fundamental lap shear test and their performance was judged with respect to maximum load before rupture. The detailed procedure of the test is already described in section 2.3.4. **Fig. 3.4** shows a comparison of the performance of ICAs with PANI powder and nano-fibre fillers. Although, it is imaginable that incorporation of filler phase of any dimension is bound to decrease the basic binding capacity of the adhesive matrix, yet there seems to be an appreciable improvement in adhesion strength of nano filled ICAs. Filler is bound to interfere with the adhesion of matrix network and create hindrance in impact transmission.

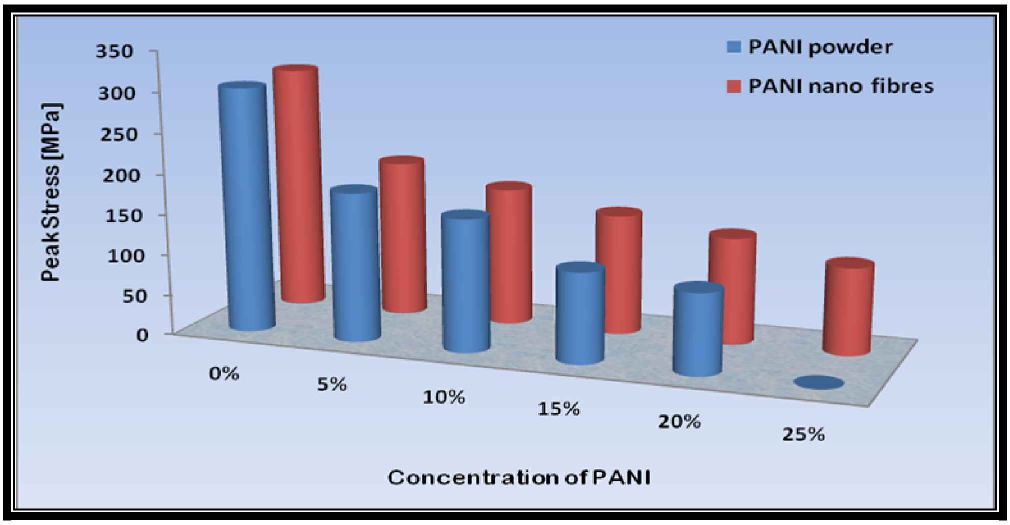


Figure 3.4. Lap shear strength of ICAs with different concentrations of PANI

As the dimension of filler decreases, the hindrance effect minimizes. Moreover, due to uniformity of size and better dispersion, nano-fibres ensure that the mechanical energy transfer across matrix filler barrier is improved. It was observed that ICA with PANI powder concentration of 25% was unable to bond the two test coupons properly and broke even before application of force during test; while nano PANI filled ICA of same concentration had a smooth surface after curing and good impact properties. It may be because agglomeration of PANI particles in the powder prevented the formation of effective matrix network, while nano dimensional fibres were diffused properly within the strong network of epoxy matrix. Such an improvisation of impact properties gives a very significant advantage to these ICAs for realising their application potential.

3.4.5. Thermal characteristics

DSC was used to investigate the cure kinetics of the ICAs filled with PANI of different morphologies under identical conditions. **Figs. 3.5** (a) and (b) show the DSC thermograms of ICAs with different concentrations of PANI as powder and nano-fibres, respectively.

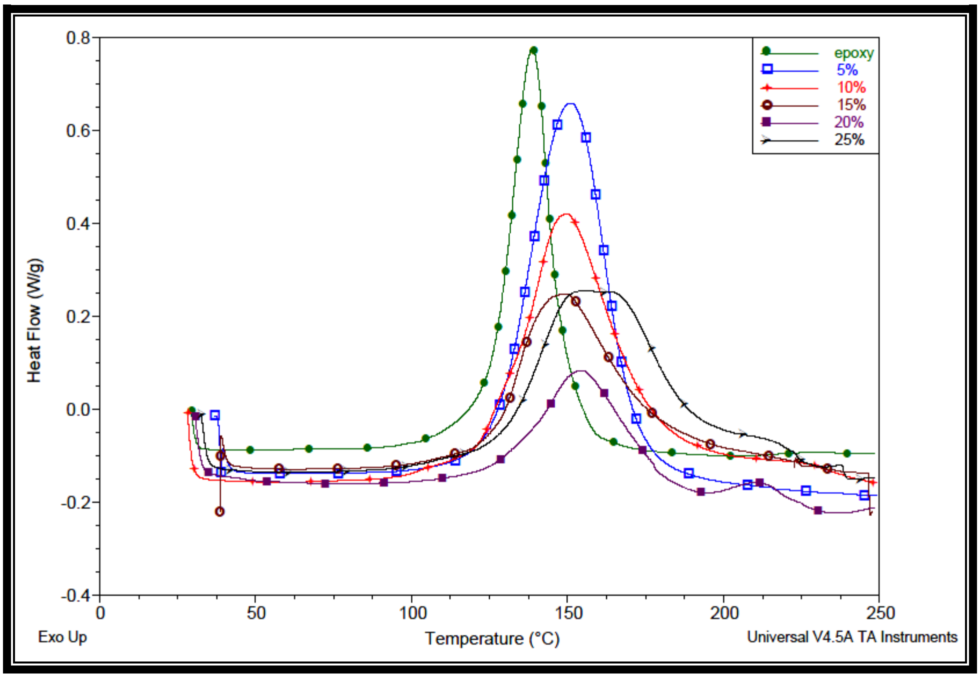


Figure 3.5(a). Curing behaviour of ICAs with PANI powder filler

The single exothermic peak of epoxy curing is evident in all samples which clearly suggests that the basic curing pattern of the epoxy remains unchanged. However, as the concentration of filler increases, the exothermic peak shifts to higher temperature in both the cases probably due to increase in non-curable filler proportion in the samples. An unusual behaviour is observed in the DSC profile of PANI nano-fibre containing ICA with 10% filler concentration. The corresponding exothermic peak is sharp and heat flow is less.

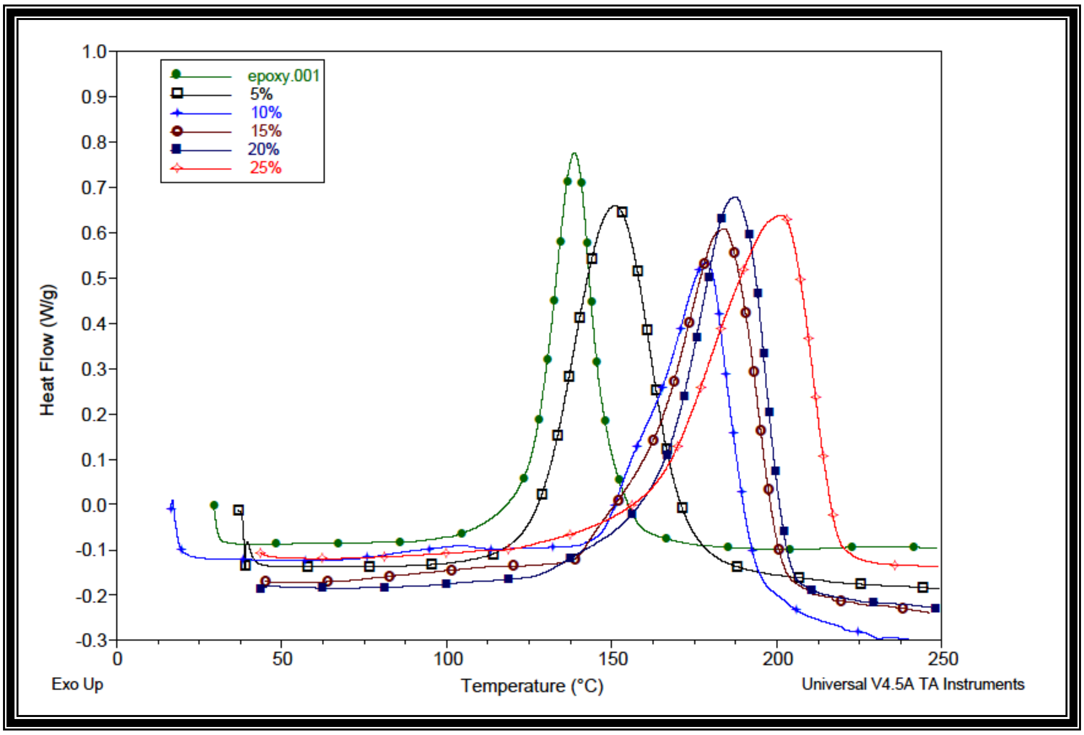


Figure 3.5(b). Curing behaviour of ICAs with PANI nano-filler

It may be significant because the percolation threshold happens to be around that concentration. Around percolation threshold filler particles form a definite pattern and an optimum diffusion of filler particles is obtained. This in turn has a definite effect on the network formation during curing as there is minimal hindrance due to filler particles. But such an effect needs uniformity of shape and small size which has been reported earlier [88].

Glass transition behaviour of samples with increase in concentration of PANI filler was studied as per procedure reported in section 2.3.1 and depicted in **Figs. 3.6** (a) and (b). Both the types of ICA samples show a similar trend of shifting of T_g range towards lower temperature with increase in concentration T_g of PANI. However, as the concentration is around percolation threshold in case of PANI nano-fibre filled ICAs, there is a sharp decrease T_g range. This unusual behaviour was confirmed by repeated scans but seems to be independent of epoxy resin curing. Such behaviour has been reported by Barrau et al [88] for polypyrrole/epoxy composites.

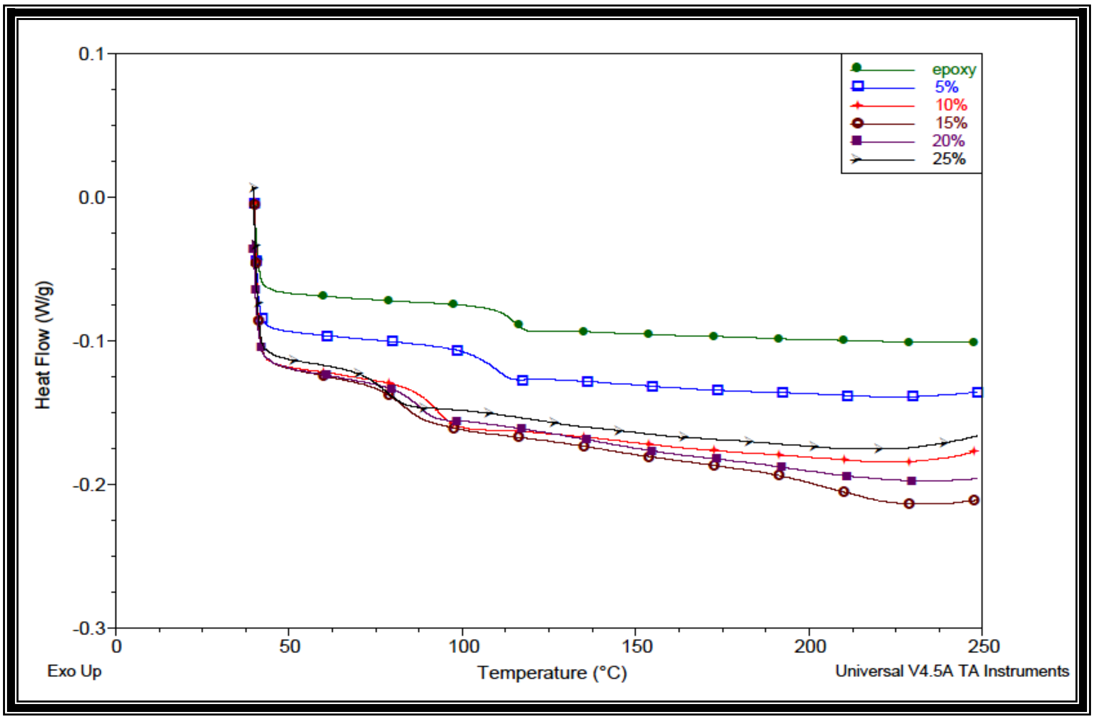


Figure 3.6(a). Variation of T_g of ICAs with PANI powder filler

This depression of T_g has been interpreted as increase of mobility of epoxy matrix chain segments around percolation threshold and is characteristic of highly uniform and minute filler dimensions. The free volume accessible to molecular motion around percolation threshold increases due to formation of infinite clusters of filler particles.

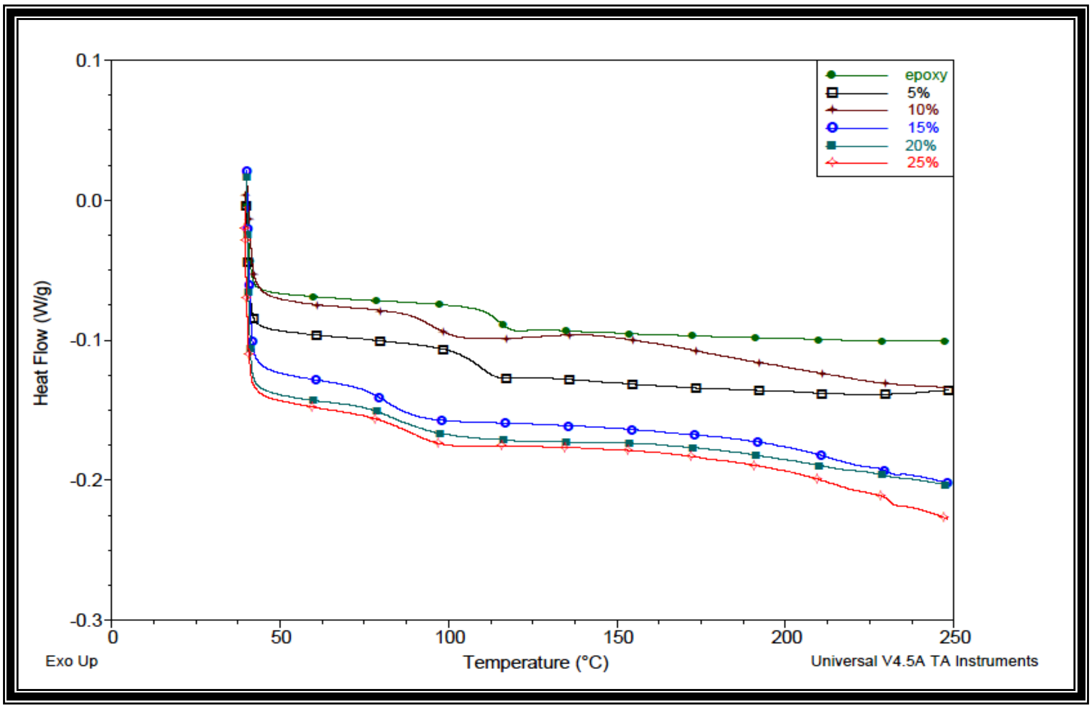


Figure 3.6(b). Variation of T_g of ICAs with PANI nano-filler

TGA thermograms of ICAs were conducted as per procedure discussed earlier in 2.3.2 and used to study the thermal degradation characteristics. It is clear from **Figs. 3.7** (a) and (b) that the thermal degradation follows almost same pattern in both the cases.

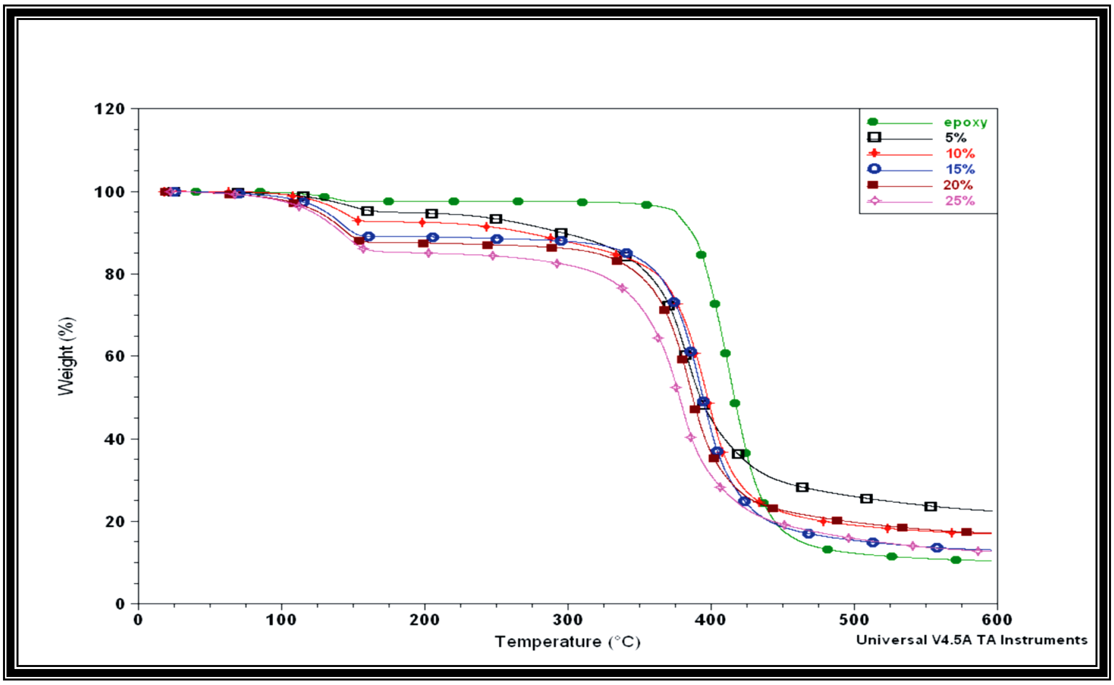


Figure 3.7(a). TGA thermograms of ICAs with PANI powder filler

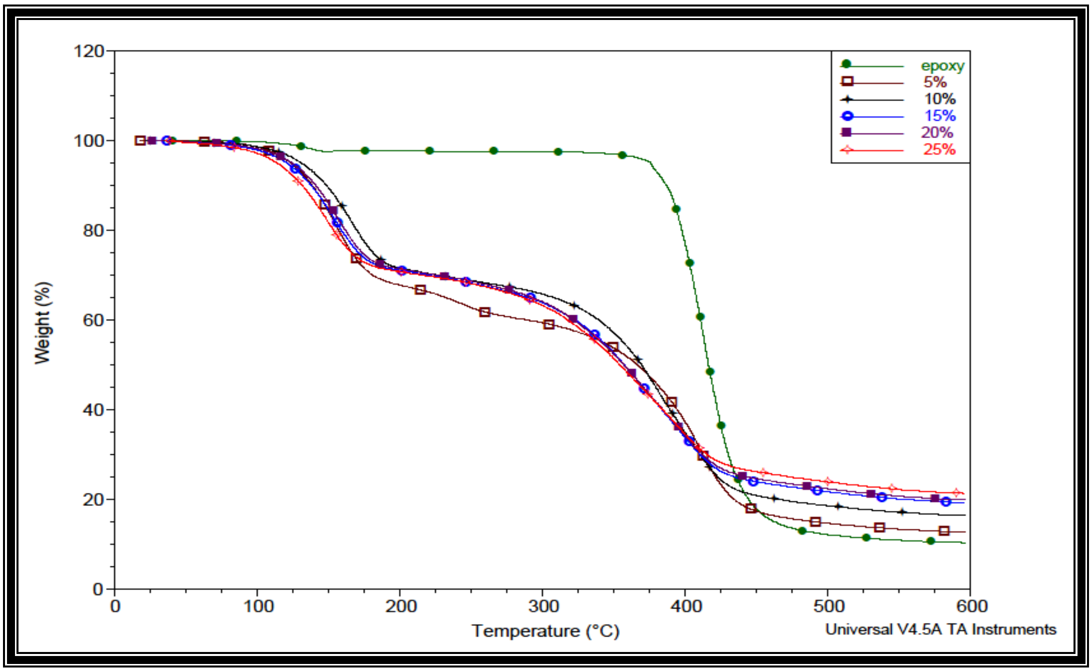


Figure 3.7(b). TGA thermograms of ICAs with PANI nano-filler

There is a two-step weight loss characteristic of epoxy systems in both the cases. First weight loss around 150 °C is probably due to the loss of volatiles and oligomers while around 350°C a sharp weight loss starts due to the degradation of epoxy matrix. ICAs with nano-fibres showed more defined weight loss around 150 °C probably because of the presence of more oligomers and volatiles due to its synthesis in organic phase.

3.4.6. Scanning electron microscopy

Since major properties of the ICAs depend on the degree of dispersion of filler inside the matrix, the morphology of the samples was studied by scanning electron microscopy. The detailed procedure is already reported in section 2.3.7. **Fig. 3.8** (a) shows irregular morphology of the PANI particles prepared by conventional one phase polymerization. Agglomeration is clearly evident and size of particles is large.

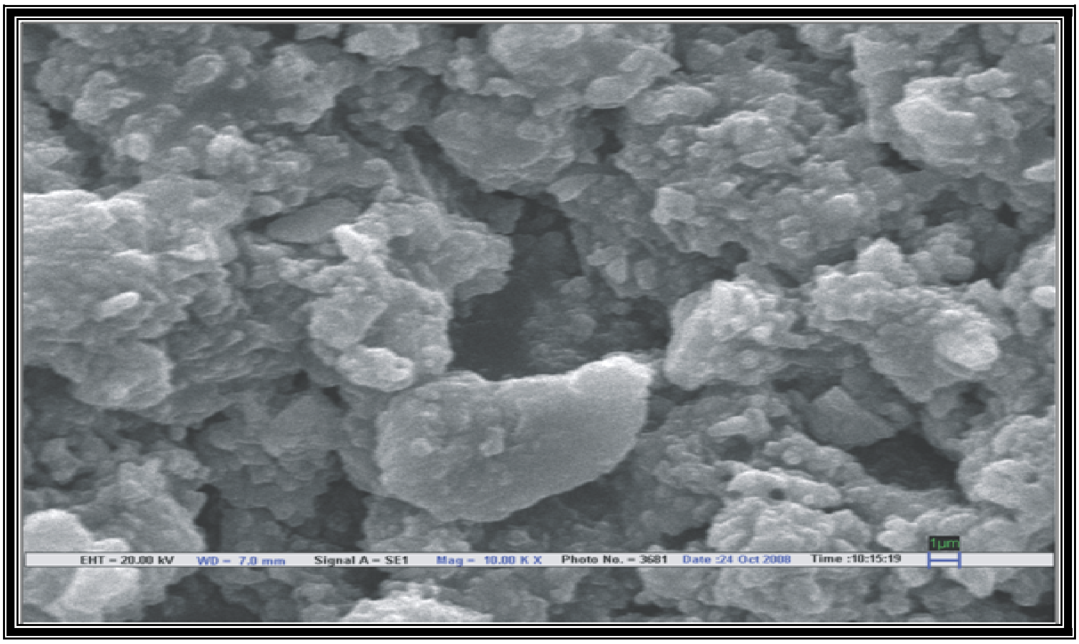


Figure 3.8(a). SEM micrograph of PANI powder

Fig. 3.8 (b) shows the SEM micrograph of PANI nano-fibres prepared by interfacial polymerization. The average diameter and length is ≈120 nm and 200 µm, respectively. **Fig. 3.8** (c) shows the fracture surface of the epoxy PANI powder composite with distinct non uniform distribution and agglomerate formation within the matrix phase. However, it is difficult to locate PANI nano-fibres in the fracture surface of ICA with PANI nano-filler as shown in **Fig. 3.8** (d). There is no distinct

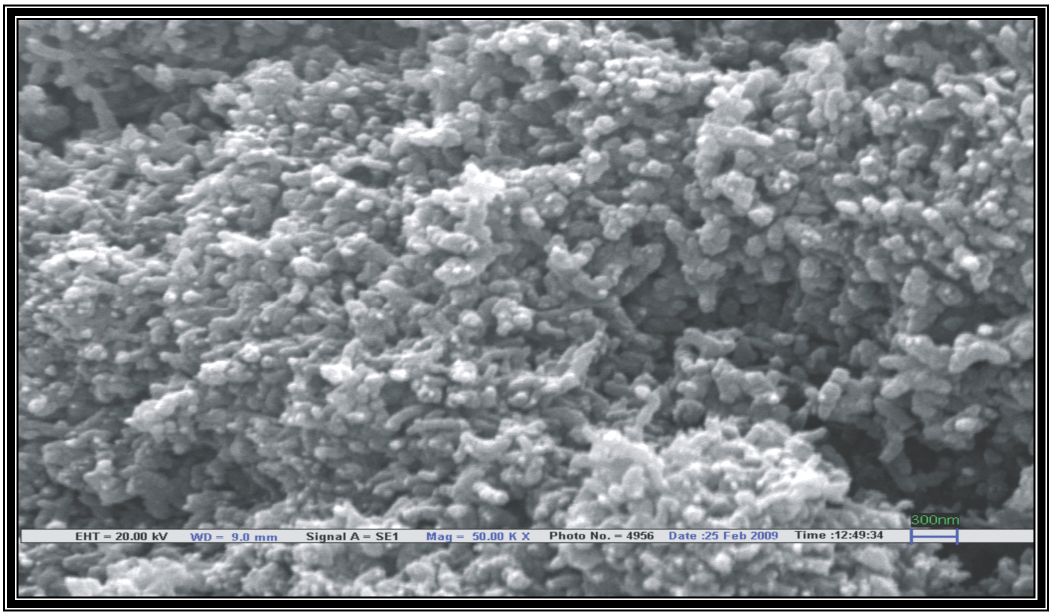


Figure 3.8(b). SEM micrograph of PANI nano-fibres

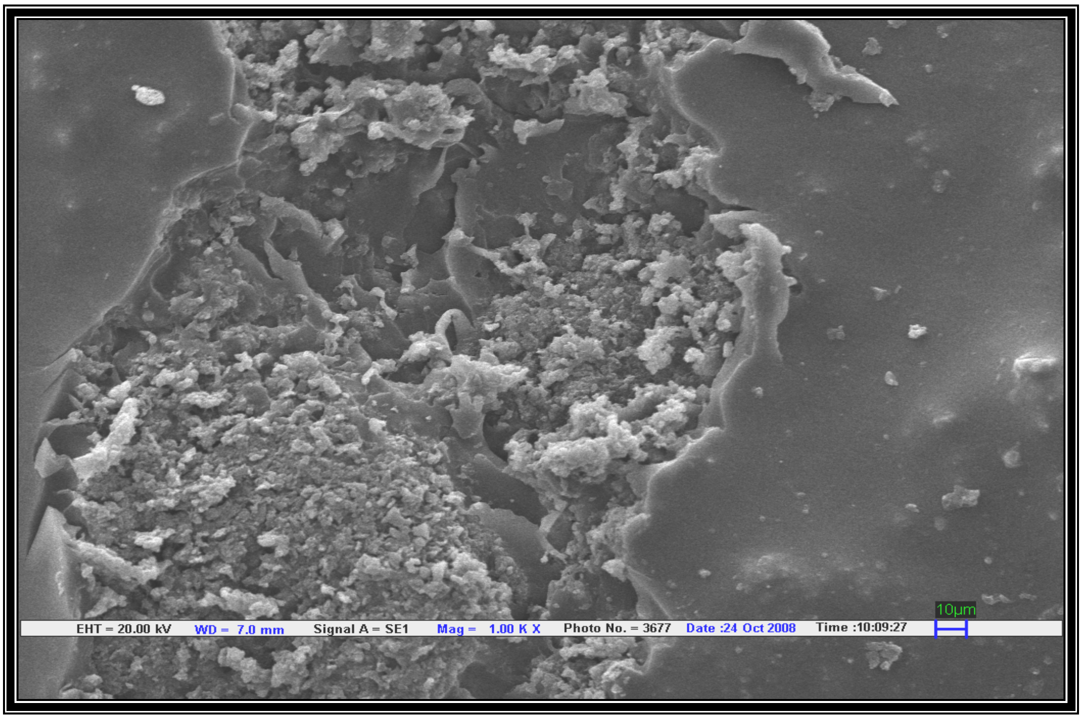


Figure 3.8(c). SEM micrograph of epoxy/PANI powder

agglomeration or visible phase differentiation which further establishes the fact that PANI nano-fibres are more uniformly dispersed within the matrix, hence establishing effective conductive channels and distributing mechanical stress uniformly.

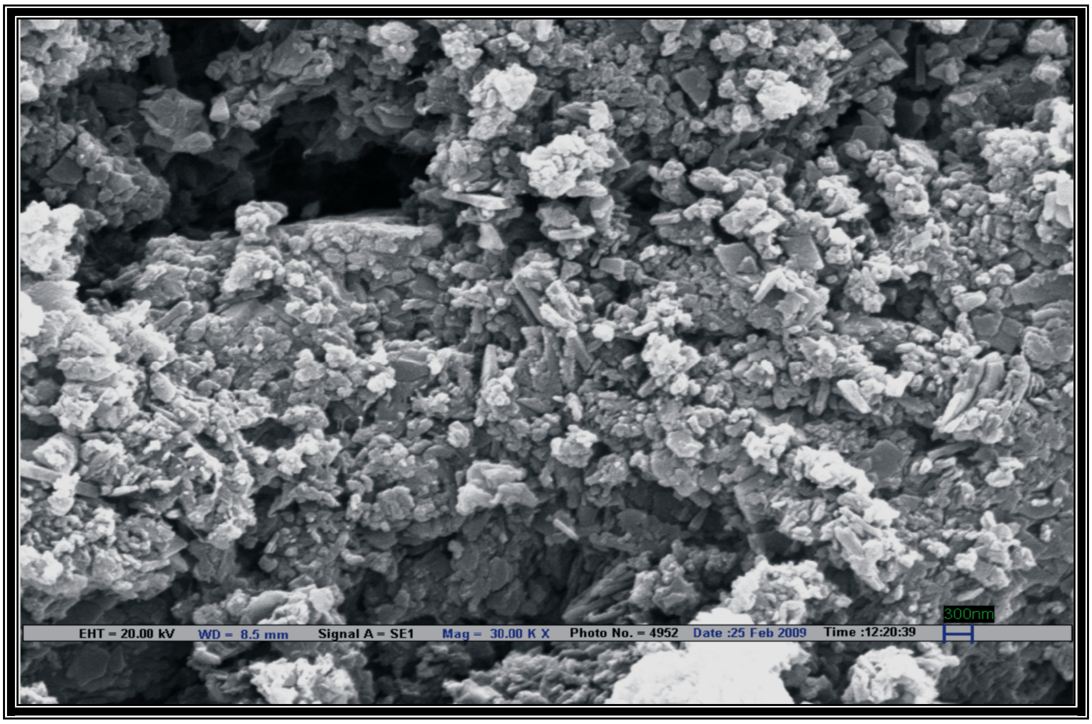


Figure 3.8(d). SEM micrograph of epoxy/PANI nanofibres

3.5. Conclusion

In this chapter, PANI nano-fibres were synthesized by interfacial polymerization and used as filler for preparing the ICAs with an epoxy/anhydride matrix. It is observed that uniformity and smaller size of PANI nano-fibres significantly improved the overall properties of the ICAs when compared to ICAs filled with PANI of macroscopic dimensions. Conductivity is established at low filler loading due to uniform diffusion and formation of conducting channels within epoxy matrix. Smaller size and high aspect ratio of nano-fibres facilitates their proper distribution and thus there is minimum hindrance to epoxy network formation. This in turn results in improvement of impact and drop test performance of the ICAs. Moreover, interpretation of SEM micrographs confirmed that the diffusion of nano-fibres inside the matrix polymer was very smooth and there is no agglomerate formation. Hence, it is concluded that incorporation of PANI nano-fibres as filler in epoxy/anhydride matrix improved the prospect of these composites for being used as ICAs.

3.6. References

1. Mir IA, Kumar D. J Adhes Sci & Technol; Accepted.
2. Theng BKG. Clay Miner 1970;18:357.
3. Paul DR. Robeson LM. Polymer 2008;49:3187.
4. Xiao Y, Li CM. Electroanal 2008;20:648.
5. MacDiarmid AG. Synth Met 2001;125:11.
6. MacDiarmid AG, Chiang JC, Halpern M, Huang WS, Mu SL, Somasiri NLD, Wu W, Yaniger SI. Mol Cryst Liq Cryst 1985;121:173.
7. Wessling B. Synth Met 1998;93:143.
8. Wang YY, Jing XL. Polym J 2004;36:374.
9. Wang YY, Jing XL. Polym Adv Technol 2005;16:344.
10. Wiznerowicz F. Wire 1994;44:102.
11. Persaud KC. Mater Today 2005;8:38.
12. Lu W, Smela E, Adams P, Zuccarello G, Mattes BR. Chem Mater 2004;16:1615.
13. Huang JX, Virji S, Weiller BH, Kaner RB. J Am Chem Soc 2003;125:314.
14. Behera DK, Bag DS, Alam S, Mathur GN. J Polym Mater 2004;21:81.
15. Wise DL, Wnek GE, Trantolo DJ, Cooper TM, Gresser JD. Electrical and optical polymer systems. New York: Marcel Dekker;1997. p.23.
16. Huang J. Pure Appl Chem 2006;78:15.
17. Zhang D, Wang Y. Mat Sci Eng B 2006;134:9.
18. Martin CR, Van Dyke LS, Cai Z, Liang W. J Am Chem Soc1990;112:8976.

19. Penner RM, Martin CR. J Electrochem Soc 1986;133:2206.

20. Martin CR. Science 1994;266:1961.

21. Martin CR. Acc Chem Res 1995;28:61.

22. Martin CR. Chem Mater 1996;8:1739.

23. Nishizawa M, Menon VP, Martin CR. Science 1995;268:700.

24. Menon VP, Martin CR. Anal Chem 1995;67:1920.

25. Wu CG, Bein T. Science 1994;266:1013.

26. Parthasarathy RV, Phani KLN, Martin CR. Adv Mater 1995;7:896.

27. Wu CG, Bein T. Science 1994;264:1757.

28. Wang CW, Wang Z, Li MK, Li HL. Chem Phys Lett 2001;341:431.

29. Wang Z, Chen MA, Li HL. Mater Sci Eng A 2002;328:33.

30. Yang SM, Chen KH, Yang YF. Synth Met 2005;152:65.

31. Cai Z, Martin CR. J Am Chem Soc 1989;111:4138.

32. Duchet J, Legras R, Demoustier-Champagne S. Synth Met 1998;98:113.

33. Wei ZX, Zhang ZM, Wan MX. Langmuir 2002;18:917.

34. Qiu HJ, Wan MX, Matthews B, Dai LM. Macromolecules 2001;34:675.

35. Liu J, Wan MX. J Mater Chem 2001;11:404.

36. Long YZ, Chen ZJ, Zheng P, Wang NL, Zhang ZM, Wan MX. J Appl Phys 2003;93:2962.

37. Wei ZX, Wan MX. J Appl Polym Sci 2003;87:1297.

38. Zhang ZM, Wei ZX, Wan MX. Macromolecules 2002;35:5937.

39. Yang YS, Liu J, Wan MX. Nanotechnology 2002;13:771.

40. Carswell ADW, O’Rear EA, Grady BP. J Am Chem Soc 2003;125:14793.

41. Zhang XY, Manohar SK. Chem Commun 2004;20:2360.

42. Nickels P, Dittmer WU, Beyer S, Kotthaus JP, Simmel FC. Nanotechnology 2004;15:1524.

43. Ma YF, Zhang JM, Zhang GJ, He HX. J Am Chem Soc 2004;126:7097.

44. Liu JM, Yang SC. J Chem Soc Chem Commun 1991;21:1529.

45. Choi SJ, Park SM. Adv Mater 2000;12:1547.

46. Hatano T, Takeuchi M, Ikeda A, Shinkai S. Chem Lett 2003;32:314.

47. Huang LM, Wang ZB, Wang HT, ChengXL, Mitra A, Yan YX. J Mater Chem 2002;12:388.

48. Kan J, Lv R, Zhang S. Synth Met 2004;145:37.

49. Kan JQ, Zhang SL, Jing GL. J Appl Polym Sci 2006;99:1848.

50. Wan MX, Li JC. J Polym Sci Part A: Polym Chem 2000;38:2359.

51. Long YZ, Chen ZJ, Wang NL, Zhang ZM, Wan MX. Phys B: Condens Matter 2003;325:208.

52. Zhang LJ, Wan MX. Nanotechnology 2002;13:750.

53. Long YZ, Zhang LJ, Ma YJ, Chen ZJ, Wang NL, Zhang Z, Wan MX. Macromol Rapid Commun 2003;24:938.

54. Long YZ, Luo JL, Xu J, Chen ZJ, Zhang LJ, Li JC, Wan MX. J Phys B:Condens Matter 2004;16:1123.

55. Long YZ, Chen ZJ, Wang NL, Ma YJ, Zhang Z, Zhang LJ, Wan MX. Appl Phys Lett 2003;83:1863.

56. Huang K, Wan MX. Chem Mater 2002;14:3486.

57. Yang YS, Wan MX. J Mater Chem 2002;12:897.

58. Pinto NJ, Carri´on PL, Ayala AM, Ortiz-Marciales M. Synth Met 2005;148:271.

59. Hwang JH, Yang SC. Synth Met 1989;29:271.

60. Pillalamarri SK, Blum FD, Tokuhiro AT, Story JG, Bertino MF. Chem Mater 2005;17:227.

61. Huang JX, Virji S, Weiller BH, Kaner RB. J Am Chem Soc 2003;125:314.

62. Huang J, Kaner RB. J Am Chem Soc 2004;126:851.

63. Huang JX, Kaner RB. Angew Chem Int Ed. 2004;43:5817.

64. Jing XL, Wang YY, Wu D, She L, Guo Y. J Polym Sci Part A: Polym Chem 2006;44:1014.

65. Jing XL, Wang YY, Wu D, Qiang JP. Ultrason Sonochem 2007;14:75.

66. Okamoto H, Okamoto M, Kotaka T. Polymer 1998;39:4359.

67. Smith JA, Josowicz M, Janata J. J Electrochem Soc 2003;150:E384.

68. Li GF, Martinez C, Janata J, Smith JA, Josowicz M, Semancik S. Electrochem Solid-State Lett 2004;7:H44.

69. Langer JJ, Czajkowski I. Adv Mater Opt Electron 1997;7:149.

70. Langer JJ. Adv Mater Opt Electron 1999;9:1.

71. Langer JJ, Framski G, Golczak S, Gibinski T. Synth Met 2001;119:359.

72. Langer JJ, Framski G, Joachimiak R. Synth Met 2001;121:1281.

73. LangerJJ, Framski G, Golczak S. Synth Met 2001;121:1319.

74. Liang L, Liu J, Windisch CF, Exarhos GJ, Lin YH. Angew Chem Int Ed. 2002;41:3665.

75. Liu J, Lin Y, Liang L, Voigt JA, Huber DL, Tian ZR, Coker E, McKenzie B, McDermott MJ. Chem Eur J 2003;9:604.

76. Chan HSO, Ho PKH, Tan KL, Tan BTG. Synth Met 1990;35:333.

77. Michaelson JC, McEvoy AJ. J Chem Soc Chem Commun 1994;79.

78. Huang JX, Virji S, Weiller BH, Kaner RB. J Am Chem Soc 2003;125:314.

79. Zhang XY, Chan-Yu-King R, Jose A, Manohar SK. Synth Met 2004;145:23.

80. Gao H, Jiang T, Han B, Wang Y, Du J, Liu Z, Zhang J. Polymer 2004;45:3017.

81. King RCY, Roussel F. Synth Met 2005;153:337.

82. Huang JX, Kaner RB. J Am Chem Soc 2004;126:851.

83. Ara´ujo PLB, Ara´ujo ES, Santos RFS, Pacheco APL. Microelectron J 2005;36:1055.

84. Zhang XY, Chan-Yu-King R, Jose A, Manohar SK. Synth Met 2004;145:23.

85. Qiu HJ, Zhai J, Li SH, Jiang L, Wan MX. Adv Funct Mater 2003;13:925.

86. Zhang XY, Goux WJ, Manohar SK. J Am Chem Soc 2004;126:4502.

87. Kumar D, Chandra R. Ind J Eng Mater Sci 2001;8:209.

88. Barrau S, Demont P, Maravel C, Bernes A, Lacabanne C. Macromol Rapid Commun 2005;26:390.

CHAPTER 4

POLYPYRROLE/EPOXY COMPOSITES AS ISOTROPICALLY CONDUCTIVE ADHESIVES

Among the intrinsically conducting polymers, polypyrrole (PPy) has been widely used for various applications due to its better conductivity and good stability. In this chapter, we report the use of PPy as conductive filler in ICAs in place of metals like Sn & Pb. PPy was incorporated as filler in epoxy/anhydride (EP) system and its application as isotropic conductive adhesive was studied in detail. PPy was synthesized by suspension polymerization using DBSA as dopant. The PPy obtained by suspension polymerization has fine particles and hence shows better dispersion in the epoxy matrix. The composites with varying PPy concentrations were studied for various properties of ICAs. The composites show good impact properties and conductivity at very low filler concentration. SEM observations established that PPy particles were dispersed in the epoxy matrix more uniformly. The overall characteristics of these conductive adhesives reported here establish that they would be prospective ICAs.

4.1. Polypyrrole

Polypyrrole is one of the most studied conducting polymers because of its rather straightforward preparation methods [1]. PPy is reasonably stable in air, presents high conductivity, good electrochemical properties, thermal stability and is easily synthesized both chemically as well as electrochemically [2]. It exhibits a wide range of surface conductivities (10^{-3} Scm^{-1} to 100 Scm^{-1}) depending on the synthesis and the nature of the counter ion or dopant [3]. Some of its important properties include electroactivity, electrochromism, environmental stability and corrosion inhibitive property. It is widely used in rechargeable batteries [4-7], electrochromic displays [8-

10], ion-exchangers [11-13], pH sensors [14], gas sensors [15-17], corrosion protection [18], biomedical applications [19] etc due to its important properties.

Pyrrole is a five membered heterocyclic compound. It can be found in heme and chlorophyll and can be synthesized by two methods: reacting furan with ammonia and dehydrogenation of pyrrolodine [20]. The general structure of PPy is a chain of mainly 2,5 coupled aromatic units (**Fig. 4.1**). PPy was first synthesized in 1916 by oxidation of pyrrole as a powder known as “pyrrole black” and in 1968 it was synthesized electrochemically [21]. As we know that PPy can be electrodeposited under various conditions and therefore its physical, chemical and electrical properties can be altered using various dopants [22-24].

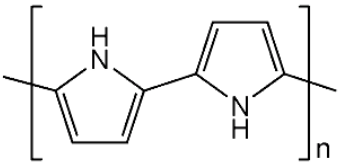


Figure 4.1. General structure of PPy

Conductivity: One of the remarkable properties of PPy that can be modified by altering the dopant ion is conductivity. Conductivity of PPy can range from those of insulators with almost no conductivity 10^{-5} to 100 Scm^{-1} [25]. Doping ions help to decrease the band gap between the energy levels. PPy is conductive because of the ability of the electrons to hop along the polymer chains and across interchains due to the π-conjugating bonds. By using smaller counter ion with coplanarity with the polymer chains, the conductivity can be increased [26]. Dopants such as hydrogen peroxide, polyethylene oxide, dodecylbenzenesulfonate, and salts containing transition metal ions have all been used [27-30]. Studies have shown that longer deposition times, lower plating potentials and temperatures, and higher concentrations of monomer and electrolyte are favourable for conductivity and stability [31]. Other modifications such as increasing the roughness of the plating surface, has also been shown to increase conductivity [26]. The addition of water into the electrodeposition solution also produces a more conductive polymer possibly because water serves as a better proton scavenger than PPy in the solution [32].

Two of the most common dopants that are used for polymerisation of PPy are polystyrene-sulfonate (PSS) or sodium dodecylbenzenesulfonate (NaDBS) [33]. PSS/PPy and NaDBS/PPy polymers have been used in many applications ranging from actuators to neural electrode coatings to neural substrates [34-40]. PPy’s properties make it an attractive choice for biosensor [41-43] and drug delivery [44, 45] applications. The ability to dope the polymer with various molecules and stimulate it electrically creates novel methods for drug delivery. The conductivity of PPy also creates the opportunity to sense specific molecules by monitoring changes in the properties of PPy directly or remotely using radio frequency (RF) technology. By further exploring the ability to manipulate and monitor the properties of PPy, more advanced interactions with its surrounding environment can be achieved.

Synthesis: PPy can be synthesized by chemical bulk polymerization, vapour phase polymerization and electropolymerization etc. Bulk chemical polymerization of pyrrole can be used to produce PPy powder easily. The monomer is dissolved in organic solvents or doping acid solutions like DBSA, p-TSA etc. Most common initiator used are $FeCl_3$ and APS. Another technique developed for producing PPy coatings is vapour phase deposition. In a typical process, polymer containing electron acceptor/initiators (i.e, $FeCl_3$, $CuCl_2$) is placed on the substrate prior to the vapour deposition. The dip coated substrates are then placed in the presence of a dry saturated vapour of the monomer pyrrole for varying periods of time, and PPy deposits on the surface as film [46]. Other methods such as UV-photo-induced PPy formation and plasma polymerized formation have also been performed to form PPy films [83, 84]. For electropolymerisation, PPy is mixed in an aqueous solution, and a potential is applied between the working and reference electrodes. The polymerisation can be carried out by potensiostatic technique (voltage held constant), galvanostatic (current is held constant), or potentiodynamic method (voltage is cycled) [47]. The polymer gets deposited on anode as an oxidation-reduction reaction occurs. The anodic oxidation results in a flux of charge and/or neutral species as the polymer forms. Plated PPy remains on the electrode surface while subsequent deposition continues which shows that PPy is conductive enough to participate in further monomer oxidation. In electropolymerisation, doping involves a redox reaction as the polymer forms. Electropolymerization usually produces thin PPy films, however, for specific uses film thickness can be increased by longer polymerization time. The film deposited on surface is infusible and insoluble because of strong inter- and intra-molecular interactions and crosslinkings [48].

Charge transport: Conjugated polymers like PPy have various oxidation levels which can be manipulated through the removal of electrons (oxidation) or the addition of electrons (reduction) by the application of a voltage (**Fig. 4.2**). For approximately every three pyrrole monomers, a positive charge forms and a counter anion is incorporated into the polymer to bring about the charge neutrality. For large dopants such as NaDBS, when the pyrrole is reduced (a negative voltage applied between the polymer and reference electrode in a solution) cations from the solution flow into the polymer to neutralize the charge, and the polymer expands. If the dopants are smaller anions, when the polymer is reduced the negatively charged dopants will flow out of the polymer into the solution to equilibrate charge. This ability to change the volume of the PPy has been used to create actuators.

It has been proposed that the electrons move through PPy by two methods. The first method involves movement of current across mobile charge carrying regions, polarons and bipolarons. Dopants ionise a polymer chain and create a polaron. As dopant concentration increases more polarons are formed and eventually bipolarons form. Electrons can then move across a single chain by movement of these charge carrier regions. The second method occurs when polarons or bipolarons from two separate polymer chains reside in the same plane. Electrons then travel from polymer chain to polymer chain by interchain hopping, producing spinless conductivity [49]. These two methods, a) transfer of polarons and bipolarons throughout a single polymer chain and b) hopping of electrons from chain to chain, account for transport of charge in PPy [25]. The dominant method of charge transfer depends on the type and the concentration of the

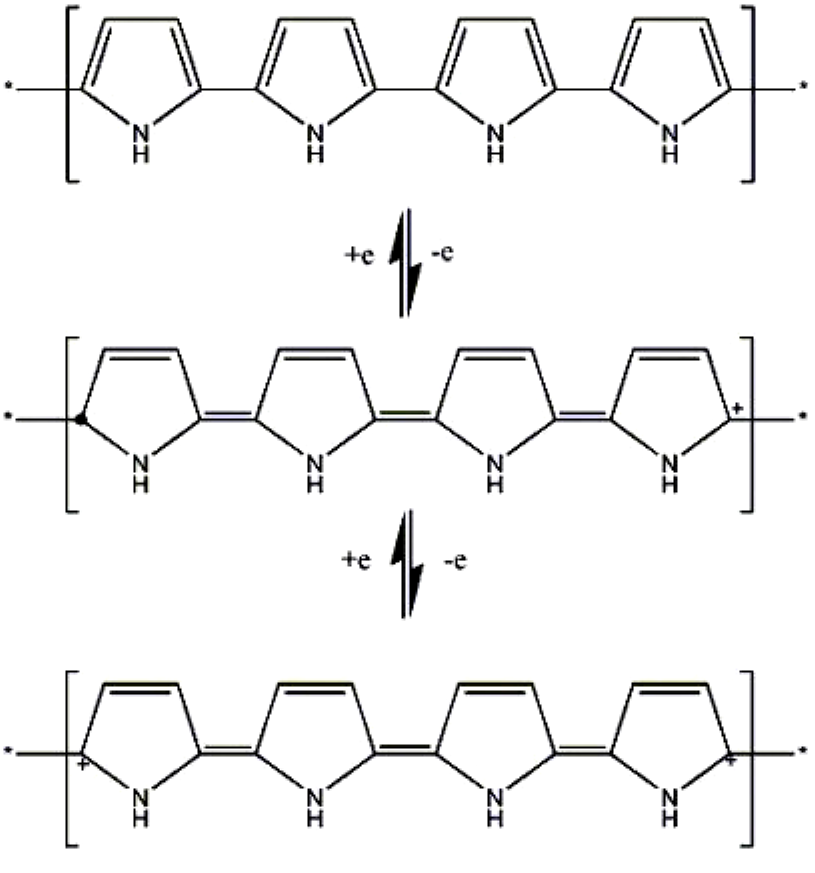


Figure 4.2. Various redox forms of PPy

dopant in the film [50]. The conjugated backbone of alternating double and single bonds allows the charge species to move along the backbone, resulting in an electrically conductive polymer.

PPy/epoxy composites

Difficulty in processing of PPy is a hindrance which prevents its effective use in many other applications. One of the most widely used technique for improving its processing properties is by forming composites with other processable polymers. Incorporating PPy in epoxy has many advantages like smoother percolation curves and low process density as compared to metal fillers. In fact, specific masses of the epoxy matrix and the PPy particles are 1.23 and 1.4, respectively [51]. Although, the approach seems to be very viable, there are very few reports of such composites available. Cassignol et al reported the use of four dispersing methods to disperse increasing amount of PPy in an epoxy matrix in order to make it electrically conductive. These composites were used to study the microstructure-conductivity relationship [52]. A correlation between percolation threshold and glass transition temperature depression in PPy/epoxy resin composites was observed by Barrau et al [53]. Similarly, Pomposo et al reported development of PPy based conductive hot melt adhesives for EMI shielding applications [54].

4.2. Experimental

4.2.1. Materials

The materials used in this study along with their suppliers are listed in **Table 4.1**.

Pyrrole was procured from SRL Ltd, India and DBSA was supplied by Himedia Labs, India, while $FeCl_3$ was purchased from Merck India and used as received. The matrix polymer was diglycidyl ether of bisphenol-F (DGEBF) Epon 862, manufactured by Hexion speciality chemicals, and purchased from Miller Stephenson chemical company, USA. The curing agent used, i.e., hexahydropthalic anhydride (HHPA) and the catalyst 2-ethyl-4-methylimidazole (2E4MZ) were obtained from Sigma Aldrich chemical company. The ratio of epoxy to curing agent was 1:0.85 and the concentration of catalyst was 1 part per hundred parts of resin.

Table 4.1. List of chemicals used and their suppliers

Material	Acronym	Source
Pyrrole (extra pure)	Py	Sisco research laboratories Pvt. Ltd, Mumbai, India
Dodecyl benzene sulphonic acid	DBSA	Himedia laboratories Pvt. Ltd, Mumbai, India
Ferric chloride L.R	$FeCl_3$	Merck specialities Pvt. Ltd. Mumbai, India
Epon 862	DGEBF	Hexion speciality chemicals, Inc. Houston, Texas, USA
Hexahydropthalic anhydride	HHPA	Sigma Aldrich chemicals Pvt. Ltd. Bangalore, India
2-ethyl-4-methylimidazole	2E4MZ	Sigma Aldrich chemicals Pvt. Ltd. Bangalore, India

4.2.2 Synthesis of polypyrrole

Chemical polymerisation of pyrrole was done in a single step procedure [55]. 0.13 moles of freshly double distilled pyrrole and 0.13 moles of DBSA were dissolved in 100 ml of deionised Millipore water by vigorous stirring to get a dispersion system. 0.26 moles of $FeCl_3$ were dissolved in 100 ml of deionised Millipore water separately. The two solutions were cooled to ≈ 0°C. Then, $FeCl_3$ solution was poured slowly over the dispersion of pyrrole and DBSA and kept at ≈ 0°C. After 4 h excessive quantity of methanol was poured into the solution to terminate the reaction. The resulting polypyrrole precipitate was vacuum filtered and washed several times with distilled water, methanol, and acetone. Finally, it was dried in oven at 80°C for 8-10 h, ground into fine powder, and stored in a desiccator.

4.2.3 Preparation of composites

The resins for the ICAs were formulated as per the procedure already reported in chapter 2 of this thesis under section 2.2.3. Various amounts of PPy powder were added to the epoxy system to obtain composites with 5, 10, 15, 20 weight percentage of PPy. The material was hand mixed thoroughly to obtain a uniform mixture.

4.3 Characterization

Various characterization techniques have been used to characterise above samples in a similar manner as in chapter 2 of this thesis under section 2.3.

4.4 Results and Discussion

4.4.1 Conductivity measurements

Conductivity of the ICA samples with different concentrations of PPy was measured in a similar manner as reported in previous chapters. In order to get consistent results, identical conditions were maintained. **Fig. 4.3** shows the evolution of conductivity in ICAs as the proportion of PPy increases.

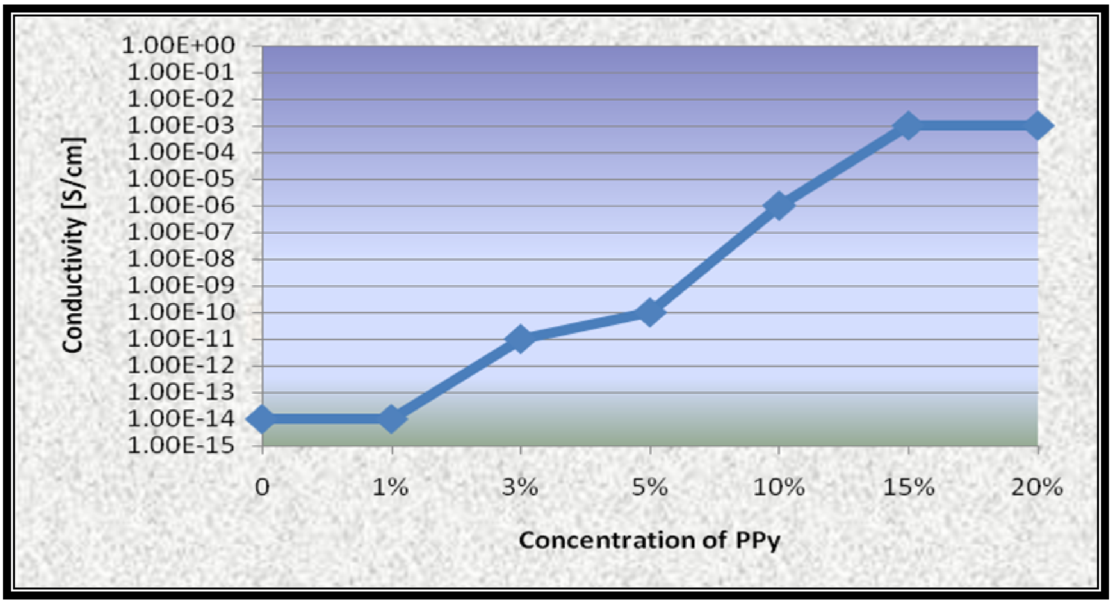


Figure 4.3. Variation of electrical conductivity with increase in PPy conc.

With respect to parent epoxy network, conductivity shows a sharp increase even with the incorporation of 3% of PPy. Even the percolation threshold taken at 10^{-6} Scm^{-1} comes at a lower PPy concentration, i.e., between 5–10%. PPy formed by dispersion polymerisation has a very minute and uniform particle size and is thus easily diffused in the epoxy matrix forming a conductive network. At the percolation threshold, this network becomes continuous and an infinite cluster of PPy particles is formed which ensures conduction within the insulating matrix network. These results are in accordance with those reported in literature [52, 53]. With the increase in PPy concentration, conductivity shows a smooth increase till it reaches a value of 10^{-3} Scm^{-1} with a PPy concentration of 15%. Above this concentration, there was no significant increase in conductivity, which may be due to saturation in conductive filler distribution and formation of clusters.

4.4.2 Curing properties

The DSC thermograms of uncured epoxy/PPy composites along with that of neat epoxy/anhydride system are depicted in **Fig. 4.4**. It is observed that a single exothermic peak is evident in all samples irrespective of the concentration of PPy in the epoxy matrix. Hence, it is clear that the basic curing profile of the epoxy anhydride system is not changed by the incorporation of PPy. Epoxy anhydride system shows a sharp exothermic peak at about 138°C corresponding to complete cross linking of the matrix. However, with the increase in PPy content, the peak starts to broaden and is slightly shifted towards higher temperature. This may be due to decrease in the curable epoxy proportion in the composites and thus increase in the curing time. ICA with 10% PPy concentration shows a slight shift towards low temperature. It may be worthwhile to note that the percolation threshold of the composites is around this concentration. Below percolation threshold the filler particles form indefinite clusters and thus there is a wide difference in modulus, but around threshold potential the particles form a definite pattern and thus an arranged pattern of filler particles is formed. This in-turn has a definite effect on network formation during curing and there is a minimal hindrance due to PPy particles. This trend is further confirmed by the sharp depression in glass transition temperature (T_g) of this composite.

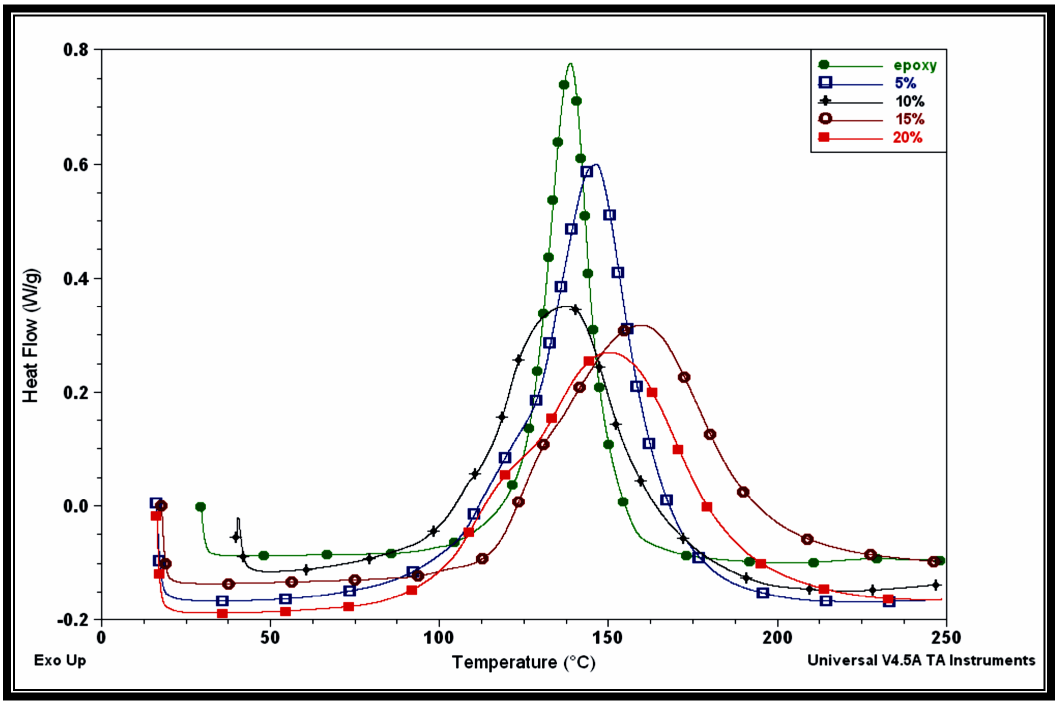


Figure 4.4. DSC thermograms of PPy/epoxy composites

After the DSC scan, samples were cooled to room temperature and scanned again at the same rate to obtain glass transition temperature (T_g) of the samples. Variation of glass transition temperature with the increase of PPy concentrations is shown in **Fig. 4.5**. As the PPy concentration increases, there is a slight shift in T_g range towards lower temperature, but it decreases sharply when the PPy concentration becomes 10%. This unusual behaviour was confirmed with a number of repeated scans and it seems to be independent of epoxy resin curing. As the concentration is around percolation threshold of the composites, there is a depression of T_g. Such type of depression in T_g has also been reported by Barrau et al [53]. It has been concluded that the depression in T_g around percolation threshold is due increase in the mobility of epoxy matrix chain segments. The transition at percolation threshold is related to formation of infinite clusters due to which free volume accessible to molecular motion of epoxy chain segments is maximum.

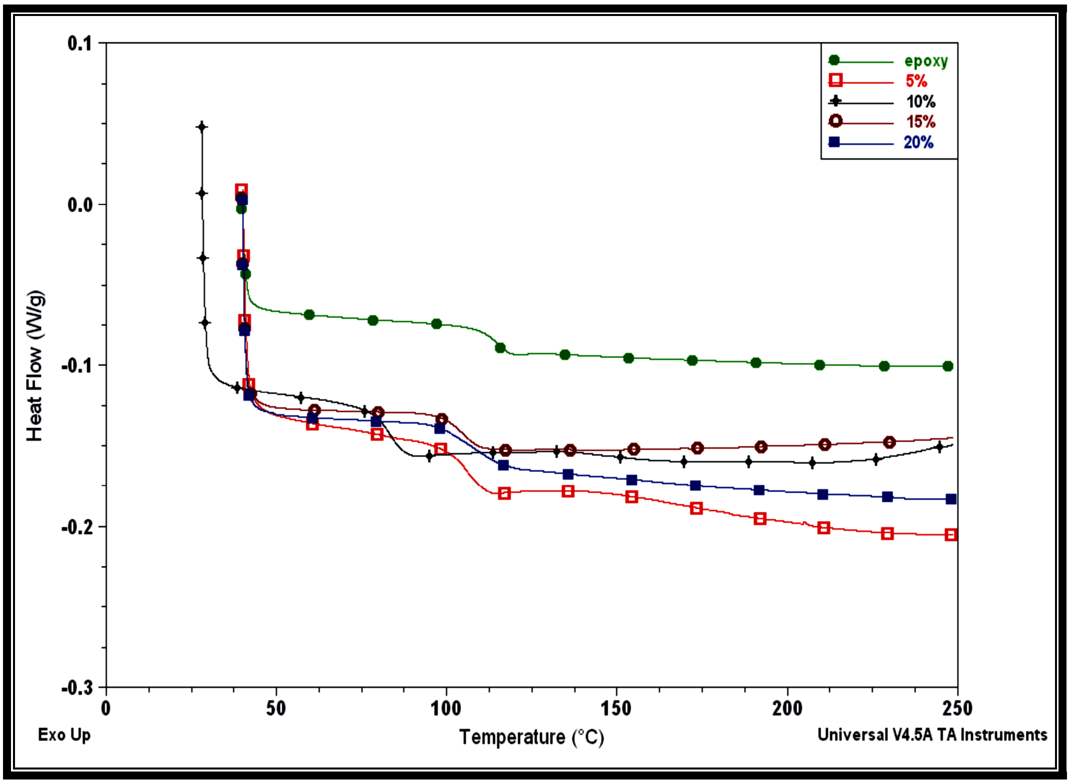


Figure 4.5. Variation of glass transition temperature with increase in PPy conc.

4.4.3 Thermogravimetric analysis

Thermal stability of the samples was studied by TGA analysis. All the samples essentially show two-step transition as depicted in **Fig. 4.6**. Epoxy system shows a slight weight loss around 150°C which can be due to loss of volatiles and is stable till around 400°C after which it shows a steep change in thermogram due to the degradation. By incorporation of PPy, the basic degradation characteristics are essentially same with a sequence of two step degradation. But, with the increase in PPy content, the weight loss around 150°C increases. This is probably due to loss of volatiles and oligomers and is characteristics of PPy phase. All the samples showed stability till 350°C and then undergo a sharp degradation till 450°C which is essentially the characteristic of epoxy system. Hence, it can be concluded from the results obtained that PPy incorporation does not have a significant effect on the thermal degradation of epoxy systems.

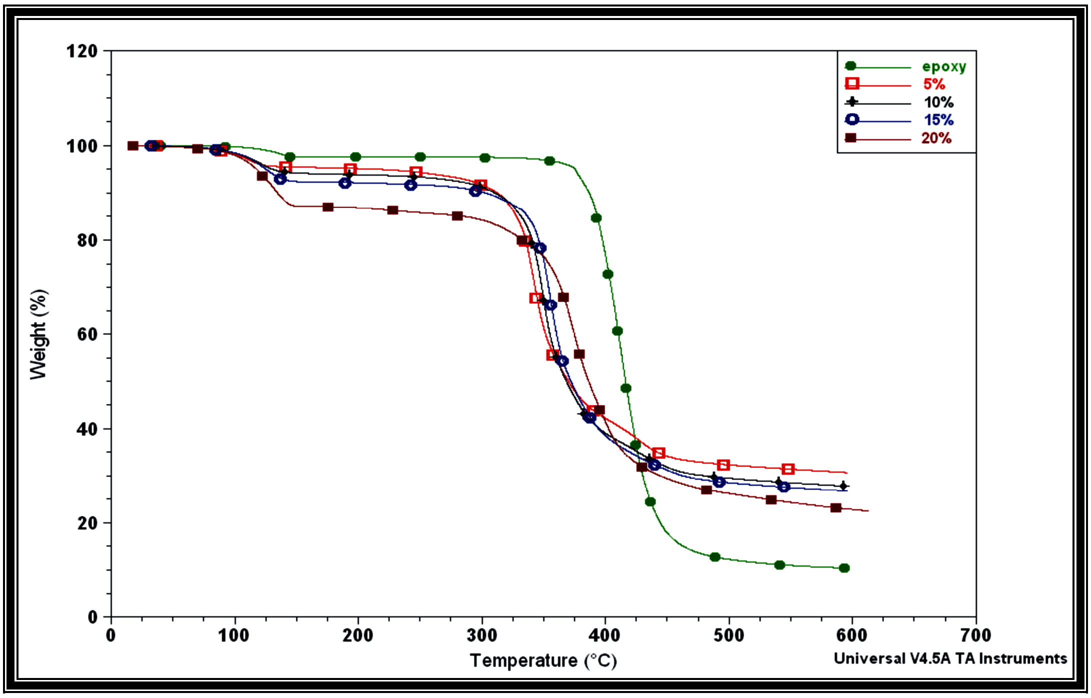


Figure 4.6. TGA thermograms of PPy/epoxy composites

4.4.4 Moisture absorption

Resistance to moisture is a very important parameter of ICAs. Moisture present in the service environment can degrade the impact properties of the adhesives, giving rise to swelling stresses in the system. This may lead to the formation of voids or growth of already present voids. Water may also affect the electrical properties of the adhesives and form oxides on the surface of metal fixtures attached by them. Hence, good ICAs should have very low moisture pickup capacity. Moisture absorption data obtained after 85°C/~100%RH aging is presented as percent weight gain in **Fig. 4.7**. It can be observed that even cured ICAs show moisture absorption but the weight gain is very small. Moisture uptake of samples was more during first 100 h. This may be due to water attached to the filler particles which are not completely adhered within the epoxy matrix network. PPy has known affinity towards humidity. This is attributed to the presence of heteroatoms and disordered structure of PPy which favours penetration of small atoms like water. These molecules are free or may be linked by hydrogen bonds to NH groups [51].

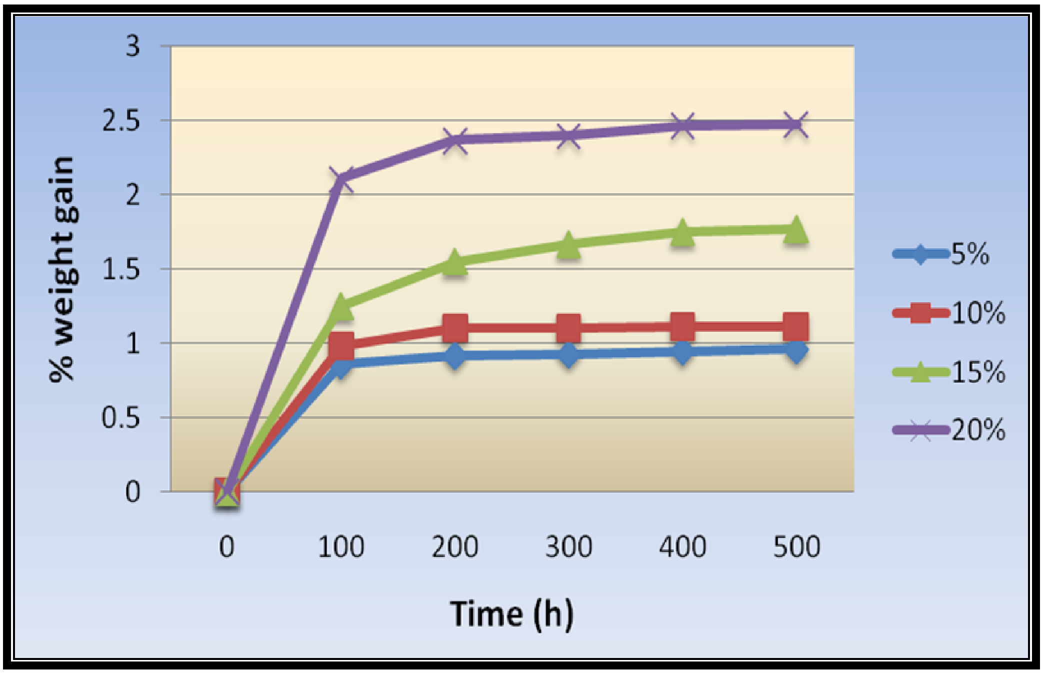


Figure 4.7. Moisture uptake of ICAs

In all the samples, there is almost saturation beyond 100 h. These results are further complimented by the fact that as the percentage of PPy increases, the weight gain increases which indicates that the moisture uptake is due to increase in proportion of PPy with respect to the cured epoxy matrix. However, the results are indicative of the fact that even under harsh conditions of temperature and humidity, ICAs showed phenomenal stability and the weight gain was too small even after 500 h of exposure to hot and moist conditions.

4.4.5 Drop test performance

High impact strength forms a very important parameter of high performance conductive adhesives. ICA joints have to absorb shocks during assembling, handling and throughout their service life and thus need to exhibit extremely good impact properties. Impact performance of any material depends on the effective damping property, i.e., the capacity of a material to dissipate energy. The impact performance of ICAs was determined using a drop test devised by NCMS, USA. For an ICA to be used for solder replacement, it has to survive 6 drops from a height of 60″ without the test assembly being detached. In this study, drop test were performed by dropping the test assembly through a channel on to concrete floor ensuring that it falls vertically. An average of five tests was taken and the results are shown in **Fig. 4.8**.

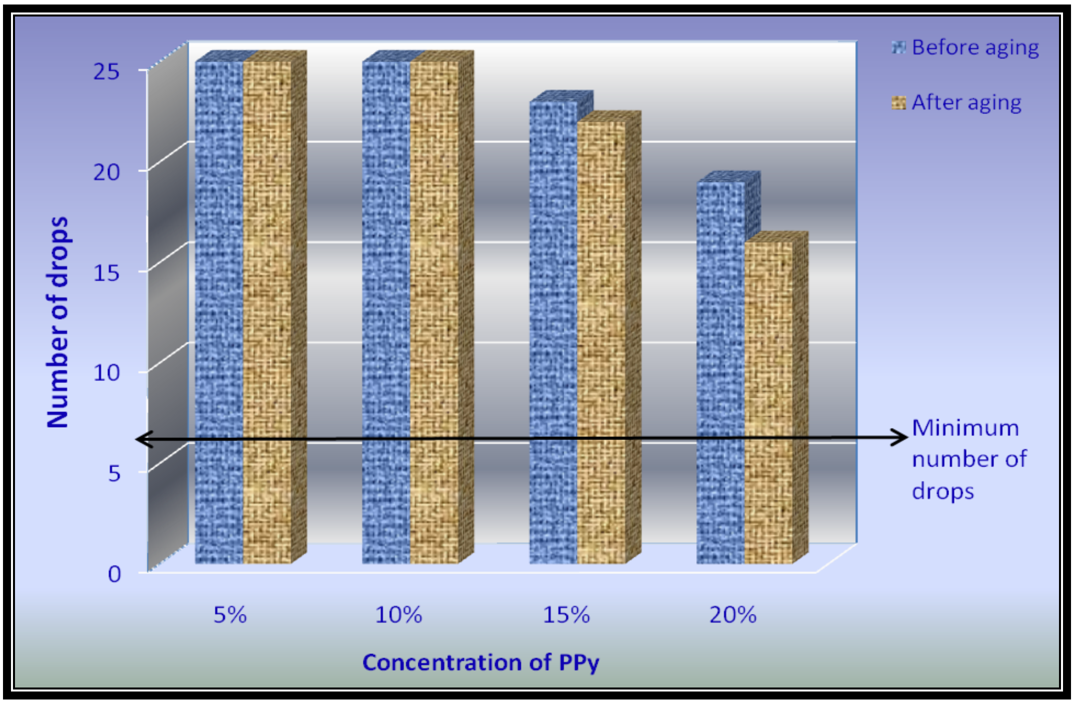


Figure 4.8. Drop test performance of ICAs

Since the powder of PPy formed was smooth and particle size is small, the impact performance of epoxy is not affected significantly. It can be observed that chips bound by ICAs containing 5 and 10% were stable even after 25 drops and the trend was not changed by aging the samples in 80°C/~100%RH for 500 h. Although, all the sample assemblies after aging continued to be intact long after the minimum 6 drops required. But with the increase in PPy concentration, drop performance decreased slightly. This again leads to the fact that moisture absorbed by partially free PPy particles leads to void propagation and thus decreases the impact performance. Although, drop performance decreases with increase in PPy concentration yet these ICAs are far more stable and can withstand the shocks even after exposure to very harsh service environment.

4.4.6 Lap shear strength

Representative data on lap shear strength are shown in **Fig. 4.9**. In all the cases, there was a drop in lap shear strength with the incorporation of PPy inside the epoxy matrix. However, it is significant to note that after a sharp decrease in lap shear at 5% PPy concentration, there is only a slight change in lap shear thereafter. It is indicative of the fact that since the particle size of PPy is uniform and small, there is an even diffusion of particles within the epoxy network without formation of agglomerates.

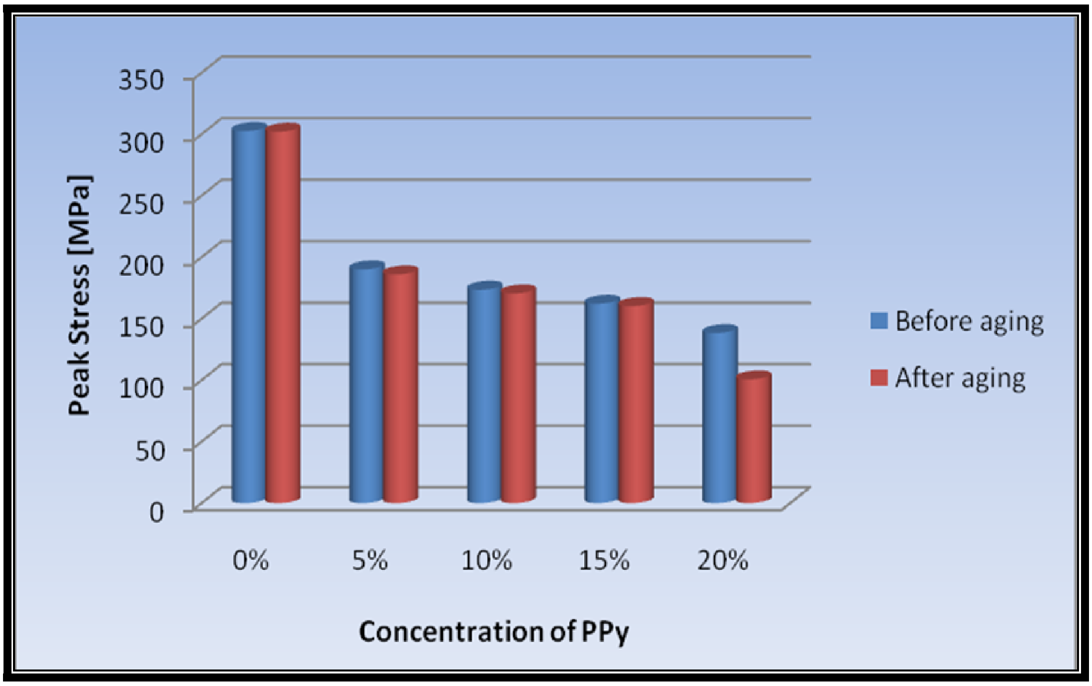


Figure 4.9. Lap shear strength of the ICAs

In most of the composites, there was almost no effect of aging on lap shear properties. When the PPy concentration increased beyond 15%, the lap shear decreased. There is probably a hint of PPy phase domination beyond that concentration and hence moisture might be enhancing the crack or void propagation leading to decrease in lap shear. Overall, we can say that these composites do not show a damping of adhesive strength under adverse environmental conditions.

4.4.7 Scanning electron microscopy

The microstructure of PPy incorporation was observed by scanning electron microscopy. **Fig. 4.10** (a) shows the surface of the epoxy/PPy composite without any distinct agglomeration of PPy particles. Some particles appear on the surface while few appear partially embedded inside the matrix. It may be observed that the smooth and well textured surface of epoxy matrix has developed contours due to PPy particles.

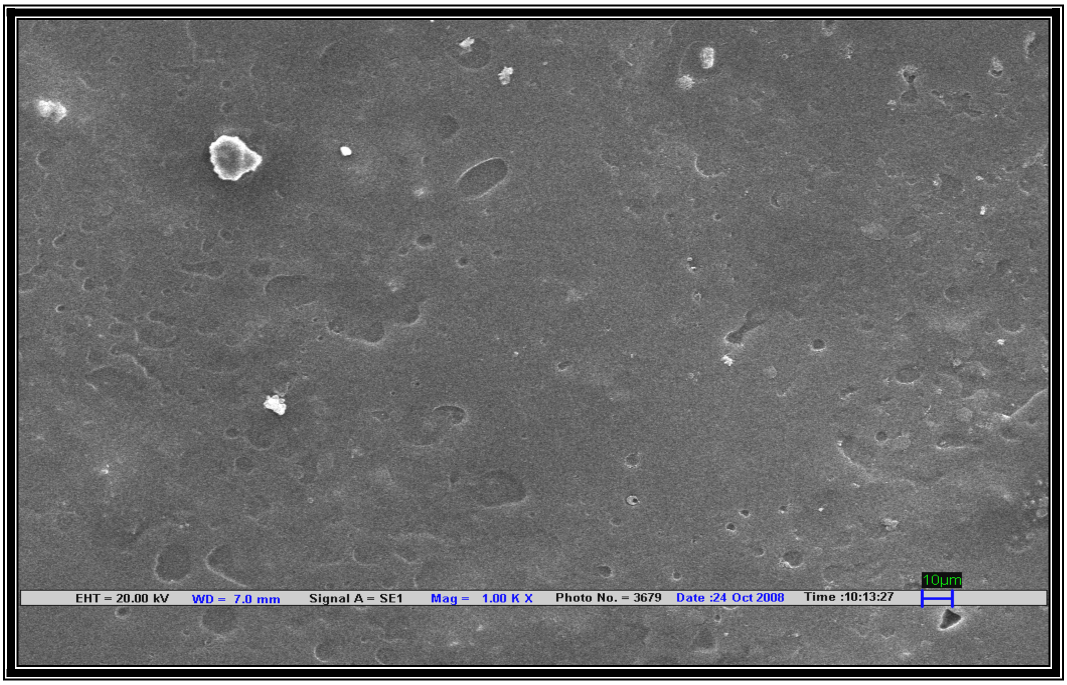


Figure 4.10(a) SEM micrograph of epoxy/PPy composite surface

The distribution of these PPy particles in the hard epoxy matrix is a bit difficult to be observed through SEM. An image of a peel fractured ICA film, **Fig. 4.10** (b) shows a cluster of PPy particles which have a strong interconnection of epoxy matrix and the particles seem to be well connected without a definite phase separation.

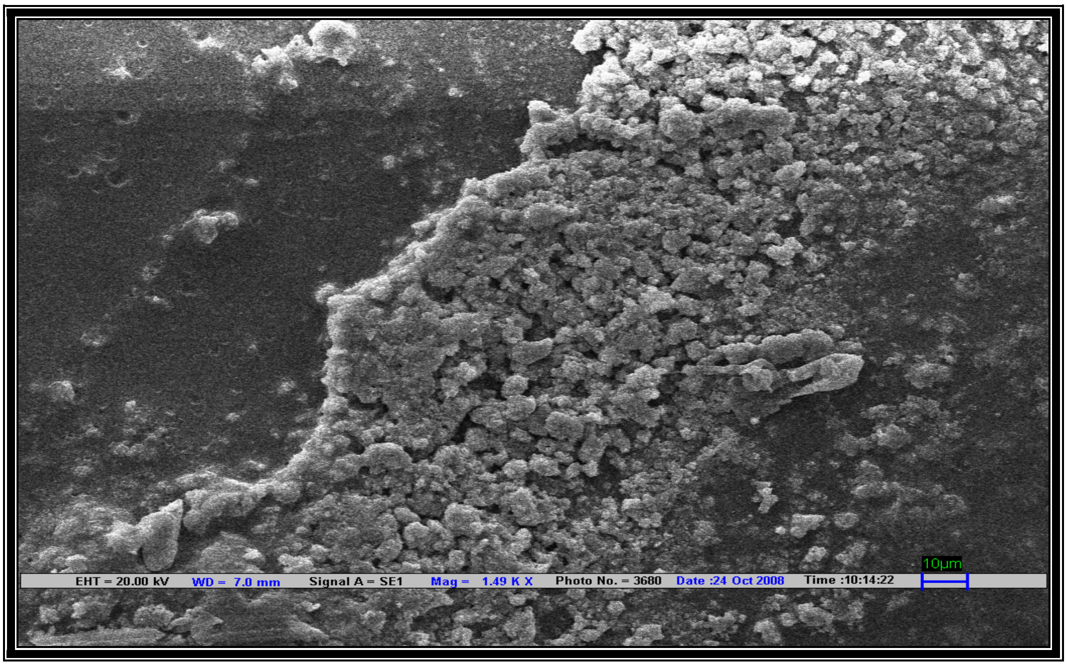


Figure 4.10(b) SEM micrograph of epoxy/PPy composites

When the fractured surface of these samples was observed under very high magnification (3000 kX), PPy particles were very difficult to be distinctly identified and appeared to be deeply embedded inside the cross-linked epoxy matrix as shown in **Fig. 4.10** (c).

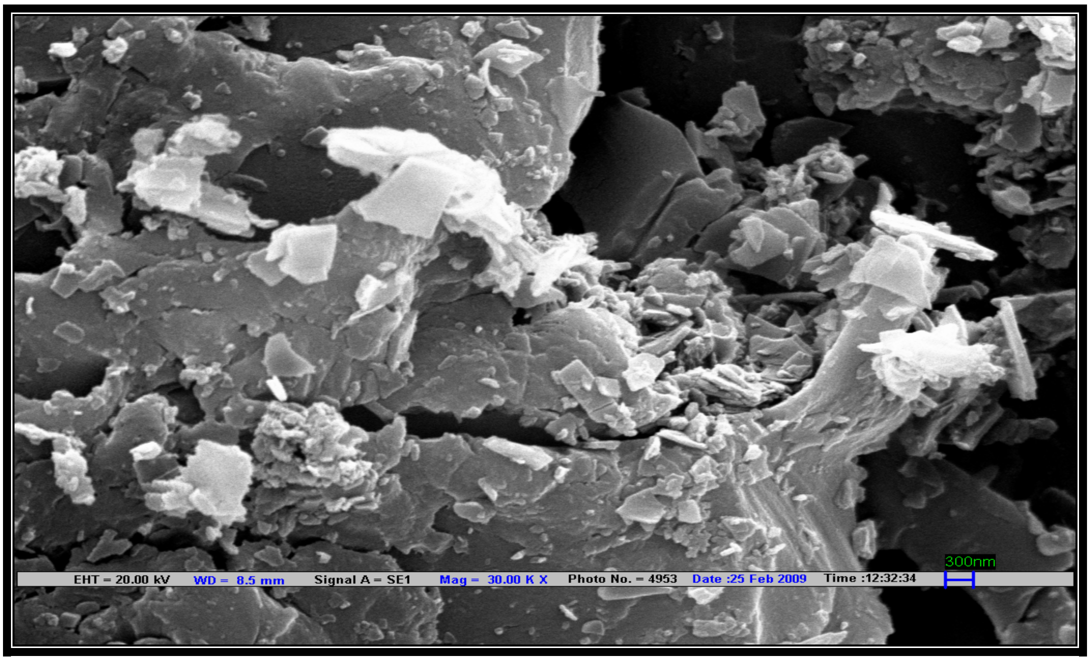


Figure 4.10(c) SEM micrograph of epoxy/PPy composite at very high magnification

4.5. Conclusion

Composites of PPy with epoxy anhydride system show prospect of being used as ICAs, although conductivity needs further improvement. PPy particles are easily dispersed within the epoxy matrix without affecting its basic properties. Conductivity shows a smooth increasing trend and reaches a value of 10^{-3} Scm^{-1} with a PPy concentration as low as 15%. No further increase of conductivity was observed on increasing the concentration of PPy. The thermal properties and curing profile of the composites are very close to that of neat epoxy system. However, a depression in T_g was observed close to percolation threshold due to increased mobility of polymeric chains around that concentration. Impact properties of epoxy matrix are affected but are still good enough for an ICA. Moisture shows a negligible effect on the overall properties of ICAs studied. Hence, incorporation of PPy in epoxy matrix forms composites which may be used as ICAs in electronic interconnections. The composite with 15% PPy showed the best properties and can be most suited in electronic application. This work has already been published in journal of adhesion [56].

4.6. References

1. Elsenbaumer RL, Reynolds JR. In: Handbook of Conducting Polymers, Ed: Skotheim TA, Marcel Dekker;1997.
2. Lin-Xia W, Xin-Gui L, Yu-Liang Y. React Funct Polym 2001;47:125.
3. Da Cruz AGB, Wardell JL, Rangel MVD, Simao RA, Rocco AM. Synth Met 2007;157:80.
4. Fedorkova A, Orinakova R, Orinak A, Talian I, Heile A, Wiemhofer HD, Kaniansky D, Arlinghaus HF. J Pow Sour 2010;195:3907.
5. Ji L, Yao Y, Toprakci O, Lin Z, Liang Y, Shi Q, Medford AJ, Millns CR, Zhang X. J Pow Sour 2010;195:2050.
6. Hwang SS, Cho CG, Kim H. Electrochim Acta 2010;55:3236.
7. Manuel J, Raghavan P, Shin C, Heo MY, Ahn JH, Noh JP, Cho GB, Ryu HS, Ahn HJ. Mater Res Bull 2010;45:265.
8. Rocco AM, De Paoli MA, Zanelli A, Mastragostino M. Electrochim Acta 1996;41:2805.
9. Deniz Is O, Koyuncu FB, Koyuncu S, Ozdemir E. Polymer 2010;51:1663.
10. Mortimer RJ, Dyer AL, Reynolds JR. Displays 2006;27:2.
11. Gohil GS, Binsu VV, Shahi VK. J Memb Sci 2006;280:210.
12. Khan AA, Inamuddin. J App Polym Sci 2007;105:2806.
13. Akieh MN, Ralph SF, Bobacka J, Ivaska A. J Memb Sci 2010, In Press.
14. Carquigny S, Segut O, Lakard B, Lallemand F, Fievet P. Synth Met 2008;158:453.
15. Hong L, Li Y, Yang M. Sens Actuat B: Chem 2010;145:25.

16. Al-Mashat L, Tran HD, Wlodarski W, Kaner RB, Kalantar-zadeh K. Sens Actuat B: Chem 2008;134:826.

17. Jang J, Bae J. Sens Actuat B: Chem 2007;122:7.

18. Hosseini MG, Raghibi-Boroujeni M, Ahadzadeh I, Najjar R, Seyed-Dorraji MS. Prog Organ Coat 2009;66:321.

19. Carta R, Jourand P, Hermans B, Thoné J, Brosteaux D, Vervust T, Bossuyt F, Axisa F, Vanfleteren J, Puers R. Sens Actuat A: Phys 2009;156:79.

20. Maw S,Smela E, Yoshide K, Sommer-larsen P, Stein RB. Sens Actuat A: Phys 2001;89:175.

21. Kudoh Y, Akami K, Matsuya Y. Synth Met 1998;95:191.

22. Scheller FW, Wollenberger U, Warsinke A, Lisdat F. Curr Opin Biotech 2001;12:35.

23. Kudoh Y. Synth Met 1996;79:17.

24. Sabouraud G, Sadki S, Brodie N. Chem Soc Rev 2000;29:283.

25. Langer R. Science 1990;249:1527.

26. Kang ET, Neoh KG, Tan KL. Prog Polym Sci 1998;23:277.

27. Wong JY, Langer R, Ingber DE. Proc Nat Aca Sci 1994;91:3201.

28. Nashat A, Langer R. Mol Cel Bio 2003;23:4788.

29. Schmidt CE, Shastri VR, Vacanti JP, Langer R. Proc Nat Aca Sci 1997;94:8948.

30. Cui X, Hetke JF, Wiler JA, Anderson DJ, Martin DC. Sens Actuat A: Phys 2001;93:8.

31. Reut J, Reut N, Opik A. Synth Met 2001;119:81.

32. Freund MS, Karp C, Lewis NS. Inorg Chim Act 1995;240:447.

33. Lyons M. Adv Chem Phys 1996;94:297.

34. Chapman B, Buckley, Kemp RG, Kaiser NT, Beaglehole D, Trodahl HJ. Phys Rev B 1999;60:13479.

35. Stucky GD. Nature 2001;410:885.

36. Khedkar SP, Radhakrishnan S.Thin Sol Film 1997;303:167.

37. Fang Q, Chetwynd DG, Gardner JW. Sens Actuat A: Phys 2002;3271:1.

38. Hosono K, Matsubara I, Murayama N, Shin W, Izu N, Kanzaki S. Thin Sol Film 2003;441:72.

39. Richardson RT, Wise AK, Thompson BC, Flynn BO, Atkinson PJ, Fretwell NJ, Fallon JB, Wallace GG, Shepherd RK, Clark GM, O'Leary SJ. Biomater 2009;30:2614.

40. Lee JY, Bashur CA, Goldstein AS, Schmidt CE. Biomater 2009;30:4325.

41. Singh M, Kathuroju PK, Jampana N. Sens Actuat B: Chem 2009;143:430.

42. Korri-Youssoufi H, Desbenoit N, Ricoux R, Mahy JP, Lecomte S. Mater Sci Eng C 2008;28:855.

43. Ahuja T, Mir IA, Kumar D, Rajesh. Sens Actuat B 2008;134:140.

44. Chansai P, Sirivat A, Niamlang S, Chotpattananont D, Viravaidya-Pasuwat K. Int J Pharm 2009;381:25.

45. Ge D, Tian X, Qi R, Huang S, Mu J, Hong S, Ye S, Zhang X, Li D, Shi W. Electrochim Acta 2009; 55:271.

46. Abrantes LM, Correia JP. Electrochim Acta 1999;44:1901.

47. Kim KJ, Song HS, Kim JD. Bull Kore Chem Soc 1988;9:48.

48. MacDiarmid AG. Synth Met 1997;84:27.

49. Cosnier S. Biosens Bioelectron 1999;14:443.

50. Dupant-Filliard A, Roget A, Livache T, Billon M. Anal Chim Acta 2001;449:45.

51. Cassignol C, Olivier P, Ricard A. J Appl Polym Sci 1998;70:1567.

52. Cassignol C, Caveraro M, Boudet A, Ricard A. Polymer 1999;40:1139.

53. Barrau S, Demont P, Meraval C, Bernes A, Lacabanne C. Macromol Rapid Commun 2005;26:390.

54. Pomposo JA, Rodriguez J, Grande H. Synth Met 1999;104:107.

55. He C, Yang C, Li Y. Synth Met 2003;139:539.

56. Mir IA, Kumar D. J Adhes 2010;86:447.

CHAPTER 5

CARBON NANOTUBE FILLED CONDUCTIVE ADHESIVE

In this chapter, we have used carbon nano-tubes (CNTs) as conductive filler in the epoxy matrix for producing ICAs. It is observed in the previous chapters that the high filler loading required for obtaining desirable conductivity in ICAs can be a problem in achieving good impact properties. Due to high electrical conductivity of CNTs, conductivity was established at a very low filler loading. Also, because of their high strength to weight ratio, the impact properties of the formulated ICAs are very good. SEM results confirmed that CNTs are uniformly dispersed in the epoxy matrix. These nano-composites with very low filler loadings showed a great prospect of being used as ICAs.

5.1 Carbon Nanotubes

Carbon nanotubes have attracted an intense interest from the scientific community and can be regarded as the most exciting new materials to have been discovered in the past 30 years. It started with the publication of the research paper by Sumio Iijima in Nature in 1991 [1]. Iijima was using high resolution transmission electron microscopy (HRTEM) to examine carbon produced by the arc evaporation of graphite in an atmosphere of helium. About a year earlier, it had been shown that this method could be used to produce C_{60} and other fullerenes in high yield, so it seemed likely that other novel forms of carbon might be formed at the same time. It was while studying the hard deposit which formed on the graphite cathode following arc evaporation that Iijima made his discovery: the central part of the deposit contained large numbers of tiny tubules of graphitic carbon, consisting of concentric graphene cylinders, typically about 10 nm in diameter, with fullerene-like end-caps. Although tubes of carbon, produced catalytically, had been known for decades, the structures discovered by Iijima were far more perfect than any that had been seen before, and promised to have exceptional properties [2]. In subsequent work, two groups showed that single-walled nanotubes could be produced in a similar apparatus in which one or both electrodes contained cobalt, nickel, or some other metal [3,4]. These single-walled tubes generally have smaller diameters than the multiwalled nanotubes (typically of the order of 1–2 nm dia.). It was reported in 1996 that single walled nanotubes, like multiwalled nanotubes, can be produced catalytically [5].

Among all carbon products, carbon nanotubes have been of great interest, both from a fundamental point of view and for potential applications. Their mechanical and unique electronic properties open a broad range of applications including nanoelectronic devices, composites, chemical sensors, biosensors and many more. Carbon nanotubes can be classified as single-walled nanotubes (SWNTs) and multiwalled nanotubes (MWNTs). SWNTs consist of a cylindrical single sheet with a diameter between 1-3 nm and a length of several micrometers. They possess a cylindrical nanostructure formed by rolling up a single graphite sheet into a tube. MWNTs consist of a coaxial arrangement of concentric single nanotubes like rings of a tree trunk separated from one another by 0.34 nm. They usually have a diameter of about 2-20 nm. The production of SWNTs or MWNTs is highly dependent on the synthesis process and conditions [6]. However, the use of CNTs in practical applications has been restricted due to their poor processability since they are insoluble and infusible [7, 8]. In order to improve their processability, they have been combined with many polymers to form nano composite materials with improved properties. Carbon nanotubes possess high flexibility, low mass density, and large aspect ratio (typically ca. 300-1000) [9, 10]. CNTs have a unique combination of mechanical, electrical, and thermal properties that make nanotubes excellent candidates to substitute or complement the conventional nanofillers in the fabrication of multifunctional polymer nanocomposites. Generally, nanotubes are stronger than steel, lighter than aluminum, and more conductive than copper. Because of these extraordinary properties of isolated carbon nanotubes, great enthusiasm exists among researchers around the world as they explore the immense potential of these nanofillers [11]. The first report of a polymer nanocomposite using CNT as filler was given by Ajayen et al [12]. Since then, there have been many papers dedicated to processing and resulting mechanical and/or electrical properties of fabricated polymer nanocomposites. However, as-grown CNTs are normally mixtures of various diameters, and lengths, not to mention the presence of impurities and other defects. Furthermore, CNT aggregation has been found to dramatically hamper the mechanical properties of fabricated nanocomposites. Finally, due to their small size, CNTs are normally curled and twisted, and therefore individual CNTs embedded in a polymer only exhibit a fraction of their potential. Thus, the superb properties of CNTs cannot as yet be fully translated into high strength and stiffness finished products [13].

In view of above mentioned demerits of CNTs there have been numerous efforts for producing CNT nano-composites with improved properties. One of the most important pre-requisite is that the CNTs must be properly dispersed inside the polymer matrix so that the stress propagation is uniform and proper conductive channels are established. As is already established, aggregation of CNTs inside the polymer matrix leads to inferior properties. So far majority of processing methods use low filler content to achieve proper dispersion but such materials may not have the best mechanical properties while they may be used for electrical applications. Various processing techniques have already been tested and efforts are on to incorporate high volume ratios of CNTs. Another important area of research is the establishment of strong chemical affinity between CNTs and surrounding polymer matrix. Various methods of CNT chemical modification have been succesful in improving thermodynamic wetting of polymer matrix [14]. Whole polymer moeities may be attched or grafted into CNTs to improve their interaction with polymer matrix [15, 16]. Combining CNTs with organic conducting polymers (CPs) has also been tested where CP either functionalizes CNT or CNT dopes the CPs [17].

The preparation method of CNT/polymer nano-composites is crucial in deciding its overall properties. Various methods have been tested but solution blending, bulk mixing, melt blending, *in-situ* polymerization etc are mainly used. Solution blending is the most common method which invloves three steps, i.e., dispersing nanotubes in a solvent, mixing it with polymer and finally recovering the composite by precipitation or solution casting. Dispersion of nanotubes in solvents is achieved by high-power ultrasonication. Another approach uses surfactants like triton X100 to improve dispersion [18]. But this approach is limited for use in polymers which dissolve in common solvents. Milling is used intensely these days to produce bulk nano-composites. This method has been used to shorten the lengths of carbon nanostructures. Similarly, high energy ball milling was used to incorporate CNTs into polymer matrices [19]. In case of thermoplastic polymers, CNT composites can be made by melt mixing. This is particularly useful for polymers which are not easily soluble and hence cannot be used in solution mixing. This procedure involves mixing of CNTs under intense shear forces using various techniques like extrusion. However, increase in viscosity with higher filler loadings can be constraint in using this process. Polymerization of vinyl polymers in presence of CNT is a classical example of *in-situ* polymerization method. The main advantage of this method is that homogenity is better and higher weight percent of filler can be incorporated. Furthermore, *in-situ* polymerization methods enable covalent bonding between functionalized nanotubes and the polymer matrix using various condensation reactions.

CNT/epoxy nano-composites have been prepared by a number of research groups [20-22]. Infact, the earliest CNT nano-composite developed was based on epoxy matrix [12]. In their study, purified nano-tubes were embedded in epoxy to study the cross-sectional images of nanotubes. Since then more such composites have been reported mostly using *in-situ* polymerization. Martin et al dispersed MWNTs in an epoxy system based on bisphenol A and studied the influence of AC and DC electric fields on alignment of conductive networks [23]. Gojny et al tried to use calendaring for dispersing CNTs in a viscous epoxy matrix [24]. A depression in glass transition temperature of conducting composites obtained by blending CNTs with epoxy resins has been observed by Barrau et al near the percolation threshold [25]. From the studies of Zhou et al on CNT/epoxy composites, a linear damage model has been combined with the weibull distribution function to establish a constitutive equation for neat and nano-phased carbon/epoxy [26]. Similarly, Li et al used MWNT of various aspect ratios to develop conductive adhesives for aerospace applications [27]. Composites with very high conductivity have been developed through resin transfer moulding technique recently [28]. In view of the above reports, it is seen that no systematic studies were carried out on CNT filled ICAs, therefore, we present various properties of such ICAs in this chapter.

5.2. Experimental

5.2.1. Materials

Multi walled carbon nanotubes (CNT) used had a diameter of 40-70 nm and length of 100 µm. The ultrasonicator from Accumax India, Delhi, model USB-2.25 was used for dispersion of CNT in HHPA. All the materials used along with their suppliers are listed in **Table 5.1**.

Table 5.1. List of materials used with their source

Material	**Acronym**	**Source**
Epon 862	DGEBF	Hexion speciality chemicals, Inc. Houston, Texas, USA
Hexahydropthalic anhydride	HHPA	Sigma Aldrich chemicals Pvt. Ltd. Bangalore, India
2-ethyl-4-methylimidazole	2E4MZ	Sigma Aldrich chemicals Pvt. Ltd. Bangalore, India
Multiwalled carbon nanotubes	CNT	Cheap tubes Inc. Brattleboro, VT, USA

5.2.2 Preparation of carbon nanotube/epoxy composites

Pre-cure composites were formulated as per the following procedure

a) Curing agent (HHPA) which is solid at room temperature was heated slightly to melt it. Calculated amounts of CNTs were added to equal amounts of HHPA so that the final concentrations of CNTs in composite will be 0.1, 0.2, 0.3, 0.4 and 0.5%. The CNT concentration is described as weight percent. Each sample was sonicated in an ultrasonicator for 30 min at 40°C to obtain dispersion.

b) The dispersion was cooled down to room temperatureand thereafter an appropriate quantity of epoxy resin was added so that the epoxy/hardener was in a ratio of 1:0.85. A certain amount of 2E4MZ, i.e., 0.1 parts per hundred parts of epoxy resin was added and mixed thoroughly.

c) The mixture was stirred by a glass rod with heat, if necessary, until a homogenous mixture was formed. The mixture was left undisturbed for some time to remove air bubbles before further use.

These samples have been characterized by various techniques as reported earlier in chapter 2 under section 2.3.

5.3 Results & Discussion

5.3.1 Conductivity measurement

Epoxy matrix is highly insulating with conductivity of the order of 10^{-14} Scm^{-1}. When the conductive filler is incorporated, the insulating matrix is traversed by the conductive filler which forms clusters. When these clusters align themselves throughout the matrix, they form conductive channels due to contact between adjacent particles. Composites containing conductive filler in insulating polymers become electrically conductive when the filler content exceeds a critical value, known as a **percolation threshold**. The percolation threshold is characterized by a sharp jump in the conductivity by many orders of magnitude which is attributed to the formation of a three-dimensional conductive network of the fillers within the matrix. **Fig. 5.1** shows the electrical conductivity of the CNT/epoxy composites as a function of CNT concentration.

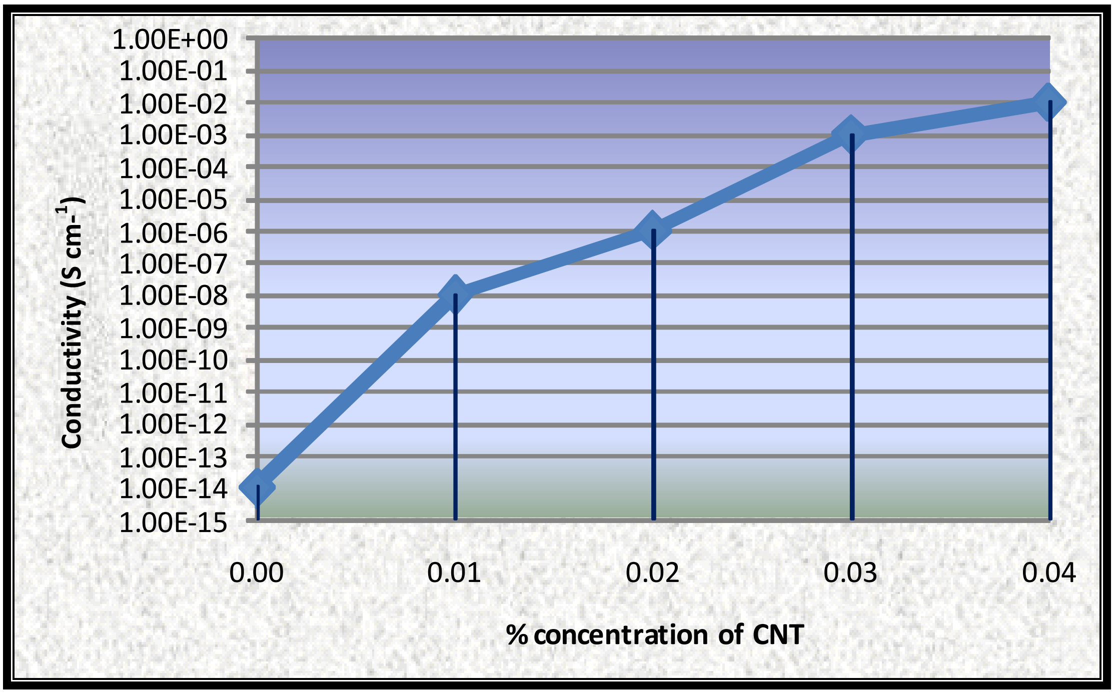


Figure 5.1. Electrical conductivity as a function of CNT concentration

There is a sharp increase in conductivity around 0.1% concentration which is due to high conductivity of CNT. The percolation threshold of these composites taken at 10^{-6} Scm^{-1} is around a very low filler concentration of 0.2%. This very low percolation threshold is due to high aspect ratio and nano-dimensions of CNTs. These findings were consistent with the previous reports of such CNT/epoxy composites [29-31]. After this value, conductivity showed a gradual increase till it almost became saturated at 10^{-2} Scm^{-1}. These results are highly significant compared to our studies with conducting polymer fillers, where high filler loadings were required to produce the same effect. The smooth propagation of conductivity indicates that the dispersion of CNTs inside the matrix is uniform and proper conductive channels have been formed. No serious effort was taken to align CNTs which might have increased the conductivity values.

5.3.2. Curing behaviour

DSC thermograms of neat epoxy and CNT/epoxy composites are shown in **Fig. 5.2.**

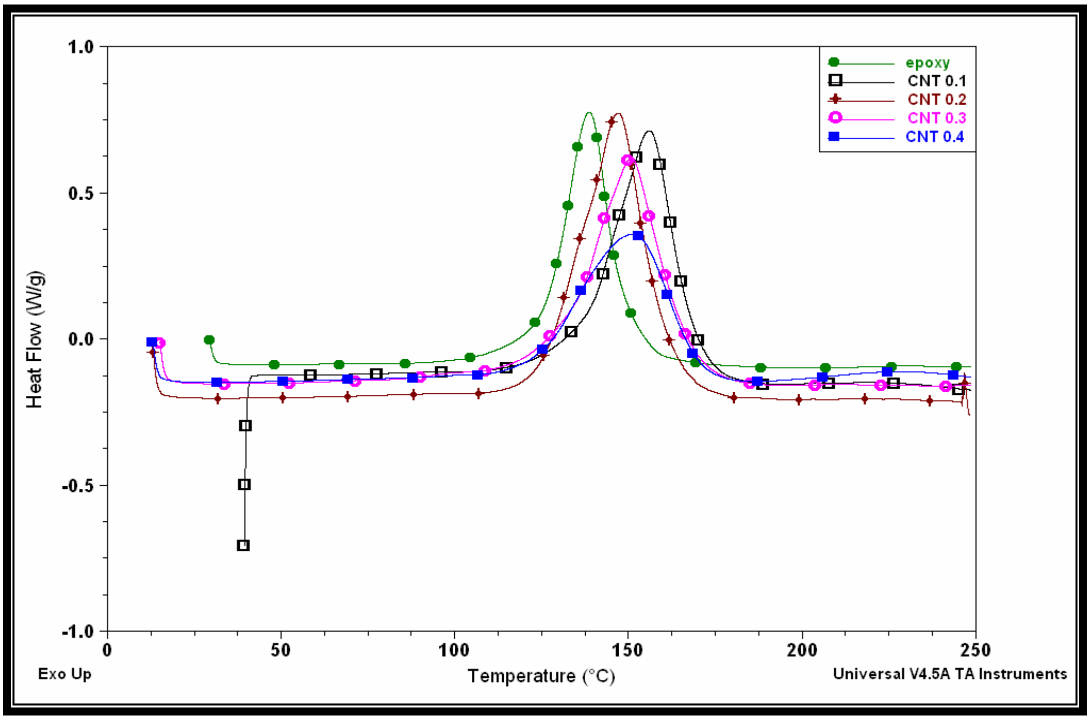


Figure 5.2. DSC thermograms of neat epoxy and CNT/epoxy composites

The exothermic peak of epoxy/anhydride system appears at 138°C, depicting the complete cross linking reaction of the epoxy system. A single curing peak is observed in all the samples, which depicts that the basic curing profile of epoxy remains unaffected by the presence of CNTs. With the increase in CNT content, the peak maximum slightly shifts towards higher temperature. This is due to an increase in uncured part in the matrix. However, as compared to our previous observations with conducting polymer fillers, peaks are sharp. The peak corresponding to the sample with 0.2% CNT concentration shows higher ΔH characteristics. It is worthwhile to note that percolation threshold of the composites is around this concentration. The reason may lie in depression in T_g which will be discussed in next section. The sample with 0.4% CNT concentration was viscous during mixing, which indicates that the cured part i.e., epoxy had decreased substantially. That is why it shows a broadening of cure peak and lesser ΔH values. All the results clearly show that due to smaller size and high aspect ratio of CNTs they provide least hindrance to cross-linking or formation of network in epoxy/anhydride systems. It is of great value for such composites as the mechanical properties of the matrix may be retained to maximum.

Glass transition values for the composites were determined by cooling the samples to room temperature and then heating the cured samples up to 250°C at the same rate. The T_g value of neat epoxy system was found to be around 115°C. The CNT-content dependence of the T_g is presented in **Fig. 5.3.** It can be observed that T_g values are affected in almost all samples, however, sample with 0.2% CNT concentration shows an unexpected behaviour. There is a sharp depression of T_g corresponding to this concentration. This behaviour was confirmed with repeated scans and seems to be independent of epoxy curing. The concentration is around percolation threshold and such behaviour has been observed by Barrau et al [25]. It is interpreted that conduction percolation is associated with a particular configuration of the conducting particles in the matrix. At the percolation threshold particles align themselves in definite infinite patterns, while before that they exist in finite size clusters. In the percolation range, the free volume accessible to the molecular motion of epoxy chain segments is maximal.

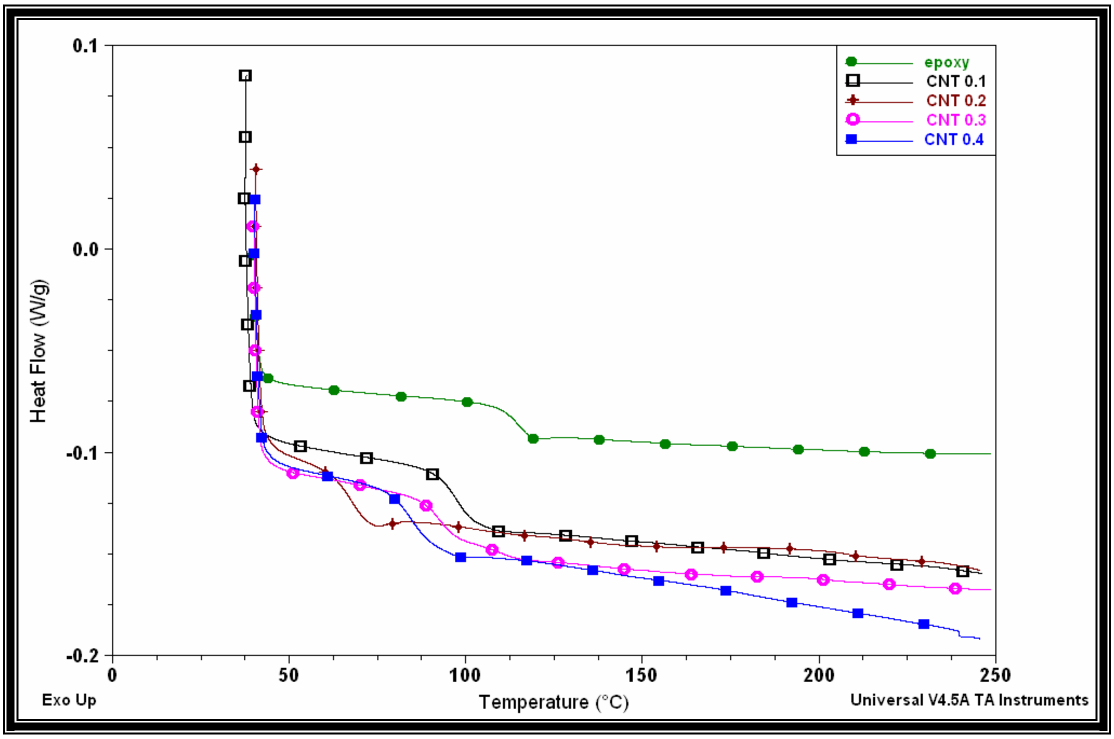


Figure 5.3. Variation of glass transition temperature Vs CNT conc.

5.3.3. Thermogravimetric analysis

The weight loss Vs temperature curve in **Fig. 5.4** shows that the overall degradation characteristics of epoxy system are retained. There is a characteristic two-step transition. TGA thermogram of neat epoxy shows a small weight loss before 150°C which may be due to loss of volatiles and then it undergoes a complete degradation around 600°C. It is observed that the concentrations from 0.1 to 0.3% show little variation in weight loss characteristics, while beyond that conc. weight loss increases around 150°C. An increase in weight loss may be due to the loss of volatiles or some moisture embedded. Hence, it can be concluded here from the results obtained that CNT incorporation does not have a significant effect on the thermal degradation of epoxy systems.

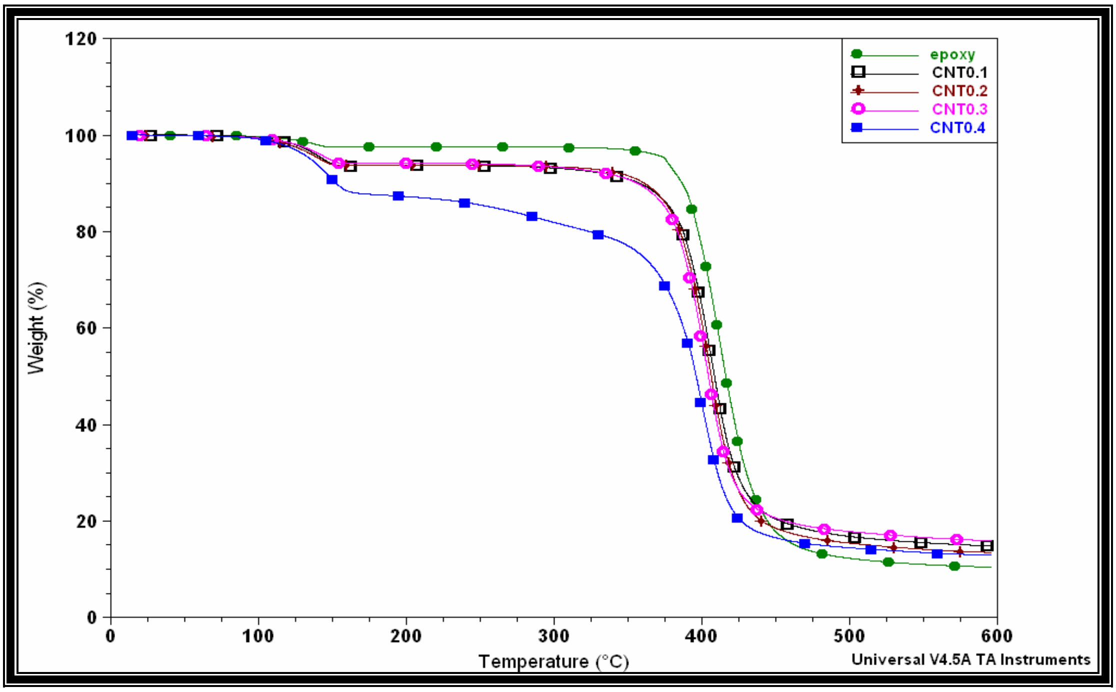


Figure 5.4. TGA thermograms of CNT/epoxy composites

5.3.4. Moisture absorption

Resistance to moisture present in the service environment is an important property of ICAs. Moisture may decrease their adhesive property or cause corrosion to metallic component joints. CNT/epoxy composite samples were subjected to 80°C/~100% RH aging and the effect was studied as weight gain over a period of time. The results obtained are plotted against time and presented in **Fig. 5.5.** It is observed that the samples are almost unaffected by the moisture as seen in the figure. There is a slight increase in weight till first 100 h and thereafter it is almost stable. The moisture absorbed may be bound to filler particles not completely adhered to epoxy network. It is evident from the results obtained that there is not even 1 % increase of weight in the samples. Thus, these composites are highly stable under environment aging. CNT due to their small size and lower loading levels are totally engulfed inside the matrix and hence do not bind water molecules. Although, as the CNT concentration increased to 0.4%, moisture absorption increased. But considering the overall effect, it is pretty clear that these ICA samples can withstand extreme conditions of heat and moisture.

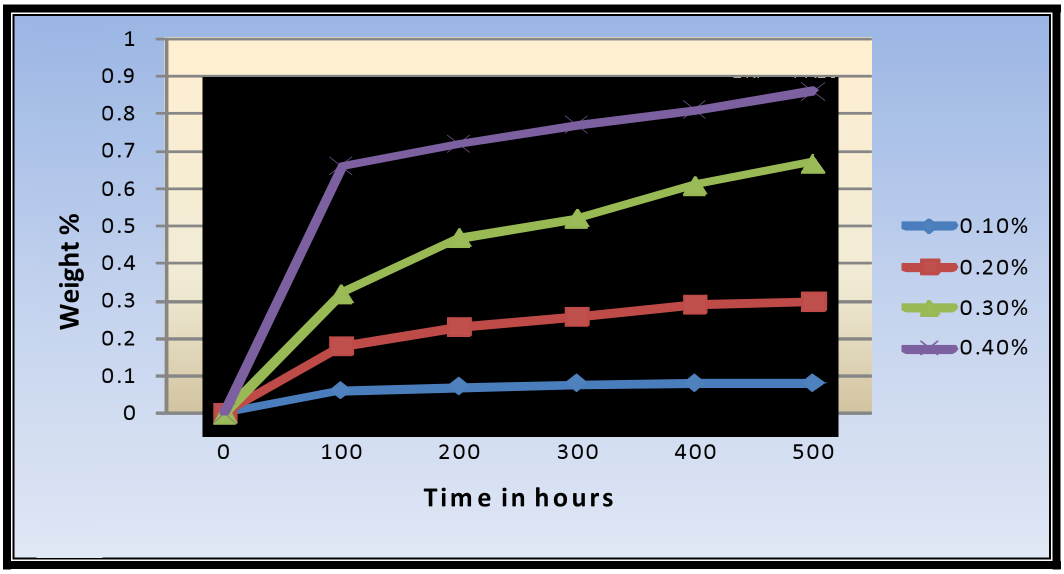


Figure 5.5. Moisture absorption behaviour with increasing CNT content

5.3.5 Drop test

The samples were studied for drop performance by recording the number of drops required to detach the chip from drop assembly and the results are shown in **Fig. 5.6**.

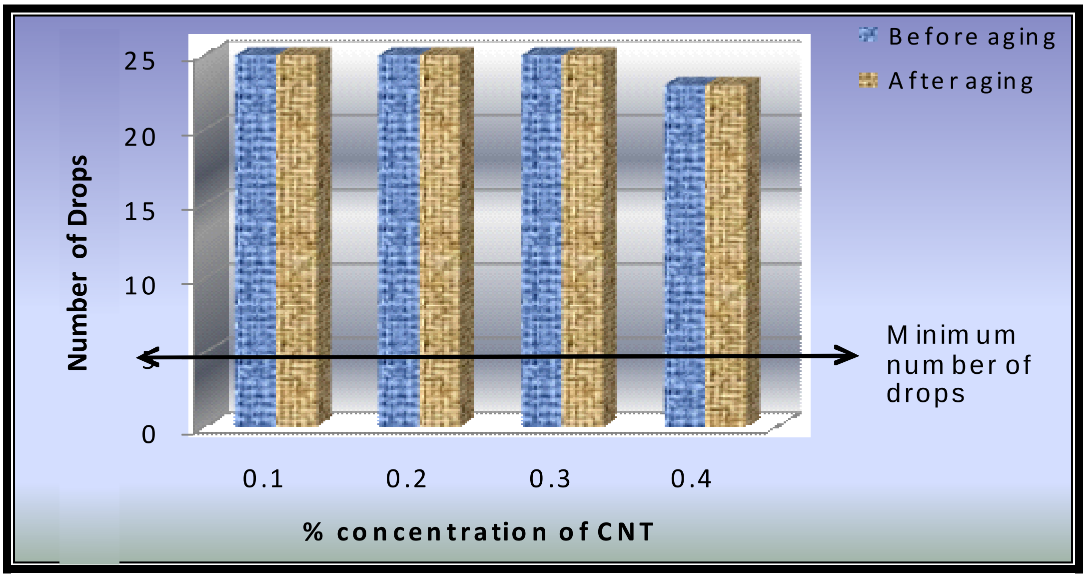


Figure 5.6. Drop test performance of ICAs

Due to good impact properties, the drop performance of all the samples was extraordinarily good. There was no visible effect even after 20 drops. The contacts formed had a smooth surface and no cracks have been found even under a simple microscope. However, assemblies joined by sample with 0.4% CNT show little weathering at the edges after 20 drops. These observations are a direct consequence of retention of maximum impact properties of strong epoxy matrix as evidenced by lap shear studies. The small size and uniform dimensions of CNTs had a very little effect on network formation of the epoxy matrix. When the drop assemblies were subjected to 80°C/~100% RH aging, drop test performance shows no significant change.

5.3.6 Lap shear strength

Lap shear strength is another critical parameter which defines the binding strength of ICAs. **Fig. 5.7** shows that the lap shear strength of ICAs of adhesives decreases with increase in CNT concentration.

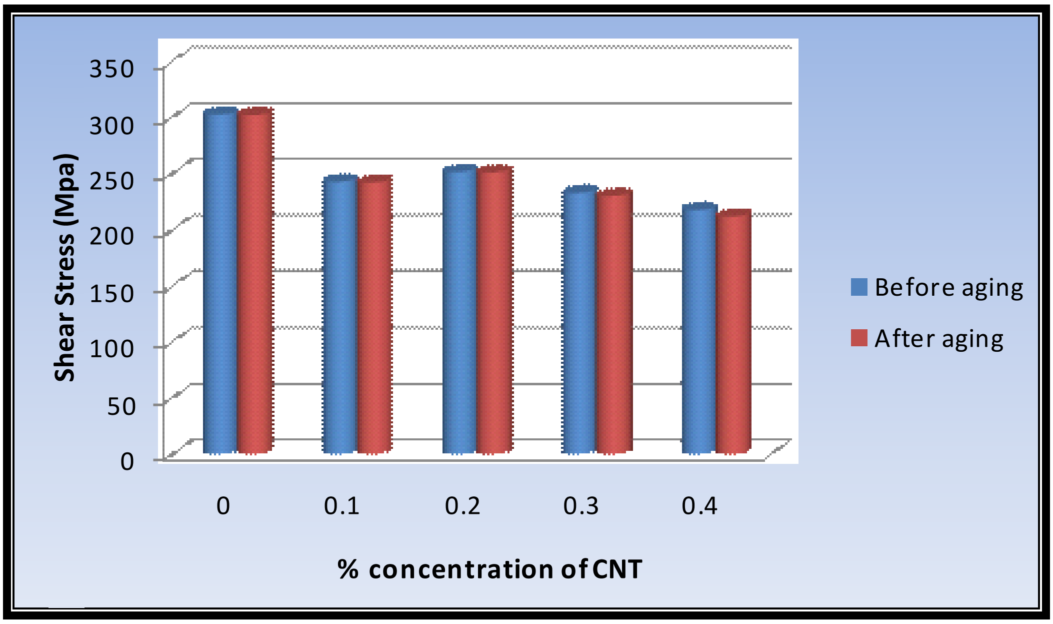


Figure 5.7. Lap shear strength of ICAs

This is the outcome of proliferation of filler phase into matrix network and decrease in transmission of mechanical energy from the matrix to the filler. But the decrease is very small and the shear strength is far greater than the desired impact strength for ICAs. The detached test coupons show that the fracture occurred at the interface of adhesive and metal surface of the test coupons rather than in the adhesive itself. It means that the observed values of lap shear are lesser than the actual impact strength of the adhesives. The etched copper surface does not undergo effective wetting hence the adhesion at that surface is poor. No cracking was observed in the adhesive material and toughness of the ICA was intact. After aging at 85°C/~100%RH until 500 h, samples show a small decrease in lap shear strength. These adhesives do not show a significant damping of adhesive strength under harsh environmental conditions. Although, epoxy matrix is not affected by moisture, filler particles loosely adhered to matrix network may absorb water and detach causing voids and crack propagation under impact. The effect of aging on lap shear also shows a slight increasing trend with increase in CNT concentration. Hence, proper dispersion of filler particles and high aspect ratio of CNTs has significantly improved the impact performance of ICAs.

5.3.7 Scanning electron microscopy

To understand the dispersion of CNTs within epoxy matrix the surface morphology was studied using SEM. **Fig. 5.8** shows the peel fractured surface morphology of the ICA with 0.4% CNT. The surface is rougher and CNTs are randomly distributed in the matrix. It is evident that the CNTs are well adhered to the surface, indicating that the interface was strong. Strong filler/matrix interface is another reason for good impact performance of these composites. No distinct agglomeration is evident, so the dispersion of CNTs in the curing agent HHPA is an efficient method of preventing re-agglomeration. All these observations clearly establish that CNTs are easily distributed within epoxy matrix and there is no distinct phase separation. This is the reason for good impact properties because the stress is easily propagated through filler moieties. Also, because of the smooth distribution conductivity is established at lower filler concentrations due to the formation of conductive channels which act as paths for charge propagation.

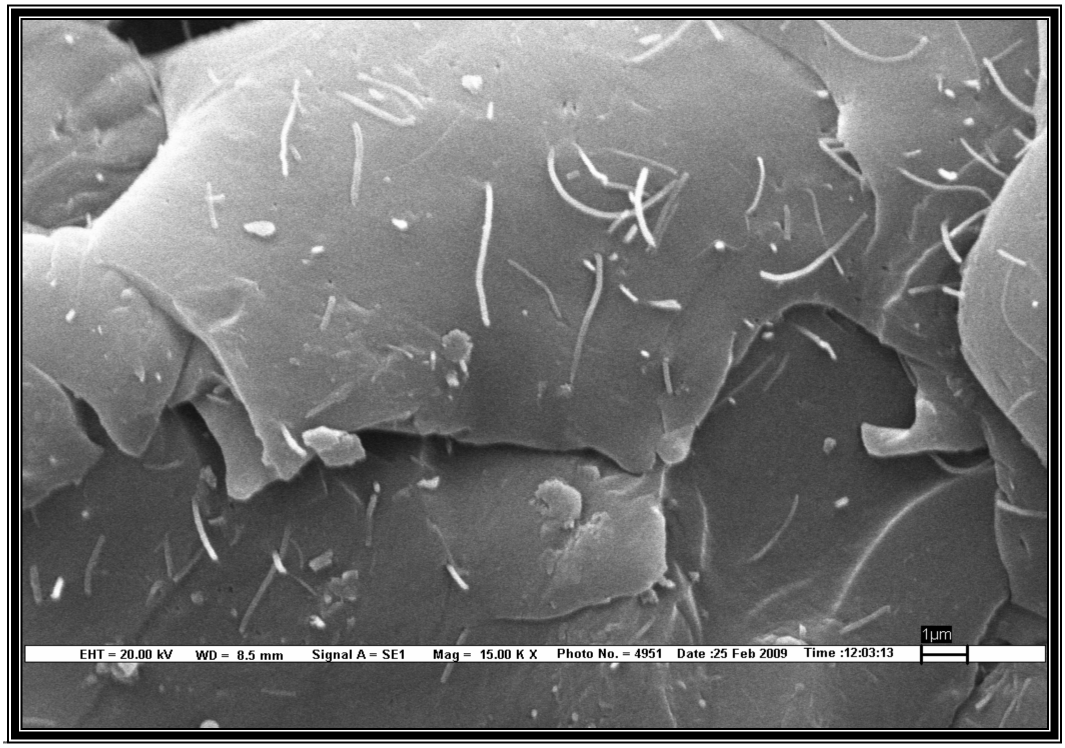


Figure 5.8 SEM micrograph of CNT/epoxy surface

5.4. Conclusion

Carbon nanotubes were used as filler in epoxy/anhydride systems and studied for their application as ICAs. From this study, it was observed that the small size and uniformity of dimensions plays an important role in defining the suitability of a material for being used as filler in ICAs. CNTs have high impact strength and good aspect ratio; hence a higher percentage of the epoxy shear strength is retained. Conductivity is established at a very low filler loading and conductivity value as high as 10^{-2} Scm^{-1} was obtained at a filler concentration of only 0.3%. The ICAs so formed not only show a good adhesion but also show least effect of aging. The surface characteristics show that there is a strong interface between matrix and filler phases, which defines the worth of an efficient composite system. Hence, it is concluded that incorporation of CNTs as filler inside the epoxy matrix produces ICAs with high electrical conductivity, great impact strength at very low filler loadings. The overall properties of these ICAs establish their use as ICAs for electronic interconnections. However, the properties may further be improved by devising some other methods like increasing the aspect ratio of CNTs which may increase the impact performance further.

5.5. References

1. Iijima S. Nature 1991; 354:56.
2. Harris PJF. Int Mater Rev 2004;49:31.
3. Iijima S, Ichihashi T. Nature 1993;363:603.
4. Bethune DS, Kiang CH, De Vries MS, Gorman G, Savoy R, Vasquez J, Beyers R. Nature 1993;363:605.
5. Dai H, Rinzler AG, Nikolaev P, Thess A, Colbert DT, Smalley RE. Chem Phys Lett 1996;260:471
6. Ahuja T, Rajesh. In: Chemical Sensors, Momemtum Press, LLC, New York, 2010
7. Dresselhaus MS, Dresselhaus G, Eklund P. In: Science of Fullerenes and Carbon Nanotubes, Academic Press, New York, 1996.
8. Hamon MA, Chen J, Hu H, Chen Y, Itkis ME, Rao AM, Eklund PC, Haddon RC. Adv Mater 1999;11:834.
9. Cooper CA, Young RJ, Halsall M. Composites, Part A 2001;32A:401.
10. Gao G, Cagin T, Goddard WA. Nanotechnology 1998;9:184.
11. Moniruzzaman M, Winey KI. Macromolecules 2006;39:5194.
12. Ajayan PM, Stephan O, Colliex C, Trauth D. Science 1994;265:1212.
13. Spitalsky Z, Tasis D, Papagelis K, Galiotis C. Prog Polym Sci 2010;35:357.
14. Tasis D, Tagmatarchis N, Bianco A, Prato M. Chem Rev 2006;106:1105.
15. Wang C, Guo Z-X, Fu S, Wu W, Zhu D. Prog Polym Sci 2004;29:1079.
16. Liu P. Eur Polym J 2005;41:2693.
17. Baibarac M, Gómez-Romero P. J Nanosci Nanotech 2006;6:1.
18. Kim YK, Shin TS, Choi HD, Kwon JH, Chung YC, Yoon HG. Carbon 2005;43:23.

19. Ghose S, Watson KA, Sun KJ, Criss JM, Siochi EJ, Connell JW. Compos Sci Technol 2006;66:1995.
20. Allaoui A, Bai S, Cheng HM, Bai JB. Compos Sci Technol 2002;62:1993.
21. Xu X, Thwe MM, Shearwood C, Liao K. Appl Phys Lett 2002;81:2833.
22. Puglia D, Valentini L, Kenny JM. J Appl Polym Sci 2003;88:452.
23. Martin CA, Sandler J, Windle AH, Schwarz M, Bauhofer W, Schulte K. Polymer 2005;46:877.
24. Gojny FH, Wichmann M, Kopke U, Fiedler B, Schulte K. Compos Sci Technol 2004;64:2363.
25. Barrau S, Demont P, Maraval C, Bernes A, Lacabanne C. Macromol Rapid Commun 2005;26:390.
26. Zhou Y, Pervin F, Lewis L, Jeelani S. Mater Sci Engineer A 2008;475:157.
27. Li J, Lumpp JK. In: Proceedings. Aerospace conference. Big sky, Montana, USA: IEEE, 2007; p. 1-6.
28. Cheng QF, Wang JP, Wen JJ, Liu CH, Jiang KL, Li QQ, Fan SS. Carbon 2010;48:260.
29. Sandler JKW, Kirk JE, Kinloch IA, Shaffer MSP, Windle AH. Ultra low electrical percolation threshold in carbon-nanotube-epoxy composites. Polymer 2003;44:5893.
30. Martina CA, Sandler JKW, Windle AH, Schwarz MK, Bauhofer W, Schulte K. Polymer 2005;46:877.
31. Moisala A, Li Q, Kinloch IA, Windle AH. Comp Sci Tech 2006;66:1285.

FINDINGS FROM THE PRESENT RESEARCH WORK

The primary focus of our research work was to develop ICAs with improved properties by replacing the metallic fillers with intrinsically conducting polymers and carbon nanotubes. It was aimed that the limitations associated with metallic fillers mainly corrosion and limited impact resistance can significantly be substantiated by using non-metallic fillers. The nature and dispersion of conductive fillers is of prime importance in deciding the final properties associated with such ICAs.

1. Due to its ease of synthesis and processing, polyaniline was selected as the first filler. PANI powder was synthesized by conventional method like chemical polymerization. Composite samples with different concentrations of PANI in epoxy/anhydride matrix show properties characteristic of an ICA. Thermal properties of the cured ICAs show that the basic curing profile of epoxy remains unaffected. There is a single curing peak in every case although the sharpness of the peak decreases and curing temperature increases slightly with increase in PANI conc. It was also observed from thermal studies that on adding PANI to resin, the T_g of the samples decreases which indicates that the presence of PANI affected the cross-linking of epoxy matrix. The TGA thermograms were very close to that of neat epoxy system. The impact properties although affected by the PANI concentration are substantially good for ICAs. **The sample with 25% PANI showed a sharp deterioration in impact properties.** The lap shear test could not be conducted for the sample with PANI conc. of 25% as the test coupon broke prior to application of force in a UTM. Similarly, drop test assembly joined by this sample showed cracks at the ends even after 5th drop and got detached after 8th drop. Electrical conductivity showed an increasing trend with the increase of PANI concentration. Although, a conductivity of 10^{-3}

Scm^{-1} was obtained at 25% PANI filler concentration but this ICA shows poor impact properties. Moisture absorption of samples increased with the increase of PANI concentration but the overall effect was too little. It seems that the moisture absorption is a characteristic of filler phase. SEM images show that PANI powder was not uniformly dispersed in the epoxy matrix due to agglomeration and large particle size. Thus, it is possible to produce isotropically conducting adhesives with improved impact properties by reinforcing PANI in an epoxy matrix. Low conductivity can be a constraint which needs to be improved. In order to get better impact properties and conductivity, PANI particles need to be finely dispersed in the matrix.

2. It is an established fact that the size and geometry of filler have a great influence on the overall characteristic of the composites. In view of this nano-fibres of PANI were introduced as filler into epoxy/anhydride matrix to produce isotropically conductive adhesives. **PANI nano-fibres were synthesized by interfacial polymerization technique.** Nanofibres developed by this technique show smooth dispersion in the matrix. **The uniformity and smaller size of PANI nano-fibres significantly improved the overall properties of the ICAs when compared to ICAs filled with PANI of macroscopic dimensions.** Conductivity is established at low filler loading due to the uniform diffusion and formation of conducting channels within epoxy matrix in this case. Although, the maximum conductivity obtained in case of PANI powder and nanofibres remains same, but the percolation threshold is established at a lower concentration in case of PANI nanofibres. Decreasing the percolation threshold is very important for conductive composites not only because it reduces the cost but also because it minimises the influence of filler on the mechanical and

thermal properties. Smaller size and high aspect ratio of nano-fibres facilitates their proper distribution and thus there is minimum hindrance to epoxy network formation. This in turn results in an improvement of impact and drop test performance of these ICAs. Drop test performance of ICAs with PANI nanofibres as filler is far better as compared to ICAs with PANI powder as filler. ICA with 25% PANI powder had failed the drop test and the assembly showed wearing at the ends even in the 5th drop. But ICA containing same concentration of PANI nano-fibres has a smooth surface, shows relatively good impact strength, and is stable far beyond the minimum requirement. **The uniformity in size and nano dimensions of these fibres enables them to effectively penetrate the matrix network and hence the damping property, i.e., the capacity to dissipate energy, increases.** The ICA with PANI powder concentration of 25% is unable to bond the two lap shear test coupons properly and broke even before application of force during test; while nano PANI filled ICA of same concentration had a smooth surface after curing and good impact properties. Such an improvisation of impact properties gives a very significant advantage to these ICAs for realising their application potential. Curing profile of the ICAs does not show any appreciable change due to nano dimensions of filler. Although, curing peaks were sharper than PANI powder filler composites. TGA thermograms show a characteristic two step weight loss of epoxy system, however in case of PANI nanofibre filled ICAs there is more weight loss around 150°C, probably due to presence of more volatiles. SEM observations confirmed that the diffusion of nanofibres inside the matrix polymer was very smooth and there is no agglomerate formation. It is concluded that incorporation of PANI nano-fibres as filler in epoxy/anhydride matrix improved the prospect of these composites for being used as ICAs.

3. Polypyrrole was synthesized by suspension polymerization using DBSA as dopant in the present work. The PPy obtained by suspension polymerization has fine particles and hence shows better dispersion in the epoxy matrix. The composites with varying PPy concentrations were studied for various properties of ICAs. Conductivity shows a smooth increasing trend and reaches a value of 10^{-3} Scm^{-1} with a PPy concentration as low as 15%. No further increase of conductivity was observed on increasing the concentration of PPy. The thermal properties and curing profile of the composites are very close to that of neat epoxy system. However, a depression in T_g was observed close to percolation threshold due to increased mobility of polymeric chains around that concentration. The depression in T_g around percolation threshold is interpreted as increase in the mobility of epoxy matrix chain segments. Since, PPy powder was smooth and particle size was small, the impact performance of epoxy is not affected significantly. It is observed that the sample assemblies bound by ICAs containing 5 and 10% were stable even after 25 drops and the trend was not changed by aging the samples in 80^oC/~100%RH for 500 h. However, it is significant to note that after a sharp decrease in lap shear at 5% PPy concentration, there is a slight change only in lap shear thereafter. It is indicative of the fact that since the particle size of PPy is uniform and small, there is an even diffusion of particles within the epoxy network without formation of agglomerates. In most of the composites, there was almost no effect of aging on lap shear properties. When the PPy concentration was increased beyond 15%, the lap shear strength decreased. Moisture shows a negligible effect on the overall properties of ICAs studied. Thus, incorporation of PPy in epoxy matrix forms composites which may be used as ICAs in electronic interconnections.

The composite with 15% PPy showed the best properties and can be most suited for the application.

4. In addition to CPs, CNTs show a bright prospect of being used as fillers. Replacing metallic fillers in ICAs with CNTs have the potential benefits of being lead free, corrosion resistant, high mechanical strength and electrical conductivity etc. So, new ICAs are being formulated by dispersing CNTs as filler in epoxy/anhydride matrix. Composites were made by dispersing different loadings of CNTs in epoxy hardener and then mixing it with epoxy resin. Conductivity of these composites was extremely good at a very low filler concentration. Conductivity values of 10^{-2} Scm^{-1} were observed at a filler concentration as low as 0.3%. This is attributed to good electrical conductivity of CNTs as well as high aspect ratio which allows them to form definite patterns and continuous conductive channels even a low concentration. Curing profiles of the ICAs show that CNTs had a very little effect on cure pattern of epoxy matrix. TGA results show a characteristic two step transition and least effect of filler. Drop test performance of samples show that CNTs are effective in stress propagation and hence energy dissipation occurs effectively. Thus, there is a very negligible effect on the drop characteristics with increase in filler concentrations. A similar trend is reported for lap shear test. Concentrations above 0.4% filler loading showed decrease in lap shear strength. These observations lead to the fact that optimum filler loading is achieved at around 0.4% CNT loading. Composite with 0.5% CNT concentration was difficult to mix and had high viscosity before curing. CNTs are very well dispersed inside the matrix as is evident from SEM images. CNTs align themselves in the tough epoxy matrix which is the reason for good impact and conducting properties.

Environmental aging characteristics of the samples showed that although a slight weight gain was observed but the overall effect of moisture was found negligible. Drop test and lap shear characteristics also show a small impact of aging. All these points indicate that the incorporation of CNTs inside the epoxy matrix produces ICAs with extremely good properties.

The main achievement of this research work lies in the fact that new filler materials for ICAs have been identified. The filler loadings in all the ICAs were lesser as compared to metal filled ICAs. Compatibility increased as evidenced by the improved impact properties. The main advantage of using organic conducting polymer fillers or CNTs is that the corrosion related to metallic filler is neglected. Further, it is established that the morphology and dimensions of filler particles have a strong effect on the overall properties of ICAs. High aspect ratio of nanofibres resulted in increase in impact properties and high conductivity at lower filler loadings. Hence, it is concluded that there is a great prospect of using conducting polymer and CNTs as fillers in ICAs. Small dimensions and uniform dispersion of filler particles makes them more suitable for finer pitch applications.

FUTURE WORK

The ICAs studied in this research work are actually a new beginning in this area. So, a lot of research work can be initiated on this theme. New matrices can be identified which can withhold impact properties at much higher filler concentrations, so that the limitations with conductivity can be eliminated. Also, matrix polymers which require low or no temperature for curing can be an added advantage. This will ease the processing and save time. Most of the adhesive matrices are thermosets and hence are not easily reworkable. Hence, new matrices may be studied which can be used to make re-flowable ICAs. It will not only ease the handling but will help in detaching the components during disposal.

There is a prospect of studying more conducting materials as fillers in ICAs. More conducting polymers or their derivatives can be studied for their application as fillers. This study has identified that morphology of fillers plays an essential role in overall properties of ICAs, so CPs with different sizes and morphology may be studied for improving the properties of ICAs. Similarly, CNTs with functionalizations may show varying effect on adhesive properties of the matrix, the identification of proper interactions will be an important study.

LIST OF PUBLICATIONS

1. **“Development of Polyaniline/Epoxy composite as a prospective solder replacement material”** IRFAN AHMAD MIR and D.Kumar. *International Journal of Polymeric Materials,* (Taylor & Francis, USA) 59(2010), 994-1007.

2. **“Development of Polypyrrole/Epoxy Composites as Isotropically Conductive Adhesives”** IRFAN AHMAD MIR**,** D. Kumar. *The Journal of Adhesion,* (Taylor & Francis, USA) 86 (2010), 447-462.

3. **“Nanocomposites of Polyaniline as conductive adhesives”** IRFAN AHMAD MIR, D. Kumar, *Journal of Adhesion Sceince & Technology,* (Sage publications, UK) accepted.

4. **“Potentiometric urea biosensor based on BSA embedded surface modified polypyrrole film”** Tarushee Ahuja, IRFAN AHMAD MIR, Devendra Kumar, Rajesh. *Sensors and Actuators B,* (Elsevier USA) 134 (2008) 140–145.

5. **“Recent advances in Isotropic Conductive Adhesives for electronics packaging applications”** IRFAN MIR and D.Kumar. *International Journal of Adhesion & Adhesives,* (Elsevier USA) 28 (2008) 362–371.

6. “**Recent Advances in the Field of Biomolecule Immobilization on Conducting Polymers for Biosensing Applications**” Tarushee ahuja, IRFAN MIR, D. Kumar, Rajesh. *Biomaterials* (Elsevier USA) 28 (2007) 791–805.

7. “**Advances in Sensors based on Conducting Polymers**” Neetika gupta, Shalini sharma, IRFAN MIR, D. Kumar. *Journal of Scientific & Industrial Research.* (CSIR, India) 65, July 2006, 549-557.

8. **“Development of carbon nanotube filled conductive adhesive for electronic interconnections”** IRFAN AHMAD MIR, D. Kumar, under review.

9. **“Carrier injection from polypyrrole coated gold electrode in pentacene field effect transistors”** IRFAN AHMAD MIR, Tarushee Ahuja, Devendra Kumar, Dai Taguchi, Takaaki Manaka, Mitsumasa Iwamoto. *Synthetic Metals (Elsevier USA)* 160 (2010) 2116-2120.