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2.0 INTRODUCTION OF ADHESIVE BONDING

Riveting, bolting, welding and soldering techniques are used for joining metals. There are matured technologies for joining such materials. In contrast to the metallic materials, adhesive bonded composite materials are often used to fabricate structural components. Though mechanical fastening is also being used for composite materials to some extent, adhesive bonding is given more preference over mechanical fastening because of some advantages [1]. Adhesive bonding provides uniform distribution of stress over the entire bond line while mechanical fastening creates large stress concentration around the drilled holes. Also, adhesive bonding technique provides more design flexibility compared to the mechanical fastening [2]. Adhesive Bonding is a technique used for joining materials, which in recent years has shown itself capable of replacing conventional methods of joining such as riveting, welding etc. and mechanical fastening in a variety of applications. The strength and durability of bonded structures in aircraft construction has been demonstrated over many years, but the extension of this experience to other structural applications has been comparatively restricted [3]. Polymer based adhesives are widely used throughout most spacecraft. The rapid increase in application of adhesives in space industry has been due to the development of synthetic resins, which do not have the limitations of natural products and which can bond both metals and other nonporous materials. Adhesive bonding is now of considerable importance and has been extensively used in aerospace structure for joining different materials [4].
2.0.1 MECHANISM OF LIQUID–SOLID ADHESION

The adhesion mechanism between liquid adhesive and the solid substrate has been explained on the basis of mechanical interlocking, adsorption, diffusion and electrostatic theory.

The theory of mechanical interlocking proposes that any substrate possesses inherent surface roughness which gives rise to mechanical interlocking of adhesive with the solid substrate [5]. However, the attainment of good adhesion between rough surfaces may not be due to only interlocking. The enhanced adhesion of adhesive to solid substrate may result also from other factors especially the increasing surface area of the substrate [6]. It has been reported that surface roughness is considered to be a factor in the context of wetting and it is a limiting factor in the case of adhesion as beyond the surface roughness of 1 micron, there is a decrease in adhesion [7].

The diffusion theory of adhesion states that the adhesion of polymer-adhesive is due to mutual diffusion of polymer molecules across the interface [8]. This requires that the macromolecules of polymers possess almost similar values of solubility parameter, \( \delta \), and is defined by:

\[
\delta = \sqrt{\frac{\Delta H_v - RT}{V}} \quad \text{...(2.1)}
\]

where \( \Delta H_v \) is molar heat of vaporization, \( R \) is gas constant, \( T \) is temperature and \( V \) is molar volume. However, in the case of dissimilar materials, where the solubility parameters are different, the inter-diffusion is not an appreciable mechanism as stated by various authors [9].

The electrostatic theory suggests that when adhesive and substrate are in intimate contact there is marked charge separation resulting in formation of electrical double layer [10]. The
interface of adhesive-substrate essentially acts as a capacitor, which is charged due to the contact of two different materials and consequently adhesion is presumed due to the existence of these attractive forces across the electrical double layer. However, the majority of the measured work of adhesion is dissipated through viscous and visco-elastic responses of the materials and this energy has not been equated with the stored electrical energy [11].

The adsorption theory states that, when intimate intermolecular contact is achieved at the interface of adhesive to polymer or metal, the adhesive adheres to them because of attractive surface forces acting between the atoms of the two surfaces [12]. These attractive forces exist due to physical adsorption and are usually defined as secondary or vander walls forces. These forces originate from molecules having permanent dipoles; dipoles induced dipoles in neighboring molecules and London dispersion forces, present in the molecules [13]. In the presence of polar groups on the polymer surface, these forces are considered to be the minor attractive force as polar groups bridge the forces of physical adsorption and the forces of chemisorption where primary covalent bond is responsible for adhesion. Thus, when the polymers are modified under various surface treatments, formation of various polar groups onto the polymer surfaces result in formation of covalent bond with adhesive. This covalent bond plays significantly to produce adhesive bonds with the polymer stronger than the cohesive strength of the polymeric materials [14].

2.0.2 ADHESION IN POLYMER-METAL JOINTS

The first step in adhesion by adhesive in a polymer/metal joint is establishment of liquid to solid molecular level contact. The adhesive is then cured and hardened. The hardened adhesive is capable of transmitting stresses from one adherend to the other and consequently intrinsic forces across the interfaces prevent them from separating under an applied load [15].
Wetting is quantitatively defined by reference to a liquid drop resting in equilibrium on a solid surface. For a liquid droplet on a solid surface in the presence of saturated vapor, the relationship between contact angle and the surface energies is given by Young’s equation \[16\]

\[ \gamma_{SV} = \gamma_{LV} \cos \theta + \gamma_{SL} \ldots (2.2) \]

Where \( \gamma_{SV} \) represents the solid-vapor, \( \gamma_{LV} \), the liquid-vapor and \( \gamma_{SL} \), the solid-liquid surface energies; When \( \theta > 90^\circ \) the droplet of liquid adhesive on the substrate does not spread spontaneously. Spontaneous spreading of adhesive droplet may be observed when,

\[ \gamma_{SV} \geq \gamma_{LV} + \gamma_{SL} \ldots (2.3) \]

It is also possible for liquid adhesive to spread and wet a solid surface even when \( \theta > 0^\circ \) but this requires the application of force to the liquid adhesive to spread it forcibly over the solid surface.

\textbf{2.0.3 POLYMER-METAL JOINTS AND ENGINEERING APPLICATIONS}

Modern fuel-efficient vehicles require lightweight material such as polymer. Thus assembly polymers are commonly used in secondary structure due to their high strength to weight ratio and low cost. Often they are joined with primary metal (steel/aluminum/titanium) structures \[17-19\]. However, joining of polymer to metal has been proved to be challenging as their joining is found to be difficult by welding or by ultrasonic bonding because of differences in thermal behavior and amplitude of vibration of these two materials \[20\]. Thus, it necessitates the use of adhesive bonding due to the advantages of possibilities of joining largely dissimilar materials; suitability of joining different thicknesses and irregular shapes; ability to perform bonding in one operation; high flexibility in manufacturing system; capability of load distribution over a large area and cost effective joining processes. Apart from lightweight the
joining of polymers to metals in an assembly is having several other merits, such as corrosion protection, good finishing, less vibration, good electrical and thermal insulation and design flexibility [21].

Epoxy resin adhesive is generally referred to be most effective for joining of these materials, as it is reactive with a number of curing agents, easy to spread over the surface of the substrates due to its low viscosity in comparison to other adhesives and also having low shrinkage [22].

2.0.4 REQUIREMENT OF ADHESIVE BONDING IN SPACE AND AVIATION

Adhesive used in spacecraft structures must meet a number of requirements like mechanical property retention over a wide temperature range, minimal strength degradation in orbital environment and negligible out gassing of volatiles [23]. The widespread use of adhesive bonding in aerospace structures can be attributed to its inherent advantages, such as, the fact that an adhesive joint can distribute the applied load over the entire bonded area and with a more uniform distribution of stress, it requires little or no damage to the adherends, adds very little weight to the structure, has a superior fatigue resistance to other joining methods, is suitable for joining dissimilar materials as well as cost effective [24]. Although adhesives offer a number of advantages, they also suffer from a number of limitations. These can include the requirement for careful surface preparations of the adherends, the joint must be designed to eliminate peel and cleavage stresses, some adhesives have a limited high temperature resistance, they are affected by service environments and are difficult to disassemble for inspection and repair [25].
2.0.5 EPOXY RESIN- A STRUCTURAL ADHESIVE USED IN SPACE AND AVIATION

Industrial bonding of load-bearing structures demands adhesives formulated from high strength, high modulus polymers. This need has been met to a large extent by the epoxies; notable those based on bisphenol A diglycidyl ether (DGEBA).

![Figure 2.1 Synthesis of Epoxy Resin](image)

Epoxy resins have excellent adhesion, mechanical and electrical properties which are widely utilized in the fields of adhesives, castings, solvent-less and high solid systems of coating, powder coating etc. The outstanding performance characteristics of epoxy resins are imparted by the bisphenol A moiety (toughness, rigidity and elevated temperature performance), The ether linkages (chemical resistance) and the hydroxyl and epoxy groups (adhesive properties and formulation latitude) are the salient features of epoxy adhesives. Synthesis of epoxy resin is shown in Figure 2.1

Epoxy adhesives, whilst not ideal, are currently the best generic adhesive types [26]. The epoxy adhesive family includes a wide variety of products with quite different properties, and suitable formulations need to be identified for each application. They do not require high
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pressure during their application and curing and are reasonably tolerant with regard to glue line thickness variations. They also exhibit strong adhesion to several materials, little or no shrinkage during cure and extremely good dimensional stability after hardening, excellent mechanical resistance and high resistance to heat [27]. The most widely used class of adhesives is the two-part epoxies, in which two liquid components are mixed, and then set (cure) to a hard, tough, solid. The epoxies can also easily be modified by the addition of fillers, and can provide adhesives with low-coefficients of thermal expansion, excellent adhesion to metals and other plastics, high temperature resistance (to 300 °C) and cryogenic stability. Several adhesives are commercially available for spacecraft applications; however space application requires low outgassing, bond durability and wide temperature range [28].

2.0.6 NOVOLAC RESIN- A STRUCTURAL ADHESIVE USED IN SPACE AND AVIATION

Phenolic (Phenol-Formaldehyde resin has a very broad application and a large output in the manufacturing of glass fiber reinforced plastic (such as molded products), adhesives and coatings [29]. These compounds have excellent thermal and flame retardance properties. Due to these properties, the phenolic resin is used in the aerospace industry (spacecraft, rockets, missiles, etc.) as structural composites. It is easy to produce at low cost [30]. The cured phenolic resin has excellent rigidity, dimensional stability and fire retardancy, however, traditional phenolic resin always suffers from inherent brittleness, high shaping pressure, and dark in color due to easy oxidation of phenolic groups [31]. To improve properties of traditional phenolic resin, many researchers tried various methods, mainly by blending them with elastomers, thermoplastic polymers, nano-fillers and fibers [32].
Although two types of phenolic resins exist (resol and novolac), structural adhesives usually contain the alkylated (methylated or butylated methylol group) resol variety. Such resins are compatible with epoxy and other polymeric materials used in formulating structural adhesives [33]. The resol phenolics possess exceptional wetting and spreading ability on metal and metal oxide surfaces due to the high concentration of strongly adsorbed phenolic and aliphatic hydroxyl groups present. They are extremely brittle and suffer high shrinkage during curing, the properties which however, prohibit their separate use as structural adhesives [34]. Various fillers and modifying resins are necessary to reduce the shrinkage and to provide stress relief. The main modifying resins most frequently co-reacted with resol phenolics are linear, high molecular weight polymers with recurring hydroxyl groups along the polymer backbone. Reaction proceeds between these hydroxyl groups and the phenolic methylol group [35].

Novolac resin is acid-catalyzed phenol-formaldehyde thermosetting resin. Formaldehyde and phenol are reacted to promote electrophilic addition of formaldehyde to the ortho and para substitutions of phenol ring. High-ortho novolac and Random novolac are two types of novolac which are available in market. The ortho/para ratios are different in them. The random novolac is used as a standard novolac which is cured with hexamethylenetetramine (HMTA) and high-ortho novolac is used for acceleration of curing in the presence of HMTA, because the phenol ring carbon of the para site has an advantage in reaction with HMTA, giving rise to formation of cross-links at a high rate [36]. The synthesis of novolac resin is shown in Figure 2.2.
2.0.7 EPOXY-NOVOLAC ADHESIVE- A STRUCTURAL ADHESIVE USED IN SPACE AND AVIATION

Epoxy-phenolic adhesives also known as epoxy-novolac adhesives are made by blending epoxy resins with phenolic resins to improve the high temperature capabilities of the standard epoxy resins. The epoxy novolac resins are synthesized by reaction of phenolic novolacs with epichlorohydrin in the same fashion as the bisphenol A resins. Phenolics are compatible with epoxy resins and will react through the phenolic hydroxyl group \[37\]. The amount of phenolic resin used is generally much greater than that required to cross-link with the epoxy, so one can debate whether, the epoxy toughens the phenolic adhesive or the phenolic increases the heat resistance of the epoxy. Epoxy novolacs generally produce a product with better-elevated temperature performance, chemical resistance and adhesion than those of the bisphenol A based resins \[38\]. Thus, epoxy novolacs are used in aerospace application as a structural adhesive system that required high temperature performance. These adhesives are good for continuous
high temperature service in the 175 °C range or for intermittent service as high as 260 °C. Shear strength of up to 3000 psi at room temperature and 1000-2000 psi at 260 °C are possible [39]. Resistance to weathering, oil, solvents and moisture is very good. However, epoxy novolacs also form very rigid and brittle polymers when fully cured because of their high cross-link density [40].

Based on above consideration, the aim of this work is to synthesis epoxy-novolac high-performance adhesive through interpenetrating polymer network (IPN) technique. The IPN is a special type of polymer blend in where the networks are formed by in-situ polymerization. The information about polymer blends and interpenetrating polymer networks are given in details below.

### 2.1 POLYMER BLENDS

Polymer blends have now come to the fore as such a major endeavor. Their current and potential technological importance is remarkable and their ubiquitous presence in consumer products is testimony to their commercial importance.

Polymer blends encompass different kinds of materials containing two or more polymeric components (homo-polymers or copolymers) and most exhibits greater or lesser degrees of phase separation. These multi-polymer systems display a broad range of behavior, ranging from toughened elastomers to high impact plastics depending upon the composition ratio, glass-transition and phase continuity. Their unique multi-phased morphology often allows for non-linear or synergistic behavior.
2.2 INTERPENETRATING POLYMER NETWORK (IPN)

Interpenetrating polymer networks (IPN) are a relatively special type of chemical combination of two polymers, both in network form. Unlike chemical blends there are no induced covalent bonds between the two polymers. This system involves interwined networks of two polymers prepared by the polymerization of a monomer in the presence of another polymer or sometimes the cross-linking of a polymer in immediate presence of the other. In this system the chains of one polymer are more or less physically and permanently entangled with those of other polymers and are thus interlocked. The physical intermolecular hooking takes place through the cross-linked bonds of different components [41].

Normal blending or mixing of polymers results in a multiphase morphology due to well-known thermodynamic incompatibility of polymers. With IPN on the other hand, the degree of mixing can be controlled, in part, through the selection of polymer pairs having small or negative heat of mixing. Because of the dual cross-linked nature of both constituents, each network of an IPN exerts a unique control over its morphological details such as phase continuity, as well as size, shape and distribution of the phase domains. In turn, the frozen or fixed multiphase morphology of IPNs provides a complex topological contribution to their physical and mechanical behavior such as glass transition, modulus, rubber elasticity and ultimate properties [42]. Thus the development of IPNs is an area of polymer technology that is challenging and economically rewarding. The material resulting from the synthesis of two networks either simultaneously or sequentially with respect to each other is termed as IPN.
In case of sequential interpenetrating polymer networks, monomer I is combined with cross-linking agent and initiator to form network I. Network I is then swollen in monomer II containing cross-linking agent and initiator to form network II [43].

When the two polymer networks are synthesized simultaneously i.e. the monomers or linear pre-polymers of the two monomers together with their respective cross-linking agents and catalysts are combined in bulk (melt), solution or dispersion, the resulting polymer networks are called simultaneous interpenetrating polymer network. It is generally believed that the simultaneous polymerization process, due to its nature results in materials with the smallest degree of phase separation and hence highest degree of interpenetration [44]. The other two important class of IPNs are semi IPNs and full IPNs. These are shown in Figure 2.3.

A semi IPN may be defined as an IPN in which one of the polymers is cross-linked and the other essentially is linear and a full IPN or simply IPN is said when both of the components are cross-linked [45].

Figure 2.3 Full IPN and Semi IPN
2.2.1 IPN-AN ADVANCED AND UNIQUE METHOD OF POLYMER BLENDING

In addition to mechanical blending and copolymerization, IPNs represent a third mechanism by which different polymers can be combined. Formation of IPNs is one method of overcoming the difficulty involved in mixing chemically incompatible polymers. While chemically different monomers can be mixed, the mixing of the corresponding polymers usually results in multiphase poly-blend unless the heat of mixing is nearly zero or negative. Even the mixing of two polymer solutions in the same solvent frequently produces two liquid phases. However, if mixing takes place on a lower molecular weight level and polymerization is achieved simultaneously with cross-linking, phase separation may be kinetically controlled, since the entanglements are made permanent by cross-linking [46].

Although phase separation depends primarily on the compatibility of the polymers and with highly incompatible polymers, the thermodynamics of phase separation is so powerful that it occurs before it can be prevented by cross-linking; the problem of extensive phase separation with moderately compatible polymers can be overcome without resorting to grafting by producing IPNs [47].

A higher degree of interpenetration, and hence a lower degree of phase separation, depends to a large extent on the compatibilities of the constituent polymers as well as the way they are combined in the final network. This blending technique offers the only method of combining cross-linked polymers [48].

2.2.2 ADVANTAGES OF IPNs

The materials resulting from the synthesis of two networks either simultaneously or sequentially with respect to each other, possess interesting characteristics compared to normal
poly-blends. The order in which the networks are formed strongly influences the resulting IPN morphology and properties and thus the manner and timing of network formation are of crucial importance. Normal blending or mixing of polymers results in a multiphase morphology due to well-known thermodynamic incompatibility of polymers. With IPNs on the other hand, the degree of mixing can be controlled, in part, through the selection of polymer pairs having small or negative heat of mixing [49].

In mechanical blends, or in block and graft copolymers, the size of the domains may fluctuate with time or applied stress and therefore induce unwanted changes in the properties of the material. This is not possible in IPNs where the structure is in some way ‘fixed’ or ‘frozen’ as soon as the cross-linking of both networks has been achieved. Thus, the morphology of IPN is fixed. Exerting external stress or temperature does not change it [50-51].

2.2.3 RELATIONSHIPS AMONG IPNs, BLENDS AND GRAFTS

A polymer blend may be defined as a combination of two polymers without any chemically bonding between them. A graft copolymer refers to a product prepared by the polymerization of monomer II in the intimate presence of polymer I, with greater or lesser extent of actual graft copolymer formation. Recent electron microscopic and kinetic evidence suggest that grafting in many systems is less extensive than previously believed, but still important. The graft copolymer may behave as a non-aqueous surface-active agent, binding the two phases together at their interface. Since most IPNs involve polymerization of one polymer in the immediate presence of other, they are also generally prone to some formation of graft copolymers. They constitute a special class however, since one or both polymers contain cross-links [52].
The interesting properties of IPNs emerge when the deliberately introduced cross-link outnumber the accidentally introduced grafts. When this condition prevails, the cross-links dominate and control the morphology and hence influence most of the physical and mechanical behavior. However, the grafts are still present and usually contribute favorably to the behavior of the IPN as a material. Idealized IPN-type structures seldom exist [53].

Frequently, covalent bond formation between the separate networks occurs because of chain transfer reactions. Again pseudo-cross-linking between the networks may occur through hydrogen bonds, ionic clusters or crystalline regions commonly present in semi-crystalline polymers. In addition to the permanent physical entanglements achieved during the synthesis, the polymers are held together in network form by these accidental covalent bonds. IPNs generally possess improved physical properties in comparison to normal poly-blends of their components. The IPNs were mostly found to exhibit a characteristic cellular structure where the first component made up the cell walls and the second component, the contents of the cells. Cellular structures have already been encountered with graft copolymers. The major difference between IPNs and graft copolymers is that cellular structures depends on the cross-link density of the two components varying from about 1000 to 500 $\text{Å}$. The phase domain sizes also depend greatly on the compatibility of the two polymers. An IPN is further distinguished from simple polymer blends, blocks or grafts in two ways: It swells but does not dissolve in solvents and further the creep and flow properties are suppressed quite remarkably [54].

### 2.2.4 IPN SYSTEMS CONTAINING EPOXY AS ONE OF THE COMPONENTS

The commonly used epoxy resins when cured with stoichiometric amounts of poly-functional amines are rather brittle and the damage tolerance to impact of composites made from
these materials is poor. Moreover, it is acknowledged that internal stress in epoxy resins cured at high temperature results from the shrinkage occurring in the cooling process from cure temperature to room temperature [55]. This internal stress reduces the adhesive strength and occasionally causes cracks in the casting materials [56].

In order to reduce the brittleness and internal stress in epoxy resin, various elastomeric additives have been explored for the last two decades.

It would be worthwhile at this point to make a survey of the related research works carried out in the recent past. To be very precise, we would be concentrating on the various works associated with the relevant polymeric materials in the form of IPN with others and among themselves. Moreover, as the network to be modified is that of epoxy in both the cases, we would like to start our review with various research works associated with epoxy either being present as a major or as a minor component in various IPN systems. Furthermore, our principal focus of review will be the mechanical, thermal and morphological aspects of poly-blend IPN systems [57].

2.2.5 IPN SYSTEMS CONTAINING EPOXY AND POLY-ACRYLATE OR COPOLYMER OF ACRYLATE OR MODIFIED ACRYLATE

Although limited but quite important and relevant research works were carried out to study the influence of elastomeric acrylates and modified acrylates on various morphological, mechanical and thermal aspects of epoxy. In the following section we are giving a brief review of the works in the relevant field.
2.2.5.1 IPN system based on Epoxy and Poly-Acrylate

Sperling et al. synthesized epoxy/acrylic IPN by the simultaneous formation of the two networks involved [58]. In this study the cross-linking of the epoxy component took place by the condensation mechanism while the acrylic network was being formed simultaneously by the addition polymerization of n-butyl acrylate in presence of di-t-butyl peroxide as initiator and diethylene glycol di-methacrylate as the co-monomer/ cross-linker for acrylic component. Phthalic anhydride was used as the cross-linker for epoxy while the initiator concentration was varied to study the influence of the rate of acrylic polymerization in relation to rate of epoxy cross-linking on the morphologies and the consequent properties of IPNs.

Electron microscopy of the various samples demonstrates that the minimum domain size and greatest molecular mixing occurs when the closet approach to simultaneity is attained. This occurs with samples prepared from 0.24 % and 0.32 % initiator respectively. When the peroxide level is higher (0.40 %) the rubber particles are large but elongated, tending to stretch out to form nearly a continuous phase. The simultaneous formation of networks limits phase dimensions sharply, as the molecules can’t form gross phases without rupturing primary bonds. In a related study on IPNs, Donatelli et. al. noted that the cross-link density of polymer I controlled the phase domain size much more than cross-links in polymer II [59].

The stress-strain data of epoxy- (poly-n-butyl acrylate) PnBA IPN show important differences among the samples. All the samples have a lower modulus than the pure epoxy homo-polymer. The toughness, indicated by the area under the stress-strain curve, is approximately doubled over samples having 0.24 % to 0.40 % initiator. The sample having the
highest initiator concentration has a lower modulus and lower ultimate stress and an elongation between 5 % and 6 %, making the area under the stress/strain curve the least of all the samples. While the sample with the lowest initiator concentration has an yield point and elongates between 8 % and 9 %, the intermediate samples show a higher modulus and greater ultimate stress but lower toughness than sample with 0.16 % initiator. It was concluded further that for a given percentage of rubber, spherical particles are the most efficient structure and give the highest toughening provided the particles are very small.

2.2.5.2 IPN systems involving Epoxy and Modified Acrylate or Copolymer of Acrylate

True homogeneity in IPNs is rare. It is observed that T_g zone of miscible epoxy/acrylic IPN made of diglycidyl ether of bisphenol A (DGEBA), cross-linked with an aliphatic diamine and diglycidyl ether of bisphenol A dimethacrylate (DGBAMA) is as sharp as those of their pure components. A single T_g could be measured from the DSC (Differential Scanning Calorimetric) curves, thus indicating miscibility between the two networks, or extensive mixing between the two components.

Morphology of the fracture surfaces of DGEBA/DGEBAMA IPN sample as determined by SEM indicates increased compatibility between polymer particles and epoxy matrix. There should be an optimum number of cross-links in the interfacial shell layer as there is no effect towards reduction in stress when the cross-links are too tight to produce any interaction or any IPN because of inhibition of mutual diffusion of segments. Thus, when it was known that decreasing the domain effectively reduces the internal stress size and further by introducing a strong interaction at the domain/matrix interface by the incorporation of cross-links.
2.2.5.3 Studies on Physical and Mechanical properties of Epoxy resin- Poly-ethyl Acrylate (PEA) IPNs system

Epoxy resin-PEA IPNs and semi IPNs were characterized with respect to their physical and mechanical behavior. This plastomer-elastomer IPN network was synthesized taking epoxy resin and PEA in four different ratios. The mechanical and physical properties of these different IPNs revealed that the modifying influence of both linear and cross-linked elastomers on the various properties of rigid, hard and brittle plastomeric epoxy resin. A wide range of properties can be achieved by blending a glassy polymer with a rubbery one. The ultimate performance depends on the relative proportions of the two components and also on the physical nature of the continuous phase. In case of IPNs prepared from a glassy and a rubbery polymer the rubber reinforcing effect plays the key role in determining various properties in addition to the interpenetration effect [60].

2.2.5.4 Studies on Physical and Mechanical Properties of Epoxy resin and Poly-methyl Methacrylate (PMMA) IPNs system

Epoxy resin-PMMA IPNs was synthesized by sequential IPN technique and characterized with respect to the physical and mechanical behavior. The modifying influences of linear and cross-linked plastomeric PMMA on another rigid, hard thermoset network of epoxy can be easily understood when the different physical and mechanical aspects of the resulting IPNs are compared to those of pure epoxy homo-polymer [61].

The aim of this work was overcoming the shortcomings of epoxy resin by way of forming plastomer-elastomer polymer blend systems by applying interpenetrating polymer networks technology.
Inspired by these all works, an attempt has been made to study the modifying influences observed when various hard novolac are incorporated into the more rigid and hard thermosetting matrix of epoxy.

2.3 CONSTRUCTION MATERIALS FOR SPACE AND AVIATION

An aircraft must be constructed of materials that are both light and strong. Materials currently used in aircraft construction are classified as either metallic materials or nonmetallic materials [62].

2.3.1 METALLIC MATERIALS

The most common metals used in aircraft construction are aluminum, magnesium, titanium, steel, and their alloys. An alloy is composed of two or more metals. The metal present in the alloy in the largest amount is called the base metal. All other metals added to the base metal are called alloying elements. Adding the alloying elements results in change in the properties of the base metal. For example, pure aluminum is relatively soft and weak. However, addition of small amounts or copper, manganese, and magnesium will increase aluminum's strength many times. Heat treatment can increase or decrease an alloy's strength and hardness. Alloys are important to the aircraft industry. They provide materials with properties that pure metals do not possess.

2.3.1.1 Aluminum

Aluminum alloys are widely used in modern aircraft construction. Aluminum alloys are valuable because they have a high strength-to-weight ratio. Aluminum alloys are corrosion resistant and comparatively easy to fabricate. The outstanding characteristic of aluminum is its
lightweight.

2.3.1.2 Magnesium

Magnesium is the world's lightest structural metal. It is a silvery-white material that weighs two-thirds as much as aluminum. Magnesium is used to make helicopters. Magnesium's low resistance to corrosion has limited its use in conventional aircraft.

2.3.1.3 Steel Alloys

Alloy steels used in aircraft construction have great strength, more so than other fields of engineering would require. These materials must withstand the forces that occur on today's modern aircraft. These steels contain small percentages of carbon, nickel, chromium, vanadium, and molybdenum. High-tensile steels will stand stress of 50 to 150 tons per square inch without failing. Such steels are made into tubes, rods, and wires. Another type of steel used extensively is stainless steel. Stainless steel resists corrosion and is particularly valuable for use in or near water.

2.3.1.4 Titanium

Titanium is a lightweight, strong, corrosion-resistant metal. Recent developments make titanium ideal for applications where aluminum alloys are too weak and stainless steel is too heavy. Additionally, titanium is unaffected by long exposure to seawater and marine atmosphere.

2.3.2 TITANIUM- AN IMPORTANT MATERIALS IN SPACE AND AVIATION

The use of titanium for structural application of spacecraft has already shown its potential during the early Mercury and Apollo program. In this context, it is also important that aerospace
industry is a larger market for titanium products primarily because of lightweight, high temperature resistance and corrosion resistance [63-64].

2.3.2.1 Background of Titanium

Titanium (Ti) is a d-block element and present in-group 4 in periodic table. Its atomic number is 22. It is a light, strong, lustrous corrosion-resistant (including in sea water and chlorine) transition metal element with a grayish color. Titanium was discovered in England by William Gregor in 1791 and named by Martin Heinrich Klaproth for the Titans of Greek mythology. It is fairly hard, non-magnetic and a poor conductor of heat. Commercial (99.2% pure) grades of titanium have ultimate tensile strength of about 63,000 psi (434 MPa), equal to that of some steel alloys, but are 45% lighter. Titanium is 60% heavier than aluminum, but more than twice as strong as the most commonly used 6061-T6 aluminum alloys [65].

<table>
<thead>
<tr>
<th>Titanium Grade</th>
<th>Chemical Composition</th>
</tr>
</thead>
<tbody>
<tr>
<td>O</td>
<td>Fe</td>
</tr>
<tr>
<td>1</td>
<td>0.18</td>
</tr>
<tr>
<td>2</td>
<td>0.25</td>
</tr>
<tr>
<td>3</td>
<td>0.35</td>
</tr>
<tr>
<td>4</td>
<td>0.40</td>
</tr>
</tbody>
</table>

Table 2.1 Chemical composition of commercial grade titanium

Titanium is always bonded to other elements in nature. It is the ninth-most abundant element in the Earth's crust (0.63% by mass) and the seventh-most abundant metal. The ASTM International recognizes 31 Grades of titanium metal and alloys, of which Grades 1 through 4 are commercially pure (unalloyed). These four are distinguished by their varying degrees of tensile strength, as a function of oxygen content, with Grade 1 being the most ductile (lowest tensile strength with an oxygen content of 0.18%), and Grade 4 the least (highest tensile strength with...
an oxygen content of 0.40%). The chemical composition and properties of commercial grade of titanium is shown in Table 2.1 and Table 2.2 [66-67].

<table>
<thead>
<tr>
<th>Titanium Grade</th>
<th>Mechanical Properties</th>
<th>Physical Properties</th>
</tr>
</thead>
<tbody>
<tr>
<td></td>
<td>Ultimate Tensile Strength (ksi)</td>
<td>Yield Strength (ksi)</td>
</tr>
<tr>
<td>1</td>
<td>35</td>
<td>25</td>
</tr>
<tr>
<td>2</td>
<td>50</td>
<td>40</td>
</tr>
<tr>
<td>3</td>
<td>65</td>
<td>55</td>
</tr>
<tr>
<td>4</td>
<td>80</td>
<td>70</td>
</tr>
</tbody>
</table>

Table 2.2 Mechanical and physical properties of commercial grade titanium

2.3.2.2 Alloy of Titanium

Titanium can be alloyed with iron, aluminum, vanadium, molybdenum, along with other elements, to produce strong lightweight alloys for aerospace (jet engines, missiles, and spacecraft), military, industrial process (chemicals and petro-chemicals, desalination plants, pulp, and paper), automotive, agri-food, medical prostheses, orthopedic implants, dental endodontic instruments and files, dental implants, sporting goods, jewelry, mobile phones, and other applications. The grades of some alloy and its chemical composition are shown in Table 2.3. The properties of some grade of titanium alloy are mentioned in Table 2.4 [68-69].
Various literature surveys reveal that the most widely used titanium alloy is Ti-6Al-4V [70]. It shows very high strength but relatively low ductility [71]. The main application of this alloy is in aircraft and spacecraft. Ti-6Al-4V is an alpha-beta alloy and having two different crystalline phases: the alpha phase which is hexagonal closed packed form and the beta phase that is a body centered cubic form. The beta-phase is favored to form when temperatures exceed 882.5°C. The beta-phase of metal shows high thermal resistance property [72]. Alpha-phase alloys are showing characteristics of high strength, high toughness and corrosion resistant property. In Ti-6Al-4V alloy, aluminum stabilizes the alpha-phase and raises the alpha to beta conversion temperature while the vanadium stabilizes the beta phase and raises the beta to alpha temperature [73]. These two-phase titanium alloys can be strengthened significantly by heat.
treatment consisting of a quench from some temperature in the alpha-beta range, followed by an ageing cycle at a somewhat lower temperature [74]. Beta-phase transformation, which would normally occur on slow cooling, is suppressed by quenching. The ageing cycle causes the precipitation of some fine alpha particles from the metastable beta, imparting a structure that is stronger than the annealed alpha-beta structure [75]. Although heat-treated alpha-beta alloys are stronger than alpha alloys, their ductility is proportionally lower [76]. These properties have made titanium alloy for choice of various applications in aerospace such as structural applications, landing gears, and blades of gas, turbines, nuclear power plants and prosthetic implants [77].

2.3.2.3 Application of Titanium and Titanium Alloy in Aerospace

Applications of pure titanium and alloys of titanium with aluminum (to refine grain size), vanadium, copper (to harden), iron, manganese, molybdenum, and with other metals can be found in aerospace markets [78].

Titanium is widely used in aerospace industry due to its high tensile strength to density ratio, high corrosion resistance, and ability to withstand moderately high temperatures without creeping. Titanium is mostly used in component of engine parts (blades, discs, rings and engine cases and airframe components (bulkheads, tail sections, landing gear, wing supports and fasteners). Titanium alloys are used in aircraft, armor plating, naval ships, spacecraft, and missiles. Two third of total titanium metal is used in aircraft engines and frames. The Ti6AL4V alloy accounts for almost 50% of all alloys used in aircraft applications. Titanium alloyed with aluminum, vanadium, and other elements is used for a variety of components including critical structural parts, firewalls and landing gear; exhaust ducts (helicopters), and hydraulic systems. The SR-71 "Blackbird" was one of the first aircrafts to make extensive use of titanium within its
structure, paving the way for its use in modern fighter and commercial aircraft. In engine applications, titanium is used for rotors, compressor blades, hydraulic system components, and nacelles. Boeing and Airbus, two major aerospace companies use highest number of titanium components in their industries. The weight of titanium used in different model of airbus and boing are shown in Figure 2.4 (a) and (b) [79].

![Figure 2.4 Weight of titanium used in different model of Airbus and Boing](image)

### 2.3.3 NONMETALLIC MATERIALS

In addition to metals, various types of plastic materials are found in aircraft construction. Some of these plastics include transparent plastic, reinforced plastic, composite, and carbon fiber materials.

#### 2.3.3.1 Transparent Plastic

Transparent plastic is used in canopies, windshields, and other transparent enclosures. It is essential to handle transparent plastic surfaces carefully because they are relatively soft and
scratch easily. At approximately 225 °F, transparent plastic becomes soft and pliable.

2.3.3.2 Reinforced Plastic

Reinforced plastic is used in the construction of radomes, wingtips, stabilizer tips, antenna covers, and flight controls. Reinforced plastic has a high strength-to-weight ratio and is resistant to mildew and rot. Because it is easy to fabricate, it is equally suitable for other parts of the aircraft.

2.3.4 INTRODUCTION OF POLYMERIC MATERIALS IN SPACE AND AVIATION

Polymeric materials are being extensively used in space systems as multilayer insulations, matrix or substrates for solar panels, adhesives, thermal control coatings for spacecraft and insulation for electrical wiring [80]. Despite having many advantages, polymeric materials are facing challenges for demanding aerospace applications. Many of the polymeric materials cannot maintain their thermal stability and mechanical properties above temperature 200 °C and lead to collapse of the composite structure. The thermal and mechanical properties of these materials are affected when exposed to harsh space environments [81]. These demanding conditions are limiting the use of polymer based materials for aerospace industry. Therefore, in order to meet the requirements of aerospace industry, research is continued to developed high performance polymers, which can maintain the desired properties under working environmental conditions for longer duration of time and serve their purpose properly [82]. During the past decade major advances have been made in the development of advanced composites based on organic polymer matrix systems with high performance fibers to replace metals in aerospace, automotive and other industrial applications [83].
2.3.4.1 Introduction and History of High Performance Polymers

High performance polymers are defined in many ways depending on the type of application [84]. High performance is a general term that can be used to describe many polymers. In term of high temperature applications, the most popular definition of performance is the polymer which can retain the useable properties at a temperature greater than 177 °C [85]. These polymers have a glass transition (T_g) greater than 200 °C and they can maintain their thermal stability (5 % weight loss) up to a temperature of 450 °C [86].

High performance polymers have long historical background. The development of high performance polymers started in late 1950s mainly to meet the requirement of aerospace industry. The most productive period for the development of high performance polymers was in between 1960 and 1970 [87]. During this period, many high performance polymers were developed with high glass transition temperature (T_g) and high thermal stability. Despite their high thermal stability, cost and processing of these polymers were the major issues [88]. The chemical structure of these high performance polymers resulted in difficult processability and poor solubility in organic solvents. Their softening points or melt viscosities were too high to process using conventional manufacturing techniques [89].

Polybenzimidazole, polyimide, polysulphone, polyether ether ketone, polyether imide, polyamide imide and polybenzoxazole are the main examples of initially developed high performance polymers. Continuous service temperature and mechanical properties of some high performance polymers are shown in Table 2.5 [90].
Polybenzimidazole could not draw the attraction to a sizeable market due to its high cost and difficult processability [91]. Polyimide film designated as Kapton was the first material among the high performance polymers, which was fabricated by DuPont [92]. Kapton attracted a big market and since then it has been the largest selling high performance polymer in the world [93].

<table>
<thead>
<tr>
<th>Mechanical properties (MPa @ 23°C)</th>
</tr>
</thead>
<tbody>
<tr>
<td>Basic unfilled resin</td>
</tr>
<tr>
<td>------------------------</td>
</tr>
<tr>
<td>Polybenziimidazole (PBI)</td>
</tr>
<tr>
<td>Poly amide imide (PAI)</td>
</tr>
<tr>
<td>Thermo plastic poly imide (PI)</td>
</tr>
<tr>
<td>Polyether imide (PEI)</td>
</tr>
</tbody>
</table>

<table>
<thead>
<tr>
<th>Continuous service temperature (°C)</th>
</tr>
</thead>
<tbody>
<tr>
<td>Polybenziimidazole (PBI)</td>
</tr>
<tr>
<td>Poly amide imide (PAI)</td>
</tr>
<tr>
<td>Thermo plastic amorphous poly imide (PI)</td>
</tr>
<tr>
<td>Polyether imide (PEI)</td>
</tr>
</tbody>
</table>

Table 2.5 Mechanical properties and continuous service temperature of high performance polymers

In aerospace industry, it is used primarily as insulation for aircraft and spacecraft wiring [94]. Other applications include high performance flexible films for photovoltaic substrates and printed circuit boards [95]. Kapton is also being used in satellites for thermal management [96]. After the commercialization of Kapton in 1970s, efforts were made to develop other high performance polymers with low cost, easy processing and improved mechanical properties [97].
One example of such polymer is thermoplastic Polyether imide designed as Ultem produced by General Electric.

2.3.4.2 Factors Contributing to High Thermal Stability of the Polymers

When linear or branched polymers such as polyethylene, polyvinyl chloride and polystyrene are heated, they decompose at temperatures up to ~250 °C [98]. The thermal properties of these polymers can be attributed to their intermolecular forces, mainly the covalent carbon-carbon bonds. The thermal stability of such polymers can be improved slightly by substituting other atoms in the chain by replacing carbon atoms, whose bond energy with carbon or with themselves is higher than the bond energy of carbon-carbon bonds. Primary bond strength is the most important factor. The difference in the bond dissociation energy between C-C and C=C are shown in Table 2.6 The most significant means of increasing the thermal stability of polymer molecules is by incorporating aromatic rings into the polymer chain. These rings hold the polymer molecule in a planar conformation and inhibit random orientation due to rotation [99].

<table>
<thead>
<tr>
<th>Bond</th>
<th>Dissociation Energy (Kcal/mole)</th>
</tr>
</thead>
<tbody>
<tr>
<td>C-C</td>
<td>74-124</td>
</tr>
<tr>
<td>C=C</td>
<td>100-145</td>
</tr>
<tr>
<td>C-H</td>
<td>83-121</td>
</tr>
<tr>
<td>C-N</td>
<td>49-82</td>
</tr>
<tr>
<td>C≡N</td>
<td>94-138</td>
</tr>
<tr>
<td>C=O</td>
<td>84</td>
</tr>
<tr>
<td>C-F</td>
<td>94-119</td>
</tr>
<tr>
<td>N-N</td>
<td>20-27</td>
</tr>
</tbody>
</table>

Table 2.6 Bond dissociation energy of compound
Aromatic rings also are more resistant to oxidative decomposition than aliphatic chains [100]. Aromatic rings and heterocyclic rings, which contain double bonds, also provide a degree of resonance stabilization, which improves the thermal properties of polymers. A heterocyclic ring containing double bonds also behaves in a similar manner as aromatic rings. Thus, more energy is required to break aromatic or heterocyclic carbon-carbon double bonds in the polymer chain that also required breaking aliphatic carbon-carbon bonds [101].

Polymers with high molecular weight and a narrow molecular weight distribution tend to be more thermally stable than polymers of lower molecular weight and broader molecular weight distribution. Low molecular weight species in polymers cause a reduction in performance, especially mechanical performance (low modulus and toughness) [102]. The regularity of the polymer’s structure and its crystallinity has pronounced advantageous effects upon performance and thermal stability [103]. Polymers primarily composed of rigid intra-chain structures, such as rigid rod polymers, are thermally more stable and exhibit higher strength and modulus than similar polymers containing flexible groups, such as ether or carbonyl groups. Rigid groups are more resistant to vibrations that lead to bond rupture. Cross-linked polymers are more thermally stable than the corresponding linear polymers since more than one bond must be cleaved to cause molecular weight reduction. In essence, to break more than one bond to cleave the polymer chain which delays the degradation process [104].

The mechanism of bond cleavage is important, especially if there is a possibility of recombination or if unzipping occurs that propagates rapidly down the polymer chain. In the unzipping process, the ends of the molecules degrade to release small fragments (generally
monomer) until the polymer is virtually destroyed [105]. Additives are commonly used to stabilize polymers exposed to certain environments; such as ultra-violate radiation coupled with moisture and elevated temperatures [106]. The addition of nano-particles in polymers has been shown to improve the thermal stability and to affect certain other properties such as increasing the modulus and lowering the coefficient of thermal expansion (CTE) [107].

2.3.4.3 Polyether Imide (PEI) – A High Performance Polymer

Polyether imide (PEI) is a newer class of amorphous thermoplastics with high temperature resistance, impact strength, creep resistance and rigidity. The structure of polyether imide is shown in Figure 2.5. The molecular architecture of this polymer is often redesigned to ease processing or optimize physical or mechanical properties. The glass transition temperature (T_g) of polyether imide is 215°C. The ether units provide a structure with flexible linkages and good melt flow characteristics [108].

![Figure 2.5 Structure of Polyether Imide (PEI)](image.png)

The aromatic imide units provide high heat resistance and good mechanical properties. Furthermore, due to the high proportion of aromatic rings; this polymer shows excellent thermal stability [109]. The bis-phenol group is symmetric, whereas the imide groups present an evident asymmetry compared to the central group, which can result in a specific dipole moment. Due to
its amorphous nature, polyether imide shows no abrupt changes in the mechanical properties below glass transition temperature ($T_g$). The material can be melt processed because of the ether linkages present in the backbone of the polymer, but still maintains properties similar to the polyimides. The high temperature resistance of the polymer competes with the poly-sulphones and poly (phenylene sulphides). The polymer is resistant to alcohols, acids and hydrocarbon solvents [110].

2.3.4.4 Polyether Ether Ketone (PEEK) - A High Performance Polymer

Polyether ether ketone (PEEK) is a high performance thermoplastic polymer, which is gaining significant interest in aviation and space industries. PEEK is a lightweight, high performance polymer that can successfully replace metals and other polymers due to its unique combination of outstanding wear performance, processing flexibility, and excellent chemical resistance. It offers significantly high thermal and chemical stability as well as mechanical properties [111-112]. The structure of PEEK is shown in Figure 2.6.

![Figure 2.6 Structure of Polyether Ether Ketone (PEEK)](image)

In aerospace industry, the standard material of construction for many years is primarily metal. The need for efficiency has driven the industry towards increasing use of polymers both as passive components, such as decorative cladding of aircraft interiors, and active components
such as fan blades [113]. There are number of advantages of polymers over metals and these are lighter in weight, higher stiffness to weight ratio, noise reduction, chemical resistance, corrosion resistance, etc. [114]. Lighter weight applies to the finished aircraft as well as individual components, the benefits of the latter relating to assembly processes. PEEK as a material excels in virtually every attribute having: excellent high temperature performance, continuous use temperature of 260 °C, glass transition temperature of 143 °C, heat deflection temperature of 310 °C, excellent tensile and fatigue strengths, excellent wear and chemical resistance, excellent fire, smoke and toxicity performance, excellent electrical properties, etc. [115].

2.3.5 INTRODUCTION OF COMPOSITE AND NANOCOMPOSITE MATERIALS IN SPACE AND AVIATION

High-performance aircraft requires an extra high strength-to-weight ratio material. Fabrication of composite materials satisfies this special requirement. Composite materials are constructed by using several layers of bonding materials (graphite epoxy or boron epoxy). These materials are mechanically fastened to conventional substructures. Another type of composite construction consists of thin graphite epoxy skins bonded to an aluminum honeycomb core. Carbon fiber is extremely strong, thin fiber made by heating synthetic fibers, such as rayon, until charred, and then layering in cross sections.

A survey of current applications of composite materials and structures in military, transport and General Aviation aircraft is presented to assess the maturity of composites technology, and the payoffs realized. The results of the survey show that performance requirements and the potential to reduce life cycle costs for military aircraft and direct operating costs for transport aircraft and are the main reasons for the selection of composite materials for
current aircraft applications. Initial acquisition costs of composite airframe components are affected by high material costs and complex certification tests, which appear to discourage the widespread use of composite materials for aircraft applications. Material suppliers have performed very well to date in developing resin matrix and fiber systems for improved mechanical, durability and damage tolerance performance. The next challenge for material suppliers is to reduce material costs and to develop materials that are suitable for simplified and inexpensive manufacturing processes. The focus of airframe manufacturers should be on the development of structural designs that reduce assembly costs by the use of large-scale integration of airframe components with unitized structures and manufacturing processes that minimize excessive manual labor [116].

Based on all these considerations above, the aim of the present work is to adhesive bonding of polyether imide to titanium and polyether ether ketone to titanium for space and aviation application. The novelty of this work is to replace metal-metal adhesive joints by plastic-metal adhesive joints. This will help to reduce overall cost of the materials as well as consumption of fuel of spacecraft and aircraft.

2.4 INTRODUCTION OF SURFACE MODIFICATION OF MATERIALS

Surface preparation of substrates prior to bonding is one of the most important factors in the adhesive bonding process. Pre-bond treatments are intended to provide cohesively strong and easily wettable surfaces. The main purpose of surface preparation is to ensure that the weakest link in the joint is either in the adhesive or in the substrate but not at the interface. Therefore, low energy surfaces must be modified chemically or physically prior to bonding so that the adhesive can adequately wet the surface and provide the attractive forces necessary for good adhesion.
There are different methods that are used for surface treatment of metals and polymers and these are discussed in details below. Passive processes only clean the substrate and remove weak boundary layers. Chemical cleaning, solvent washing and mechanical abrasion are considered as passive surface processes. Active surface treatments are chemical or physical processes that do not merely clean the surface or remove weak boundary layers but also transform the inherent surface chemistry to improve wetting characteristic of materials. Examples of the active surface treatments are anodization process and plasma process [118].

2.4.1 SURFACE MODIFICATION OF TITANIUM

Surface treatment of the titanium and its alloys is critical in improving the initial strength and long-term durability of the adhesive joint. The surface treatments are utilized to remove the contaminants comprising the weak boundary layer and for creation of a stable adherend surface which may be chemically and mechanically compatible with the adhesive. For optimizing the durability of the adhesive joints, the surface treatments that enhance surface wettability and introduce macro-and to a greater degree micro roughness are favored. In order to improve the adhesion on titanium, numerous methods of surface preparation have been developed. Most of them are multi-step procedures, which consist of a conditioning step for cleaning and texturing the surface (e.g. abrasive blasting, chemical cleaning, alkaline or acidic pickling) and a pre-treatment step for promoting adhesion (e.g. anodizing, sol–gel or plasma) [119].

2.4.1.1 Surface Modification of Titanium by Anodization Method

Anodic oxidation, sometimes called anodization, is an electrochemical technique used for modification of oxide film on titanium. This technique is a simple process, which involves connecting the Ti substrate to an anode in electrolyte solution, and then application of current.
Electrochemical processes like sulphuric or phosphoric acid anodization produces colored oxide layers [120]. Some works point out that the oxide layer consists mainly of TiO₂. Other workers notice that the oxide layer is composed of titanium sub-oxides (TiO, Ti₂O₃). To remove oil or other organic contamination from titanium surfaces; alkaline cleaning in NaOH-based solution is a suitable way [121]. Two pickling processes are common. In the case of acidic pickling, the solutions used are based on HF and HNO₃ [122]. To avoid these hazardous ingredients, it is common to use an alkaline etching with highly concentrated NaOH solutions [123]. Pre-treatments like chromic acid anodizing lead to higher durability due to their high degree of microroughness (Group 3) [124]. According to Group 3, the increase in surface area leads to an increased mechanical interlocking of the adhesive to the adherend. The obtained micro-roughness is a desirable feature of metal pre-treatments because of the propensity to form a mechanical micro composite interphase. The chemical stability of fresh oxide layers in moisture could also have an influence on the adhesion strength. Investigations on chromic acid anodized oxide layers in hot/wet conditions exhibit a transition from amorphous to crystalline titanium oxide. The environmental concerns over existing wet chemical surface pre-treatments pushed the focus of recent developments to dry treatments like laser or plasma pre-treatment [125].

One of the important factors in anodizing titanium and its alloys in accordance with this invention is the pH of the electrolyte, which must be at least 10.5 [126]. The necessary high pH is provided by the inclusion in the electrolyte of either one or both of the aforementioned alkali metal salts of ethylenediaminetetraacetic acid and diethylenetriaminepentaacetic acid, and an alkali-metal hydroxide [127]. These components of the electrolyte also serve as a sequestering, or chelating, agent, which combine with stray metallic ions in the electrolyte and thus prevents the same from interfering with the anodizing process [128]. Such stray metallic ions may include
titanium or alloying metals of the work piece, which is anodized, or impurities contained in the components of the electrolyte [129]. The electrolyte continuously absorbs carbon dioxide from the atmosphere, and since this gas lowers the pH of the solution it is necessary to add additional amounts of the alkali-metal hydroxide in order to maintain the proper pH level [130]. The alkali metal silicate furnishes oxygen for the anodizing process [131]. Because of cost considerations, sodium meta-silicate and sodium per-borate are preferred for these compounds, but any of the soluble alkali metal silicates and per-borates can be employed, such as those of potassium [132]. For the same reason, the sodium salt of either ethylenediaminetetraacetic acid or diethylenetriaminepentaacetic acid is preferred as the compound which provides proper pH level for the electrolyte and which serves as the sequestering agent therein, although the same substitution of lithium or potassium may be made for this component of the electrolyte [133]. The anodizing process can be performed with the electrolyte maintained at normal ambient temperatures within the range of about 65 ° to 100 ° F. Higher temperatures permit expulsion of some of the per-borate from solution and hence should not be used [134].

2.4.1.2 Surface Modification of Titanium by Plasma Nitriding Method

Plasma nitriding is an industrial surface hardening treatment for metals. Plasma nitriding is a plasma activated thermo-chemical diffusion process that introduces nitrogen into the surface of titanium alloy at temperature ~700 °C [135]. The nitrogen ions then combine with titanium alloy to form titanium nitrides. This in turns increases the hardness and roughness of surface [136]. In plasma nitriding, the reactivity of the nitriding media is not due to the temperature but due to the gas in ionized state. In this technique intense electric fields are used to generate ionized molecules of the gas around the surface to be nitrided. Such highly active gas with ionized molecules is called plasma, naming the technique [137]. The gas used for plasma
nitriding is usually pure nitrogen, since no spontaneous decomposition is needed (as is the case of gas nitriding with ammonia).

Plasma nitriding process involves a number of stages, which include heating, sputter cleaning, nitriding and cooling [138]. The heating is usually carried out using external means till all the volatile compounds in the vacuum chamber are removed. This is followed by sputter cleaning of the work-piece surface and simultaneous heating, through ion bombardment, in addition to external heating. The sputter cleaning is carried out at a relatively low pressure than the nitriding pressure. The actual nitriding process starts after achieving the nitriding temperature and it can run from few hours to several tens of hours depending on the material being nitrided and the properties required thereof [139].

In the plasma nitriding processes, nitrogen gas (N₂) is usually considered to play the important role. Other gasses like hydrogen or Argon are also used. Indeed, Argon and H₂ can be used before the nitriding process during the heating of the parts to clean the surfaces to be nitrided. This cleaning procedure effectively removes the oxide layer from surfaces and may remove fine layers of solvents that could remain. This also helps the thermal stability of the plasma plant, since the heat added by the plasma is already present during the warm up and hence once the process temperature is reached the actual nitriding begins with minor heating changes. For the nitriding process H₂ gas is also added to keep the surface clear of oxides. This effect can be observed by analysing the surface of the part under nitriding [140].

Titanium nitride is a material, which has many remarkable properties, which lend themselves to a wide range of applications. Titanium nitride coating has been used in steel industry, due to its high hardness and corrosion resistance properties. It is useful for increasing
the wear resistance of high-speed steel cutting tools. Titanium nitride coating has high conductivity and diffusion barrier properties and employed in semiconductor metallization schemes [141]. In addition TiN films have been used for gold surfaces, wavelength selective transparent optical films, thin film resisters, tool bit coatings and due to its strong inferred reflection energy saving, coatings for windows etc. [142]. Titanium nitride is a refractory interstitial nitride with a golden color, extreme hardness, corrosion resistance and relatively high conductivity [143]. The color of TiN also varies strongly with composition. With increasing nitrogen content, the color changes from Ti grey to light yellow (Ti$_2$N) to golden (TiN) [144]. Such variations of color and other properties with composition implies that when composition may not be directly measured, external properties such as lattice parameter and color may be used to get a rough idea of composition. Varying nitrogen content of the samples can also cause the introduction of sub stoichiometric Ti-N phases leading to a wide range of microstructures [145]. Some properties of TiN have been summarized in Table 2.7 and compared to those of titanium

<table>
<thead>
<tr>
<th>Properties</th>
<th>TiN</th>
<th>Ti</th>
</tr>
</thead>
<tbody>
<tr>
<td>Structure</td>
<td>FCC</td>
<td>HCP</td>
</tr>
<tr>
<td>Color</td>
<td>Golden</td>
<td>Grey</td>
</tr>
<tr>
<td>Density</td>
<td>5.4 g/cm$^3$</td>
<td>4.54 g/cm$^3$</td>
</tr>
<tr>
<td>Melting Point</td>
<td>2950 °C</td>
<td>1940 °C</td>
</tr>
<tr>
<td>Thermal Conductivity</td>
<td>30 W/ m. K</td>
<td>13 W/ m. K</td>
</tr>
<tr>
<td>Vicker’s Hardness</td>
<td>21-24 HV</td>
<td>0.55-2.5 HV</td>
</tr>
<tr>
<td>Young’s Modulus</td>
<td>590 GPa</td>
<td>120 GPa</td>
</tr>
</tbody>
</table>

Table 2.7 Properties of titanium nitride (TiN) and titanium (Ti)
2.4.2 SURFACE MODIFICATION OF POLYMERIC MATERIALS

Polymers have been applied successfully in fields such as adhesives, protective coatings, composites and thin-film technology. In general, special surface properties with regards to chemical composition, hydrophilicity, cross-linking density and roughness are required for the success of these applications. Polymers very often do not possess the surface properties needed for these applications. However, they have excellent bulk, physical and chemical properties and are inexpensive and easy to process. For these reasons, surface modification techniques, which can transform these inexpensive materials into highly valuable finished products, have become an important part of the polymers and many other industries [146].

The situation with polymer substrates is even more complex than with metals. These materials have lower surface energies and lower tensile strength than metals, and most importantly, polymeric surfaces are more dynamic than metals. Thus there is a greater probability of variation in the surface that will affect the ultimate joint performance [147].

2.4.2.1 Plasma Treatment on Polymeric Materials

Plasma treatment is a popular method of dry surface preparation for polymers. The treatment is believed to oxidize the surface of the polymer and increase the roughness of the polymer. Relative bond strength improvements of ten to several hundred times are possible depending on the substrate and gas used for plasma. Plasma treatment has become a very popular treatment for small to medium size parts. Glow-discharge under low-pressure plasma is a popular technique, which results in better uniformity in surface modification of the polymers [148]. Moreover, it is a dry treatment method, which is better suited for industrial applications. It is now well established that the glow discharge treatment creates physical and chemical changes such as cross-linking, degradation formation of free radicals and oxygen functionalization [149].
The temperature of gases in a glow discharge generally remains low and the plasma play a predominant role in the surface modification of polymers. It is possible to strike glow discharge with either a direct current (DC) or radio frequency (RF) power source. In the industry, RF glow discharge is generally employed for surface modification of polymer.

2.4.2.2 Working of Plasma Treatment on Polymeric Materials

Gases or mixtures of gases, which are used for plasma treatment of polymers, include nitrogen, argon and oxygen [150]. Plasma is created when a neutral gas is given sufficient energy from an electronic discharge source to create new product in the form of ions and radicals. The source of free electrons is generally a high-energy glow discharge such as a high voltage electrode. These resulting collisions of electrons and gas molecules result in a net energy transfer to the molecules producing meta-stable fragments and energized ions. The resulting product is a mixture of highly excited ions. Plasma generated from oxygen (O₂) carrier gas typically consists of O⁺, O⁻, O₂⁺ and O₃⁺ ions. The plasma particles are extremely unstable and their energetic state are highly reactive with particles or surfaces that they interact [151].

When polymeric substrate is placed under the plasma, the electrons generated in the plasma equipment collide on the exposed surface with energies necessary to break the molecular bonds on the surface. The resulting free radicals react rapidly with the products of the plasma, or with adjoining free radicals on the same or different chain, to form various chemical functional groups on the surface of the substrate. Increased surface energy results from this reaction. This occurs without significantly affecting the balance of the part [152].

The plasma treatment affects molecules only to the depth of several molecular layers [153]. Generally, short treatment times (seconds to minutes) are necessary to modify polymer surface. Although providing excellent surface adhesion on many hard-to-bond plastics and long
shelf life, conventional plasma treatment also has shortcomings. It requires a low pressure (partial vacuum) and thus, the parts must be processed in a vacuum chamber. Atmospheric pressure plasma treatment represents a new generation of surface treatment technology that allows the plasma to be sustained at atmospheric pressure in a way that permits the surface treatment of polymers and other substrates. An atmospheric plasma source may be viewed as an electrical switch that turns chemical reactions on and off. When it is on, a high concentration of atoms and radicals are delivered to a surface to modify materials of choice [154].

Based on the above consideration, the aim of this work is to modify the surfaces of polyether imide (PEI) and polyether ether ketone (PEEK) by treatment of low-pressure plasma. The surface of titanium is modified by the treatment of anodization and plasma nitriding techniques. This surface modification of polymeric materials and titanium is expected to improve the adhesive bond strength due to increase of surface energy of polymeric materials as well as titanium.

### 2.5 SURFACE ENERGY MEASUREMENT

Surface energy is the deciding factor on how a liquid adheres to a surface of material. The higher the surface energy of the solid substrate in relation to the liquid, the better will be the wettability [155]. Surface treatment improves wettability by creating higher energy on the surfaces. These high-energy surfaces allow the liquid to spread over a solid surface upon contact. The angle at which the solid-liquid contact occurs at equilibrium can be measured with a goniometer and studied as a quantification of how much surface modification was induced by the surface treatment on solid surfaces [156].

A liquid, which spreads completely on a surface, would have a contact angle nearer to $0^\circ$. Surface energy reflects contributions from two distinct components. The polar component ($\gamma_P$)
of surface energy represents energy related to polar interactions and hydrogen bonding. The dispersive component ($\gamma_D$) of surface energy encompasses interactions caused by van der waals and weaker intermolecular forces. The total surface energy is attained from the sum of these two individual components.

$$\gamma = \gamma_p + \gamma_D \quad (2.10)$$

To measure surface energy, a liquid drop is placed on the surface. Solid surface energies are obtained by contact angle measurements with at least two fluids of known surface tension [157].

2.6 **FRACTURE ANALYSIS OF ADHESIVE JOINTS**

The surface characteristics of the polymer and the metal, choice of adhesives, stress distribution of the joints and strain rate during testing predominantly governs fracture and failure modes in metal-polymer adhesive joints. During mechanical testing of the joint, each of these factors may contribute to the failure mechanism, depending on the circumstances. Generally, the following four types of failures may occur for adhesive joints of polymer to metal; interfacial failure of polymer to adhesive, subsurface layer failure of polymer, cohesive failure of adhesive and interface failure of metal to adhesive [158].

2.7 **PERFORMANCE OF JOINTS UNDER ENVIRONMENTAL CONDITIONS**

Water must be considered a dominant factor in determining the permanence of adhesive bonded joints in most weathering service environments. The adhesive may be affected by water in a variety of ways, depending on whether water can permeate the adhesive structure itself to produce significant property changes or more via some pathway to reach the interfacial area and
affect adhesion. Salt water is the substance, which gives the greatest problems in the environmental stability of adhesive joints. The rate of diffusion of water through the adhesive from one adherend to the other may be of importance in minimizing stresses arising from incipient dimensional changes. Water entering a joint may cause swelling and thereby introduce stresses into the joint, which could weaken it. Reference has already been made to water attacking adherends consisting of fibers in plastic matrices, but with metallic adherends water may attack the oxide layer or be involved in corrosion of the bulk adherend [159]. Moisture has a profound effect on the service life of adhesive joints made with some adhesives between some adherends. There are four aspects of the problem, which need to be drawn together when looking at joints, which have been exposed to moisture or are to be designed to withstand such exposure. These comprise the ability of moisture to diffuse through the adhesives, its susceptibility to displacement from the substrate, the corrosion susceptibility of the substrate in presence of moisture and lastly, the role of any primer or sealing agent in modifying the first three considerations. For moisture to affect an adhesive joint between two metal adherends it must enter the joint by diffusion into the adhesive from an exposed edge. Moisture might also assist failure by creating surface corrosion of the adherend, which can lead to surface flaws such as pits or inclusions of a weak corrosion product [160]. Because temperature is a common factor in all service environments, its effect on bond performance should be considered. Even though thermosetting resins in adhesives have no softening point, they still show a change in joint strength at higher temperatures that seems to be quite independent of any thermal degradation process [161]. It is evident that the adhesive fails by a brittle mode at low temperature but at room temperature, many adhesives begin to fail by a ductile mode. Thus the recorded bond
strength decrease with increasing temperature is probably due to a plastic flow phenomenon [162].

2.8 RESEARCH GOAL

Inspired by excellent thermal and mechanical properties of novolac and epoxy resin, the aim of this dissertation is to develop an IPN adhesive with the help of mixture of the above two resins and to explore the potential of it for aerospace application. Another direction, which has not been explored, yet is the manufacture of nano-adhesive based on epoxy-novolac IPN adhesive. Therefore, another objective of this work is to manufacture the carbon nanofiber reinforced epoxy-novolac IPN adhesive. The most important area of this work is to replace the surface treated metal-metal adhesive joint by surface treated polymer-metal adhesive joint and expose this joint in different environmental condition for application of space and aviation. This replacement may be considered to be an approach towards reduction in the overall weight of the material meant for space and aviation, reduce fuel consumption and cost effectiveness. Based on above-mentioned issues the most important questions to be addressed in this dissertation are:

(a) What are the problems that may be encountered during the processing of epoxy-novolac IPN adhesive and CNF reinforced epoxy-novolac IPN adhesive?

(b) Epoxy-novolac adhesive has already been established. However, synthesis of epoxy novolac IPN adhesive has not yet been established. In this context, the question need to be addressed entails what is the novelty and why it is useful as a structural adhesive in space and aviation?

(c) Epoxy-novolac IPN adhesive has never been tested as a structural adhesive for space and aviation application. Inspired by its thermal and mechanical properties, one of the objectives
of this work is to evaluate the potential of epoxy-novolac IPN adhesive as structural one and also to judge the carbon nanofiber reinforced epoxy-novolac adhesive in this respect.

(d) The environmental condition degrades the thermal and mechanical properties of adhesives. Therefore, the question that needs to be addressed is how and to what extent the exposure of the said adhesive to environmental condition will affect the thermal and mechanical properties of epoxy-novolac IPN adhesive?

The work only includes the initial evaluation of the IPN adhesive in aerospace application. Detailed evaluation of the material for any specific application is out of the scope of this work. However, recommendation for the future work will be given on the basis of the results obtained in this work. On the basis of these recommendations, IPN adhesive can be further evaluated in detail for a specific application.

It is obvious that most of the studies conducted in the past have been primarily focused on the surface modification of polyether imide and polyether ether ketone by radio frequency (RF) plasma. This surface treatment method affects wetting and physicochemical characteristics of polymer. A limited number of studies on the surface modification of polyether imide and polyether ether ketone by Direct Current (DC) glow discharge plasma have come to our notice. The DC plasma treatment on polymer surfaces highly affects the above properties. It has also highlighted that various parameters of glow discharge such as duration of exposure, process power and discharge gas significantly affect the wetting characteristics of the polymer. After certain duration of exposure, the wetting characteristics of the polymer deteriorate. However, the rationale behind it has not been understood very clearly.
2.9 OUTLINES OF THESIS

The thesis mainly divided into two parts. Part 1 includes the synthesis and characterization of epoxy-novolac IPN adhesive through simultaneous and full IPN technique. Part 2 mainly relates to the adhesive bonding of titanium with respected polyether imide (PEI) and polyether ether ketone (PEEK) by applying the above epoxy-novolac IPN adhesive. Two separate chapters are included for the solvent bonding and solvent vapor bonding of polycarbonate.

An overview of the present work is described in the introductory chapter. The present work is based on performances of plastics-metal adhesive joint under harsh environments. The need of this material with increased performance and challenges faced by astronauts are mentioned. The project is defined in the light upcoming requirements for space sector.

A brief history of adhesive bonding and interpenetrating polymer network is mainly presented in the literature review (Chapter 2). Firstly, an introduction to adhesive bonding and its importance for aerospace application is presented in this chapter. After this discussion, novel interpenetrating polymer network is described suitably. Thus, construction materials, which are prominently used in aerospace, are also discussed here. Then, the most emerging field of polymer composite has been described. Surface modification techniques such as anodization technique and plasma technique; and its effect on titanium and polymeric surfaces are mentioned in this chapter. Surface energy and morphology of fracture surfaces of materials are described in this chapter. Finally, Performance of adhesive joints under different environments is discussed in Chapter 2.

Chapter 3, describes the experimental procedures used in the present investigation for synthesis of epoxy-novolac IPN adhesive and the surface modification polyether imide (PEI) and
polyether ether ketone (PEEK) by DC glow discharge, and also, for the titanium by plasma nitriding and anodization. This chapter also highlights various methodologies applied for surface characterizations, adhesive joining, strengths and fracture characteristics under lap-shear tensile test.

In chapter 4, characteristics result of epoxy-novolac IPN adhesive is discussed. The epoxy-novolac IPN adhesive is synthesized by mixing of different proportion of novolac with respect to epoxy resin. The objective of this chapter is to find out the best epoxy-novolac IPN adhesive system.

Surface modification and surface characterization of polyether imide (PEI) and polyether ether ketone (PEEK) is described in chapter 5. Low-pressure DC glow discharge plasma is used for surface modification of above two polymers.

Chapter 5 explains the surface modification and surface characterization of titanium. Two types surface modification technique are used. One is anodization technique and another is plasma nitriding technique.

In chapter 7, lap-shear tensile strength results of epoxy-novolac IPN adhesive bonded titanium to polyether imide and titanium to polyether ether ketone is discussed. The objective of this chapter is to find out the best IPN adhesive bonded titanium to polyether imide and titanium to polyether ether ketone.

Chapter 8 deals with performance of IPN adhesive bonded titanium to polyether imide and titanium to polyether ether ketone under different environmental conditions. This chapter is related to chapter 7. In chapter 7, lap-shear tensile strength results exhibit the best IPN adhesive system. This adhesive system is applied for bonding of titanium with polyether imide and polyether ether ketone separately and exposed to different environmental conditions. The results
are compared with carbon nanofiller reinforced IPN adhesive bonding of titanium to polyether imide and titanium to polyether ether ketone.

Chapter 9 summarizes the undertaken research and highlights the main finding of this work. On the basis of these finding, some conclusions are made and recommendations are given for future work.

Chapter 10 and Chapter 11, mainly deals with solvent bonding of polycarbonate and solvent vapor bonding of polycarbonate. These two works are separately given in two different chapters. Introduction, experimental details, results, discussion and conclusion of solvent bonding and solvent vapor bonding of polycarbonate are discussed in two different chapters.
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