Chapter 2
Experimental
2.1 Materials

2.1.1 Solvents

Dimethyl acetamide (DMAc) (Spectrochem, Mumbai) was purified by distilling over phosphorous pentoxide (S. D. Fine Chemicals, Mumbai). Methyl isobutyl ketone (E-Merk, Mumbai), methyl ethyl ketone (Nice Chemicals, Cochin), diglyme (Spectrochem, Mumbai), acetone (CDH, Mumbai), chloroform and n-hexane (Qualigens, Mumbai) were used as received. Toluene (Qualigens, India) was refluxed and distilled over sodium. Tetrahydrofuran (THF) (Qualigens, Mumbai) was refluxed over calcium hydride and distilled before use. Ethanol (Qualigens, Mumbai) was distilled and used.

2.1.2. Aminoacids/diamines

4-Aminobenzoic acid and 3-aminobenzoic acid (Aldrich, USA) were used as received. 4,4'-Diaminodiphenylmethane (DDM), 4,4'-diaminodiphenylsulphone (p-DDS), 3,3'-diaminodiphenylsulphone (m-DDS) and 4,4'-diaminodiphenyl ether (DDE) [Merck, USA] were
used without further purification. 1,3-Bis(3-aminopropyl)-1,1,3,3-tetramethyldisiloxane (Fluka, Switzerland) and 1,6-diaminohexane and 4,7,10-trioxa-1,13-tridecanediamine (Aldrich, USA) were used as received.

2.1.3. Other reagents and materials

4-Chloronitrobenzene (CDH Ltd., Mumbai), bisphenol-A (S.D. Fine Chemicals, Mumbai), triphenyl phosphine (SISCO Research Lab., Mumbai), benzyltriethylammonium chloride (BTEA) (Spectrochem, Mumbai) calcium chloride (Qualigens, Mumbai) and nickel aluminium alloy (S.D. Fine Chemicals, Mumbai) were used as received. Anhydrous sodium acetate (Glaxo Lab., Mumbai) was dried at 120°C for 3 h and used. Hydroxyl-terminated polybutadiene (HTPB) [hydroxyl value: 41.7 mg KOH/g, M_w: 15,200 and M_n: 5,500 (GPC, polystyrene standard); VSSC (in-house); Thiruvananthapuram] was used as received. Solid carboxyl-terminated butadiene-acrylonitrile copolymer (CTBN-S)-Nipol 1072 [carboxyl content: 0.07-0.08 ephr (eq./100 parts of resin); M_n: 65,000 g/mol, acrylonitrile content: 26-28 %, Zeon Chemicals, USA] and liquid CTBN – Hycar 1300 x 8 [carboxyl content: 0.052 ephr; M_n: 3500 g/mol, acrylonitrile content: 26-28 %, B. F. Goodrich, USA] were used as received. Anhydrous sodium sulfate (S.D. Fine Chemicals, Mumbai) was dried at 120°C and used. Calcium hydride (Spectrochem, Mumbai) was used as received. 1-Chloro-2,3-epoxypropane (epichlorohydrin) (SISCO Research Lab., Mumbai) was distilled and used. Hydrazine hydrate (S.D. Fine Chemicals, Mumbai) and sodium metal (Nice Chemicals, Mumbai) were used as received. 3-Aminopropyl-terminated polydimethylsiloxane (amine value: 39.2 mg KOH/g; Petrarch, USA) was used.
Silane treated, E-glass fiber (Unnathi Corporation, Ahmedabad) of density 2580 kg/m³ and linear density 4.97 x 10⁻⁴ kg/m were used as received. Kapton H polyimide film of thickness 125 μm and Kapton films of thickness 25 and 125 μm aluminized on one side of the film, obtained from DuPont, USA were used for atomic oxygen exposure studies. Carbon-polyimide and glass-polyimide composites, made in VSSC from T-300 carbon fabric and E-glass fabric using nadic end-capped addition curable imide as the matrix resin, were used for atomic oxygen exposure studies.

2.1.4. Anhydrides

Acetic anhydride (Qualigens, Mumbai) was distilled before use. Trimellitic anhydride (Aldrich, USA) was purified by recrystallization from acetic anhydride.

*Itaconic anhydride*: It was prepared from itaconic acid (Sigma, USA) following the procedure described below. About 19.5 g of itaconic acid and 11 g of P₂O₅ (excess) were added to 135 ml of chloroform taken in a 500 ml round bottom flask. A mechanical stirrer and a water condenser were fitted to the flask and the contents of the flask were stirred continuously at 55-60°C till the insoluble portion of itaconic acid disappeared. The reaction mixture was cooled to room temperature and the chloroform solution was decanted from the brown residue remaining at the bottom of the flask. Excess chloroform was removed by distillation. Itaconic anhydride which crystallized out was dried under vacuum for 3 h at room temperature (m.p. 67-69°C). Yield: 90%.

*Maleic anhydride*: Commercially available maleic anhydride (SISCO Chem., Mumbai) was purified by the following procedure. 50 g of maleic anhydride was refluxed with 65 ml of acetic anhydride for 3 h. It was then distilled to remove acetic acid (b.p. 126°C) and acetic anhydride (b.p. 140°C). The fraction of liquid boiling at 200°C was
collected. It was solidified by cooling and dissolved in minimum quantity of chloroform under reflux condition. The solution was cooled and the crystals formed were separated and dried under vacuum for about 3 h (m.p. 50-53°C). Yield: 93%.

2.1.5. Epoxy resins

Epoxy resins, viz., Araldite GY 250 (DGEBA; epoxy value = 5.0-5.5 eqv/kg; difunctional) and Araldite EPN 1138 (Novolac epoxy; epoxy value = 5.5-5.7 eqv/kg; polyfunctional) manufactured and supplied by M/s. Hindustan Ciba-Geigy, India Ltd., Mumbai, were used. 1,3-bis(3-glycidyloxypropyl)tetramethyldisiloxane (epoxy value = 5.3 eqv/kg; Fluka, Switzerland) was used as received.

Epoxidized hydroxyl terminated polybutadiene (EHTPB) was synthesized from HTPB following the procedure of Latha et al.12. HTPB was epoxidized using performic acid generated in situ by the reaction of formic acid with hydrogen peroxide. 150 g of HTPB and 167 ml of hydrogen peroxide were added to a three necked round bottom flask containing 1.5 L of toluene and stirred well in a water bath at 25°C. Formic acid (112 ml) was added to this reaction mixture drop-wise over a period of 1 h. Drop-wise addition of formic acid is required to maintain the concentration of the acid in the medium as low as possible, which otherwise may open up the epoxy ring of EHTPB. It was then washed with water several times to remove excess acid, neutralized with sodium bicarbonate solution and finally dried over anhydrous sodium sulphate overnight. Toluene was distilled off from the resin under vacuum at 80°C using a flash evaporator. The resin obtained was finally dried under vacuum at 40°C. It has the epoxy value of 5-5.4 eqv/kg, Mw of 17,300 and Mn of 5800 (GPC).
The structures of the four epoxy resins used in the present study are shown in Fig. 2.1.

2.2. Synthesis of imide-diacids (IDAs)\textsuperscript{80,163}

\textit{N-(4-carboxyphenyl(trimellitimide)):} 13.7 g (0.1 mole) of 4-aminobenzoic acid was dissolved in 175 ml of distilled DMAc taken in a 500 ml three necked round bottom flask fitted with a condenser, mechanical stirrer and a CaCl\textsubscript{2} guard tube. To this 21.12 g (0.11 mole) of trimellitic anhydride was added over a period of 20 min under constant stirring and the reaction was continued for 3 h at room temperature. A small quantity of the reaction mixture was precipitated in water. It was filtered, dried and characterized to confirm the formation of amic acid. Then the temperature of the reaction mixture was raised to 70°C and 0.7 g (0.01 mole) of anhydrous sodium acetate was added. After the complete dissolution of sodium acetate, 12 ml (0.13 mole) of acetic anhydride was added drop wise under constant stirring. The reaction was continued for 13 h at 70°C under constant stirring to ensure the complete imidization. The reaction mixture was poured into 3 L of distilled water taken in a beaker under constant stirring. The imide-diacid which precipitated out was filtered, washed several times with distilled water till it was free from acid. It was then dried in air for two days and then in an air oven at 100°C for 6 h. Finally it was dried under vacuum at 60°C for 3 h. The imide-diacid was obtained as a white powder in 90% yield and is referred to as IDA-I. Using a similar experimental procedure, \textit{N-(3-carboxyphenyl)trimellitimide} (IDA-II) was synthesized by reacting 3-aminobenzoic acid with trimellitic anhydride. This compound was obtained as a white powder in 90% yield.
2.3. Synthesis of diimide-diacids (DIDAs)\textsuperscript{80}

2.3.1 From aromatic diamines

2,2-Bis[4-(4-trimellitimidophenoxy)phenyl]propane (DIDA-V):
Disodium salt of bisphenol-A, prepared through the reaction of
bisphenol-A with sodium hydroxide solution, was reacted with 4-chloronitrobenzene to obtain 2,2-bis[4-(4-nitrophenoxy)phenyl]propane which was reduced to the corresponding diamine using Raney Nickel catalyst and hydrazine hydrate in ethanol to obtain 2,2-bis[4-(4-aminophenoxy)phenyl]propane. Diimide-diacid viz., DIDA-V was synthesized through the reaction of the above diamine with trimellitic anhydride in 1:2 mole ratio in DMAC at room temperature followed by chemical imidization as detailed in the section 2.2.

Diimide-di acids such as methylene-bis[N-(4-phenylene)-4’-(carboxy)phthalimide] (DIDA-I), sulfuryl-bis[N-(4-phenylene)-4’-(carboxy)phthalimide] (DIDA-II), sulfuryl-bis[N-(3-phenylene)-4’-(carboxy)phthalimide] (DIDA-III) and oxy-bis[N-(4-phenylene)-4’-(carboxy)phthalimide] (DIDA-IV) were obtained through the reaction of trimellitic anhydride with 4,4’-diaminodiphenylmethane, 4,4’-diaminodiphenylsulfone, 3,3’-diaminodiphenylsulfone and 4,4’-diaminodiphenylether respectively in 2:1 mole ratio in DMAC followed by chemical imidization adopting the experimental procedure described in the Section 2.2.

2.3.2 From aliphatic diamines

Diimide-di acids from hexamethylene diamine and 4,7,10-trioxadodecanediamine were synthesized by reacting them with trimellitic anhydride (1:2 mole ratio) in DMAC followed by chemical imidization as per the procedure described in Section 2.2 and these diimide-di acids are referred to as DIDA-VI and DIDA-VII respectively.

2.3.3 From siloxane linkage containing diamine

Siloxane linkage containing diimide-diacid (DIDA-VIII) was synthesized by reacting 1,3-bis(3-aminopropyl)-1,1,3,3-tetramethyl-disiloxane with trimellitic anhydride in 1:2 mole ratio
followed by chemical imidization adopting the procedure described in Section 2.2.

2.4. Synthesis of monoitaconamic acid

11.88 g (0.06 mole) of 4,4'-diaminodiphenyl methane was dissolved in methyl isobutyl ketone (MIBK) in a 250 ml three necked round bottom flask, fitted with a magnetic stirrer. A solution of itaconic anhydride [5.6 g (0.05 mole)] in 20 ml of MIBK was added drop by drop maintaining the temperature of the flask at -12 to -10°C. After the addition of itaconic anhydride, the temperature was allowed to raise to room temperature. The product which precipitated out in the reaction medium was filtered, washed several times with MIBK and then with acetone to remove the unreacted diamine. The product was dried under vacuum at 60°C for 10 h. This monoitaconamic acid is referred to as MIA.

2.5 Synthesis of maleimidobenzoic acids

Maleimidobenzoic acids were synthesized through the reaction of 4- and 3-aminobenzoic acids with maleic anhydride in 1:1 mole ratio in acetone followed by chemical imidization as detailed in the Section 2.2 and they are referred to as MBA-I and MBA-II respectively.

2.6 Pre-reaction of epoxy resins with CTBN-L or CTBN-S

Liquid carboxyl-terminated butadiene-acrylonitrile copolymer (CTBN-L) and solid carboxyl-terminated butadiene-acrylonitrile copolymer (CTBN-S) were pre-reacted with excess amount of Araldite GY 250 or Araldite EPN 1138 prior to making the adhesive formulation of toughened epoxy-imide resins, in order to avoid the presence of
unreacted CTBN molecules, which may otherwise form a weak layer at the glueline.\textsuperscript{31}

Pre-reaction of CTBN-L with GY 250 or with EPN 1138 was carried out as follows. 0.05 g of triphenyl phosphine (TPP) (0.25 parts per 100 g of CTBN-L) was added to 100 ml of MEK taken in a 500 ml round bottom flask fitted with a water condenser, mechanical stirrer and a water bath. The temperature of the bath was raised to 80°C. On complete dissolution of TPP in MEK, 20 g of CTBN-L and 20 g of GY 250 or EPN 1138 were added to it under constant stirring. The contents were stirred for 6 h at 80°C. The excess MEK was partially removed under vacuum. The solid content of this solution was determined by evaporating a weighed quantity of the solution to constant weight in a hot air oven at 100°C. The completion of the reaction was confirmed by monitoring the acid value. The acid value of the pre-reacted resin was found to be nil. In the case of CTBN-S, it was masticated in a two-roll mill and cut into small pieces and dissolved in MEK to get approximately 20% solution. The solid content of this solution was determined following the procedure described above. Required quantity of this solution to get 20 g of CTBN-S was reacted with 20 g of GY-250 or EPN 1138 in presence of TPP following the procedure described above.

During the pre-reaction, the carboxyl group of CTBN undergoes esterification with epoxy group to produce epoxy-end-capped CTBN by epoxy-carboxyl addition reaction.

2.7 Synthesis of siloxane-imide-epoxy resin

Siloxane-imide-epoxy resin was synthesized by epoxidizing siloxane linkage containing diimide-diacid [DIDA-VIII].\textsuperscript{102-104} In a typical experiment 2 g (0.0034 mole) of DIDA-VIII was epoxidized by reacting it with 20.36 ml (0.2618 mole) of epichlorohydrin in presence of
0.07752 g (0.0034 mole) of benzyltriethylammonium chloride (catalyst) at 110°C for 45 min under nitrogen atmosphere. Hydrochloric acid formed in the medium reacted with the excess epichlorohydrin to form glycerol dichlorohydrin,\textsuperscript{102} which is water-soluble. The reaction mixture was washed several times with water to remove glycerol dichlorohydrin and HCl, if any, present in the medium. Toluene was added to the reaction mixture and the remaining epichlorohydrin/water\textsuperscript{102} was removed by distilling at 110°C, as the toluene and epichlorohydrin/water forms an azeotropic mixture. Finally the viscous resin was dried under vacuum for 6 h at 60°C. This resin is referred to as Glye-VIIIa. In a similar way Glye-VIIIb, Glye-VIIIc and Glye-VIIIId were prepared by reacting DIDA-VIII with epichlorohydrin in the mole ratios 1:100, 1:150 and 1:200 respectively.

### 2.8 Pre-reaction of siloxane-imide-epoxy resin

In a 100 ml three necked flask fitted with a magnetic stirrer, a condenser and 1.03 g of Glye-VIIIc having epoxy value of 1.75 eqv/kg, 0.51 g of siloxane epoxy resin, 0.5 g of amine-terminated polydimethylsiloxane and 0.5 g of 1,3-bis(3-aminopropyl)-1,1,3,3-tetramethyldisiloxane were taken in 10 ml of tetrahydrofuran. The flask was kept in a water bath and stirred at 63-65°C for 12 h. The prepolymer was characterized by GPC. It has $M_w$ of 20,000 and $M_n$ of 3900. This prepolymer was evaluated as atomic oxygen resistant coating and the details are given in the later part of this chapter.

### 2.9 Preparation of epoxy-imide polymers

Epoxy resin was mixed with imide-diacid/diimide-diacid in the required epoxy equivalent to carboxyl equivalent ratio and mixed thoroughly in a pestle and mortar and applied on a Teflon coated glass
cloth and it was folded in such a way that the mixture formed a layer between them. This was kept in between two Teflon sheets and cured in an air oven under contact pressure to avoid phase separation.

**Cure schedule:** The cure schedule was fixed based on DSC scan of epoxy resin-imide-diacid/diimide-diacid mixture. From the DSC data, the initial, maximum and the final cure temperatures ($T_{ic}$, $T_{max}$ and $T_{fe}$ respectively) were determined. The temperature of the oven was raised to $T_{ic}$ and maintained at this temperature for 30 min. The temperature of the oven was further raised to $T_{max}$ and maintained at this temperature for 1 h. Finally, the oven temperature was raised to $T_{fe}$ and the coupons were kept at this temperature for 30 min. The oven was allowed to cool to room temperature before the samples were removed.

Using a similar method adopted for the preparation of epoxy-imide polymers, epoxy-imide polymers containing siloxane linkages were prepared by the following three routes: (i) by reacting siloxane-epoxy viz., 1,3-bis(3-glycidyloxypropyl)tetramethyldisiloxane with diimide-diacid (DIDA-V) or monoitaconamic acid (MIA) or maleimidobenzoic acids (MBA-I/MBA-II), (ii) by reacting Araldite GY 250 with siloxane containing diimide-diacid (DIDA-VIII) and (iii) by reacting siloxane epoxy with DIDA-VIII. These epoxy-imide polymers were used for the thermal, spectral analysis and morphological studies. Wherever thick test specimens were required, they were made using Teflon mould of specific dimension to which the epoxy-imide mixture was transferred and cured under pressure.

**Epoxy-imide resins modified with reactive liquid rubbers:** Required quantity of EHTPB was mixed with Araldite GY 250/Araldite EPN 1138 followed by mixing with the required quantity of the imide curative. For CTBN-L and CTBN-S modified systems, Araldite GY 250/Araldite EPN 1138 pre-reacted with CTBN-L/CTBN-S was mixed with the required quantity of the corresponding epoxy resin (to obtain 10 phr of CTBN) and the imide curative. The modified systems were cured
following the cure schedule adopted for the corresponding unmodified systems.

2.10 Characterization

2.10.1 IR spectral studies

FTIR spectra of the mixture of epoxy resin and imide group containing curative (as a smear on an NaCl crystal) and that of the cured polymers (in KBr pellet) were recorded using Nicolet 510P FT-IR spectrometer. The instrument employed a pyroelectric detector, which scanned the samples in the form of smear on NaCl plate or as KBr pellets, and generated the spectra depicting percentage transmittance versus wave number, by averaging 32 scans at a resolution of 4 cm⁻¹.

2.10.2 NMR spectral studies

¹H-NMR spectra were recorded at 300 MHz on a Brucker Avance 300 spectrometer and at 400 MHz on a Brucker AMX 400 spectrometer. ¹³C-NMR spectra of the samples were recorded on a Brucker AMX 400 and a Brucker Avance 300 spectrometer operating at 100 MHz and 75 MHz respectively. Samples were run as a solution in deuterated solvents such as CDCl₃, DMF-d₇ and DMSO-d₆ in 10/5 mm tubes at room temperature with an accumulation of 1000 to 5000 scans as necessary to obtain adequate signal/noise ratio. Gated decoupling technique was used for quantitative analysis. All chemical shifts were reported with respect to internal tetramethylsilane standard.

2.10.3 Elemental analysis

Percentages of carbon, hydrogen and nitrogen present in different compounds were determined by a Perkin Elmer Elemental Analyzer (Model PE 2400). The analysis is based on the flash dynamic catalytic
combustion of samples to simple gases. The system uses a steady state wave-front chromatographic approach to separate the mixture of gases. The separated gases are detected as a function of thermal conductivity.

2.10.4 Chemical analysis

Epoxy value of different epoxy resins, acid value of different imide acids/diimide-diacids, and hydroxyl value of toughening agents were determined using various chemical methods.

2.10.4.1 Determination of epoxy value

Epoxy value was determined using pyridine hydrochloric acid method. A known weight of epoxy resin was refluxed with a known excess of pyridinium hydrochloride in pyridine (0.1N) at reflux temperature for 1 h. During heating all epoxy rings present in the sample were opened up by pyridinium hydrochloride, and the amount of unreacted pyridinium hydrochloride was estimated by titrating the cooled mixture against NaOH (0.1N) using phenolphthalein as an indicator. Thus, the number of epoxy equivalents present per kg of the sample was calculated as shown below.

\[
\text{Epoxy value} = \frac{\text{Volume of NaOH} \times \text{Normality of NaOH}}{\text{Weight of the sample in kg}}
\]

2.10.4.2 Determination of acid value

Acid value of a monomer or a polymer sample was determined by dissolving the sample in a previously neutralized toluene/methanol mixture or in DMSO and titrating it with standard alcoholic KOH solution (0.1 N) using cresol-red indicator. At the end-point, the colorless
acid solution turned to wine red color. Acid value of the sample was calculated as mg KOH/g by using the following equation,

\[
\text{Acid value} = \frac{\text{Normality of KOH} \times \text{Volume of KOH} \times 1000}{\text{Weight of the sample in g}}
\]

### 2.10.4.3 Determination of hydroxyl value

A known weight of the sample was refluxed with a known excess of acetic anhydride in pyridine (1:8 mole ratio) for 3 h in a water bath. During heating hydroxyl groups present in the sample were acetylated. Unreacted acetic anhydride was then hydrolyzed and determined by titration with NaOH (0.5N) using phenolphthalein indicator. Hydroxyl value of the sample in mg KOH/g was calculated by using the following equation,

\[
\text{Hydroxyl value} = \frac{\text{Normality of KOH} \times 56.1 \times \text{Volume of KOH} \times 1000}{\text{Weight of the sample in g}}
\]

### 2.10.5 Determination of molecular weights

Molecular weights were determined by GPC with Waters ‘Alliance’ instrument using HR1 and HR2 microstyrage columns and THF as the eluent with a flow rate of 1 ml/min. Waters 410 RI detector was used. The molecular weights reported are based on polystyrene standards.\(^{166}\)

### 2.10.6 Thermal analysis

Thermo-analytical techniques were used to study the chemical transformations like curing, phase changes like melting and glass transitions, and thermal stability of the different polymer systems.
2.10.6.1 Differential scanning calorimetry

The cure characteristic of different resin systems were studied using differential scanning calorimetry (DSC). A Mettler DSC-20 analyzer with aluminium sample pans was employed at a heating rate of 10°C/min from ambient temperature to 350°C, in nitrogen atmosphere or in air. The dynamic DSC curve of epoxy resin-curative mixture was obtained as a plot of heat of the reaction versus temperature. The temperatures corresponding to initiation \(T_i\), peak or maximum \(T_{\text{max}}\) and completion \(T_{\text{f}}\) of cure were noted from the thermograms. The glass transition temperature \(T_g\) of the cured epoxy-imide samples were determined by DSC.

2.10.6.2 Thermogravimetric analysis

Thermogravimetric analysis (TGA) was performed on a DuPont 900 thermal analyzer in conjunction with 951 TGA unit at a heating rate of 10°C/min under nitrogen atmosphere over a temperature range of 30°C to 900°C. The thermo-balance operates on null balance principle with a sensitivity of 2 micrograms and an accuracy of 1%. The non-isothermal thermograms were recorded as the plot of mass of the sample versus temperature. The temperatures corresponding to initial \(T_i\), maximum \(T_{\text{max}}\) and final/end \(T_f\) decomposition, as well as percentage char yield were obtained from the thermograms.

2.10.7 X-ray diffractometry studies

X-ray diffraction (XRD) patterns were recorded on a Philips 1729 instrument using Cu-K\(\alpha\) radiation with nickel filter and PW 1710 diffractometer control unit.
2.10.8 Morphological Studies

Morphology of fractured surfaces of toughened epoxy-imide resins was examined using scanning electron microscopy (SEM). A Hitachi Model S-2400 SEM was used. This instrument has a resolution of 4 mm at an accelerating voltage of 25 KV and ultimate vacuum of $10^{-7}$ torr. The specimen surface was made electrically conductive by coating a thin layer of gold using the plasma vapor deposition technique in a Fine Coat Ion Sputterer JF-1100. A fine electron beam is scanned across the surface of the sample in synchronization with the beam in a cathode-ray tube. The signal produced by the scattered electrons modulates the beam in the cathode-ray tube, producing the image.\(^{168}\)

2.11 Evaluation of adhesive properties

2.11.1 Surface preparation of stainless steel coupons

AlSI-304 cold roll stainless steel coupons of dimensions 100 mm x 25 mm x 1.6 mm were used. Stainless steel coupons were first degreased by wiping with acetone/n-hexane. The area to be bonded was abraded with emery paper No. 36 and cleaned with detergent and tap water. It was then chemically etched using chromic acid solution (36 g of saturated solution of sodium dichromate in 100 g of conc. H$_2$SO$_4$) for 60 min at 60°C as per ASTM D 2651. Coupons were then thoroughly washed with tap water to remove all traces of acid. The effectiveness of the surface was checked by waterbreak-free test, in which properly cleaned surface will hold a continuous film of water rather than a series of isolated droplets. The coupons were dried in an air oven at 110°C for 1 h, cooled to room temperature and then used for bonding. The whole process of cleaning, etching and drying were carried out just prior to adhesive
application in order to ensure the availability of freshly prepared metallic oxide surface for bonding.

2.11.2 Evaluation of adhesive lap shear strength (LSS) of bonded coupons

Lap shear test involves two adherends (substrates) which are overlapped by a certain length (Fig. 2.2). The adhesive forms a layer between the overlap area. All lap shear tests were performed in tension until failure. The lap shear test which is used in common for metallic substrates is the single lap test.

![Fig. 2.2. Assembly of stainless steel coupons for the evaluation of lap shear adhesive strength](image)

LSS was determined as per ASTM D-1002 using stainless steel coupons of dimensions 100 mm x 25 mm x 1.6 mm. The epoxy resin - IDA/DIDA mixture was applied on cleaned stainless steel substrates and the steel coupons were then bonded in such a way that the bonded area was approximately 300 mm². The bonded coupons were kept in an air oven under a contact pressure and cured following the cure schedule as described in section 2.9. The stainless steel coupons were destructively tested in a Universal Testing Machine (UTM) (Instron Model No. 4549) at a cross-head speed of 10 mm/min. Knowing the failure load (L) in kg and
bonded area (A) in cm\(^2\), the LSS of the joint in MPa can be calculated as 

\[(L/A) \times 0.098\]. Tensile lap shear strength at 100°C, 125°C and 150°C was measured after equilibrating the test coupons at the required temperature for a period of 10 min in a hot chamber attached to the Instron. To obtain lap shear strength value at a particular temperature, five bonded coupons were tested. LSS value reported is an average of at least three measurements, which fell in the range of ± 1 MPa.

2.12 Evaluation of epoxy-imides as matrix resins for composites

2.12.1 Preparation of unidirectional (U.D.) composites

U.D. composites were made using E-glass fiber as the reinforcement and epoxy-imide resin as the matrix resin. The fiber and the resin were taken in such a way to adjust the resin content to 40 wt.% of the total weight of the composite. Araldite GY 250/EPN 1138 was pre-reacted with DIDA-V in the required equivalent ratio in MEK/DMAc (8:1 by volume) at 70°C for 6 h. Glass fibers were impregnated with the above solution. The calculated number of tows of glass fiber were impregnated with the above solution and dried overnight under inert atmosphere at room temperature. It was then dried for 8 h at 40°C and for 8 h at 70°C under vacuum to remove solvents completely. The prepreg strands were then stacked together and compressed in a mould of dimension 18 cm x 0.6 cm x 0.3 cm under a pressure of 2 MPa and cured in a hydraulic press of capacity 35 MPa and a platen area of 0.3 m\(^2\) at desired temperatures to obtain the U.D composite. The moulded composite was cut using a diamond wheel cutter into specimens of the required dimensions for interlaminar shear strength (ILSS).
2.12.2 Testing of unidirectional composites

The U.D. composites were tested for their inter laminar shear strength (ILSS) using UTM (Instron, Model 4202). The ILSS test may produce a relative displacement between the two laminae in the laminate along the plane of their interface. The ILSS of the U.D. composites was determined at room temperature as per ASTM D 2344, in an Instron using specimens of size 30 mm x 6 mm x 3 mm. The test specimens were end-rested on two supports with a span to thickness ratio of 5 and centre-loaded at a cross-head speed of 1.3 mm/min. Five specimens were tested in each case and the average value of these five was taken. ILSS was calculated using the equation,

\[ \text{ILSS (MPa)} = \frac{(0.75 \times 10^{-6}) P}{bd} \]

where P-breaking load in N, and b and d are width and thickness of the specimen (in meters) respectively.

2.13 Evaluation of siloxane containing epoxy-imide polymers as atomic oxygen resistant (AO) coatings

2.13.1 Preparation of coatings

10 % solution of siloxane containing epoxy-imide polymer was applied on unaluminized side of a Kapton film (125 µm) of dimension 30 mm x 25 mm using a brush. This procedure was repeated until the coating thickness of about 5 µm was achieved. The coating was allowed to stand at room temperature in a dust-free environment for 24 h and then dried at 35°C for 8 h and at 45°C for 5 h. Then, it was kept under vacuum at 50°C for 5 h, 80°C for 5 h and then at 120°C for 6 h. Keeping the coating at 120°C was essential to get a tack-free coating.
In a similar way, quartz plate, C-polyimide composite, glass polyimide composite and aluminized Kapton of 25 μm thickness were coated with siloxane-containing epoxy-imide polymer.

2.13.2 Exposure of uncoated and coated samples to atomic oxygen

Uncoated Kapton (125 μm), aluminized Kapton, C-polyimide composite and glass-polyimide composite, and epoxy-imide coated samples were exposed to AO in a plasma barrel system (March Plasmod Plasma Barrel System) operating at RF frequency of 13.56 MHz and 75 Watts current input. The system was operated under oxygen flow of 7.23 standard cubic centimeter per min (SCCM). The mass loss of all the samples was measured at different time intervals using a Mettler Toledo balance and exposure of the samples to air during weighing was kept to the minimum to prevent rehydration. From the mass loss of the uncoated Kapton film atomic oxygen fluence, i.e., total number of incident atomic oxygen per unit area expressed in atoms/cm² can be calculated using the equation,

\[ \text{Fluence (F)} = \frac{\Delta M}{A \cdot \rho \cdot E} \]

where \( \Delta M = \) initial mass of the sample – mass at that time of measurement (in g), \( A = \) area in cm², \( \rho = \) density in g/cm³ and \( E = \) erosion yield in cm³/atom. Erosion yield of Kapton (polyimide) as obtained from AO exposure study in space environment is \( 3 \times 10^{-24} \text{g/cm}^3 \). Density of Kapton is 1 gm/cc. From these measurements the fluence for a given period of exposure can be calculated by substituting the above values.
The mass loss of the coated and uncoated samples were plotted against the atomic oxygen fluence.

2.13.3 Surface analysis

Surface analysis of the uncoated and coated samples before and after exposure to atomic oxygen was carried out using SEM following the procedure described in the Section 2.10.8 for morphological studies.