CHAPTER 2

LITERATURE REVIEW

This chapter describes the literature survey of the existing knowledge on the different space environment conditions and its interaction with materials, different classes of materials which are currently in use for space vehicle structures and also its performance weaknesses towards space environmental hazards. A critical review has been performed in selection of matrix phase and different methods in developing multifunctional nanocomposite for space application.

2.1 Reviews of international status

Polymeric and polymer based nanocomposite materials has been widely employed as structural raw material in the aerospace sector as it possess high strength to weight ratio, high toughness, low co-efficient of thermal expansion, resistance to stress corrosion cracking, better structural rigidity and ease in processing polymeric materials. Wright et al., (1991), studied and reviewed in detail the applications of polymers in aerospace technology sector, which embraces all kinds of textile based, organic and inorganic fiber reinforced polymer composite, high temperature polymer surface coatings and high performance adhesives and also all categories of nanofillers reinforced multifunctional nanocomposite materials. There is an increase in demand for light weight, multifunctional spacecraft structural materials which does not compromise its performance even at surviving in the hazardous environmental conditions such as high vacuum, thermal cycling, ionizing and penetrable space radiation, atomic oxygen erosion, micrometeoroids and space debris impacts (Huang et al. (2002); Xu et al., (2011); He, (2008)). Outgassing effect has constantly been an apprehension for polymeric materials under hard vacuum and thermal cycling it may also induce variations in material elemental composition, structural dimensions, and eventually decrease the performance effectiveness of the polymers
(Grossman et al., 2003). These outgassing contaminants get condensed on the surface of sensitive complex spacecraft components and triggers corrosion in surface materials and also induce pollution, these damages affects the functionality of those affected components and at times even lead to material failures (Schlappi, 2010). It can also cause significant structural alteration that would easily distress the performance functionality and durability of the subtle modules and jeopardize the astronaut’s lives in the spacecraft (James et al. (1992); Zhang et al. (2002); Wang et al. (2011)). Cynthia L. Lach et al., (1992) investigated the influence of temperature and gap opening rates on the efficacy of elastomeric O-ring present in the solid rocket booster system of the “Challenger” space shuttle. As this deformation failure of the O rings instigated the explosion. This made researchers to build thorough understanding on material behavior (failure, aging mechanism, stability etc.) before selecting the materials for extreme service conditions.

Real time space flight real time experimentation and exposure of spacecraft materials to specific environment and analyzing its performance during space missions are really critical and also expensive. Similarly, the spacecraft materials designer must have a thorough knowledge about the different types of space environmental hazards present in the near earth and deep space environments and also its interaction with the spacecraft materials. This familiarity facilitates suitable selection of raw materials to exploit its performance functionality, increased mission duration, deep space exploration and condensed risk factors. David et al., (2010), offered an approach for evaluating the performance functionality of different classes of materials (limited to a definite spacecraft or mission), which in turn delivered an outline of different space environmental effects on spacecraft materials performance. Miller et al. (2010) concisely conveyed the degradation effect experienced by spacecraft materials during several space
missions. They also compared the ground simulation and real time space flight data in order to envisage the durability study of materials as well as simulated results. National Aeronautics and Space Administration (NASA, 2008) and European space agency (ESA) Meshishnek (1995), established stipulations for selection of polymer materials and Fayazbakhsh et al., (2010), offered a scheme for selecting materials for space applications considering the outgassing effect. These critical studies have significant inferences for the research and development on spacecraft materials technology, as well as the selection and performance assessment of aerospace polymer composite materials. The various space environments and its effects on spacecraft materials will be discussed in forthcoming chapter, which also addresses the critical evaluation and selection of high performance thermoplastic nanocomposite materials for deep space application.

2.2 Space environment and materials

The space environment extends from the minimum altitude of 160 km from Earth's surface. From the beginning of the Earth's atmosphere, transient through the outer space and planetary atmospheres are considered as space environment. International Astronautic Federation (IAF) did a rough separation of terms: aeronautics (aerodynamic flight) and astronautics (space orbital flight) based on altitude difference which is 100 km, known as the Karman line. The two factors which control the space environment are the Earth and the Sun while the other factor is planets specific spacecraft missions. Before space exploration was born in early 1970s, the outer space was considered to be filled with asteroids, meteors, comets and other celestial objects which confirmed the existence of a distinctive space environment above the earth surface. The commercial jet usually operates at an altitude of ~5-10 km above sea level that interacts with the atmosphere present at this altitude. The spacecraft interacts with its harsh space environment at an altitude above ~100 km above sea level. The knowledge about the harsh space environment
interaction with spacecraft has been studied based on the structural damages and failures occurred during numerous space missions. A footstep towards modern space explorations was started during the successful launch of SPUTNIK in 1957. The EXPLORER 1 space vehicle confirmed the existence of Van Allen belt (trapped protons and electrons) circles around the Earth which can be considered as a leap towards the study of space radiation interaction with materials. This led to the progress in radiation shielding effectiveness of the material and electronic components. MARINER space mission vehicle’s missing star tracker lock outlined to particulate contaminants presence, GEMINI space mission vehicle’s windows contamination was due to silicone rubber window gaskets, Effect of the spacecraft surface charging in GEO environment which affected ROSEN space mission vehicle paved way for developing simulation codes by the NASA charging and analysis program (NASCAP) and also for launching SCATHA spacecraft in order to study the effects of spacecraft surface charging occurrences.

During the period of 1980s, atomic oxygen erosion effect over spacecraft structural materials has been identified as a threat to spacecraft and compelled to build ground simulation facility for simulating and studying the behavior of the materials in simulated LEO and GEO environment (Daniel Hastings et al. 2004). In the period of space shuttle age, researchers found that the STS-3 space shuttle surface was shining luminously as shown in figure 1 and the material surface erosion was high during its travel through LEO environment which was due to the effect of high velocity atomic oxygen flux interaction with space shuttle structural materials such as kapton (Banks et al., 2004). Since the construction of the International Space Station (ISS) in LEO, many technological research works have been attempted in testing the diverse space environment effect on different materials. Polymer Erosion and Contamination Experiment (PEACE) has tested 40 different thin film polymers that are exposed to the LEO space environment conditions
by placing it in the exterior of the ISS (for 4 years) as a shared work of Materials International Space Station Experiment 2 (MISSE 2).

Figure 2.1: Space Shuttle illumination due to atomic oxygen interaction (Banks et al., (1989); Banks et al. (2008)).

The MISSE 2 PEACE precisely determined the AO erosion yield of different polymeric materials after prolonged exposure to the LEO space environment (de Groh et al., 2006). The dehydrated pre-flight and post-flight mass and precise density measurements of the exposed materials were employed to define the accurate atomic oxygen high fluence ($8.43 \times 10^{21}$ atoms/cm$^2$) erosion yield data. The future of spacecraft structural materials estimated to be made space durable, lighter in weight, reusable and reprocessable, superior performance with longer service life time, radiation shielding effectiveness, excellent damage tolerance and high thermal stability, surface charging and atomic oxygen erosion resistant.

2.2.1 Classification of different Space Environment

The space environmental effects experienced by space vehicle are usually a mixture of natural space environment (based on orbits) and artificial environment (created by the spacecraft itself). The space environments can be characterized based on the constituents present: the neutral thermosphere, the plasma (Banks et al., 1989), the high energy radiation
and the particulate atmosphere (Adam J.H, 1982). The neutral thermosphere comprised of ambient gas molecules and molecules that are outgassed by the spacecraft structural materials. The plasma environment consists of neutral particles, ions and electrons.

This plasma is formed by ionization of molecules or charge interchange with the neutral gas. The radiation environment has been separated into two components as both are a fusion reaction by-products from Sun, one is electromagnetic (EM) radiation and the other is charged particle radiation. The EM radiation environment includes the solar photon flux (reflected and emitted) from the planet Earth, and the electromagnetic interference (EMI) generated by the spacecraft systems or due to plasma arcing. The charged particle radiation environment consists of the solar wind and flares, Galactic cosmic rays (GCRs), the Van Allen radiation belts having an ambient flux of high energy charged particles such as electrons, protons, heavy ions, neutrons and also alpha rays, beta and gamma rays. The particulate environment consists of micro meteoroids, orbital debris, and degraded contaminants released by the spacecraft.

The space environment can also be defined by the orbital boundary based upon planet earth such as Lower earth orbit (LEO), Medium earth orbit (MEO) and Geosynchronous earth orbit (GEO) also based upon the gravitational field of earth, altitude and the type of environment present. The harsh space environment interactions with the spacecraft were collective effect of all the orbital environmental paths. The characteristics of the five orbits are listed in Table 2.1. Before discussing the various space radiation hazards, a brief description must be detailed for both the Sun and Earth’s atmospheric conditions which are the principal source for space environmental conditions in our solar system.
Table 2.1: Classification of space environment based on Orbits

<table>
<thead>
<tr>
<th>Orbit</th>
<th>Altitude (km)</th>
<th>Types of constituents present</th>
</tr>
</thead>
</table>
| LEO   | 100-1000     | • Ultraviolet radiation (UV) emitted from the Sun  
|       |              | • Naturally originating micrometeoroids from asteroid belt, planetary collisions and comets (Tennyson, R. C. 1997).  
|       |              | • Ionosphere: Ionized molecules due to X-rays and UV  
|       |              | • Atomic oxygen fluence  
|       |              | • High vacuum ($10^{-3}$ to $10^{-9}$ Torr)  
|       |              | • Solar flares  
|       |              | • Key source of incident ambient plasma  
|       |              | • South Atlantic Anomaly (SAA) - Auroral zone  
|       |              | • Cosmic rays |
| MEO   | 1000-36000   | • Intense UV radiation  
|       |              | • Plasma environment  
|       |              | • Trapped high energy radiation belt |
| GEO   | >36000       | • Plasma sheet  
|       |              | • Outer trapped radiation belt  
|       |              | • Solar storms, solar flares and solar events  
|       |              | • Charged particle radiations  
|       |              | • Galactic Cosmic rays  
|       |              | • Plasma environment induced surface charging |

2.3 The Sun and space environment

The Sun is a little yellow dwarf star out of billions of stars in our galaxy. It is made of helium, hydrogen (major constituents), iron, oxygen, and carbon. The Sun is driven by nuclear fusion reaction of hydrogen and it’s a G-type main sequence star with a core temperature of roughly several millions of degree Celsius (Kivelson and Russell, 1995; Baker, 2002).
At such high temperatures, the Sun is physically in the plasma phase. The major impact of the Sun on the space environment is through emission of electromagnetic flux and the solar particle flux. The Sun emits the fusion reaction ensuing energy in the form of electromagnetic radiation across the whole electromagnetic spectrum, from exceedingly high energy cosmic rays to long wavelength radio waves as shown in figure 2.2.

![Electromagnetic spectrum and diverse radiations](image)

**Figure 2.2:** Electromagnetic spectrum and diverse radiations

Typically, the solar particle flux (plasma emission) can be classified as higher energy plasma bursts and inconstant lower energy plasma. The former is related with the solar flares, Coronal mass ejection (explosion of Sun’s plasma and magnetic field) and proton events. The latter corresponds to the solar wind and also co-rotating interaction regions (interaction between the fast and slow solar wind). The Sun holds a strong magnetic field which makes charged particles (protons and electrons) to move away from it at speeds of 290 to 690 km/s. This stream of charged particles moving off from the Sun is called the *solar wind*. Sporadically bursts of charged particles are called *solar flares*. The solar wind controls the interplanetary environment and can straight reach to the GEO environment and also for other orbits through geomagnetic
activity. The variation in the solar activity such as Sun spot cycle also affect the space environmental changes, the disparities are deceptively associated to rise in the extreme ultraviolet (EUV) radiation emission from the Sun and surge in geomagnetic activity connected to solar wind variations. Sun spots are dark coloured cooler regions of the Sun which are related to the amplified Sun’s magnetic field. In the solar activity, solar maximum (highly active) designates extreme numbers of Sun spot occurrences in the Sun and cause outbreak of solar flares and the vice versa is solar minimum (less active). The emission of charged energetic particles combined with variations in EUV flux are the reason behind rise in the atmospheric temperature which usually occurs during solar maximum (Daniel Hastings et al., 2004).

2.4 The neutral earth’s atmospheric conditions

There is a momentous variation in temperature and pressure with increase in the altitude, which define a number of atmospheric layers from the earth’s surface as shown in figure 2.3. These include the condensed layer of troposphere (0 to 20 km) which encompasses nitrogen (78%), oxygen (21%), moisture and the tropopause separates it from the stratosphere. The dry and less condensed stratosphere (20 to 50 km) is composed of ozone molecules and the temperature rises due to absorption of UV radiation. Similarly, the stratopause region divides the stratosphere and mesosphere. The mesosphere (50 to 80km) is coldest region (-100 °C) and thermosphere (80 extends to 640 km and 1000 km) the temperature is high but still not sensed due to low atmospheric density. In the troposphere and mesosphere, temperature generally falls with increasing altitude, whilst in the stratosphere and thermosphere, temperature rises with increasing altitude. Further, ionosphere consists of ions where the aurora (variable patterns of light) occurs. The exosphere region originates from the thermopause and spreads to the deep
space which comprises of hydrogen and helium at low concentrations and some photo-
dissociated atomic oxygen molecules near the extremity of this region.

![Diagram showing atmospheric regions]

**Figure 2.3:** Different atmospheric regions with respect to the altitude.

In the case of molecules presence in various atmospheres, the uppermost thermosphere
typically embraces oxygen ($O_2 = 32\%$), argon ($Ar = 39\%$), nitrogen ($N_2 = 28\%$), atomic oxygen
($O = 16\%$), helium ($He = 4\%$) and atomic hydrogen ($H = 1\%$). The LEO environment consists
of mainly atomic oxygen elements with traces of $N_2$, atomic $H$, $He$, atomic $N$, and argon. The
figure 2.4 graphically portrays the variations in the concentration of gaseous molecules
depending upon the increase in the altitude. The spacecraft travelling at a speed of 28 km/hr
when interacts with these molecules produces sufficient energy to erode the spacecraft surface of
the material though intense physical or chemical reactions.
Earth’s gravitational force ($9.8 \text{ m/s}^2$) dominates the effect of free falling on objects present in earth. Above earth’s surface, spacecraft entering deep space are being influenced only by the gravitational pull of the Sun and the moon.

The Earth’s magnetosphere protects the earth’s surface and the orbiting spacecraft from harmful high energy charged particles originating from solar flares and solar wind. The charged particles entering at the cusp of north and south magnetic poles experiences collision with the earth’s atmosphere which resulted in formation of aurora. This magnetosphere and interplanetary magnetic field indirectly manages the effect of charge particle and solar events interaction with the spacecraft also cause geomagnetic storm. The combined effect of earth’s atmosphere and the Sun are the prime source for the major space environmental hazards such as hard vacuum, atomic oxygen, UV radiations, ionizing high energy radiations, plasma and micrometeoroids and orbital debris impact on spacecraft materials are to be discussed in forthcoming sections.

2.5 Major space environmental hazards and its effect of materials

2.5.1 High Vacuum

The pressure decreases with increase in altitude due to the thinning of air at higher altitudes. The atmospheric pressure at sea level is 760 Torr (1 Torr = 1.3 mbar) which decreases
to deep space vacuum pressure of $10^{-3} – 10^{-9}$ Torr with increase in altitude. The table 2.2 (a) interprets various vacuum level ranges present. The hard vacuum causes outgassing effect which refers to the trapped volatiles emission being released from the surface of the spacecraft structural and typical electronics components. The pressure difference between the inner materials bulk and the outer part induces a pressure lag inside the materials and leads to desorption of trapped molecules from the surface of these materials (Jianguo Huang, 2015). The outgassing effect is controlled either by outgassing resistant property of materials itself or by providing escaping path arrangements being made for outgassing the volatiles. The main impact of outgassing effect are the spacecraft surface contamination, loss in the dimensional stability and other damaging consequences on material performance and its properties. Sometimes, the outgassed volatiles get deposited and contaminate the line of sight section in the spacecraft exteriors and affect their optical property that also degrades the performance of nearby delicate functional devices. The intensified contamination problem ensues when the contaminants interact with other space environmental hazards such as atomic oxygen, ultraviolet radiation and thermal cycling effect and also due to high temperature and moisture. Additional problem generated by harsh vacuum is cold welding of mechanical parts that have very minute parting among them.

**Table 2.2 (a):** Vacuum level ranges (Karl 2016)

<table>
<thead>
<tr>
<th>VACUUM RANGE</th>
<th>LEVEL (torr)</th>
</tr>
</thead>
<tbody>
<tr>
<td>Low Vacuum (Rough)</td>
<td>760 to 25</td>
</tr>
<tr>
<td>Medium Vacuum (Rough)</td>
<td>25 to $1 \times 10^{-3}$</td>
</tr>
<tr>
<td>High Vacuum (Hard)</td>
<td>$1 \times 10^{-3}$ to $1 \times 10^{-9}$</td>
</tr>
<tr>
<td>Ultra High Vacuum</td>
<td>$1 \times 10^{-9}$ to $1 \times 10^{-12}$</td>
</tr>
<tr>
<td>Extremely High Vacuum</td>
<td>$&lt;1 \times 10^{-12}$</td>
</tr>
<tr>
<td>Outer Space</td>
<td>$1 \times 10^{-6}$ to $&lt;3 \times 10^{-17}$</td>
</tr>
</tbody>
</table>
The cold welding occurs when two similar or dissimilar metals fuse together under high vacuum condition. It is due to the formation of solid state metallic bonding between them. This type of welding is possible only on contamination free metal surfaces. The susceptibility of material to cold weld depends on limited separation distance between mechanical parts and also dependent upon compressive stresses between mating surfaces, temperature, abrasion and time. The liability of dissimilar metals to cold weld is enhanced by similarity in their crystal structures and atom sizes and also due to mutual solubility (Dursch et al. 1991).

As the temperature increases mobility of the polymer chains also increases and the weaker polymer bonds undergo scission reaction and cause outgassing. Polymers possessing high crosslink density, no volatile organic compound (VOC) emission, presence of polymerizable monomers presence and high molecular functionality possess better outgassing properties.

**Table 2.2 (b): Outgassing properties of selected polymers (Campbell, 1984)**

<table>
<thead>
<tr>
<th>Material</th>
<th>Trade Name</th>
<th>Application</th>
<th>TML (%)</th>
<th>CVCM (%)</th>
</tr>
</thead>
<tbody>
<tr>
<td>Polybenzimidazole (PBI) [in water]</td>
<td>CELAZOLE</td>
<td>Bearings</td>
<td>2.50</td>
<td>0.00</td>
</tr>
<tr>
<td>Polyetherimide (PEI)</td>
<td>ULTEM</td>
<td>Interiors</td>
<td>0.40</td>
<td>0.00</td>
</tr>
<tr>
<td>Polyimide</td>
<td>KAPTON</td>
<td>Thermal insulation</td>
<td>1.30</td>
<td>0.02</td>
</tr>
<tr>
<td>Polyamideimide (PAI)</td>
<td>TORLON</td>
<td>Spacers</td>
<td>0.58</td>
<td>0.00</td>
</tr>
<tr>
<td>Polyethylene Terephthalate (PTFE)</td>
<td>ERTALYTE</td>
<td>Wire sleeve</td>
<td>0.13</td>
<td>0.00</td>
</tr>
<tr>
<td>Epoxy</td>
<td>Araldite AV100</td>
<td>Adhesive</td>
<td>0.78</td>
<td>0.14</td>
</tr>
</tbody>
</table>
For most metals, sublimation losses will be negligible. However, the exclusion of surface oxygen may be beneficial to the mechanical properties in some cases. In some instances, oxide films can move into emerging cracks and thus encourage crack growth and crack propagation (Henry, 1969). Banks et al., (2008), expressed silicone contaminants when interacted with the atomic oxygen forms a stable SiO$_2$ which is an intense contaminant layer. Campbell et al., (1984) assessed the outgassing properties of numerous organic and inorganic materials for their outgassing properties using ASTM Test Method E 595-84. The evaluation was performed on a small sample (approximately 200 mg cut into very small pieces) heated to 125°C for 24 hours in a vacuum of $10^{-6}$ to $10^{-7}$ Torr with the vacuum-condensable materials collected on a 25°C copper collector. The outgassing property of materials has been measured based on the collected volatile condensable materials (CVCM), total mass loss (TML), and the water vapor regain data. The outgassing properties of typical spacecraft materials are shown in Table 2.2 (b). All non-metallic materials must fulfill requirements of TML % and CVCM % values under 1 % and 0.1 % respectively are acceptable for aerospace application as per ASTM-E595 (ASTM. 1993) or equivalent procedure specified in ECSS-Q-70-02A (ECSS (2000); Lobascio et al. (2003)).

2.5.2 Thermal Cycling

The spacecraft temperature fluctuates as it arrives and departs from the earth's atmosphere. The atmospheric temperature at altitudes from 180 to 500 km is typically greater than 200 °C (denotes complete Sun exposure) but, due to the exceedingly low atmospheric pressures at LEO altitudes, spacecraft undergo slight conductive heat transfer.
Figure 2.5: Post-flight picture displays failure of thin film samples from the MISSE-4.

The spacecraft’s temperature in the LEO is principally reliant on the loss or gain of solar radiant energy received from the Sun’s radiation, reflected solar radiation from Earth surface (albedo), and Earth's atmosphere emitting out long wave solar radiation (Kent A. Watson, 2003). Throughout the 90 minutes LEO cycle, the spacecraft surface temperature oscillates from -100 to +90 °C and the maximum fluctuation is from -120 to +120 °C. In GEO, the temperature fluctuation is superior within the range of -150 to +150 °C. These variations will straight away affect the polymer bulk and bond strength of the polymeric material, and also initiate cracks, stress concentrations, thermal degradation and ageing (Hancox, 1998). Pochiraju, et al. (2008), modeled the thermo-oxidative behavior in high temperature polymer matrix composite (HTPMC) materials which aged at 288 °C for about 1864 hrs. After thermal ageing, the polymer composite exhibited interstitial matrix cracking perpendicular to fiber ends. Thermal cycling can also exaggerate the micro cracking in the graphite/epoxy composite initiated by the UV radiation exposure (W B. Liau, 1998). The difference in the CTE of substrate and the coating material or two dissimilar materials may lead thermal cycling effect and also synergistic effect along with AO which in turn generates micro cracks and failure as shown in figure 2.5. High performance thermally stable polymer based structural materials are required in order to overcome these effects. Thermal cycling also induces outgassing effect in the surface of the spacecraft materials.
2.5.3 Atomic oxygen

Spacecraft in LEO encounter a low-density atmosphere consisting predominantly of most reactive atomic oxygen and helium (Judith C. Yang, 2010). The UV radiation with wavelengths of 100 to 200 nm from the Sun, cause photo dissociation of oxygen (O\textsubscript{2}) molecule into highly reactive and unstable atomic oxygen (O) species in the ionosphere region. The AO density varies with the increase in the altitude. It is densely populated in the region of 150 to 500 km range (density = 1 x 10\textsuperscript{10} to 1 x 10\textsuperscript{7} atoms/cm\textsuperscript{3}) as shown in figure 2.6. At an altitude above 1000 km range (density = 1 x 10\textsuperscript{2} to 1 x 10\textsuperscript{6} atoms/cm\textsuperscript{3}) AO decreases in with increasing altitude, while other gaseous elements (atomic hydrogen and nitrogen) are negligible. Although the concentration of AO in LEO is low (pressures of ~ 10\textsuperscript{-7} torr), the high orbital velocity (7.8 km/s) of spacecraft in LEO environment causes the AO flux on ram orientated spacecraft surfaces to be very high with collisional energies of ~5 eV (480 kJ/mol) (Peters, Linton, and Miller, 1983; Gull et al., 1985; Peters, Gregory, and Swann, 1986). Surface erosion was seen on ram or front facing spacecraft surfaces of numerous categories of materials.

![Atomic Oxygen Flux, atoms/cm\textsuperscript{2} \cdot s\textsuperscript{-1}](image)

**Figure 2.6:** AO flux as a fraction of solar activity (Peplinski, 1984)
The total amount of AO exposure depends on many factors including spacecraft altitude, orbital inclination, attitude, mission duration, and solar activity (Tascione, 1988). AO formation is dependent upon solar radiation; its concentration is dependent upon solar activity. Figure 2.6 shows AO flux as a fraction of solar cycle activity at altitudes ranging from 300 to 900 km (Peplinski, 1984). Spacecraft in LEO orbit will be exposed to less AO during periods of low solar activity than one orbiting during periods of high activity. AO erosion in polymeric materials causes bond breakage and thus forms volatile oxides (e.g., CO) or oxides that do not adhere to the surface (e.g., silver oxides).

![Diagram of AO erosion mechanism]

**Figure 2.7:** Typical mechanism of AO erosion in polymeric materials (Tennyson, 1993)

Note that AO does not always lead to erosion; it may also give rise to a stable oxide that stays on the surface. For example, silicon exposed to AO develops a stable silicon dioxide coating. The typical mechanism behind atomic oxygen surface erosion has been explained in figure 2.7. The effects of atomic oxygen on various polymeric materials to metals such as polyimide (Hiroyuki Shimamura et al., 2012; Mei Lv et al., 2015), polysiloxane-block-polyimide film (Eiji Miyazaki et al., 2010), polytetrafluoroethylene (Xiao et al., 2010) have been extensively investigated in the recent years through onboard space mission and ground simulated
laboratory experiments (Haris et al., 1997). Though several research works about effects of AO exposure on polymer and polymer based composite materials have been attempted (Kim et al., 2006; Bank et al., 2008), only limited research work have been done based on effects of AO exposure on CNT based micro and macroscopic composite materials (Kim et al., 2013; Moon et al., 2011).

Davide Micheli et al., 2012, from his research work defined the interesting properties of carbon based nanostructured materials, instituting themselves as very promising materials for the future aerospace composite technology.

2.5.4 Plasma environment and its interaction

The space plasma (energies < 100 keV) is an ionized gas in which electrons and positively charged ion densities are almost equal and fluctuates with solar activity and altitude. Plasma sources are the geomagnetic sub-storm activity, planetary ionosphere and the solar wind. The plasma region is categorized by electron densities of $10^{10}$ m$^{-3}$ to $10^{11}$ m$^{-3}$ at an altitude of 1,000 km and then drops to about $10^9$ m$^{-3}$ at its outer boundary (Daniel Hastings et al. 2004). The variation in the plasma density with respect to the altitude has been graphically represented in figure 2.8. The changes in spacecraft velocities and variations in the electron and ion thermal energy, electrons can impact on any part of the spacecraft surface, while ions can only ram the leading edge surfaces. This effect leads to a charge buildup (negatively), which can lead to ion arcing and sputtering, and also re-attraction of contamination (James et al., 1994). At LEO, there are large numbers of plasma particles present near the spacecraft surface that are susceptible to differentially charging. This effect can be neutralized by providing conductive paths between them. The GEO plasma environment is characterized by collision-less and rarefied plasma and
also sudden injections of high energy plasma (typically with a mean energy of a few tens of keV) associated with sub storms.

![Figure 2.8: Variation in the plasma density with respect to altitude (Daniel Hastings et al. 2004)](image)

These events are believed to be the major source of surface charging on GEO spacecraft, making them of particular interest here. The impending damages caused by the plasma interactions with the spacecraft materials are malfunctioning of electronic devices (communications; navigation data), causing spacecraft surface charging, secondary electron (electron ejection from substrate) and auger electron emission, sputtering of vehicle surface materials. Among these, sputtering and surface charging interactions induce major effect over the material properties and its performance (Vincent et al., 2008).

2.5.4.1 Sputtering:

The process by which atoms present near the surface of the material is removed by the incident particle (must possess energy greater than the binding energy of the targeted site atoms). This can pose a problem for surfaces on which thin films have been deposited. In addition, the released material may contaminate neighboring surfaces. In case of plasma interaction with
metals, it generates secondary electron emission and cause vacancies and defects in the crystal structure. Plasma interaction with polymer generates free radicals on the surface. The reactivity of the generated free radicals can cause both or either cross-linking (stable) and degradation (unstable) of polymers (C. A. L. Westerdahl et al. 1974).

2.5.4.2 Surface charging

It is the process by which a spacecraft or particular part gathers all electrical charge from its surrounding environment. It has been generated from the low-energy plasma and photoelectric currents (due to Sunlight). A standardized recommended design for spacecraft charging effect on materials has been made by Rodgers and Hilgers (2000). Spacecraft charging is dependent on the characteristics of the space environment, including where the spacecraft is exposed to the Sun or the eclipse, geomagnetic activity, Sun’s activity, and the solar electron flux density.

Spacecraft charging can be classified into two types absolute charging and differential charging. When the whole spacecraft accumulates a net charge relative to its environment such that it has a potential difference is known as absolute charging. Differential charging occurs when dissimilar sections of the spacecraft charge to different potentials. The plasma ionizes the molecules that are outgassed from the spacecraft where it gets attracted towards the negatively charged surfaces and cause contamination (Vincent et al., 2008). Plasma arc discharging occurs when the electric fields created by differential charging exceeds its breakdown potential (Herr et al., 1994). Arcing creates an electromagnetic (EM) fields that couples into spacecraft electronics parts and cause critical damage and malfunctioning. Arcing also causes physical damage to the structural materials that result in reduction of properties and its performance. Differential charging can further be classified into internal charging and surface charging based on plasma arcing. Internal charging occurs when the charge accumulation arises inside the dielectric
materials of the spacecraft due to the penetration of high energy electrons (>10 keV). If dielectric breakdown occurs in the surface materials such as Kapton (Polyimide), it may then lead to either arc discharge or charge leakage. In order to overcome this effect, conductive coating has been done on the surface of the material. Surface charging occurs when arc discharge is generated between the neighboring surfaces. It happens because of two reasons; charge difference occurs between the surfaces and when threshold voltage is surpassed (Roger et al., 2000). Watson et al. (2003) studied the durability of polyimide (PI)/CNT nanocomposite films for electrostatic charge mitigation in space plasma environment. Nurit et al., (2015) developed a flexible CNT-PI nanocomposite films for electrostatic discharge (ESD) protection in space environment.

2.5.5 Space radiation environment and its interaction with materials

The space radiation environment typically comprises of high energy radiation and photons as shown in figure 2.9. Space radiation interaction factor plays a critical role in selection of materials for structural and electrical applications. These radiations lose their energy when they interact with materials through ionization and non-ionization process. The irradiation dosage is measured based on energy absorbed by the material and in S.I units it is termed as Gray (Gy), where 1 Gy is equal to 1 J/kg. The ionizing radiations (occurs in either particle or wave form) possess enough energy to eject orbital electrons from atoms, thus generating ions and charge distributions. These radiations cause functional failure of electronic devices and thus damage the performance and properties of structural materials of the spacecraft. Typical examples include X-ray, gamma ray and cosmic rays. The non-ionizing Radiation does not possess enough energy to eject an electron, instead it makes atoms to vibrate or it causes agility of atoms inside the molecules and damages the materials property by creating atomic displacements.
Typical examples include microwaves, radio waves and visible light. Damage to electrical devices is generally categorized as non-ionizing thermal damage (thermal shock), displacement damage (creation of vacancies or interstitials), total ionization dose damage (device malfunctioning) and single event effects (circuit damage and random failure rate) (Ma et al., 1989). The space radiation can be classified into man-made artificial radiation and natural space radiation environment. The former is due to nuclear based electrical power being employed in spacecraft for example; radioisotope thermoelectric generator having power output of 2.7 W for transit navigation satellite in 1961 and the latter consists of solar UV, galactic cosmic rays (GCR), ionizing photon or electromagnetic radiation and solar particle events (SPE).

2.5.5.1 Ultraviolet irradiation (UV):

The UV radiation originates from the Sun in the form of EM radiation (wavelength = 200 and 400 nm) and has energy greater than 376.6 kJ/mol. As the polymer chain bond energy is only
about 250 to 450 kJ/mol, the UV radiation has enough energy to break the weak chemical bonds. Usually, EM radiation fluence for a spacecraft with a working lifetime of 25–30 years is only 10–100 MGy (Cheng et al., 2016). The synergistic effects of vacuum and UV results in bond breaking, indirect atomic displacements (Tennyson et al. 1982), chain scission, outgas volatile elements (ensuing in mass loss and degradation) or forming crosslinks (Leger et al., (1987); Chen et al. (2014)). Grossman and Gouzman, 2003, identified space environment effects on silicone paint in low earth orbits and observed the surface alterations. In the presence of oxygen, the free radicals form oxygen hydro-peroxides and it easily disrupts the double bonds present in the backbone of the chain leading to brittle failure and this phenomenon is called UV photoxidation. Polymers containing no double bonds or π electron (such as polyethylene) are relatively unaffected by UV light. The PEI is the only polymer with excellent resistance to UV due to the presence of imide groups and it has also been used in the Hubble Space Telescope. Carbon based materials can also hinder damaging effect of UV.

2.5.5.2 Galactic cosmic rays:

These are high energy particles (atom fragments) arriving from outer space as a resulting effect of supernova or colliding galaxies. Galactic cosmic rays contain earth radiation belt particles (Van Allen’s belt) and solar cosmic rays, whose flux is only about 1–4/cm² s and the energy is as high as 10²–10¹³ MeV. The typical composition of galactic cosmic rays is 89 % proton and 10 % α particles -Helium nuclei and 1 % heavier nuclei (Meyer (1985); Boezio et al. (2012)).

2.5.5.3 Earth’s trapped radiation belt: (Van Allen, 1971)

The radiation belt comprises of high energy charged particles such as protons and electrons trapped by Earth's magnetic field. It consists of two belt regions: a low altitude zone (inner belt)
which extends approximately from hundreds of kilometers to ~ 6,000 km and is occupied by high energy (0.1–400 MeV) protons and high energy (1-10 MeV) electrons. The outer belt is a high altitude region (10,000-60,000 km) and is predominately made up of high-energy electrons (Cheng et al., 2016). The trapped radiations interaction with the materials establishes a major radiation hazard for spacecraft. Radiation effects include total ionizing dose (TID), single events effects (SEEs), displacement damage and deep dielectric charging. In the case of deep dielectric charging, high-energy trapped electrons can penetrate into dielectric materials on a spacecraft structure and discharge, causing damage to electrical circuits and structural materials. This in turn results in performance degradation or the incompletion of a desired mission (Janet L, 2004).

2.5.5.4 Ionizing Photon radiations:

Photon radiation is the transfer of energy by electromagnetic (EM) radiation that has zero rest mass and no charge. Typical ionizing EM radiations include ultraviolet radiation, x-rays, and gamma rays.

2.5.6 Ionizing radiation interaction with materials

The ionizing radiations of concern here include electron radiation, the neutral radiation that include photons (gamma, UV and X rays) and also neutron particle. In the fission fragments such as alpha (^3_2\alpha \text{ or } He^{2+}), beta (-^1_0\text{e}) and gamma particle (^0_0\gamma), the gamma radiation and neutron possesses greater penetrating capability in matter than that of the other two. The alpha particle and beta particle can be blocked by a sheet of paper and aluminum or glass or polymeric material (low density material) respectively. Electromagnetic radiation such as x-rays and gamma rays are typically blocked by highly dense materials such as lead. The neutron particle whose interaction is less does indirect ionization and penetrates further inside the material. The figure 2.10 portrays the types of ionizing radiation interaction with material.
2.5.6.1 Neutron radiation and its interaction with materials:

The neutron radiation consists of neutral particles having mass slightly greater than a proton (939.6 MeV c\(^{-2}\)). While photons (gamma, X-ray) principally interact with the electron cloud surrounding the nucleus of the atom in which they are traveling, but neutrons interact directly with the nucleus. Neutrons interaction with a material is mainly by elastic scattering (energy transferred to the nucleus), inelastic scattering (energy absorbed by target nuclei and emit photons), and neutron capture (low energy neutron captured by nuclei and its atomic number increased to 1). Maximum energy is transferred if the mass of the nucleus is equal to the mass of the neutron. Thus, hydrogen having nucleus of one proton (atomic number = 1) is a good absorber of neutrons. Whereas, Lead with 82 protons and 126 neutrons (atomic number = 86) does not absorb. Thus, polymeric materials possessing high hydrogen content are unaffected by neutron radiation and also absorb fast neutrons.

Figure 2.10: Radiation interaction with materials (Courtesy- article nucleotidings.com)
2.5.6.2 Gamma radiation:

Gamma rays from EM radiations possess high frequency (> $10^9$ Hz) and therefore high energy (>100 KeV) with very short wavelength i.e less than 10 pico-meter and consequently they have no net electric charge and cannot be deflected by electric and magnetic fields (Klueh, 2002)

2.5.6.3 X-rays:

X-ray photons are created by the interaction of energetic electrons with matter at the atomic level. The Bremsstrahlung interactions involve deceleration of a charged particle (electron) when deflected by atomic nuclei which in turn generates x-ray photons. Not much damage has been generated to exposed materials while compared to gamma radiation.

2.5.7 Neutral photons (Gamma rays, X-rays) interaction mechanisms:

The three primary interactions of photons with matter are the photoelectric effect, Compton scattering, and pair production.

2.5.7.1 The photoelectric effect (low energy: E < 200 keV):

In photoelectric effect, the photon transfers all of its energy to eject an orbital electron ($E_e^\text{-}$), whose energy is equal to the incident photon energy ($E_\gamma$) and less than that of the binding energy or ionization energy ($B \cdot E_e$) needed to remove the electron.

$$E_e^- = E_\gamma - B \cdot E_e$$  \[1\]

2.5.7.2 The Compton scattering (intermediate energies: 200 keV to 1.5 MeV):

It is an elastic scattering of the photon by an atomic electron and in turn atomic electron gets excited. The resulting photon with reduced energy gets refracted from its original path.

2.5.7.3 Pair production: (high energy: E > 1.5 MeV):

The interaction between the incident photon and the Coulomb force of the nucleus cause some of the photon energy (1.02 MeV) to generate an electron/positron pair with same mass
(each 0.511 MeV). The rest of the photon energy is given as kinetic energy to the electron/positron pair. The unstable positron (positively charged electron) combines with a free electron and whole mass energy gets converted into ejection of two gamma photons of energy 0.51 MeV each which is known as annihilation radiation. (Vincent, 2008)

### 2.5.8 Radiation interaction effect over metals and polymers:

There are various types of radiation induced damages that occur in the spacecraft materials during its mission. The radiation induced damages in the electronic devices have already been discussed briefly in section 2.5.5. The damages caused by ionizing radiation at the molecular level of the materials and the mechanical effects are focused in the forthcoming reviews.

Ionization (electron is removed or added to a neutral atom) process has the ability to disrupt molecular bonds. In the case of metals, metallic bonding consists of positive ions with free valence electrons, which holds the ions together. Ionizing radiation increases the kinetic energy of the electrons or excites the electron to a higher energy level and comes back to normal energy level. In both the case, there is no permanent damage due to ionization, only impermanent internal heat generation that causes reduction in some material properties depending upon the density of the material. The metals are also severely damaged by radiation induced events such as displacement damage (Interstitials, vacancies) (Klueh, 2002). When the high energy radiation interacts with the high atomic number (Z=13) materials such as aluminium it generates secondary radiation emissions such as X-rays and bremsstrahlung. From the NASA study in 2002, it was determined that materials with high hydrogen contents, such as polyethylene and other polymers, can reduce primary and secondary radiation to a greater extent than metals (Lyndon, 2002).
Radiation normally affects polymers in two basic manners, resulting from excitation or ionization of atoms. The two mechanisms are chain scission, a random rupturing of bonds, which reduces the molecular weight (i.e., strength) of the polymer, and cross-linking of polymer molecules, which results in the formation of large three-dimensional molecular networks. Most often, both of these mechanisms occur as polymeric materials are subjected to ionizing radiation, but frequently one mechanism predominates within a specific polymer. As a result of chain scission reaction, very-low-molecular-weight fragments, evolution of volatile gas and unsaturated bonds may obtain. Crosslinking generally results in an initial increase in tensile strength, while impact strength decreases and the polymer become more brittle with increased dose.

A polymeric material (organic) is made of carbon (C) atoms which is the backbone of any hydrocarbon materials. The four valence electrons present in the C atoms forms covalent bond with the neighboring C atoms or H atom and thus together form a polymer chain. Covalent bond energies are in the low eV range. Radiation possessing high energy to rupture the covalent bond can induce bond breakage from highly reactive unstable free radicals. These free radicals either encourage degradation of polymeric materials or form stable cross-linking. These radiation effects also alter the polymer bulk properties and reduce its performance.

In polymers with carbon-carbon chains (backbones), it has been observed that crosslinking generally occurs if the carbon has one or more hydrogen atoms attached, whereas scission occurs at tetra-substituted carbon. The polyethylene (PE) exposed to high energy radiation shows an increase in the tensile strength at room temperature due to crosslinking until dosage of 10 Mrad (1 rad = 0.01 Gy); with further increase of the radiation dose the tensile strength of PE decreases. Elongation at break also increases slightly and then decreases sharply.
It may be due to increased crosslinking density observed in many other polymers (Kabakchi et al. (1972); Madani (2012)). Polyimide displays an excellent resistance towards degradation and loss of material properties when it is exposed to high energy radiations, such as gamma radiations and electron beams (Heiland et al., 1996). Polymers containing aromatic molecules generally are much more resistant to radiation degradation than are aliphatic polymers. This resistance towards high-energy radiation arises because the polymer containing high concentration of aromatic groups, which scavenges small free radicals, such as hydrogen atoms and which can degrade absorbed energy to heat through the manifold of vibration states associated with these groups. Thus, both polystyrenes, with a pendant aromatic group, and polyimides, with an aromatic group directly in the polymer backbone, are relatively resistant to high doses (>4000 kGy). This is the reason behind selecting polyimide (Kapton) and polyetherimide as a suitable candidate for applications in aerospace industry.

2.5.9 Micrometeoroids and Orbital debris:

Micrometeoroids originate naturally from planetary or asteroidal collisions and cometary ejecta (Tennyson et al. (1997)). Hyper-velocity debris at LEO altitudes are man-made and consist mainly of unused satellites and rockets, and mostly of small objects such as aluminum oxide fuel particles, paint chips and fragmentation of objects from collisions of these bodies in orbit (Tennyson et al. (1997)). Space debris varies with the solar cycle as the Sun’s activity increases, the atmosphere heats up, increasing the drag force on space debris in orbit. Typical velocities of debris particles range from few kilometers per second up to 16 km/s, making these particles a threat to spacecraft. The Hubble’s solar array suffered impacts at ultrahigh velocities ranging from 2.9 to 11.5 km/s from particles 7–98 µm in diameter (Paul et al. (1997)). The damages include accelerated growth of particle and molecular contamination, reduction in
mechanical properties due to debris impact and crack propagation. Gilsang et al. 2014, MWCNTs protective surface provided better protection over debris impact and impeded the crack propagation due to bridging effect, the film-protected specimens showed less increase in surface roughness and a reduction in the degradation of tensile strength.

The selection of spacecraft structural materials is to be finalized based upon considering the above cited hazardous environments and its interaction with the materials. The current requirement for space vehicle structural material design incudes development of light weight structures by employing polymer based composite with multi-functionality characteristics. It must also offer better performance, dimensionally be stable, recyclable, ease in processing, tailor made properties and long service life span for deep space exploration.

2.6 Polymers for space application

The principal aim of developing novel light weight space structural materials is to attain performance improvement with high strength to weight ratio, tailor made properties, enhanced damage tolerance, thermally stable with low co-efficient of thermal expansion, both electrical and thermally conductive, enhanced stability in ionizing radiation environment, does not generate secondary radiations, extended service life, resistance to dielectric corrosion, reusability, thorough understanding of material behavior and ease in processing and also reduced costs. The development of light weight structures could reduce a spacecraft's mass by up to 40 percent and benefits to save on fuel and transport more payload or people, in the case of deep space manned missions.

Based on these considerations, the recent development for choice of structural materials for the spacecraft heavily depends on polymer based matrix materials for composites structures. Due to their high toughness, high elasticity, good insulation, low density, high or low melting
point, ease in processing, prevents secondary radiation generation, dielectric property, lower shrinkage, tailor-able properties and high damage tolerance, polymeric materials have been widely used in the space technology. These polymer materials are used as lubricants, optical fiber materials for optoelectronic devices, temperature control cladding materials, insulating paint, printed circuit board, and high strength composite materials in spacecraft structures. The deep space environmental conditions demands spacecraft materials to sustain their performance even under the impact of high vacuum, space radiation, thermal cycling, atomic oxygen, space debris and tiny meteoroids impact (He 2008). The selection of polymers used in the space environment is very challenging and involves various complex factors. The polymeric materials must withstand the severe space environmental conditions without compromising the performance and extended service life time.

Polymer is a general term that defines wide variety of long chain macromolecules which includes plastics and elastomers. The polymers can be classified based on molecular chain arrangement and chemical structure as thermoplastics and thermosetting polymers. Based on the polymer long chains arrangement it can be also sub-classified into semi-crystalline (regular arrangement) and amorphous polymers (irregular arrangements). The amorphous polymers usually possess properties such as low shrinkage, more transparent, greater low temperature toughness, high creep and softening temperature (no melting temperature). The crystalline polymers are typically opaque, have sharp melting temperature, high shrinkage, low creep and better dimensional stability.

The material that softens when heated above the glass transition temperature and becomes hard after cooling is called thermoplastics. The intermolecular forces between the chains are effectively strong to prevent motion of the molecules past one another the polymer
solid at room temperature, but will lose strength and flow when heated. It consists of lengthy molecular chains made by joining two or more monomer molecule as shown in table 2.3. The thermoplastic possess strong covalent bonds that join the atoms together along the length of the polymer chain (Each polymer chain is a discrete molecule), but no covalent bonding can be found in-between the lengthy chains. The lack of bonding between the molecular chains cause thermoplastics to soften and melt when heated which that in turn allows them to be recycled. The thermoplastic monomers are bi-functional and grow only as linear polymer chain, which means that they possess only two reactive sites in the molecule where pairing can arise with other molecules. The polymer chains are only entangled and intertwined due to weak van der Waals forces in a thermoplastic and are not crosslinked. This entanglement or intertwining characteristics provide the necessary stiffness and strength (resisting sliding of chains when force applied) to the polymer as a whole. Typical examples include Polyetherimide (PEI), polyetheretherketone (PEEK), Polybenzimidazole (PBI), polyethylene (PE) etc.

*Thermosetting* polymers are also produced by addition and condensation reactions, but are formed from tri-functional monomers that possess three reaction sites, and this allows the covalent bonding to form along the chain and also crosslinking across the chains. The polymer becomes hard and rigid when heated above the melting temperature and cooled down to room temperature. The crosslinking of polymer chains is the prime reason behind the superior tensile strength and elastic modulus, but it also imparts low toughness and brittleness. They do not possess melting temperature and hence they cannot be recycled.
### Table 2.3: Merits and demerits usage of thermoplastic and thermoset polymer

<table>
<thead>
<tr>
<th>POLYMER</th>
<th>MERITS</th>
<th>DEMERITS</th>
<th>STRUCTUTRAL ARRANGEMENT</th>
</tr>
</thead>
</table>
| THERMOPLASTIC | • Less Reactive  
• No crosslinking  
• Fast Processable  
• High ductility  
• High fracture toughness  
• High impact resistance  
• Highly recyclable  
• Remolding and Reshaping  
• No volatile emission during processing  
• Superior toughness  
• Fusion weld and welded joint  
• Shrinkage resistance  
• Superior shelf life | • Very high viscosity-  
• poor fiber wettability  
• Elevated processing conditions  
• Poor resistance to polar solvents | ![Diagram](image1.png) |
| THERMOSET  | • Low processing conditions  
• Low viscosity  
• Good compression properties  
• Good fatigue resistance  
• Good creep resistance  
• Highly resistant to solvents  
• Good fiber wetting for composites | • Long processing time  
• Low ductility  
• Low fracture toughness  
• Low impact resistance  
• Absorb moisture  
• Limited shelf life  
• Cannot be recycled | ![Diagram](image2.png) |
The heat is usually required to accelerate the curing process by mixing hardener and resin together and pressure is applied to squeeze out volatile byproducts. The typical examples include epoxy, cyanate ester, phenolic etc.

2.6.1 Thermosetting polymers used in space application

The most widely used thermoset resins for advanced composite structures includes epoxies, phenolic, cyanate esters (CE), bismaleimides (BMI), and polyimide.

2.6.1.1 Epoxy:

Epoxy resins possess better strength and chemical resistance. They offer high performance at elevated temperatures, with hot/wet service temperatures up to 121°C. The high-performance application of epoxy is limited due to moisture absorption at low service temperature that is adversely affected by moisture content. It has also been used as high temperature adhesive in joining parts. LEO environment exposure of carbon fiber/epoxy composite (Baluch et al., 2013), graphite/epoxy composite (Kim et al., 2006) resulted in mass loss along with degradation in other mechanical properties. When exposed to radiation it produces volatile by-products and degrades the mechanical performance (Scott et al., 1986).

2.6.1.2 Bismaleimides (BMI):

Cured BMI thermosets such as 4, 4-bismaleimide diphenyl methane/o, o’-diallyl alcohol of bisphenol A (Matrimid 5292, Ciba Geigy) provide excellent high-temperature performance. BMI thermosetting resin has similar properties to those of epoxies but offers better temperature performance, especially hot/wet service temperatures up to 232 °C (462). Proton irradiation causes surface degradation of carbon fiber (CF)/BMI composites by altering their surface chemical structure and surface morphology at a microscopic level (Yu et al., 2011). The higher fluence beyond 5 × 10^{15} \text{ cm}^{-2} of electron beam irradiation over CF/BMI composite results in
superior amount of chain scission and led to the degradation in thermal and mechanical properties of the composites.

2.6.1.3 Phenolic resin:

Phenol–formaldehyde resin is low-cost, flame-resistant, and low-smoke resins. The Phenolic-Impregnated Carbon Ablator (PICA) heat shield, a lightweight material designed to withstand high temperatures. (NASA, July 3, 2015). Carbon–phenolic ablative materials for re-entry space vehicles have also been studied (Pulci et al., 2010).

2.6.1.4 Cyanate ester (CE):

CE provides excellent toughness and strength, low moisture absorption, and superior electrical properties with a hot/wet service temperature around 149 °C. CE resins provide low dielectric loss, high glass-transition temperature of 220-290 °C, good adhesive properties. CE also can be blended with epoxies and BMI (Nair et al., 2001). However, cyanate resins pose a safety risk because they produce poisonous hydrogen cyanide during the cure reaction process.

2.6.1.5 Polyimide:

Thermosetting polyimide possesses good chemical resistance, better adhesion and heat as well as superior mechanical properties. Fire retardancy can be enhanced by the addition of phosphorus substituents. Thermosetting polyimides can provide hot/wet use temperature 260 °C to 320 °C. AO exposure of polyimide composite induces oxidation and degradation of polyimide (PI) molecular chains (Baixing et al., 2012). Disadvantages include the need for a multi-stage cure process and the toxicity of the monomer 4, 4’-methylenedianiline (Lou et al., 2004).

The complications faced during usage of thermosetting polymers in space application are volatile emission during radiation interaction, free radical generation which in turn affects the performance properties, high surface erosion low shelf life, low toughness (debris impact
damage), low impact resistance and reusability. The shift towards high performance thermoplastic matrix based composite would be a suitable solution for such problems.

2.7 Selection of high performance thermoplastic polymers for space application

The use of thermoplastics in spacecraft structures is very limited while compared with the much greater use of thermosets. Some sectors of the space industry are keen to increase the use of thermoplastics as the matrix phase in composite materials, and the number of applications is gradually increasing. Thermoplastics provide several important advantages over thermosets when used in composite materials, most notably better impact damage resistance, higher fracture toughness, recyclable, better radiation resistance, vibration-damping properties and higher operating temperatures.

The thermoplastic matrices such as Polytetrafluoroethylene (PTFE) for high frequency space circuits and polycarbonate (PC) for astronauts helmet visor and shuttle windshield, in the case of high performance thermoplastic category it is polyimide (Kapton) for solar array and for thermal management, PEEK for spacecraft wiring and polyamideimide (Torlon) for adhesive and blended with other polymers hold vast applications in space industry. There are other two high performance thermoplastic polymers such as PEI which possess immense space durable properties but the only drawback is requirement of high processing temperature conditions and PBI also has excellent mechanical, thermal and fire resistance properties but possess immense processing difficulty. Not much research work has been carried out in exploring the PEI and PBI being employed as a space vehicle structural material. The structure property relationship of each polymer is based on property requirement for space application is to be explained as follows
2.7.1 Polyetherimide (PEI)

It is an amorphous thermoplastic polymer, with amber to transparent colour and the structure of PEI is depicted in figure 2.10. The amorphous structure of the PEI is the prime factor for its excellent dimensional stability and the mechanical properties highly isotropic, comparing to other semi-crystalline (Offringa, 1996; Sroog, 1991). The presence of the ether linkages (induce chain flexibility) is sufficient enough to allow the material to be melt flow and processable. The PEI also retains most of the desirable properties of polyimides (J.A Brydson, 1999; Bor et al., 2008). The presence of rigid imide group in the chemical structure is the prime reason for the polymer to possess high glass transition temperature and tensile modulus even at elevated temperature conditions (>200 °C).

![Molecular structure of PEI polymer](image)

**Figure 2.11:** Molecular structure of PEI polymer

It also possesses enhanced radiation resistance over gamma rays and ultraviolet radiation, which is due to the presence of delocalized π electrons that does not allow free radical generation and instead causes delocalization. It is soluble to solvents that are partially halogenated. However, the ether groups justify the flexibility of the molecular chain. PEI also demonstrates good electrical properties and remains stable over a wide range of temperatures and frequencies. As a consequence the material has gained rapid acceptance as a high temperature engineering thermoplastics material competitive with the poly-sulphones, poly-phenylene sulphides and poly-ketones. They exhibit the following key characteristics i.e. high tensile strength property (unfilled) and impact resistance; heat deflection temperature of 200 °C;
superior toughness and cryogenic conditions performance; Enhanced thermal and thermo-oxidative stability; Inherent flame resistance property with very low smoke emission, superior than polyethersulphone polymer; exceptional resistance to long-term creep and stress corrosion cracking; possess high purity, low outgassing in vacuum; excellent radiation resistance and electrical insulation properties. The superior hydrolytic stability and ease in processing are the advantages of PEI which is missing in many of polyimides.

The PEI polymer possess low moulding shrinkage of 0.005-0.007 cm/cm and also has high polymer melt strength which facilitates possibility of processing of PEI through thermoforming and blow moulding techniques. Maruti et al. (2017) manufactured 3D printed structure using polyimide (Kapton) as the raw material by employing mask-projection stereolithography. This type of manufacturing requires a photo-crosslinkable site in the polymeric (or monomeric) material. The 3D printing was manufactured using polyimide solution through free radical generation. The Additive Manufacturing Facility (AMF) is the first commercial 3D printer in space which could print a small satellite as well as an organic matter in microgravity. Among the polymers that the AMF is able to print with is polyetherimide (PEI) which possess space durable properties and ensures stability (Michael, 2017). Made in Space already uses acrylonitrile butadine styrene and polyethylene in the additive manufacturing facility which is adopted by NASA’s artificial low Earth orbit satellite. PEI represents the third material incorporated into its AMF processes. It is also been employed as a rigidization materials inflatable structures (Cadogan et al., 2001).

2.7.2 Polybenzimidazole (PBI):

PBI is a thermoplastic and has the highest Tg of 435°C among any high performance polymer. It possesses excellent fire resistant property. These characteristics are a consequence of
the inherent chemical stability of the benzimidazole functionality present in the polymer backbone as shown in figure 2.11.

![Molecular structure of PBI polymer](image)

**Figure 2.11:** Molecular structure of PBI polymer

Polybenzimidazoles have been reported in the literature since early 1960s (Cassidy, 1980). While being known for their excellent thermo-oxidative stability, PBIs was thought to be intractable ‘brick-dusts’. However, in the last few years (Powers et al., 1986) work at Hoechst Celanese has demonstrated that PBI can be made with high molecular weight, moldable and soluble in dimethylacetamide (DMAc) allowing for the facile preparation of PBI matrix resin composites containing continuous fiber reinforcement. Celazole PBI (sintered powder) can be molded in a variety of stock shapes or directly molded into finished articles. PBI has excellent resistance to inorganic acids and bases, even at elevated temperatures. In addition, it retains its strength when exposed to a broad range of organic chemicals and solvents. PBI maintains significant tensile properties up to 371°C and also has heat deflection temperature resistance of 435 °C which is the highest value of distortion temperature among thermoplastic polymers (Sandor et al., 1990). PBI has an excellent resistance to radiation. It does not require UV stabilizers for a long-term exposure to UV radiation. The exposure to gamma radiation, EB radiation induces cross-linking and increasing thermal stability. No degradation is observed after cumulative exposure up to 1 MGy (Saleem et al., 2014). PBI can be processed by compression moulding (sintering) typically at 440 to 450 °C in preheated moulds and by film casting from
solutions using dimethylacetamide (Jingshuai 2010). It can be used for preparing nanocomposites using carbon based nanofillers (Li Zhang et al., 2011).

2.8 Carbon Nanotube reinforced thermoplastic nanocomposites

From the literature survey, it is evident that not enough research work has been attempted on the effects of actual deep space environmental interaction over carbon nanotube reinforced polymeric nanocomposites. There have been few theoretical simulations (Paci et al. (2009); Xu et al. (2009)) and ground simulated tests (Nicholson et al. (2005); Rossia et al. (2015)) that evaluated the effect of ionizing radiation on CNT materials. The CNTs does not get readily affected by AO exposure. It is believed that the different degree of graphitization drives the difference in observed AO erosion yields (Hopkins et al. 2016). Miller et al. (2010) and de Groh et al. (2010) have reported that higher residual impurities, presence of residual catalyst and high number of defective sites in carbon nanomaterials are mostly responsible for the higher reactivity towards oxygen and subsequent higher erosion yields. The CNTs possess excellent stability in radiation environment as compared to other nanofiller reinforcements, which is due to the presence of delocalized π electron in its structure. When CNTs interacts with the high energy radiation, delocalization occurs within its structure and does not allow ionizing radiation to generate free radicals and this in turn hinder chain scission reaction. The CNTs also have the advantage of excellent electrical conductive, mechanical and thermal properties along with high aspect ratio making it suitable for aerospace application. The MWCNTs possessing high electrical conductivities are highly considered as suitable nanofillers for developing electrically conductive polymer based nanocomposites. The reinforced CNTs induce sufficient electrical conductivity in the polymer matrix to dissipate the electrostatic charge (ESC) build-up on the space structural materials (Jenkins 2001). Consequent discharging by the insulators (unfilled
polymer matrix) can potentially cause catastrophic damage to sensitive spacecraft components (Robinson 1989).

Moreover, the electrical conductivity of the CNTs reinforced polymer nanocomposites was found to be stable even under bending and flexible action, which is an added advantage over commonly used, and typically fragile, AO erosion resistant indium tin oxide (ITO) surface coatings (Nurit et al. 2015). Addition of CNTs in the polymer matrix increases the thermal stability of the nanocomposite as a whole and also increases the thermal conductivity of the space structural material. The outer space above earth’s atmosphere comprises of distinctive and hazardous environmental conditions that can degrade or impair the spacecraft structural material properties and cause a drop in their performance. Synergistic effects between AO, UV, ionizing radiation, thermal cycling, meteoroids, space debris, and other hazards should be taken into consideration when selecting materials for use on spacecraft structures. The four major areas where CNTs based nanocomposites have potential use in space structural applications are: ESC mitigation, improved mechanical properties, stability in the radiation environment and enhanced thermal conductivity. Further, immense research attempts are required to thoroughly analyze the nanotubes durability and performance in actual space environmental conditions.

Since the innovation of carbon nanotubes (CNTs) in 1991 by Iijima, CNTs has been employed as a reinforcement filler in diverse areas of research (Iijima 1991 and 1993). Both experimental and theoretical methodologies recommend the remarkable mechanical properties of CNTs which is ~100 times greater than the steel at a fraction of the mass (Mojtaba et al., (2016); Goze et al., (1999); Dresselhaus et al. (2001)). CNTs belonging to the fullerene family are geometrically idealized to be a cylinder formed by concentrically rolled graphene sheets. Similar to the structure of graphite, the $sp^2$ hybridized CNT has each of its atoms bonded to three
neighboring atoms in a hexagonal array. The type of CNT would depend upon the number of concentric cylinders. CNTs principally exist as SWCNTs, double-walled carbon nanotubes (DWCNTs) or as MWCNTs. CNTs are known for their intrinsically high mechanical, thermal and electrical properties. The sigma bonds which make up the C–C bonding in CNTs attributes to their excellent mechanical characteristics. Elastic modulus of 1.2 TPa and tensile strength of about 50–200 GPa have been reported for CNTs (Qian et al., 2002). Their high axial and low lateral thermal conductivity also add to their significance. Although theory predicts a room temperature thermal conductivity of 6,000 W/mK (Che et al., 2000), Kim et al., (2001), estimated the thermal conductivity of MWCNTs to be 3,000 W/mK, and Pop et al., (2006) reported 3,500 W/mK for SWCNTs. This is significantly higher than the thermal conductivity of diamond (1,000–2,200 W/mK) which is reported to be one of the best known thermal conductors (Sukhadolou et al., 2005). The oxidative thermal stability for both MWCNTs and SWCNTs are greater than 600 °C which compares strongly with that of 450–650 °C for graphite. Their coefficient of thermal expansion is very minimal which supports the excellent thermal conductivity of these materials. The extraordinary multi-faceted properties of CNT confer to these materials a significant potential to be used in a wide-variety of applications. The intrinsic tendencies of the CNTs to exist as agglomerates due to their van der Waals forces of attraction (0.5 eV/nm) (Walters et al., 2001), by large limits the realization of the complete potential of these materials as nano scale reinforcements in different host matrices. Carbon nanotubes (CNTs) offers enhanced mechanical property improvement in the polymer matrix, principally due to their exceptionally large aspect ratio which could be as high as $10^6$ (Breuer et al. 2004) combined with a large interfacial area $> 1300$ m$^2$/g (Peigney et al. 2001). The two factors such as quantum effects and improved relative surface area are the major reason for the properties of nano
structured materials to differ considerably from other micro and macro structured materials. Comparatively MWCNTs are available at lower cost and are usually less agglomerated, high aspect ratio, and more rigid than that of SWCNTs (Shyam et al. 2013).

The reason for choosing MWCNTs as reinforcing filler for space application is due to the various advantages over SWCNTs, such as low product cost per unit, as ease of mass production, comparatively lower agglomeration, enhanced chemical and thermal stability. Moreover in SWCNTs and graphene, the mechanical and electrical properties of nanotubes can be affected and also there is a chance of defects formation over the tube walls when surface modified using covalent and non-covalent functionalization techniques. During chemical treatment process, the structural defects occur in the SWCNT and MWCNT nanotube wall due to the C=C bond breakages. However, intrinsic properties of carbon nanotubes can be preserved by the surface modification of MWCNTs, where the outer wall of MWCNTs is exposed to chemical modifiers (Jia et al. (2018); Eatemadi et al. (2014)). The SWCNTs have been rarely used as reinforcing filler in a polymer matrix mainly because of the difficulty in efficient dispersion as they tend to agglomerate due to the increased electrostatic force of attraction between them. It is also due to the presence of non-reactive surface character in the SWCNTs. In general, SWCNTs tend to agglomerate as bundles in a solution and if dispersed, re-agglomerate soon thereafter due to electrostatic force of attraction. In the case of carbon nanofibers (CNF), it possesses numerous advantages over CNTs such as low production cost, ease in functionalization and low cost. The stacked-cup nanofibers has various drawbacks when compared to nanotubes which includes increased AO erosion and outgassing due to open more reactive sites due to open edges of CNFs. Thus MWCNTs acts as suitable nanofiller reinforcement in the PEI and PBI matrices for deep space application.
2.8.1 **Surface modification of MWCNT:**

It is an approach widely adopted to render the surface of the inert CNTs compatible to interact efficiently with the polymer and also weaken their intrinsic van der Waals forces of attraction (de-agglomerate). Functionalization both by chemical and physical means has been mostly reported.

2.8.1.1 **Physical functionalization**

It is done by polymer wrapping (Vander Waals forces and p-p stacking), surfactant adsorption on CNT surface (physical adsorption) and endohedral techniques (capillary principle). Although this technique would not damage CNTs a weak CNT-polymer interaction could be expected out of these approaches. Non-covalent or physical treatment of CNTs result in the outer tube walls to be subjected to more treatment than the inner tubes (Cohen et al., 2004). Mechanical property enhancements cannot be expected to be on a larger scale because the chance for the interfacial strength to improve is minimal because of lack of chemistry. The techniques of chemical and physical modifications are however, relatively expensive which limits modification of the CNT for large scale applications. Mohan et al., 2016 studied the effect of nitrogen plasma functionalization (Shahzad et al., 2013) and achieved significant improvement in the mechanical and thermal properties.

2.8.1.2 **Chemical functionalization:**

It is done either on the side walls of the nanotubes or by creating defects on CNT surfaces by acid treatments. This is expected to result in a very strong matrix-CNT interaction with a trade off on the structural characteristics of CNTs. The sp² hybridization of carbon is transformed to sp³ to create active sites for effective interaction with polymer accompanied with the loss of p conjugation bonds on the outer walls. But, covalent functionalization such as strong acid treatment
affects the geometry of the CNTs resulting in increased filler percolation thresholds (Bose et al., 2008). The phonon scattering length is also expected to be lowered which in turn lead to decrease in the thermal conductivities (Padgett et al., 2004). Covalent treatments are mainly aimed at improving polymer-CNT compatibility and CNT dispersion. Effective achievement of this could lead to improved structural characteristics accompanied with losses in electrical and thermal conductivity of the composite. Mohan et al., 2017 studied the effect of partial acid treatment of CNTs and its positive effect over improvement in the thermal, mechanical properties of PEI/Acid-MWCNTs nanocomposite. Oxygen containing functional groups (OH, C=O, and COOH) can be attached over the walls of MWCNTs through acid oxidation procedures. These functional groups presence encourages CNT dispersion in the polymer matrix and enhances the chemical compatibility (Balasubramanian et al., (2005); Gojny (2003)). May-Pat et al. (2011) reported that, mild acid oxidation treatment generates hydroxyl and carboxyl functional groups on the CNT surface with minimum CNT damage, which produces enhanced mechanical properties of MWCNT/PET composites. Venkata et al. (2010) stated that viscosity of functionalized carbon nanotubes reinforced epoxy composite increased compared to pristine CNT/epoxy composites. The mechanical properties of MWCNTs/epoxy composites are improved significantly with the addition of MWCNTs.

2.8.2 Processing techniques for Thermoplastic/CNTs Nanocomposites:

The level of CNT dispersion visible on the composite morphology is a direct function of the type of polymer and CNT employed the processing approach and the process factors. The morphology and the macroscopic properties of the composite are deduced by the thermo-mechanical history during processing. The major processing methodologies are solution casting (Safadi et al. (2002); Qian et al. (2000)), melt mixing (Menzer et al., (2011); Socher et al. (2012);
Sathyanarayana et al. (2013)) and solution mixing (Chen et al., 2006), such as in situ polymerization of the monomer in the presence of CNTs (Lin et al. (2005); Wu et al. (2008)), have been adopted for the synthesis of polymer-MWCNT composites. The solution processing, in situ polymerization and melt mixing are discussed briefly in the following sections.

2.8.2.1 Solution processing

It is one of the widely employed methods which involve dispersion of the CNT in a suitable solvent by sonication or stirring processes followed by mixing with a polymer solution and then the solvent evaporation process and drying with or without vacuum. Ultra sonication is widely employed in order to break the CNT agglomerates as the shear in the solution mixing process is significantly low. The type of ultra-sonication (ultrasonic bath or horn), bath temperature, and rate of sonication (frequency and time) and the nature of the solvent would have a strong influence on the properties of the product. This method can be successful with the right choice of solvent and complete removal of the solvent during the drying stage. However it is not easily scalable. It is widely adopted for preparing composites based on thermosetting matrices where a significant magnitude of shear is not required as the low viscosity of the host would result in good infiltration of the CNT agglomerates facilitating dispersion.

2.8.2.2 In situ polymerization

The polymerization process is carried out in the presence of CNTs along with the monomer. This projected to form a very good chemical affinity between the polymer chains and the CNTs, but depending on the nature of the reactants a non-covalent interaction is a definite probability. The polymerization of the monomer in the presence of an initiator is carried out with CNTs in the vicinity enabling the production of composites with high CNT loadings. A mix of polymer grafted CNTs and free polymer chains are obtained which creates a favorable
environment for the development of a highly compatible polymer-CNT interface. The low viscosity of the starting monomer facilitates better infiltration into the CNTs and consequently their dispersion. CNT based composites of polystyrene (PS), poly (methyl methacrylate) (PMMA), and vinyl monomers are commonly produced using this approach. Yuan et al. showed significant enhancement in the mechanical properties of PS-MWCNT composites prepared by a combination of in situ polymerization followed by melt mixing owing to strong interfacial adhesion between the CNT grafted PS and the PS matrix (Yuan et al., 2009).

2.8.2.3 Melt Compounding:

Owing to its simplicity and adaptability for a commercial scale up melt mixing/compounding seems to be the most commonly employed approach for thermoplastic polymer/MWCNT nanocomposites. This method is most suitable for polymers that cannot be processed with the solution processing approach owing to its inability to dissolve in commonly employed solvents. The higher magnitude of shear during the melt mixing process facilitates the breakup of the CNT agglomerates followed by simultaneous dispersion and distribution in the polymer melt. For a melt mixing process to give optimum dispersion quality optimization of all the process parameters like the screw configuration, screw speed, throughput/residence time, barrel temperatures, filler feeding position etc. is imperative.

2.8.3 Thermoplastic/ MWCNTs nanocomposites for space application

Siyuan et al. (2014) described the effect of adding acid functionalized (f-) MWCNTs as a reinforcing filler material in the PBI matrix. They have also studied the vital role of the MWCNTs as an effective reinforcement material for shielding high-energy radiation. The tensile strength property results portrayed potential reinforcing capability of f-MWCNTs in PBI
nanocomposites. Even at comparatively low loading of 0.25 wt. % of the f-MWCNTs, the PBI+f-MWCNTs shows minor reinforcement effects in terms of e-beam shielding properties.

Stienstra et al. (2006) reported the performance of aromatic polyetherimides (PEI) under simulated Low Earth Orbit (LEO) conditions. The effects of the polymer backbone structure on the thermo-optical stability under simulated ultraviolet (UV) radiation and atomic oxygen (AO) exposure were also investigated. The UV-induced degradation of all PEI films appears to be confined within a thin surface layer of approximately 0.5 µm, leaving the underlying material largely unaffected.

Santos et al. (2017), reported the effect of functionalized MWCNTs reinforcement in enhancing the mechanical and thermal properties of the PEI matrix. The dispersion of functionalized MWCNTs has been confirmed using morphological observations. PEI/MWCNTs nanocomposites were further processed into a laminate structure using carbon fiber as reinforcement. The MWCNTs addition improved the fracture resistance, the enhancement in the inter-laminar shear strength (ILSS) and compression shear test (CST) is about 16% and in the case of 58% respectively. Using weibull distribution, they verified that the laminate with MWCNT presents a lower dispersion of the results and greater reliability.

Iqbal et al. (2011), investigated the thermo-mechanical properties of compression molded PBI, PBI neat film, and nanocomposite films using TGA, dynamic mechanical analysis (DMA), and tensile testing. TGA results showed that compression-molded PBI possess high thermal stability up to a temperature of 550 °C. Thermal stability of PBI film improved about 15% by loading up to 2% carbon nanofibers (CNFs). A significant improvement in tensile strength of about 15% was achieved by dispersing 2 wt. % of CNFs in PBI film. The SEM micrographs confirmed the presence of uniform dispersion of CNFs in the PBI polymer solution. Analysis of
fractured surfaces revealed that the failure has been translated from ductile to brittle fracture. These reported results lead to the inference that PBI with excellent mechanical and thermal properties an excellent candidate for aerospace applications.

Iqbal et al. (2015), studied the effects of various high energy radiation (gamma radiation and electron radiation) on mechanical, thermal and optical properties of polybenzimidazole (PBI). TGA results of exposed and unexposed samples shows that both radiations have induced cross-linking in PBI matrix, which eventually enhanced the thermal stability of the polymer. These radiation induced effect on tensile strength property of PBI is insignificant. The radiation induced cross-linking effect aided in sustaining the stiffness of the polymer matrix even at high temperature condition. The results obtained clearly indicate the enhanced radiation resistance of the PBI polymer.

Najafi and Shin (2005), reported the degradation of poly (methyl methacrylate) (PMMA)/CNTs nanocomposite thin film exposed to e-beam radiation and UV ozone as a function of CNT concentration. The PMMA-CNT samples were exposed to 20 keV e-beam radiation for 15 min and the deteriorations occurred in the polymer film has been measured. The damages incurred by the radiation and also the etched depth of PMMA films have been analyzed and compared. The CNT reinforcement in the PMMA matrix imparted a dramatic influence on nature of the degradation by both high energy radiation sources.

Zhenhao et al. (2016) studied the reinforcement effectiveness of MWCNTs in enhancing the proton radiation shielding property of the poly (methyl-methacrylate) (PMMA). It was experimentally evaluated by comparing the proton transmission properties and secondary neutron generation of the PMMA/MWCNT nanocomposite with pure PMMA and aluminum. The results showed that the addition of MWCNTs in PMMA matrix can further reduce the
secondary neutron generation of the pure polymer, while no obvious change was found in the proton transmission property. On the other hand, both the pure PMMA and the nanocomposite were 18%–19% lighter in weight than aluminum for stopping the protons with the same energy and generated up to 5% fewer secondary neutrons. Furthermore, the use of MWCNTs showed enhanced thermal stability over the pure polymer, and thus the overall reinforcement effects make MWCNT an effective filler material for applications in the space industry.

2.9 Statistical mathematical modeling

2.9.1 Design of Experiments (DoE) approach for polymer nanocomposites:

DoE is a statistical tool for modeling and optimizing the experimental runs when the desired responses are influenced by several factors and levels. Compared to a conventional experimental approach when only one-factor-at-a-time (OFAT) is varied, DoE has several benefits. It can be used to analyze the factor interactions which is impossible with OFAT, to estimate error variation in the experiment, and to economically plot response contours (Mason et al. 2003). In the DoE approach, a chain of structured assessments are designed in which premeditated changes are made to the input factor variables of a system and the effects of these changes on a pre-defined response are assessed. All possible dependencies are planned in the first place, and the data needed to assess them are laid out. The main advantages of statistical design are producing comparatively precise data with least number of experimental trials thereby reducing the consumption of expensive materials and also saving time. It helps in evaluating the factor effects mathematically and also covers a large experimental region with minimum number of experimental runs. DoE helps in deducing the relationship between the system output responses and the vital factor variables. The different steps in DoE include selection of design,
conduct of experiments, regression analysis and generation of contour diagrams, response surfaces and factor plots.

The first step in DoE is to identify the vital factor variables (input) and the response (output) that is to be measured. The number of levels in each factor denotes the range for which the effect of that variable is desired to be known. This methodology involves coding of levels for the independent factor variables which is achieved by the identification of maximum (+1) and minimum (-1) levels. This lead to a significant change in the properties measured and also determination of midrange of the factor levels. The experimental plan determines the setting parameter for each run of the test. The response is then measured for each run. The changes in the response with respect to the change in input factor variables are to be observed. These changes are then attributed to the input factor variables either by single or interaction effect (Bhagawan 2008).

The second step is choice of selecting an experimental design based upon the objectives of the experiment and the number of vital factors to be investigated. The type of designs includes comparative; screening; response surface method RSM and optimal fitting of a regression model (Gunst, 1989).

2.9.1.1 Comparative objective:

The primary goal of the experiment is to comparatively analyze the significance level of one of the important factor (and its levels) from several other vital factors over the change in the response of a system or process.

2.9.1.2 Screening objective:

The main purpose is to screen out the few important main effects from the many less important ones.
2.9.1.3 **Response surface method (RSM) objective:**

To estimate interaction and quadratic effects of the factors, and therefore give us an idea of the (local) shape of the response surface we are investigating.

2.9.1.4 **Optimal fitting of a regression model objective:**

If we want to model a response as a mathematical function (either known or empirical) of a few continuous factors and we desire "good" model parameter estimates (i.e., unbiased and minimum variance), then a regression design is needed.

### 2.9.2 Types of design techniques

Choice of a design also depends on the amount of resources available and the degree of control over human errors. For nanocomposites design study, the design techniques available are factorial design (Tillekeratne et al. 2006), the Taguchi method (Barick et al. 2013), and the response surface methodology (RSM).

#### 2.9.2.1 Factorial design:

The factorial design can be full or fractioned design depending whether all factors and all experiment levels are needed (Mason et al. 2003). It can be used to develop an empirical model of the response variables in terms of the factors. The limitation of this method is it has no repeat experiments, so it is unable to estimate error variation or model adequacy.

#### 2.9.2.2 Taguchi method

The Taguchi method is a fractional factorial that offers simpler design than conventional factorial design. It is commonly applied to detect main effects. It has been used to observe the main processing factors in polyamide microcellular nanocomposite preparation (Yuan et al. 2005), the main effects in thermoplastic vulcanizate nanocomposite preparation (Barick et al. 2013), and the effect of material content (Lahijani et al. 2013). Because it was developed from a
fractioned factorial, the efficiency of the design, in term of runs, is very good. However, its limitation is that it’s not possible to observe curvature area.

2.9.2.3 **Response surface methodology (RSM):**

In contrast, RSM is dedicated to evaluate the relationship between of the vital factors and observed responses. The primary utility of using RSM is that it offers a methodology of strictly selecting less number of factors in a design space to efficiently represent all the possible factors that affect the responses of a system (Balachandran et al. (2010); Krishnaiah (2015)). The Central Composite designs (CCD) and Box-Behnken designs (BBD) are the two major Response surface designs.

2.9.2.3.1 **Box-Behnken Design (BBD):**

Box-Behnken Design (Banerjee et al. 2012) is a three-level quadratic design that does not contain fractional factorial design. The sample combinations are treated in such a way that they are located at midpoints of edges formed by any two factors. The design is rotatable (or in cases, nearly rotatable). One advantage of a Box-Behnken design is that it requires fewer design points than a full factorial CCD and a fractional factorial CCD. The limitation of this method is prediction at the corners of the design space is very poor and only three levels per parameter is present. Minimum three factors are required in order to run the design. It is impossible to reduce the design runs as linear 2 ways interaction is mandatory in BBD which is not in CCD.

2.9.2.3.2 **Central Composite Design (CCD):**

CCDs are very flexible and availability of several varieties of CCDs enables their use under different experimental regions of interest and operability. CCD is a rotatable design that provides equal precision for fitted response at points (factor level combinations) that are equal distances from the center of the factor space. The CCD is a rotatable design which would require
5 levels of each factor (-a, -1, 0, +1, +a). The three types of CCD are Face-centered composite design (FCCD), rotatable and inscribed. The right variety of CCD is chosen based on the region of interest and the region of operability (Montgomery 1997; Anderson 2004).

The FCCD design contains an imbedded factorial design with center points. It is used to find the best set of values, for a set of factors, giving an optimal response. In this design, the star points are at the center of each face of the factorial space, so $\alpha = \pm 1$. This design requires 3 levels of each factor. Minimum 2 factors are required in order to perform the design analysis. Assuming $Tr$ as the true response of a processing method, the response depends on vital factors that are manageable, i.e., $F_1, F_2, F_k$. The relationship between true response and the factors can be denoted as equation 2.

$$Tr = f (F_1, F_2, ... F_k) + Er$$

Where,

- $f$ - True response function
- $Er$ - Statistical or mechanical error often expected to have a normal distribution with mean zero and variance
- $F_1, F_2, ... F_k$ - Independent variables (stated in units of measurement such as MPa, °C, m/s², etc.).

RSM experiments usually transforms the independent variables into dimensionless coded variables where the standard deviation is similar to that of the independent variables and taking mean as zero. Usually coded variables are calculated using the following formulae:

$$Actual \ X_{ab} = (X_{ab} - \gamma)/\gamma$$

... [3]
Where,  
\[ \gamma = \frac{\text{maximum } X_{ab} + \text{minimum } X_{ab}}{2} \]  
\[ \gamma' = \frac{\text{maximum } X_{ab} - \text{minimum } X_{ab}}{2} \]  

Where, \( X_{ab} \) is the \( a^{th} \) natural variable for the \( b^{th} \) experimental run.

The design consists of a center point, 4 factorial points and 4 axial points (the axial points are parallel to every variable axis on a circle having a radius equal to 1.0 keeping center points as the origin). As shown in figure 2, the points represent the factor level combinations that establish the 9 design experimental runs. The total experimental runs required in FCCD can be deduced using the following equation.

\[
\text{Experimental runs (FCCD)} = 2^f + 2f + n \ldots \]

Where, \( f \) - Number of vital factors
\( n \) - Center points.

The responses are demonstrated by employing a second order polynomial quadratic regression equation which helps in assessing the quadratic effect, main and interactive effects of the vital factors over the resulting composite properties (Rai et al. 2016).

2.9.3 Interpretation of design analysis data

The interpretation can be done based on the following aspects which denote the relationship between vital factor variables and the responses.

2.9.3.1 Null hypothesis testing:

It quantifies the significance level of each term in the polynomial model. If \( p \)-value is low, it indicates that the null hypothesis is false and denotes the selected factors are statistically significant for each response measured. The factors which are essential for plotting in the contour plots can also be determined using this \( p \)-value.
2.9.3.2 R-squared value:

The higher the R-squared values, the better the polynomial is at either describing the system or making predictions about the system.

2.9.3.3 Regression analysis:

Regression analysis is a statistical procedure used to predict the response values from the values of one or more known factor variables. It also measures the relationship between each of the independent variables and the dependent variable. The regression analysis generates a response equation, which consists of the main, quadratic and the interaction terms. The general form of a regression equation for a response consisting of 2 factors \((k = 2)\) is 2\(^{nd}\) order polynomial approximation of the true response function \((R)\) can be expressed using the coded variables as stated in equation 1.

\[
R = E (Tr) = \beta_0 + \beta_a x_a + \beta_b x_b + \beta_{ab} x_a x_b + \beta_{aa} x_a^2 + \beta_{bb} x_b^2 \quad \ldots \ [7]
\]

Where,

- \(R\) - Response function
- \(x_a, x_b\) - Main effect of factor (a) and factor (b)
- \(\beta\) - Regression co-efficient
- \(x_a x_b\) - Interaction between two factors (a) and (b)

The common method used in RSM is regression scheme based on the least square method. This method is usually used to identify the regression coefficient. The above equation suits well to the true response surface as an approximation and the equation can be expressed as

\[
R = \beta_0 + \sum_{a=1}^{k} \beta_a x_a + \sum_{a=1}^{k} \beta_{aa} x_a^2 + \sum_{a < b=1}^{k} \beta_{ab} x_a x_b \quad \ldots \ [8]
\]

Where,
In the above mentioned equation, the $\beta_0$, $\beta_a$, $\beta_{ab}$, $\beta_{aa}$ are the mean values of responses that are linear, interaction and quadratic constant coefficients correspondingly.

DoE has been successfully utilized to optimize the performance and model the properties of polymer nanocomposites (Mirmohseni et al 2010). Thus DoE can be used as an effective tool to model and optimize the properties of polymer nanocomposites.

Based on the detailed literature review conversed from section 2.1 to 2.9, the various space environmental conditions and its interaction with the material, the problem statement for this dissertation is formulated.

### 2.10 Problem statement

In respect to the reviews highlighted from section 2.1 to 2.9, it is obvious that most of the research work was principally focused on effect of space environmental conditions over the change in thermo-mechanical properties of thermosetting fiber reinforced polymers such as epoxy/CF composite, polyimide/CF and thermoplastic aromatic polyimide (Kapton). It has also highlighted the effect of atomic oxygen erosion, high energy radiation (gamma, electron beam), vacuum outgassing and plasma environment in degrading the material properties of the composite after short period of exposure. Very limited research work has been attempted in employing high performance thermoplastic polymers such as PEI and PBI based composites for specialty application. The significance of improving the interfacial interaction between MWCNTs and the PEI and PBI matrices for space application are yet to be investigated. The space durable properties of high performance thermoplastic polymer and the effectiveness of
MWCNTs dispersion and reinforcement in the PEI and PBI matrices have not been investigated till date.

The existing knowledge from the available literature indicates that PEI and PBI matrices possess better mechanical, thermal, radiation resistance, AO and vacuum outgassing resistance than that of other polymers. From the primary properties of PEI and PBI, it is expected that when the polymers are exposed to extreme space environmental conditions, excessive exposure may cause trivial surface erosion and chain scissions in the polymer molecule up to certain extent, which in turn may affect the mechanical performance of the polymer and also initiate degradation of material. From the existing knowledge of the literature review, there is no research study that has established these effects on PEI and PBI based nanocomposites towards usage as structural or functional material in space application.

Based on these considerations, the present investigation aims to develop functionalized MWCNTs reinforced PEI and PBI based nanocomposite for space application. The MWCNTs have been functionalized using both partial acid treatment and nitrogen gas based low pressure plasma. The reinforcement effectiveness of dual functionalized MWCNTs in enhancing the thermo-mechanical properties related to space environmental durability has also been examined.

The morphological changes and effectiveness of surface functionalization over the dispersion of nanotube in the polymer matrix has been analyzed using Transmission electron microscopy (TEM). Spectroscopical analysis such as Fourier transforms infrared spectroscopy (FTIR) and x-ray photoelectron spectroscopy (XPS) has been employed to validate the surface functionalization of nanotube and development of interfacial adhesion between the polymer and the filler. The change in flow property of the polymer nanocomposite with respect to the MWCNTs loading has been analyzed using rheological study.
The PEI/MWCNTs and PBI/MWCNT nanocomposite has been exposed to Low earth orbit (LEO) environment and Geosynchronous earth orbit (GEO) environment such as electron beam and gamma radiation and also cryogenic to elevated temperature condition thermal cycle test. Thermal decomposition kinetics study has been performed to validate the thermal properties of the nanocomposite. The change in the tensile properties of PEI/MWCNTs and PBI/MWCNTs nanocomposite before and after exposure to space environmental conditions has also been studied using tensile testing machine.

Further, twin screw extrusion process of PEI/MWCNTs nanocomposite has been optimized using response surface methodology. The filler content (wt. %) and screw speed (rpm) has been acknowledged as the significant factors for manufacturing the nanocomposite depending upon its properties for space application. The non-linear quadratic regression equations has been deduced and employed to model the properties of importance and the various surface and contour plots were comprehended for optimizing the responses and the predicted responses has been validated based on experimental data.