CHAPTER 2
EXPERIMENTAL

This chapter deals with materials, testing equipments and experimental methods adopted for the present investigation. For the sake of convenience this chapter is divided into two parts. Part A covers the various materials used in this research programme such as polymers, fillers and others along with their chemical structure, physical properties and brief discussions about their industrial applications. Part B covers theory, equipments and experimental techniques adopted for the characterization of polymer composites.

PART A - MATERIALS AND EQUIPMENTS

This section gives details of polymer materials such as nylon 66, nylon 6, polytetrafluoroethylene (PTFE), polycarbonate (PC), polypropylene (PP), and ultra-high molecular weight polyethylene (UHMWPE), and fillers such as molybdenum disulphide (MoS\(_2\)), graphite, carbon black (CB), nanoclay and short glass fiber. This section also deals with equipments used to fabricate the composites and testing equipment’s that have been used to carry out this research work. Details of the polymers were collected from different sources[1,2].

2.1 MATERIALS
2.1.1 Nylon 6,6

The name nylon was given by the DuPont, USA which produced the first polyamide 66 (PA 66) in 1939. It caused a real revolution in the world of textiles, when the first premium man-made fiber was introduced. It is used in structural parts. The mechanical properties of nylon homopolymers are among the high temperature can be as high as 120°C, but properties can degrade with time due to oxidation. The biggest disadvantage of nyons as engineering materials is their tendency to absorb moisture. Nylon 6,6 is made of hexa methylene diamine and adipic acid, which give nylon 6,6 a total of 12 carbon atoms, and its molecular formula is C\(_{12}\)H\(_{22}\)O\(_2\)N\(_2\). It is a semi crystalline polymer and its structural formula is shown in Figure 2.1.
Figure 2.1 Structure of nylon 66

<table>
<thead>
<tr>
<th>Common name</th>
<th>Poly (hexamethylene adipamide)</th>
</tr>
</thead>
<tbody>
<tr>
<td>Trade names</td>
<td>Zytel (DuPont), Maranyl (ICI), Ultramid A</td>
</tr>
<tr>
<td>Class</td>
<td>Aliphatic polyamides</td>
</tr>
</tbody>
</table>

Table 2.1 Typical properties of nylon 66

<table>
<thead>
<tr>
<th>Properties</th>
<th>Nylon 66</th>
</tr>
</thead>
<tbody>
<tr>
<td>Glass transition temperature (°C)</td>
<td>50</td>
</tr>
<tr>
<td>Melting temperature (°C)</td>
<td>255</td>
</tr>
<tr>
<td>Density (crystalline) at 25°C (g/cc)</td>
<td>1.24</td>
</tr>
<tr>
<td>Density (amorphous) at 25°C (g/cc)</td>
<td>1.07</td>
</tr>
<tr>
<td>Tensile strength (MPa)</td>
<td>3300</td>
</tr>
<tr>
<td>Tensile modulus (MPa)</td>
<td>875</td>
</tr>
<tr>
<td>Flexural strength (MPa)</td>
<td>2827</td>
</tr>
<tr>
<td>Flexural modulus (MPa)</td>
<td>53</td>
</tr>
<tr>
<td>Izod impact strength (notched) J/m</td>
<td>363</td>
</tr>
<tr>
<td>Heat deflection temperature (1.82 MPa) °C</td>
<td>1.2</td>
</tr>
<tr>
<td>Water absorption, 24hr (%)</td>
<td>82</td>
</tr>
<tr>
<td>Surface hardness (Shore D)</td>
<td>1.131</td>
</tr>
</tbody>
</table>

Nylon 66 has a melting point of 255°C, high for a synthetic fiber, though not a match for polyesters or aramids such as Kevlar. This fact makes it the most resistant to heat and friction and enables it to withstand heat setting for twist retention. Its long molecular chain results in more sites for hydrogen bonds, creating chemical “springs” and making it very resilient. It has a dense structure with small, evenly spaced pores. This means that nylon 66 is difficult to dye, but once dyed it has superior colorfastness and is less susceptible to fading from sunlight and ozone and to yellowing from nitrous oxide.

High mechanical strength, great rigidity, good deep-drawing behaviour, good dimensional stability under heat, good toughness even at low temperatures, favorable tribological properties, good resistance to chemicals, very good electro-insulating
properties, good dimensional stability, rapid processing. Nylon 66 has high lubricity and moderate strength. It is tough, inexpensive, but has poor dimensional stability due to water absorption (hygroscopic nature). PA is commonly used to make high-lubricity parts such as bearings, blow moldings molds and clothing fabrics.

**Applications:** Nylon 6 and nylon 66 are engineering thermoplastics which have found great attractions in wide variety of engineering applications due to their desirable mechanical properties, suitable tribological characteristics and ease of processing. The properties can also be improved further when suitable particulates, short fibers or special additives are incorporated into the PAs. However, the type and content of the additives depend on the final usage of the product. The good wear resistance and self-lubricating characteristics as well as good strength and stiffness of PAs make these thermoplastics promising candidate in the bearing applications where two different bodies are in contact at severe sliding conditions [1,2]. Compared to nylon 6, nylon 66 is harder and has better wear properties. It is often used for slider pads, switches, plugs, wheel cover, chair bases, spectacle frames, insulating liners for railways, nose cones for defense, vacuum cleaner housings, mono-filaments, connectors, and radiator end tanks.

Nylon was intended to be a synthetic replacement for silk and substituted for it in many different products after silk became scarce during World War II. Nylon fibres are used in many applications, including fabrics, bridal veils, musical strings and rope. The most important applications for nylon include automotive engineering, chemical engineering, electrical engineering, mechanical engineering in general, wind power generation, materials handling, instrumentation, packaging, apparel, airbags, carpet fiber, tires, ropes, hoses, conveyor belts, plumbing and sanitary ware applications.

Nylon 66 Zytel 101 L, lubricated grade having MFI 30-40g/10min was supplied by M/s DuPont, India Limited is used in this study.

### 2.1.2 Nylon 6

Polyamides (PAs) are a group of thermoplastic polymers containing amide groups (−CONH) in the main chain. They are popularly known as nyons. Polyamide 6 (PA 6) [NH− (CH\(_2\))\(_5\)−CO]\(_n\) is made from \(\varepsilon\)-caprolactum. Nylon 6 is formed by ring-opening polymerization of \(\varepsilon\)-caprolactum. Its molecular formula is C\(_6\)H\(_{11}\)ON and its structural formula is shown in Figure 2.2.
Figure 2.2. Structure of nylon 6

Alternative name  poly-ε-caproamide
Trade names  Capron, Ultramid, Nylatron
Class  Aliphatic polyamides

**Properties:** Nylon 6 is a crystalline thermoplastic with a low thermal coefficient of linear expansion. The reinforced resins, in particular, undergo very little dimensional change when the temperature changes. Characteristics of PA 6 are; hard and tough thermoplastic, good abrasion resistance, low coefficient of friction, high tensile strength, good dimensional stability, low tendency to warp, resistant to lubricants, engine fuels, grease, etc., good resistance to coolants, paints and solvent cleaners, possess high HDT, attacked by strong acids, phenols, cresols at elevated temperatures, poor UV resistance, low coefficient of thermal expansion and high sensitive to moisture. The typical properties of PA 6 used in this study is presented in Table 2.2.

<table>
<thead>
<tr>
<th>Properties</th>
<th>Nylon 6</th>
</tr>
</thead>
<tbody>
<tr>
<td>Glass transition temperature (°C)</td>
<td>47</td>
</tr>
<tr>
<td>Melting temperature (°C)</td>
<td>220</td>
</tr>
<tr>
<td>Density (crystalline) at 25°C (g/cc)</td>
<td>1.23</td>
</tr>
<tr>
<td>Density (amorphous) at 25°C (g/cc)</td>
<td>1.084</td>
</tr>
<tr>
<td>Tensile strength (MPa)</td>
<td>80</td>
</tr>
<tr>
<td>Tensile modulus (MPa)</td>
<td>3000</td>
</tr>
<tr>
<td>Flexural strength (MPa)</td>
<td>850</td>
</tr>
<tr>
<td>Flexural modulus (MPa)</td>
<td>2414</td>
</tr>
<tr>
<td>Izod impact strength (notched) J/m</td>
<td>53</td>
</tr>
<tr>
<td>Heat deflection temperature (1.82 MPa) (°C)</td>
<td>58</td>
</tr>
<tr>
<td>Water absorption, 24hr (%)</td>
<td>3.0</td>
</tr>
<tr>
<td>Surface hardness (shore D)</td>
<td>79</td>
</tr>
</tbody>
</table>

Most of the application involves in electrical sector like electrical motor casings for portable power tools, grips and handles for tools, portable lamp housing battery boxes, distributor caps for automobiles. The domestic application includes electric food mixers, grinders, juicers, electric casing, furniture, hair dryers, washing machines, radio, television receivers and transmitters.
Polyamides are large volume plastics widely used for structural and packaging applications. Their market spread is continuously growing due to their properties such as chemical and mechanical resistance, less coefficient of friction, good barrier properties to gases, clarity, printability, etc. The ultimate properties of end products are, of course, heavily dependent on the chemical structure of PA and on the process used to produce the manufactured articles and can be further increased using nanoparticles as additives to enhance the polymer performance.

**Applications:** Gear teeth, pinions, ball bearing cages, switch parts, spools, electro-insulating parts; semi-finished products, pipes, profiles; machine parts, parts subject to wear such as friction bearings, roller bearing cages, engine parts, water pump impellers and also parts of door locks; fan and blower wheels, parts of housings, fuel filters, clips, chain tension rails; sliding bearings for swivel chairs and folding tables, sliding feet and fittings, connecting parts in furniture.

Solid nylon is used for mechanical parts such as machine screws, hair combs, gears and other low- to medium-stress components previously cast in metal. Engineering-grade nylon is processed by extrusion, casting, and injection molding. Nylon is available in glass-filled variants which increase structural and impact strength and rigidity, and molybdenum sulfide-filled variants which increase lubricity.

Nylon 6 E 28, extrusion grade with an MFI 20-25 g/10 min was supplied by M/s. Gujilon India Ltd., India, is used in this study.

### 2.1.3 Polytetrafluoroethylene

Polytetrafluoroethylene (PTFE) is truly a unique material and still the most widely used of all the fluoropolymers. PTFE has a combination of chemical, electrical and thermal performance unmatched by any other commercially available material. PTFE is a highly crystalline polymer which is very resistant to attack by corrosives and solvents. It also has extremely good thermal resistance at temperatures up to 340 °C. PTFE is used in a broad range of applications, including gasketing, pump parts, bearings, and anti-stick applications. PTFE molecular formula is C₂F₄ and its structural formula is shown in Figure 2.3.

\[
- [\text{CF}_2 - \text{CF}_2 ] -
\]

**Figure 2.3 Structure of PTFE**
Trade names: Teflon, Hostaflon, Fluon, Algoflon, Halon, Polyflon, Fluoroplast

Class: Poly(α-olefins)

**Properties:** Three major forms of PTFE exist: granular, fine powder, and micropowders. Granular is produced by suspension polymerization in the absence of a surfactant. It is a spongy, porous form of irregular particle shape as polymerized, and it is typically ground to a particle size to suit fabrication and end-use needs. Fine powder is coagulated from dispersion which is polymerized in the presence of an emulsifying agent. It can be supplied as the dispersion or in a coagulated form. It is extremely sensitive to mechanical shear. Micropowder can be produced as a low molecular weight form of powder or by scission of powder products by gamma or electron beam irradiation. It is typically a waxy or friable powder.

**Table 2.3. Typical characteristic properties of PTFE**

<table>
<thead>
<tr>
<th>Properties</th>
<th>PTFE</th>
</tr>
</thead>
<tbody>
<tr>
<td>Glass transition temperature (°C)</td>
<td>399</td>
</tr>
<tr>
<td>Melting temperature (°C)</td>
<td>327</td>
</tr>
<tr>
<td>Density (crystalline) at 25°C (g/cc)</td>
<td>2.30</td>
</tr>
<tr>
<td>Density (amorphous) at 25°C (g/cc)</td>
<td>7-28</td>
</tr>
<tr>
<td>Tensile strength (MPa)</td>
<td>340</td>
</tr>
<tr>
<td>Tensile modulus (MPa)</td>
<td>No break</td>
</tr>
<tr>
<td>Flexural strength (MPa)</td>
<td>350</td>
</tr>
<tr>
<td>Flexural modulus (MPa)</td>
<td>187</td>
</tr>
<tr>
<td>Izod impact strength (notched) J/m</td>
<td>333</td>
</tr>
<tr>
<td>Heat deflection temperature (1.82 MPa) °C</td>
<td>0.0</td>
</tr>
<tr>
<td>Water absorption, 24hr (%)</td>
<td>42</td>
</tr>
<tr>
<td>Surface hardness (shore D)</td>
<td>2.1</td>
</tr>
</tbody>
</table>

**Applications:** Granular and fine powder forms are used in electrical wire insulation, seals, and gaskets, and in valve and pipe fittings and linings for harsh chemical applications. Fine powders are also prepared in fiber, filament, and porous fabric forms. Dispersions are used in glass cloth coatings to provide weather protection, mechanical strength, and chemical resistance. Micropowders are used as additives to inks, lubricants, and plastics to provide lubricity, anti-burning, and nonstick properties.

The molecular configuration of PTFE imparts its surfaces with a high degree of anti-adhesiveness, and for the same reason these surfaces are hardly wettable.
PTFE possesses the lowest friction coefficients of all solid materials, between 0.05 and 0.09. The static and dynamic friction coefficients are almost equal, so that there is no seizure or stick-slip action. Wear depends upon the condition and type of the other sliding surface and obviously depends upon the speed and loads. PTFE coatings for composite have been developed to overcome the inherent softness of fluoropolymers used for surface release. They minimize the unwanted adhesion of products to production machinery, and reduce cleaning time; product wastage; contamination of product; and damage to machinery. They minimize the use of liquid lubricants and the wear that naturally results from two surfaces moving in contact. Reduces wear, heat generation; running costs, maintenance costs, machine downtime, and operational limitations. It has exceptional chemical and corrosion resistance, low coefficient of friction, resists abrasion, is flame resistant, can withstand extremes of temperature, and is chemically inert. These non-reactive qualities make PTFE a good candidate for use in containers and pipes used for reactive or corrosive chemicals. PTFE’s good surface release and low friction properties make is useful in applications which do not have heavy mechanical demands.

PTFE (NC010 601E) used in this study is manufactured by DuPont company.

2.1.4 Polycarbonate

Polycarbonates (PCs) are among the strongest, toughest and most rigid engineering thermoplastics. Its molecular formula is C\(_{16}\)H\(_{14}\)O\(_3\). In addition, they have a ductility normally associated with the softer, lower modulus thermoplastics. This polymer, a branch of polyester, was developed in 1958, its main structure being bis-phenol Bayer, in West Germany, is first to produce and market PC. The typical properties of PC are; density - 1.124 g/cc, and glass transition temperature is 145-150 °C. MoS\(_2\) typical properties are; density - 2.1 g/cc, water absorption - < 0.01 % and particle size 30-100µm.

![Figure 2.4 Structure of polycarbonate](image)

**Figure 2.4 Structure of polycarbonate**
Alternative name: Bisphenol-A polycarbonate
Trade names: Lexan (GE), Makrolon (Bayer)
Class: Polyesters

PC is an extremely tough thermoplastic with outstanding strength, dimensional stability and electrical properties, high heat distortion temperature and low-temperature resistance (down to −100°C). It is available in transparent optical, translucent, and opaque grades (many colors). PCs have only fair resistance to chemicals as evidenced by the stress cracking caused by many solvents. The weathering tendencies can be stabilized against ultraviolet radiation by the use of proper additives. PC compounds are used for injection moldings and extrusions for glazing panels, helmets, face shields, dashboards, window cranks and gears.

Properties: PC is a clear, colorless polymer used extensively for engineering and optical applications. PC resin is generally stable to water, mineral and organic acids. It is available commercially in both pellet and sheet form. Outstanding properties include impact strength and scratch resistance. The most serious deficiencies are poor weatherability and chemical resistance. PC is many times stronger than acrylic, yet has the toughness and ductility associated with the softer and more rubbery materials. PC has high resistance to deformation under load and at temperature extremes. They possess excellent impact strength, good dimensional stability, very good thermal stability, exceptional machinability, high dielectric strength and high volume resistivity.

Table 2.4. Typical properties of polycarbonate

<table>
<thead>
<tr>
<th>Properties</th>
<th>PC</th>
</tr>
</thead>
<tbody>
<tr>
<td>Glass transition temperature (°C)</td>
<td>145</td>
</tr>
<tr>
<td>Melting temperature (°C)</td>
<td>225</td>
</tr>
<tr>
<td>Density (crystalline) at 25°C (g/cc)</td>
<td>1.20</td>
</tr>
<tr>
<td>Density(amorphous) at 25°C (g/cc)</td>
<td>2380</td>
</tr>
<tr>
<td>Tensile strength (MPa)</td>
<td>62.1</td>
</tr>
<tr>
<td>Tensile modulus (MPa)</td>
<td>93.1</td>
</tr>
<tr>
<td>Flexural strength (MPa)</td>
<td>2340</td>
</tr>
<tr>
<td>Flexural modulus (MPa)</td>
<td>850</td>
</tr>
<tr>
<td>Izod impact strength (notched) J/m</td>
<td>405</td>
</tr>
<tr>
<td>Water absorption, 24hr (%)</td>
<td>85</td>
</tr>
<tr>
<td>Surface hardness (shore D)</td>
<td>1.124</td>
</tr>
<tr>
<td>Molecular weight of repeat unit (g/mol)</td>
<td>254.3</td>
</tr>
</tbody>
</table>
Polycarbonates are almost clear like glass and can be colored to desired shades. They are very tough almost unbreakable, and have excellent dimensional stability over a wide range of temperature from sub-zero to sterilization temperatures. Because of its good ductile properties, they can be nailed, sawed, punched, drilled, cold-drawn, sheared and riveted without any cracks. It has excellent chemical resistance and safe for potable water, food processing and packaging. It also has good electrical resistance and machining qualities. In addition PC has a high glass transition temperature in the proximity of 145-150 °C, its melting temperature is 225°C and yet this polymer is not brittle like PS.

Although there may be a loss of toughness with heat aging, the material still remains stronger than many thermoplastics. PCs are transparent materials and resistant to a variety of chemicals, but they are attacked by a number of organic solvents like ketones, chlorinated hydrocarbons, high-octane gasoline, strong acids and alkalis etc.

**Applications:** While the performance characteristics PC are utilized singly or in combinations, they are most commonly relied on their high impact strength, water-clear transparency, good creep resistance, wide use temperature range, dimensional stability, abrasion resistance, hardness, and rigidity despite its ductility. Perhaps one of the best known trade names in plastics is Lexan which has mechanical engineering applications like machine guards, guides, bushings, shields and other applications in signs insulators, compact discs, window glazing, security glazing and optical lenses.

Because of its toughness and impact resistance, it is used for the manufacture of helmets, shields, street lamp covers, factory and school windows, machine guards etc. Because of its high temperature resistance, it is also used as housing for high voltage lamps, aircrafts, instrument panel etc. Its physiological harmlessness had made it suitable for refrigerator parts, food vending machines and various household appliances. Because of its easy machinability and fabrication PC sheets are widely used in place of metals and glass.

PCs of opaque grades are used for thin wall mechanical parts and large exterior parts. PC offers impact properties that can meet requirements for instrument panels without the need for padding. Hardware applications include drapery fixtures, furniture’s, plumbing and sophisticated electrical and electronic products. PC also finds its applications in housing internal parts of printers, copier terminals, circuit
boards, wiring blocks, connectors in telephones and other industrial components. PC (Makrolon 2856) used in this study was manufactured by M/s. Bayer India limited has an MFI 10g/10min.

2.1.5 Polypropylene

Polypropylene (PP) is a low-density, hard, stiff, creep-resistant plastic with good resistance to chemicals, good wear resistance, low water absorption, and is relatively low cost. Its mmolecular formula is C₃H₆ and it belongs to poly(α-olefins) family. PP can be spun into filaments, converted into weaves, injection moulded, and is commonly produced in a large variety of forms. Glass filled polypropylene is widely used for its enhanced mechanical properties. It is used for food and chemical containers, domestic appliances, furniture, car parts, twine, toys, tubing, cable sheath, and bristles. The density and melt flow rate of neat PP were 0.90 g/cc and 11 g/10 min. The typical properties of PP are given in Table 2.4.

Structure of PP

\[
\begin{align*}
\text{CH}_3 \\
- [ \text{CH}_2 - \text{CH}] - 
\end{align*}
\]

<table>
<thead>
<tr>
<th>Properties</th>
<th>PP</th>
</tr>
</thead>
<tbody>
<tr>
<td>Glass transition temperature (°C)</td>
<td>-10</td>
</tr>
<tr>
<td>Melting temperature (°C)</td>
<td>173</td>
</tr>
<tr>
<td>Density at 25°C (g/cc)</td>
<td>0.95</td>
</tr>
<tr>
<td>Tensile strength (MPa)</td>
<td>36</td>
</tr>
<tr>
<td>Tensile modulus (MPa)</td>
<td>1657</td>
</tr>
<tr>
<td>Flexural strength (MPa)</td>
<td>25.6</td>
</tr>
<tr>
<td>Flexural modulus (MPa)</td>
<td>1650</td>
</tr>
<tr>
<td>Izod impact strength (notched) J/m</td>
<td>27</td>
</tr>
<tr>
<td>Heat deflection temperature (1.82 MPa) °C</td>
<td>104</td>
</tr>
<tr>
<td>Surface hardness (shore D)</td>
<td>65</td>
</tr>
</tbody>
</table>

Polypropylene of J-170 grade (whose density is 0.9 g/cc and Tₘ is 155-170 °C) was obtained from Honam Petrochemical Co., China.
2.1.6 Ultra high molecular weight polyethylene

Ultra high molecular weight polyethylene (UHMWPE) is a linear polymer with a molecular weight in the range of 3,100,000 to 6,000,000. Therefore, UHMWPE has a molecular weight average 10 times that of conventional high density polyethylene resin. The high molecular weight gives UHMWPE a unique combination of high impact strength, low coefficient of friction and abrasion resistance making it more suitable for many applications where lower molecular weight grades fail. UHMWPE is a self-lubricating material which exhibits excellent wear and abrasion properties in addition to extremely high impact strength. Markets which would utilize these attributes would be snowboard bottoms, material handling, packaging, food processing and automotive just to name a few.

UHMWPE is a versatile, high performing material that stands up to demanding applications in many industries. It is often chosen for wear and sliding surface for bulk materials and ores, where it provides a low friction surface that resists wear and chemicals. These properties are also important on equipment for lining industry, paper-making, chemical, textile, and water and wastewater treatment facilities. UHMWPE’s ability to retain its mechanical properties to near absolute zero makes it ideal for winter sports equipment and cryogenic applications.

Many applications of UHMWPE are an ideal replacement to PTFE (Teflon), due to its low coefficient of friction & non-stick properties. Being a good insulator, most anti-static applications can be utilized and UV-stabilized grades are offered for outdoor applications with no physical changes with environment.

UHMWPE of XM-220 grade (whose average particle size is 30-50 μm density is 0.94 g/cc and T_m is 135 °C) were obtained from Mitsui Petrochemical Industries, Ltd.,

2.1.7 Fillers

Traditionally, fillers were considered as additives, due to their unfavorable geometrical features, surface area or surface chemical composition, could only moderately increase the modulus of the polymer, while strength remained unchanged or even decreased. Particulate filler reinforcements for polymer composite systems are available in numerous different size and shapes including spherical, cubic, platelet or any other regular or irregular geometry [3-4]. Each type and form imparts their
own specific properties to the final product. Particulate filler reinforced composites have been reported to offer many advantages over neat resin matrices including; increased stiffness, strength and dimensional stability, increased toughness or impact strength, increased heat distortion temperature, increased mechanical damping, reduced permeability to gases and liquids, modified electrical properties, and reduced costs [5].

2.1.8 Solid lubricants/Tribological additives

Different types of solid materials most widely used at the present time include (i) specific fillers (layer-lattice solids): molybdenite or molysulfide (MoS$_2$) and graphite, (ii) polymers: PTFE (polytetrafluoroethylene), polychlorofluoroethylene, silicones and (iii) less frequently used materials: ceramics, e.g., boron nitride (BN), aramid or carbon fibers; miscellaneous, e.g. calcium fluoride, cerium fluoride, tungsten disulfide, mica, borax, silver sulfate, cadmium iodide, lead iodide and talc.

Among the above-listed materials, MoS$_2$ and graphite are the predominant solid lubricants. In dry powder form, these are effective lubricants due to their lamellar structures. Solid/dry lubricants are useful under conditions when conventional liquid lubricants are inadequate [6-7], namely high temperatures, conditions of reciprocating motion, and extreme contact pressures.

2.1.9 Molybdenum disulfide

Molybdenum disulfide is the inorganic compound with the formula MoS$_2$. This black crystalline sulfide of molybdenum occurs as the mineral molybdenite. It is the principal ore from which molybdenum metal is extracted. The natural amorphous form is known as the rarer mineral jordisite. MoS$_2$ is less reactive than other transition metal chalcogenides, being unaffected by dilute acids. In its appearance and feel, molybdenum disulfide is similar to graphite. Indeed, like graphite, it is widely used as a solid lubricant because of its low friction properties, sometimes to relatively high temperatures.

MoS$_2$ with particle sizes in the range of 1-100 µm is a common dry lubricant. Few alternatives exist that can confer the high lubricity and stability up to 350 °C in oxidizing environments. Sliding friction tests of MoS$_2$ using a pin on disc tester at low loads (0.1-2 N) give friction coefficient values of < 0.1 [3,4]
MoS$_2$ is often a component of blends and composites where low friction is sought. A variety of oils and greases are used, because they retain their lubricity even in cases of almost complete oil loss, thus finding a use in critical applications such as aircraft engines. When added to plastics, MoS$_2$ forms a composite with improved strength as well as reduced friction. Polymers that have been filled with MoS$_2$ include nylon, teflon and vespel. Self-lubricating composite coatings for high-temperature applications have been developed consisting of MoS$_2$ and titanium nitride by chemical vapor deposition [5].

The use of molybdenite as a lubricant was apparently recorded in the early 17$^{th}$ century by John Andrew Cramer [8]. Its lubrication performance often exceeds that of graphite, and it is also effective in vacuo or under an inert atmosphere up to 1200 °C, temperatures at which graphite cannot be used. The temperature limit of 400 °C for the use of molybdenite in air is imposed by oxidation. It begins to sublime at 450 °C. It is insoluble in water, dilute acids, and most organic solvents. When used as a lubricant, the particle size should be matched to the surface roughness of the plastic or metal substrate. Large particles may result in excessive wear by abrasion caused by impurities, while small particles may promote accelerated oxidation [6-7].

Figure 2.5 [6-7] shows a comparison of the crystal structures of MoS$_2$ and graphite. Molybdenite’s hexagonal crystal structure is composed of molybdenum ions sandwiched between layers of sulfur ions. The sulfur layers are strongly bonded to the molybdenum, but are not strongly bonded to other sulfur layers, rendering it softness, easy shear and perfect cleavage [6]. Thus, the principle of action of molybdenite as a dry lubricant is based on the formation of bonds between the metal and sulfur. These bonds slip under shear forces, but are continuously reformed, thereby holding the lubricating film on the surface [9].

(a) (b)

Figure 2.5. Comparison of crystal structures of (a) MoS$_2$ and (b) Graphite
**Application:** MoS$_2$ finds many industrial applications where it is either impossible or impractical for components to be lubricated using liquid lubricants. MoS$_2$ is a material approved for roller and slide bearings, sliding rails and guides, cams and cam plates, bolts, joints, hinges, cardan shafts, steering racks, threaded spindles across the entire machinery and mechanical engineering industry. MoS$_2$ is approved for wheel bearing lubricant, as well as multipurpose lubricant for kingpins, track rod joints, cardan shafts and spline shafts. MoS$_2$ used for improved wear protection in the case of boundary lubrication; waterproof and corrosion preventive. MoS$_2$ based coatings are used for friction reduction and control. Dry-film lubricants like moly coatings are extremely useful for working parts which operate in an environment unsuitable for wet lubricants, or are positioned in awkward places that make wet lubrication very difficult. Different MoS$_2$ coatings have variable degrees of corrosion and wear resistance qualities. The coating is suitable for heavily loaded mechanical applications, but not safe for food contact applications. MoS$_2$ used in our research investigation has a particle size of $< 10\mu$ and manufactured by Thomson & Grek limited.

### 2.1.10 Graphite

Graphite is one of the oldest and most widely used (due to its lower price compared to MoS$_2$ or BN) solid lubricants. It is obtained both as a soft mineral and as a manmade (synthetic) product. Graphite powders are used as solid lubricants in three ways: (i) in dry films, (ii) as an additive in liquids (oils) or semi-solids (greases) and (iii) as a component of self-lubricating (internally lubricated) composites [8-9].

Most commercial grade amorphous graphite is formed from the contact or regional metamorphism of anthracite coal. It is considered a seam mineral and is extracted using conventional, coal-type mining techniques. Synthetic graphite, also known as “artificial graphite,” is a man-made product. Synthetic graphite is manufactured by heat-treating amorphous carbons, i.e. calcined petroleum coke, pitch coke, etc., in a reducing atmosphere at temperatures above 2500 °C. At high temperatures, the “pregraphitic” structures present in these “graphitizable carbons” become aligned in three dimensions. The result is the transformation of a two-dimensionally ordered amorphous carbon into a three-dimensionally ordered crystalline carbon. Feedstocks for synthetic graphite production are chosen from
product streams that have a high concentration of polynuclear aromatic structures that can coalesce to graphene layers under the influence of heat [10-11].

In polymer applications, crystalline vein graphite, in addition to lubricity, may offer superior performance since it has slightly higher thermal and electrical conductivity, which result from its high degree of crystalline perfection and good oxidation resistance. Amorphous graphite is the least “graphitic” of the natural graphites. However, the term “amorphous” is a misnomer since this material is truly crystalline. Amorphous graphite is typically lower in purity than other natural graphites due to the intimate contact between the graphite “microcrystals” and the mineral ash with which it is associated. While MoS$_2$ coatings have traditionally been applied on components subjected to high-pressures, whilst graphite coatings have been used in applications at high temperatures. The morphology of lake graphite is consistently laminar regardless of particle size.

![Figure 2.6. Scanning electron micrograph (SEM) of flake graphite pinacoid structure](image)

The filler material was graphite powder with particle size 300 mesh, 98% purity which was procured from Brakes India Limited, Nanjanagud manufactured by graphite India Limited.

### 2.1.11 Carbon black

Carbon black is a material produced by the incomplete combustion of heavy petroleum products. It is used as a pigment and reinforcement in rubber and plastic products. The application of carbon black vulcan XC-72R in polymeric electrolyte fuel cells; heat transfer and growth of primary black carbon particles in gas mixture.

Carbon black powder obtained from M/s. Cabot, India with particle sizes in the range 30-35 μm, pigment grade was used as received.
2.1.12 Glass fibers

Glass fiber also called as fiber-glass is the material made from extremely fine fibers of glass. It is used as a reinforcing agent for many polymer products; the resulting composite material, properly known as fiber-reinforced polymer (FRP) or glass-reinforced plastic (GRP). Glass fiber is formed when thin strands of silica-based or other formulation glass is extruded into many fibers with small diameters suitable for textile processing. It lowers warpage and reduces creep, particularly at higher temperatures. E-glass fibre, silane coupling agent (0.5-1.0%), 3mm to 4mm length Chopped Strand, coupling agent silicon titride 0.6 to 0.8 µm manufactured by Owens Corning (India) Ltd.

Types of glass fibers

Glass fiber reinforcements are classified according to their properties. At present there are five major types of glass used to make fibers. The letter designation is taken from a characteristic property:

A-glass is a high-alkali glass containing 25% soda and lime, which offers very good resistance to chemicals, but lower electrical properties.

C-glass is chemical glass, a special mixture with extremely high chemical resistance

D-glass has a low dielectric constant with superior electrical properties. However, its mechanical properties are not so good.

E-glass is electrical grade with low alkali content. It manifests better electrical insulation and strongly resists attack by water. More than 50% of the glass fibers used for reinforcement is E-glass.

Short glass Fiber improves tensile and flexural strength, tensile and flexural modulus (or stiffness), short-term temperature (HDT) resistance over neat resins, potential to reduce the abrasion by fibers by maintaining a low friction film.

Among the fibre reinforcements, glass, and carbon fibres are the most likely candidates and are widely employed. Among these fibers, glass fiber especially E-Glass is the most commonly used, both in the textiles industry and in polymer composites, where it accounts for 90% of the reinforcement used. E glass is so named (electrical glass) because of its high electrical resistivity. These types of glass fibres are made of alumino borosilicates glass with very low sodium oxide content. They are often preferred because of its good chemical durability and high softening point. E-glass fibres also have good stiffness, strength and weathering properties.
The glass fibres used in this study is E-glass (silane coated chopped strand, 3-5 mm length) fibre obtained from Owen Corning glass, India.

2.13 Nanoclay

Organically modified montmorillonite (o-MMT) (Nanomer I.31PS) was obtained from M/s. Sigma, Bangalore. It was surface modified MMT clay: (Na)-modifiers-gamma-aminopropyl triethoxysilane, octadecylamine (CEC ~145 meq/100 g). The 1.31PS and 1.44PS grades are containing silane modification. Silane coupling agents enable trouble-free nanomer dispersion under mild shearing conditions and better silicate layer stability. Processing temperature limits for the 1.31 and 1.44 series are 540 F (280°C) and 460 F (240°C), respectively. 1.44PT features better heat stability than standard 1.44P, particularly in long residence time processing. Typically, they have mean particle sizes in the range of 15-20 μm.

Nanomer nanoclays are high purity, surface modified montmorillonite clay intended for use in a wide variety of plastics. When properly dispersed into polyolefins, nanomer products create a nanocomposite with improved mechanical properties and flame resistance. Nanocor has commercial Nanomer nanoclay powder and nanoMax® nanoclay masterbatches available for polyolefin resin systems. Some of the typical properties of montmorillonite are given in Table 2.4.

<table>
<thead>
<tr>
<th>Properties</th>
<th>Nanoclay(montmorillonite)</th>
</tr>
</thead>
<tbody>
<tr>
<td>Chemical formula</td>
<td>(Na, Ca)<em>{0.33}(Al, Mg)</em>{2}Si_{4}O_{10}(OH)<em>{2} nH</em>{2}O</td>
</tr>
<tr>
<td>Molecular weight (M_w)</td>
<td>540.46</td>
</tr>
<tr>
<td>Density (g/cc)</td>
<td>2 - 2.7 (average 2.35)</td>
</tr>
<tr>
<td>Shape</td>
<td>Platelet</td>
</tr>
<tr>
<td>Surface area</td>
<td>750 m$^2$/g when exfoliated</td>
</tr>
<tr>
<td>Modulus (GPa)</td>
<td>178</td>
</tr>
<tr>
<td>Hardness</td>
<td>1-2</td>
</tr>
</tbody>
</table>

Table 2.4. Typical physical properties of montmorillonite

The nanoclay (synthetic hectorite, Laponite XLS, used in this study was obtained from Rockwood Co. USA. The composition of Laponite XLS is 92.32 wt% Mg$_{5.34}$Li$_{0.66}$Si$_{8}$O$_{20}$(OH)$_{4}$Na$_{0.66}$ and 7.68 wt % Na$_{4}$P$_{2}$O$_{7}$.
2.2 EQUIPMENTS

Prepared composites have been characterized by physical, chemical, mechanical and analytical techniques. Physical methods such as density, surface hardness and percentage swelling were used to characterize the prepared composites. Analytical instruments such as DSC, TGA and DMA are used to characterize composites. The morphological behaviour of polymer composites was evaluated by scanning electron microscopy (SEM). The following equipments are used for the preparation and characterization of polymer composites.

2.2.1 Extruder

The extruder used in this study for fabrication of composites is a twin screw co-rotating. The screw is 924 mm long and 28 mm in diameter (i.e., l/d = 33) and the extruder has a nominal output of 10-20 kg/hr. There are three mixing zones composed of kneading blocks arranged. The mixing blocks of the screws are with modular design. There are total five heating and cooling zones along the barrel including the adapter and the die areas with sensors to control the process parameters. The temperatures of these five zones were set at the required temperatures of the respective composites. The temperature profile followed for the melt processing of the composite is given in the respective chapters.

2.2.2 Injection moulding machine

The test specimens were prepared as per the ASTM standard specifications using various moulds in injection moulding machine (80T model ES 330/80 HLS, International Equipments, China, 50T model. The injection moulding machine consists of two major parts viz., injection and clamping units with the necessary control systems wherein the mould is fixed and operated by applying the optimized processing conditions for making the test specimens.

The following paragraphs provide a brief theory, techniques and experimental procedure adopted for each of the above methods.

2.2.3 Density

Densities of composites are measured using Mettler electronic balance, Toledo, Switzerland, model AG 204 with a weighing accuracy of ± 0.0001 g according to ASTM 792-86.
2.2.4 Universal testing machine

The tensile behaviours of nanocomposites were carried-out as per ASTM D 638 using 4302 model universal testing machine (UTM), using Lloyds (UK), LR 100K, 100KN, with an accuracy of ± 2 MPa. A minimum of five samples were tested at room temperature for each nanocomposites and average values are reported. The microprocessor UTM machine is used with all the attachments for the measurement of tensile behaviour of nanocomposites.

2.2.5 Izod impact pendulum tester

The izod impact strength (unnotched) of pristine polymer and its composites were measured using a pendulum impact testing equipment (Model CEAST Pendulum Impact Tester, Italy) as per ASTM D 256A.

2.2.6 Surface hardness tester

Hand operated durometer was used to measure the surface hardness of the prepared composites. Surface hardness test of composites was performed as per ASTM D 785 using Shore D (plastic) durometers (M/s. Techno instruments Co., India).

2.2.7 Differential scanning calorimeter

All calorimetric measurements were made by differential scanning calorimeter (DSC) Universal V4.3A (Q2000), TA Instrument, USA, as per ASTM D 3417, D 3418 under nitrogen atmosphere in the temperature range from -50 to 250°C at a heating rate of 10°C/min. The DSC instrument was calibrated using pure indium metal. All measurements were carried out with an accuracy of ± 0.01 °C.

2.2.8 Dynamic mechanical analyser

The dynamic mechanical properties of nanocomposites were carried out with dynamic mechanical analyzer (DMA) (Model Q800 made by TA Instruments Inc., USA). The DMA equipment consists of a probe mechanically connecting the entities such as a force transducer to control the force applied to the sample, an oscillatory applied force (or applied strain), a position transducer to measure the displacement and a temperature – controlled sample specimen. There is a provision for the sample mounting and deforming in a defined manner viz., torsion, compression, tension and
bending geometries by the equipment probe and surrounded by a furnace and monitored by a thermocouple along with suitable measuring systems. The operational range of instrument is from -100 to 300 °C.

2.2.9 Thermogravimetric analyzer

The thermal stability of all nanocomposites was analyzed by using thermogravimetric analyzer (TGA) TA Q50 thermal analyzer, Universal V4.3A, TA Instrument, USA, under nitrogen atmosphere at a heating rate of 20°C/min in the temperature ranges of 30 - 800°C. About 6-8 mg of the sample was used for analysis under a continuous nitrogen gas flow of 60 ml/min and the weight loss with respect to temperature was recorded.

2.2.10 Pin–on-disc sliding wear testing machine

Pin-on-disc machine Ducom model LR 20 E(India) made and high precision Mettler electronic balance (Switzerland), Model AG 204 was used to conduct wear test and investigate the coefficient of friction, wear loss and specific wear rate for all the prepared composites according to ASTM G99.

2.2.11 Laser assisted etching machine

Laser etching machine 75 W pulsed Nd-YAG laser marking machine (make LASER CHEVAL, France) was used for etching all the prepared composites.

2.2.12 Surface roughness tester

The surface roughness of laser etched surface was measured with instrument HANDY SURF E35A manufactured by ZEISS. The average roughness, R_a values were recorded for composites before and after Laser etching.

2.2.13 Optical polarized microscope

The surface morphological studies of composites were carried out by using optical polarized microscope of Carl Zeiss l 800, Zeiss Instruments, Germany. The optical microscope consists of polarizing units and analyzer.

2.2.14 Scanning electron microscopy

The morphology of the nanocomposites was analyzed using scanning electron microscopy (SEM) on a JEOL equipment model JSM-5300 with 10 kV of voltage acceleration. The photomicrographs of nanocomposites were recorded from cryofractured surfaces of the specimen after coating with a thin layer of gold.
PART B - THEORY AND TECHNIQUES

2.3 Physical properties

The physical methods are used to evaluate the physical properties such as density, chemical interaction, dimensional stability and other properties of composites.

2.3.1 Density

Density is a non-mechanical property of great importance. In many applications, the density criterion combined with strength and stiffness gives a sound basis for comparison of polymers with different materials, such as metals and alloys. In the case of plastic materials particularly, the density is often of a major significance as an indication of the end-use possibilities of the material. Density also depends upon the blend compositions and their physical and chemical interactions [12-13].

Densities of composites were measured according to ASTM D 792-86 (displacement) method using Metler Toledo electronic balance. This technique is applicable for solid samples such as film, sheet or powder. The accuracy of density obtained by this method is ± 0.0001 g/cc. The Mettler electronic balance should be standardized as per standard before using the composite specimen.

2.3.2 Water uptake behaviour

Procedure to measure percent swelling of composites in water is briefly explained as follows: a known weight of \( w_1 \) dried samples were immersed in water and allowed to attain a state of equilibrium at room temperature. After it attains equilibrium, the weight of the swollen material was noted down \( w_2 \) [14-15]. The percentage of water uptake was calculated by the relation;

\[
\text{Percentage swelling} = \frac{W_2 - W_1}{W_1} \times 100
\]

\[ (2.1) \]

2.3.3 Void content [ASTM D2734]

Void content measures the voids in reinforced polymers and composites. Information on void content is useful because high void contents can significantly reduce the composites' strength. Monitoring lot-to-lot void contents can also act as a measure of the consistency of the composites' manufacturing process.
The composites under this investigation consist of two components. The theoretical density of composites in terms of weight fraction can easily be obtained as per the following equation [16]:

\[
\rho_{ct} = \frac{1}{\left(\frac{W_s}{\rho_s}\right) + \left(\frac{W_m}{\rho_m}\right) + \left(\frac{W_n}{\rho_n}\right)}
\] (2.2)

where, \(W\) and \(\rho\) represent the weight fraction and density respectively. The suffix \(s\), \(m\), \(n\) and \(ct\) stand for the naturally occurring filler, matrix, filler or second component and the composite materials respectively. The actual density (\(\rho_{ce}\)) of the composite can be determined experimentally by simple water immersion technique. The voids significantly affect some of the mechanical properties and even the performance of composites in the workplace. Higher void contents usually mean lower fatigue resistance, greater susceptibility to water penetration and weathering resistance [16]. The knowledge of void content is desirable to estimate the quality of the composites. It is understandable that a good composite should have fewer voids. The volume fraction of voids (\(V_v\)) of the composites is calculated using the following equation:

\[
V_v = \frac{\rho_{ct} - \rho_{ce}}{\rho_{ct}}
\] (2.3)

The theoretical and measured densities of the composites along with the corresponding volume fraction of voids are presented in the forth coming chapters.

2.3.4 Surface hardness

Hardness is defined as the resistance of a material to deformation, indentation or scratching. Hardness test can differentiate the relative hardness of different grades of particular plastics and also reveals the dimensional stability. Dimensional stability of the blends depends significantly on nature of the components and their compositions.

Hardness is the property of a material showing resistance to surface indentation. The specimens were kept under the indenter of shore A and shore D testers and the deflection on the scale was noted. The indentation value reflects the resistance to local deformation, which is a complex property and related to modulus, strength, elasticity, plasticity and dimensional stability. It also gives an idea about the
degree of crosslinking. A minimum of six readings were note down for each sample at different positions and an average value was recorded.

2.4 Mechanical properties

The mechanical properties have been carried out using universal testing machine (UTM). The following paragraph briefly describes the procedure adopted for measuring the mechanical properties of composites.

2.4.1 Tensile properties

Tensile strength, tensile modulus and percentage elongation at break measurements are among the most important indications of the strength in a material and are the most widely specified properties of the materials. The tensile property data are more useful in preferential selection of a particular type of plastics from a large group of plastic materials [17].

Tensile properties such as tensile strength, percentage elongation at break and tensile modulus were determined as per ASTM D 638 using universal testing machine (UTM), with an accuracy of ± 2 MPa. A minimum of five samples were tested at room temperature for each composites and an average values are reported. The microprocessor controlled UTM machine is used with all the attachments for the measurement of tensile behaviour of composites.

The specimens from the flexible sheets were prepared with the help of a punching die, whereas from the rigid sheets, dumb-bell shaped specimens were prepared by cutting 165 mm long and 14 mm wide rectangular pieces and then shaping them by filing. The edges of the specimens were conditioned as per the standard before testing. A gauge length of 25 mm full scale, cross head speed of 1 cm/min and load of 100 kg was adopted. A minimum of six samples were tested at room temperature for each composition and an average value was taken. Mathematical expressions used to calculate the tensile behaviour are as follows:

- Tensile strength = Load at break/Cross sectional area \hspace{1cm} (2.4)
- Percentage Elongation at break = Strain x 100 \hspace{1cm} (2.5)
- Tensile modulus = Slope at straight line portion of the stress vs. strain curve \hspace{1cm} (2.6)
2.4.2 Izod impact strength

The impact properties of polymeric materials are directly related to the toughness of the materials. Generally, the rubbery phase in moderate concentration, when dispersed throughout a rigid glassy thermoplastic matrix, a significant improvement in impact strength is obtained without any major sacrifice in other mechanical and thermal properties [18-19].

Scope: Notched Izod Impact is a single point test that measures a material’s resistance to impact from a swinging pendulum. Izod impact is defined as the kinetic energy needed to initiate fracture and continue the fracture until the specimen is broken. Izod specimens are notched to prevent deformation of the specimen upon impact. This test can be used as a quick and easy quality control check to determine if a material meets specific impact properties or to compare materials for general toughness. ASTM impact energy is expressed in J/m. Impact strength is calculated by dividing impact energy in J by the thickness of the specimen. The test result is typically the average of 5 specimens. The higher the resulting number, the tougher is the material.

Specimen size: The standard specimen for ASTM is 64 x 12.7 x 3.2 mm. The most Common specimen thickness is 3.2 mm, but the preferred thickness is 6.4 mm because it is not as likely to bend or crush. The depth under the notch of the specimen is 10.2 mm.

The testing machine consists of a heavy base with a vise for clamping the specimen in place during the test. The specimen is clamped into the pendulum impact test fixture with the notched side facing the striking edge of the pendulum. The pendulum is released and allowed to strike through the specimen. A pendulum type hammer is fitted to the machine through a rigid frame and is operated by a holding and releasing mechanism. The pendulum is connected to a pointer and a dial mechanism that indicates that the excess energy remaining in a pendulum after breaking the specimen. The dial is calibrated to read the impact values directly in standard units. A hardened striking nose is attached to the pendulum.

2.5 Thermo-analytical techniques

Thermal analysis is one of the most powerful techniques available for understanding thermo-physical properties of materials. Among several thermal techniques available for such studies, HDT, DSC, TGA and DMA continue to
A comprehensive coverage of this important field of thermal characterization of polymers including theory and instrumentation was given by Turi [30]. A brief coverage of DSC, TGA and DMA techniques are highlighted in the following paragraphs. The heat deflection temperature (HDT) test is used for quality control and for screening and ranking materials for short-term heat resistance which indicates the continuous service temperature for any application. The long-term heat resistance test is useful to determine the permanence effect of heat on any property by selection of an appropriate test method.

2.5.1 Differential scanning calorimetry

DSC was introduced commercially during the early 1960’s, and it was found to provide a convenient and useful method for monitoring the course of exothermic reactions including those involved in the interlocking of the polymer composites. Its main advantages are; (i) the modest requirements in terms of sample size, of the order of milligrams and (ii) it can provide quantitative data on overall reaction kinetics with relative speed and ease.

One of the major applications of DSC is the measurement of transition temperatures such as $T_g$, $T_m$, $T_{\text{cryst}}$, curing temperature range and degree of crosslinking or state of cure of the polymers [31-32]. In the absence of endothermic or exothermic reactions, the DSC heat flow output is proportional to the sample heat capacity and $T_g$ may be determined from the characteristic discontinuity in heat capacity. The $T_g$ of cross linked polymer in general shows an increase with increasing degree of crosslinking and provides a useful index of the degree of cure. The temperature (extrapolated) at which a steep-jump in specific heat capacity occurs is taken as the $T_g$ of the specimen.

All calorimetric measurements were made by differential scanning calorimetry (DSC) This instrument has advanced Tzero, modulated DSC technologies and a reliable 50-position auto sampler. The DSC instrument consists of sample and reference pan with facilities for a controlled rate of heating/cooling temperature and a continuous heat-flow measuring arrangement. This is also coupled with a data recording microprocessor controlled device. Arrangement of gas or air flow at a controlled rate provides the facility of setting the condition as per test requirement. The test can be carried out at a temperature range from -180 to 725 °C with an accuracy of ± 0.01 °C.
Technique: The temperature scale of the instrument was calibrated with high purity indium as a melting point standard (156.6 °C), while the heat flow calibration was done with a high purity alpha alumina disc supplied by the company as a calorimetric standard. In this investigation, all calorimetric measurements were made by dynamic DSC scans. About 6-8 mg of sample was taken in an aluminium pan for dynamic (constant rate of rise in temperature) DSC studies. The DSC scans were recorded in the temperature range -50 to 200 °C at a heating rate of 10 °C/min. The DSC cell was operated with a flow of dry oxygen-free nitrogen. An empty aluminium pan was used as the reference material. The DSC instrument consists of sample and reference pan with facilities for a controlled rate of heating/cooling temperature and a continuous heat-flow measuring arrangement. Arrangement of gas or air flow at a controlled rate provides the facility of setting the condition as per test requirement.

2.5.2 Thermogravimetric analysis

The thermal stability of all composites and their composites were analyzed by using TGA. The TGA instrument consists of an analytical balance supporting a platinum crucible for the specimen, the crucible situated in an electric furnace and a microprocessor controlled system.

TGA is finding increasing utility in the investigation of pyrolysis and thermal degradation behaviour of solids [20-21]. In addition to that, both qualitative and quantitative analysis is also possible. When a sample is subjected to TGA analysis, the decomposition occurs at a very slow rate until a critical temperature is reached. Then the pyrolysis rate increases very rapidly to maximum, after which, as the sample disappears, the rate of weight loss drops more rapidly. Such behaviour is the characteristic of a large number of decomposition processes, including many polymer pyrolysis [22].

Thermal stability: The relative thermal stability of the composites was evaluated by comparing decomposition temperatures at various percent weight losses. The oxidation index (OI) was calculated based upon the weight of carbonaceous char (CR) as related by the empirical equation;

$$\text{OI} \times 100 = 17.4 \times 0.4 \times \text{CR}$$

2.7

Technique: The TGA module was operated with a flow of dry oxygen free nitrogen. (The temperature scale of the instrument was calibrated with high purity calcium oxalate (CaC$_2$O$_4$·H$_2$O)). The sample size taken in each analysis is around 8-10 mg.
The TGA scans are recorded at a constant heating rate in the temperature range from ambient to 800 °C. Thermal analysis was carried out at a heating rate of 20 °C/min. The results of TGA data are given in respective places in concerned chapters. For thermal analysis, completely polymerized and dried samples were taken.

2.5.3 Dynamic mechanical analysis

This technique is generally used for the qualitative characterization of viscoelastic properties of polymers. In this test, the ability of materials to store and/or dissipate mechanical energy imparted on deformation is being measured. These tests can be performed over a wide range of rates, frequency and temperature as well as time for relaxation studies. From each cycle, the DMA calculates both the modulus and the phase, i.e., the response delay caused by viscoelastic changes taking place in the sample. From these fundamental measurements the storage and loss modulus, compliance and viscosity can be calculated. These parameters can be calculated as a function of applied stress-strain and frequency as well as temperatures. The modulus information obtained from dynamic mechanical testing is very useful for researchers, manufacturers and users of polymers in structural applications.

The storage and loss modulus of viscoelastic polymers measure respectively the energy stored and the energy lost during oscillation. The former represents the elastic part, and the latter represents the viscous part. The storage ($E'$) and loss ($E''$) moduli are expressed as:

$$E' = \left( \frac{\sigma_s}{\varepsilon_s} \right) \times \cos \delta$$

$$E'' = \left( \frac{\sigma_s}{\varepsilon_s} \right) \times \sin \delta$$

The phase lag between the displacement of specimen and applied force determines the damping properties of the material. The phase lag is reported in the form of loss tangent:

$$\tan \delta = \frac{E''}{E'}$$

The viscoelastic properties of the polymers as function of temperature can be characterized by dynamic mechanical thermal analysis. The common method is to apply an oscillating force to the sample and measure the resulting displacement, from which we can determine storage modulus ($E'$), loss modulus ($E''$), and $\tan \delta$. DMA experiments can be run at elevated temperatures, and the values of $E'$, $E''$ and $\tan \delta$ at different temperatures and the glass transition can be determined.
Techniques: The dynamic mechanical properties of composites were carried out with DMA. The DMA equipment consists of a probe mechanically connecting the entities such as a force transducer to control the force applied to the sample, an oscillatory applied force (or applied strain), a position transducer to measure the displacement and a temperature – controlled sample specimen. There is a provision for the sample mounting and deforming in a defined manner viz., compression, tension and bending geometries by the equipment probe and surrounded by a furnace and monitored by a thermocouple along with suitable measuring systems.

Rectangular samples having a size of about 20 ×2×10 mm (lxtxw) were tested in the single cantilever mode to measure the storage modulus (E'), the loss modulus (E'') and the phase angle as expressed by tan δ. All data were obtained using a fixed frequency of 1 Hz and fixed strain of 3 %. Samples were cooled from room temperature to 30 ºC, kept isothermally at this temperature for 5 min to equilibrate subsequently. DMA thermograms were recorded in the temperature range 30 to 200 ºC at a heating rate of 3 ºC/min, under nitrogen gas purge. The Tg was taken at the temperature of the maximum in the loss modulus curve.

2.6 Wear properties
2.6.1 Sliding wear technique by pin–on-disc experimentation

Pin-on-disc machine Ducom model LR 20 E(India) made and high precision Mettler electronic balance (Switzerland), Model AG 204 was used to conduct wear test and investigate the coefficient of friction, wear loss and specific wear rate for all the prepared composites according to ASTM G99.

This test method covers a laboratory procedure for determining the wear of materials during sliding using a pin-on-disc apparatus. Materials are tested in pairs under nominally non-abrasive conditions. The principal areas of experimental attention in using this type of apparatus to measure wear are described. The coefficient of friction may also be determined. The pin specimen is pressed against the disk at a specified load usually by means of an arm or lever and attached weights. The amount of wear is determined by weighing specimens before and after the test. Wear results are usually obtained by conducting a test for a selected sliding distance and for selected values of load and speed.

Scope: This test method covers a laboratory procedure for determining the wear of materials during sliding using a pin-on-disc apparatus. Materials are tested in pairs
under nominally non-abrasive conditions. The principal areas of experimental attention in using this type of apparatus to measure wear are described. The coefficient of friction may also be determined.

For the pin-on-disk wear test, two specimens are required. One, a pin with a radius tip, is positioned perpendicular to the other, usually a flat circular disk. A ball, rigidly held, is often used as the pin specimen. The test machine causes either the disk specimen or the pin specimen to revolve about the disk center. In either case, the sliding path is a circle on the disk surface. The plane of the disk may be oriented either horizontally or vertically. The pin specimen is pressed against the disk at a specified load usually by means of an arm or lever and attached weights.

In this investigation, pin-on-disc machine was used for evaluating the sliding wear frictional properties of the composites. In this test rig, pivoted liver loaded with dead weight applies the normal load as shown in Figure 2.7. The main advantages of this type of loading method are the less frictional losses and good mechanical advantage in the loading. A pin is pressed against a rotating disc such that the contact surface of the pin will be flat. The cured composite laminates were cut using a diamond tipped cutter to yield wear test coupons of size 8mm diameter. The test samples were then glued using an adhesive to pins of size 8mm diameter and 25mm length.

![Diagram of pin on disk experimental parameters](image)

**Figure 2.7. Pin on disc experimental parameters**

where, $F$ is the normal force on the pin, $d$ is the pin or ball diameter, $D$ is the disk diameter, $R$ is the wear track radius, and $w$ is the rotation velocity of the disk.

**Method of testing:** The test specimens were weighed and initial weights were recorded using a high precision digital electronic balance after thorough cleaning. After recording initial weight, specimen fixed to the holder such that the flat face of the layup come in contact with the rotating hardened steel disc as shown in Figure.2.8.
The setup had an arrangement to vary the motor speed and consequently the rpm of the disc. Selecting the suitable track on the disc, sliding distance and rpm, the sliding velocity can be chosen. The final weights were recorded and the wear losses in grams were calculated.

![Schematic diagram of pin-on-disc test set-up](image)

**Figure 2.8. Schematic diagram of pin-on-disc test set-up**

Technical specification of the pin-on-disc Machine used for this investigation is:

- **Speed**: 3000 RPM (maximum), RPM indicator digital type with proximity sensor
- **Sliding velocity**: 14 m/s (maximum)
- **Drive system**: A. C. Motor - Siemens make with A. C. Drive - ABB control
- **Data acquisition**: 16 channel ADC card - Dynalog make
  - Range 100 N and 200 N (maximum) - Resolution 1N, senstronics
- **Load cells**: make, two numbers, normal load that can be applied using dead weight of 250 N maximum.
- **Disc dimensions**: 160 mm diameter and 8 mm thickness. Surface roughness of the disc 25 µm, hardness 62 HRC. Temperature and heater for disc heating: four thermocouples, temperature heating for pin one element, temperature range up to 400°C
The specific wear rate \( K_S \) (g/N-m), was calculated from the equation;

\[
K_S = \frac{W}{F_N \times d}
\]

where, \( W \) is the weight loss in grams, \( F_N \) is the normal load in Newton, \( d \) is the sliding distance in meters.

The coefficient of friction is calculated from the equation;

\[
\mu = \frac{F_f}{F_N}
\]

\( F_f \) is the frictional force (Newton) and \( \mu \) is the coefficient of friction.

The Ducom wear and friction monitor – TR 20E series has become the industry standard in wear and friction analysis. The TR 20 Series tribometer is specifically designed for fundamental wear and friction characterization. This instrument consists of a rotating Disk against which a test pin is pressed with a known force. A provision for measurement of compound wear and frictional force is provided. The TR 20E Series comes with the WinDucom software for data acquisition and display of results. The WinDucom instrumentation and data acquisition permits the measurement of: (i) RPM, (ii) wear, (iii) frictional force and (iv) temperature and the detailed specifications the wear tester are given in Table 2.7.

### Table 2.7 Equipment specification and specimen size

<table>
<thead>
<tr>
<th>Parameter</th>
<th>Unit</th>
<th>Min</th>
<th>Max</th>
<th>Remarks</th>
</tr>
</thead>
<tbody>
<tr>
<td>Pin size</td>
<td>mm</td>
<td>3</td>
<td>12</td>
<td>Diameter or diagonal with different holders</td>
</tr>
<tr>
<td>Ball diameter</td>
<td>mm</td>
<td>10</td>
<td>12.7</td>
<td></td>
</tr>
<tr>
<td>Disk Size</td>
<td>mm</td>
<td>16 x 8</td>
<td></td>
<td></td>
</tr>
<tr>
<td>Wear Track Diameter</td>
<td>mm</td>
<td>20</td>
<td>145</td>
<td></td>
</tr>
<tr>
<td>Disk Rotation</td>
<td>RPM</td>
<td>200</td>
<td>2000</td>
<td></td>
</tr>
<tr>
<td>Normal Load</td>
<td>N</td>
<td>5</td>
<td>200</td>
<td>In steps of 5 N</td>
</tr>
<tr>
<td>Wear</td>
<td>( \mu )</td>
<td>0</td>
<td>2000</td>
<td></td>
</tr>
<tr>
<td>Frictional Force</td>
<td>N</td>
<td>0</td>
<td>200</td>
<td></td>
</tr>
</tbody>
</table>

**Test parameters:** Load - values of the force in Newtons at the wearing contact. Speed - the relative sliding speed between the contacting surfaces in m/s and Distance - the accumulated sliding distance in meters.

**Significance**

The amount of wear is determined by weighing both specimens before and after the test. The amount of wear in any system will, in general, depend upon the
number of system factors such as the applied load, machine characteristics, sliding speed, sliding distance, the environment, and the material properties. The value of any wear test method lies in predicting the relative ranking of material combinations. Since the pin-on-disk test method does not attempt to duplicate all the conditions that may be experienced in service (for example; lubrication, load, pressure, contact geometry, removal of wear debris, and presence of corrosive environment), there is no insurance that the test will predict the wear rate of a given material under conditions differing from those in the test.

2.7 Laser assisted etching (LAE)

A study has been conducted using a 75 W pulsed Nd-YAG laser marking machine (make LASER CHEVAL France) to etch the surface of nylon 66/PTFE specimens. To investigate the possibility of this type of laser providing a solution to the problem of etching materials, machining and subsequent analyses like morphological study using optical microscopic images and surface roughness.

The processing parameters of the machine are marking speed of 250 characters per sec with micro pulse duration. The surface roughness of laser etched surface was measured with instrument surface roughness measuring instrument. The average roughness, $R_a$ values were recorded for composites before and after Laser etching and surface images were taken using optical microscope.

When the glass plastic was exposed for higher laser power for longer duration in air media the material burns more vigorously resulting in more char formation. This results in increase in surface roughness and micro hardness. However, in water media the over burning and degradation of material does not occur as in the case of air and argon and the surface of glass plastic appears very clean and precise. The measured change in micro hardness under water media was considerably less than that in air and argon media. The specification of Nd YAG Laser Q - switched engraving machine are; capacity -75 watts, size - 110 x 110 mm, precision - 0.01 mm to 50 mm; control software – LENS; machinability - marking and engraving of any profiles on all metals, ceramics and few types of plastics and speed - 250 characters/sec.

An experimental study conducted to determine the surface finish characteristics of carbon and aramide fibre-reinforced plastics by CO$_2$ laser [23]. The Heat Affected Zone depends strictly on the feed rate. The higher the speed of laser beam, the smaller the volume of damage and the better the cut finish [24-27]. Caprino
[28] developed a simple one-parameter thermal model, predicting the maximum feed rate as a function of beam power.

2.7.1 Laser/Polymer interactions

The interaction between laser light and polymeric materials depends on the material formulation, laser wavelength and laser parameters. The absorption of the laser energy changes the optical characteristics of the polymer. A pyrolysis reaction in the sample releases small amounts of gas, which cause a foamed surface structure. The irregular foam structure scatters light, making the area appear lighter.

![Figure 2.9 Process of foaming in laser assisted etching](image)

2.7.2 Carbonization

In this technique, the plastic surface decomposes when absorbing the laser light due to the high intensity of the laser pulse. This results in char formation on the surface of the plastic, creating a dark colored mark.

![Figure 2.10 Carbonization in laser assisted etching](image)

2.8 Roughness measurements

The equipment used to measure roughness is Handysurf (HANDY SURF E35A manufactured by ZEISS). A rough surface will feature a number of peaks and troughs Figure 2.11 of random heights and depths. The distance between the highest peak and deepest trough is not necessarily a good measure of the roughness, as they may appear only once on the entire surface. This can be performed by measuring an
area of the surface (Figure 2.11 shows a single line; normally the surface would be scanned in the x and y directions) and finding the line about which the average displacement (i.e., the average of all peaks and troughs) is 0; this is where the surface would be if it was perfectly flat. The roughness is then calculated as the deviation from this imaginary perfect surface. At all measured points, the deviation is first squared (i.e., multiplied by itself; hence, negative deviations become positive), the average (mean) of these squares is found, and then the square root of this number is taken. This gives a reasonable estimate of the surface roughness, but note that the actual deviation from the imaginary ideal surface will normally have greater amplitude.

![Figure 2.11 A rough surface in cross section](image)

The dotted line indicates the average level of the surface the rough surface deviates from this perfectly flat surface in both directions. Surface roughness can be calculated as the rms deviation from this.

### 2.9 Scanning electron microscopy

The morphology of the composites was analyzed using scanning electron microscopy (SEM). The micrographs of the composites were taken on a JEOL equipment model JSM-5300 having 10 kV of voltage acceleration with probe microanalysis Sl. No. 320 after gold (100 Å) coating. The magnification is displayed on the respective microphotographs of the samples. The cryofractured specimen’s morphology of the various composites is well documented in the literature [29-33]. The combination of rubbery and glassy polymer networks gives interesting SEM photomicrographs. Since morphology plays a major role in affecting polymer performance, it has been extensively studied using SEM.

Since its commercial introduction in the early sixties, the SEM has been used in a number of situations requiring greater resolution than the light optical microscopes. Here, a fine beam of electrons is scanned (focused) on the surface of an opaque sample to which a light conducting film has been applied by evaporation. An
image of the surface of the sample can be obtained from the intensity of the secondary electrons. A fixed energy electron beam is scanned across the surface of the sample. The results appear on the read-out device as a visual image of the surface of the sample. The resulting image has a great depth of field and a remarkable three-dimensional appearance. The results are similar to those obtained from an optical microscope except that the magnification is considerably greater in SEM. Conventional SEM images are formed by scanning a focused beam of electrons across the surface of a composite specimen and detecting the secondary electrons that are ejected by the specimen.

**Technique:** The SEM micrographs/images of the composites were taken on a JEOL equipment model JSM-5300 with probe microanalysis Sl. No. 320 after gold (100 Å) coating. The magnification is displayed on the respective microphotographs of the samples.

### 2.10 Statistical analysis

The experimental data were analyzed by using MINITAB software wherein the regression equations are used to find the correlation between variables. Based on the analysis, the coefficients corresponding to factors that were statistically significant was considered for the regression model. Factors with positive coefficients have a positive effect on the property and those with negative coefficients decreases the property. The regression equation for each of the properties was refined by taking the coefficients that are significant based on the statistical significance level of 0.1. Analysis of variance (ANOVA), Durbin–Watson value is used to find the type of correlation between the variables.

**Durbin–Watson statistic:** In statistics, the **Durbin–Watson statistic** is a test statistic used to detect the presence of autocorrelation (a relationship between values separated from each other by a given time lag) in the residuals (prediction errors) from a regression analysis. It is named after James Durbin and Geoffrey-Watson.

**Computing and interpreting the Durbin–Watson statistic**

If $e_t$ is the residual associated with the observation at time $t$, then the test statistic is

$$d = \frac{\sum_{t=2}^{T} (e_t - e_{t-1})^2}{\sum_{t=1}^{T} e_t^2},$$

2.13
where, $T$ is the number of observations. Since $d$ is approximately equal to $2(1 - r)$, where $r$ is the sample autocorrelation of the residuals, $d = 2$ indicates no autocorrelation. The value of $d$ always lies between 0 and 4. If the Durbin–Watson statistic is substantially less than 2, there is evidence of positive serial correlation. As a rough rule of thumb, if Durbin–Watson is less than 1.0, there may be cause for alarm. Small values of $d$ indicate successive error terms are, on average, close in value to one another, or positively correlated. If $d > 2$, successive error terms are, on average, much different in value to one another, i.e., negatively correlated. In regressions, this can imply an underestimation of the level of statistical significance.

The wear model for the tested materials was developed based on the applied load, sliding velocity and sliding distance. Furthermore regression analysis and analysis of variance (Anova) are employed to investigate the characteristics of the materials. The dry sliding wear of composites depend on several parameters such as size, shape, contents, environment and test conditions such as load, speed and temperature [34-36].

The p-value quantifies the significance of each term in the regression polynomial model. If the p-value is less than the statistically significant value of 0.1, the relation between the factor and the response is statistically significant. Factors with positive coefficients must be kept as more significant than negative coefficients.

An $R^2$ value is very important when the objective is to optimize, then higher $R^2$ values are important implying that the polynomial model is a very good predictor of the response. The higher the $R^2$ values were, the better the polynomial was at either describing the system or making predictions about the system [37-41].

For most of the responses under the study, the $R^2$ values obtained were 70% indicating that the polynomials represent a good description of the relationship between the four factors and the responses. In general, the fit was better for some responses than for others.
2.11 References

41. MINITAB software package, Statguide, WWW.Minitab.com.