CHAPTER – 4
MATERIALS AND METHODS

The concept and technology of fiber reinforced polymer composites have undergone a sea change and thus exploring the availability of different types of fiber reinforcements and polymer resins. The performance of hybrid fiber-reinforced polymer laminated composite is judged by its length, shape, orientation, composition as well as mechanical properties of fibers and matrix. Hence this chapter provides an insight regarding the details of the ingredients or the reinforcements selected and the methods employed in the research work.

4.1 EXPERIMENTAL MATERIALS

4.1.1 Polymer Matrix

In fiber-reinforced composites, matrix phase supports the fibers and keep them in their position, transfers the load to strong fibers, protect the fibers from damage and prevents crack propagation depending upon the composite type. Polymer matrix is structurally more complex but they are cheap and can be easily processed; available in various forms and types. Although there are many different types of polymer matrix in use in the composite industry, the majority of structural parts are made with three main types, namely polyester, vinylester and epoxy.

Polyester Resins

Polyester resins are the most widely used resin systems, particularly in the marine industry. By far the majority of dinghies, yachts and workboats built in composites, FRP Chemical Process Plants, FRP Storage Tanks and FRP Pipes make use of this resin system. Polyester resins used in the present work are of the ‘unsaturated’ type. Unsaturated polyester resin is a thermoset, capable of being cured from a liquid or solid state when subject to the right conditions. Unsaturated polyester differs from saturated polyester such as Terylene, which cannot be cured in this way. It is usual to refer to unsaturated polyester resins as polyester resins or simply as polyesters [45].

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The unsaturated polyester amounts to about 75% of all polyester resins used in USA. The advantages of the unsaturated polyester are its dimensional stability and affordable cost as well as ease of handling, processing, and fabricating. Some of their special properties are high acid & water resistance, high corrosion resistance, good electrical properties, fire retardants, temperature resistance up to 80°C and higher mechanical strength of laminates. These resins are probably of the highest value for they have a balance between performance and structural capabilities. They have low cost and have good properties such as low viscosity. One disadvantage of unsaturated polyesters is, it has an impact of light and UV light [96].

In chemistry the reaction of a base with an acid produces a salt. Similarly, in organic chemistry the reaction of an alcohol with an organic acid produces ester and water. By using special alcohols, such as glycol, in a reaction with di-basic acids, polyester and water will be produced. This reaction, together with the addition of compounds such as saturated di-basic acids and cross-linking monomers, forms the basic process of polyester manufacture. As a result there is a whole range of polyesters made from different acids, glycols and monomers, all having varied properties. There are two principal types of polyester resin used as standard laminating systems in the composites industry. They are,

- Orthophthalic polyester resin - the standard economic resin used by many people.
- Isophthalic polyester resin - now becoming the preferred material in marine industries where its superior water resistance is desirable. Also some of the important characteristics of Isophthalic polyester are their higher tensile and flexural strengths and also better chemical and water resistivity.

The idealized chemical structure of typical Isophthalic Polyester is shown in Figure 4.1. Note the positions of the ester groups (CO - O - C) and the reactive sites (C* = C*) within the molecular chain.
Most polyester resins are viscous, pale colored liquids consisting of a solution of polyester in a monomer, which is usually styrene. The addition of styrene amounting to 50% helps it easier to handle by reducing its viscosity. The styrene also performs the vital function of enabling the resin to cure from a liquid to a solid by 'cross-linking' the molecular chains of the polyester, without the evolution of any by-products. These resins can therefore be moulded without the use of pressure and are called 'contact' or 'low pressure' resins. Polyester resins have a limited storage life as they will set or 'gel' on their own over a long period of time. Often small quantities of inhibitor are added during the resin manufacture to slowdown this gelling action. The use of a polyester resin in molding requires addition of several ancillary products such as catalyst, accelerator and additives like pigments, filler etc.

Resins can be formulated to the moulder's requirements simply by the addition of the catalyst prior to moulding. As has been mentioned, given enough time an unsaturated polyester resin will set by itself. This rate of polymerization is too slow for practical purposes and therefore catalysts and accelerators are used to achieve the polymerization of the resin within a practical time period. Catalysts are added to the resin system shortly before the use to initiate the polymerization reaction. The catalyst does not take part in the chemical reaction but simply activates the process. An accelerator is added to the catalyzed resin to enable the reaction to proceed at workshop temperature and/or at a greater rate. Since accelerators have little influence on the resin in the absence of a catalyst the polyester manufacturer to create a 'pre-accelerated' resin sometimes adds them to the resin. The molecular chains of the polyester can be represented as shown in Fig. 4.2, where 'B' indicates the reactive sites in the molecule.

**Fig. 4.1 Idealized Chemical Structure of a Typical Isophthalic Polyester**
The addition of styrene ‘S’ in the presence of a catalyst, crosslinks the polymer chains at each of the reactive sites to form a highly complex three dimensional network as shown in Fig. 4.3.

The cross-linking or curing process is called ‘polymerization’. It is a non-reversible chemical reaction. The ‘side-by-side’ nature of this cross-linking of the molecular chains tends to mean that polyester laminates suffer from brittleness when shock loadings are applied.

Great care is needed in the preparation of the resin mix prior to molding. The resin and any additives must be carefully stirred to disperse all the components evenly before the catalyst is added. This stirring must be thorough and careful as any air introduced into the resin mix affects the quality of the final molding. This is especially so when laminating with layers of reinforcing materials air bubbles can be formed within the resultant laminate, which can weaken the structure. It is also important to add the accelerator and catalyst carefully in measured amounts to control the polymerization reaction which gives the best material properties.

**Catalyst and Accelerators**

Catalysts are added to the resin system shortly before use to initiate the polymerization reaction. The catalyst does not take part in the chemical reaction but simply activates the process. An accelerator is added to the catalyzed resin
to enable the reaction to proceed at workshop temperature and/or at a greater rate. Since accelerators have little influence on the resin in the absence of a catalyst they are sometimes added to the resin by the polyester manufacturer to create a 'pre-accelerated' resin. A very wide range of catalyst-accelerator-inhibitor system is available for use with polyester resins. For example, a general purpose hydroquinone-inhibited resin can be cured very rapidly by using an active peroxide catalyst, such as methyl ethyl ketone peroxide, in combination with an active accelerator, such as Cobalt Naphthenate or cobalt octate. Finally it is to be remembered that too much catalyst will cause too rapid a gelation time, whereas too little catalyst will result in under-cure [43].

It is occasionally desirable (and sometimes necessary) to start and even complete cure at lower temperatures, so that the polymerization heat can be readily dissipated. This is of particular importance when using the wet hand lay-up method for large or complicated units, where it may not be possible to apply heat. In these cases, Methyl Ethyl Ketone peroxide (MEKP) is generally used as the catalyst (refer Fig. 4.4 for their activity of a general-purpose polyesters in catalyzed with 1.0% MEKP).

![Fig. 4.4 Reactivity of a general-purpose polyester resin catalyzed with 1% MEKP.](image)

**4.1.2 FIBER REINFORCEMENTS**

Fiber reinforcements are the most important class of reinforcements, as they satisfy the desired conditions and transfer strength to the matrix constituent, influencing and enhancing their properties as desired. Mainly the different types
of fibers available are glass fibers, silicon carbide fibers, graphite fibers, boron fibers, aramid fibers, metal fibers, nylon fibers etc. [96].

4.1.2.1 Woven Steel Fiber Reinforcement

As current infrastructure ages, and load demand continues to increase, both rehabilitation (restoring to original capacity) and strengthening measures must be made. Fiber reinforced polymer (FRP) materials have been successfully used for rehabilitation and strengthening efforts for the past two decades. Recently, a new form of FRP: steel fiber reinforced polymer (SFRP), has been introduced as an alternative to more conventional carbon or glass fiber reinforced polymers (C/GFRP). SFRP materials are composed of ultra high strength steel fibers embedded in a polymeric matrix. The fibers are of a very small diameter so that the steel can have the microstructure of pearlite. The result is a high tensile strength steel, up to eleven times stronger than typical steel plate [77].

Steel fibers possess many advantages such as ease of production, more ductile, apart from not being too sensitive to surface damage and possess high strengths and resistance to temperature. Steel wire is the most extensively used reinforcement in most large-scale metal filament applications. Steel wire is used for its capacity to enhance the tensile strength. Steel wires reinforced with plastic ensure high strength, lightweight and good fatigue resistance, besides these continuous fibers are easy to handle, unlike glass fibers.

In this work plain weave (PW) type of steel fiber mesh was used as one of the reinforcement in the preparation of SFRP hybrid composite specimens. The selected PW type of steel mesh was tested for chemical analysis at established metallurgical laboratory and the composition is shown in Table 4.1. The equipment used for the chemical analysis was optical emission spectrometer (BAIRD-DV6). The PW type of steel mesh has areal density of 490 gsm, the diameter of steel fiber being 95microns and the fibers in wrap and fill directions being respectively 100 X 100 per inch length.
4.1.2.2 Woven Nylon Fiber Reinforcement

Nylon is a thermoplastic silky material was the first commercially successful polymer and the first synthetic fiber to be made entirely from coal, water and air. These are formed into monomers of intermediate molecular weight, which are then reacted to form long polymer chains. 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. It replaced silk in military applications such as parachutes and flak vests, and was used in many types of vehicle tires. Nylon fibers are used in many applications, including fabrics, carpets, musical strings, and ropes.

There are several commercial nylon products, such as nylon 6, 11, 12, 6/6, 6/10, 6/12, and so on. Of these, the most widely used nylon products are formed of nylon 6 and nylon 6/6. Nylon is produced by melt spinning and is available in staple, tow, monofilament, and multi-filament form. The fiber has outstanding durability and excellent physical properties. Nylons are semi-crystalline polymers. The amide group \(-\text{CO-NH}^{-}\) provide hydrogen bonding between polyamide chains, giving nylon high strength at elevated temperatures, toughness at low temperatures, combined with its other properties, such as stiffness, wear and abrasion resistance, low friction coefficient and good chemical resistance. These properties have made nylons the strongest of all man-made fibers in common use. Because nylons offer good mechanical and thermal properties, they are also considered as very important engineering thermoplastics. For example, 35% of total nylon produced is used in the automobile industry, others are mainly used in
tubing extrusion, injection molding, and coatings of metal objects. The most common properties of Nylon 6/6 are mentioned below [68]:

- Tenacity-elongation at break ranges from 8.8g/d-18% to 4.3 g/d-45%. (Its tensile strength is higher than that of wool, silk, rayon, or cotton)
- 100% elastic under 8% of extension
- Specific gravity of 1.14
- Melting point of 263°C
- Extremely chemically stable
- Degraded by light as natural fibers
- Permanent set by heat and steam
- Abrasion resistant, resilient and wear resistance
- Lustrous- Nylon fibers have the luster of silk
- Filament yarn provides smooth, soft, long lasting fabrics

In this research, the other reinforcement selected is plain weave (PW) type of nylon fiber mesh. The plain weave type of mesh is preferred because it possess good strength and can be reinforced to provide light weight and other characteristics mentioned above. The PW type of nylon fiber mesh has areal density of 100 gsm, the diameter of steel fiber being 300 microns and the fibers in wrap and fill directions being respectively 40 X 40 per inch length.

4.2 MATERIALS SELECTED
Hybridization of reinforcing fibers in polymer laminated composites possess many advantages over usual composite materials, Therefore in this research work an attempt has been made to obtain a positive hybrid effect by selecting the following ingredients:

- Isophthalic polyesters as a matrix, with attractive mechanical, chemical and electrical properties accompanied with dimensional stability, cost and ease of processing and fast curing.
- Steel fibers as one of the reinforcement possessing many advantages such as their production is easy, more ductile, apart from not being too
sensitive to surface damage, high strengths and temperature resistance.

- **Nylon** as the other reinforcement, which has high toughness and impact resistance, durability, high elongation and high resistance to many chemicals.

The properties of the composite depend to a great extent on the combination of the properties of the matrix and the fibers. Table 4.2 shows selected properties of isophthalic polyester resin along with the above-mentioned reinforcement materials. In this table it is possible to see some basic differences between polymer matrices and reinforcements. The density of steel fibers is higher, which requires superior properties in other areas to justify its use.

<table>
<thead>
<tr>
<th>Property</th>
<th>Iso-Polyester</th>
<th>Nylon</th>
<th>Steel</th>
</tr>
</thead>
<tbody>
<tr>
<td>Density, Kg/m³</td>
<td>1210</td>
<td>1400</td>
<td>7100</td>
</tr>
<tr>
<td>Tensile Strength, MPa</td>
<td>71.1</td>
<td>600</td>
<td>320</td>
</tr>
<tr>
<td>Youngs Modulus, GPa</td>
<td>3.9</td>
<td>8.3</td>
<td>200</td>
</tr>
<tr>
<td>Poisons Ratio</td>
<td>0.32</td>
<td>0.28</td>
<td>0.3</td>
</tr>
</tbody>
</table>

### 4.3 SPECIMEN PREPARATION

In this work, the interply hybrid composite specimens were fabricated using hand lay-up method using the above-mentioned matrix and reinforcements. In this method, plain weave type of reinforcement mats is manually placed onto the mould in the required orientation. The resin is then impregnated into the ply by brushing liquid resin onto the reinforcement and then the rollers are used to thoroughly wet the reinforcement with the resin matrix material to enable good compaction and to remove entrapped air. The reinforcement mats both steel and nylon were approximately trimmed with certain allowance (5-10%) to the required dimensions. Then the polyester resin was mixed thoroughly with catalyst in specified ratio to initiate the polymerization reaction. Later, an accelerator is added to the catalyzed resin in specified ratio to enable the reaction to proceed at
workshop temperature and/or at a greater rate. During the mixing care should be taken so that too much catalyst will cause too rapid a gelation time, whereas too little catalyst will result in under-cure [43].

A thin plastic sheet was then laid on a flat surface, on to which mold releasing agent is thoroughly applied; otherwise on solidification laminate adheres to the surfaces. A layer of polyester resin was coated on the sheet and then composite laminate is fabricated by laying the steel and nylon woven mesh in a symmetric stacking sequence layer by layer such that a layer of resin exists between two layers to obtain the desired laminate thickness. While laying, care was taken to avoid air bubble and wrinkling of fabric to the maximum extent possible by using the rollers. Now a milder sheet was taken and mold release agent applied on to it, and then a layer of resin mix was applied. And this was placed on the last layer of the composite stacked sequence. A flat board was then placed on this sheet and dead loads were applied on to this prepared composite so that it is applied with uniform pressure (approx 150 KPa) to enable compaction. Necessary precautions were taken to minimize voids in the material and maintain homogeneity. Entire process of lay-up was carried at room temperature. In order that the symmetric hybrid composite specimen acquires the mechanical properties, the mould was allowed to a curing period of about 48 hours. Finally the prepared sample was ripped off the mold.

After curing, covering releasing agents are removed from the composite laminate, cleaned, and edge trimmed. At this stage the composite laminate is ready with the resin fully cross-linked, and inspected to detect the presence of voids and delaminations, followed by final machining to cut, trim or shape the desired part.

4.4 INVESTIGATION METHODOLOGY

In this work, the specimens considered for experimentation were macroscopic specimens since they have several advantages & provide more information. In order to reach the goals of this study, the research was divided into six phases:
1. Preparation of hybrid laminated specimens

During the literature survey it was evident that for achieving superior mechanical properties, higher fiber volume fraction is necessary. In practice, with certain limits the fibers need to be fully coated with resin to be effective, and there will be an optimum packing of the fibers. In addition, the manufacturing process used to combine fiber with resin leads to varying amounts of imperfections and air inclusions [45,118]. Hence in this first phase of the work, matrix percentage was selected as 40% & was maintained constant throughout the investigation. The remaining 60% was used as fiber percentage between steel and nylon fibers. The hybrid specimens were prepared by stacking steel and nylon mats in a symmetric fashion using 15%, 30% & 45% steel content with the remaining percentage as nylon content and 40% isophthalic polyester matrix for three different bi-directional fiber orientations namely 0/90°, 30/60° and ± 45°. All the specimens prepared were in accordance with ASTM standards, the details of which are mentioned in the respective chapters and sections.

2. Experimental investigation of mechanical behavior

In this phase, to characterize the mechanical behavior of hybrid composite laminates, the specimens were subjected to tensile, compression, flexure and impact loads to analyze the effect of steel content and fiber orientation along with hardness test. Further the experiments were also on single ended notched (SEN) specimens for tensile and compressive loads to analyze the effect of volume fraction of steel, orientation and also for various notch depths (2, 4, 6 & 8 mm in tensile and 1, 2, 3 & 4 mm in compression specimens).

3. Experimental investigation on Delamination

In this phase experiments were conducted on double cantilever beam (DCB) and end-notch flexure (ENF) type of test specimens to analyze the delamination process for four artificial crack lengths (a = 5,10,15 and 20mm and three loads (p =10, 20 and 30N). Also experimental investigation to study and explore delamination due to change in fiber orientation, percentage of steel content and service temperatures due to flexural and compressive loads was also taken up.
4. **Strength degradation of hybrid composites**

Since composites are susceptible to degradation when exposed to low and high temperature, in this phase experimentations were carried out on the above mentioned specimen configurations exposed to freezing (0°C) and elevated temperatures (50°C & 70°C) for a duration period of 2 hours. The different experiments carried out to determine the strength degradation due to different types of loads such as tensile, compressive, flexural and impact loads.

5. **Machinability studies on hybrid composites**

In this phase of the research, turning experiments were carried out on cylindrical hybrid composite specimens for varied steel content mentioned above in order to analyze the variation of cutting & thrust force for three different cutting speeds (21.67m/min, 32.04m/min and 46.18m/min) and three tool rake (α) and relief (γ) angle (5°&7°, 5°&17° and 10°&7°) combination using HSS tool. The machining was carried out in dry condition for five depths of cut such as 0.5, 1, 1.5, 2 and 3mm. In addition two different types of tool materials namely High-speed steel (HSS) and Carbide tipped tools were used to study the effect of tool material on cutting forces.

6. **Statistical Modeling**

Multilevel Factorial Design model was selected to validate the experimental results using the factors controlling the performance of the variables of interest. The factors selected to study the response are the same factors used in the experimentation, for the modeling purpose suitable number of runs based on the model are selected and the percentage contribution of each parameter are estimated.