Chapter 1

General Introduction

1.1 Introduction

Polymeric materials constitute a widely used category of materials based on elastomers, plastics and fibres. When considering materials for load bearing applications, designers are increasingly examining the advantages of using plastics materials, both thermosets and thermoplastics. The advantages of thermoplastics over others are their low specific gravity and low cost of fabrication particularly by the injection moulding technique. The term composite is used in materials science to mean a material made up of a matrix substance containing reinforcing agents. The reinforcement of materials such as mud and clay by hair, straw and vegetable fibres has been long established in man's history, enabling him to improve his buildings and extend his engineering abilities. By definition, composite is a material composed of two or more distinct components. Composites are divided into two basic forms, composite materials and composite structure. Composite materials are composed of reinforcing structures surrounded by a continuous matrix whereas composite structure exhibits a discontinuous matrix.

1.2 Classification of composites

The composites have been classified generally into particulate composites, fibrous composites, laminated composites and hybrid composites.
1.2.1 Particulate composites

Particulate composites consist of particles dispersed in a matrix. These particles are divided into two classes, skeletal and flakes. The first one consists of continuous skeletal structures filled with one or more additional materials. Flakes consist generally of flat flakes oriented parallel to each other. These particles may have any size, shape and configuration. Inorganic fillers like calcium carbonate, aluminium trihydrate and organic fillers like wood flour, shell flour, etc. are examples of particulate reinforcements.

1.2.2 Fibre reinforced composites

Fibre reinforced composites consist of fibres of high strength and modulus embedded in a matrix with distinct interfaces between them. Both matrix and fibres retain their physical and chemical properties and exhibit synergism. Fibrous composites are divided into two broad areas—continuous and short fibre reinforced composites. Fibres of length less than 50 mm are considered to be short fibres whereas fibres of length greater than 50 mm are regarded as continuous. Incorporation of short fibres into polymer matrices offers many attractive features like ease of fabrication, better economics at both the incorporation and fabrication stages, i.e. production of complex shaped articles is possible with short fibres, which is completely impossible with long fibres.

1.2.3 Laminated composites

In laminated composites, the individual layers of materials are bonded together to form an element or plate. When the constituent materials in each layer are the same, the laminated layers are called a laminate (e.g. plywood, papers, etc.). If the layers are of different constituent materials or of the same material with different reinforcing pattern, the laminate is said to be a hybrid laminate.
1.2.4 Hybrid composites

The term 'hybrid' is generally used to denote the incorporation of two or more different types of materials into one single matrix. The level of mixing can be either on a small scale (fibres, tows) or on a large scale (layers). The purpose of hybridisation is to construct a new material that will retain the advantages of its constituents. There are several types of hybrid composites, classified according to the way in which the constituent materials are arranged. Figure 1.1 shows the various types of hybrid constructions. These include sandwich hybrids also known as core-shell (Figure 1.1a), in which one material is sandwiched between another, interply or laminated (Figure 1.1b) where alternate layers of the two (or more) materials are stacked in a regular manner. In intraply (Figure 1.1c), tows of two or more constituent types of fibres are mixed in a regular or random manner and in intimately mixed hybrids (Figure 1.1d), the constituent fibres are made to mix as much as possible so that no concentration of either type are present in the material.

Figure 1.1. Different hybrid configurations: (a) sandwich type, (b) interply, (c) intraply and (d) intimately mixed.
1.3 Fibres-matrices-interface

1.3.1 Types of fibres used for reinforcement

Fibres are mainly classified as natural and manmade. These two categories are further classified into various types as shown in Figure 1.2.

![Figure 1.2. Classification of fibres.](image-url)
(a) **Natural fibres**

Fibres which obtained from natural sources like minerals, animals and plants are classified as natural fibres.\(^5\)^\(^6\)

(i) **Mineral fibres**

Fibres under this category are composed of naturally occurring materials. A good example is asbestos. The most common type is chrysotile, representing more than 95% of asbestos production in the world. Chemically it is magnesium silicate (\(\text{Mg}_6\text{(OH)}_4\text{Si}_2\text{O}_5\)). Nowadays use of this fibre is limited because long exposure to this may cause bronchial cancer.

(ii) **Animal fibres**

Fibres obtained from living organisms are known as animal fibres e.g. wool, obtained from domestic sheep, silk fibre, obtained from silkworm-cocoon, etc. In contrast to all other natural fibres such as cotton, flax, wool etc., silk does not have a cellular structure. In this respect and the way in which it is formed, silk closely resembles synthetic fibres.

(iii) **Plant fibres**

These fibres are classified into three types depending on the part of plant from which they are extracted

i) Bast or stem fibres (jute, mesta, banana)

ii) Leaf fibres (sisal, pineapple, screw pine)

iii) Fruit fibres (coir, cotton, areca nut, oil palm)

The extraction methods, the amount and lengths of various plant fibres and their mechanical properties are given in Tables 1.1 and 1.2.
Table 1.1. Extraction methods, amount and length of various plant fibres.

<table>
<thead>
<tr>
<th>Fibre</th>
<th>Method</th>
<th>Amount</th>
<th>Length (mm)</th>
</tr>
</thead>
<tbody>
<tr>
<td>Banana</td>
<td>Manual/raspador</td>
<td>1.5 wt % of stem</td>
<td>300-900</td>
</tr>
<tr>
<td>Coir</td>
<td>Retting/mechanical</td>
<td>8 wt % of nut (this weighs 0.1 kg)</td>
<td>75-150</td>
</tr>
<tr>
<td>Jute</td>
<td>Retting and beating/chemical</td>
<td>3-4 wt % of stem</td>
<td>1500</td>
</tr>
<tr>
<td>Linseed</td>
<td>Retting/dry scratching</td>
<td>20-25 wt % of dry straw</td>
<td>-</td>
</tr>
<tr>
<td>Mesta</td>
<td>Retting and beating/chemical</td>
<td>Same as jute</td>
<td>-</td>
</tr>
<tr>
<td>Palmyrah</td>
<td>By hand (by beating)</td>
<td>0.5 mg per stalk</td>
<td>300-600</td>
</tr>
<tr>
<td>Pineapple</td>
<td>By hand/decorticator</td>
<td>2.5–3.5 wt % of green leaves</td>
<td>900-1500</td>
</tr>
<tr>
<td>Ramie</td>
<td>Decorticator</td>
<td>2.5–3.5 wt % of bark</td>
<td>900-1200</td>
</tr>
<tr>
<td>Sisal</td>
<td>Manual (beating)/microbial retting/decorticator</td>
<td>3-4 wt % of green leaves</td>
<td>900-1200</td>
</tr>
<tr>
<td>Sunhemp</td>
<td>Manual/retting</td>
<td>2-4 wt % of green stalk</td>
<td>-</td>
</tr>
</tbody>
</table>

Source: Ref. 5.

Table 1.2. Mechanical properties of some plant fibres.

<table>
<thead>
<tr>
<th>Fibre</th>
<th>Initial modulus (GN/m²)</th>
<th>Ultimate tensile strength (MN/m²)</th>
<th>Elongation at break (%)</th>
<th>Flexural modulus (MN/m²)</th>
</tr>
</thead>
<tbody>
<tr>
<td>Sisal</td>
<td>9-22</td>
<td>568-640</td>
<td>3-7</td>
<td>12.5-17.5</td>
</tr>
<tr>
<td>Pineapple</td>
<td>34-82</td>
<td>413-1627</td>
<td>0.8-1</td>
<td>0.25-0.40</td>
</tr>
<tr>
<td>Banana</td>
<td>7-20</td>
<td>54-754</td>
<td>1-4</td>
<td>2-5</td>
</tr>
<tr>
<td>Jute</td>
<td>18</td>
<td>226</td>
<td>1.3</td>
<td>0.3-0.5</td>
</tr>
<tr>
<td>Mesta</td>
<td>-</td>
<td>-</td>
<td>1-2</td>
<td>0.35-0.65</td>
</tr>
<tr>
<td>Flax</td>
<td>-</td>
<td>780</td>
<td>2-4</td>
<td>0.18-0.25</td>
</tr>
<tr>
<td>Sunhemp</td>
<td>-</td>
<td>760</td>
<td>2-4</td>
<td>12.5-17.5</td>
</tr>
<tr>
<td>Palmyrah</td>
<td>4-6</td>
<td>180-215</td>
<td>7-15</td>
<td>-</td>
</tr>
<tr>
<td>Cotton</td>
<td>-</td>
<td>200-400</td>
<td>6-7</td>
<td>0.03-0.10</td>
</tr>
</tbody>
</table>

Source: Ref. 5.
(b) **Manmade fibres**

The manmade fibres are classified into two different categories, regenerated fibres and synthetic fibres depending on the way in which they are prepared.

(i) **Regenerated fibres**

The fibres which are regenerated either from organic or inorganic systems are classified in this category. Polymers from natural sources are dissolved and regenerated after passing through a spinneret to form fibres (e.g. rayon). These fibres are used for reinforcing plastics and rubbers.

Glass fibres are the most common of all reinforcing fibres for polymer matrix composites. The principal ingredient in all glass fibres is naturally occurring silica (SiO₂). The two types of glass fibres commonly used in the FRP industry are E and S glass. Other types are C glass, for applications requiring greater corrosion resistance to acids, D glass for electrical application, A glass for making window glass and bottles and L glass or lead glass for applications requiring radiation protection.

(ii) **Synthetic fibres**

Fibres which have been prepared by chemical synthesis are called synthetic fibres. Examples include nylon, carbon, boron, organic fibres, ceramic fibres and metallic fibres. Among the commercially available fibres, Kevlar fibres exhibit high strength and modulus (Table 1.3). Kevlar is the DuPont trade name for poly(p-phenylene diamine terephthalamide). It is an aromatic polyamide (aramid) in which at least 85% of the amide linkages are attached directly to two aromatic rings.
Table 1.3. Properties of Kevlar and other competitive materials.

<table>
<thead>
<tr>
<th>Properties</th>
<th>Nylon 66</th>
<th>Kevlar 29</th>
<th>Kevlar 49</th>
<th>E-Glass</th>
<th>Steel</th>
</tr>
</thead>
<tbody>
<tr>
<td>Specific gravity</td>
<td>1.14</td>
<td>1.44</td>
<td>1.45</td>
<td>2.55</td>
<td>7.86</td>
</tr>
<tr>
<td>Tensile strength</td>
<td>1000</td>
<td>2750</td>
<td>2760</td>
<td>1700</td>
<td>1960</td>
</tr>
<tr>
<td>(MN m⁻²)</td>
<td></td>
<td></td>
<td></td>
<td></td>
<td></td>
</tr>
<tr>
<td>Tensile modulus</td>
<td>5.52</td>
<td>82.7</td>
<td>131</td>
<td>68.9</td>
<td>200</td>
</tr>
<tr>
<td>(MN m⁻²)</td>
<td></td>
<td></td>
<td></td>
<td></td>
<td></td>
</tr>
<tr>
<td>Elongation at break (%)</td>
<td>18</td>
<td>5.2</td>
<td>2.4</td>
<td>3.0</td>
<td>2.4</td>
</tr>
</tbody>
</table>

Source: Ref. 3.

1.3.2 Matrices

The key difference between thermoplastic and more traditional thermoset based composites lies in the behaviour of matrix during processing. The thermoplastic matrix need not undergo a cure process to achieve its final mechanical properties; all that required is melting, shaping and subsequent solidification. The range of conventional thermoplastic composites and their resultant properties depend on the average length of fibres on moulding.

The most important among common polymeric matrices are polyester and epoxy resins. Cured epoxy resins form the prime matrix of high performance glass, aramid, and carbon fibre composites whereas the unsaturated polyester resins are primarily used in industrial applications. The advantages of the former include their resistance to water, a variety of chemicals and weathering and ageing resistance. Polyimides represent the largest class of high-temperature polymer matrices used in composites today and have service temperatures between 250-300°C. Polyimides are available as thermoplastic polymers or as thermosets. Thermo-setting resins are crosslinked with peroxide to obtain high modulus, strength and creep resistance. However, they exhibit extreme brittleness. Thermoplastic resins are
easier to fabricate than thermosetting resins. Besides, they can be recycled. PEEK is a semicrystalline aromatic thermoplastic. Thermoplastic resins such as PMMA have higher fracture energies. The typical properties of thermoplastic and thermosets are listed in Table 1.4.

Table 1.4. Representative properties of some polymeric matrix materials.

<table>
<thead>
<tr>
<th>Properties</th>
<th>PEEK</th>
<th>Poly-ether sulfone</th>
<th>Polyamide-imide</th>
<th>Polyphenylene oxide</th>
<th>Polyimide</th>
<th>Epoxy</th>
<th>Phenolics</th>
<th>Polyester</th>
</tr>
</thead>
<tbody>
<tr>
<td>Tensile strength (MPa)</td>
<td>92</td>
<td>75</td>
<td>105</td>
<td>70</td>
<td>120</td>
<td>35-85</td>
<td>50-55</td>
<td>35-53</td>
</tr>
<tr>
<td>Flexural modulus (GPa)</td>
<td>40</td>
<td>28</td>
<td>35</td>
<td>28</td>
<td>35</td>
<td>15-35</td>
<td>-</td>
<td>20-30</td>
</tr>
<tr>
<td>Density (g/cc)</td>
<td>1.30</td>
<td>1.25</td>
<td>-</td>
<td>1.32</td>
<td>1.46</td>
<td>1.38</td>
<td>1.30</td>
<td>1.38</td>
</tr>
<tr>
<td>Water absorption, 24 h (%)</td>
<td>0.1</td>
<td>0.2</td>
<td>0.25</td>
<td>0.2</td>
<td>0.3</td>
<td>0.1</td>
<td>0.1-0.2</td>
<td>-</td>
</tr>
</tbody>
</table>

1.3.3 Interface

Fibre reinforced composite materials have three phases. Surface of fibre side, surface of matrix and the interface between fibre and matrix. These phases are collectively referred to as the interface. The characteristics of the interface are dependent on the bonding at the interface, the configuration, the structure around the interface and the physical and chemical properties of constituents. Therefore, the interface has a strong influence on the property of the composite material. These interface effects are seen as a type of adhesion phenomenon and are often interpreted in terms of the surface structure of the bonded material, i.e. surface
factors such as wettability, surface free energy, the polar group on the surface and surface roughness of the material to be bonded.

The composite material performance can be estimated from the characteristics of fillers and matrices and the configuration of filler using the law of mixtures. In the most basic form of law of mixtures, the characteristics of a composite material are represented as a function of characteristics of constituent components and their volume fractions as shown in Figure 1.3. For a composite material (characteristics: $X_C$) that consists of component A (characteristics: $X_A$, volume fraction: $f_A$) and component B (characteristics: $X_B$, volume fraction: $f_B$), the basic formulae of law of mixtures are as follows.

$$X_C = f_A X_A + f_B X_B$$  \hspace{1cm} (1.1)

$$\frac{1}{X_C} = \frac{f_A}{X_A} + \frac{f_B}{X_B}$$  \hspace{1cm} (1.2)

The parallel and series models (curves 1 and 2) are given in Figure 1.3.

The two curves exhibit theoretical upper and lower limits respectively, based on a simple composite effect in general. A basic formula that generalises Equations (1.1) and (1.2) is

$$X_C^n = f_A X_A^n + f_B X_B^n$$  \hspace{1cm} (1.3)

where $n (-1 \leq n \leq 1)$ represents the properties of the combination mode, i.e. the parallel model is predominant when $n$ is close to 1 and the series model, when $n$ is close to -1. According to the logarithmic law of mixtures, composite characteristics is given by the equation,

$$\log X_C = f_A \log X_A + f_B \log X_B$$  \hspace{1cm} (1.4)

This function is in between the parallel model and the series model and referred to as logarithmic law of mixtures as shown in curve 3 (Figure 1.3). The law of mixtures is valid for a composite system when there is no interaction in the
interface. However, it is natural to consider that interaction will occur in the interface due to contact between A and B. Then considering the creation of interfacial phase C, different from A and B, the following equation can be presented.

\[
X_C = f_A X_A + f_B X_B + K f_A f_B
\] (1.5)

This is referred to as quadratic law of mixtures as shown in curve 4 (Figure 1.3). The parameter K involves an interaction between components A and B and provides an expression for the interfacial effect.

\[
f_A = (1-f_B)
\]

**Figure 1.3.** Relation between the properties of composites and various laws of mixture.
1.4 Processing techniques

The choice of manufacturing technique for the fabrication of fibre reinforced plastics or composite materials is intimately related to the performance, economics and application of the materials. It also depends on a number of factors such as component numbers required, item complexity, number of moulded surfaces and type of reinforcement. Important moulding methods for fabrication of polymer matrix composite structural parts may be classified under matched die mould, contact mould (also called open mould), filament winding and pultrusion.

There are two important stages in all moulding processes: laying and curing. The laying is the process in which moulding materials are laid on a mould in the mould cavity or on the mould surface that conforms to the shape of the part to be fabricated. The process of curing helps the resin to set, thereby providing the fabricated part a stable structural form.

The moulding materials are obviously reinforced plastics, either in the form of separate resin and reinforcements, or in the form of composites like bulk moulding compound (BMC) and sheet moulding compound (SMC) prepregs. These composite forms of moulding materials eliminate the mess of using wet resins during the lay-up process. A bulk moulding composite compound is prepared by mixing chopped strands or particulate reinforcements with a pre-mixed resin (normally polyester resin) paste. Fillers, thickeners, catalysts and other additives are also blended. The final mix is, either in the bulk form or extruded in the form of a rode and then stored for future use in the matched-die compression moulding process. A sheet moulding compound is, on the other hand, fabricated in the form of a sheet. Chopped strands or other particulate reinforcements are sandwiched between two layers of polyester resin pastes coated on two polyethylene carrier films. This resin-reinforcement-resin sandwich covered on two sides by the carrier films is thoroughly compacted by forcing it through a series of rollers and stored as rolls. Sometimes continuous rovings are also added in between two resin layers to improve directional properties. Carrier films are
removed prior to using them in moulds. BMCs and SMCs can be used in several moulding processes. Prepregs are prepared by pre-impregnating fibre fabrics with resin. The system is only partially cured. The final cure takes place during the moulding process. Prepregs can be used in all important moulding processes. However, high quality products are realised, when curing is done in an autoclave. Prepregs yield superior products having all kinds of shapes with uniform resin content and consistent quality. Different moulding techniques are given in Figure 1.4.

Figure 1.4. Different moulding techniques.
1.5 Factors influencing composite properties

1.5.1 Fibre volume fraction

One of the important factors affecting composite properties is the fibre content i.e. percentage by volume.

Fibre volume fraction $v_f$ is defined as the ratio of fibre volume $V_f$ to the total composite volume $V_C$.

$$v_f = \frac{V_f}{V_C} \quad (1.6)$$

Matrix volume fraction $v_m$ is defined as the ratio of matrix volume $V_m$ to the total composite volume $V_C$.

$$v_m = \frac{V_m}{V_C} \quad (1.7)$$

For a composite made of fibre and matrix materials, there is an optimum spacing between fibres at which the fibre tensile strength will be fully exploited.\(^{13}\) This optimum spacing is the minimum allowable spacing between fibres, below which the structure will start to disintegrate under loading before the tensile failure. This minimum spacing then defines a maximum volume fraction allowable for a composite.

1.5.2 Strength, modulus and chemical stability of fibre and matrix

The mechanical properties of fibre reinforced composites depend on the strength and modulus of the reinforcing fibre.\(^{14-16}\) Choice of the matrix depends on final requirements of the product in addition to low cost, ease of fabrication, environmental conditions, and chemical resistance of the matrix. The function of matrix in a fibre composite will vary, depending on how the composite is stressed. For compressive loading, the matrix prevents the fibres from buckling and also provides a stress transfer medium, so that when an individual fibre breaks, it does
not lose its load carrying capability. The physical properties of the resin influencing the behaviour of shrinkage during cure are modulus of elasticity, ultimate elongation, tensile and flexural strength, compression and fracture toughness.

1.5.3 Influence of fibre orientation

Orientation of fibres relative to one another has a significant influence on the strength and other properties of fibre reinforced composites. With respect to orientation three extremes are possible. Longitudinally aligned fibrous composites are inherently anisotropic, in which, maximum strength and reinforcement are achieved along the direction of fibre alignment. In the transverse direction, fibre reinforcement is virtually non-existent, fracture usually occurs at very low tensile stress, which may be less than the strength of the matrix. In randomly oriented composites, strength lies between these two extremes.

Uniaxial fibre filled composites can have very high longitudinal tensile strength, but the longitudinal compressive strength is generally less because of the buckling of the fibre.\textsuperscript{17-19} Transverse compressive strength is limited by the strength of matrix and so is less than the longitudinal compressive strength.\textsuperscript{18} By randomly orienting fibres in a plane or by making multilayered laminates in which the fibres in the various layers have different orientation directions, composites can be constructed which are essentially isotropic in plane, i.e. such composites have desirable properties in all directions in a plane. If fibres are aligned in all three directions, desirable properties can be achieved in three dimensions. However, to achieve good properties in two or three dimensions, there must be a sacrifice of property compared to the longitudinal direction of a uniaxially oriented fibre composite.
1.5.4 Influence of fibre length

The strength of a fibre reinforced composite depends not only on the tensile strength of the fibres, but on the degree to which an applied load is transmitted to the fibres. The extent of load transmittance is a function of fibre length and the magnitude of fibre-matrix interfacial bond. The critical aspect ratio which would result in fibre fracture at its midpoint can be expressed as

\[
(1/d)_c = \frac{S_f}{2\tau}
\]

where
- \( l \) - length of fibre
- \( d \) - diameter of fibre
- \( (1/d)_c \) - critical aspect ratio
- \( S_f \) - tensile strength of fibre
- \( \tau \) - fibre-matrix interfacial shear strength

The rule of mixtures for discontinuous fibre composites may be expressed as

\[
S_c = V_f S_f \left[ 1 - \frac{l_c}{2l} \right] + V_m S_m
\]

where
- \( S_c \) - tensile strength of composite
- \( S_f \) - tensile strength of fibre
- \( V_f \) - volume fraction of fibre
- \( V_m \) - volume fraction of matrix
- \( S_m \) - tensile strength of matrix
- \( l_c \) - critical fibre length

1.5.5 Coupling agents

Studies on the composite materials have shown that the bonding between the reinforcing fibre and the matrix has a significant effect on the properties of the composite. Good bonding at the interface can be achieved by modifying the fibre-matrix interface with various surface reactive additives or coupling agents.
An important technique for improving compatibility and dispersability between filler and matrix is to develop a hydrophobic coating of a compatible polymer on the surface of the filler before being mixed with the polymer matrix. Generally, coupling agents facilitate the optimum stress transfer at the interface between filler and matrix. The selection of a coupling agent which can combine both strength and toughness to a considerable degree is important for a composite material.

The most common coupling agents are silane, isocyanate and titanate based compounds, whose chemical composition allows them to react with the surface of fibre. The coatings are applied to the fibre before they are compounded with the polymer matrix. Coupling action will be explained in a later section.

1.6 Theories of adhesion

The mechanisms of adhesion are explained by four main theories: mechanical theory, adsorption theory, diffusion theory and electrostatic theory.

1.6.1 Mechanical theory

According to this theory, the adhesive interlocks around the irregularities or pores of the substrate. A rough surface will have a larger potential bonding area than a smooth one. The metal plating of the polymer acrylonitrile-butadiene styrene (ABS) is probably an example of mechanical adhesion. To obtain satisfactory adhesion, it is necessary to carry out a pre-treatment with chromic acid, which dissolves rubber particles near the polymer surface, leaving a porous structure. A metal from solution may then be deposited into the porous structure providing a mechanical lock.
1.6.2 Adsorption theory

The adhesive macromolecules are adsorbed on to the surface of the substrate and are held by various forces of attraction. The adsorption is usually physical, i.e. due to van der Waals forces. However, primary bonding (ionic or covalent) and hydrogen bonding are involved in some cases. If primary bonds are involved, the term chemisorption is used. This theory assumes a definite interface between the adhesive and adherent. Hydrogen bonding is believed to be important in the bonding of tire cords to rubber. There is good evidence that hydrogen bonding is involved in the self-adhesion of corona treated polyethylene.20,21

The direct evidence of chemical bonding in adhesion is observed in silane coupling agents. Kokta and co-workers22 have provided strong evidence for chemical bonding between isocyanate coupling agent and natural fibre reinforced polyethylene systems. Although the exact nature of the interactions at the interface may be uncertain, the adsorption theory of adhesion is the most widely accepted mechanism.

1.6.3 Diffusion theory

The adhesive macromolecules diffuse into the substrate, thereby eliminating the interface. It requires that the macromolecules of the adhesive and adherent have sufficient chain mobility and they are mutually soluble. Diffusion will also take place when two pieces of the same plastics are heat sealed. Voyutskii23 provided experimental evidence for this theory based on autohesion experiments i.e. bonding experiments where the adhesive and substrate are identical. He studied the bonding of rubbers at elevated temperature and found that joint strength increases with increasing period of contact, increasing temperature, increasing pressure and decreasing molecular weight. The strength is also found to be affected by the addition of plasticisers and with crosslinking.
1.6.4 **Electrostatic theory**

In this theory, the adhesion is due to electrostatic forces, arising from the transfer of electrons from one material of an adhesive joint to another. Evidence in support of this theory includes the observation that the parts of a broken adhesive joint are sometimes charged.\(^{24}\) It has been shown that peeling forces are often very much greater than that can be accounted for by van der Waals forces or chemical bonds.

1.7 **Interface modification**

1.7.1 **Surface modification of polymers**

(a) **Chemical treatment**

When a polymer is treated with highly oxidative chemicals such as chromic anhydride/tetrachloroethane, chromic acid/acetic acid, and chromic acid/sulphuric acid under suitable conditions, polar groups are introduced on the polymer surface and the surface characteristics are improved.\(^{25,26}\) The surface of the polymer is highly oxidised by nascent oxygen generated during the reaction.

\[
K_2Cr_2O_7 + 4H_2SO_4 \rightarrow Cr_2(SO_4)_3 + K_2SO_4 + 4H_2O + 3[O]
\]  
(1.10)

The surface of polyolefins can be activated by treating it with the chemicals through the formation of polar groups such as \(\text{C}=\text{O}, \text{-OH, -COOH and -SO}_3\text{H}\). Rasmussen *et al.*\(^{27}\) determined these polar groups qualitatively in detail. The following mechanism for the formation of oxygen containing polar groups has been proposed.\(^{28}\)
(b) **Corona discharge treatment**

Corona discharge treatment results in the formation of high polarity functional groups such as carbonyl at the polymer surface. Various mechanisms have been proposed for the improvement of the adhesive properties of polyethylene by corona discharge treatment, some attributed it to electric formation \(^{20}\) and others to hydrogen bonding.\(^ {29}\)

(c) **UV irradiation**

UV irradiation on polymer matrices has the following advantages: (1) reaction occurs at ordinary temperature and pressure, (2) selective reaction is possible and (3) light energy can be focused on the surface of the matrix. Modification is carried out by introducing functional groups: (1) by applying UV light to oxidise the material surface or allowing the material to contact a gas or sensitiser to cause a photochemical reaction (2) by allowing UV irradiation induced graft polymerisation at the material surface. Adhesive strength increases with the increasing degree of treatment. To modify a polymer surface, carboxylic acid group is produced at the surface by introducing double bonds through irradiation in acetylene followed by photo oxidation.\(^ {30}\) The reaction is given by
In addition, there are many surface modification processes that use triplet sensitisers to permit oxidation reactions. In a typical process, polyisocyanate is applied on a polyolefin together with a sensitiser such as benzophenone and then irradiated with UV light. The sensitiser has an oxidising effect to produce hydroxyl groups over the polymer surface. These hydroxyl groups finally react with isocyanate to provide a functional polymer. In some cases, adhesive properties can be improved by UV irradiation alone which is known as

\[
P E \xrightarrow{U V} O H \xrightarrow{R(NCO)} O C N H R (NCO)_2
\]  

(d) Plasma treatment

The plasma utilised for polymer treatment is generally called non-equilibrium low temperature plasma. In low temperature plasma for polymer treatment, relatively few electrons and ions are present in the gas. Here, energy of electrons are in the range of 1 to 10 eV. This energy causes molecules of gas A to be ionised and excited. As a result, radicals and ions are produced as shown below.

\[
\begin{align*}
\text{Ionisation} & : \quad A + e_f \rightarrow A^+ + 2e \\
\text{Excitation} & : \quad A + e_f \rightarrow A^* + e \\
\text{Radical dissociation} & : \quad A^* \rightarrow A^* _1 + A^* _2 \\
\text{Luminescence} & : \quad A^* \rightarrow A + h\nu \\
\text{Electron addition} & : \quad A + e \rightarrow A^-
\end{align*}
\]

The activated particles react with polymeric materials so that polymeric radicals are produced on the surface layer of materials. This causes the surface layers to be oxidised, crosslinked or decomposed. On the other hand, free radicals are
produced from molecules of the gas and are polymerised, so that the resultant polymers of A coat the surface of the material.

In the presence of inert gas such as He or Ar, crosslinking can be introduced into the surface layer of material by plasma treatment. Hansen and Schonhorn named this as "Crosslinking by Activated Species of Inert Gases" (CASING). As a result, bond strength is enhanced because crosslinking strengthens the surface layer.

1.7.2 Surface modification of fillers

Reinforcing fibres can be modified by physical and chemical methods.

(a) Physical methods of modification

Physical treatments change the structural and surface properties of the fibre and thereby influence the mechanical bonding in the matrix. These include electric discharge using corona or cold plasma. Corona treatment is one of the most interesting techniques for surface oxidation activation. This process changes the surface free energy of the fibres. In the case of cold plasma treatment, depending on the type and nature of the gases used, a variety of surface modifications like crosslinkages could be introduced. Surface free energy could be increased or decreased and reactive free radicals could be produced.

(b) Chemical methods of modification

When two materials are incompatible, it is often possible to bring about compatibility by introducing a third material that has properties in between those of the other two. There are several mechanisms of coupling in materials.

- Weak boundary layers—coupling agents eliminate weak boundary layers.
- Deformable layers—coupling agents produce a tough flexible layer.
- Restrained layers—coupling agents develop a highly crosslinked interface region with a modulus in between those of the substrate and the polymer.
- Wettability—coupling agents improve the wetting between polymer and substrate.
- Chemical bonding—coupling agents form covalent bonds with both materials.
- Acid base effect—coupling agents alter the acidity of the substrate surface.

The development of a definite theory for the mechanism of bonding by coupling agents in composites is a complex problem. In addition to chemical bonding theory it also includes the morphology of the interface, the acid-base reactions at the interface, surface energy and the wetting phenomena.

(i) Silane coupling agents

Silane coupling agents impart hydrophilic properties to the interface especially when amino-functional silanes such as epoxies and urethane silanes are used as primers for reactive polymers. Organosilanes are the main type of coupling agents in glass reinforced polymers. Most of the silane coupling agents can be represented by the following formula:

\[
R-(\text{CH}_2)_n-Si(\text{OR}')_3
\]

with \(n=0-3\); \(\text{OR}'\) the hydrolyzable alkoxy group and \(R'\) the functional organic group which causes the reaction with the polymers. This could be a copolymerisation reaction and/or the formation of an interpenetrating network.\(^\text{39}\) This curing reaction of a silane treated substrate enhances the wetting by the resin.

(ii) Impregnation of fibres

A better combination of fibre and polymer is achieved by an impregnation of the reinforcing fibres with polymer dispersions compatible with the polymer.
matrix. For this purpose polymer solutions or dispersions of low viscosity are used. When cellulose fibres are impregnated with a butyl benzyl phthalate plasticised PVC dispersion, excellent properties were achieved.

(iii) **Graft copolymerisation**

An effective method of natural fibre chemical modification is graft copolymerisation, which is initiated by free radicals of the cellulose molecule. The cellulose is treated with an aqueous solution with selected ions and is exposed to a high energy radiation. Then the cellulose molecule breaks and radicals are formed. Afterwards, the radical sites of the cellulose are treated with a suitable solvent compatible with the polymer matrix, e.g. vinyl monomer, acrylonitrile, methyl methacrylate and polystyrene. The resulting copolymer possesses properties characteristic of both cellulose fibre and grafted polymer. The treatment of cellulose fibres with polypropylene maleic anhydride (MAH-PP) copolymers provide covalent bonds across the interface.

(iv) **Isocyanate treatment**

The mechanical properties of PVC, PE or PS based composites reinforced with wood fibres can be improved by an isocyanate treatment of the cellulose fibres or the polymer matrix. Poly(methylene) poly(phenyl) isocyanate (PMPPIC) in the pure state or in solution in the plasticiser can be used. PMPPIC is chemically linked to the cellulose matrix through strong covalent bonds. When PMPPIC is used as a bonding agent for PS matrix, the delocalised π electrons present in the benzene rings of both of them provide strong interactions, so that there is an adhesion between PMPPIC and PS matrix.

1.8 **Characterisation of interface**

The type of interaction along the interface will exert a great influence on various properties of the composite material. Therefore, to improve the
performance of a composite material, it is absolutely necessary to characterise the structure of the interface. Some of the methods for analysis of the interface are electron spectroscopy for chemical analysis (ESCA), auger electron spectroscopy (AES), infrared spectroscopy (IR), Fourier transform infrared spectroscopy (FTIR), secondary ion mass spectroscopy (SIMS), scanning electron microscopy (SEM), inverse gas chromatography (IGC), etc. which are well-known. ESCA is widely used at present in the surface analysis of elements and the qualitative analysis of functional groups. An alternative approach to acid/base characterisation is based on the technique of inverse gas chromatography (IGC). Environmental scanning electron microscopy (ESEM) allows wet, oily and electrically non-conductive specimens to be observed without special preparation (gold coating) and at relatively high pressures. ESEM is useful for investigating wood polymer interactions at fracture surfaces and polymer distributions in wood polymer composites (WPC). Solid state $^{13}$C-NMR spectroscopy using cross polarisation and magic angle spinning is especially useful for characterising wood and WPCs. Elemental composition can be determined in energy dispersive analysis of X-rays (EDAX). This type of analysis is particularly useful in determining the depth of penetration of a chemical used for wood modifications and to ascertain if the chemical is homogeneously distributed throughout the wood.

1.9 Natural fibre reinforced polymer composites and their applications

Fibre reinforced plastics (FRP) have been widely accepted as materials for structural and non-structural applications in recent years. The main reason for interest in FRP for structural applications, is due to high specific modulus and strength of the reinforcing fibres. Glass, carbon, kevlar and boron fibres are commonly used for reinforcement. However, these are highly expensive and therefore their use is limited only in aerospace applications.

Nowadays throughout the world different natural fibres are available and these are undergoing a high-tech revolution that could see them replace synthetic
materials in applications such as boat hulls, building materials, bath tubs and archery bows.⁴⁵ Their manifold virtues include low cost, light weight and ease of recycling. According to a recent report, in Germany, car manufacturers are aiming to make every component recyclable or biodegradable.⁴⁵ Daimer-benz is a world leader in using natural fibres in its vehicles. Since 1995, the door panels in the mercedes-cars have been made from plastics reinforced with flax fibres. Composites reinforced with jute fibres take the place of wood in packaging and building applications in South and South-East Asia.

Thermoplastic materials are being used increasingly due to their lower cost, light weight and better flexibility in part design. The use of cellulosic materials in thermoplastic composites is highly beneficial because the strength and toughness of plastics can be improved. The potential advantages of these natural fibres are low cost, light weight, flexibility, reduced wear of processing machinery, biodegradability, ease of recycling and no health hazards. Also, the hollow nature of vegetable fibres imparts acoustic insulation properties to certain types of matrices. Effect of sisal, coir, bamboo, banana, hemp and wood fibres as reinforcing agents have been studied in an attempt to produce reinforced building products. It was found that pineapple, banana and bamboo fibre reinforced cement composites were successful in building applications.⁴⁶⁴⁷ Jute and kenaf fibres have been reported to work very well in geotextile applications as a natural separator between different materials in the layering of back fill.⁴⁸

In 1981 Belmares and his research group in Mexico together with Parfoort and his research group in Belgium carried out an investigation on the reinforcement of polyester resin with palm, sisal and henequene.³ Their work explored the reinforcement of polyester resin with palm fibres, a low-cost fibre abundant in Mexico, for improving its mechanical properties, reducing water absorption and biodegradation in order to make them competitive with glass reinforced polyester resin. Palm fibres coated with a poly(vinyl acetate)/fumarate emulsion also increased the flexural properties of composites with polyester resin. Another
important aspect of these composites, is the prevention of biodegradation of cellulose fibres in the polyester. When a microbicidal agent (ZnCl₂) was added to the laminated samples, the tensile strength remained almost the same even after 45 days of soil biodegradation in palm fibre reinforced polyester composites.¹³

Polyethylene-henequene-sand laminates has been reported to have a relatively low density, high weathering resistance and low water absorption.⁴⁹ PVC-ixtler-sand laminates⁵⁰ show good mechanical properties and are found to be suitable for construction materials. In general, building and especially roofing applications are expected of these composites. Pine craft pulp reinforced polyethylene laminates showing good flexural properties at low humidities have been produced for application in building and packaging. Pregrafted and ungrafted pulp fibres from aspen and spruce have been combined with polystyrene by hot pressing⁵⁰ and as a result a general improvement in mechanical properties was observed at high fibre contents.

Extruded composites of plasticized PVC and short cellulose fibres have been investigated by Goettler.⁵¹ Pronounced increase in tensile modulus and both yield and ultimate tensile strength are observed. Single step processing of reinforcement and polymer with good product performance are key characteristics of the material whose field of application lies in vinyl hose industry. The effects of various fibre reinforcements like abaca fibre, bagasse, bamboo, banana, sun-hemp, jute, oil-palm, sisal and coir on thermosetting resins have been reported.⁵²⁻⁶¹

The major drawbacks associated with the use of natural fibres as reinforcement in thermoplastic matrix to achieve composite material with improved mechanical properties and dimensional stability are the poor wettability and weak interfacial bonding with the polymer due to inherently poor compatibility. Without effective wetting of the fibre, strong interfacial adhesion cannot be achieved. The lack of interfacial interaction leads to internal strains,⁴⁰ porosity⁶² and environmental degradation.⁶³ Kokta and co-workers⁶⁴⁻⁶⁸ have extensively studied the effect of different chemical modifications such as poly(methylene)
poly(phenyl isocyanate) (PMPPIC), silane and monomer grafting on the mechanical properties and dimensional stability of natural fibre reinforced polymer composites (polyethylene, polystyrene and PVC). They have reported that chemically modified cellulose fibre filled thermoplastic composites offer superior physical and mechanical properties. Felix and Gatenholm reported the effect of compatibilising agents and nature of adhesion in composites of cellulose fibres and polypropylene. Ali et al. reported the improvement of jute fibre composites through UV-cured films of urethane acrylate. Improvement of interfacial strength by grafting of a polypropylene chain by an ester bond capable of co-crystallising or entangling with the matrix in cellulose fibre reinforced PP composites was reported by Jolly and co-worker. Improvement of adhesion between PE and regenerated cellulosic fibres by surface fibrillation is also reported. Recently, from our laboratory, Thomas and co-workers have reported on the use of sisal, coir, pineapple, oil-palm and banana fibre as potential reinforcing agents in polyethylene, polystyrene, styrene butadiene rubber, natural rubber and thermosets (epoxy resin, phenolformaldehyde, polyester). Among polyester, epoxy, and phenol formaldehyde composites of sisal fibre, the phenolic type resin performed as a better matrix than epoxy and polyester resins with respect to tensile and flexural properties due to the high interfacial bonding in phenolic composites.

To sum up, it must be stated that at the present time high strength, high toughness and long term durable products can be made from natural fibres and polymers using high technology. By developing low cost chemical pre-treatment of natural fibres and low cost manufacturing processes, developing nations will soon be able to produce cheap building materials using the indigenous natural fibres. The primary benefit in terms of the environment would be forest conservation. Natural fibres have the added advantage of being biodegradable. Fibres are biodegradable but the polymers or resins used in composites are not. However, the quantity of polymers using can be reduced by reinforcing with these natural fibres.
1.10 Scope and objectives of the work

As discussed in the previous sections, natural fibres have several advantages. They are abundant, inexpensive, renewable and of low density. In addition to being amenable to modification, they are biodegradable and thus do not contribute to environmental pollution. Therefore, there is every need to develop natural fibre reinforced composites. Among the natural fibres, pineapple leaf fibre (PALF) exhibits highest strength and modulus and appreciable crystallinity. Thus, the reinforcement obtained with these fibres is of great significance. The physical properties, mechanical and dielectric characteristics, tensile behaviour and surface morphology of PALF have been reported. The mechanical properties of PALF reinforced elastomer composites have been studied by Bhattacharyya et al.

However, very little or no work has been reported in literature on the use of pineapple leaf fibre as a reinforcement in thermoplastics. Among the ‘big four’ thermoplastics, polyethylene is widely used in packaging, industrial goods, household products, engineering applications, etc. Hence, a study on the influence of PALF on the different properties of polyethylene is of theoretical interest and practical relevance. Thus, an investigation of PALF reinforced low density polyethylene (LDPE) composites has been undertaken. The results of these studies are presented and discussed at length in the thesis.

In the course of their use, materials are subjected to different loads or deformation levels. Thus, the stress-strain properties of PALF/LDPE composites is of relevance not only for characterising their mechanical behaviour but also for engineering design of componets based on them. The uniaxial stress-strain properties of fibre reinforced composites are dependent on many factors like fibre-matrix adhesion, volume fraction of fibre, fibre aspect ratio, fibre orientation, processing method, stress transfer efficiency at the interface, etc. Surface modification with coupling agents provide better stress transfer at the fibre-matrix interface. Fibre length and fibre orientation are of critical importance to engineers and designers who wish to predict the failure behaviour of short fibre reinforced
plastics. Thus, the investigations on PALF/LDPE composites have been made with reference to fibre length, fibre loading, orientation, processing method (solution mixing and melt mixing) and chemical treatment of fibre using coupling agents. In structural applications, it is necessary to make allowance for the degradation that can occur due to heating in some of the mechanical properties of materials. Therefore, the study of the mechanical behaviour of composites at different temperatures is undertaken.

A study of the flow behaviour of materials in the melt state is essential to achieve a complete understanding of processing operations, and also to improve the efficiency and quality of product manufacture. The variation of viscosity with shear rate and temperature is an important factor for the successful exploitation of these materials using different moulding techniques. Therefore, the processing characteristics of the composites have been investigated in terms of mixing behaviour (dependence of torque versus time of mixing) and rheological properties (variation of melt viscosity with shear rate, extrudate morphology, etc).

Owing to the polymeric nature of polyethylene, the composites based on LDPE would exhibit viscoelasticity, i.e. the properties are dependent on time/frequency. In dynamic experiments, time lag exists between stress and strain resulting in such characteristics as damping coefficient, storage modulus and loss modulus. These properties have also been used to provide information about structural motions and thermal transitions ($T_s$ and $T_m$) in polymers. Thus, the viscoelastic behaviour of PALF/LDPE composites has been investigated using dynamic mechanical analysis technique. The dependence of storage modulus and damping factor on temperature and effects of parameters like fibre length, loading, orientation, etc. have been studied.

Stress relaxation (i.e. decay of stress with time at constant strain) is another manifestation of viscoelastic behaviour of polymeric materials. Therefore, the stress relaxation characteristics of PALF/LDPE composites have been investigated in terms of relative stress and relaxation modulus as functions of logarithmic time.
The dependence of rate of relaxation and relaxation mechanism on fibre level, loading, orientation, chemical treatment, strain level, thermal ageing, etc. have been studied for providing insight into the viscoelastic nature of these composites.

Thermogravimetry has been widely used as an analytical tool for studying the degradation of polymeric materials under the influence of temperature. TG/DTG studies carried out on PALF/LDPE composites have revealed interesting thermal characteristics, particularly the effect of chemical treatment of fibres.

In packaging, static charge accumulation is one of the most serious problems. This situation can be alleviated by using antistatic materials. In order to have an insight into the use of PALF/LDPE composite as an antistatic material, a study on dielectric properties (dielectric constant, volume resistivity, dielectric loss factor) of composites is undertaken.

A specific source of embrittlement in plastics materials, which has frequently posed adverse problems in service is the phenomenon of environmental stress cracking. The failure is caused by any condition in which an external stress is imposed on a specimen which is in contact with an external environment (temperature, water, and UV radiation). The absorption of moisture by plastic material generally softens and toughens in the short term behaviour. In the longer times, especially at moderately elevated temperature, water is frequently degradative, leading to premature failure. So emphasis is given in this work to investigate the water absorption behaviour and radiation effects.

Scanning electron microscope and optical microscope methods have been used to understand morphological changes in PALF and PALF/LDPE composites. Chemical treatment by coupling agents resulted in interesting changes in fibre characteristics. SEM fractographs have been used to provide better understanding of failure modes in these composites under different conditions of fibre loading and size, test conditions and environmental conditions.
1.11 References


