2.1 Composites

Composite is a material made up of two or more distinct phases with a recognizable interface or boundary. There can be a variety of materials which could be used for the formation of composites such as ceramics, metals, plastics, carbon fibres, glass, etc. Polymer composites are plastics within which there are embedded particles or fibres with the major component being the polymer (matrix) and the particles being additives (dispersed phase). Such composites exhibit quite different properties than the original materials individually. This arises due to various effects:

1) polymer molecules wrapping around the stiff additive particles/ fibres
2) interfacial forces between the two phases
3) distribution of stress/ applied load
4) reinforcing effect, etc.

A major driving force behind the development of composites has been to produce materials with improved specific mechanical properties over existing materials. In addition, polymer composites are useful in applications where the environment would be detrimental to other materials. Cost is ever present in the engineering equation and it is the balance of cost and performance that determine whether or not a polymer composite will be preferred over an alternative structural material option.

2.1.1 Classification of Composites

Composites, in general are classified either based on the structural components or the matrix and based on the type of the matrix used they are classified as follows,

Ceramic Matrix Composites (CMC) - Ceramic matrices are often used with carbon, ceramic, metal and glass fibres. These are used in rocket engine parts and protective shields. Glass matrices are mostly reinforced with carbon and metal oxide fibres. Heat resistant parts for engine, exhausts and electrical components are their primary applications. Carbon matrices with carbon whiskers or carbon fibres as reinforcement are used for desired properties. Carbon in the form of diamond and graphite has high heat capacity per unit weight and therefore selected as ablative materials.
Metal Matrix Composites (MMC)- Metal matrices of iron, nickel, tungsten, titanium, aluminium, and magnesium are generally used for high temperature usage in oxidizing environment.

Polymer Matrix Composites (PMC)- The reinforcing filler particles are dispersed in a thermoset or a thermoplastic resin in these composites. Henceforth, the focus in this thesis would be restricted to polymeric composites, which provides the framework for further discussions.

Based on the type reinforcement used the composites are classified as follows:

Fibre Reinforced Composites- these contain reinforcements having much greater length than their cross-sectional dimensions. They may be continuous (with lengths running the full length of the composite) or discontinuous (of short lengths). These fibres may be unidirectional, cross woven or random. Typical examples are glass fibre reinforced plastics, carbon fibres in epoxy resins, wood (a composite of cellulose in a matrix of lignin), vehicle tyres in which rubber is reinforced with nylon cords.

Particulate Filled Composites- these include materials reinforced by spheres, rods, beads, flakes, and many other shapes of roughly equal axes. The example of these are polymeric materials incorporated with different fillers such as glass spheres or finely divided powders, polymers with fine rubber particles, etc.

Laminar Composites- these are composed of two or more layers held together by the matrix binder. These have two of their dimensions much larger than the third. Wooden laminates, plywood and some combinations of metal foils, glasses, plastics, film and papers are laminar composites. Some ceramic and metallic composites also fall in this category.

Skeletal Composites- These are composed of continuous skeletal matrix filled by a second matrix. For example, honeycomb structure of the polymer filled with additives.

2.1.2 Advantages of Composites

The chief among the many advantages that composites offer over traditional materials are
✔ High strength
✔ Lower weight
✔ Great freedom of shape or flexibility in design
✔ High dielectric strength
✔ Dimensional stability and fatigue endurance
✔ Corrosion and environmental resistance
✔ Low tooling costs

Composites literally have an endless number of applications. Due to their high strength to weight ratio, they have applications ranging from aerospace to sports goods. Because of their electrical insulating properties, composites are used widely in appliances, tools and other machinery. Additionally, corrosion-resistant composite tanks and pipes offer extended service life over metals. Strong and stiff glass fibers carry loads imposed on the composite while the resin matrix spreads the load across the fibers.

### 2.2 Fillers for Polymer Composites

Historically, fillers have been used in polymers, paints, thickening agents, extenders or composites as cost effective materials. Actually, they play a more important role than being a mere inert additive (Mascia et al. 1982, Gachter R. 1987, Lutz J. T. 1989, Murphy J. 1996 and Pritchard G. 1998). More appropriately, they are christened functional fillers, mineral additives or reinforcing agents. For decades, mineral fillers have been added to thermoplastics and thermosets to form composites. Compared to neat resins, these composites have a number of improved properties including tensile strength, heat distortion temperature and modulus. Thus for structural applications, composites have become very popular and are sold in billion-pound quantities. Clearly, the idea of adding fillers to thermoplastics and thermosets to improve properties, and in some cases decrease the cost, has been very successful for many years. However, as one desirable property is changed, nearly all of the other physical and mechanical properties are affected. Hence, it is essential to optimize the filler type, composition and the processing parameters to obtain the best performance from these materials. Fillers are the solid additives incorporated into the polymer to modify its physical (usually) mechanical properties. Fillers can constitute either a major or a minor part of a composition. The structure of filler particles ranges from precise
geometrical forms, such as spheres, hexagonal plates, or short fibers, to irregular masses.

2.2.1. Characteristics of Fillers

The overall value of filler is a complex function of intrinsic material characteristics, e.g. density, melting point, crystal structure, and chemical composition; and of process dependent factors like, particle size distribution, surface chemistry, purity, bulk density, etc.

2.2.1.1. Particle Size and Distribution

Filler particle size distribution and shape affect rheology and loading limits of filled compositions and generally are primary selection criteria. Particles with fibrous, needle-like, or other irregular shapes yield compositions more resistant to flow, as compared to compositions filled with ‘spheres’ or other fillers with more regular morphologies. Thus fillers with regular shapes can be used in compositions at higher loadings than fillers with regular morphologies. Filler morphology plays the major role in reinforcement, for example fibrous material due to high aspect ratio gives better reinforcement compared to particulate filler, but often at the cost of processability and expense. Finer the particle size, higher the values of tensile strength, modulus and hardness. Coarser particles will tend to give compounds less strong than pristine polymer, but if the particle size is sufficiently fine there is an enhancement in the properties upto an optimum loading of filler, and the phenomenon is known as reinforcement. The particle shape also has an influence; for example; plate like clay particles tend to be oriented during processing to give products that are anisotropic. Other particles tend to have an uneven surface and are difficult to wet the polymer whilst others are porous and may absorb additives and render them ineffective.

2.2.1.2. Surface Area

Surface area is the available area of fillers, be it on the surface or in the cracks, crevices, and pores. Surface area is important because many processing factors are dependent on the surface area, e.g., ease of filler dispersion, rheology, and optimum filler loading.
2.2.1.3. Surface energy or wettability

A hydrophilic surface, like that found on a typical amorphous silica particle is expected to disperse readily in water and most liquids miscible in water. The wettability is a function of the surface area and chemical composition of the surface. Many commercial types of filler are surface-coated or chemically treated to modify their surface chemistry and wetting properties.

2.2.1.4. True Density & Bulk Density

The average mass per unit volume of the individual particles is called true density or specific gravity. This property is most important when volume or mass of filled composition is a key performance variable. Bulk density refers to the total amount of space or volume occupied by a given mass of dry powder. Bulk density is also a key factor in the economics of shipping and storing fillers.

2.2.1.5. Thermal Stability

Fillers for high temperature application must not decompose under conditions of processing or use. To preserve the structural strength of filled compositions over a wide range of temperatures, all components of the composition should have similar coefficient of thermal expansion.

2.2.1.6. Chemical Nature

Chemical nature of the surface has a vital effect. Mineral fillers usually have pendant polar groups on the surfaces, for example hydroxyl groups, which render them attractive to water and not to polymer. To improve the wetting of polymers to fillers and hence obtain better products mineral fillers are often treated. For example, calcium carbonate may be treated with stearic acid, the acid group attaching itself to filler particles while aliphatic chain is compatible with the polymer. Some of the clays are amine treated whilst others are coated with glycol or similar product. Other important features of filler include hardness, refractive index, color, brightness, etc. Some of the important characteristics of fillers that have a considerable influence on its properties in consonance with a polymer matrix are the average particle size, particle size distribution, particle shape, particle integrity, surface properties and
abrasion. Fine particles increase the mechanical properties but are difficult to disperse thereby increasing the viscosity. The shape of the filler particle is found to have a tremendous effect on flexural modulus. Aspect ratio, defined as the ratio of the longest length of a particle to its thickness thereby becomes extremely significant. As a mineral’s shape progresses from a cube to a block to a plate to a flake to a fibre, the aspect ratio increases as shown in the figure 2.1. The melt viscosity of the composite is found to be a function of the filler loading level, surface area and aspect ratio. Narrower distribution of similarly shaped particles results in a higher melt viscosity. A critical aspect ratio is necessary in a composite to allow a functional filler to receive an applied stress. A primary particle is the smallest unit that has a coherent shape. Aggregates are defined as primary particles that have been fused together. Agglomerates represent an additional degree of structuring, where primary particles or aggregates are bonded together in nonintergrown unions such that the total surface area does not differ significantly from the sum of individual areas. Some minerals like talc and mica are easily delaminated along the crystallographic planes. Although friability of minerals is a factor, their structural strength can be so tough that abrasivity becomes an issue. Abrasion properties are quantified by the moh’s hardness scale. Sharp edges and rod shaped particles have greater abrasive effects than smooth or rounded particles.

![Figure 2.1. Aspect ratios of various fillers](image)

### 2.2.2. Classification of Fillers

There is a plethora of fillers to choose from these days and the selection is mostly done based on the end application (Sekutowski, 1996 and Rothon R. N, 1999). Both
natural and synthetic compounds are used as fillers. Most of the fillers like calcium carbonate, clays, talc, mica, wollastonite, glass fibre, silica, aluminium hydroxide, magnesium hydroxide and magnesium carbonate are used extensively in thermoplastics. Relative abundance and high purity of calcium carbonate, lamellar structure and softness of mica and talc, high aspect ratio of wollastonite, special reinforcing capabilities of glass fibre, antiblocking nature of silica, flame retardance of aluminium hydroxide, coating applications of magnesium hydroxide and smoke suppressant characteristics of magnesium carbonate vouch for their functional uses.

Fillers can be classified according to their source, function, composition or morphology.

2.2.2.1. Particulate Filler

These are types that remain in discreet form in a matrix, having relatively low aspect ratio. Size of the filler varies from coarser, fines to ultrafines including micro and nanoscale. They embrace not only fillers of regular shape such as sphere but also many of irregular shape possibly having extensive convolution and porosity. Table 2.1 gives the important filler used in polymer.

2.2.2.2. Fibrous Filler

A general term used to refer to filamentary materials, with a finite length that is at least 100 times its diameter, which is typically 0.01 to 0.13 mm. In most cases it is prepared by drawing from a molten bath, spinning, or deposition on a substrate. Fiber can be continuous or specific short length normally no less than 3.2 mm. Whiskers are the short single crystals fiber or filaments made from a variety of materials, with diameter ranging from 1 to 25 micron and aspect ratio from 100 to 15000. Table 2.1 gives the important filler used in polymer.

2.2.2.3. Nanoscale fillers

Nanofillers are those fillers whose any one of its dimensions is lesser than 100 nanometer. Various types of Nanoscale fillers are as follows.
2.2.2.3.1. Layered silicates

The layered silicates commonly used in nanocomposites belong to the structural family known as the 2:1 phyllosilicates. Their crystal lattice consists of two-dimensional layers where a central octahedral sheet of alumina or magnesia is fused to two external silica tetrahedron by the tip so that the oxygen ions of the octahedral sheet do also belong to the tetrahedral sheets. Figure 2.2 shows the structure of 2:1 layered silicates. The layer thickness is around 7Å and the lateral dimensions of these layers may vary from 300 Å to several microns and even larger depending on the particular silicate. These layers organize themselves to form stacks. Different types of fillers have been depicted in table 2.1.

![Figure 2.2. The structure of 2:1 layered silicates](image-url)
Table 2.1. Fillers for polymer

<table>
<thead>
<tr>
<th>Particulate</th>
<th>Fibrous</th>
</tr>
</thead>
<tbody>
<tr>
<td><strong>Organic</strong></td>
<td><strong>Inorganic</strong></td>
</tr>
<tr>
<td>Wood Flour</td>
<td>Glass</td>
</tr>
<tr>
<td>Cork</td>
<td>Calcium Carbonate</td>
</tr>
<tr>
<td>Nutshell</td>
<td>Alumina</td>
</tr>
<tr>
<td>Starch</td>
<td>Beryllium Oxide</td>
</tr>
<tr>
<td>Polymers</td>
<td>Iron Oxide</td>
</tr>
<tr>
<td>Carbon</td>
<td>Magnesia</td>
</tr>
<tr>
<td>Protein</td>
<td>Magnesium Carbonate</td>
</tr>
<tr>
<td></td>
<td>Titanium Oxide</td>
</tr>
<tr>
<td></td>
<td>Zinc Oxide</td>
</tr>
<tr>
<td></td>
<td>Zirconia</td>
</tr>
<tr>
<td></td>
<td>Silicates(^a)</td>
</tr>
<tr>
<td></td>
<td>Barium ferrite</td>
</tr>
<tr>
<td></td>
<td>Barium Sulfate</td>
</tr>
<tr>
<td></td>
<td>Molybdenum disulfide</td>
</tr>
<tr>
<td></td>
<td>Silver</td>
</tr>
<tr>
<td></td>
<td>Silicon carbide</td>
</tr>
<tr>
<td></td>
<td>Clays</td>
</tr>
</tbody>
</table>

\(^a\)talc, mica, calcium silicate

with a regular Van der Walls gap in between them called the interlayer or the gallery. Isomorphic substitutions of Si\(^{4+}\) for Al\(^{3+}\) in the tetrahedral lattice and of Al\(^{3+}\) for Mg\(^{2+}\) in the octahedral sheet causes an excess of negative charges within the
layers. These negative charges are counterbalanced by alkali or alkaline earth cations such as Ca$^{2+}$ and Na$^+$ situated in the interlayer. Montmorillonite, hectorites and saponite are most commonly used layered silicates. In particular, the smectite group of clay minerals such as montmorillonite, saponite and hectorite are mainly been used because they have excellent intercalation abilities (Pinnavaia et al. 2001). Their chemical formulas are shown in Table 2.2.

This type of clay is characterized by a moderate negative surface charge (known as cation exchange capacity, CEC and expressed in meq/ 100g). The charge of the layer is not locally constant as it varies from layer to layer and must rather be considered as an average value over the whole crystal. As clearly shown in figure 2.2, MMT, oxygen atoms from each alumina octahedral sheet also belong to the silica tetrahedral sheets, the three of them consisting of 7Å thin layer. These layers are linked together by Van der Waals bonds and organized in stacks with a regular gap between them called ‘interlayer’ or ‘gallery’. Within the layers, isomorphic substitution of atoms as Al$^{3+}$ with Mg$^{2+}$ or Fe$^{2+}$ can occur generating an excess of negative charge, the amount of which characterizes each clay type and is defined through the Cation exchange capacity (CEC). The CEC value for MMT depends on its mineral origin, yet is typically 0.9-1.2 meq/g. In natural clays, ions such as Na$^+$, Li$^+$ or Ca$^{2+}$ in their hydrated form balance excess negative charge; this means natural MMT is only miscible with hydrophilic polymers like polyethylene oxide and polyvinyl alcohol. In order to make possible for MMT to be miscible with other kinds of polymers, it is essential to replace the alkali ions with cationic-organic surfactants, such as alkylammonium ion. In this way the natural clay can be rendered

Table 2.2. Chemical formula for the 2:1 phyllosilicates

<table>
<thead>
<tr>
<th>2:1 phyllosilicate</th>
<th>General formula</th>
</tr>
</thead>
<tbody>
<tr>
<td>Montmorillonite</td>
<td>M$<em>x$(Al$</em>{4-x}$Mg$_x$)Si$<em>8$O$</em>{20}$(OH)$_4$</td>
</tr>
<tr>
<td>Hectorite</td>
<td>M$<em>x$(Mg$</em>{6-x}$Li$_x$)Si$<em>8$O$</em>{20}$(OH)$_4$</td>
</tr>
<tr>
<td>Saponite</td>
<td>M$_x$Mg$_6$(Si$_8$-xAl$_x$)Si$<em>8$O$</em>{20}$(OH)$_4$</td>
</tr>
</tbody>
</table>

M = monovalent cation; x = degree of isomorphous substitution (between 0.5 to 1.3)
'organophilic' and then named ‘organoclay’, or ‘nanoclay’, which is capable of yielding a nanocomposite interacting with an organic matrix. It is worth saying that the layers (platelets) have been proven to be not totally rigid, but have a certain degree of flexibility, and this feature can affect the mechanical behavior of the resulting composite.

### 2.2.2.3.2. Nano Zinc oxide rods

Inorganic UV blockers are more preferable to organic UV blockers as they are non-toxic and chemically stable under exposure to both high temperatures and UV. Inorganic UV blockers are usually certain semiconductor oxides such as TiO2, ZnO, SiO2 and Al2O3. Among these semiconductor oxides, titanium dioxide (TiO2) (Xin et al. 2004; Burniston et al. 2004; Jonatahn 2003; and Yang et al. 2003) and zinc oxide (Saito, M. 1993; Xiong et al. 2003) are commonly used.

It was determined that nano-sized titanium dioxide and zinc oxide were more efficient at absorbing and scattering UV radiation than the conventional size and were thus better able to block UV (Xin et al. 2004; Saito et al.). This is due to the fact that nanoparticles have a larger surface area per unit mass and volume than the conventional materials, leading to the increase of the effectiveness of blocking UV radiation. For small particles, light scattering predominates at approximately one-tenth of the wavelength of the scattered light. Rayleigh’s scattering theory stated that the scattering was strongly dependent upon the wavelength, where the scattering was inversely proportional to the wavelength to the fourth power. This theory predicts that in order to scatter UV radiation between 200 and 400 nm, the optimum particle size will be between 20 and 40 nm (Burniston et al. 2004).

Various research works on the application of UV-blocking treatment to fabric using nanotechnology were conducted. UV-blocking treatment for cotton fabrics was developed using the sol-gel method. A thin layer of titanium dioxide is formed on the surface of the treated cotton fabric which provides excellent UV-protection; the effect can be maintained after 50 home launderings (Xin et al. 2004; Daoud, et al. 2004). Apart from titanium dioxide, zinc oxide nanorods of 10 to 50 nm in length were applied to cotton fabric to provide UV protection (Wang et al. 2004). According to the
study of the UV-blocking effect, the fabric treated with zinc oxide nanorods demonstrated an excellent UV protective factor (UPF) rating.

2.2.2.3.3. Nano Silver

Silver, in its many oxidation states (Ag⁰, Ag⁺, Ag²⁺, and Ag³⁺) has long been recognized as having an inhibitory effect towards many bacterial strains and microorganisms commonly present in medical and industrial processes (Clement et al. 1994; Jiang et al. 2004). As early as 344 B.C., Aristotle may have advised his student, Alexander the Great, to store boiled water in silver vessels to thwart waterborne diseases (Russell et al. 1994). One of the most powerful naturally occurring antiseptic materials with a severe bactericidal effect and believed low toxicity towards mammalian tissue, the deposition and insertion of silver ions to various products has been a highly appealing approach for the prevention of biofilm formation (Ahearn et al. 1995).

Technologies utilizing nanoparticles are based on the notion that materials constructed from particles below a critical length dimension display very unique chemical and physical properties (Poole et al. 2003). The properties of a “building block” nanomaterial are highly dependent upon the nanoparticles’ size, shape, and composition. However, it is the size dependence which allows nanoparticles to be engineered to have specific properties to serve various functions, including medical applications (Bruchez et al. 1999).

Particles in the nanometer size range can exhibit properties very different from macroscale bulk and even atomic scale materials. One of the most highly desirable properties of metal nanoparticles is increased catalytic activity (Iijima et al. 1986; Yacamán et al. 2001). Nanoscale silver materials are also extremely chemical durable (Toshikazu, T. 1999). This section describes the physical characteristics of metal nanoparticles and the bactericidal properties of nano-silver.

2.2.2.3.4. Carbon Nanotubes

The carbon nanotubes (CNT), discovered by Iijima have many interesting properties such as high mechanical strength, and a remarkable crystalline structure. These attributes make CNT suitable for wide range of potential uses. Carbon nanotubes
occur in two distinct forms, single-walled nanotubes (SWNT), which are composed of a graphene sheet rolled into a cylinder (Figure 2.3) and multi-walled nanotubes (MWNT), which consist of multiple concentric graphene cylinders. Compared with multiwalled nanotubes (Okamoto et al. 2001), single-walled nanotubes are expensive and difficult to obtain and clean, but they have been of great interest owing to their expected novel electronic, mechanical, and gas adsorption properties.

Figure 2.3. Single layered and multiwalled Carbon nanotube

Carbon nanotubes based materials have inspired scientists for a range of potential applications. The use of carbon nanotubes in polymer/carbon nanotubes composites has attracted wide attention. The carbon nanotubes have unique atomic structure, very high aspect ratio, and extraordinary mechanical properties (strength and flexibility). These properties make them ideal reinforcing fibers in nanocomposites. “Carbon nanotubes reinforced composites have been investigated for flame-retardant performance, improved electrical conductivity (Wong et al. 2003) and electrostatic charging behavior, optical emitting devices, and in lightweight, high strength composites”.

2.2.2.3.5. Graphite

While most nanocomposite researches have focused on exfoliated clay platelets, the same concept can be applied to another layered material, graphite, to produce nano platelets and nanocomposites. Graphite is the stiffest material found in nature (Young’s Modulus of 1060 MPa), having a modulus several times that of clay, and also has excellent strength and electrical and thermal conductivity. The key to
utilizing graphite as platelet nano reinforcement is in the ability to exfoliate Graphite Intercalated Compounds [GICs]. Since the late 1990’s, some research groups reported graphite nanocomposite systems using intercalated, expanded, or exfoliated graphite flakes in polymers such as nylon6, polystyrene, PP, and polyisoprene (Chen et al. 2003). If the appropriate surface treatment can be found for graphite nanoflakes, its exfoliation and dispersion in a polymer matrix will result in a composite with not only excellent mechanical properties but electrical and thermal properties as well, opening up many new structural applications as well as non-structural ones where electromagnetic shielding and high thermal conductivity are requirements.

2.2.2.3.6. Ceramic nanofiber

The term ceramic fiber refers to products made of refractory materials used in the ceramic industry. Ceramic fibers are made of metal oxides, metal carbides, metal nitrides and mixture thereof. Example of material used for ceramic fibers are aluminum silicate, alumina, zirconium, boron nitride, silicon nitride thoria, magnesia, hafnia, beryllia, titanium oxide etc. Ceramic fibers are distinguished from glass in that the amount of sodium, lithium or potassium in the product is limited to less than 2%. These fibers have one distinguish advantage over glass fibers, that they possess better thermal resistance, expressed as high heat insulating property and higher melting point (Susan et al. 2003).

Polymer nanocomposites combine the concept of composites and nanometer size materials. In the conventional composites (thermoplastic or thermoset), the filler may enhance one property while compromising on others. In contrast to the conventional systems where the reinforcement is on the order of microns, discrete constituents of the order of a few nanometers exemplify polymer nanocomposites (Wypych G. 2003). This empowers us to tailor revolutionary material combinations. These new materials circumvent classic material performance trade-offs by accessing new properties and exploiting unique synergism between materials. This only occurs when the length-scale of morphology and the fundamental physics associated with a property coincide on the nanoscale. Size does matter and the physics, which dominates the processes at the nanometer length scale, has qualitative differences from the physics that dominates our macroscopic world.
Uniform dispersion of these nanoscopically sized filler particles produces ultra-large interfacial area per unit volume between the nanofiller and host polymer. This immense internal interfacial area and the nanoscopic dimensions fundamentally differentiate polymer nanocomposites from traditional composites and filled thermoplastics. Considering the number of potential nano-sized materials, polymeric resins, and applications, the field of polymer nanocomposites is immense. Development of multicomponent materials, whether microscale or nanoscale, must simultaneously balance four interdependent areas: constituent-selection, fabrication, processing, and performance. This is still in its infancy for polymer nanocomposites. Developing an understanding of the characteristics of this interphase region, its dependence on nanoelement surface chemistry, the relative arrangement of constituents and, ultimately, its relationship to the properties, is a current research frontier in nanocomposites. Equally important is the development of a general understanding of the morphology-property relationships for mechanical, barrier, and thermal response of these systems.

2.3. Advantages of Nanocomposites over Conventional Composites

Some of the major advantages that nanocomposites offer over traditional polymeric composites are

- Dramatic improvements in mechanical properties like tensile and flexural modulus, strength, elongation and toughness at much lower concentrations of the additive.
- Greater thermal stability and higher HDT.
- Excellent fire retardant characteristics.
- Considerable improvement in barrier properties due to the tortuous path created by the flaky fillers when dispersed in the polymer matrix.
- Very good transparency because of the length scale involved that decreases scattering.
- Relatively better biodegradation.
- Good scratch resistance.
- Easier processing due to avoidance of cumbersome fabrication techniques and filler loading levels.
In recent years polymer/clay or polymer/layered-silicate nanocomposite materials (Giannelis et al. 1999; Theng B. K. G., 1979) have aspired efforts to disperse clay-based fillers in almost any polymer available, usually expecting that complete exfoliation of the inorganic fillers in the polymer would yield the best performing systems. Although it has been long known that polymers can be mixed with appropriately modified clay minerals and synthetic clays (Theng B. K. G. 1974), the field of polymer/clay nanocomposites has gained a large momentum recently. Two were the major findings that pioneered the revival of these materials.

2.4. Bionanocomposites

Attempts to improve the properties of materials through the addition of reinforcing fillers, either inorganic or organic, are not new. For years, synthetic polymer composites have been developed and applied in various industrial fields, domestic equipment, the automotive industry, and even in aerospace. However, these synthetic materials come from limited, non-renewable sources, and are not easily decomposed (Lu et al. 2009; Tokiwa et al. 2009) by microorganism present in nature. In addition, global warming, caused in part by carbon dioxide released by the combustion of fossil fuels, has become an increasingly important problem and the disposal of items made of petroleum based plastics such as fast food utensils, packaging containers, and carrier bags also creates a serious environmental problem (Wool and Sun, 2005). As we begin the 21st century, there is an increased awareness that non renewable resources becoming scarce and dependence on renewable resources is growing (Rowell et al. 2008). A growing environmental awareness all over the world and the pressures to use evermore “greener” technologies (Bismarck et al. 2008) have encouraged researchers and industrialists to consider natural plant fibers as an alternative reinforcing agent or filler to produce composite materials known as biobased composites (Thakur et al. 2010). Natural fiber composites are also claimed to offer environmental advantages such as reduced dependence on non-renewable energy/material sources, lower pollutant emissions, lower greenhouse gas emissions, enhanced energy recovery etc. (Joshi et al. 2004) There are various types of the natural fibers and are classed according to their source; plants, animals or minerals. In general, it is the plant fibers that are used to reinforce plastics in the composite
industry. A detailed list of commercially available natural fibers (Eichhorn et al. 2001) is given in the table 2.3.

**Table 2.3.** Commercially important fiber sources

<table>
<thead>
<tr>
<th>Fiber source</th>
<th>Species</th>
<th>World production (10³)</th>
<th>Origin</th>
</tr>
</thead>
<tbody>
<tr>
<td>Wood</td>
<td>(&gt;10,000 species)</td>
<td>1,750,000</td>
<td>Stem</td>
</tr>
<tr>
<td>Bamboo</td>
<td>(&gt;1250 species)</td>
<td>10,000</td>
<td>Stem</td>
</tr>
<tr>
<td>Cotton lint</td>
<td>Gossypium sp.</td>
<td>18,450</td>
<td>Fruit</td>
</tr>
<tr>
<td>Jute</td>
<td>Corchorus sp.</td>
<td>2,300</td>
<td>Stem</td>
</tr>
<tr>
<td>Kenaf</td>
<td>Hibiscus cannabinus</td>
<td>970</td>
<td>Stem</td>
</tr>
<tr>
<td>Flax</td>
<td>Linum usitatissimum</td>
<td>830</td>
<td>Stem</td>
</tr>
<tr>
<td>Sisal</td>
<td>Agave sisilana</td>
<td>378</td>
<td>Leaf</td>
</tr>
<tr>
<td>Roselle</td>
<td>Hibiscus sabdariffa</td>
<td>250</td>
<td>Stem</td>
</tr>
<tr>
<td>Hemp</td>
<td>Cannabis sativa</td>
<td>214</td>
<td>Stem</td>
</tr>
<tr>
<td>Coir</td>
<td>Cocos nucifera</td>
<td>100</td>
<td>Fruit</td>
</tr>
<tr>
<td>Ramie</td>
<td>Boehmeria nivea</td>
<td>100</td>
<td>Stem</td>
</tr>
<tr>
<td>Abaca</td>
<td>Musa textiles</td>
<td>70</td>
<td>Leaf</td>
</tr>
<tr>
<td>Sunn hemp</td>
<td>Corolaria juncea</td>
<td>70</td>
<td>Stem</td>
</tr>
</tbody>
</table>

By far the most abundant are the wood fibers (Siqueira et al. 2010) from trees (see table 2.3), however other fiber types are emergent in use. A common choice for reinforcement of biobased composites is cellulose. The cellulose fiber family, including kenaf, flax, ramie, hemp and jute has been widely used as a composite.
reinforcement for its outstanding properties including good mechanical and thermal stability, non-abrasiveness and biocompatibility (Geyer et al., 1994; Bullions et al., 2006). However, because of their hydrophilic nature, these fibers make imperfect bonds with the polymer matrix, which is generally of hydrophobic nature. Various ways of improving the interface to overcome this problem have been used, such as by the addition of surfactants or compatibilising agents, and by grafting a matrix-compatible polymer onto the fiber surface (Escamilla et al., 1999; Viet et al., 2007). Recently an cellulose composite has also been introduced by Nishino et al., (2007). It is well known that cellulose fiber networks as in the case of paper provides good mechanical properties because of the degree of hydrogen bonding obtained between the fibers in the network. The greater the hydrogen bonding, the stronger the composite material and nature of hydrogen bonding depends on the size of the cellulose fibers or whiskers.

![Figure 2.4. Comparision of hydrogen bonded cellulose network in nano-size (A) and micro-size (B).](image)

Renewable biomaterials offer a broad range of commodities, including forests, crops, and farm and marine animals; all of which have many uses. The idea of using plant-based fiber as reinforcement has been around since the beginning of human civilization. The use of straw reinforced clay for making stronger bricks is one of the earliest composites referred to in the literature. Plenty of examples can be found of plant-based fibers being used for reinforcement of petrobased thermoplastic polymers such as polypropylene (PP), polyethylene (PE), nylon and polyvinylchloride (PVC). Plant fibers have also been used to reinforce biodegradable polymers such as cellulose
ester, polyhydroxybutyrate (PHB), polyester amide, polylactic acid (PLA) and starch derivatives and blends (Peijs et al. 2005).

2.5. Synthetic methods used for preparation of nanomaterials

Basically nanomaterials are prepared by approaches like bottom up and top down:

![Figure 2.5. Different methods used for preparation of nanomaterials](image)
2.5.1. Top-Down Approach:

In this approach nanomaterials are derived from bulk substrate by removing material from it, till the desired sized nanomaterials is achieved. It can be chemical, mechanical or chemo-mechanical process. It is a simple and easy method for preparing nanomaterials. Top-Down approach consists of various methods like:

1. High energy ball milling
2. Lithography
3. Laser ablation
4. Gas-phase condensation
5. Aerosol Spray

The biggest problem with the top-down approach is the imperfection of surface structure.

2.5.2. Bottom-Up Approach

Bottom-Up approach builds up of a material from the bottom i.e atom-by-atom, molecule-by-molecule, or cluster-by-cluster. This approach has a potential of creating less waste and is more economical. Bottom-Up approach consists of various methods like:

1. Sol-gel
2. Colloidal precipitation
3. Electrodeposition
4. Hydrothermal synthesis
5. Gas-phase agglomeration

Many of these techniques are still underdevelopment or are just beginning to be used for commercial production of nanopowders.

In the present work, we had used chemo-mechanical process (Top-Down approach) for preparation of cellulose nanofibers and nano-whiskers.
2.6. Preparation of Polymer Nanocomposites

Preparation of polymer nanocomposites was accomplished either by melt blending process, via solution or by in situ polymerization.

2.6.1. In-Situ Polymerization

In-situ polymerization was the first method used to synthesize nanocomposites. Nowadays, it is the conventional process used to synthesize thermoset nanocomposites. For thermosets such as epoxies or unsaturated polyesters, a curing agent or peroxide, respectively, is added to initiate the polymerization. For thermoplastics, the polymerization can be initiated either by the addition of a curing agent or by an increase of temperature (Messersmith et al. 1995).

2.6.2. Solution Method

Polar solvents can be used to synthesize polymer nanocomposites. The nano-particles is first dispersed in the solvent. Then, the polymer, dissolved in the solvent, is added to the solution. The last step consists in removing the solvent by evaporation usually under vacuum. Nanocomposites based on high-density polyethylene (Jeon et al. 1998), polyimide (Yano et al. 1993) and nematic liquid crystal polymers (Kawasumi et al. 1998) have been synthesized by this method. The driving force for polymer intercalation from solution is the entropy gained by desorption of solvent molecules, which compensates for the decrease in conformational entropy of the intercalated polymer chains (Theng, B. K. G. 1979). The major advantage of this method is that it offers the possibilities to synthesize nanocomposites based on polymers with low or even no polarity. Nevertheless this technique leads to poor dispersion, besides it is applicable only to polymers that are soluble into common solvents. More, since a large amount of solvent needs to be used to achieve appreciable filler dispersion, and the same quantity of solvent has to be removed after mixing, this method results to be long and tedious, then suitable only for laboratory applications.

2.6.3. Melt Intercalation

The melt intercalation process was first reported by Vaia (Vaia et al 1993) consists of blending a molten thermoplastic with an nanoparticle in order to optimize the
polymer-nanomaterial interactions. The mixture is then annealed at a temperature above the glass transition temperature of the polymer and forms a nanocomposite. The polymer chains experience a dramatic loss of conformational entropy during the mixing. The proposed driving force for this mechanism is the important enthalpic contribution of polymer/nano interactions during the blending and annealing steps.

The melt intercalation process has become increasingly popular because of its great potential for application in industry. The melt intercalation is more flexible than the previous two routes thanks to the absence of solvents and chemical reaction; besides it’s testing with nylon-6 (Liu et al. 1999), polysiloxane and even polystyrene (Vaia et al. 1996) yielded noteworthy results. On the other hand, when non-polar matrices (Burnside et al. 1995) like Polypropylene are involved a third component, such as MAgPP, has to be added to the polymer/nanocomposite system, even though the nanomaterial was already organically modified. The aim of this new constituent is to improve the matrix filler interactions by reducing the interfacial tension between them.

2.7. Applications of Nanocomposites

Mechanical property improvements have resulted in major interest in nanocomposite materials in numerous automotive and general/industrial applications. These include potential for utilization as mirror housings on various types of vehicles, door handles, engine covers and intake manifolds and timing belt covers. More general applications currently being considered include usage as impellers and blades for vacuum cleaners, power tool housings, mower hoods and covers for portable electronic equipment such as mobile phones, pagers etc.

2.7.1. Gas Barriers

The gas barrier property shows substantial improvement from incorporation of relatively small quantities of nanomaterials. The oxygen transmission rates for polymer nanocomposites, are usually less than half that of the unmodified polymer. Further the extent to which both the amount of nano incorporated in the polymer, and the aspect ratio of the filler contributes to overall barrier performance. In particular, aspect ratio is shown to have a major effect, high ratios (and hence tendencies towards
filler incorporation at the nano-level) quite dramatically enhances the gaseous barrier properties. Such excellent barrier characteristics have resulted in considerable interest in nanocomposites in food packaging applications, both flexible and rigid. Specific examples include packaging for processed meats, cheese, confectionery, cereals and boil-in-the-bag foods, also extrusion-coating applications in association with paperboard for fruit juice and dairy products, together with co-extrusion processes for the manufacture of beer and carbonated drinks bottles.

2.7.2. Oxygen barriers

Passive barrier characteristics are provided by nanoparticles incorporated via melt processing techniques whilst the active contribution comes from an oxygen-scavenging ingredient. Oxygen transmission results reveal substantial benefits provided by nano incorporation in comparison to the base polymer (rates approximately 15-20% of the bulk polymer value, with further benefits provided by the combined active/passive system). The increased tortuosity provided by the nanoparticles essentially slows transmission of oxygen through the composite and drives molecules to the active scavenging species resulting in near zero oxygen transmission for a considerable period of time.

2.7.3. Food packaging

Nanocomposites are currently showing considerable promise for this application. It is likely that excellent gaseous barrier properties exhibited by nanocomposite polymer systems will result in their substantial use as packaging materials in future years.

2.7.4. Fuel Tanks

The ability of polymer nanocomposites to reduce solvent transmission through polymers has been demonstrated. Considerable interest is now being shown in these materials as both fuel tank and fuel line components for cars.

2.7.5. Films

The presence of filler incorporation at nano-levels has also been shown to have significant effects on the transparency and haze characteristics of films. In comparison
to conventionally filled polymers, nanoparticle incorporation has been shown to significantly enhance transparency and reduce haze. With polymers, this effect has been shown to be due to modifications in the crystallization behavior brought about by the nanoparticles; spherilitic domain dimensions being considerably smaller. Similarly, nano-modified polymers have been shown, when employed to coat polymeric transparency materials, to enhance both toughness and hardness of these materials without interfering with light transmission characteristics.

2.7.6. Environmental Protection

Water laden atmospheres have long been regarded as one of the most damaging environments, which polymeric materials can encounter. Thus an ability to minimize the extent to which water is absorbed can be a major advantage. Specifically, increasing aspect ratio was found to diminish substantially the amount of water absorbed, thus indicating the beneficial effects likely from nanoparticle incorporation in comparison to conventional microparticle loading.

2.7.7. Flammability reduction

The ability of nano incorporation to reduce the flammability of polymeric materials was presented by Gilman of the National Institute of Standards and Technology in the US. Gilman demonstrated the extent to which flammability behavior could be restricted in polymers such as polypropylene with as little as 2% nanoclay loading. In particular heat release rates, as obtained from cone calorimetry experiments, were found to diminish substantially by nano incorporation. With the nanoparticle approach, this is usually achieved whilst maintaining or enhancing other properties and characteristics.

2.7.8. Antimicrobial based application

A number of healthcare and consumer products already take advantage of the antibacterial property of nano-silver. Recent research has confirmed the bactericidal effect of silver-impregnated materials, as well as open corridors for new and improved antimicrobial medical and consumer products.
The potential exists for the manufacture of several polymer/nano-silver composite materials for medical applications, including antibacterial wound dressings and bandages, catheters, and implantable hip and joint replacements that inhibit postsurgical bacterial infections. The development of new technologies for coating materials with films of silver nanoparticles could also be beneficial in the food processing industry where pipelines are susceptible to biofilm formation. Silver-impregnated polymers and silver-coated glass both have potential as antimicrobial food packaging materials.

2.8. Cellulose

Cellulose is a renewable, biodegradable and most abundant biopolymer available in the biosphere (Lee et al. 2009) and is produced in nature at an annual rate of $10^{11}-10^{12}$ tons (Zhao et al. 2007). Cellulose is the main constituent of the plants serving to maintain their structure. It is also found in bacterial, fungi, algae and even animals (Samir, et al. 2005). The properties of cellulose like good tensile strength, low density, biodegradability etc. leads to rising research interest. Cellulose is the structural material of the fibrous cells with high level of strength and stiffness per unit weight and has a straight carbohydrate polymer chain consisting of β-1-4 glucopyranose units and a degree of polymerization of about 10,000 (Kamel S. 2007). The molecules aggregate and are present in the form of microfibrils. The hydroxyl (−OH) groups in the cellulose structure play a major role in governing the reactivity and physical property of the cellulose.

Natural Cellulosic fibers are synthesized mainly in plants and cellulose constitutes 40-50% of wood, 80% of flax and 90% of cotton fiber. In recent years, many researchers and manufacturers use natural fibers to replace man-made fibers as reinforcement material and fillers to make environmentally safe products because they have many advantages. Cellulose fibers can be mechanically disintegrated to the structural nanoscale fibrils (Ahola, et al. 2008). The word fibril has been described by various researchers to describe relatively long and very thin pieces of cellulosic material. Microfibrils are defined as the fibers of cellulose of 0.1-1μm in diameter (Chakraborty et al 2005), with corresponding minimum length of 5-50 μm and nanofibrils are at least one dimension in nanometer scale (1-100 nm).
Cellulose is a water insoluble polysaccharide (Klemm et al. 2005). In all native celluloses, the molecules are found in fibril form, with the microfibril highlighted as a primary constituent of the supramolecular structure. Within the microfibrils, the cellulose chains are organized as stacked sheets separated into molecular layers that have interchain hydrogen bonds connecting neighboring chains together in the X-Y direction (Nishiyama et al. 2010). Refer Figure 2.6. These positions of atoms of the unit cell of cellulose were determined using a combination of synchrotron X-ray and neutron diffraction (Nishiyama et al. 2002, 2003b). Furthermore, computational studies (Qian et al. 2005) have provided justification of the molecular spacing of the unit cell with dimensions of a 7.784 Å, b 8.201 Å, c 10.380 Å (Nishiyama et al. 2002), and give insight into the bonding differences within the cellulose superstructure; intersheet bonding is approximately eight times weaker than in-plane intrasheet bonding (Qian et al. 2005).

**Figure 2.6. Structure of cellulose fiber**

Advantages of the cellulose over synthetic materials are as follows,

- Low density
- Renewable resources
- Biodegradability
- Non-food agricultural based economy
- Low energy consuming per unit product
- Low abrasivity
- Greater longevity of the process equipment
- Reduced carbon dioxide emissions in the environment
Polymer Composites Based on Cellulosics Nanomaterials

Chapter 2

- High specific strength and modulus
- High sound attenuation of lignocelluloses based composites
- Relatively reactive surfaces which can be used for grafting

2.8.1. Nano-Cellulose

Recently, active research on the isolation of cellulose micro-fibrils from the plants has been undergoing to use them as a reinforced material in the nanocomposites (Azizi-Samir et al. 2004, Azizi-Samir et al. 2004, Takagi et al. 2008, and Yang et al. 2007). The potential of cellulose nanofibrils as reinforcement provides a new direction for the development of value-added novel composites. These cellulose nanofibrils have been extracted from cell walls by a chemical (Bondeson et al. 2006) or mechanical treatment (Nakagaito et al. 2004, Dufrene et al. 2000) and combination of those treatments.

Cellulosic materials intended for use as nano-fillers in composites are usually subjected to hydrolysis by strong acids such as sulfuric or hydrochloric acid, which causes a selective degradation of amorphous regions of cellulose and, consequently, the splitting of micro-fibril beams. As a result of cellulose hydrolysis, the disintegration of its hierarchical structure takes place to form crystalline nanofibres or nanocrystals, usually referred to in literature as nanowhiskers. The morphology of the nanocrystals obtained depends on the source of cellulose and hydrolysis conditions used, such as acid concentration, the ratio of acid to cellulose, temperature and reaction time (Mirosława et al. 2000).

Before considering different possible methods by which it is possible isolate cellulosic nanostructures understanding some of the basic definitions are very essential. Many researchers (Hubbe et al. 2008, Favier et al. 1995a and b, Durfense et al. 2000, Americaen Forest product association, 2005, Oksman and Sain 2006, Marcovich et al. 2006, Wu et al. 2007, Abe et al. 2007, Cheng et al. 2007 ) have been described the word fibril as relatively long and very thin pieces of cellulose. Even paper manufacturers uses the term fibril to denote thin cellulosic strands that remain attached on the outer surface of the fiber after refined pulp. Therefore to avoid this confusion the word nanofiber has come in to use (Bhatnagar and Sain 2005, Chkraborthy et al. 2006a and b, Dalmas et al. 2006, Klemm et al. 2006; Abe et al.
In general nanofibers are the elementary assemblies of the distinct units that can have diameter on 10 nm and constitute fiber or strand network. Due to its unique structural and physical aspects it has got unique tensile, optical, electrical and chemical properties. Very long and straight crystals of cellulose are called as whiskers (Favier et al. 1995a, b, Hajji et al. 1996, Dufresne 2000, Ruiz et al. 2000; Schroers et al. 2004; Kvien et al. 2005; Ljungberg et al. 2005; Hamad 2006). The dimensions of the crystals are in the range of 8-20 nm thickness and length sometimes more than 1 µm (Terech et al. 1999).

2.8.2. Methods for preparing nano-cellulose:

1. Refining
2. Homogenization
3. Acid hydrolysis
4. Microbial
5. Enzymatic

2.8.1.1. Refining Process

Refining is a process of isolation of micro or nano fibrils from the pulp fibers by mechanical action. Figure 2.7 shows the actual photo of refiner. Figure 2.8 shows the schematic representation of the Lab disc which consist two discs having number of ridges on the surface. Out of two discs one is stationary and other one is rotating disc which is driven by a three phase electrical motor. Stationary disc is called as stator, whereas, the rotating disc is called as rotor. (See Figure 2.9) Distance between the stationary and rotating disc was maintained at 5 thou (1 thou = 1/8 cm) and the rotating disc was operated at 1440 rpm. The pulp slurry comes in between these discs where combination of frictional, shear and compression force acts on the fiber. This results into fibrillation (separation) of cotton fibers.

The extent of fibrillation depends on the size of the bar; as finer size results into better fibrillation. There are various interactions taking place during the refining process. Initially, the bunch of fibers gets picked in between the stator and rotor followed by
edge to edge, edge to surface, surface to surface interactions and then end of refining. This results into isolation of microfibrils or nanofibrils from the cotton fibers. In here, the extent of fibrillation depends on the distance between the stator and rotor. Lesser the distance more efficient will be the fibrillation. But, if the distance is too small, chances of blockage are more. So, to avoid this, initially fibrillation should be done at larger distance of stator and rotor. And, further fibrillation can be carried out by reducing the distance between them.

Figure 2.7 is the view of disc refiner in open condition. From the figure 2.9, it can be clearly seen that, at centre the size of the bar is more and gradually decreases as we move towards the periphery. Due to the centripetal force, the pulp slurry moves from centre to periphery. As the slurry moves towards the periphery of the disc, it gets more and more sheared by the action between the bars, leading to better and uniform fibrillation. Schematic representation of the Lab-Disc Refiner and geometry of the stator and rotor (A)-Inside geometry of the bar (B)-Inside view has been depicted in figures 2.8 and 2.9 respectively.

Figure 2.10 and 2.11 represents the mechanism of action and different types of forces which act during the refining process respectively. This forces acts when the fibers are in between the stator and rotor in various contact modes as:

Edge to edge – compression force
Edge to surface – bending force
Surface to surface – tension and shearing

Figure 2.7. Photograph of the Lab-Disc Refiner
Figure 2.8. Schematic representation of the Lab-Disc Refiner

Figure 2.9. Geometry of the stator and rotor (A)-Inside geometry of the bar (B)-Inside view
Figure 2.10. Actions of refining during fibrillation process

Figure 2.11. Different forces which acts during the refining process
1.8.1.2. Homogenization Process

Product fluid is pumped through the inlet fitting into the nozzle by a high pressure pump. The nozzle has a small orifice that comes in variety of sizes that range from 0.1 to 0.25 mm. forcing the fluid the orifice of the nozzle at high pressure produces a high velocity jet This constitutes first step in the size reduction process. Exiting the nozzle is a high velocity jet of product, which enters the absorption cell (Figure 2.13.) completes the mixing process, producing a thoroughly homogenized product. The geometry of the absorption cell is designed to create a second high- velocity stream, which flows in the opposite direction and around the original fluid jet from the nozzle. (Figure 2.14.) The interaction between these two streams produces a combination of high velocity, shear, cavitation and impact forces, which completely break apart the particles in the fluids.

Figure 2.12. Set-up of the high pressure homogenizer used during
2.8.1.3. Acid Hydrolysis Process

In this process nanocellulose is produced by hydrolysis using hydrochloric acid or sulphuric acid. Acids led to the dissolution of the amorphous regions present in cellulose fibers, forming micro-crystalline cellulose. This, on further hydrolysis gets converted into nano-cellulose.
2.8.1.4. Microbial Process

In this process, nano-cellulose is obtained by hydrolysis using microbial agents like Cal-dicellulosiruptor, Fibrobacter succino-genes, Cytophaga hutchinsoniii etc.

2.8.1.5. Enzymatic Process

In this process, hydrolysis of fibers is carried out in the presence of enzymes like cellulase. This results in nano-cellulose.

2.9. Synthesis and Applications of Nanocellulose

Cellulose based nanocomposites are largely used due to their potentially high stiffness, required for reinforcement. This property can be achieved with the reducing amount of amorphous material by breaking the structure of the plant in individualized nano-fibers with high crystallinity. Cellulose nano-fibers and the composite materials reinforced with this kind of fillers have found many potential applications in important fields like electronic and electrical industry (Hubbe et al. 2008), constructions, biomedicine and cosmetics (Dong et al. 2007; Hoenich et al. 2006; Ivanov 2007; Hou et al. 2008) paper industry (Marques et al. 2007), packaging(Fama et al. 2009), building materials (Wegner et al. 2005), textile industry (Fijan et al. 2009) and others (Kamel, 2007). The fact that almost any cellulose material could be considered as a potential source for isolation nano-cellulose structures represents another important advantage in using cellulose elements as reinforcing phase in polymeric matrix composites.

Frone et al. investigated the aspects regarding the isolation of cellulose micro- and nano- fibers. They performed the acid hydrolysis of micro-crystalline cellulose at varying time durations of 150 and 300 min. Long duration (300 min) acid hydrolyzed microcrystalline cellulose were found to have smaller diameters and higher aspect ratio. Lee et al. prepared cellulose nanofibrils from microcrystalline cellulose by using high pressure homogenizer at 20,000 psi. They passed the microcrystalline cellulose through the homogenizer for 20 times and investigated the size of the cellulose nanofibrils obtained. The obtained nanofibrils were used as reinforcing agent in hydroxypropyl cellulose. They found that, 5–10 times homogenized microcrystalline cellulose gave an optimized improvement in the mechanical properties of the
composite. (Cellulose nanofibrils by high pressure homogenizer) Li et al. isolated nano-sized cellulose from never-dried wood pulp, in a sheet form. Thickness of the material was ten times smaller than the previously reported structures. This helped them in concluding that the intersheet

Chakraborty et al. obtained cellulose microfibrils using high shear refining and cryocrushing. They had soaked bleached northern black spruce pulp for overnight and disintegrated in fiber disintegrator for 15 mins. Subsequently most of the water was drained out to achieve desired concentration. This was then sheared thoroughly in a laboratory PFI refiner for up to 125000 revolutions. Though refiner produced high shear capable of forming individual microfibrils at the surface of the fiber bundles, this step was not suitable for effectively isolating microfibrils into individual entities separated from the walls of the thicker fibers. Therefore after the refining process, cryocrushing was done using high impact grinder in the presence of liquid nitrogen. The microfibrils prepared by above process were characterized using microscopy and found that most of the fibers were conveted into microfibrils having diameter distribution as 11% above 1 µm, 71% in the range of 0.1-1 µm and 18% below 0.1µm (Chakraborthy et al. 2005).

Qingqing et al. have worked on molecularly thin Nanoparticles from cellulose. They had isolated nanostructes from from never dried cellulose wood pulp, in sheet form that had submicrofibrillar dimensions. They had used oxidation procedure developed by Saito and co-workers (Tsuguyuki et al. 2006) which was combined with extensive ultrasonication to liberate nanoscale cellulose nanofibrils. From the AFM characterization it was observed that the prepared cellulose nanofibrils had diameters ten folds smaller than the previous report. This work also provided indirect evidence in support of and is consistant with the hypothesis that the intersheet van der waals bonding of the cellulose fibril is significantly weaker than than the intersheet hydrogen bonding of the cellulose microfibril (Qingqing et al. 2009). Previously Johnson et al. also shown that the ultrasonication would yield as much as 98% nanocellulose after 20 mins of sonication converting bulk of the sample in to nanoscale cellulose.

Mehdi et al. had extraxted cellulose nanofibrils from kenaf core fibers by employing chemo-mechanical treatments. The prepared cellulose fibrils were characterized using
environmental electron microscopy and transmission electron microscopy. The results revealed that most of the fibers had diameter in the range of 10 to 75 nm. Thermogravimetric analysis shown that thermal stabilities of these fibers were increased by chemomachanical treatments (Mehdi et al. 2010).

Eyholzer et al. worked on preparation and characterization of water redispersible nanocellulose in powder form from refined bleached pulp by carboxymethylation and mechanical disintegration. The mechanical disintegration was carried using high shear homogenizer. It was that the chemical modification of the product reduced the crystallinity of the product significantly whereas in case of the product obtained after mechanical disintegration but without pretreatment, reduction in the crystallinity was insignificant. TGA experiments evidenced a dramatic decrease in thermal stability of the carboxylated samples as the onset temperature of the cellulose had dropped from 300°C to 200°C. Therefore this type of cellulose can be used in the composite where processing temperature in not more than 200°C. At the same time SEM and sedimentation results confirmed that carboxymethylation was essential to obtain water redispersible powders capable of forming stable suspensions.

Florent Dalmas et al. studied deformation mechanical behavior of flexible nanofibers filled nanocomposites. Cellulose nanofibrils were obtained from sugar beet pulp. The chemical treatment described by Dinand et al. 1996, was used. This treatment allows to obtain a final aqueous suspension of cellulose nanofibrils, which does not sediment or flocculate. The cellulose nanofibrils prepared using above methods were used as the reinforcing agent to prepare poly(styrene-co-butyl acrylate) nanocomposites. By studying two different types of nanofibers using different processing routes two main effects like the role of interactions existing at the contacts between the nanofibers and the influence of fiber entanglement were highlighted. Different assumptions were made and found consistent with the experimental results. High reinforcement effect was achieved for cellulose filled materials suggesting that the presence of a rigid cellulose nanofibrils network, liked by strong hydrogen bonds within the material. The formation of such a network is possible only above the nanofibril percolation threshold (which can be very low as suggested by the high nanofibrils aspect ratio) but is detectable by tensile test for cellulose content higher than 1.5 vol%. Beyond this filler content, the strength of the contacts between nanofibrils (and thus, the
rigidity of the nanofibril network) governs the compositemechanical behavior. Indeed, an important decrease of the composite ultimate strain is observed for high cellulose contents. This network is irreversibly damaged for low strain level, inducing a strong decrease in the composites mechanical properties after predeformation.

Iwamoto et al. had done nanofibrillation of pulp fibers for the processing of transparent nanocomposites. Pulp fibers were fibrillated uniformly into nano-sized fibers using a grinder with a specially designed set of grinding disks. To investigate the effect of the fibrillation through the grinder on the physical properties of the composites, dissolved pulp fibers were subjected to various passes through the grinder, and the resulting fibrillated pulp fibers were used to make fibrillated pulp fibers/acrylic resin composites. Scanning electron microscopy observations showed that above five passes, the structure of the fibrillated pulp fibers did not change significantly. The light transmittances of the composites were increased to 80% up to five passes through the grinder, and did not change after further passes. However, the tensile test and thermal expansion analysis indicated that a degradation of the fibrillated pulp occurred during the grinding treatment. To evaluate the fiber degradation, the degree of crystallinity and degree of polymerization of cellulose were measured. Both decreased as the number of passes through the grinder increased. In addition, to reduce the thermal expansion of composites, the fibrillated pulp fibers were additionally treated by sulfuric acid. The thermal expansion of composites was decreased, because the amorphous region of cellulose was removed.

Bittencourt et al. have done preliminary studies on the production of nanofibrils of Cellulose from never dried cotton using eco-friendly enzymatic hydrolysis and high energy sonication. In this study never dried cotton fibers were used as the starting material for producing nanofibrils as it has more accessible structure for the action of enzyme as compared to the dried cotton. Enzymatic hydrolysis was followed by high energy sonication for 20 to 50 mins resulting nanofibrils. TEM results shown that the above process produces nanostructures with 50 nm diameter.

Panthapulakkal et al. worked on preparation and characterization of cellulose nanofibrils films from wood fiber and their thermoplastic polycarbonate composites. Cellulose nanofibers were prepared from wood fibers by mechanical defibrillation and the diameter obtained was in the range of 1-100 nm. Nanofiber films were prepared
and characterized in terms of strength properties, crystallinity and thermal properties. Strength and modulus of the composites were 240 MPa and 11 GPa respectively. Nanocellulose-polycarbonate composite by incorporating nanofiber film in between the layers of the polycarbonate followed by compression moulding at 210°C and a pressure of 1MPa for 1 minute. Evaluation of the strength properties of the polycarbonate and its composites showed a trend that demonstrated an improvement in the tensile strength and modulus with nanofibre reinforcement. The modulus of the PC improves about 100% by incorporating about 18% of the nanofibres, and an increase of 30% is observed in the tensile strength for the composite with the same fibre content (Panthapulakkal et al. 2011).

Huda et al. had prepared wood fiber reinforced Poly(lactic acid) as well wood fiber reinforced composites and compared with each other. The mechanical, thermal and morphological properties of these composites were studied. It was observed that PLA/dood fiber composites had mechanical properties of sufficient magnitude to compare with conventional thermoplastic composite. Addition of wood fibers into PLA resulted significant improvement in the mechanical properties as compared with virgin polymer. 20% concentration of wood fibers in to PLA/wood fibers composites improved flexural strength by 19% and modulus by 115% whereas tensile strength and modulus improved by 5% and 77% respectively (Huda et al. 2005).

Marcovich et al. used nanocellulose modified with polyaniline as a reinforcement in polyurethane which can be used for shape memory applications. The modified nanocrystals were prepared by in situ polymerization method, growing polyaniline on the surface of the cellulose nanofibrils. These cellulose nanocrystals exhibits good mechanical as well as conductive properties. These nanocrystals were added into thermoplastic polyurethane composites showing shape memory properties. Electrical measurements were performed to understand the electrical performance of the conductive composite. effect of reinforcement on the final properties of the polyurethane composites were clearly observed (Marcovich et al. 2006).

Seydibeyolu et al. carried out fibrillation of cellulose fiber to convert it from microfibrils to nanoscale fibers and studied how these fibers affected thermoplastic polyurethane composites. The source of nanopcellulose and hard and the fibrillation was carried using high pressure homogenizer. The cellulose fiber mats were kept
between the layers of the polyretahen and the composite was prepatred using compression moulding at 200°C and a pressure of 100-200 bar for a compression time of 1-4 minutes. The results shown that polyurethane reinforced with microfibrils as well as nanofibrils had better heat stability. Addition of 16.5% of cellulose nanofibrils into polyurethane increased strength by 500% and the stiffness by 3000% compared with virgin polymer matrix. With these improvements, the use of polyurethane and many other polymers can be expanded (Seydibeyolu et al. 2008).

Karaaslan et al. prepared hemicelluloses and cellulose whiskers reinforced biocompatible hydrogels. The hemicelluloses were modified with 2-hydroxyethylmethacrylate prior to adsorption onto the cellulose whiskers in aqueous medium. Synthesis of the hydrogels was accomplished by in situ radical polymerization of the methacrylic groups of the adsorbed coating to form a network of poly(2-hydroxyethylmethacrylate) (PHEMA) matrix reinforced with cellulose whiskers. The mechanical, swelling and viscoelastic properties, of water-swollen hydrogels were investigated. Results indicated that the number of effective crosslinks between polymer chains and the average chain length between crosslinking points was significantly different from PHEMA hydrogels that had been crosslinked by a conventional chemical method, using a cross-linking agent. The resulting hydrogels had enhanced toughness, increased viscoelasticity, and improved recovery behavior. With respect to the mechanical and swelling properties, it can be hypothesized that these nanoreinforced PHEMA hydrogels have potential for use in load-bearing biomedical applications such as articular cartilage replacement (Karaaslan et al., 2011).

Ping et al., prepared nanocomposites of poly(lactic acid) reinforced with cellulose nanofibrils. Cellulose nanofibrils were prepared by chemo-mechanical process. The prepared nanofibrils were dispersed into organic solvent (N,N-Dimethylacetamide) and after this poly(lactic acid) was dissolved. The polyethylene glycol was added to as the compatibilizer to improve the interfacial interactions between hydrophobic poly(lactic acid) and hydrophilic cellulose nanofibrils. The composites were prepared by solution casting method and were characterized to evaluate the performance properties. The strength results indicated that by adding PEG to PLA and cellulose
nanofibrils matrix, the tensile strength and the elongation rate increased by 56.7% and 60% respectively compared with the composites prepared in the absence of compatibilizer. Improvement in the intermolecular interactions were confirmed from FTIR analysis. From the morphological study also it was evident that interace between the cellulose nanofibrils and poly(lactic acid) were effectively improved which is very important as far stress transfer behaviour is concerned (Ping Qu et al., 2010).

Marielle et al. prepared polyurethane based composites based on microcrystalline cellulose as the reinforcement. The resulting composites shown increased stain to failure alongwith increased strength and stiffness. The optimum properties of the composites were obtained at 5% concentration of cellulose. The average tensile strength of the composites was 257 MPa, compared with 39 MPa for the neat polyurethane (Marielle et al. 2007).

Wang et al., worked on polypropylene nanocomposites based on cellulose nanofibrils as an reinforcing agent. They mentioned that cellulose nanofibrils can be prepared by either physical treatment that high pressure homogenization, high shear refiner and chemical treatments like acid hydrolysis. In this they had prepared cellulose nanofibrils by from tregenreated cellulose fiber. The geometrical characteristics of the cellulose nanofibrils were studied using optical microsacope, scanning electron microscope and their crystalline structure was investigated using wide angle X-ray diffractometer. It was observed that tensile strength of the neat polymer increased with increasing concentration of cellulose nanofibers but elongation had decreased from 230% to 80% which means that the composites become much brittle as compared to control PP. SEM observations shown that large holes on the surface of the PP which is an indication of poor adhesion of the cellulose nanowhiskers with polypropylene matrix (Wang et al., 2006).

Massodi et al., prepared epoxy composites based on cellulose nanofibrils as the reinforcing agent. They had prepared cellulose nanofibers according toa procedure described by Saito and Isogai (2006) [Saito T, Isogai A Introduction of aldehyde groups on surfaces of native cellulose fibersby TEMPO-mediated oxidation. Colloids and Surfaces A: Physicochem. Eng. Aspects 2006. 289: 219-225]. The films of the cellulose were prepared usingmillipofre ultrafiltration apparatus with
polytetrafluoroethylene membranes. These films were used as the reinforcement for biobased epoxy resin. A bio-based epoxy was used to reinforce the CNF/Epoxy composites. The bio-based epoxy is an epoxy resin that is made from 37% bio-content obtained as co-products of other green industries including woodpulp and bio-fuels production. The composites were prepared by hand layup using the sheet type process. Swelling behavior of cellulose nanofibers in water as well as epoxy resin was studied. It was observed that swelling of the fibers affect the porosity and permeability of the fiber mats as it reduces pore size and decreases permeability thus swelling plays important role in mould filling simulations. Mechanical results obtained were compared with the fiber glass and carbon fibers reinforced and it was observed that cellulose nanofibers reinforced epoxy composites had drawback of lower strength and fatigue properties. The investigation performed shown that fracture behavior of the composite can be enhanced by introducing crack resistance mechanisms such as fiber bridging (Massodi et al., 2011)

Dongsheng et al., prepared cellulose nanowhiskers by acid hydrolysis process using 60% sulphuric acid for 2 hr for 55 °C and it was used as for preparing paper composite. Unidirectional reinforced nanocomposite paper was fabricated from cellulose nanowhiskers and wood pulp under an externally applied magnetic field. A magnetic field was applied in order to align the nanowhiskers in the pulp as it was being formed into a sheet of paper. ESEM micrographs demonstrated unidirectional alignment of the nanowhiskers in the all-cellulose composite paper. Comparing with control paper sheets made from wood pulp only, the storage modulus in the all-cellulose nanocomposites increased dramatically. The storage modulus along the direction perpendicular to the magnetic field was much stronger than that parallel to the magnetic field. This new nanocomposite, which contains preferentially oriented microstructures and has improved mechanical properties, demonstrates the possibility of expanding the functionality of paper products and constitutes a promising alternative to hydrocarbon based materials and fibers (Dongsheng et al., 2010).

Mathew et al., prepared starch nanocomposites based on cellulose nanowhiskers derived from tunicates. Nanocomposites materials were prepared using sorbital plasticized waxy maize starch matrix. In this had studded nanocellulose up to 25% concentration and studied their effect on mechanical deformation behavior of the
nanocellulose reinforced starch composites. The performance of the composites was explained on the basis of morphological and structural behavior (Dufresne et al., 2002). The nanocomposites exhibit good mechanical strength due to strong interactions between tunicate whiskers, plasticizer and starch. They mentioned that crystallinity of the composite decreased with increase in concentration of the filler due to resistance to chain rearrangement imposed by the whiskers. SEM morphology shown the even distribution of the whiskers and plasticizer in to the matrix which had resulted in improvement in the mechanical properties of the composites (Mathew et al., 2008).

Jihoon Lee et al., worked on improving the mechanical properties of the poly(cinyl alchol) by incorporating cellulose nanowhiskers as an reinforcement. PVA and cellulose nanowhiskers fibers were prepared by electrospinning process. After electrospinning, the fiber webs were carefully detached from the aluminum foil and metal drum for imaging and mechanical tests. To make it easy to peal off the electrospun fiber webs from the substrates, a thin film of poly(propy-lene) (PP) was attached to the aluminum foil and the metal drum before electrospinning. PP coating on the aluminum foil and metal drum had no significant effect on the electro-spinning process because the PP thin film will not be left on the metal drum surface but not came with the PVA nanofi-ber web. However, by using PP coated metal. the PVA based electrospun fiber webs were pealed off easily. They had observed that 15 wt% cellulose nanowhiskers loaded iso-tropic PVA electrospun fiber webs show 86% higher tensile and 105% higher modulus. Aligned PVA electrospun fiber webs with 15 wt% cellulose nanowhiskers show 95% higher tensile and 118% higher modulus (Jihoon Lee et al., 2012).

Even Medeiros et al., had worked on poly(vinyl alcohol) fibers reinforced with cellulose nanowhiskers by electrospinning process. It was observed that the reinforced composites had 2.4 fold increase in their mechanical properties by addition of only 6.6% cellulose nanofibrils without significant changes in elongation at break (Medeiros et al., 2008).

Nakagaito et al., studied the effect of morphological changes from pulp fibers to nanofibrillated cellulose on mechanical properties of the high strength plant fiber based composites. They fibrillated kraft pulp fibers and impregnated with phenilic
resin and compression moulded at pressure of 100 MPa to produce high strength cellulose nanocomposites. To evaluate how the degree of fibrillation of pulp fiber affects the mechanical properties of the final composites, kraft pulp subjected to various levels of refining and high pressure homogenization treatments was used as raw material with different phenolic resin contents. It was found that fibrillation solely of the surface of the fibers is not effective in improving composite strength, though there is a distinct point in the fibrillation stage at which an abrupt increase in the mechanical properties of composites occurs. In the range between 16 and 30 passes through refiner treatments, pulp fibers underwent a degree of fibrillation that resulted in a stepwise increment of mechanical properties, most strikingly in bending strength. This increase was attributed to the complete fibrillation of the bulk of the fibers. For additional high pressure homogenization-treated pulps, composite strength increased linearly against water retention values, which characterize the cellulose’s exposed surface area, and reached maximum value at 14 passes through the homogenizer (Nakagaito et al., 2004).

Rojas et al., prepared nanocomposites of cellulose nanowhiskers reinforced polystyrene by electrospinning process. The morphology of the microfibers was examined by using scanning and transmission electron microscopies. Surface porosity, unique ribbon-shapes, and the presence of twists along the fiber axis were observed in the composite microfibers. It was noticed that 10 and 20% solutions of PS dissolved in THF were easily electrospun, whereas the 30% solution was difficult to process because of the high viscosity of the solution, which caused material clogging at the spinneret’s tip. It was observed that there was significant improvement in the strength of the composite. They had mentioned that the manufactured nanocomposite fibers and respective nonwovens are of potential value given the highly porous structures they form and the large surface areas which are often required in high-performance applications (Rojas et al., 2009).

Sain et al., had prepared nanocellulose from hemp fibers by chemo-mechanical process and had diameter in the range of 50-100 nm. It was used as the reinforcing agent in biopolymers such as poly(lactic acid) and polyhydroxy butyrate. They had mentioned that cellulose has number of hydroxyl groups present it surface which try to attach with the another fibril by hydrogen bonds and hence reduces the interaction
with the matrix. Therefore it is essential to chemically modify the surface functionality of the cellulose nanofibrils. The cellulose nanofibers were incorporated in polymer by melt blending. The results showed that styrene maleic anhydride coated and ethylene acrylic acid coated fibers improves their potential to interact with both acidic and basic type of resins. TEM results shown that partial dispersion of the nanofibers in to the polymer matrix. In both PLA and PH, SMA coated nanofibers as a reinforcement enhanced mechanical properties over the systems containing uncoated nanofibers or virgin polymer. As per the theoretical calculations made in this article showed that the PLa has largest potential to improve the mechanical properties compared to the PHB system (Sain et al., 2007).

Francisco et al., used commercial refined wood pulp and nanocofibers were prepared by chemical treatment followed by mechanical disintegration. Nanocomposites of poly(vinyl acetate) latex adhesive were prepared by incorporation of varying concentrations of cellulose nanofibers. The resulting composites were analyzed using dynamic mechanical analysis. It was observed that presence of cellulose nanofibers had strong influence on the viscoelastic properties of the poly(vinyl acetate) latex. At any given concentration, the cellulose nanofibrs showed superior reinforcing potential especially glass transition as well as rubbery plateau of poly(vinyl acetate) and polyvinyl alcohol. The nanofibers obtained by mechanical disintegration process had more effect as compared to only chemically treated fibers (Francisco et al., 2007).

Henriksson et al. worked on cellulose nanopaper structures of high toughness. The wood pulp were subjected to pretreatment followed by mechanical disintegration into microfluidics homogenizer. The used wood nanofibrils to prepare porous cellulose nanopaper of remarkable high toughness. Nanopapers of different porosities with different molae masses were prepared by vacuum filtration. This nanopaper shown very high toughness in uniaxial tension and this is associated with a strain to failure as high as 10%. Despite a porosity of 28% for the toughest nanopaper, the Young’s modulus (13.2 GPa) and tensile strength (214 MPa) are remarkably high (Henriksson et al. 2008).

Teixeira et al. prepared cellulose nanofibrils reinforced thermoplastic cassava starch composites. Cellulose nanofibrils were directly extracted from the cassava bagasse. The cellulose nanofibrils were characterized by SEM and AFM and found to be
around 2–11 nm thick and 360–1700 nm long. These nanofibrils were used as reinforcement in a thermoplastic cassava starch matrix plasticized using either glycerol or a mixture of glycerol/sorbitol (1:1) as plasticizer. Nano-composite films were prepared by a melting process. The nanocomposite was characterized by DMA and tensile properties were found to be depend on the nature of the plasticizer used. The glycerol/sorbitol mixture hinders the stress transfer at the filler/matrix interface probably because of the transcristallization phenomenon of starch chains around the nanofibrils surface. These phenomena seem to be more favored when using the glycerol/sorbitol mixture than when using glycerol alone. The reinforcing effect of these nanofibrils in glycerol plasticized starch was limited, especially because of an additional plasticization phenomenon induced by sugars originating from starch hydrolysis during the acid extraction (Teixeira et al. 2009).

Azeredo et al. studied effect of nanocellulose alongwith plasticizer on properties properties of the composite. The composites were prepared by casting process. The optimization was done withrespect to tensile strength, Youngs modulus and glass transition temperature and water vapour permeability. Mechanical and barrier properties of chitosan films were improved by addition of cellulose nanofibers. A nanocomposite film with 15% cellulose nanofibers and plasticized with 18% glycerol was comparable to synthetic polymers in terms of strength and stiffness, but their elongation was poor, indicating that the film may be used only for applications that do not require a great flexibility and/or water vapor barrier (Azeredo et al.2010).

Danuta published review paper on Multifunctional Bacterial Cellulose/Chitosan Composite Materials for Medical Applications. They mentioned that modifying bacterial cellulose with chitosan during biosynthesis of results into composites which has numbers of valuable features such as good mechanical properties in wet state, high moisture keeping properties, bacteriostatic activity against Gram negative and Gram positive bacteria and bactericidal activity against Gram positive bacteria. This make modified bacterial cellulose an excellent material for medical applications (Danuta 2004).