Chapter 1

Introduction
1.1. General Aspects:

With the improvement of science and technology, the people of the modern civilized world are becoming more dependent on the advanced materials. In this regard, the chemist from all over the world has contributed a lot for the modernization of our society. One of such major gift that chemist has ever bestowed to the human society is the “polymer” or “polymeric materials” without which the world have been in a totally different position [1-7]. However, as the environmental and health effects of chemicals or chemical processes have started considering, therefore, there has been an expanding search for new materials with high performance at affordable cost in recent years [8-13]. With growing environmental and health awareness, there has been a significant focus within the scientific, industrial, and environmental communities on the use of eco-friendly materials, and subsequently the terms such as “renewable”, “recyclable”, “sustainable”, and “triggered bio-degradable” became buzzwords, to the scientific, industry and environmental community [14-20]. The development or selection of a material to meet the desired structural and design requirements calls for a compromise between conflicting objectives. This can be overcome by resorting to multi-objective optimization in material design and selection [21-26].

The development of sustainable materials has not only been a great encouraging factor for materials scientists, but also an important provider of opportunities to improve the living standard of people around the globe. This can also provide a potential for economic improvement based on these materials even though major thrust for their use has been driven by the needs of the industrialized countries [27-31]. For example, natural fibres such as jute, sisal, hemp, pineapple, etc., whose extraction is an important process that determines the properties of fibres, can generate rural jobs since those fibres have established their potential as reinforcing fillers in many polymers, and products based on these have found increasing use on a commercial scale in recent years. Another example for the generation of jobs by agro-based materials is provided by the use of rice husk, which constitutes more than 10% of a world rice production. These examples underline not only the development of new materials, but also possible generation of additional employment through the collection, transportation and development of new materials. It is reported that increasing use of renewable materials would create or secure employment in rural areas, the distribution of which would be agriculture, forestry, industry, etc.
The use of natural polymers was superseded in the 20th century as wide-range of synthetic polymers was developed based on raw materials from low cost petroleum [32, 33]. However, since 1990s, there is a simultaneous and growing interest in developing bio-based products and innovative process technologies that can reduce the dependence of fossil fuel and move to a sustainable materials basis. The main reasons for development of such material are stated below: [34]

(i) Growing awareness in declining the environmental impact of polymers or composites due to increased consciousness to eco-friendliness,
(ii) Dwindling petroleum resources, shrinking pressures for the dependence of petroleum products with increasing attention in exploiting the use of renewable materials; and
(iii) Accessibility of enriched information on the properties and morphologies of natural materials such as lignocellulosic fibres, through modern instruments at diverse levels, and hence better understanding of their structure-property relationships.

These factors have greatly increased the understanding and development of new materials termed as biocomposites.

Commodity polymer-based composite materials are now well established all over the world. Because of their high specific strength, modulus and long durability compared to conventional materials such as metals & alloys, these materials have found wide applications. However, the use of large volumes of polymer-based synthetic fibre composites in different sectors has led to disposal problems. Therefore, researchers have been looking for the reduction of such environmentally abusive materials, and triggering greater efforts to find materials based on natural resources in view of the latter’s eco-friendly attributes. In parallel, researchers have also focussed their works on the processing of nanocomposites (materials with nanosized reinforcement) to enhance mechanical properties. Similar to traditional microcomposites, nanocomposites use a matrix where the nanosized reinforcement elements are dispersed. The reinforcement is currently considered as a nanoparticle when at least one of its dimensions is lower than 100 nm. This particular feature provides nanocomposites unique and outstanding properties never found in conventional composites. Bio-based nanocomposites are the next generation of materials for the future [35-41].
1.2. Bio-based Polymers:

Modern scenario of the polymer market is mostly occupied by synthetic polymers and most of these polymers are non-degradable. The non-degradable nature of polymer causes disturbance in the earth ecosystem. Besides this, the earth has finite resources in terms of fossil origin fuel. The escalating increase of price of petroleum based products and alternative disposal method are also a great concern. Hence, the use of fossil-based products is not sustainable. So, there is an urgent need to overcome the dependence on such conventional polymers by using bio-degradable polymers and composites. In order to produce fully renewable and biodegradable composites, both the polymeric matrix and the reinforcement must be derived from renewable natural resources such as agricultural and biological origin. Also, the use of natural polymers, which are normally biodegradable, can pave new direction in designing of newer greener composites and could widen the spectrum of applications in different sectors such as automobiles, furniture, packing and construction industrial parts.

1.2.1. Bio-based matrix:

“Bio” is a Greek word that means “life”. Bio-based materials, therefore, refer to products that consist mainly of a substance, or substances, derived from living matter (biomass) and either occurs naturally or are synthesized. The term “bio-based materials” should not be confused with “biomaterials,” which has another meaning and relates to biocompatible materials used in and adapted to medical applications, which include implantable medical devices, tissue engineering, and drug delivery systems [42]. The range of bio-based materials, from natural fibres to biopolymers, is making significant advances in petroleum-based materials industries [43]. Renewable resource-based chemicals and bio-based polymers, such as starch, 1, 3-propanediol, soy, polyl, polylactic acids, and so on, are gaining momentum in commercialization as supplements and possible replacements for petroleum based products. For decades, cellulosic polymers have played a key role in a wide range of applications, such as apparel, food, and varnishes etc. Since 1980s, an increasing number of starch polymers have been introduced, which have made them one of the most important groups of commercially available bio-based materials.

Bio-based materials, are commonly thought to be greener alternatives than their petroleum-based counterparts, which are nonbiodegradable, have potentially devastating effects on animal and ocean life, and for the most part, have an inherently
toxic life cycle from their production through their final disposal. Bio-based materials frequently are labelled as produced from “renewable” resources, although this term is used loosely because biomass production requires non-renewable inputs, which include fossil fuels, and ties up other finite resources such as land and water. The claim that bio-based materials are friendlier to the environment than their petroleum-based counterparts is being scrutinized closely [34].

1.2.1.1. Starch Polymers:

Starch is one of the most exciting and promising raw materials for the production of biodegradable products. It is the major polysaccharide reserve material of photosynthetic tissues and of many types of plant storage organs such as seeds and swollen stems. The primary crops used for its production consist of potatoes, corn, wheat and rice. In all of these sources, starch is produced in the form of granules, which vary in size and somewhat in composition based on the resources. Starch granule is composed of two main polysaccharides, amylose and amylopectin with some minor components such as lipids and proteins. Amylose is linear polymer of (1→4)-linked α-D-glucopyranosyl units with some slight branches by (1→6)-α-linkages (Figure 1.1). Amylose can have a molecular weight between $10^4$ and $10^6$ g mol$^{-1}$, with solubility in boiling water [44, 45].

![Figure 1.1. Structure of amylose.](image)

Amylopectin is a highly branched molecule composed of chains of α-D-glucopyranosyl residues linked together mainly by (1→4)-linkages but with (1→6)-linkages at the branched points. Amylopectin consists of hundreds of short chains of (1→4)-linked α-D-glucopyranosyl interlinked by (1→6)-α-linkages (Figure 1.2). It is an extremely large and highly branched molecule with a molecular weights ranging from $10^6$ to $10^8$ g mol$^{-1}$. Therefore, it is insoluble in boiling water, in body, both fractions are readily hydrolyzed at the acetal link by enzymes. Amylases attack α-(1→4)-link of starch while the α-(1→6)-link of amylopectin is by enzyme glucosidases.
The crystallinity of starch granules is attributed mainly to the amylopectin and not to amylose, which although linear, presents in a conformation that hinders its regular association with other chains [46, 47].

Starch has received significant interest during the past two decades as a biodegradable thermoplastic polymer. Starch offers an attractive and cheap alternative in developing degradable materials. Starch is not truly thermoplastic as most synthetic polymers. However, it can be melted and made to flow at high temperatures under pressure and shear. It has been widely used as a raw material in film production because of increasing prices and decreasing availability of conventional film-forming resins based on petroleum resources. Starch films possess low permeability and are thus potential materials for food packaging. Starch is also useful for making agricultural mulch films because it degrades into harmless products when placed in contact with soil microorganisms [48, 49].

By itself, starch is a poor alternative for any commodity plastic because, it is mostly water soluble, difficult to process, and brittle. Therefore, research on starch includes exploration of its water adsorptive capacity, the chemical modification of the molecule, its behaviour under agitation and high temperature, and its resistance to thermo mechanical shear. Although starch is a polymer, its stability under stress is not high. Above 150 °C, the glucoside links start to break, and after exceeding 250 °C the starch grain endothermally collapses. At low temperatures, a phenomenon known as

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Figure 1.2. Structure of amylopectin.
retrogradation is observed. This is a reorganization of the hydrogen bonds along with alignment of the molecular chains during cooling. In extreme cases below 10 °C, precipitation is observed. Thus, though starch can be dispersed into hot water and cast as films, the above phenomenon causes brittleness in the film [50].

Plasticised starch is essentially starch that has been modified by the addition of plasticisers to enable processing. Thermoplastic starch is plasticised to completely destroy the crystalline structure of starch to form an amorphous thermoplastic starch. Thermoplastic starch processing involves an irreversible order-disorder transition termed as gelatinisation. Starch gelatinisation is the disruption of molecular organization within the starch macromolecules and this process is affected by starch-water interactions. Most starch processing involves heating in the presence of water and some other additives; like sugar and salt to control the gelatinisation in the food industry, and glycerol as a plasticiser for biodegradable plastics applications. Most of the commercial researches on thermoplastic starches involve the use of modified starches and or blends with additives and other appropriate polymers for its application as biodegradable plastics [51]. The starch molecule has two important functional groups, the –OH group that is susceptible to substitution reactions and the C–O–C bond that is susceptible to chain breakage. The hydroxyl group of glucose has a nucleophilic character. To obtain various properties, starch can be modified through its –OH group. One example is the reaction with silane to improve its dispersion in polyethylene [52]. Crosslinking or bridging of the –OH groups changes the structure into a network subsequently increases the viscosity, reduces water retention and increases its resistance to thermo mechanical shear.

One of the approaches to modify this starch is by acetylation to from starch acetate. Acetylated starch do have advantages as a structural fibre or film-forming polymer as compared to native starch. The acetylation of starch is a well-known reaction and is relatively easy to synthesize. Starch acetate is considerably more hydrophobic than starch and has been shown to have better retention of tensile properties in aqueous environments. The degree of acetylation is easily controlled by trans esterification, allowing polymers to be produced with a range of hydrophobicities. Starch has been acetylated [with a high content (70%) of linear amylose] and its enzymatic degradation has been studied. Apart from acetylation and esterification, some other modification of starch such as carbonilation of starch with phenyl isocyanates, addition of inorganic esters to starch to produce phosphate or nitrate starch
esters, production of starch ethers, and hydroxypropylation of starches via propylene oxide modification has been performed. Generally all these modifications involve hydroxyl group substitution on the starch that will lower gelatinisation temperatures, reduce retrodegradation and improve flexibility of final product [46].

Starch has been used for many years as an additive to plastic for various purposes. Starch was added as a filler [53] to various resin systems to make films that were impermeable to water but permeable to water vapour. The use of starch as a biodegradable filler in LDPE was reported [54]. A starch-filled polyethylene film was prepared which became porous after the extraction of the starch. This porous film could be readily invaded by microorganisms and rapidly saturated with oxygen, thereby increasing polymer degradation by biological and oxidative pathways [55]. Otey et al. in a study on starch-based films, found that a starch– polyvinyl alcohol film could be coated with a thin layer of water-resistant polymer to form a degradable agricultural mulching film [51]. Starch-based polyethylene films were formulated and containing up to 40% starch, urea, ammonia and various portions of low density polyethylene (LDPE) and poly(ethylene-co-acrylic acid) (EAA). The EAA acted as a compatibilizer, forming a complex between the starch and the PE in the presence of ammonia. The resulting blend could be cast or blown into films, and had physical properties approaching to those of LDPE [56, 57].

Additionally, crosslinking of starch may be induced by the addition of organic/inorganic esters, hydroxyethers, aldehydes and irradiation. Kulicke et al. examined solution phase crosslinking of starch with epichlorohydrin and trisodium trimetaphosphate [58]. Jane et al examined the crosslinking of starch/zein cast films for improving water resistance [59]. The possibility of chemically combining starch or starch-derived products with commercial resins in such a manner that the starch would serve as both filler and a crosslinking agent may provide a possible approach for incorporating starch into plastics.

Commercial starch polymer based products are provided in Table 1.1 given below:
Table 1.1. Starch polymer based products and suppliers [46, 60].

<table>
<thead>
<tr>
<th>Base Polymer</th>
<th>Source Type</th>
<th>Advantages</th>
<th>Disadvantages</th>
<th>Potential Applications</th>
<th>Manufacturer (Product name)</th>
</tr>
</thead>
<tbody>
<tr>
<td>Starch</td>
<td>Renewable</td>
<td>Low cost, Fast bio-degradation</td>
<td>Poor mechanical properties, Hydrophilicity</td>
<td>Foams, Films and bags, Moulded items, Starch-based composite</td>
<td>Novament (Mater-bi™), Biotec (Bioplast®, Bioflex®, Biopur®), National Starch (ECO-FOAM), Buna Sow Leuna (Sconacell), Starch Tech (ST1, ST2, ST3), Novon (Poly-NOVON®)</td>
</tr>
</tbody>
</table>

One of the first starch based products was developed probably by the National Starch in the brand name ECO-FOAM™ and used as packaging material. ECO-FOAM™ materials are derived from maize or tapioca starch and include modified starches. This relatively short-term, protected-environment packaging use is ideal for thermoplastic starch polymers. National Starch now has additional thermoplastic starch materials, blends and speciality hydrophobic thermoplastic starches for a range of applications including injection moulded toys, extruded sheet and blown film applications [61]. Novament has been developing thermoplastic starch based polymers since 1990. Mater-Bi™ polymers are based on starch-blend technologies and product applications include biodegradable mulch films and bags, thermoformed packaging products, injection moulded items, personal hygiene products and packaging foam [62].
Similarly, Biotech GmbH produces Bioplast™ based on starch for a wide range of applications including accessories for flower arrangements, bags, boxes, cups, cutlery, edge protectors, golf tees, horticultural films, mantling for candles, nets, packaging films, packaging materials for mailing, planters, planting pots, sacks, shopping bags, straws, strings, tableware, tapes, technical films, trays and wrap films [63]. Recently Plantic Technologies Ltd produced soluble Plantic™ thermoformed trays for confectionery packaging [46].

1.2.1.2. Soy Protein (SP):

Proteins are abundant in nature and widely available in various forms in plants (soy, corn, whey protein, and wheat gluten) and in animals (collagen, gelatin). SP has been used to develop bioplastics for various applications [64]. Among all those proteins, soy protein is one of the less expensive bio-polymers abundant worldwide. It was first introduced by Henry Ford in automobile manufacturing as alternating source for plastics and fibres [65].

**Table 1.2. Typical composition of soy protein preparation.**

<table>
<thead>
<tr>
<th>Component (%)</th>
<th>Protein</th>
<th>Fat</th>
<th>Fibre</th>
<th>Ash</th>
<th>Carbohydrates</th>
</tr>
</thead>
<tbody>
<tr>
<td>Soy flours</td>
<td>56</td>
<td>1.0</td>
<td>3.5</td>
<td>6.0</td>
<td>33.5</td>
</tr>
<tr>
<td>Concentrates</td>
<td>72</td>
<td>1.0</td>
<td>4.5</td>
<td>5.0</td>
<td>17.5</td>
</tr>
<tr>
<td>Isolates</td>
<td>96</td>
<td>0.1</td>
<td>0.1</td>
<td>3.5</td>
<td>0.3</td>
</tr>
</tbody>
</table>

Its purification process is benign and environment friendly. This protein can also be used as resin due to its ability to form ductile and viscous polymers. Soy protein is generally available in four different forms as soy protein isolate (SPI), soy protein concentrate (SPC), soy flour (SF), and soy meal. Chemically, SPI contains 90% protein and 4% carbohydrates, SPC contains 70% protein and 18% carbohydrates, SF, which requires less purification, contains about 55% protein and 32% carbohydrate and finally soy meal has 40% protein. Soy protein is globular, reactive and often water soluble, as compared to helical or planar, non-reactive and water resistant synthetic polymers [66, 67]. The typical compositions of these different sources are given in the Table 1.2.

Soy protein isolate and soy concentrate are most widely used in design and engineering of biodegradable plastics. This protein has many side groups like –NH₂ and
OH, in which crosslinking reactions are easy to perform. Generally soy proteins are categorised on the basis of their sedimentation rate in fractional ultracentrifugation. Approximately 90% of the proteins in soybeans are globulins, and exist as dehydrated storage proteins. The major components are classified according to their sedimentation properties and are listed in Table 1.3. Based on Svedberg numbers (S), soy protein has mainly four fractions that include 2S, 7S, 11S, and 15S [68]. The main constituents of soy protein, the 7S fraction, is also called conglycinin and it comprises of many important enzymes and storage proteins. The 7S fraction is about 30% of the total soy protein by weight. The 11S fraction comprises about 52% of the total soy protein and is usually called glycinin [69]. The other two minor fractions are present as 2S (8%) and 15S (5%).

**Table 1.3.** Approximate distribution of the major components of soy proteins.

<table>
<thead>
<tr>
<th>Fraction</th>
<th>Content</th>
<th>Principle components</th>
</tr>
</thead>
<tbody>
<tr>
<td>2S</td>
<td>8</td>
<td>Trypsin inhibitor, Cytochrome</td>
</tr>
<tr>
<td>7S</td>
<td>35</td>
<td>Lipoxygenase, Amylase, Globulins</td>
</tr>
<tr>
<td>11S</td>
<td>52</td>
<td>Globulins</td>
</tr>
<tr>
<td>15S</td>
<td>5</td>
<td>Polymers</td>
</tr>
</tbody>
</table>

It can be seen that storage proteins, 7S (conglycinin) and 11S (glycinin) are the principal components of soy protein. 7S has a quaternary structure and is highly heterogeneous according to Kinesilla. Its principal component is beta-conglycinin, a sugar containing globulin. The fraction also comprises of enzymes (beta-amylase and lipoxygenase) and hemagglutinins. 11S fraction consists of glycinin, the principal protein of soybeans. 11S has also a quaternary structure and is composed of three acidic and three basic subunits with isoelectric points between pH 4.7–5.4 and 8.0–8.5, respectively. The polypeptides in native glycinin are tightly folded and stabilized via intermolecular disulphide bonds. The ability of soy proteins to undergo association–dissociation reactions under known conditions is related to their functional properties and particularly to their texturization. The major amino acid contents of soy protein are given in Table 1.4. It can be seen that soy protein consists mainly of the acidic amino acids (aspartic and glutamic acids) and their corresponding amides (asparagine and glutamine), non-polar amino acids (alanine, valine and leucine), basic amino acids (lysine and arginine), uncharged polar amino acid (glycine) and approximately 1% of
cystine. High proportions of glutamic and aspartic acid are found in soy proteins making it more hydrophilic than any other proteins. The sulfhydryl groups and disulfide bonds of 7S globulin are zero and two per molecule, respectively. In contrast, 11S globulin has two sulfhydryl groups and 20 disulfide bonds per molecule. The presence of various polar groups and reactive amino acids such as cystine, arginine, lysine, and histidine in the structure of soy protein enable them for convenient chemical and physical modifications, thereby improving the tensile and thermal properties of the biopolymer [70].

Table 1.4. Amino acid contents of some protein sources used for bioplastics.

<table>
<thead>
<tr>
<th>Amino acid</th>
<th>Amino acid content mol-%</th>
</tr>
</thead>
<tbody>
<tr>
<td><strong>Non-polar</strong></td>
<td></td>
</tr>
<tr>
<td>Valine</td>
<td>5.00</td>
</tr>
<tr>
<td>Leucine</td>
<td>8.10</td>
</tr>
<tr>
<td>Isoleucine</td>
<td>4.80</td>
</tr>
<tr>
<td>Phenylalanine</td>
<td>5.20</td>
</tr>
<tr>
<td>Methionine</td>
<td>1.30</td>
</tr>
<tr>
<td>Tryptophan</td>
<td>1.30</td>
</tr>
<tr>
<td>Alanine</td>
<td>4.20</td>
</tr>
<tr>
<td>Proline</td>
<td>5.10</td>
</tr>
<tr>
<td>Cystine</td>
<td>1.30</td>
</tr>
<tr>
<td>Glycine</td>
<td>4.10</td>
</tr>
<tr>
<td><strong>Polar</strong></td>
<td></td>
</tr>
<tr>
<td>Serine</td>
<td>5.20</td>
</tr>
<tr>
<td>Threonine</td>
<td>3.80</td>
</tr>
<tr>
<td>Tyrosine</td>
<td>3.80</td>
</tr>
<tr>
<td><strong>Acid residues</strong></td>
<td></td>
</tr>
<tr>
<td>Glutamic acid</td>
<td>19.00</td>
</tr>
<tr>
<td>Aspartic acid</td>
<td>11.50</td>
</tr>
<tr>
<td><strong>Basic residues</strong></td>
<td></td>
</tr>
<tr>
<td>Lysine</td>
<td>6.20</td>
</tr>
<tr>
<td>Arginine</td>
<td>7.50</td>
</tr>
<tr>
<td>Histidine</td>
<td>2.60</td>
</tr>
</tbody>
</table>
1.2.2. Reinforcing Biofibres:

In 1908, cellulose fibre reinforced phenolics composites were made and later it was extended to urea and melamine. In 1940, fibre reinforced composites received the commodity status with glass fibre in unsaturated polyesters. Composites are finding use in different fields ranging from guitars, tennis racquets, cars, microlight aircrafts and electronic components to artificial joints. Because of growing environmental awareness, the use of traditional composites, usually made of glass, carbon or aramid fibres being reinforced with epoxy, unsaturated polyester resins, polyurethanes, or phenolics, are considered unfavourably. The most significant disadvantage of traditional composite materials is the problem of suitable disposal after the end of life time. In the present polymer technology, it is essential that every material should exclusively be adapted to the environment. New fibre reinforced materials called biocomposites were created by implanting natural reinforcing fibres, e.g. jute, flax, hemp, ramie, etc. into bio based polymer matrix derived from virgin derivatives of cellulose, starch, lactic acid, etc [60, 71-74]. This is a challenging field of research with unlimited future prospects. The researches in this area are being pursued with great interest to develop newer bio composites.

Over the last few decenniums biofibre composites have been undergoing a notable transformation. These materials have become more and more satisfactory as new compositions and improvements have been intensively researched, developed and subsequently applied. The depletion of fossil fuel made biocomposites pointedly important and biocomposites have become engineering materials with a very diverse range of properties. The growth of natural fibre-thermoplastic composites, products that are progressively used in building materials and automotive interior parts, has been well recognized. These products have a number of key advantages in comparison with synthetic fibre-reinforced composites which includes low weight, low cost, lack of abrasiveness during processing, and the wide availability of the reinforcing fibres (wood or agricultural fibre) from renewable resources. This century could be called the cellulosic century, because more and more renewable plant resources are being discovered. It has been generally stated that natural fibres are renewable and sustainable, but they are in fact, neither. The living plants are renewable and sustainable from which the natural fibres are taken, but not the fibres themselves [75-80].

The plants, from which the natural fibres produce, are classified as primary and secondary depending on their utilization. Primary plants are those grown for their fibre
content while secondary plants are plants in which the fibres are produced as a by-product. Jute, hemp, kenaf, and sisal are examples of primary plants where as pineapple, oil palm and coir are the examples of secondary plants. Table 1.5 shows the main fibres used commercially in composites, which are now produced throughout the world [81]. There are six elementary types of natural fibres. The fibre classifications are shown in Table 1.6. The natural fibres are lignocellulosic in nature which is generally the most ample renewable biomaterial of photosynthesis on earth. In terms of mass units, the net primary production of natural fibre per year is estimated to be $2 \times 10^{11}$ tons as compared to $1.5 \times 10^8$ tons for synthetic polymers [82]. Lignocellulosic materials are widely distributed in the biosphere in the form of plants, trees (wood), and crops. Cellulose, in its several forms, constitutes approximately half of all polymers utilized in the industry worldwide.

**Table 1.5.** Commercially major fibre sources.

<table>
<thead>
<tr>
<th>Fibre source</th>
<th>World production (10^3 ton)</th>
<th>Fibre source</th>
<th>World production (10^3 ton)</th>
</tr>
</thead>
<tbody>
<tr>
<td>Bamboo</td>
<td>30,000</td>
<td>Coir</td>
<td>100</td>
</tr>
<tr>
<td>Jute</td>
<td>2300</td>
<td>Ramie</td>
<td>100</td>
</tr>
<tr>
<td>Kenaf</td>
<td>970</td>
<td>Abaca</td>
<td>70</td>
</tr>
<tr>
<td>Flax</td>
<td>830</td>
<td>Grass</td>
<td>700</td>
</tr>
<tr>
<td>Sisal</td>
<td>378</td>
<td>Hemp</td>
<td>214</td>
</tr>
<tr>
<td>Sugar cane bagasse</td>
<td>75,000</td>
<td></td>
<td></td>
</tr>
</tbody>
</table>

**Table 1.6.** Different types of fibre and their example.

<table>
<thead>
<tr>
<th>Fibre Type</th>
<th>Example</th>
</tr>
</thead>
<tbody>
<tr>
<td>bast fibres</td>
<td>jute, flax, hemp, ramie and kenaf</td>
</tr>
<tr>
<td>leaf fibres</td>
<td>abaca, sisal and pineapple</td>
</tr>
<tr>
<td>seed fibres</td>
<td>coir, cotton and kapok</td>
</tr>
<tr>
<td>core fibres</td>
<td>kenaf, hemp and jute</td>
</tr>
<tr>
<td>grass and reed fibres</td>
<td>wheat, corn and rice</td>
</tr>
<tr>
<td>all other types</td>
<td>wood and roots</td>
</tr>
</tbody>
</table>
1.2.2.1. Jute fibre:

Jute (*Corchorus capsularis* L.) is an important tropical crop and grows in some of Asian countries like India, Bangladesh, China, Thailand, Myanmar, Nepal and Indonesia. It occupies the second place in terms of world production levels of cellulosic fibres. Jute, a rainy season crop, grows best in warm and humid climates with temperature between 24 °C to 37 °C. India, China, and Bangladesh are the main producers of jute. To grow jute, farmers scatter the seeds on cultivated soil. About four months after planting, harvesting begins. The plants are usually harvested after they bloom, but before the blossoms go to seed. Jute plants are thinned out when they are about 6 inches (15 centimetres) tall. Jute is graded or rated according to its colour, strength, and fibre length. There are two types of Jute fibre: (a) White Jute (*Corchorus capsularis*) and (b) Tossa Jute (*Corchorus olitorius*). The fibres are off-white to brown and 3 to 15 feet (0.9 to 4.5 meters) long. Jute is pressed into bales for shipment to manufacturers. Jute grows in alluvial soils and can survive in heavy flooding. It will only grow in areas with high temperatures, sand or loam soils, and having annual rainfall over 1,000 millimetres. Large-scale jute cultivation is virtually confined to northern and eastern Bengal, mostly in the floodplains of the Ganges and Brahmaputra Rivers. More than 97 % of the world's jute is produced in Asia, including 65 % in India and 28 % in Bangladesh. Jute has played a vital role in the socioeconomic development in some of these countries [83]. Jute and its products have played an important role in this country’s work force. It is one of the inexpensive lignocellulosic fibres and is currently the bast fibre with the highest production volume.

1.2.2.1.1. Chemical constituents and structural aspects of Lignocellulosic fibre:

The major constituents of lignocellulosic fibres are cellulose, hemicellulose and lignin. The amount of cellulose, in the bio-fibres can vary depending on the species and the age of the plant or species. Cellulose is better described as a high molecular weight homopolymer of β-1,4-linked anhydro-D-glucose [84] units in which every unit is corkscrewed 180° with respect to its neighbours, and the repeat segment is frequently taken to be a dimer of glucose, known as cellobiose (Figure 1.3) [85]. It contains alcoholic hydroxyl groups. These hydroxyl groups form intramolecular hydrogen bonds inside the macromolecule itself and among other cellulose macromolecules as well as with hydroxyl groups from the air. Therefore, all of the natural fibres are hydrophilic in nature [86].
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Figure 1.3: Structure of cellobiose.

Even though the chemical assembly of cellulose from different natural fibres is the same, the degree of polymerization shows a discrepancy. The mechanical properties of a fibre are significantly related to degree of polymerization. Among various natural fibres “Bast fibres” generally show the highest degree of polymerization. Approximately, the degree of polymerization for bast fibre is around 10000 [87].

Lignin is a phenolic compound, commonly resistant to microbial degradation, but the pre-treatment of fibre renders it susceptible to the cellulose enzyme [88, 89]. The actual chemical nature of the primary component of biofibre, the lignin, still remains vague [90-91]. No method has so far been available by which it is possible to isolate the lignin in the native state from the fibre. Hence the exact structural formula of lignin in natural fibre has yet not been established although most of the functional groups and units which make up the lignin molecule have been identified. It is highly unsaturated or aromatic in nature due to the high carbon and low hydrogen content. It is characterized by its related hydroxyl and methoxy groups. Ethylenic and sulfur-containing groups have also been found in lignin [92]. The chemical environment of lignin in lignocellulosic materials has been a challenging subject of research [93, 94]. Polysaccharides such as cellulose and hemicellulose are laid down first during synthesis of plant cell walls and lignin fills the spaces between the polysaccharide fibres, cementing them together. Thus it works as a structural support material in plants. This lignification process causes hardening of cell walls, and the carbohydrate is protected from chemical and physical damage. The topology of lignin from different sources may be different but has the same basic composition. Lignin is believed to be linked with the carbohydrate moiety though the exact nature of linkages in biofibre is not well known [95]. One of the linkages is alkali sensitive and formed by an ester-like combination between lignin hydroxyls and carboxyls of hemicellulose uronic acid. The other ether-type linkage occurs through the lignin hydroxyls combining with the hydroxyls of cellulose. The lignin, being poly functional, exists in combination with more than one neighbouring chain molecule of cellulose and/or hemicellulose, making a crosslinked structure. The lignocellulosic material possesses many active functional
groups [96] like primary and secondary hydroxyls, carbonyls, carboxyls (esters), carbon-carbon, ether, and acetal linkages. Like all the lignocellulosic fibre, the physical and chemical properties of jute fibre is also depend on the three chemical components viz. cellulose, hemicellulose and lignin. The chemical composition and structural parameters of jute fibres are represented in Table 1.7.

**Table 1.7. Chemical composition and structural parameters of jute [86, 91, 95, 96].**

<table>
<thead>
<tr>
<th>Chemical composition</th>
<th>wt. (%)</th>
<th>Chemical composition</th>
<th>wt. (%)</th>
</tr>
</thead>
<tbody>
<tr>
<td>Cellulose</td>
<td>61-71.5</td>
<td>Pectin</td>
<td>0.2</td>
</tr>
<tr>
<td>Lignin</td>
<td>12-13</td>
<td>Wax</td>
<td>0.5</td>
</tr>
<tr>
<td>Hemicellulose</td>
<td>13.6-20.4</td>
<td>Moisture content</td>
<td>12.6</td>
</tr>
</tbody>
</table>

1.2.2.1.2. Properties of jute:

The lignocellulosic fibres reveal substantial deviation in diameter along with the length of individual fibres. The qualities and properties of lignocellulosic fibres generally depend on features like size, maturity, as well as processing methods implemented for the extraction of fibres. The modulus of fibre reduces with proliferation in diameter. The internal structure and chemical composition of fibres are responsible for the properties such as density, electrical resistivity, ultimate tensile strength, initial modulus, etc. The strength and stiffness of fibre is generally correlated with the angle between axis and fibril of the fibre, *i.e.*, the smaller this angle, the higher the mechanical properties. The chemical constituents and complex chemical structure of natural fibres also affect the properties significantly. Because of the very complex structure of lignocellulosic fibres, it is not possible to correlate the fibre strength exactly with cellulose content and microfibrillar angle. However, individual fibre properties can vary extensively depending on the source, separating technique, age, moisture content, speed of testing, etc. The lignin content of the fibres influences its structure [87], properties [75, 87, 95-106] and morphology [107]. The waxy substances of natural fibres generally influence the fibre’s wet ability and adhesion characteristics [108, 109].

Jute is 100% bio-degradable and recyclable and thus environmental friendly. It has high tensile strength, low extensibility, and ensures better breathability of fabrics. Therefore, jute is very suitable in agricultural commodity bulk packaging. It helps to make best quality industrial yarn, fabric, net, and sacks. It is one of the most versatile
natural fibre that has been used for packaging, textiles, non-textile, construction, and agricultural sectors. Bulking of yarn results in a reduced breaking tenacity and hence an increased breaking extensibility when blended as a ternary blend. Unlike the other fibre e.g. hemp, jute is not a form of Cannabis. Jute stem has very high volume of cellulose and hence it also can save the forest and meet cellulose and wood requirement of the world. The best varieties of Jute are Bangla Tosha - Corchorus olitorius (Golden shine) and Bangla White - Corchorus capsularis (Whitish Shine). Raw Jute and jute goods are interpreted as Burlap, Industrial Hemp, and Kenaf in some parts of the world. The best source of Jute in the world is the Bengal Delta Plain, which is occupied by Bangladesh and India [110]. Image of jute crops grow in India is shown below (Figure 1.4):

![Image of jute crops](image-url)

**Figure 1.4.** Image of jute crops.

*The physical properties of jute are given below:*

- The cells of jute fibre vary from 0.05-0.19 inch in length and 20-22\(\mu\)m in thickness.
- The Aspect Ratio (L/D) (mm) is about 152-365.
- Externally the fibre is smooth and glossy.
- It has specific gravity of 1.29. It is a very good insulator of heat and electricity.
- It is highly hygroscopic fibre. Water absorption by jute takes place in two phases, i.e., molecular phase and capillary phase.
- The tenacity of jute varies from 3.5-4.5 (g/denier) at 4 cm test length. The tenacity may be as high as 6-7 g/denier.
Its breaking elongation under normal atmospheric condition is 1-1.2%.

**The chemical properties of jute are:**

- In chemical composition, jute is different from linen and cotton. It is composed of a modified form of cellulose called lignocellulose (*bastose*).
- It develops yellow colour by iodine and sulphuric acid.
- It is more sensitive to the action of chemicals, than cotton or linen. Therefore, it cannot be bleached on treatment with alkalis. Bleaching powder weakens, and breaks down the fibre significantly.
- The use of sodium silicate, soda ash, or sodium hydroxide is not recommended for treatment of jute. Lime water makes the fibre brittle. Ammonia provides a harsh feel and decreases its lustre.

**1.2.2.1.3. Cost aspects, availability & sustainable development:**

The world’s supply of petroleum resources is being dwindling; the demand for sustainable and renewable raw materials is on high. So the use of available natural fibres has become an unavoidable task for scientists and industries. In order to confirm a reasonable profit to the farmers, non-traditional outlets have to be explored for natural fibres. One of such promising way is the natural fibre reinforced polymer composites. The price for lignocellulosic fibres which are viable for different applications differs a lot depending on the changed economy of the countries where such fibres are widely available [91]. It is one of the cheapest natural fibres in the world. In recent years, prices of natural fibres were not stable, especially for flax fibres [101], which is about 30% more expensive than glass fibres. For these economic reasons, a substitution of glass fibres by natural fibres seems not to be easily realized. However, lignocellulosic fibres offer several advantages; the most fascinating aspect about natural fibres is their positive environmental impact. They also present safer handling and working conditions compared to synthetic reinforcements. The worldwide availability is an additional factor.

**1.2.2.2. Surface treatments:**

The fabrication of polymer composites containing lignocellulosic fibres will often result in fibres physically spread in the polymeric environment. However in majority of cases, poor adhesion and subsequently insufficient mechanical properties result. Hence, surface treatment of the lignocellulosic fibres is playing a dynamic role.
Generally, surface treatment of lignocellulosic fibres is not mandatory to develop the bonding for the synthesis of biodegradable composites, in view of the analogous chemical scenery of both the biofibre and biopolymer matrix, which have a hydrophilic environment, unlike the situation with commodity polymers, which have an affinity to be hydrophobic. However, to improve many specific aspects of biodegradable composites, such as providing superior adhesion and diminished moisture sensitivity, surface treatment can be useful. Although better adhesion between the bio polymer matrix and lignocellulosic fibres is contributed by the similar polarities of the two materials, these results in an increase in water absorption of the composite. Hence, these fibres need appropriate surface treatments.

Different surface treatment methods namely chemical, physical, or combination of physical–chemical and physical–mechanical are employed. These modification methods are different for different types of fibres [86]. Dewaxing and alkali treatments are generally done for surface modification of jute fabrics. Jute is first treated with 2% liquid detergent at 70 ºC, followed by washing with distilled water and finally dried in oven. The washed fabrics are then dewaxed by treatment with a mixture of alcohol and benzene (1:2) for 72 h at 50 ºC, washed with distilled water and finally dried. The fabrics were then treated with 5% (w/v) NaOH solution for 30 min at room temperature, and washed with distilled water for several times to leach out the absorbed alkali. The fabrics were then kept immersed in distilled water for overnight and washed repeatedly to avoid the presence of any traces amount of alkali. The alkali treated fabrics were dried in an oven and stored at ambient temperature in a desiccator [111]. This treatment has helped to improve its interaction with the matrix materials, and increase adhesion of fibres with the matrix through surface roughness of fibre, leading to increased strength or other properties of composites through higher fibre incorporation and possibly providing greater durability of the composites.

A variety of moulding methods can be used according to the end-item design requirements. The principal factors impacting the methodology are the nature of the chosen matrix and reinforcement materials. Another important factor is the gross quantity of material to be produced. Large quantities can be used to justify high capital expenditures for rapid and automated manufacturing technology. Small production quantities are accommodated with lower capital expenditures but higher labour and tooling costs at a correspondingly slower rate. Based on the type of resins, the fabrication process may be of two types. The processes used for thermosetting resins
are: compression moulding, hand lay up, resin transfer moulding, vacuum assisted resin transfer moulding (VARTM), pultrusion etc. The processes for thermoplastic resins include injection moulding, extrusion moulding, needle punched, direct long fibre thermoplastic moulding (D-LFT) etc.

1.2.2.3. Jute reinforced Bio-composites:

Jute is one of the most common bast fibres having high tensile modulus and low elongation at break. If the low density (1.45 g/cm$^3$) of jute fibre is taken into consideration, then its specific stiffness and strength are similar to the respective quantities of glass fibre [112-114]. The specific modulus of jute fibre is better than glass fibre, and on a modulus per cost basis, jute is far superior. There are many reports that use jute as reinforcing agent for the synthesis of biodegradable composite. Mitra et al. [115] have reported the studies on jute-reinforced composites, their limitations and some solutions through chemical modifications of fibres. Flexural strength, flexural modulus and the dynamic strength of chemically modified jute-poly (propylene) composites have been found to increase by 40%, 90% and 40% respectively compared to unmodified jute- poly (propylene) composites [116] due to the chemical modification of jute with maleic anhydride grafted polypropylene. The effect of different additives on performance of biodegradable jute fabric-Biopol composites has been reported [117]. Biopol biodegradable polyester is a thermoplastic which has gained industrial consideration since it has a tensile strength comparable to that of isotactic poly (propylene) and is fully biodegradable. In absence of any additive, both tensile strength and bending strength of composites are found to increase around 50% whereas elongation at break reduced only 1% as compared to pure Biopol sheet. In order to study the effects of additives, the jute fabrics were soaked with several additive solutions of different concentrations. During such treatments dicumyl peroxide was used as the initiator. The effects of various surface modifications of jute on performance of biodegradable jute-Biopol composites as prepared by hot-press technique have been reported by Mohanty et al. [111, 118]. The surface modification of jute, involving dewaxing, alkali treatment, cyanoethylation and grafting are made with the aim to improve the hydrophobicity of the fibre in order to obtain decent fibre-matrix adhesion in the resulting composites. Differently chemically modified jute yarn-Biopol composites [107] showed maximum enhancement of mechanical properties like tensile strength, bending strength, impact strength and bending-modulus by 194%, 79%, 166%
and 162% respectively in comparison to pure Biopol. With 10 and 25% acrylonitrile
grafted yarns, the tensile strength of composites was enhanced by 102 and 84 % in
comparison to pure Biopol. Thus with the increase of grafting percent in yarn, the
mechanical properties of the composite were found to decline. The composites made
from alkali treated yarns produced better mechanical properties than dewaxed and
grafted yarns. Orientation of jute yarn played an important role on the properties. The
enhancement of mechanical properties of composites were noticed only when the
properties of composites were measured along the yarn wrapping direction. Unlike jute
yarn, the enhancement of mechanical properties of jute fabric-Biopol composites did
not show any variation with the direction of measurement of properties [119]. An
enhancement in more than 50% tensile strength, 30% bending strength and 90% impact
strength of resulting composites as compared to pure Biopol sheets was observed under
the experimental conditions used. Scanning electron microscopy also showed that the
surface modifications improved the fibre matrix adhesion. The improvement in
adhesion may be attributed to the formation of rough surface due to the removal of
natural and artificial impurities from the surface of jute by the treatment with alkali
[120]. In addition, alkali treatment leads to fibre fibrillation, i.e., breaking down the
fibre bundle of fabrics into smaller fibres which improves the effective surface area
available for contact with matrix polymer. Degradation studies showed that after 150
days of compost burial more than 50% weight loss of the jute/Biopol composites
occurred.

Sarkar et al. and other researchers have broadly investigated the properties of
alkali treated jute fibre reinforced with vinyl ester resin [121, 122]. In their studies, they
compared the mechanical, thermal, dynamic, and impact fatigue behaviour of treated
composites to those of untreated jute fibre–vinyl ester composites. Longer alkali
treatment removed the hemicelluloses and improved the crystallinity, enabling better
fibre dispersion. The dynamic, mechanical, thermal and impact properties were
superior owing to the alkali treatment. The effects of hybridization [123] on the tensile
properties of jute–cotton woven fabric reinforced polyester composites were
investigated as functions of the fibre content, orientation and roving texture. It was
observed that tensile properties along the direction of jute roving alignment (transverse
to cotton roving alignment) increased steadily with fibre content up to 50% and then
showed a decreasing trend. The tensile strength of composites with 50% fibre content
parallel to the jute roving is about 220% higher than pure polyester resin. Jute fibre
reinforced PP composites were evaluated in terms of the effect of matrix modification [111], the influence of gamma radiation [124], the effect of interfacial adhesion on creep and dynamic mechanical behaviour [125], the influence of silane coupling agent [126], and the effect of natural rubber [127]. The properties of jute/plastic composites were studied, including the thermal stability, crystallinity, modification, transesterification, weathering, durability, fibre orientation on frictional and wear behaviour, eco-design of automotive components, and alklylation [128-131]. Polyester resin was used as matrix for jute fibre reinforced composites and the relationship between water absorption and dielectric behaviour [132], impact damage characterization [133], weathering and thermal behaviour, and effect of silane treatment [134] were examined. Behera et al. [135] has developed jute reinforced soy milk based composites using non-woven and woven jute fabrics. They have studied and reported the mechanical properties, viz., tensile strength, tensile and flexural modulus, flexural strength and elongation at break. Composites having 60 wt % jute fabric possessed the best mechanical properties. Hydrophilicity of the composites was assessed by the measurement of contact angle and water absorption after immersing in water at ambient temperature as well as in boiling condition. Biodegradability of the composites was evaluated in compost soil burial condition. Fourier transform infra-red and optical microscope analyses of the buried samples confirmed the degradation of the composites.

1.3. Nanomaterials:

Nanomaterials are such a stuff which has at least one dimension in nanometre scale i.e. 1 to 100 nm. Nanomaterials can be classified into two categories viz. nanostructured material and nanophase/nanoparticle materials. Nanostructured materials usually refer to condensed bulk materials that are made of grains (agglomerates), with nanometric size range. The latter are generally the dispersive nanoparticles. Nanotechnology is the study and control of nanomaterial which also deals with the design, fabrication and application of nanostructures. Nanomaterials, a new branch of materials research, are attracting a great deal of attraction because of their potential applications in areas such as optics, electronics, magnetic data storage, catalysis and polymer nanocomposites (PN).

Incorporation of inorganic/organic nanoparticles as additives into polymer systems has resulted in PN displaying multifunctional, high performance polymer
characteristics beyond what conventional filled polymeric materials acquire. Multifunctional features attributable to PN consist of improved mechanical properties, thermal properties and/or flame retardancy, moisture resistance, chemical resistance, decreased permeability, and charge dissipation. Through control/alteration of the nanoscale additives, one can maximize the property enhancements of selected polymers to meet or exceed the needs. Uniform dispersion of these nanoscale materials produces super interfacial area per volume between the nanoparticle and the polymer. There are different types of commercially available nanoparticles such as montmorillonite organoclays, carbon nanofibres, carbon nanotubes, nanosilica, nanotitanium dioxide, nano ZnO and others that can be incorporated into the polymer matrix to form PN [136].

The term “nano” is derived from the Greek word nanos meaning “dwarf”, though in nanoscience and nanotechnology, it is used to indicate the size of the used material \(10^{-9}\) metre). PN are polymers (thermoplastics, thermosets or elastomers) that have been reinforced with small quantities of nano-sized particles having high aspect ratios \((l/h > 300)\) [137]. Thus, one component of nanocomposite has at least one dimension (length or width or thickness) in the nanometre range. The advantages of nanocomposites over macro composites include reduced filler amount and better properties than obtained for the conventional composites. Different types of thermoplastic and thermosetting polymer nanocomposites, viz. clay/polymer nanocomposites, carbon nanotube/polymer nanocomposites, metal/polymer nanocomposites (metals like Au, Ag, Cu, Cd, Zn, Fe, etc. and their oxides, sulphides, etc.) are good demonstration of nanotechnology. The main significance of polymer nanocomposites are:

- Superior physical properties; modulus, dimensional stability, etc.
- Improved chemical resistance, weatherability and biodegradation
- Better barrier properties; reduced gas permeability to oxygen and carbon dioxide
- Enhanced flame retardance and slow smoke emission
- Improved optical clarity over that of conventional filler
- Increased heat distortion temperature

Nanotechnology is one of the most popular regions for present research and development in basically all technical disciplines. This obviously includes polymer science and technology and even in this field the investigations cover a broad range of
topics. The areas include bio-polymer-based materials, nanoelectronics, miniemulsion particles, nanoparticle drug delivery, fuel cell electrode polymer bound catalysts, electrospun nanofibres, imprint lithography, polymer blends layer-by-layer self-assembled polymer films, and nanocomposites. Even in the field of nanocomposites, many diverse topics exist including composite reinforcement, barrier properties, flame resistance, electro-optical properties, cosmetic applications, bactericidal properties etc. There are different types of commercially available nanofillers that can be incorporated into the polymer matrix to form polymer nanocomposites. Depending on the application, the researcher must determine the type of nanoparticle needed to provide the desired effect. The commonly used nanoparticles are:

1.3.1. Clay

Nanoclay is the most widely investigated nanoparticle in a variety of different polymer matrices for a spectrum of applications. The origin of natural clay i.e. bentonite is most commonly formed by the in-situ alteration of volcanic ash. Bentonite contains montmorillonite but also can contain glass, mixed layer clays, illite, kaolinite, quartz, zeolite, and carbonates. The expanding clays are phyllosilicates, smectite, and montmorillonite, and the nonexpanding clays are talc, kaolin, and mica. Clay soil has particles size of less than 2 µm. Silica is the dominant constituent of the montmorillonite clays, with alumina being essential. The chemical structure of montmorillonite is illustrated in Figure 1.5, showing its structure consisting of the tetrahedral silicate layer and the octahedral alumina layer. The tetrahedral silicate layer consists of SiO$_4$ groups linked together to form a hexagonal network of the repeating units of composition Si$_4$O$_{10}$. The alumina layer consists of two sheets of closely packed oxygens or hydroxyls, between which octahedrally coordinated aluminium atoms are imbedded in such a position that they are equidistant from six oxygens or hydroxyls. The two tetrahedral layers sandwich the octahedral layer, sharing their apex oxygens with the latter. The layer thickness is around 1 nm 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 with a regular van der Waals gap in between them called the interlayer or the gallery. The chemical formula of montmorillonite clay is Na$_{1/3}$(Al$_{5/3}$Mg$_{1/3}$)Si$_4$O$_{10}$(OH)$_2$. In its natural state Na$^+$ cation resides on the montmorillonite clay surface [136, 139].
The dispersion of clay tactoids in a polymer matrix can result in the formation of three types of composites, as shown in Figure 1.6.

(i) **Phase separated (microcomposite) structure:** It is a conventional composite that contains clay tactoids dispersed simply as a segregated phase, resulting in poor mechanical properties of the composite.

(ii) **Intercalated structures:** The second type is intercalated polymer-clay nanocomposite, which is formed by the infiltration of one or more molecular layers of polymer into the clay host galleries.

(iii) **Exfoliated structures:** In this case, the host clay layers have lost their registry and are well separated into single layers within a continuous polymer matrix. The exfoliated polymer-clay nanocomposites, characterized by low clay content, a monolithic
structure, and a separation between clay layers that depends on the polymer content of the composite.

Exfoliation is particularly desirable for improving specific properties that are affected by the degree of dispersion and resulting in interfacial area between polymer and clay nanolayers. Exfoliated nanocomposites usually provide the best properties enhancement due to the large aspect ratio and surface area of the clay.

1.3.2. Zinc oxide (ZnO)

ZnO a wide, direct band gap (3.37eV, 298K) semiconductor with extonic Bohr radius of 1.8 nm has been intensively studied in the past decade [140]. Its excitation binding energy is about 60 MeV, which is much larger than other band gap semiconductors [141]. Because of the high UV–protection property in the range of wave-length 240-380 nm and low refractive index (n=1.9), ZnO is considered as an ideal UV protector and usually added into cosmetics for ultra-violet protection [142-145]. So far, various nanostructures of ZnO, such as nanowires, nanorods, nanobelts, nanotubes, and nanocables have been fabricated by means of various methods, including vapour phase transport, metal organic vapour phase epitaxy, aqueous thermal deposition and electrochemical deposition. Inorganic UV absorbers are used widely owing to their higher chemical stability, thermal stability, nontoxicity, and non-irritant compared with organic absorbers. Besides, it is very interesting multifunctional material for its applications in solar cells, sensors, displays, gas sensors, varistors, piezo-electric devices, electro-acoustic transducers, photodiodes and UV light emitting devices [146]. However, ZnO nanoparticles, like other nanoparticles, possess high surface energy, which may result in the agglomeration of particles when ZnO nanoparticles are dispersed in organic solvent and matrices.

In polymer composite, nano ZnO is widely used as photostabilizer. Besides UV stabilizing effect, ZnO nanopowder can also improve thermal stability of polymer. In recent years, most of the researchers have examined the role of ZnO nanoparticles in exterior coatings to improve photostability [147], as a component of UV coatings for nanocomposites or modelling UV permeability of nano-ZnO filled coatings [148, 149]. Laachachi and co-workers have reported the increased thermal properties of PMMA by incorporation of ZnO and organo-montmorillonite [150].
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1.3.3. Titanium dioxide (TiO₂)

Titanium dioxide adopts at least eight (8) structures. Besides its four polymorphs found in nature (i.e. rutile, anatase, brookite, TiO₂ (B)), additional high-pressure forms have been synthesized: TiO₂ (II) with the α-PbO₂ structure, TiO₂ (H) with hollandite, baddelleyite with ZrO₂, Cotunnite with PdCl₂ [151]. The anatase phase of TiO₂ has long been considered as the most photoactive of these four phases [152-156]. TiO₂ has received a great attention due to its strong oxidizing power of the photo-generated holes, chemical inertness, non-toxicity, low cost, high refractive index and other advantageous surface properties. TiO₂ was first industrially introduced to replace toxic lead oxides as a white paint pigment in 1900’s. It is used as a white pigment in paints, plastics, paper and cosmetic products which represent the major end-use sectors of TiO₂. TiO₂ has also been used for photo-assisted degradation of organic compounds and reduction of inorganic compounds. As a semiconductor oxide, a wide-band gap TiO₂ is easy to be irradiated by sunlight (especially UV light) to create the excited electron–hole pairs which could separate and the resulting charge carriers might migrate to the surface where they react with adsorbed water and oxygen to produce radical species. These radicals attack any adsorbed organic or even micro-organic molecules, resulting in complete or selective decomposition; or transformation of inorganic molecules into their oxidized and/or reduced states. Furthermore, due to presence of wide band gap of ~3.2 eV, TiO₂ can be used as semiconductor devices. Its other applications are studied for antifouling, antimicrobial, deodorizing and photovoltaic effects.

TiO₂ is regarded as the best photocatalyst for the decomposition of many organic pollutants in water and air [157]. It can be used in various processes such as the odour elimination from drinking water, the degradation of oil spills in surface water systems and the degradation of harmful organic contaminants like herbicides, pesticides and refractive dyes [158-160]. Nanosized TiO₂ powder has a large specific surface area, and good photo catalytic activities since reactions take place on the TiO₂ surface.

1.3.4. Cellulose and cellulose derivatives:

Cellulose is one of the most fascinating organic resources, an almost inexhaustible raw material, and a key source of sustainable materials on an industrial scale in the biosphere. Natural cellulose based materials (cotton, wood, linen, hemp, etc.) have been used by our society as engineering materials for millennia and their use
continues today as verified by the extent of the world wide industries in building materials, paper, textiles, etc. Generally, cellulose is a fibrous, tough, water-insoluble natural polymer that plays a vital role in maintaining the structure of plant cell walls. It was first discovered and isolated by Anselme Payen [161] in 1838, and since then, numerous physical and chemical prospects of cellulose have been extensively studied. Cellulose has been used for about 150 years for wide spectrum of products and materials in daily life. Many polymer researchers are with the opinion that polymer chemistry had its origins with the characterization of cellulose. Cellulose differs in some respects from other polysaccharides produced by plants, the molecular chain being very long and consisting of one repeating unit. Cellulose can be characterized as a high molecular weight homopolymer of $\beta$-1,4-linked anhydro-D-glucose units in which every unit is corkscrewed $180^\circ$ with respect to its neighbours, and the repeat segment is frequently taken to be a dimer of glucose, known as cellobiose.

Naturally, it occurs in a crystalline state. From the cell walls, cellulose is isolated in microfibrils by chemical extraction. In all forms, cellulose is a very highly crystalline, and high molecular weight polymer. Because of its infusibility and insolubility, cellulose has driven the step-by-step creation of novel types of materials. Breakthrough were the development of cellulose esters and cellulose ethers as well as of cellulose regenerates and the discovery of the polymeric state of molecules. The very first thermoplastic polymeric material of cellulose was manufactured by Hyatt Manufacturing Company in 1870 to make celluloid in which they had reacted cellulose with nitric acid to form cellulose nitrate. The chemical modification of cellulose on an industrial scale led to a broad range of products based on cellulose from wood. The first example was the fabrication of regenerated cellulose filaments by spinning a solution of cellulose in a mixture of copper hydroxide and aqueous ammonia [85].

Natural cellulose has earned in the materials society a tremendous level of awareness that does not emerge to be yielding. The cellulose biopolymer imprimatur such interest not only because of their unsurpassed quintessential physical and chemical properties but also because of their inherent renewability and sustainability in addition to their abundance. They have been the subject of a wide array of research efforts as reinforcing agents in nanocomposites due to their availability, low cost, renewability, light weight, nanoscale dimension, unique morphology and most importantly they have low environmental, animal/human health and safety risks. Currently, the isolation, characterization, and search for applications of novel forms of cellulose, variously
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termed crystallites, nanocrystals, whiskers, nanofibrils, and nanofibres, is generating much activity. Novel methods for their production range that begins at the highest conceptual level and works down to the details methods involving enzymatic/chemical/physical methodologies for their isolation from wood and forest/agricultural residues to the bottom-up production of cellulose nanofibrils from glucose by bacteria [38, 162]. Some fungi can secrete enzymes that catalyze oxidation reactions of either cellulose itself or the lower molecular weight oligomers produced from the enzymatic hydrolysis of cellulose. Of these, the peroxidases can provide hydrogen peroxide for free radical attack on the C2–C3 positions of cellulose to form ‘aldehyde’ cellulose, which is very reactive and can hydrolyze to form lower molecular weight fragments while other oxidative enzymes can oxidize glucose and related oligomers to glucuronic acids. Such isolated cellulosic materials with one dimension in the nanometre range are referred to generically as nanocelluloses [163]. These nanocelluloses provide important cellulose properties—such as hydrophilicity, wide spectrum of chemical-modification capacity, and the formation of versatile semi-crystalline fibre with very large aspect ratio which is the specific features of nanoscale materials. On the basis of their dimensions, functions, and preparation methods, which in turn depend mainly on the cellulosic source and on the processing conditions, nanocelluloses may be classified in three main subcategories.

(i) Microfibrillated cellulose (MFC): MFC is normally produced from highly purified wood fibre (WF) and plant fibre (PF) pulps by high pressure homogenization according to the procedures developed at ITT Rayonnier [164]. Pulp is produced by using a mixture of sodium hydroxide and sodium sulphide and thus so-called kraft pulp (almost pure cellulose fibres) is obtained. Pulping with salts of sulfuric acid leads to cellulose named sulphite pulp (which contains more by-products in the cellulose fibres). MFC particles are considered to comprise of several elementary fibrils. Each one of them consisting of 36 cellulose chains has a high aspect ratio or ~10-100 nm wide and 0.5-10 µm in length. MFCs are ~100% cellulose, and contain both amorphous and crystalline regions. In food and cosmetic industries, MFCs have been used as a thickening agent [165].

(ii) Nanocrystalline cellulose (NCC): NCC is the term frequently used for the cellulose nanocrystals or cellulose whiskers prepared from natural cellulose by acid hydrolysis. NCC is the enlightened crystalline segments of elementary nanofibrils after the amorphous segments have been removed via the treatment with strong acids at eminent
temperature. The nanocrystals formed from wood pulp are shorter and thinner than the MFC. NCCs have a high aspect ratio (3–5 nm wide, 50–500 nm in length), are ~100% cellulose, and are highly crystalline (54–88%). Most likely, from the result of acid hydrolysis process, the end of the cellulose nanocrystals are narrowed due to which they look like whiskers. This hierarchical structure of natural fibres, based on their elementary nanofibrilar components, leads to the unique strength and high-performance properties of different species of plants. The mechanical properties of cellulose can be characterized by its properties in both the ordered (so-called crystalline) and disordered (so-called amorphous) regions of the molecule. The chain molecules in the disordered regions contribute to the flexibility and the plasticity of the bulk material, while those in the ordered regions contribute to the elasticity of the material. As they are almost defects free, the modulus of cellulose nanocrystals is close to the theoretical limit for cellulose. It is potentially stronger than steel and similar to Kevlar [166, 167].

(iii) Bacterial Nanocellulose (BNC): BNCs are also known as bacterial cellulose, microbial cellulose, or biocellulose. BNCs are microfibrils concealed by aerobic bacteria, such as acetic acid bacteria of the genus Gluconacetobacter, as a pure component of their biofilms. The resulting microfibrils are microns in length, have a large aspect ratio with morphology depending on the specific bacteria and culturing conditions. These bacteria are wide-spread in nature where the fermentation of sugars and plant carbohydrates takes place. In contrast to other forms of cellulose i. e. MFC and NCC, materials isolated from cellulose sources, BNC is formed as a polymer and nano material by biotechnological assembly processes from low-molecular weight carbon sources, such as d-glucose. The bacteria are cultivated in common aqueous nutrient media, and the BNC is excreted as exopolysaccharide at the interface to the air. The resulting form-stable BNC hydrogel is composed of a nanofibre network (fibre diameter: 20–100 nm) enclosing up to 99% water. This BNC is proved to be very pure cellulose with a high weight-average molecular weight (MW), high crystallinity, and good mechanical stability. The bio-fabrication approach opens up the exciting option to produce cellulose by fermentation in the sense of white biotechnology and to control the shape of the formed cellulose bodies as well as the structure of the nanofibre network during biosynthesis. The resulting unique features of BNC lead to new properties, functionalities, and applications of cellulose materials [168-175].
1.4. Different additives for jute based bionanocomposites:

The chemicals or substrate or materials, which are necessary to incorporate into the virgin polymers to obtain the desired level of properties for their different applications are known as additives for polymers. All the chemicals or materials cannot be an additive for polymers. They should fulfil some criteria to act as an additive for polymers. They should be efficient in their function, i.e. the purpose for which they are being incorporated into the polymer, and should efficiently work for that. They should be stable under processing as well as service conditions. The additive should not degrade or decompose or alter its nature during processing and under service conditions. They should not bleed or bloom. They should be non-toxic and should not impart any taste, odour or colour to the polymer matrix. The additives should be inert other than their own functions. They should be available in sufficient quantity as required and should have low cost. The physical state of additive may be solid, liquid or even gaseous. The semi-liquid like rubbery and gel are also used in some cases. However, gaseous additives are only used in case of foam products.

1.4.1. Crosslinking agent

Crosslinking agents are additives used to enhance crosslinking or bonding between polymer chains, so that the resultant polymer mainly exists in a 3D network form in biopolymers, which could increase reaction rate and significantly improve the dimensional stability, mechanical properties, wear resistance, impact strength of polymer nanocomposites. These are used in small quantities to provide a stable bond between two otherwise nonbonding and incompatible surfaces [176]. They play remarkable role in improving the affinity, compatibility, and adhesion between fibres and polymers in composite. Among the many available crosslinking agents, glutaraldehyde has undoubtedly establish the extensive application in various fields such as leather tanning industry, enzyme technology, chemical sterilization, and biomedical and pharmaceutical sciences. Glutaraldehyde, a linear, 5-carbon dialdehyde, is a clear, colourless to pale straw-coloured, pungent oily liquid that is soluble in all proportions in water and alcohol, as well as in organic solvents. It is mainly available as acidic aqueous solutions (pH 3.0–4.0), ranging in concentration from less than 2% to 70% (w/v). Glutaraldehyde has had great success because of its commercial availability and low cost in addition to its high reactivity. It reacts rapidly with amine groups at around neutral pH and is more efficient than other aldehydes in
generating thermally and chemically stable crosslinks [177]. The simple structure of glutaraldehyde is not indicative of the complexity of its behaviour in aqueous solution and its reactivity. Knowledge of the structure and mechanism of crosslinking reagents is important for their use. However, the structure of glutaraldehyde in aqueous solution has been the subject of more debate than any of the other crosslinking reagents. In fact, glutaraldehyde structure in aqueous solution is not limited to the monomeric form (Figure 1.7, structure I). Figure 1.7 gives an overview of the possible molecular forms of glutaraldehyde in aqueous solution [178].

![Diagram of possible forms of glutaraldehyde in aqueous solution](Figure 1.7)

**Figure 1.7.** Possible forms of glutaraldehyde in aqueous solution.

### 1.4.2. Plasticizer

A great devotion has been made to thermoplastic SP and starch because thermomechanical processing technique is an easy and effective way to prepare complete biodegradable materials [179]. However, both soy protein and starch are very brittle, weak and difficult to process into useful films. In a state to improve the processing assets of soy protein and starch, plasticizers have to be added into the matrix to
overcome the brittleness of pure biopolymers. Plasticizer has the ability to reduce internal hydrogen bonding between macromolecule chains as well as to increase the molecular spacing of them [180]. The most effective plasticizers will resemble most closely in the structures of the polymers they plasticize. The best plasticizers for soy protein and starch are compounds containing hydroxyl groups, such as glycerol [181]. Glycerol is a simple naturally occurring polyols. It is an odorless, colorless, viscous liquid, and generally considered as non-toxic. It is widely used in pharmaceuticals. It contains three hydroxyl groups which are accountable for its solubility in water and hygroscopic nature. The chemical structure of glycerol is depicted in Figure 1.8.

![Figure 1.8. Chemical structure of glycerol.](image)

1.5. Review of Literature:

Mohanty et al. [111, 182] has developed the chemical surface modification of jute fabrics to improve the interfacial properties. The modification involves bleaching, dewaxing and alkali treatment. The mechanical properties of composites like tensile and bending strengths have increased as a result of surface modification. Wang et al. [183] has developed a new technique including chemical (room temperature alkaline, acid steam and 80°C alkaline) and physical (high pressure steam) for treatment of natural fibres. They have used scanning electron microscopy (SEM) to study the effects of chemical and physical treatments on the morphological development of jute fibres from micro-to-nano-scale. The thermal stability of the jute fibres has been found to enhance after treatment. Khanam and co-workers [184] has carried out fibre surface treatment to produce good interface between the fibre and the matrix to improve the mechanical properties. They have reported that the untreated sisal fibre shows lower tensile, flexural properties than the treated one. The sisal fibre reinforced composites are resistant to all chemicals except carbon tetrachloride.

Chabba et al. [185] have prepared environment-friendly, fully biodegradable, ‘green’ composites using glutaraldehyde (GA) modified soy protein concentrate (MSPC-G) and flax fabric. The polymer has been cross-linked with GA to increase its
tensile properties and to improve its process ability. Fracture stress, young modulus and moisture resistance have been found to improve in glutaraldehyde modified MSPC-flax fabric composite compared to glutaraldehyde modified SPC-flax fibre composite. Chabba and Netravali [186] have blended the cross-linked soy protein concentrate (SPC) with poly (vinyl alcohol) for improving its toughness and thermal properties. Chabba et al. [66] has also prepared green composites based on plant based fibres and resins. They have modified deflated soy flour by cross-linking with glutaraldehyde and the composites using cross-linked soy flour (CSF) and flax yarn. They have studied the effect of glycerol on mechanical properties of the soy flour composite. CSF polymer has shown improved tensile properties and thermal stability, compared to unmodified SF resin. Lodha and Netravali [187] have investigated the effect of stearic acid on tensile and thermal properties of ramie fibre-reinforced soy protein isolate (SPI) resin green composites. It is observed that part of the stearic acid crystallized in SPI resin and the crystallizability is affected by the addition of glycerol as a plasticizer. The fabricated green composites are found to have enormous potential for certain indoor applications. SEM photomicrographs of some of the fractured tensile surfaces of the ramie/SPI and ramie/modified soy protein isolate (MSPI) composites do not show any resin whereas a few other fibres clearly show resin sticking to the surface. The presence of resin on some fibre surfaces for the SPI and MSPI resins clearly indicates good interfacial interaction between the fibre and the resins.

Khondker et al. [188] has fabricated long fibre reinforced unidirectional thermoplastic composites using jute yarns (both untreated and treated). They have used two types of polymeric materials (biodegradable poly (lactic) acid and non-biodegradable homo-polypropylene) as matrix. The jute/PP composites, specimens with only 20% of jute fibre content have shown remarkable improvement in tensile and bending properties when compared to those of the virgin PP specimens. Park et al. [189] has fabricated the composite using cellulose acetate powder, eco-friendly triethyl citrate plasticizer and organically modified clay. The tensile strength and modulus of cellullosic plastic reinforced with organoclays are improved by decreasing the plasticizer content. The heat deflection temperature is improved and the water vapour permeability is reduced. But the impact strength is decreased. Nam et al. [190] has used ramie fibres to reinforce SPC and obtained composites with excellent mechanical properties. Kumar and Zhang [191] have aligned the ramie fibres in vertical, horizontal as well as both vertical and horizontal to enhance the strength of soy protein composite.
The materials in which ramie fibres are aligned vertically, exhibit the highest water resistance and mechanical properties compared to either horizontal or vertical one. They have coated the soy protein isolate with 2,2-diphenyl-2-hydroxyethanoic acid to get the arylated soy protein in order to further improve the water resistance property of the composite. This work provides a novel idea to improve the water resistance and modulus by reinforcing the protein matrix with natural fibres.

Goda et al. [192] has explored the effect of mercerization on tensile properties of ramie fibres. They have treated the ramie fibre with 15% NaOH solution. The results show that tensile strength of the treated ramie fibre has increased by 4–18% than that of the untreated ramie fibre. They also have found that fracture strain of the treated ramie fibre drastically increases. Kim and Netravali [193] have used modified soy flour (MSF) and ramie fibre to prepare biodegradable, green composites. They have modified defatted soy flour by a lab-scale filtration system to improve its mechanical, interfacial and thermal properties through increasing the protein content. Tensile stress and Young’s modulus of MSF resins are 35.5 and 1411.7 MPa, respectively, which is significantly higher than those (12.7 and 379.3 MPa) of SF resins. Interfacial shear strength of single ramie fibres with MSF resins ranges from 8.8 to 15.2 MPa, which were about 40-50% higher than those obtained with SF resins. Nanocomposites, with nanoparticles dispersed, have been studied extensively due to their capability to improve mechanical, physical, thermal and barrier properties with very low nanoparticles loading of 1-5 wt% [194-198]. Huang and Netravali [199] have used phytagel and nano-clay particles to improve the mechanical, thermal and moisture resistance of soy protein concentrate (SPC) resin. The Phytagel-modified SPC resin (PH-SPC) has shown improved tensile strength, modulus, moisture resistance, and thermal stability as compared to the unmodified SPC resin. The incorporation of 40% Phytagel and 20% glycerol led to an overall 340% increase in the tensile strength (over 50 MPa) and approximately 360% increase in the Young’s modulus (over 710 MPa) of the SPC resin. Nano-clay has been uniformly dispersed into PH-SPC resin to further improve the properties.

Pandey and Singh [200] have studied the effect of plasticizer on the nanocomposites of starch and reported that the mechanical properties are improved for the composites where plasticizer has been added after mixing of clay in the starch matrix. Darder et al. [201] has worked in the intercalation of the cationic biopolymer chitosan in Na+-montmorillonite and reported that the chitosan layer is first adsorbed
through a cationic exchange procedure and the second layer is adsorbed in the acetate salt form. He has used this material in the development of bulk modified electrodes exhibiting numerous advantages as easy surface renewal, ruggedness, and long-time stability. He has applied the resulting sensors in the potentiometric determination of several anions and has found that the sensor showed high selectivity towards the monovalent anions. Biodegradable starch based materials has been prepared by Averous et al. [202] from wheat starch, polyesteramide and glycerol by melt blending. They have noticed that the polyester amide blended thermoplastic starch overcomes the weakness of pure thermoplastic starch like low mechanical properties, high moisture sensitivity and high shrinkage in injection. Viville et al. [203] has grafted polymer chains onto clay nano platelets by coordination-insertion polymerization of ζ-caprolactone in toluene with montmorillonite type clay. The work highlights the possibility of producing organic-inorganic nanohybrids, where the nanoscale components are linked to each other through electrostatic interactions.

Cao et al. [204] has prepared nanocomposites from polycaprolactone-based waterborne polyurethane and a suspension of cellulose nanocrystals. The cellulose nanocrystals are obtained by acid hydrolysis of flax fibre. The prepared composites show significant increase in Young’s modulus and tensile strength with increasing filler content. Chen and Evans [205] have prepared nanocomposites of glycerol plasticized starch with untreated montmorillonite and hectorite. The nanocomposites prepared by them have shown an increase in modulus for a given volume fraction of clay. Jute fabric reinforced starch/polyvinyl alcohol/clay composites have been prepared by Ray et al. [206]. They have found that the composites having higher amount starch show superior mechanical properties than the others. Jong et al. [207] has blended soy protein concentrate with styrene-butadiene latex to form elastomer composites. This elastomer has shown an increase in the shear elastic modulus in a small strain region and also improved the recovery behaviour. Thomas et al. [208] has reviewed and evaluated various properties of starch/clay/glycerol nanocomposites. The sequence of addition of starch, glycerol and clay has a significant effect on the properties of composites. MMT modified with octadecylammonium chloride has been used as organoclays for nanocomposites preparation. Poly (hydroxyl butyrate)/layered silicate nanocomposites have been successfully prepared by Maiti and co-workers [209]. The nanocomposites exhibit a higher storage modulus, better biodegradation behaviour as compared to the neat Poly (hydroxyl butyrate).
1.6. Application & Market:

Unlike many biopolymer products being developed and marketed, very few biodegradable composites have been developed, with most of their technologies still in the research and development stages. This is despite the fact that the environmentally friendly composites, where biodegradability is important, provide designers new alternatives to meet challenging requirements. These include aquatic and terrestrial environments, municipal solid waste management and compostable packaging, while those for automobiles include parcel shelves, door panels, instrument panels, armrests, headrests and seat shells. Accordingly, a wide range of biodegradable products have been produced using LC fibres and biopolymers for different applications, ranging from automotive vehicles including trucks, construction (hurricane resistant housing and structures, especially in the USA) and insulation panels, to special textiles (geotextiles and nonwoven textiles) [210]. The hurricane resistant housing, structures and a variety of products developed using soy oil with LC fibres could be the predecessor for diverse range of applications for the biodegradable composites. Other identified uses for these materials include bathtubs, archery bows, golf clubs and boat hulls. This is further underlined with the estimated global market of about 900,000 metric tons of wood plastics and natural fibre composites as per Steven Van Kourteren, Consultant, Principia Partners [211]. Hence the market for biodegradable composites can be expected to grow in near future. This is based on continued technical innovations, identification of new applications, persistent political and environmental pressures, and investments mostly by governments in new methods for fibre harvesting and processing of natural fibres [212, 213].

1.7. Objectives and plan of work:

Biopolymer based materials immobilized with nanoparticles have recently dominated over the traditionally available petroleum based polymer materials. Due to their outstanding mechanical properties and biodegradability, bio based polymer nanocomposites are now a days considered to be promising future material. These materials have the potential to overcome the disadvantages possesses by material commercially obtained from petrochemical supply chain. Moreover, the use of bio based polymer nanocomposites plays a vital role in sustainable development so called the development of newer methods for production of environmentally benign ‘greener products’.
Among the various biodegradable polymers, two of the most studied and promising polymers are starch and soy flour (SF). They are natural and renewable biodegradable polymers which are produced by many plants as a source of stored energy. The presence of various polar and reactive groups in the structure of starch and soy flour augment them to crosslink with some crosslinking agent such as glutaraldehyde, thereby improving the mechanical and thermal properties. However, the potentiality of such material has been less explored in synthesizing bio based composites. Besides having various advantages, SF based material too exhibits certain disadvantages. For example soy protein based plastics have poor flexibility and water resistance. Although several plasticizers like glycerol, polyethylene glycol, sorbitol etc, have been used to improvise the flexibility of SF but found to provide less mechanical strength and high water sensitivity. In this respect, biofibres evolved to be one of the promising materials in improving the mechanical strength of such material. The salient features of natural fibres over the conventional counterparts include comparatively low cost, low weight, high specific modulus, less hazards, copious and renewable resources. The applications of natural fibres in the sectors such as automobiles, furniture, packing and construction industries sectors are now of highly demanding. Currently, kenaf, bamboo and palm-tree fibres are used as reinforcing agent at micro and macro levels to improve the thermal and mechanical properties of natural biodegradable polymers. Similarly, palm tree and kenaf natural fibres are used as reinforcing agents for the development of self-bonded polymer bio-composite. Besides the above mentioned natural fibres, jute fibre is one which can be used as reinforcing agent and can be used for fabrication of polymer composite. Jute, mainly comprising of cellulose and lignin, is an extensively demanding materials in cloth and other such industries. The most attractive features of such fibre are that they are cheap, widely available and most importantly can be modified to a cost – effective and environmental friendly green products with improvised physical properties like thermal, mechanical etc. The combination of bio-polymer and jute fibre crosslinked with glutaraldehyde can lead to a bio based polymer composites and their properties can be improved by dispersing the nanofillers into their matrix.

Nano technology deals with the material in sub-micron level. It has been successfully applied in many fields. Nano structured material will have substantially different properties from a larger dimensional material (conventional composite) of same composition. Nano materials can provide reinforcing efficiency because of their
high aspect ratio. The properties of nanocomposites are greatly influenced by the size scale of its component phases and degree of mixing between the two phases. Without proper dispersion the nano materials will not offer improved mechanical properties over that of conventional composites. Among the various nanofillers, clay, ZnO, TiO$_2$ and cellulose whisker are extensively used for modification of conventional polymer composite. The immobilization of nanoparticles results in high interfacial area between the matrix and the filler. This in turn assists the polymer nanocomposites to show high thermo – mechanical performance.

Keeping in mind the advantages of bio based polymer and increasing demand of a greener products, it is proposed to develop a bio based polymer nanocomposites comprising of soy flour/starch, jute, glutaraldehyde, and clay/ZnO/TiO$_2$/cellulose whisker either alone or in combination for improved thermo – mechanical properties. Efforts will be made to develop a treatment/process which can confer properties like fire retardation, UV resistance etc. all at the same time.

**The plan of work has been segregated as follows:-**

The plan of research is divided into different parts. Following the standard procedure mentioned in the literature the main approaches will be done as given below:

- Surface modification of the jute fabric.
- Preparation of bio-nanocomposites employing natural polymers (like soy flour and starch), jute fabric, plasticizer, clay, cross linking agent and other additives (like TiO$_2$, ZnO, Cellulose whisker etc.).
- Dispersion of clay and other additives in deionised water using magnetic stirrer, mechanical stirrer and ultra sonicator. Mixing of the slurry containing clay and other additives into dispersed soy flour/starch etc. for preparation of polymeric slurry. Impregnation of jute fabric with polymeric slurry followed by drying.
- Characterization the composites using FT-IR, tensile tester, thermogravimetric analyser (TGA), X-ray diffractometer (XRD), scanning electron microscope (SEM), transmission electron microscope (TEM) etc. Evaluation of properties in terms of moisture absorption, dimensional stability, etc.
- Study of the biodegradability of the nanocomposites.
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[138] http://braungroup.beckman.illinois.edu/IanBlitz.html (20-08-2014)


