Chapter 1 Introduction

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Progresses in the field of materials science and technology have given birth to fascinating and wonderful materials known as 'composites'. The aim of composites is to develop products with unique properties that cannot be attained from individual constituents. They are developed because no single, homogeneous structured material can be found that has all of the desired properties for a given application [1]. A composite material can provide superior and unique mechanical and physical properties because it combines the most desirable properties of its constituents while suppressing their least desirable properties.

1.1 Composites and fillers
Composites consist of two (or more) distinct constituents or phases, which when combined result in a material with entirely different properties from those of the individual components. Typically, a manmade composite would consist of a reinforcement phase of stiff, strong material, frequently fibrous in nature, embedded in a continuous matrix phase (Figure. 1.1). Two of the main functions of the matrix are to transmit externally applied loads, via shear stresses at the interface, to the reinforcement and to protect the latter from environmental and mechanical damage [2]. The advantage of such a coupling is that the high strength and stiffness of fibers may be exploited.

![Figure 1.1 Formation of composite](image)

Traditionally, fillers were considered as additives, which due to their unfavorable geometrical features, surface area or surface chemical composition, increases the strength of polymer. Their major contribution was in lowering the cost of materials by replacing the more expensive polymer. The term reinforcing filler has been coined to describe discontinuous additives, the form, shape, and/or surface chemistry of which have been
suitably modified with the objective of improving the mechanical properties of the polymer, particularly strength. Fillers exist in a variety of systems such as organic, inorganic, biological, biomimetic, and polymeric materials [3]. On the one hand the replacement aims at reducing costs, on the other, a synergistic effect of different fillers might be obtained due to the complicated cooperative interactions.

Inorganic reinforcing fillers are stiffer than the matrix and deform less. This causes an overall reduction in the matrix strain, especially in the vicinity of the particle and hence particle matrix adhesion is poor. As shown in Figure.1.2, the fiber “pinches” the polymer in its vicinity, reducing strain and increasing stiffness [4]. Reinforcing fillers are characterized by relatively high aspect ratio, $\alpha$, defined as the ratio of length to diameter for a fiber, or the ratio of diameter to thickness for platelets and flakes. For spheres, which have minimal reinforcing capacity, the aspect ratio is unity. A useful parameter for characterizing the effectiveness of a filler is the ratio of its surface area, $A$, to its volume, $V$, which needs to be as high as possible for effective reinforcement. In developing reinforcing fillers, the aims of process or material modifications are to improve their compatibility and interfacial adhesion with the chemically dissimilar polymer matrix. Such modifications may enhance and optimize not only the primary function of the filler but may also introduce or enhance additional functions. The main problem of using inorganic fillers is that they are very expensive.

![Figure. 1.2 A cylindrical reinforcing fiber embedded in polymer matrix (a) under undeformed state and (b) under tensile load](image-url)
1.1.1 Classification of Composites
According to the nature of the reinforcement used, composites are classified into particulate, fibrous, laminate and hybrid composites.

Particulate reinforcement
Particulate fillers are employed to improve high temperature performance, reduce friction, increase wear resistance and to reduce shrinkage [5]. In many cases particulate fillers are used to reduce the cost, under these conditions the additive is filler, whereas when a considerable change in the properties of the composite occurs, the additive is reinforcement. The particles will also share the load with the matrix, but to a lesser extent than a fibre. A particulate reinforcement will therefore improve stiffness but will not generally strengthen. Hard particles in a brittle matrix will cause localized stress concentrations in the matrix, which will reduce the overall impact strength.

Fibrous reinforcement
Fibrous reinforcement represents physical rather than a chemical means of changing a material to suit various engineering applications [6]. The measured strength of most materials is much less than that predicted by theory because flaws in the form of cracks perpendicular to the applied load are present in bulk materials. Fibres of non polymeric materials have much higher longitudinal strengths in this form because the larger flaws are not generally present in such small cross sectional areas. In the case of fibres from polymeric materials such as Kevlar, the orientation of the polymeric molecules along the long dimension produces strength in that direction. The fibres dispersed in the matrix may be continuous or discontinuous. In continuous fibre reinforcement, the transference of the load from matrix to the fibres will be easy and very effective whereas in
discontinuous (or short) fibre reinforcement, the fibres must be of sufficient length to have load transference effectively (Figure. 1.3 (a)). In short fibre composites, the properties of the composite vary with fibre length. Most continuous (long) fibre composites in fact contain fibres that are comparable in length to the overall dimensions of the composite part.

**Laminates**

A laminate is fabricated by stacking a number of laminas in the thickness direction (Figure. 1.3 (b)). Generally three layers are arranged alternatively for better bonding between reinforcement and the polymer matrix, for example plywood and paper. These laminates can have unidirectional or bi-directional orientation of the fibre reinforcement according to the end use of the composite. A hybrid laminate can also be fabricated by the use of different constituent materials or of the same material with different reinforcing pattern. In most of the applications of laminate composite, man made fibres are used due to their good combination of physical, mechanical and thermal behaviour.

**Hybrid composites**

Composite materials incorporated with two or more different types of fillers especially fibres in a single matrix are commonly known as hybrid composites (Figure. 1.3 (c)). Hybridisation is commonly used for improving the properties and for lowering the cost of conventional composites. There are different types of hybrid composites classified according to the way in which the component materials are incorporated. Hybrids are designated as i) sandwich type ii) interply iii) intraply and iv) intimately mixed [7]. In sandwich hybrids, one material is sandwiched between layers of another, whereas in interply, alternate layers of two or more materials are stacked in regular manner. Rows of two or more constituents are arranged in a regular or random manner in intraply hybrids while in intimately mixed type, these constituents are mixed as much as possible so that no concentration of either type is present in the composite material.
1.1.2 Factors affecting the performance of composites

Many factors combine to affect the properties of a composite material. However, the properties of composites are dictated by the intrinsic properties of the constituents. The two most important factors that affect the performance of composites are (i) The architecture of fillers and (ii) filler–matrix interface

(i) Filler architecture

Filler geometry to some extent is influenced by the way in which the fillers are extracted and processed. The aspect ratio (the ratio of filler length to diameter) is an important characteristic for any materials to be used as fillers. Thus fillers with high aspect ratio are long and thin, while that with low aspect ratio are shorter in length and broader in the
transverse direction. These high aspect ratio fillers tend to impart more strength to the matrix as compared to the low aspect ratio fillers.

(ii) The filler–matrix interface

The interface between filler and matrix is also crucial in terms of composite performance. The interface serves to transfer externally applied loads to the reinforcement via shear stresses over the interface. Controlling the ‘strength’ of the interface is very important. Clearly, good bonding is essential if stresses are to be adequately transferred to the reinforcement and hence provide a true reinforcing function. Owing to the general incompatibility between natural fillers and most matrix polymers, methods of promoting adhesion are frequently needed. Several approaches have been explored, including chemical modification of the filler prior to composite manufacture and introducing compatibilizing agents to the polymer/filler during processing.

1.2 Natural rubber (NR),

Natural rubber is chemically cis 1, 4 polyisoprene; its structure is given in figure 1.4. It is an elastomer (an elastic hydrocarbon polymer) that was originally derived from latex, a milky colloid produced by some plants. The commercial major source of natural rubber latex is the para rubber tree (Hevea brasiliensis). Apart from this other plants containing latex include gutta-percha (Palaquium gutta),[8] rubber fig (Ficus elastica), Panama rubber tree (Castilla elastica), spurges (Euphorbia spp.), lettuce, common dandelion (Taraxacum officinale), Russian dandelion (Taraxacum kok-saghyz), Scorzonera (taus-saghyz), and guayule (Parthenium argentatum). Although, these are not the major sources of natural rubber. To obtain latex the plants are tapped, that is, an incision made into the bark of the tree and the sticky, milk colored latex sap is collected and refined into a usable rubber. Further it is vulcanized, a process by which the rubber is heated in the presence of sulfur, to improve its resilience, elasticity and durability. The purified form of natural rubber is known as polyisoprene, which can also be produced synthetically. NR is normally very stretchy and flexible and extremely waterproof and hence is used extensively in many applications and products, as is synthetic rubber. The use of rubber is widespread, ranging from household to industrial products. Tires and tubes are the largest
consumers of rubber. The unique mechanical properties of NR result from both its highly stereoregular microstructure and the rotational freedom of the \( \alpha \)-methylene C-C bonds. While the entanglements resulting from the high molecular weight which contributes to its high elasticity. The properties of NR can be tailored by the addition of fillers of varying surface chemistry and aggregate size/aspect ratio to suit the application concerned [9]. The performance of a polymer is determined by various factors, including the nature of the individual components, type of vulcanizing agent, processing parameters, and, to a certain extent, the application for which it is intended [10,11].

![Structure of natural rubber](image)

**Figure.1.4 Structure of natural rubber**

### 1.2.1 Fillers used in natural rubber

Carbon black (C-black) and silica are the main fillers used in the compounding of NR [5]. For C-black filled rubbers, reinforcement is generally attributed to the nanoscale particle size, large specific surface area, high structure degree of C-black and, the formation of extensive rubber-C-black interactions [12,13]. Generally, on addition of fillers the increase in modulus is achieved at the expense of strength and elongation at break. There are some exceptions, particularly C-black, which induces an increase in both strength and modulus. We already know that C-black is produced by the incomplete combustion of heavy petroleum products such as FCC tar, coal tar, ethylene cracking tar, and a small amount from vegetable oil. Due to its origin from petroleum, it causes pollution and gives black color to the rubber. Recently, International Agency for Research on Cancer (IARC) evaluated that, it is possibly carcinogenic to humans. Hence research was focused on the development of other reinforcing agents to replace C-black in rubber compounds. Silica
and other types of fillers have a weaker polymer-filler interaction and are extensively used where a high degree of reinforcement is not essential [14,15].

Sombatsompop et al., [16] introduced untreated fly ash particles into NR vulcanizates, and found that the mechanical properties of fly ash-filled NR vulcanizates appeared to be very similar to those of commercial silica-filled vulcanizates at silica content of 0-30 phr. Above these concentrations, the properties of the fly ash-filled compounds remained unchanged, the fly ash particles being used as an extender. David et al., [17] studied the mechanical properties of twaron/natural rubber composites.

**Carbon black (C-black)**

Carbon black is a colloidal form of elemental carbon. It owes its reinforcing character to its colloidal morphology, the size and shape of the ultimate units, and to its surface properties. The particles of carbon black are not discrete but are fused clusters of individual particles. Carbon black is prepared by incomplete combustion or by thermal cracking of hydrocarbons. They are classified into furnace blacks, channel blacks, thermal blacks, lamp black and acetylene black depending on their method of manufacture. The major types of rubber reinforcing carbon blacks are manufactured by the furnace process. The predominant purpose of furnace type carbon blacks in elastomers is the reinforcement they impart to the vulcanisates [18,19]. Carbon black has reactive organic groups on the surface that cause affinity to rubber. Incorporation of carbon black into rubber gives enhanced modulus, improved fatigue, abrasion resistance and better overall technological properties. Details of a range of furnace blacks generally used for rubber reinforcement are given in table 1.1 [20].

**Kaolin**

Kaolin or china clay consists chiefly of the mineral kaolinite and has been selected based on its abundant availability and low cost to favor synthesis of a product having industrial utility.

Kaolinite \([\text{Al}_4\text{Si}_4\text{O}_{10}(\text{OH})_8]\) is a dioctahedral aluminosilicate, which is built with a tetrahedral \(\text{SiO}_4\) sheet and an octahedral \(\text{AlO}_4(\text{OH})_2\) sheet linked together by oxygen atoms. The crystal consists of several of these layers extending in a two-dimensional
array, which are stacked along the c-axis and held together essentially by (i) hydrogen bonds between the external hydroxyls of the octahedral sheet and the basal oxygens of the adjacent layer tetrahedral sheet, (ii) van der Waal’s attractive forces, and (iii) electrostatic interactions due to net fractional charges of opposite sign on each basal surface (Figure. 1.5). Although the surface silicate sheet of kaolinite is not particularly amenable to covalent attachment, the relatively reactive aluminol surface is similar to that in the case of montmorillonopkites and has the potential to be functionalized via Al-O-R bonds. In fact, a number of polar organic molecules such as urea, dimethyl sulfoxide, formamide, hydrazine, fatty acid salt, potassium acetate, and so on, are reportedly able to disrupt the interlayer bonding between the adjacent siloxane and hydroxy aluminium surfaces and to penetrate the interlayer space to form a complex by hydrogen bonding to both surfaces [21]. Such a process is known as intercalation. Successful intercalation agents decrease the electrostatic attraction between the lamellae by causing an increase in the dielectric constant when the compounds penetrate between the layers [22].

<table>
<thead>
<tr>
<th>Name</th>
<th>Abbreviation</th>
<th>ASTM Desig.</th>
<th>Particle size (nm)</th>
</tr>
</thead>
<tbody>
<tr>
<td>Super abrasion furnace</td>
<td>SAF</td>
<td>N110</td>
<td>20-25</td>
</tr>
<tr>
<td>Intermediate SAF</td>
<td>ISAF</td>
<td>N220</td>
<td>24-33</td>
</tr>
<tr>
<td>High abrasion furnace</td>
<td>HAF</td>
<td>N330</td>
<td>28-36</td>
</tr>
<tr>
<td>Easy processing channel</td>
<td>EPC</td>
<td>N300</td>
<td>30-35</td>
</tr>
<tr>
<td>Fast extruding furnace</td>
<td>FEF</td>
<td>N550</td>
<td>39-55</td>
</tr>
<tr>
<td>High modulus furnace</td>
<td>HMF</td>
<td>N683</td>
<td>49-73</td>
</tr>
<tr>
<td>Semi-reinforcing furnace</td>
<td>SRF</td>
<td>N770</td>
<td>70-96</td>
</tr>
<tr>
<td>Fine thermal</td>
<td>FT</td>
<td>N880</td>
<td>180-200</td>
</tr>
<tr>
<td>Medium thermal</td>
<td>MT</td>
<td>N990</td>
<td>250-350</td>
</tr>
</tbody>
</table>
1.2.2 Blends and composites of natural rubber

The blending of rubbers produces new materials with a wide range of applications because they have the potential to combine the attractive properties of both the constituents in the blends. Usually, the outdoor properties of high diene rubbers such as polybutadiene (BR), nitrile rubber (NBR), styrene-butadiene rubber (SBR) or NR can be very significantly improved by the incorporation of low-unsaturated rubbers such as ethylene propylene diene monomer (EPDM) rubber [23,24,25,26,27]. Arayapranee and Rempel [28] studied the properties of NR/EPDM blends with or without Methyl Methacrylate-Butadiene-Styrene (MBS) as a compatibilizer. They found out that the incorporation of the EPDM in NR exhibits better stable mechanical properties as compared to the NR rich blend due to good thermal and weathering resistance of EPDM. The addition of graft copolymer into the 50/50 NR/EPDM blend increased the Mooney viscosity with an increase in graft copolymer concentration. The curing time became shorter with increasing graft copolymer content due to an increased compatibilizer interaction between NR and EPDM. Consequently, the tensile strength and elongation at break show improvement by the addition of the graft copolymer. Sombatsompop and Kumnuantip [29,30] introduced tire- tread reclaimed rubber into two natural rubber
grades and investigated various properties of the blends. They found that the Mooney number, shear viscosity and cure rate increased with reclaimed content, while the cure time was independent of the reclaimed content. Sreeja & Kutty [31] studied the cure characteristics and mechanical properties of NR/RR blends using EV system. They observed that the scorch time and tensile properties of the blends reduced with the reclaimed loadings. Hanafi et al., [32] checked the tensile properties of natural rubber filled with halloysite tubes and found out that the optimum tensile strength was obtained at 20 phr.

1.2.3 Methods of preparation of composites

Various commercial methods such as extrusion, injection molding and casting or compression molding are used to prepare composites. Generally two methods are used to prepare composites of natural rubber.

(i) Solution casting and (ii) Dry blending process

(i) Solution casting process

In this process polymer solution along with filler is stirred for long time to obtain homogenous suspension. The solvent is then evaporated at elevated temperature. This method has some disadvantages such as high consumption of solvent and time and it is not used commercially.

(ii) Dry blending process

This process is carried out on a two roll mixing mill where polymer along with filler is mixed until homogenous mixing occurs. It is then followed by vulcanization to obtain composites. However, this method is superior because (i) it is environmentally safe due to absence of organic solvents and (ii) it is compatible with the current industrial processes, such as extrusion and injection molding. Also, like other methods this method yields composites with structures ranging from intercalated to exfoliate, depending on the degree of penetration of the polymer chains [33].
1.3 Biocomposites of natural rubber

Biocomposites are composite materials comprising one or more phase(s) derived from a biological origin. In terms of the reinforcement, this could include plant fibres such as cotton, flax, hemp and the like, or fibres from recycled wood or waste paper, or even by-products from food crops. Fowler et al., [34] studied the technology, environmental credentials and market forces of biocomposites. They observed that there is a huge range of potential reinforcing fibers/fillers and an extensive range of processing options to ensure the right fiber at the right price. In parallel, significant developments have been seen in the realm of biopolymers in recent years due to more environmentally aware consumers, increased price of crude oil and global warming. They are used in variety of applications, like therapeutic aids, medicines, coatings, food products and packing materials.

The manufacture of true biocomposites demands that the matrix be made predominantly from renewable resources, although the current state of biopolymer technology dictates that synthetic thermoplastics and thermosets dominate commercial biocomposite production.

1.3.1 Polysaccharide as fillers

Natural fibers are pervasive throughout the world in plants such as grasses, reeds, stalks, and woody vegetation. They are also referred to as cellulosic fibers, related to the main chemical component cellulose, or as lignocellulosic fibers, since the fibers usually often also contain a natural polyphenolic polymer, lignin, in their structure. Results suggest that these agro-based fibers are a viable alternative to inorganic/ mineral based reinforcing fibers The use of lignocellulosic fibers derived from annually renewable resources as a reinforcing phase in polymeric matrix composites provides positive environmental benefits with respect to ultimate disposability and raw material use [35]. Compared to inorganic fillers, the main advantages of natural materials are listed below:

- wide variety of fillers available throughout the world
- nonfood agricultural based economy
low energy consumption
- high specific strength and modulus
- comparatively easy processability due to their nonabrasive nature, which allows high filling levels, resulting in
- significant cost savings
- relatively reactive surface, which can be used for grafting specific groups.

In addition, the recycling by combustion of natural materials filled composites is easier in comparison with inorganic fillers systems. Therefore, the possibility of using natural fillers in the plastic industry has received considerable interest. Automotive applications display strong promise for natural fiber reinforcements [36,37]. Potential applications of agrofiber based composites in railways, aircraft, irrigation systems, furniture industries, and sports and leisure items are currently being researched [38]. Various researchers have tried to use biofillers in place of commercially used fillers. A variety of fibers like sisal [39], bamboo [40], short coir fibres [41] etc. have been used to prepare biocomposites of NR. However, the use of polysaccharide as fillers or reinforcing agents in NR has not been extensively reported in the literature [42,43]. Carvalho et al., [44] prepared starch/NR composite by blending NR latex and starch paste. Jobish et al., [45] studied the mechanical and thermal properties of chitosan/natural rubber composites and concluded that the thermal stability of chitosan increases on formation of blend with natural rubber. Fernandes et al., [46] synthesized natural rubber/expoxidized natural rubber/cellulose II blend and found out that vulcanization increases in the presence of cellulose. Zaman et al., [47] synthesized jute/natural rubber composite and concluded that this composite showed excellent biodegradable properties. There have been many attempts investigating effects of the addition of rice husk ash into rubber [48,49].

Use of polysaccharide such as starch, cellulose and chitin have received significant importance due to their
- Abundance availability
- Low cost
- Renewability
- Biodegradability and
- Non-toxic nature
1.3.2 Starch

Starch is a natural, renewable, and biodegradable polymer produced by many plants as a source of stored energy. It is the second most abundant biomass material in nature and is found in plant roots, stalks, crop seeds, and staple crops such as rice, corn, wheat, tapioca, and potato [50,51]. Worldwide, the main sources of starch are maize (82%), wheat (8%), potatoes (5%), and cassava (5%) [52]. The starch powder consists of microscopic granules with diameters ranging from 2 to 100 μm, depending on the botanic origin, and with a density of 1.5. The basic formula of this polymer is \((C_6H_{10}O_5)_n\), and the glucose monomer is called α-D-glycopyranose (or α-D-glucose) when in cycle. Depending on their botanic origin, starch raw materials have different conversion factors, size, shape, and chemical content. It consists of mainly two glucosidic macromolecules: amylose and amylopectin (Figure 1.6). In most common types of starch the weight percentages of amylose range between 72 and 82%, and the amylopectins range from 18 to 28%. However, some mutant types of starch have very high amylose content (up to 70% and more for amylomaize) and some very low amylose content (1% for waxy maize).

Amylose is defined as a linear molecule of glucose units linked by (1-4) α-D-glycoside bonds, slightly branched by (1-6) α-linkages. Amylopectin is a highly branched polymer consisting of relatively short branches of α-D-(1-4) glycopyranose that are interlinked by α-D-(1-6)-glycosidic linkages approximately every 22 glucose units [53].

![Figure. 1.6 Structure of starch](image)
1.3.3 Cellulose

Cellulose is the most abundant renewable organic material produced in the biosphere, having an annual production over $7.5 \times 10^{10}$ tons [54]. Cellulose is widely distributed in higher plants, in several marine animals (for example, tunicates), and to a lesser degree in algae, fungi, bacteria, invertebrates, and even amoeba (protozoa), for example, *Dictyostelium discoideum*. In general, cellulose is a fibrous, tough, water-insoluble substance that plays an essential role in maintaining the structure of plant cell walls. It was first discovered and isolated by Anselme Payen in 1838, [55] and since then, multiple physical and chemical aspects of cellulose have been extensively studied. Several reviews have already been published reporting the state of knowledge of this fascinating polymer [56,57]. Regardless of its source, cellulose can be characterized as a high molecular weight homopolymer of -1,4-linked anhydro-D-glucose units in which every unit is corkscrewed $180^\circ$ with respect to its neighbors, and the repeat segment is frequently taken to be a dimer of glucose, known as cellobiose (Figure 1.7). Each cellulose chain possesses a directional chemical asymmetry with respect to the termini of its molecular axis: one end is a chemically reducing functionality (i.e., a hemiacetal unit) and the other has a pendant hydroxyl group, the nominal nonreducing end.

Figure 1.7 Structure of cellulose
1.3.4 Chitin

Chitin is the other polysaccharide used extensively. It constitutes the structure of the external skeleton in shellfish and insects and is one of the major components of the fibrous material of cellular walls in mushrooms and algae [58,59]. In terms of structure, chitin may be compared to the polysaccharide cellulose and, in terms of function, to the protein keratin. It has also proven useful for several medical and industrial purposes. It is a modified polysaccharide that contains nitrogen; it is synthesized from units of N-acetylglucosamine (to be precise, 2-(acetylamino)-2-deoxy-D-glucose). These units form covalent β-1,4 linkages (similar to the linkages between glucose units forming cellulose). Therefore, it may be described as cellulose with one hydroxyl group on each monomer substituted with an acetyl amine group (Figure 1.8). This allows for increased hydrogen bonding between adjacent polymers, giving the chitin-polymer matrix increased strength. In its pure form, chitin is leathery, but in most invertebrates it occurs largely as a component of composite materials. It is used in industry in many processes. It is used as an additive to thicken and stabilize foods and pharmaceuticals. It also acts as a binder in dyes, fabrics, and adhesives. Industrial separation membranes and ion-exchange resins can be made from chitin. It has some unusual characteristics that accelerate healing of wounds in humans. This combined with, its flexibility and strength makes it favorable for use as surgical thread. Its biodegradability is such that it wears away with time as the wound heals.

Figure. 1.8 Structure of chitin
1.3.5 Disadvantages of polysaccharide as fillers

- Despite these attractive properties, natural fillers are used only to a limited extent in industrial practice due to difficulties associated with surface interactions. The inherent polar and hydrophilic nature of polysaccharide and the nonpolar characteristics of most of the thermoplastics result in difficulties in compounding the filler and the matrix and, therefore, in achieving acceptable dispersion levels, which results in inefficient composites.

- Moreover, the processing temperature of composites is very low because these biofillers start to degrade at high temperature (around 230 °C). This limits the type of thermoplastics that can be used in association with polysaccharide fillers to commodity plastics such as polyethylene, polypropylene, poly(vinyl chloride), and polystyrene.

- Another drawback of biofillers is their high moisture absorption and the resulting swelling and decrease in mechanical properties. Moisture absorbance and corresponding dimensional changes can be largely prevented if the hydrophilic filler is thoroughly encapsulated in a hydrophobic polymer matrix and there is good adhesion between both components. However, if the adhesion level between the filler and the matrix is not good enough, a diffusion pathway can preexist or can be created under mechanical solicitation. The existence of such a pathway is also related to the filler connection and therefore to its percolation threshold.

Hence, several researchers have modified these biopolymers into nanosize for better encapsulation in hydrophobic polymers.

1.4 Nanocomposites of natural rubber

Recently there is considerable interest in polymer composites having rigid particles, with at least one dimension in the nanometer range, as fillers. This class of materials which has attracted the attention of academicians as well as industrialists is known as ‘Nanocomposites’.
1.4.1 Advantages of nanofillers

Nanofillers have strong reinforcing effects, and studies have also shown their positive impact in barrier packaging. The pioneer work on nanocomposites that was initiated by researchers at Toyota in the early 1990’s created nanoclay reinforced polymers, opening a new research path on composites. Due to their nanometric size effect, these composites have some unique properties. Nanoparticles (fills) not only enhance mechanical properties, but also physical properties. Their properties depend on the nature and effectiveness of interactions at the interfacial region, that is, on both the surface area and the dispersion of the particles. The surface area depends on the dimensions of the dispersed particles from 0.5 to 250 g/m² for natural fibers and up to 1000 g/m² for cellulose nanofibrils, exfoliated clays, and carbon nanotubes [60].

1.4.2 Classification of nanoparticles

One of the most wide sprayed classifications of nanoparticles is based on particle shape:

(i) **Particulate nanoparticles**, such as metallic nanoparticles or carbon black are generally iso-dimensional and show moderate reinforcement due to their low aspect ratio. They are used to enhance resistance to flammability and decrease permeability or costs.

(ii) **Elongated particles** that show better mechanical properties due to their high aspect ratio. Such particles include cellulose nanofibrils (also called whiskers or nanocrystals) and carbon nanotubes.

(iii) **Layered particles**, like nanoclays, also referred to as layered polymer nanocomposites. This latter family is the most used industrially and can show different degrees of dispersion, as shown in Figure. 1.9, namely, intercalated nanocomposites (intercalated polymer chains between layered nanocomposites), exfoliated nanocomposites (separation of individual layers), and flocculated or phase-separated nanocomposites, which are also called microcomposites and consequently show the poorer physical properties. Exfoliation is sought by nanocomposite
producers as it gives, by far, the best results. In light of reviewed classifications for fillers, biopolymer nanocrystals fit the last category, “layered particles”.

Figure. 1.9 Schematic representation of three types of polymer composites

1.4.3 Natural rubber/clay nanocomposites
Polymer matrix/clay-based nanocomposites have largely dominated the polymer literature [61,62,63,64,65], since their first applications as reinforcement in the automotive industry. The packaging industry has focused its attention mainly on layered inorganic solids like clays and silicates due to their availability, significant enhancement, and relatively simple processability [66]. Several studies have reported the effectiveness of nanoclay to decrease water vapor [67,68,69] and oxygen permeabilities [70,71,72] and improve mechanical properties. Attention has been more recently directed toward organic and renewable fillers. The use of clay minerals such as montmorillonite (MMT) [73,74] and organoclays [75,76,77] has also been extended to NR, and they seem to be a potential substitute to carbon black. Hrachova et.al., [78] studied the effect of MMT modification on mechanical properties of vulcanized natural rubber composites and found out that the mechanical properties improved by addition of MMT to natural rubber. Usuki et al., [79,80] first reported the superior nylon 6 MMT nanocomposites, polymer-layered silicate nanocomposites have attracted great interest from researchers due to their academic and industrial importance [81,82]. The special structure of MMT play
important roles in improving mechanical, thermal and diffuse barrier properties of polymer-layered silicate nanocomposites [83,84,85]. Many polymer matrices have been used to prepare polymer-MMT nanocomposites (such as polyimide, polyurethane, polypropylene, polyaniline) [86,87,88,89,90]. Due to poor compatibility of MMT with organic monomers and polymer matrices, it is necessary to modify MMT. At present, alkylammonium and alkylphosphonium are used widely to treat MMT [91,92]. To further improve the properties of polymer-clay nanocomposites, alternate functional modifiers are being used to prepare polymer-clay nanocomposites [93,94,95,96].

Single-walled carbon nanotubes (SWNTs) have been widely used with different kinds of polymers. Some work has been done on incorporating the SWNTs in rubber. The concept of nano-sized filler-reinforced elastomer was demonstrated by the incorporation of nanoparticles in a rubbery polymer matrix such as SWNTs into silicone rubber [97]. Although rubbers are known to be a thermal and electrical insulator, incorporation of conductive fillers into these materials could produce composite materials with some electrical conductivity. The interest in ceramic particle reinforced composites has begun a decade ago. SiC nanoparticles have become popular recently as the reinforcement phase for polymer or ceramic matrices [98,99,100,101]. In the last few years, SiC has attracted more interest due to its desirable properties for potential applications as semiconductor devices [102]. Niihara [103] has reported that nano-sized (20-300 nm) ceramic composites provided considerably higher fracture toughness and strength than conventional ceramic composite. K.Kueseng and K.I.Jacob [104] studied the natural rubber nanocomposites with SiC nanoparticles and carbon nanotubes.

1.5 Bionanocomposites of natural rubber

Bionanocomposites are novel materials born out of the growing interest in nanomaterials and in the development of materials derived from renewable sources [105]. Polysaccharide such as starch, cellulose and chitin are potential renewable sources of nanosized reinforcements. The use of starch is receiving significant attention because of the abundant availability of starch, low cost, renewability, biocompatibility, biodegradation and non-toxicity [106].
1.5.1 Polysaccharide nanoparticles
Among the biopolymers cellulose NPs were used first as reinforcing phase by Favier et al., in 1995 [107], new nanocomposites materials with original properties were obtained using cellulose whiskers and micro fibrillated cellulose and led to the development of studies on chitin whiskers [108, 109, 110] and starch nanocrystals [111, 112, 113, 114, 115] by analogy. In comparison to nanoclay, studies on these bionanofillers are scarce.

1.5.2 Preparation of starch nanocrystal

Structure of starch
Starch occurs as a flour-like white powder insoluble in cold water. This powder consists of microscopic granules with diameters ranging from 2 to 100 μm, depending on the botanic origin, and with a density of 1.5 [116]. Starch structure has been under research for years, and because of its complexity, a universally accepted model is still lacking. However, in this past decade a model seems predominant. It is a multiscale structure, shown in Figure 1.10.

![Multiscale structure of starch](image)

Figure. 1.10 Multiscale structure of starch
Many interesting reviews and articles on structure of starch have been published. Starch’s composition was first determined by studying the residue of its total acid hydrolysis. As discussed earlier it consists of mainly two glycosidic macromolecules amylopectin and amyllose. Minor components associated with starch granules are of three types:

(i) cell-wall fragments,
(ii) surface components, and
(iii) internal components.

The main constituents of surface components are proteins, enzymes, amino acids, and nucleic acids, whereas internal components are composed mainly of lipids. The proportion of these components depends on the botanical origin.

An X-ray diffraction study showed that starch is a semicrystalline polymer [117]. Starch granules consist of concentric alternating amorphous and semicrystalline growth rings. They grow by apposition from the hilum of the granule. The number and thickness of these layers depends on the botanical origin of starch. They are thought to be 120-400 nm thick. Details on the structure of the amorphous growth ring are not found in literature.

More recently SEM observations have enabled the observation of blocklets structure [118,119,120]. Although the blocklet concept is not commonly mentioned in the literature, it was heavily supported and brought back to discussion by Gallant et al., [121]. They suggested that both semicrystalline and amorphous growth rings are subdivided into respectively large (diameter 20-500 nm for wheat) and small (25 nm) spherical blocklets. More recently, Tang et al., [122] supposed the blocklets of the amorphous region and the surface pores (as mentioned earlier) to be defective blocklets, with lower branching molecules. On average, two endto- end blocklets would constitute a single semicrystalline growth ring. These blocklets have an average size of 100 nm in diameter and are proposed to contain 280 amylopectin side chain clusters [123].

Schematically, the semicrystalline growth rings consist of a stack of repeated crystalline and amorphous lamellae. The thickness of the combined layers is 9 nm regardless the botanic origin [124]. In reality, it is believed that the crystalline region is created by the interwining of chains with a linear length above 10 glucose units to form double helixes [125] that are packed and form the crystallites, and the amorphous region corresponds to branching points.
Tang et al., [107] illustrated this model, making amylopectin the backbone of the blocklet structure. Amylose molecules are thought to occur in the granule as individual molecules, randomly interspersed among amylopectin molecules and in close proximity with one another, in both the crystalline and amorphous regions [92]. Depending on the botanic origin of starch, amylose is preferably found in the amorphous region (e.g., wheat starch), interspersed among amylopectin clusters in both the amorphous and the crystalline regions (e.g., normal maize starch), in bundles between amylopectin clusters, or cocrystallized with amylopectin (e.g., potato starch) [126].

Native starches contain between 15 and 45% of crystalline material. Depending on their X-ray diffraction pattern, starches are categorized in three crystalline types called A, B, and C. Hizukuri et al., [127,128] postulated that amylopectin chain length was a determining factor for crystalline polymorphism. Imberty et al., [129,130] proposed a model for the double helices packing configuration to explain difference between A and B types starches. A-type structures are closely packed with water molecules between each double helical structure, whereas B-types are more open and water molecules are located in the central cavity formed by six double helices, as shown in Figure.1.11. It was later envisaged that branching patterns of the different types of starch may also differ [131]. It was suggested that the B-type amylopectin branching points are clustered, forming a smaller amorphous lamella, whereas A-type amylopectin branching points are scattered in both the amorphous and the crystalline regions, giving more flexibility to double helices to pack closely. Gerard et al., [132] recently confirmed that the distance between two α-(1-6) linkages and the branching density inside each cluster are determining factors for the development of crystallinity in starch granules. Clusters with numerous short chains and short linkage distance produce densely packed structures which crystallizes into the A allomorphic type. Longer chains and distances lead to a B-type. The C-type starch pattern has been considered to be a mixture of both A- and B-types because its X-ray diffraction pattern can be resolved as a combination of the previous two. It has been suggested by Bogracheva et al., [133] that C-type starch granules contain both types of polymorph: the B-type at the center of the granule and the A-type at the surrounding.
Figure. 1.11 Double helixes packing configuration of starch according to crystalline type.

Several attempts of structural characterization of C-type starch were conducted using acid hydrolysis by Wang et al., [134,135]. They revealed that the core part of C-type starch was preferably hydrolyzed and that hydrolyzed starch showed an A-type diffraction pattern, suggesting that B-type polymorphs consists of mainly the amorphous regions and are more readily hydrolyzed than A-types constituting mainly the crystalline region. This is in agreement with the previous conclusions of Jane et al., [98] that B-type starches are more acid-resistant than A-types. These conclusions are of importance for starch nanocrystal production. Another V-type was also identified as the result of amylase being complexed with other substances such as iodine, fatty acid, emulsifiers, or butanol. This crystalline form is characterized by a simple left helix with six glucose units per turn [136]. Jenkins and Donalds [137] concluded that an increase in amylose content has the effect of increasing the size of the crystalline lamella and acts to disrupt their packing. Two mechanisms to explain this disrupting have been introduced: first, cocrystallization between amylose and amylopectin chains and, second, the penetration of amylose into amorphous regions.

Synthesis of polysaccharide nanoparticles such as starch and cellulose is carried out using acid hydrolysis. Various strong acids such as sulfuric acid, hydrochloric acid, phosphoric acid were employed to polysaccharide for acid hydrolysis.

First interest in starch nanocrystals has been studied by analogy with cellulose whiskers to be used as reinforcing fillers in a matrix. In 1996, Dufresne et al., [138] reported a method for producing “microcrystalline starch” and which they reported to be agglomerated particles of a few tens of nanometers in diameter. The procedure consisted of hydrolyzing starch (5 wt %) in a 2.2 N HCl suspension for 15 days. Because it was
shown that classical models for polymers containing spherical particles could not explain the reinforcing effect of microcrystals, further studies on the morphology of these microcrystals were conducted by Dufresne and Cavaille in light of aggregate formation and percolation concept [139]. In 2003, Putaux et al., [140] revealed the morphology of “nanocrystals resulting from the disruption of the waxy maize starch granules by acid hydrolysis”. After 6 weeks of hydrolysis, TEM observations (Figure. 1.12) showed (a) a longitudinal view of lamellar fragments consisting of a stack of elongated elements with a width of 5-7 nm and (b) a planar view of an individualized platelet after hydrolysis. Shapes and lateral dimensions were derived from the observation of individual platelets in planar view: a marked 60-65 °C acute angles for parallelepipedal blocks with a length of 20-40 nm and a width of 15-30 nm. However, more recent publications report bigger starch nanocrystals (40-70 nm for potato starch nanocrystals; [141,142] and 60-150 nm [143,144] for pea starch nanocrystals; and 50 [145] and 70-100 nm [146] for waxy starch nanocrystals), with round edges [147] and found as grape-like aggregates of 1-5 μm. The heterogeneity in particle size could be explained by the differences in starch types and also by the difficulty to obtain well-defined pictures of non-aggregated nanocrystals.

Acid hydrolysis has been used for a long time to modify starch and its properties. Nageli [148] reported low molecular weight acid-resistant fraction after the hydrolysis of potato starch at room temperature in a 15% H₂SO₄ suspension for 30 days. The fraction would be known as Nageli amylodextrin. Lintner [149] also gave his name to a hydrolysis process consisting of a 7.5% (w/v) HCl suspension of potato starch at 30-40 °C to produce a high molecular weight starch suspension called “lintnerized starch”.

Only a few studies have reported the use of acid hydrolysis to produce microcrystalline starch [150] and starch nanocrystals [151]. For all starches, a two-stage hydrolysis profile can be evidenced, namely, an initial fast hydrolysis step, presumably due to the hydrolysis of the amorphous regions of starch granules, and a second slower step, presumably due to the hydrolysis of the crystalline regions [152,153]. Some authors distinguish three steps of hydrolysis: a rapid one, a slow one, and a very slow one, [154] presumably corresponding to the hydrolysis of amorphous layers, semicrystalline layers and crystalline ones, respectively. There are two common hypotheses to account for the slower hydrolysis rate of the crystalline domain. The first one is that the dense packing of
starch in the crystalline regions does not readily allow the penetration of $\text{H}_3\text{O}^+$ [117]. The second one is that the hydrolysis of the glucosidic bonds requires a change in conformation from chair to halfchair [155].

![Figure 1.12 TEM of starch nanocrystals: longitudinal view and planar view.](image)

The obvious factors influencing hydrolysis kinetics are time, acid type, acid concentration, and temperature. The influence of acid and starch type has been studied extensively by various researchers [156,157,158,159]. They showed, through different characterization techniques (alkali fluidity number, number average molecular weight, intrinsic viscosity) that, for the same equal normalities, $\text{HCl}$ and $\text{HNO}_3$ gave the highest thinning effect followed respectively by $\text{H}_2\text{SO}_4$ and $\text{H}_3\text{PO}_4$. Angellier et al., [160] also obtained a lower yield of hydrolysis with $\text{H}_2\text{SO}_4$ compared to $\text{HCl}$ for the production of nanocrystals but showed that final suspensions were more stable with $\text{H}_2\text{SO}_4$ due to the presence of sulfate groups at the surface. The difference in the rate and yield of hydrolysis among starch types was attributed to the difference in granule sizes and number of pores on the granule surface [146]. Jayakody and Hoover studied further the susceptibility of different cereal starches to hydrolysis [161]. Roughly, the extent of hydrolysis was more pronounced in waxy maize than in oat, rice, normal maize, amylomaize V (50-60% amylose), and amylomaize VII (70% amylose) starches. They concluded that (i) the first stage of hydrolysis (amorphous regions) is influenced by the
granule size, pores on the surface, amylase content, and the amount of lipid-complexed amylose chains and (ii) the second step of hydrolysis (crystalline region) is influenced by the amyllopectin content, mode of distribution of R(1-6) branches between the amorphous and the crystalline regions, and degree of packing of the double helices within the crystallites (i.e., the parameters also influencing crystallinity). Wang et al., [162] observed as expected that the rate of hydrolysis increased when increasing the concentration of acid while the temperature was kept constant at 50 °C. Angellier et al., [146] in the intent of producing starch nanocrystals studied the influence of these parameters using a surface response methodology. They concluded that both the acid concentration and the temperature should not be too high: acid concentration was kept at 3.16 M and the temperature was kept at 40 °C. However, techniques for following the extent of hydrolysis are numerous.

The use of acid hydrolysis and even though a variety of starch sources has been used, they all refer to the same two processes: (1) Dufresne et al., process using HCl as previously discussed [163] and (2) Angellier et al., optimized the process using H_2SO_4, [128].

In most recent studies, new processes have been tried out to produce starch nanoparticles by (i) precipitation of amorphous starch by Ma et al., [164] and Tan et al., [165] (ii) combining complex formation and enzymatic hydrolysis by Kim and Lim, [166] yielding nanocrystals (i.e. complexed with lipids), and (iii) microfluidization by Liu et al., [167]. It is worth noting that such starch nanoparticles are following totally different strategies than starch nanocrystals as described in Figure. 1.13. Consequently, ensuing nanoparticles have different properties, crystallinity, and shape.

Ma et al., [132] prepared starch nanoparticles by precipitating a starch solution within ethanol as the precipitant. However, this process for producing starch nanoparticles does not allow producing nanocrystals. Kim and Lim studied alternative ways to obtain starch nanoparticles [134]. They proposed a process for preparing nanoscale starch particles by complex formation with other components. Experiments were conducted with n-butanol. However, the complex contained a large portion of amorphous matrix so that its selective removal by enzymatic hydrolysis was needed. The disadvantage of this method is that most of the starch was hydrolyzed (85-90%) and the resulting yield of the nanoparticles
was extremely low. Starch nanoparticles obtained by this method display a spherical or oval shape, with diameters in the range of 10-20 nm.

Figure. 1.13 Different approaches of producing crystalline and amorphous starch nanoparticles

Liu et al., carried out a method in which 5% slurry of high amylose corn starch was run through a Microfluidizer for several passes (up to 30) [135]. The particle size of the samples obtained from more than 10 passes was below 100 nm and the gel-like suspension remained stable for more than a month. The thermal stability was not affected, and because no chemical or thermal degradation occurred during the treatment, the reported yield was almost 100%. However, in this method the resultant starch colloids were obtained from breaking down both amorphous and crystalline domains, rendering an amorphous diffraction pattern after 10 passes.
1.5.3 Preparation of cellulose nanocrystals

Structure of cellulose

Cellulose constitutes the most abundant renewable polymer resource available today. As a chemical raw material, it is generally well-known that it has been used in the form of fibers or derivatives for nearly 150 years for a wide spectrum of products and materials in daily life. What has not been known until relatively recently is that when cellulose fibers are subjected to acid hydrolysis, the fibers yield defect-free, rod-like crystalline residues. Cellulose nanocrystals have garnered in the materials community a tremendous level of attention that does not appear to be relenting. These biopolymeric assemblies warrant such attention not only because of their unsurpassed quintessential physical and chemical properties (as will become evident in the review) 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 low cost, light weight, nanoscale dimension, and unique morphology. Surprisingly, a focus on nanoscale phenomena involving these materials has not been realized until the past few years in which a virtual collection of information has become available.

In nature, cellulose does not occur as an isolated individual molecule, but it is found as assemblies of individual cellulose chain-forming fibers. This is because cellulose is synthesized as individual molecules, which undergo spinning in a hierarchical order at the site of biosynthesis. Typically, approximately 36 individual cellulose molecules assemble into larger units known as elementary fibrils (protofibrils), which pack into larger units called microfibrils, and these are in turn assembled into the familiar cellulose fibers. However, celluloses from different sources may occur in different packing as dictated by the biosynthesis conditions.

In the 1950s, Ranby reported for the first time that colloidal suspensions of cellulose can be obtained by controlled sulfuric acid-catalyzed degradation of cellulose fibers [168, 169,170]. This work was inspired by the studies of Nickerson and Habrle [171 61] who observed that the degradation induced by boiling cellulose fibers in acidic solution reached a limit after a certain time of treatment. Transmission electron microscopy
(TEM) images of dried suspensions revealed for the first time the presence of aggregates of needle-shaped particles, while further analyses of these rods with electron diffraction demonstrated that they had the same crystalline structure as the original fibers [172,173]. Simultaneously, the development by Battista [174,175] of the hydrochloric acid-assisted degradation of cellulose fibers derived from high-quality wood pulps, followed by sonification treatment, led to the commercialization of microcrystalline cellulose (microcrystalline cellulose). Stable, chemically inactive, and physiologically inert with attractive binding properties, microcrystalline cellulose offered a significant opportunity for multiple uses in pharmaceutical industry as a tablet binder, in food applications as a texturizing agent and fat replacer, and also, as an additive in paper and composites applications. After the acid hydrolysis conditions were optimized, Marchessault et al., [176] demonstrated that colloidal suspensions of cellulose nanocrystals exhibited nematic liquid crystalline alignment. Since the discovery of spectacular improvements in the mechanical properties of nanocomposites with cellulose nanocrystals, [177,178] substantial research has been directed to cellulose nanocrystal composites because of the growing interest in fabricating materials from renewable resources.

The main process for the isolation of cellulose nanocrystals from cellulose fibers is based on acid hydrolysis. Disordered or paracrystalline regions of cellulose are preferentially hydrolyzed, whereas crystalline regions that have a higher resistance to acid attack remain intact [179,180]. Thus, following an acid treatment that hydrolyzes the cellulose rod-like nanocrystals are produced. The obtained cellulose nanocrystals have a morphology and crystallinity similar to the original cellulose fibers; examples of such elements are given in Figure. 1.14. The actual occurrence of the acid cleavage event is attributed to differences in the kinetics of hydrolysis between amorphous and crystalline domains. In general, acid hydrolysis of native cellulose induces a rapid decrease in its degree of polymerization (DP), to the so-called level-off DP (LODP). The DP subsequently decreases much more slowly, even during prolonged hydrolysis [146,181]. LODP has been thought to correlate with crystal sizes along the longitudinal direction of cellulose chains present in the original cellulose before the acid hydrolysis. This hypothesis was based on the reasonable assumption that disordered or para-crystalline domains are regularly distributed along the microfibers and therefore they are more
susceptible to acid attack (in contrast to crystalline regions that are more impervious to attack). Also, homogeneous crystallites were supposed to be generated after acid hydrolysis. These assumptions were actually confirmed by X-ray crystal diffraction [182] electron microscopy with iodine-staining, small-angle X-ray diffraction, and neutron diffraction analyses [183]. Contrary to cellulose nanocrystals, starch nanocrystals are not almost 100% crystalline, but rather 45% crystalline, with variations depending on the botanic origin, as recently presented by Le Corre et al., [184]. Typical procedures currently employed for the production of cellulose nanocrystals consist of subjecting pure cellulosic material to strong acid hydrolysis under strictly controlled conditions of temperature, agitation, and time. The nature of the acid and the acid-to-cellulosic fibers ratio are also important parameters that affect the preparation of cellulose nanocrystals. A resulting suspension is subsequently diluted with water and washed with successive centrifugations.

Figure. 1.14 TEM images of dried dispersion of cellulose nanocrystals derived from (a) tunicate (b) bacterial (c) ramie and (d) sisal.
Specific hydrolysis and separation protocols have been developed that depend on the origin of the cellulosic fibers. Most common sources include among others, cellulose fibers from cotton [185,186] ramie [187,188,189] hemp [190], flax [191,192], sisal [193,194], wheat straw [195], palm [196], bleached softwood [197] and hardwood [198] pulps, cotton linters pulp [199,200], microcrystalline cellulose [201], sugar beet pulp [202], bacterial cellulose [203], jute and Tunicates [204]. Similar to preparation of starch nanocrystals here also sulfuric and hydrochloric acids have been extensively used for cellulose nanocrystals preparation. Other acids such as phosphoric [205] and hydrobromic [206] have also been reported for such purposes. If the cellulose nanocrystals are prepared by hydrolysis in hydrochloric acid, their ability to disperse is limited and their aqueous suspensions tend to flocculate [207]. On the other hand, when sulfuric acid is used as a hydrolyzing agent, it reacts with the surface hydroxyl groups of cellulose to yield charged surface sulfate esters that promote dispersion of the cellulose nanocrystals in water [208]. However, the introduction of charged sulfate groups compromises the thermostability of the nanocrystals [209]. Also, differences in the rheological behavior have been shown between suspensions obtained from sulfuric acid hydrolysis and those obtained from hydrochloric acid. In fact, the sulfuric acid treated suspension has shown no time-dependent viscosity, whereas the hydrochloric acid-treated suspension showed a thixotropic behavior at concentrations above 0.5% (w/v) and antithixotropic behavior at concentrations below 0.3% [178]. Post-treatment of cellulose nanocrystals generated by hydrochloric acid hydrolysis with sulfuric acid has been studied to introduce, in a controlled fashion, sulfate moieties on their surfaces. Cellulose nanocrystals generated from hydrochloric acid hydrolysis and then treated with sulfuric acid solution had the same particle size as those directly obtained from sulfuric acid hydrolysis; however, the surface charge density could be tuned to given values by sulfuric acid hydrolysis. With respect to the morphology of the particles, a combination of both sulfuric and hydrochloric acids during hydrolysis steps appears to generate spherical Cellulose nanocrystals instead of rod-like nanocrystals when carried out under ultrasonic treatment [210]. These spherical Cellulose nanocrystals demonstrated better thermal stability mainly because they possess fewer sulfate groups on their surfaces [211].
The concentration of sulfuric acid in hydrolysis reactions to obtain Cellulose nanocrystals does not vary much from a typical value of ca. 65% (wt); however, the temperature can range from room temperature up to 70 °C and the corresponding hydrolysis time can be varied depending upon the source of cellulose. In the case of hydrochloric acid-catalyzed hydrolysis, the reaction is usually carried out at reflux temperature and an acid concentration between 2.5 and 4 N with variable time of reaction depending on the source of the cellulosic material. Bondenson et al., [212] investigated optimizing the hydrolysis conditions by an experimental factorial design matrix (response surface methodology) using microcrystalline cellulose that was derived from Norway spruce (Picea abies) as the cellulosic starting material. The factors that were varied during the process were the concentrations of microcrystalline cellulose and sulfuric acid, the hydrolysis time and temperature, and the ultrasonic treatment time. The responses that were measured were the median size of the cellulose particles and the yield of the reaction. Prolongation of the hydrolysis time induced a decrease in nanocrystal length and an increase in surface charge [156]. Reaction time and acid-to-pulp ratio on nanocrystals obtained by sulfuric acid hydrolysis of bleached softwood (black spruce, Picea mariana) sulfite pulp was investigated by Beck-Candanedo et al., [169]. They reported that shorter nanoparticles with narrow size polydispersity were produced at longer hydrolysis times. Recently, Elazzouzi-Hafraoui et al., [213] studied the size distribution of Cellulose nanocrystals resulting from sulfuric acid hydrolysis of cotton treated with 65% sulfuric acid over 30 min at different temperatures, ranging from 45 to 72 °C. By increasing the temperature, they demonstrated that shorter crystals were obtained; however, no clear influence on the width of the crystal was revealed.

To the best of our knowledge, there are no commercial starch and cellulose nanocrystals available in the market. In fact, only two patents, in Chinese and from the same authors, dealing with starch nanocrystals have been found [214,215].

The aim of producing such polysaccharide nanocrystals or nanoparticles is to use them as fillers in polymeric matrices to improve their mechanical and barrier properties.
1.5.4 Polysaccharide nanocystal reinforced polymers and their properties

After 2006, most work has been oriented towards the use of new environment-friendly polymers such as waterborne polyurethane [216] (WPU also called organic solvent free polyurethane), starch (waxy maize [217], cassava [218], pullulan [219] (obtained by starch fermentation), PLA [220] [65] polyvinyl alcohol (PVA), [221] and, most recently, soy protein isolate (SPI)[222] [66].

Processing.

There are various methods reported for the preparation of composites. Dufresne and Cavaille, [223] Angelier at al., [185] reported preparation of composite by hot pressing. Casting-evaporation was found out to be another approach for preparation of composites. From 2006 to present, authors have opted for a simpler casting-evaporation method at 40 °C for 24 h. Ma et al., [224] and Garcia et al., [225] prepared the composites of starch nanoparticles by casting-evaporation at 50 °C. Dufresne et al., [100] also prepared composites of natural rubber containing starch and cellulose nanocrystals by casting-evaporation method. Most recently, compression molding was used to prepare glycerol-plasticized starch nanocrystal composites at 120 °C from a freeze-dried powder [193].

Mechanical Properties

Using starch nanocrystals as a reinforcing phase in a polymeric matrix has been evaluated from a mechanical point of view both in the nonlinear (tensile test) and linear range (DMA). Dufresne and Cavaille [226] found that starch nanocrystals brought great reinforcing effect especially in the rubbery plateau region, that is, at temperatures higher than $T_g$ of the matrix. Later, this observation was confirmed by most authors. The reinforcing effect of starch nanocrystals was evidence from tensile tests results. In most of the cases the introduction of nanofillers resulted in an increase in both the elastic modulus and the tensile strength of the composite together [227,228,229,230]. The reinforcement increased with the amount of nanofillers in most of the cases [202]. Whereas, increasing relative humidity was shown to have a strong negative impact on the reinforcing effect. Zheng et al., [231] reported an increase in strength and Young’s modulus, together with a decrease in the elongation at break, at low pea starch
nanocrystal loading level (lower than 2 wt %) in a soy protein isolate (SPI) matrix. They attributed this result to a uniform dispersion. For higher content, the authors believe that nanocrystals get self-aggregate which decreases the surface for interactions with the soy protein isolate matrix and destroys the ordered structure. This leads to a decrease of strength and modulus at 40 wt % filler content to values close to those obtained for the unfilled matrix. Another interesting reported phenomenon is the observation, for some composite, of a constant elongation at break with increasing filler content. Indeed, Wang and Zhang [232] reported the preparation of a high strength WPU-based elastomer reinforced with 1-5% waxy maize starch nanocrystals. Low filler content allowed better dispersion of the starch nanocrystals in the WPU matrix, allowing stronger interactions. The same observations have been made on NR/starch nanocrystals composites, by different authors, and for 5 and 30% starch nanocrystals from different botanic origins [233].

The reinforcing effect of starch nanocrystals is more significant in thermoplastic starch than in natural rubber. The higher reinforcing effect observed with the former matrix is assumed to result from strong interactions between the filler and amylopectin chains and a possible crystallization at the filler/ matrix interface [200]. Also, the reinforcing effect of starch nanocrystals within a thermoplastic starch matrix was higher than with tunicin or sugar cane bagasse cellulose whiskers [234]. An interesting and innovative approach to use polysaccharide nanocrystals as fillers is the investigation of a synergistic reinforcement of waterborne polyurethane by both starch nanocrystals and cellulose whiskers [235]. The authors attributed results to the formation of a new type of network allowed by strong hydrogen bondings interactions both between the nanofillers and between the nanofillers and the WPU matrix.

**Reinforcing Effect**

The literature is significantly lacking in a comprehensive explanation of the reinforcing mechanism of starch nanocrystals, contrary to cellulose nanocrystals, for instance. Similar to cellulose nanocrystals, the reinforcing effect of starch nanocrystals is generally ascribed to the formation of hydrogen bonded percolating filler network above a given starch content corresponding to the percolation threshold. However, this assumption is
difficult to prove because the connecting particles should be starch clusters or aggregates with ill-defined size and geometry [236]. This phenomenon should most probably affect the mechanical properties of the composites in the linear range. This percolation mechanism should depend on among other parameters the dimensions of the primary starch nanoparticles, the isolation process, processing method of nanocomposite films, and interactions with the polymeric matrix.

Water Uptake

Biopolymers change their dimensions with varying moisture content because the cell wall of polymers contain hydroxyl and other oxygen containing groups, which attract moisture through hydrogen bonding [237]. Their porous nature accounts for the large initial uptake at the capillary region. The hydroxyl group (-OH) in biopolymers build a large amount of hydrogen bonds between the macromolecules in the plant fibre cell wall. Subjecting the plant fibres to humidity causes the bonds to break. The hydroxyl group then forms new hydrogen bond with water molecules, which induce swelling [238]. The schematic representation of swelling process in cellulose is given in figure 1.15.

The hydrophilic nature of these polysaccharide nanocrystals generally limits the formation of nanocomposites to water-soluble polymers only. In hydrophobic matrices repulsive forces lead to aggregation and poor interfacial contact. Though the approach leads to good filler dispersion, composites cannot be obtained by simply melt blending the filler with the polymer as desired in industrial processes.

Several authors have assessed water uptake of the composites containing polysaccharide nanocrystals. Dufresne and Cavaille reported that as the amount of starch nanocrystals increases the water uptake increases [118]. The unfilled natural rubber matrix displayed the lowest water uptake value, and the addition of starch nanocrystals induced an increase in water diffusivity [100]. The critical volume fraction of starch nanocrystals at the percolation is difficult to determine due to their heterogeneity and ill-defined geometry. Other authors preferred a conditioning technique, at different relative humidity, to assess the water sensitivity of films.
1.6 Modification of polysaccharide nanoparticles
For the processing of composite materials, starch and cellulose nanocrystals are used in the form of aqueous suspensions and the matrices are latexes. To disperse starch nanocrystals in nonpolar solvent surfactant was used [239,240]. However, a large amount of the surfactant is needed to maintain the stability of the suspension. Such a drawback hinders the use of this technique for composites processing in organic solvents [241]. Therefore, physical or chemical modifications on polysaccharide nanocrystals have been extensively studied, among which the surface chemical modification is a sound approach and a lot of relevant research work has been done [242]. In the past years, it has been
reported that some polymers such as poly(tetrahydrofuran), poly(propylene glycol) momobutyl ether, poly(carprolactone) and poly(styrene) [243] were used to chemically modify the properties of starch nanocrystals. However, the polymer modified starch nanocrystals aggregation still exists and the solubility with organic solutions is not satisfactory. Starch nanocrystals with short grafting agents was also reported [244], but the grafting extent is not sufficient to induce a partial solubilization of starch molecules located at the surface of the nanocrystals. Heterogeneous esterification of polysaccharide nanofibres with organic acids usually resulted in significant bulk modification, characterised by loss of crystallinity and high degree of substitutions [245]. Cellulose has also been esterified homogeneously in ionic liquids to produce cellulose acetate but the crystal structure of modified cellulose once regenerated is destroyed [246]. By restricting the modification only to the surface of cellulose nanofibres, the highly crystalline bulk structure of cellulose can be retained, while the surface is rendered hydrophobic. The mechanical properties of natural rubber filled with polysaccharide are dominated by many factors, such as the dispersing ability, the interfacial combination. As polysaccharide contain many hydroxyl groups with strong polarity, its compatibility with NR is poor. Hence, the mechanical properties (elasticity and tear) of composite filled by direct loading of polysaccharide NPs will deteriorate. A large amount of work has been contributed to improve the mechanical properties of polysaccharide/NR composites. In the 1970s, Buchanan et al., prepared crosslinked starch xanthide–styrene butadiene rubber (SBR) master batches. It was demonstrated that crosslinked starch xanthide could improve the fatigue life and abrasion resistance, when used to partially replace carbon black in a premium tread [247,248]. Goodyear Company employed modified cornstarch which was called filler of biological polymer to partly replace traditional fillers like black carbon or white carbon to improve the properties of tyres. Those tyres reinforced with cornstarch possess many advantages, such as light quality, low rolling resistance, low noise and low emission of carbon dioxide [249]. Rouilly et al., [250] prepared the composite by blending dimethylaminoethyl methacrylate grafted latex and starch. Nakason et al., [251] synthesized grafted copolymer by grafting NR with methyl methacrylate, and then blending the copolymer with NR and cassava starch. The results
showed that the induction period of cure of the composite decreased with the increase of cassava starch loading.

There is no doubt that, polysaccharide nanocrystals are promising fillers. This field is at the moment much less reported in the literature. It is worth noting that the main interest of starch in addition to a low cost is that the raw material is relatively pure. This point is important to broaden their further application, and there are significant scientific and technological challenges to take up.

Based on the above discussions our broad objectives were:

- To investigate the performance of polysaccharides as green reinforcing agents and substitutes for carbon black in natural rubber.
- To improve the reinforcing ability of polysaccharides through chemical modification and hence to synthesise hydrophobic nanofillers.
- Synthesis and characterization of bionanocomposites of natural rubber reinforced with nanosized polysaccharide derivatives and compare their performance with conventional composites.
- To develop bionanocomposites of natural rubber with high filler loading.
- To explore other possible applications of nanosized polysaccharide derivatives.
1.7 References


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