

CHAPTER II

BACKGROUND AND LITERATURE SURVEY

2.1 Nanocomposite Material

Nanocomposites are a relatively new class of composites that exhibit ultrafine phase dimensions of 1-1000 nm. As most of the present-day polymers used for preparing nanocomposites are synthetic materials, their processability, biocompatibility, and biodegradability are much more limited than those of natural polymers. Other advantages of the natural nanofillers are their lower cost relative to synthetic nanofillers and renewable resources. The use of various natural fibers such as starch and cellulose as reinforcing phase in nanocomposites has been reported.

Favier *et al.*, (1995) prepared polymer nanocomposites reinforced by cellulose whiskers films. A dispersion of cellulose whiskers can be produced by H_2SO_4 . The suspensions of cellulose whisker were homogeneously mixed with polymer lattices ($T_g=0^\circ C$) resulting from the copolymerization of styrene (35% w/w), butylacrylate (65% w/w), and a small amount of acrylic acid. When reinforced by a small percentage of tunicin whiskers, the polymer films showed improved mechanical properties which were particularly striking when the films were heated above the glass transition of the polymer.

Dufresne *et al.*, (1999) investigated transcrystallization in Mcl-PHAs/cellulose whisker composites. Nanocomposite materials were prepared from an elastomeric medium-chain-length poly(hydroxyalkanoate) (Mcl-PHA) latex as semicrystalline matrix using a colloidal suspension of hydrolyzed cellulose whiskers as a filler. Tunicin whiskers induce mechanical properties through the formation of a rigid filler network. However, owing to the semicrystalline nature of the matrix, this whisker network originates from the formation of interwhiskers links through transcrystalline layers grown on cellulose surface. This results in a disastrous decrease of the mechanical properties of the semicrystalline Mcl-PHA composite filled with tunicin whiskers as soon as the melt temperature of the matrix is reached.

Anglès and Dufresne (2001) characterized the mechanical behavior of glycerol plasticized/cellulose whisker nanocomposite films. The mechanical

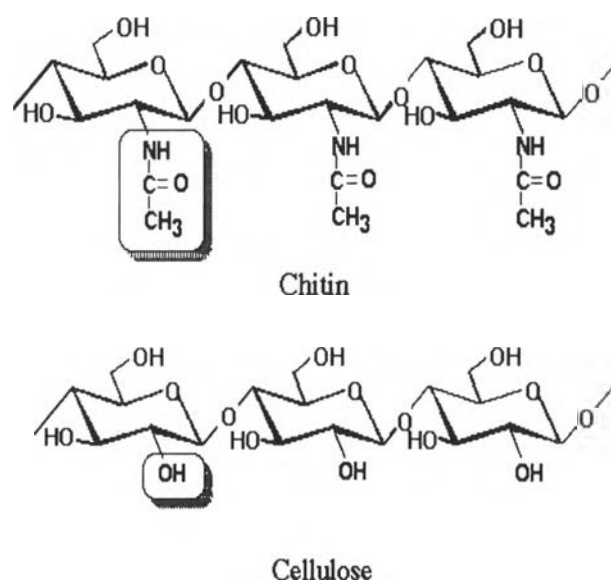
behavior of resulting films was characterized in both the linear and the nonlinear range. The reinforcing effect of tunicin whiskers strongly depended on the ability of cellulose filler to form a rigid network, resulting from strong interactions between whiskers such as hydrogen bonds, and therefore on the moisture content. It was shown that increasing water content induced the crystallization of amylopectin chains and the accumulation of plasticizer in the cellulose/amylopectin interfacial zone.

Anglès and Dufresne (2000) prepared nanocomposite materials by using glycerol plasticized starch as the matrix and a colloidal suspension of cellulose whiskers as the reinforcing phase. The results lead to the conclusion that both plasticizers (glycerol and water) redistribute within the matrix, diffusing toward the cellulose surface. This relocalization effect decreases the plasticizing effect of glycerol and water in the bulk amylopectin matrix, resulting in an increase of the Tg of amylopectin-rich domains. The accumulation of plasticizer in the cellulose/amylopectin interfacial zones improves the ability of amylopectin chains to crystallize, leading to the formation of a possible transcrystalline zone around the whiskers.

Dubief *et al.*, (1999) prepared polysaccharide microcrystals reinforced amorphous poly (β -hydroxyoctanoate) nanocomposite. Nanocomposite materials were prepared using a latex of poly (β -hydroxyoctanoate) as a matrix and using a colloidal suspension of hydrolyzed starch or cellulose whiskers as a natural and biodegradable filler. The resulting properties were strongly related to the aspect ratio L/d of the filler.

2.2 Chitin

Chitin is a high molecular weight biopolymer found predominantly in the hard external shell of crustaceans, and also in the flexible internal backbone of the squid. The structure of chitin has an acetamide group substituted at the C- β carbon position, resulting in mainly β -(1 \rightarrow 4)-2-deoxy-D-glucopyranose structure units.



Chitin has been known to form microfibrillar arrangements in living organisms. These fibrils are usually embedded in a protein matrix and have diameters from 2.5 to 2.8 nm. Crustacean cuticles possess chitin microfibrils with diameters as large as 25 nm. Three polymorphic crystal structures of chitin are known, α -, β - and γ -structures. Crystal structures of three chitins have been extensively studied. α -Chitin is the tightly compacted, mostly in crystalline orthorhombic form where the chains are arranged in an anti-parallel fashion with strong intermolecular bonding in the main chain. α -Chitin are extracted from the shell of crabs, lobsters and shrimps. β -Chitin, obtained from the pen of loligo and squid has the monoclinic form where the chains are parallel, with weaker intermolecular hydrogen bonding than α -Chitin caused by the parallel arrangement of the main chains.

Chitin has very attractive typical characteristics such as biocompatibility, biodegradability, non-toxicity, infection prevention, acceleration in wound recovery, etc.

2.3 Chitin Whisker

Whisker is a short single crystal fiber which is prepared by acid hydrolysis. Whiskers can be used as a reinforcing phase in polymeric matrix. The suspension of

chitin whisker can be prepared by acid hydrolysis. This suspension displays a colloidal behavior, the stability of which is attributed to the presence of positive charge (NH_3^+) at the surface of the crystallites, resulting from the protonation of amino groups. The use of chitin whiskers as reinforcing phase in nanocomposite material has been studied.

Paillet and Dufresne (2001) studied chitin whisker reinforcing a latex of styrene and butyl acrylate. The colloidal chitin dispersion was mixed with the latex with various amounts in order to obtain nanocomposite films. The blend films were prepared by solution casting. Results from DSC measurements showed that the T_g of the matrix was not modified upon chitin whisker addition. For mechanical properties, when reinforced by a low weight fraction (lower than 10 wt%) of chitin whiskers, the polymer films did not show any significant improved mechanical properties. For higher percentages of chitin whiskers, the composite glassy shear modulus increased up to $\sim 2\text{GPa}$ for the 20 wt% filled material.

Morin and Dufresne (2002) prepared nanocomposite materials were obtained from a colloidal suspension of high aspect ratio β -chitin whisker as a reinforcing phase and poly (caprolactone) as the matrix. The chitin whiskers, prepared by acid hydrolysis of *Riftia* tubes, consisted of slender parallel-piped rods with an aspect ratio close to 120. A procedure was optimized to prepare latex of poly (caprolactone). After mixing and stirring the two aqueous suspensions, solid films were obtained by either freeze-drying and hot-pressing or casting and evaporating. The reinforcing effect of chitin whiskers was discussed on the basis of different types of mechanical models, and it was concluded that these whiskers form a rigid network assumed to be governed by a percolation mechanism. The formation of this network allows the thermal stabilization of the material for temperatures higher than the melting temperature of the poly (caprolactone).

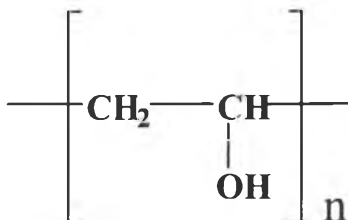
Nair and Dufresne (2003A) studied processing and swelling behavior of crab shell chitin whisker reinforced natural rubber. Chitin whisker reinforced natural rubber nanocomposites were developed from colloidal suspension of chitin whiskers and latex of both unvulcanized and prevulcanized natural rubber. Chitin whiskers were prepared by acid hydrolysis of chitin from crab shells which consisted of slender parallel-piped rods with the average length around 240 nm and an aspect

ratio close to 16. The composite films were obtained by casting and evaporating. The processing and swelling behavior of composite films were evaluated. It was concluded that the whiskers form a rigid network assumed to be governed by a percolation mechanism in the evaporated samples only. Comparatively, better resistance of evaporated samples than hot-pressed ones against swelling in an organic solvent medium is good evidence for the existence of a rigid chitin network.

Nair and Dufresne (2003B) analyzed the mechanical behavior of the resulting nanocomposite films in both the linear and the nonlinear range. Dynamic mechanical analysis revealed the presence of a small percentage of crystallinity in vulcanized rubber prepared by evaporation or in unvulcanized natural rubber prepared by hot pressing method. DMA also showed that the rubbery modulus of unvulcanized evaporated natural rubber is significantly improved by the incorporation of chitin whiskers. Successive tensile test experiments help to understand the existence of a three-dimensional chitin network formed as a result of hydrogen bonding within the evaporated samples.

Nair and Dufresne (2003C) modified the surface of chitin whiskers and investigated the effect of the incorporation of the modified whiskers into a natural rubber matrix on the properties of the ensuing nanocomposite. Different chemical coupling agents were tested, namely, phenyl isocyanate (PI), alkenyl succinic anhydride (ASA), and 3-isopropenyl- α - α -dimethylbenzyl isocyanate (TMI). FTIR spectroscopy, TEM, and contact angle measurements were performed to prove the occurrence of the surface modification without any major morphological changes associated with the various treatments applied. All of the results lead to the conclusion that the various chemical treatments improve the adhesion between the filler and the matrix. However, the mechanical performances of the composites strongly decrease after the chemical modification. This loss of performance, more pronounced for the isocyanate treatments, could be due to the partial or total destruction of the three-dimensional network of chitin whiskers assumed to be present in the unmodified composites.

2.4 Poly (vinyl alcohol) (PVA)

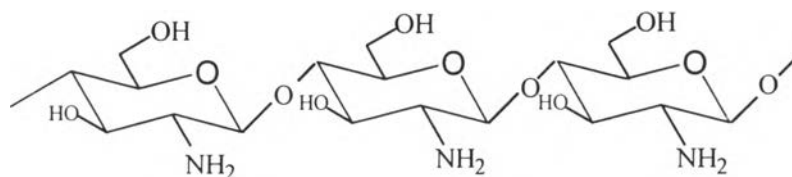


Poly (vinyl alcohol) (PVA) is a nontoxic water-soluble synthetic polymer, which is widely used in biochemical and biomedical applications. PVA has good film forming, highly hydrophilic properties. The use of PVA in medical research has been studied.

Cerchiara *et al.*, (2003) evaluated the in vitro characteristics of PVA 10,000 and PVA 15,000 substituted with different alkyl chains and crosslinked with bis-chloro-ethoxy-ethane as an injectable drug carrier. β -carotene was used as a lipophilic model drug. Physical mixtures of the drug and the spray-dried polymer were prepared and the release of the drug from the mixtures was evaluated in vitro at pH 7.4. The results indicated that the substituted PVA 10,000 and PVA 15,000 provided faster drug release with respect to the pure drug at pH 7.4.

Chuang *et al.*, (1999) investigated properties of the poly (vinyl alcohol)/chitosan blend and its effect on the culture of fibroblast in vitro. The SEM photographs show the PVA/chitosan blended membrane undergoes dramatic changes on the surface and bulk structure during the membrane formation. Therefore, adhesion and growth of fibroblasts on the PVA as well as PVA/chitosan blended membranes were investigated. Cell morphologies on the membranes were examined by SEM and cell viability was studied using MTT assay. It was observed that the PVA/chitosan blended membrane was more favorable for the cell culture than the pure PVA membrane. Cells cultured on the PVA/chitosan blended membrane had good spreading, cytoplasm webbing and flattening and were more compacting than on the pure PVA membrane.

2.5 Chitosan



Chitosan is the *N*-deacetylated derivative of chitin. It is used as a haemostatic agent, wound dressing, bacteriostatic agent and a spermicide. Chitosan is biodegradable and biocompatible to human and most of the animals (Felse and Panda, 1999). The use of chitosan in medical research has been reported.

Lai *et al.*, (2003) prepared and characterized drug-loaded alginate and chitosan sponges. The mechanical properties of the sponges were assessed using texture analysis and the microstructure examined using scanning electron microscopy. The dissolution of a model drug (paracetamol) from the sponges was assessed as a function of polysaccharide composition. It was noted that the sponges had a flexible yet strong texture, as assessed macroscopically. Dissolution studies indicated that systems containing chitosan alone showed the slowest release profile, with the mixed systems showing a relatively rapid dissolution profile. The use of chitosan and alginates together, therefore, appears to allow the formulator to manipulate both the mechanical properties and the drug release properties of the sponges.

Kofuji *et al.*, (2004) observed the release of prednisolone (PS) from chitosan (CS) gel beads. Carrageenan solution was injected into air pouches (AP), which were prepared subcutaneously on the dorsal surface of mice, in order to induce local inflammation. Chitosan gel beads retaining PS were then implanted into the AP to investigate the therapeutic efficacy of sustained PS release against local inflammation. *In vivo* PS release from CS gel beads was governed by both diffusion of the drug and degradation of the gel matrix. Inflammation indexes were significantly reduced after implantation of chitosan gel beads when compared with injection of prednisolone suspension. Thus, extension of the duration of drug activity by chitosan gel beads resulted in improved therapeutic efficacy. These

observations indicate that chitosan gel beads are a promising biocompatible and biodegradable vehicle for treatment of local inflammation.