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**Nano-Structured Materials Utilized in Biopolymer based Plastics
for Food Packaging Applications**

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Abstract

Most materials currently used for food packaging are non-degradable, generating environmental problems. Several biopolymers have been exploited to develop materials for eco-friendly food packaging. However, the use of biopolymers has been limited because of their usually poor mechanical and barrier properties, which may be improved by adding reinforcing compounds (fillers), forming composites. Most reinforced materials present poor matrix–filler interactions, which tend to improve with decreasing filler dimensions. The use of fillers with at least one nanoscale dimension (nanoparticles) produces nanocomposites. Nanoparticles have proportionally larger surface area than their microscale counterparts, which favors the filler–matrix interactions and the performance of the resulting material. Besides nanoreinforcements, nanoparticles can have other functions when added to a polymer, such as antimicrobial activity, etc. in this review paper, the structure and properties of main kinds of nano structured materials which have been studied to use as nanofiller in biopolymer matrices are overviewed, as well as their effects and applications.

Keywords: Nanoparticle, nanocomposite, biodegradable, biodegradable film

1. Introduction

The word “Nano” comes from the Greek for “dwarf” and denotes nanometer (10^{-9} m). The concept of nanotechnology was introduced by Richard Feynman in 1959 and the National Nanotechnology Initiative (Arlington, VA, USA) defines nanotechnology as ‘the understanding and control of matter at dimensions of roughly 1-100 nm, where unique phenomena enable novel applications’ (Azeredo, 2009; Kumar et al., 2009; Neethirajan and Jayas, 2011; Sekhon, 2010). European Food Safety Authority (EFSA) definition of a nanomaterial is “Nano-scale refers to a dimension of the order of 100 nm and below. But there are size-related effects that can appear at larger size (Barlow et al., 2009). Generally, current available definitions mainly based on size parameter (s) and fall short in terms of applicability to particulate materials that only have a size fraction in the nano-scale, or that contain primary nanostructures in highly agglomerated or aggregated forms. To overcome these shortcomings, Kreyling et al. (2010) postulate a new definition for nanoparticulate materials based on their volume specific surface area (VSSA) as derived in supplementary material. This definition will regard a particulate material a nanomaterial if it has a VSSA equal to, or greater than $60 \text{ m}^2/\text{cm}^3$ volume of the material. A practical aspect of this definition is that the parameters, specific surface area (SSA) and bulk material density (ρ), needed to derive VSSA are easily obtainable for the materials in question. The proposed definition is not intended to replace any of the existing definitions that are based on the size distribution of the primary particulate structures, or the size distribution of the agglomerated material. According to the European Commission adopted new official definition of nanomaterials in 2011, Nanomaterials was defined as: "a natural, incidental or manufactured

material, containing particles, in an unbound state or as an aggregate or as an agglomerate and where, for 50% or more of the particles in the number size distribution, one or more external dimensions is in the size range 1-100 nm."

The use of plastics is ubiquitous in food packaging where they provide mechanical, chemical, and microbial protection from the environment and allow product display. This is so, because synthetic polymers bring in enormous advantages, such as thermo-sealability, flexibility in thermal and mechanical properties, permit integrated processes (i.e. plastic packages can be formed, filled and sealed in a continuous manner within the production line), lightness and low price. Polymers most frequently used in food packaging are polyethylene, polypropylene, polystyrene, polyvinyl chloride (PVC), and polyethylene terephthalate (PET), all nonpolar and derived from non-renewable petroleum resources, and give non-biodegradable plastic materials, become a major source of waste after use. For this, packaging materials for foodstuff, like any other short-term storage packaging materials, represent a serious global environmental problem the so-called "white pollution" (Arora and Padua, 2010; Lagaron and Lopez-Rubio, 2011; Zhao et al., 2008; Sorrentino et al., 2007; Zan et al., 2004). One of the more promising approaches to overcome these problems is the use of annually renewable or environmentally-friendly resources. Accordingly, a variety of renewable biopolymers, such as polysaccharides (e.g., starch, alginate, pectin, carrageenan, agar, chitosan); proteins (e.g., gluten, gelatin, casein, whey protein), polyesters (e.g., polylactic acid,...) and their composites, derived from plant and animal resources have been investigated for the development of edible/biodegradable packaging materials to substitute for their non-biodegradable petrochemical-based counterparts (Mangiacapra et al., 2006; Rhim and Perry, 2007; Alves et al., 2010). Economic and

environmental aspects are contributing to the growing interest in natural polymers, due to their biodegradability, low toxicity, low manufacture costs, low disposal costs and renewability (Puppi et al., 2010). The global market for biodegradable polymers exceeds 114 million pounds and is expected to rise at an average annual growth rate (AAGR) of 12.6% to 206 million pounds in 2010 (Mahalik and Nambiar, 2010).

Biopolymer based packaging materials are notorious for water sensitive, brittleness and their poor mechanical, gas and moisture barrier properties and low heat distortion temperature which limit their industrial use (Tunç and Duman, 2010; Arora and Padua, 2010; Ghanbarzadeh and Oromiehi, 2009; Liu et al., 2009; Azeredo et al., 2009).

The most frequently used strategies to enhance performance and processing properties are the use of polymer blends, coating articles with high barrier materials, the use of multilayered films containing other films, chemically modification of natural biopolymers and producing composite plastic with using different fillers (Arora and Padua, 2010; Sorrentino et al., 2007).

Composites typically consist of a polymer matrix or continuous phase and a discontinuous phase or filler. Fillers are organic or inorganic materials and having certain geometries (fibers, flakes, spheres, particulates). Several composites have been developed by adding reinforcing compounds (fillers) to polymers to enhance their thermal, mechanical, and barrier properties. However, many reinforced materials present poor adhesion at the interface of their components. Macroscopic reinforcing components often contain defects, which become less important as the particles of the reinforcing component are smaller (Azeredo, 2009; Falguera et al. 2011). The use of nanoscale fillers is leading to the development of new composite crop that called “nanocomposites”. Polymer nanocomposites (PNCs) are the latest materials aimed at solving the

aforementioned problems (Duncan, 2011). Nanobiocomposites consist of a biopolymer matrix reinforced with particles (nanoparticles) having at least one dimension in the nanometer range (1 to 100 nm) (Kumar et al., 2011).

Nanocomposites exhibit increased barrier properties (solvent or gas resistance), increased mechanical strength, and improved modulus, dimensional stability and heat resistance (e.g., melting points, degradation and glass transition temperatures) compared to their neat polymers and conventional composites. Therefore, the application of nanocomposites promises to expand the use of edible and biodegradable film and help to reduce the packaging waste associated with processed foods and will support the preservation of fresh foods, extending their shelf life. In addition, inorganic particles may be used to introduce multiple functionalities like color and odors but also to act as reservoirs for the controlled release functions of drugs or fungicides (Arora and Padua, 2010; Sorrentino et al., 2007).

The effectiveness of nanofillers on improving physical, mechanical and other properties of polymer nanocomposites strongly depends on a number of factors, including geometrical properties (size, shape, aspect ratio), mechanical properties (ultimate tensile strength, elastic modulus), loading level, degree of dispersion and exfoliation, and their interfacial properties (intensity of adhesion to the polymer matrix) (Chan et al., 2002; Moghbelli et al., 2009; Choudalakis and Gotsis, 2009). Because of their very high surface area to volume ratio strong interfacial adhesion would be potentially exist between nanoparticle and matrix which in turn leads to form composites with unique outstanding properties (such as higher mechanical, thermal and barrier properties) in comparison to their conventional microcomposite counterparts. Bionanocomposites also offer extra benefits like low density, transparency, good flow, better

surface properties, and recyclability (Avella et al., 2005; Sorrentino et al., 2007; Kristo and Biliaderis, 2007; Zhao et al., 2008; Azeredo, 2009).

Besides reinforcing nanoparticles, there are several types of nanostructure materials which present other functions such as providing active or “smart” properties to the packaging system (e.g, antimicrobial activity, biosensing, etc). Some particles can have multiple applications, and sometimes the applications can overlap, such as titanium dioxide which can act as reinforcing and antimicrobial components (Sozer and Kokini, 2008; Zhou et al., 2009).

This review paper is concerned with properties and application of organic and inorganic nano-structured materials with good potential of reinforcement activity that can be incorporated into biopolymer based packaging materials as ‘nano-additives’ and highlights some recent results on the use of nano-biocomposites for food packaging applications.

2. Various classifications of nano-structured materials

As shown in Fig. 1, nanoscale particles are classified into three categories depending on their dimensions as follows:

- I. Nanoparticles: When the three dimensions of particulates are in the order of nanometers, they are referred as equi-axed (isodimensional) nanoparticles or nanogranules or nanocrystals (e.g. silica) and nanospherical (e.g. metal oxides like TiO_2 , ZnO)
- II. Nanotubes: When two dimensions are in the nanometer scale and the third is larger, forming an elongated structure, they are generally referred as ‘nanotubes’ or nanofibers/whiskers/nanorods (e.g. carbon nanotubes (CNTs), Titania nanotubes (TiNTs) and cellulose whiskers).

III. Nanolayers: The particulates which are characterized by only one dimension in nanometer scale are nanolayers/nanosheets. These particulate is present in the form of sheets of one to a few nanometer thick to hundreds to thousands nanometers long (e.g., clay (layered silicates), layered double hydroxides) (Jordan et al., 2005; Kumar et al., 2009; Chiu and Lin, 2011).

These nanoscale particles (NSPs) can further be classified in three types as natural, incidental, and engineered nanoparticles depending on their pathway.

Natural nanoparticles, which are formed through natural processes, occur in the environment (e.g, magneto-tactic bacteria, minerals, etc.). Incidental nanoparticles occur as the result of manmade industrial processes (diesel exhaust, coal combustion, welding fumes, etc.). Mostly, both natural and incidental nanoparticles may have irregular or regular shapes. Engineered nanoparticles most often have regular shapes (Fig. 2) (Bouwmeester et al., 2009).

Two building strategies are currently used in synthesis of engineered nanoparticles: a “top-down” approach and the “bottom-up” approach. The commercial scale production of nanomaterials currently involves basically the “top-down” approach, in which nanometric structures are obtained by size reduction of bulk materials, by using milling, nanolithography or precision engineering. The newer “bottom-up” approach, on the other hand, allows nanostructures to be built from individual atoms or molecules through crystal growth or chemical synthesis (Cushen et al., 2011; Azeredo, 2009; Kumar et al., 2009; Yuan and Su, 2004).

These nanoscale particles (NSPs) can further be distinguished in two types:

- (1) Inorganic nano-structured materials.
- (2) Organic nano-structured materials.

The inorganic nano-structured materials include titanium dioxide, silver, zinc oxide, gold nanoparticles, carbon nanotubes, nano-layered clay, and their nano-composites.

Organic nano-structured materials include cellulosic whiskers, lignocellulosic, chitin whisker, starch nanocrystal, and their nanocomposites. However, each one has an especial concept, architecture and properties. Thus, in this review, they have been discussed in separate groups. From commercial viewpoint, up to now, metal oxides (e.g. zinc or titanium oxides) have been the most important group of nano materials. From this point, a second significant group is nanoclays, naturally occurring plate-like clay particles and third group is nanotubes.

3. Inorganic nano-structured materials and their bionanocomposites

3-1. Titanium dioxide nanomaterials

3-1-1. TiO₂ Nano-particles

3-1-1-1. Structure

Titanium dioxide, C.I. No. 77891, also known as titanium (IV) oxide with chemical formula TiO₂ has been extensively applied in the food industry as color additive. TiO₂ nano-particles possess interesting high stability, relatively low-cost production (Anwar et al., 2010), long lasting, safe, has potential activity against all kind of microbes (Cerrada et al., 2008), optical and high refractive index rating, dielectrical, catalytical property and UV protecting agent, which results in industrial applications such as pigments (Pigment White 6), fillers, catalyst supports, and photocatalysts (Mahshid et al., 2006).

TiO₂ can exist in both crystalline and amorphous forms. The amorphous form of TiO₂ is photocatalytically inactive (Watson et al., 2004). There are three famous crystalline structures for

TiO₂ have been known as anatase (tetragonal, band gap = 3.2 eV which is equivalent to a wavelength of 388 nm) rutile (tetragonal, band gap = 3.02 eV) and brookite (orthorhombic, band gap = 2.96 eV) (Anwar et al., 2010; Wongkaew et al., 2010; Khataee and Kasiri, 2010; Lee, 2004). The fundamental structural unit in these three TiO₂ crystals forms from TiO₆ octahedron units and has different modes of arrangement. Anatase is most stable at sizes less than 11 nm, brookite at sizes between 11-35 nm, rutile at sizes greater than 35 nm (Lin, 2006). The most commonly seen phases are anatase and rutile (Xiaobo, 2009). The transmission electron micrographs of the anatase and rutile TiO₂ are shown in Fig. 3 (Khataee and Kasiri, 2010; Yeung et al., 2009).

Anatase is metastable at lower temperatures and useful catalyst in photochemistry because of its higher surface area and high photo activity. The rutile is thermodynamically more stable than the anatase and brookite. On heating concomitant with coarsening, the anatase and brookite are converted to the rutile. These transformation sequences imply very closely balanced energetic as a function of particle size (Xiaobo, 2009; Wu et al., 2008). In reality, the crystal structure of TiO₂ nanoparticles depended largely on the preparation method. Up to now, a number of methods including electrospinning (Sheikh et al., 2010; Qiu and Yu, 2008), hydrothermal synthesis (Anwar et al., 2010), supercritical carbon dioxide (Wu et al., 2008), vapor phase hydrolysis (John and Surender, 2005), the most common methods sol-gel (Robert and Weber, 1999; Wongkaew et al., 2010; Karami, 2010), ultrasound assisted sol-gel technique (Prasad et al., 2010) and microorganisms like *Lactobacillus sp.* and *Sacharomyces Cerevisae* (Jha et al., 2009) have been used to prepare TiO₂ nanomaterials such as nanotubes and nanoparticles.

3-1-1-2. Photocatalytic properties and UV absorbance

One of the important properties of the inorganic solid TiO₂ nanomaterials is its photocatalytic activity. Titanium dioxide irradiation by light with more energy compared to its band gaps generates electron–hole pairs that induce redox reactions at the surface of the titanium dioxide. Consequently, electrons in TiO₂ jump from the valence band to the conduction band, and the electron (e⁻) and electrical hole (h⁺) pairs are formed on the surface of the photo-catalyst. The created negative electrons and oxygen will combine into O₂⁻, the positive electric holes and water will generate hydroxyl radicals. Ultimately, various highly active oxygen species can oxidize organic compounds of cell to carbon dioxide (CO₂) and water (H₂O) and mineral acids. Since TiO₂ has a relatively high energy band gap (3.2 eV), TiO₂ nano-particles can only be excited by high energy UV irradiation with a wavelength shorter than 387.5 nm and absorption this wavelength. Hence, TiO₂ nanoparticles can absorb approximately 2–3% of solar light energies. In principle, food packaging films incorporating TiO₂ nanoparticles may protecting food content from the oxidizing effects of UV irradiation while maintaining good optical clarity, as TiO₂ nanoparticles are efficient short-wavelength light absorbers with high photostability. Many investigations confirm that the other material such as silver and ZnO increases the photocatalytic activities of titanium dioxide by extending the light absorption range of TiO₂ from UV to visible light (Wong et al., 2010, Wodka et al., 2010; Amin et al, 2009; Akhavan, 2009; Cheng et al., 2006; Vohra et al., 2005). Wong et al., (2010) employed nitrogen- and carbon-doped TiO₂ substrates to show photocatalytic activities under visible-light illumination against human pathogens.

3-1-1-2. Applications and effects on biopolymers matrices

3-1-1-2-1. Antimicrobial activity

The antimicrobial activity of TiO₂ nanoparticles is photocatalyzed and thus TiO₂-based antimicrobials are only active in the presence of UV illumination but not in the dark. Titanium dioxide can decompose common organic matters such as odor molecules, both Gram-negative and Gram-positive bacteria and viruses (Banerjee et al., 2006; Xu et al., 2006a; Fu et al., 2005). TiO₂ photocatalysis, promotes peroxidation of the polyunsaturated phospholipids of microbial cell membranes and consequently its derived functions (semi permeability, respiration, oxidative phosphorylation reactions) are the main cause of cellular death (Maness et al., 1999). TiO₂ used to inactivate many microorganisms including: bacteria such as: *E.coli* (Nadtochenko et al., 2008; Chawengkijwanich and Hayata, 2008), *S. aureus* (Asahara et al., 2008), *Salmonella typhimurium*, *Vibrio parahaemolyticus*, *Bacillus cereus* and *Listeria monocytogenes* (Kim et al., 2003; Tsai et al., 2010), *Clostridium perfringens* spores (Lanao et al., 2010), *Bacillus subtilis* (Armela et al., 2007), molds such as *Penicillium Expansum* (Maneerat and Hayata, 2006), yeasts such as *S. cerevisia*, algae such as *Chlorella vulgaris*, and viruses such as phage MS2 (Sjogren and Sierka, 1994), *B. fragilis bacteriophage*, *Poliovirus I*, *Cryptosporidium parvum*, and *Giardia intestinalis* (Gamage and Zhang, 2010) and use as alternative means for *L. monocytogenes* biofilm disinfection in food processing (Chorianopoulos et al., 2010) (Fig. 4).

3-1-1-2-2. Oxygen and ethylene scavenger activity

Oxygen (O₂) is responsible for the deterioration of many foods either directly or indirectly by browning of fruits, rancidity of vegetable oils and aerobic microorganisms. Also, the presence of oxygen is essential for photo-mineralization of the organic matter (Piero et al., 2005), thus nanocrystalline titania (TiO₂) can act as O₂ scavenger in food packaging under ultraviolet

radiation to maintain very low O₂ levels and very suitable for packaging of wide variety of oxygen-sensitive products (Xiao-e et al., 2004; Mills et al., 2006). The incorporation of O₂ scavengers into food package can maintain very low O₂ levels, therefore several authors suggested the use of TiO₂ for packaging a wide variety of oxygen-sensitive products. Also TiO₂ interactions with ripening gas (ethylene), slow down the maturation rate of climacteric fruits and extend the shelf life of ready to use fruit and vegetables (Costa et al., 2011). It's a crucial point for import-export of this food. Photoactive titanium dioxide can oxidize ethylene to H₂O and CO₂ (Llorens et al., 2011).

It has been approved by the American Food and Drug Administration (FDA) for use in human food, drugs and cosmetics and compounded in food contact materials such as cutting board, plastic packaging and other surfaces in contact with unprotected food (maximum allowable amount for food is 1% TiO₂). An anticipated use as a new material technology for future requirements is in the hygienic design of food processing facilities (Sikong et al., 2010).

A number of studies have been accomplished on properties of TiO₂ - synthetic polymers based nanocomposites (Zhu et al., 2011; Polizos et al., 2010; Cerrada et al., 2008; Nakayama and Hayashi, 2007; Zan et al., 2004). However, a few researches have been carried out on TiO₂-biopolymer based nanocomposite (nanobiocomposit). Zhou et al. (2009) have reported that adding small amounts (<1wt%) of TiO₂ nanoparticles (anatase, particle size <20 nm) to whey protein isolate film, significantly increase the tensile properties due to electrostatic attraction between negatively charged carboxylic or sulphhydryl groups from certain amino acids of WPI and positively charged Ti_4^+ -water complex during the preparation of WPI- TiO₂ film solution and hydrogen bonding or O-Ti-O bonding. However, it decreased the moisture barrier properties

due to diminish in cross-linking within WPI film matrix. The addition of higher amounts (>1wt%) of TiO₂ improved moisture barrier properties which attributed to low water solubility of TiO₂ compared with WPI and the prolonged tortuous pathway of water vapor caused by TiO₂ nanoparticles, but lowered the tensile properties of this film due to inhomogeneous distribution of TiO₂ and aggregation of TiO₂ in the WPI matrix. They regarded 1% TiO₂ nanoparticles as the optimum weight ratio of TiO₂/WPI to make blend films with relatively balanced physical properties and improved mechanical properties. With 1% TiO₂ the obtained nanocomposite film could block more than 70% visible light and more than 90% UV light (Fig. 5). This result, also confirmed with Li et al. (2011). Improvement in physical–mechanical and relaxation properties of nanocomposites based on chitosan graft copolymers with poly(vinyl alcohol) and nanodispersed titanium oxide, were observed by Ozerin et al. (2009).

3-1-2. Titania nanotubes (TiNTs)

3-1-2-1. Structure and properties

Titania nanotubes have a large surface area, tubular structure, small diameter, thin walls, small crystal size and their walls are composed of nanoparticles, therefore exhibit high photocatalytic performance (Qiu and Yu, 2008; Tongpool et al., 2007; Peng et al., 2005). The main methods to fabricate titania nanotube arrays are electro chemical anodization (Kontos et al., 2010; Yang and Pan, 2010; Xiao et al., 2009) and the sol-gel template method (Gang et al., 2009).

3-1-2-2. Applications and effects on biopolymers matrices

Anti-bacterial and other physical properties of TiO₂/chitosan nanocomposite have been investigated by Visurraga et al. (2010). TiNTs did not affect the structure of the films minimal variation in optical properties was observed, and light barrier properties of the films remained

stable over the storage period. Also, they observed the films were effective in reduction of microbial concentration (Tam et al., 2008).

3-2. ZnO nano-particles

3-2-1. Structure and properties

Zinc oxide (ZnO) has found many applications in daily life such as in drug delivery, cosmetics, and medical devices and pigments due to its strong antimicrobial effect on a board spectrum of microorganisms (Jones et al., 2008; Emamifar et al., 2010, Emamifar et al., 2011; Li et al., 2010; He et al., 2011; Padmavathy and Vijayaraghavan, 2008; Jiang et al., 2009), attenuate (absorb and/or scatter) the UV radiation or UV-blocking (Zhao and Li, 2006), high photostability, non-toxicity, low irritancy, low cost, environmentally friendly, dye adsorption (Salehi et al., 2010) and white appearance (Zhai et al., 2010; Vigneshwaran et al., 2006).

ZnO is a polar inorganic crystalline material and has a hexagonal quartzite structure with lattice constants of a and c being 3.250 and 5.207 Å, respectively, a direct band gap of 3.37 eV (368 nm), and large excitation binding energy of 60 meV at room temperature (Kuo et al., 2010). Zinc oxide shows different physical and chemical properties depending upon sizes and morphology of nanostructure. The shapes of ZnO nanostructures can be as spherical nanoparticles, nano-rods, nanowires, needles, and flower-like structures depend on the method of preparation. (Fig. 6) (Park et al., 2007). Methods have been developed to synthesize zinc oxide nanocrystals including warm ultrasonic bath (Wei and Chang, 2008), vapor phase growth, vapor-liquid-solid process, soft chemical method, electrophoretic deposition, sol-gel process, homogeneous precipitation, etc (Bigdeli et al., 2010).

The particle properties of ZnO, such as crystallinity and morphology, can be controlled by adjusting factors such as the source species, pH value, reaction temperature, time and solvent (Kuo et al., 2010; Kanade et al., 2006). ZnO powders can absorb infra-red light and infra-red electromagnetic wave with 5–16.68 dB in the range of 2.45–18GHz.

3-2-2. Applications and effects on biopolymers matrices

ZnO is used to reinforce polymeric nanocomposites (Vigneshwaran et al., 2006). ZnO nanoparticles in the polypropylene based nanocomposites reduced the extent of photo-oxidation and the storage modulus (E') and strain at break (ϵ_b) increased with increasing nanoparticle content (Zhao and Li, 2006). It increased the glass transition temperature (T_g) and changes in ΔC_p during transition in PVC based nanocomposite (Elashmawi et al., 2010) and also caused to increase in thermal stability and decrease in tensile strength (UTS) and ϵ_b in chitosan/poly vinyl alcohol films strain (Denice et al., 2010). Effects of ZnO nanoparticles (stabilized by soluble starch and carboxymethyl cellulose) as filler in a glycerol plasticized-pea starch (GPS) matrix, have been investigated (Ma et al., 2009; Yu et al., 2009). At low filler level (below 4 wt %), nano-ZnO enhanced the pasting viscosity, storage modulus, glass transition temperature, tensile yield strength and Young's modulus of GPS/nano-ZnO nanocomposites. Nano-ZnO impregnation also improved the absorbance of UV radiation and the water vapor barrier in comparison to pure GPS. This improvement in nanobiocomposite properties attributed to the strong interaction between nano-ZnO filler and the GPS matrix contributed

3-3. Zirconium Phosphate (ZrP)

3-3-1. Structure and properties

Most researches in zirconium phosphates and phosphonates chemistry have been focused on layered low-dimensional 1D structure, and their derivatives for their own nature, easily accessible and able to be functionalized for many applications. α - and γ -phases formula are $\text{Zr}(\text{HPO}_4)_2 \cdot \text{H}_2\text{O}$ and $\text{Zr}(\text{HPO}_4)_2 \cdot 2\text{H}_2\text{O}$, respectively, (Utracki et al., 2007; Vivani et al., 2008; Vaivars et al., 2003; Trobajo et al., 2000).

Zirconium bis (monohydrogen orthophosphate) monohydrate (Fig. 7), is an important class of crystalline material with many notable features, such as desired aspect ratio, thermal and chemical stability, catalytic activity, selective heavy metals removal from waters and intercalation properties in polymers (Pan et al., 2006; Pan et al., 2007; Feng et al., 2007; Zhang et al., 2009; Tai et al., 2010).

It exhibits prosperous intercalation chemistry feature due to its reactivity, which arises from the high acidity in its protonic form region (Geng et al., 2004) and the presence of medium strong acid groups in its interlayer. The intercalation chemistry is, thus, often driven by an acid-base reaction. Therefore, compounds with a functional group which can accept protons, such as amines, alkanols, glycols and ketones are the preferred guests (Sun et al., 2005).

Synthetic α -ZrP exhibits similar structural characteristics to natural montmorillonite (MMT) clay. Compared with natural MMT clay, the main drawbacks of MMT clay are its wide particle size distribution and difficulty in achieving full exfoliation in polymer matrices and α -ZrP has several additional advantages, including much higher purity and surface energy and ion-exchange capacity, more controllable surface functionality and easier processing of intercalation/exfoliation due to α -ZrP has different elements within its structure (Sue and Gam,

2004; Sun et al., 2007a; Sun et al., 2007b). But these layered phosphates are unable to swell in water, unlike smectite clays, and it is therefore necessary to pres well them with alkylamines, alcohols, or amino acids before intercalating large cations (Pastor et al., 1996).

Synthetic α -zirconium phosphate layer structures have been prepared via these three different approaches reported by Sun et al., (2007a). By controlling the concentration of reactants, temperature, pressure, and using a complexing agent, α -ZrP with a wide variation in aspect ratios has been prepared.

The size distribution of synthetic α -ZrP nanoplatelets can be more tightly controlled by varying reactant concentration, temperature, and reaction time. As a result, polymer nanocomposites containing fully exfoliated α -ZrP nanoplatelets can be easily prepared (Boo, 2007).

3-3-2. Applications and effects on biopolymers matrices

ZrPs would be possible to disperse with tailored properties in a polymer matrix in order to modify its characteristics or to enhance its usefulness for specific applications (Casciola et al., 2005). More recently, nanocomposites based on polymers have been obtained by dispersing α -ZrP in polyvinylidene fluoride (Casciola et al., 2005), in epoxy resins (Sue and Gam, 2004; Moghbelli et al., 2009), polyvinyl alcohol (Liu and Yang, 2009; Yang et al., 2010), polystyrene (Tai et al., 2010), polyvinyl acetate (Vaivars et al., 2003), PET (Wang et al., 2009a) and Polycaprolactone (Duan et al., 2007; Furman et al., 2009).

However, using α -ZrP nanoplatelets as nanofiller in natural biopolymers for food packaging applications is very limited. Structure and properties of starch nanocomposite films reinforced with layered zirconium phosphate have been investigated by Wu et al. (2009, 2010). They

reported that polar starch and ZrP interacted and formed strong hydrogen bonds, resulting improved compatibility. Incorporation of ZrP enhanced the tensile strength, strain at break and water resistance of the starch based nanocomposites, but decreased the thermal stability of them. This could be attributed to increase in acidity of α -ZrP with temperature increasing, which in turn induces the decomposition of the glycoside bonds. Yang et al. (2010) succeeded to synthesize oxidized starch/PVA/ α -zirconium phosphate nanocomposites for obtaining special mechanical and barrier properties. However, degradation temperature of the resulted nanocomposites was increased which was attributed to hydrogen bonding between α -ZrP and PVA/OST which restricted the movement of molecular chains. Also, Wu et al. (2010b) have prepared chitosan/ α -ZrP nanocomposite films and observed that addition of α -ZrP reduced the moisture uptake and improved the strain at break, tensile strength, thermal stability of the nanocomposite films.

3-4. Nano-clay

3-4-1. Structure and properties

The packaging industry has focused its attention mainly on layered inorganic solids like clays, due to their availability, low cost, significant enhancements and relative simple processability (Silvestre et al., 2011; Azeredo, 2009; Sorrentino et al., 2007).

Researches on the preparation and characterization of Polymer-Clay Nanocomposites (PCNs) intended for food packaging have been published only since the late 1990s (Brody et al., 2008). Historically, the term clay has been understood to be made of small inorganic particles (part of soil fraction less than 2 mm), without any definite composition or crystallinity (Hussain et al., 2006). Their basic building blocks are tetrahedral (T) sheets in which silicon is surrounded by four oxygen atoms, and octahedral (O) sheets in which a metal like aluminum is surrounded by eight oxygen atoms. Therefore, in 1:1 layered structures (e.g. in kaolinite) a tetrahedral sheet is fused with an octahedral sheet, whereby the oxygen atoms are shared. On the other hand, the crystal lattice of 2:1 layered silicates or 2:1 phyllosilicates (montmorillonite, vermiculite, rectorite, hectorite and saponite) is based on the pyrophyllite structure $\text{Si}_4\text{Al}_2\text{O}_{10}(\text{OH})_2$ and consists of two-dimensional layers where a central octahedral sheet of alumina is fused to two external silica tetrahedral by the tip, so that the oxygen ions of the octahedral sheet also belong to the tetrahedral sheets, as shown in Fig. 8 (Pavlidou and Papaspyrides, 2008; Choudalakis and Gotsis, 2009; Chivrac et al., 2009; Bordes et al., 2009).

The layers are located on top of each other like the pages of a book. The distance observed between two platelets of the primary particle, named gallery, inter-layer spacing or d-spacing (d_{001}). This value does not entirely depend on the layer crystal structure, but also on the type of the counter cation and on the hydration state of the silicate. To increase the d-spacing and then enhance the nanostructure effects, a chemical modification of the clay surface, with the aim to match the polymer matrix polarity, is often carried out (Ray and Okamoto, 2003; Alexandre and Dubois, 2000). Cationic exchange is the most common technique for chemical surface modification, but other original techniques such as the organosilane grafting and the use of

monomers or block copolymers adsorption are also used (Avérous and Halley, 2009). These substitutions induce a negative charge inside the clay platelet, which is naturally counter balanced by inorganic cations (Li^+ , Na^+ , Ca^{2+} , K^+ , Mg^{2+} , etc.) located into the inter-layer spacing, which increases the clay hydrophilic character.

Most polymers are considered to be organophilic compounds. In order to render the layered silicates miscible with non-polar polymers, one must exchange the alkali counter-ions with a cationic-organic surfactant. Alkylammonium ions are mostly used, although other “onium” salts can be used, such as sulfonium and phosphonium. Surfactants can also be used to improve the disperseability of the clay. The surfactants were able to increase spacing between clay layers (d-spacing) to different extents, depending on the number of polar units in the copolymer molecule. The resulting clays are called organomodified layered silicates (OMLS) and in the case of montmorillonite MMT, are abbreviated OMMT.

Organoclays are cheaper than most other nanomaterials, since they come from readily available natural sources, and are produced in existing, full-scale production facilities. Properties, preparations and applications of organoclays were reviewed by de Paiva et al. (2008).

The layer thickness is around 1 nm and the lateral dimensions may vary from 30 nm to several microns, and even larger, depending on the particulate silicate, the source of the clay and the method of preparation. Therefore, the aspect ratio of these layers (width/thickness) is very high, with values greater than 1000 (Ray and Okamoto, 2003; Alexandre and Dubois, 2000).

Depending on the strength of the interfacial interaction, three types of morphology are possible in nanocomposites (Fig. 9): tactoid, intercalated and exfoliated (full delamination). In aggregated materials the polymer does not fit between the layered clay, leading to a microphase separated

final structure. In intercalated systems, the polymer is located between clay layers, increasing interlayer spacing. Some degree of order is retained in parallel clay layers, which are separated by alternating polymer layers with a repeated distance every few nanometers. Exfoliated systems achieve complete separation of clay platelets in random arrangements. The main goal for the successful development of clay based nanocomposites is to achieve complete exfoliation of the layered silicate in the polymer matrix (Avérous and Halley, 2009; Ray et al., 2006).

3-4-2. Applications and effects on biopolymers matrices

High barrier properties against oxygen, carbon dioxide, ultraviolet, moisture and volatile compounds are perhaps the most important properties that a nanocomposite based food packaging can offer. The transparency and high barrier performance makes PCNs attractive as packaging materials and protective films (Zenkiewicz and Richert, 2008; Utracki et al., 2007). The improvement of the gas/water vapour barrier properties by incorporation of nanoclay fillers in the polymer matrix depends on the aspect ratio of the dispersed clay filler. Increasing the aspect ratio of the clay will increase the effective path length for the permeant to penetrate through the system (Adame and Beal, 2009).

Many studies have reported the effectiveness of nanoclays in decreasing oxygen (Bae et al., 2009 a, b ; Mangiacapra et al., 2006; Vartiainen et al., 2010; Zeppa et al., 2009), water absorption and water vapor (Kumar et al., 2010a; Lavorgna et al., 2010; Tang et al., 2008; Tang et al., 2009a; Vercelheze et al., 2012; Guilherme et al., 2010; Almasi et al., 2010; Chivrac et al., 2010a,b; Casariego et al., 2009), carbon dioxide and volatile compounds permeabilities (Tunc et al., 2007) in biopolymers such as pectin, gelatin, starch, chitosan, soy protein isolate and wheat gluten. It is

reported that gas permeability through polymer films can be reduced by 50–500 times even with small loadings of nanoclays. Such improvements in gas barrier properties of nanocomposite materials are attributed to two separate phenomena resulting from the addition of the inorganic phase. Firstly, the inclusion of the inorganic phase results in decreasing of the polymer chain mobility and flexibility which in turn increase chain arrangement regularity in polymer matrix and lower the penetrant mobility in the nanocomposite and changes the diffusibility (Drozdov et al., 2003). Secondly, impermeable inorganic nanoparticles in polymer formulations increase the tortuosity of the diffusive path for a penetrant molecule. A simple permeability model for a regular arrangement of platelets has been proposed by Nielsen and is presented in Fig. 10. The nanoclays are evenly dispersed and considered to be rectangular platelets with finite width, and thickness. Their orientation is perpendicular to the diffusion direction. The platelets act as impermeable barriers to the diffusing molecules, forcing them to follow longer and more tortuous paths in order to diffuse through the nanocomposite (Choudalakis and Gotsis, 2009; Zeppa et al., 2009; Paul and Robeson, 2008). The effects of sheet length, concentration and, orientation, polymer clay interaction and degree of delamination on the relative permeability have been explored by modifying a simple tortuosity based model (Lu and Mai, 2007; Sorrentino et al., 2007; Bharadwaj, 2001).

While tortuosity is usually the primary mechanism by which nanoclay impact the barrier properties of PNCs, this is not always the case. The other way that nanoparticulate fillers influence the barrier properties is by causing changes to the polymer matrix itself at the interfacial regions. If the polymer–nanoparticle interactions are favorable, polymer strands located in close proximity to each nanoparticle can be partially immobilized. The result is that

gas molecules traveling through these interfacial zones have attenuated hopping rates between free volume holes, or altered density and or size of holes (Duncan, 2011).

Clays have been also investigated to improve the mechanical strength of biopolymers, making their use feasible in packaging applications (Rhim, 2011; Weiss et al., 2006). Altinisik et al. (2009) reported that tensile strength and modulus of a chitosan–clay nanocomposites film was enhanced when the clay weight ratio was increased up to 2 wt% which attributed to formation of an exfoliated state and the uniform dispersion of montmorillonite in the chitosan matrix. However, with further increasing up to 5 wt% in nanoclay concentration loss in tensile strength was observed which could be attributed to aggregation of montmorillonite particles with high surface energy.

Other authors observed improved functional properties of other polysaccharide biopolymer like alginate (Benli et al., 2011), lignin (Guigo et al., 2009), agar (Jang et al., 2010, 2011; Rhim, 2011; Rhim et al., 2011), cellulose acetate and methyl cellulose (Rodríguez et al., 2011; Tunç & Duman, 2010, 2011; Rimdusit et al., 2008), starch-carboxy methyl cellulose (Almasi et al., 2010), pectin (Vartiainen et al., 2010) and natural guar (Wang et al., 2011; Wang & Wang, 2009) by addition of nanoclays.

A number of studies have been published on protein/clay nanocomposites. Clays have been reported to improve the mechanical strength of whey protein, making it use feasible. The optical and tensile properties of WPI-based films were greatly influenced by blending with organically modified MMT, Cloisite 30B. Water vapor barrier properties of these films were significantly improved by blending small amounts of nano-clays (5%) (Sothornvit et al, 2009, 2010).

Nanoclay can also be used to improve the functional properties of other protein based films. The presence of MMT in Wheat gluten (WG) nanocomposite films led to a significant reduction of the water sensitivity of WG-based materials. Significant changes in the permeability of films towards water vapour and aroma compounds were observed, while O₂ and CO₂ permeabilities remained unchanged. Finally, a slight improvement in tensile properties was obtained for filler contents higher than 2.5 wt% (Tunc et al., 2007; Guilherme et al., 2010). Also, there was a significant improvement in mechanical and barrier (water vapour and oxygen permeability) properties and thermal stability of the soy protein isolate (SPI) (Lee and Kim, 2010; Kumar et al., 2010 a,b) and corn zein films (Luecha et al., 2010) with the addition of MMT. The surface electrostatic interaction between the protein (+ charged) and the MMT layers (– charge) as well as the hydrogen bonding between the -NH and Si-O groups was understood to be the interacting mechanism for protein/MMT system (Chen and Zhang, 2006).

The dispersed clay improves the thermal stability of the matrix systematically with the increase of clay loading because the dispersed clay enhances the formation of char on the surface of polymer matrix and as a consequence, reduces the rate of decomposition for chitosan films (Xu et al., 2006b; Wang et al., 2005a) and starch nanobiopackage materials compared to the pure matrix (Avella et al., 2005; Chung et al., 2010; Lim et al., 2009; Lu et al., 2009; Magalhães and Andrade, 2009).

Amongst the most important properties of polymeric materials, the glass transition temperature (T_g), which determines the conditions in which the material can be used and stored, is of great interest (Mbey et al., 2011). Some authors (Hassan Nejad et al., 2010; Liu et al., 2010; Aouada et al., 2011; Wang et al., 2009b) reported a T_g and T_m increasing effect of nanoclay on starch

biodegradable films. According to Almasi et al., (2010), this reinforcing effect depends strongly on intercalation of nanoclay layers within the starch chains in amorphous regions and MMT ability to increase the starch matrix cohesiveness and to modify the starch chains orientation. Also, this is due to a barrier effect associated to clay that limits the heat diffusion through the starch matrix (Mbey et al., 2011). On the other hand, nanoclay effects on T_g of polymers have been controversial. Some authors reported T_g decreasing effects on biopolymer films (Gao et al., 2011; Souza et al., 2011). They proposed with the addition of clays, the intermolecular attraction of thermoplastic starch matrix seemed to be interrupted by the charged clays, subsequently the film backbone chains gained additional segmental mobility which led to the decrease of T_g . They also observed, with increased hydrophilic property of the clays, T_g reduced at the beginning and then went up. Clay with medium hydrophilic property had a greater effect on transition temperatures of the films.

During synthesis of nanocomposites, polymer chains from the bulk try to penetrate inside the silicate layers and as mentioned above, depending on penetration extent, an intercalated or exfoliated structure is formed. If polymer chains are not able to penetrate effectively, microcomposites formation takes place. There are a number of parameters that decide this degree of diffusion, viz. modification of clay, polar-polar interactions, molecular weight of polymer, packing density inside the gallery, concentration of filler, etc (Alexandre and Dubois, 2000). However, the sequence of mixing can also affect the nature of the resulting product, whether it will be a nano-level or micro-level distribution. Pandey and Singh (2005) studied the behavior of starch / plasticizer (glycerol) with clay to investigate the cause of intercalation and to study, which molecule enters the clay gallery with what preference. Starch / clay / glycerol (75 /5/20)

were mixed in the following ways: i) Starch was gelatinized with water followed by plasticization and then clay slurry was added. This mixture was heated for 30 min to boiling and the obtained composite samples were designated as STN1, ii) The clay slurry was mixed with starch in water and heated to boiling for 30 min with constant vigorous stirring, followed by the addition of plasticizer. These samples were named as STN2, iii) Starch, clay slurry and glycerol were mixed together and heated for 30 min to boiling and were designated as STN3 and iv) glycerol was mixed with clay slurry and stirred for 5 h at room temperature followed by addition of starch. This mixture was heated to boiling for 30 min and samples were named STN4.

The possible ways of interaction by which the four types of composites could be obtained are illustrated in Fig. 11. Starch and glycerol tend to migrate to clay galleries as both encounter polar-polar attraction forces with clay. Glycerol is preferred over starch in this competition due to its smaller molecular size. The rate of diffusion of both starch and glycerol inside the layers decreases when mixed together (STN1) because of mutual attraction forces, which formed a mass-like structure resulting in slow transport around the tectoides and consequently delay in migration inside the silicate layers. If already plasticized starch is mixed with clay, almost a microcomposite is formed and whatever the increase in gallery height observed is due to the migration of some glycerol inside the layers. The best nanocomposites were formed when first starch-clay was mixed followed by plasticization (STN2). In this case, the starch chains were involved in only one dominant polar-polar attraction with clay and confinement occurs without interference. At this moment, the plasticizer molecules encounter double attraction towards the gallery space; first with clay and second due to electrostatic hydrogen bonding formation with starch chains. Since the plasticizer is small in size, it can be accommodated in gaps of starch

chains between the silicate spacing. This process leads to an efficient plasticization of the starch matrix retaining the elongation of resulting product. Since complete diffusion of plasticizer is not possible due to presence of interactions between plasticizer and starch, it was concluded that both components in the STN3 samples have moved faster towards the gallery than in STN1 and slower than in STN2. When another set of the composites (STN4) were prepared by the mixing of starch in the mixture of clay and glycerol, a WAXD pattern showing a greater gallery height than STN1 but less than STN2 and STN3 was found. One most probable explanation may be, as soon as starch chains meet glycerol present in the gallery, close packing starts, which may generate a solid-like structure after a definite penetration of starch chains. At this stage of penetration, other chains diffusion becomes difficult, resulting in a microcomposite (Fig. 11). These results show that the sequence of addition of components had a significant effect on the nature of composites. Diffusion of plasticizer inside the clay is easier than diffusion of biopolymer. Biopolymer chains must penetrate through clay galleries first, followed by plasticization in order to maintain the plasticization efficiency.

Nanoclays also show antimicrobial activity. The antimicrobial activity of clay minerals is based on a strong adsorption of toxins produced by bacteria. Sothornvit et al, (2009, 2010) investigated the effect of nanoclay type on the antimicrobial properties of whey protein isolate/clay nanocomposite films. They used three different types of nano clays, Cloisite Na⁺, Cloisite 20A, and Cloisite 30B. The antimicrobial activity of WPI/nano-clay composite films depended on type of MMTs and microorganisms tested. The control WPI films showed no antimicrobial activity against both Gram-negative (*E. coli* O157:H7) and positive bacteria (*L. monocytogenes*). Incorporation of Cloisite 30B in WPI films showed a distinctive bacteriostatic effect against

Rhim et al. (2006) also found that a chitosan/Cloisite 30B nanocomposite films exhibited bactericidal effects against the Gram-positive bacteria including *S. aureus* and *L. monocytogenes*, and bacteriostatic effects against the Gram-negative bacteria *S. typhimurium* and *E. coli*. They explained the antimicrobial activity of the composite films might be attributed to the quaternary ammonium group in the silicate layer of Cloisite 30B, which disrupts bacterial cell membranes and causes cell lysis. Other authors also, observed the antimicrobial activity of chitosan–MMT nanocomposites against *Escherichia coli* and *Staphylococcus aureus* (Han et al., 2010; Hsu et al., 2011). These results imply that nano-clays may be incorporated into polymer matrix not only as a filler to improve film properties but also as an antimicrobial agent to provide functional properties. Sterilizing effect and adsorption of toxins are pointed out as some practical potential bio- applications of nano-clay (Wilson, 2003).

3-5-1. Structure and Properties

The diagram illustrates a silicate polymer chain. It features a backbone of silicon (Si) atoms connected by oxygen (O) atoms. Some silicon atoms are bonded to hydroxyl groups (OH), labeled "isolated hydroxyl groups". Other silicon atoms are bonded to oxygen atoms that are part of a hydrogen bond network, labeled "hydrogen bond". The structure is shown as a continuous chain with dashed lines indicating the polymer nature.

Nano-SiO₂ deviates from a stable silicon–oxygen structure for lack of oxygen in its surface. Its molecular formula is SiO_{2-x}, in which x ranges from 0.4 to 0.8. Because of its small size, large specific surface area, high surface energy, as well as a lot of unsaturated chemical bonds and hydroxyl groups on the surface, nano-SiO₂ is easy to disperse into the macromolecular chains (Tang et al., 2009b; Xiong et al., 2008).

Silicon dioxide (E551), is a permitted food additive which is preferably insoluble. SiO₂ used in food contact surfaces and food packaging. The coating is applied using a continuous process as a thin amorphous film of 50 nm or less to prevent cracking of the barrier if the product is flexed. The flexibility of the coatings may be increased by the addition of other additives during production. The source compounds for SiO₂ used in the production of the nanoscale SiO₂ coatings includes organosilicates, silanes, chlorosilanes and tetraethylorthosilane (Chaudhry et al., 2008).

3-5-2. Applications and effects on biopolymers matrices

Tang et al., (2009b) increased tensile strength and water resistance properties of the starch/poly(vinyl alcohol) (PVA) films with loading nano-sized silicon dioxide particles into the starch/PVA blend. They emphasized that intermolecular hydrogen bond was formed between nano-Silicon dioxide and starch or n-SiO₂ and PVA, and the strong chemical bond C–O–Si was also formed in nano-SiO₂/starch/PVA hybrid materials, which improved the miscibility between film components. This reason confirmed by IR analysis (Yao et al., 2011). The nano-SiO₂ content significantly impacted on the water resistance of TPS:PVA films. The increase of SiO₂ nanoparticle leads to the decrease of both water solubility and water uptake (Abbasi, 2011).

Improvements in mechanical properties of the starch based nanocomposite films, not only was including tensile strength but also enhancement in strain at break was reported as resulting from nano-Silicon dioxide addition. With increasing nano-SiO₂ weight percent, the water resistance, and water vapor permeability and optical transparency of the films was also improved (Tang et al., 2008b). Xiong et al. (2008) successfully produced starch-based biodegradable films containing with similar results and advantages. They also observed improved melting temperature in nanosilica–starch based nanocomposite which attributed to restriction of the movement of molecular chains by C–O–Si bonds.

3-6. Carbon nanotubes (CNTs)

3-6-1. Structure and Properties

Carbon nanotubes are cylindrical tubes of carbon with 5 nm internal and 10 nm external diameters and very high aspect ratios (the ratio of length to width, e.g.>300). These tubes are allotropes of carbon called fullerenes (Fig. 12). Carbon nanotubes are produced in two forms namely; single wall (SWCNTs) and multiwall nanotubes (MWCNTs). Compared with SWCNTs, MWCNTs is low price and abundant enough.

The CNTs has the history since 1960s, in mid-1990s only, it was shown by Iijima that the CNTs can be made in the quantities required for the reinforcement of polymer and their evaluation. three main methods used for single and multi-walled carbon nanotubes synthesis include arc-discharge laser ablation, gas-phase catalytic growth from carbon monoxide and chemical vapor deposition (CVD) from hydrocarbons methods (Kumar et al., 2009; Bradley et al., 2011; Sanguansri and Augustin, 2006; Gacitua et al., 2005; Dai, 2002; Thostenson et al., 2001).

Some of prominent characteristics of CNTs include high strength, good electrical and thermal conductivity and other functional properties like antistatic, crystallization behavior and antimicrobial effects, , chemical and contaminants absorber and flame-retardant (Sekhon, 2010; Nepal et al., 2008; Upadhyayula et al., 2009; Wei et al., 2011; Zhao et al., 2011).

Single walled carbon nanotubes (SWNTs) exhibit strong antimicrobial activity. Kang et al. (2007) observed direct contact of E.coli cells and CNTs, is known as the CNT antibacterial mechanism, caused cell membrane damage. SWNTs have highly stronger antibacterial efficiency compared to MWNTs against E. coli (Kang et al., 2008).

CNTs exceptional mechanical properties (tensile strength on the order of 100 GPa, stiffness 1000 GPa, failure strain up to 0.4 and elastic modulus 1.7 TPa,). These experimental parameters are close to the theoretically predicted values and they demonstrate the great potential for improving the mechanical properties, especially the fracture toughness, of polymer nanocomposites (Rozenberg and Tenne, 2008; Pavlidou and Papaspyrides, 2008; Chen et al., 2005; Sanchez-Garcia et al., 2010). Nanotubes may exhibit significant waviness. The effects of waviness on the elastic moduli of CNT-reinforced polymer composites have been shown to be significant (Gibson et al., 2007).

3-6-2. Applications and effects on biopolymers matrices

Cao et al. (2007) reported that the addition of multiwalled carbon nanotubes (MWCNTs) as filler-reinforcement into a plasticized starch (PS) matrix improved tensile strength Young modulus and strain at break properties of the nanocomposite. Strain at break, tensile strength and Young's modulus reached a maximum value as the MWCNTs content was 1.0, 3.0 and 3.0 wt%,

respectively. Water uptake of the nanocomposites at the presence of MWCNTs also decreased due to the strong hydrogen bonding between MWCNTs fillers and PS matrix. The T_g values shifted to higher temperatures with increasing CNTs content, indicating that the MWCNTs were compatible with PS matrix and reduced the flexibility and mobility of starch molecular chains. However, the huge outer diameter and smooth surface of MWCNTs decrease compatibility in these type composites. Therefore, Zhanjun et al., (2010), introduced hydrophilic (Carboxylic acid) groups on the surface of MWCNTs. These modified CMWNTs could improve thermal stability and electrical conductivity as well as tensile strength and modulus of TPS matrix. Even at concentrations as low as 0.055 wt.%. MWCNTs, improvements in the mechanical properties (including tensile strength, modulus, strain and tensile toughness) were also reported in starchbased composite, also increased (Fama et al., 2011). Similar advantages were observed by Ma et al., (2008) with except reduction in toughness.

Zheng et al., (2007) have investigated the influences of various sizes of MWNTs, on the mechanical and water resistance properties of soy protein isolate (SPI) based films. They observed that SPI nanocomposites containing 0.25wt.% of 10–15nm MWNT was simultaneously reinforced and toughened. A MWNT with moderate size could provide the highest tensile strength and Young modulus. The improvement of water resistance and mechanical properties was mainly attributed to interactions at the interface of SPI chain and wrapped MWNTs and the interface between penetrating SPI chains and the internal wall of MWNTs.

Carbon nanotubes have been also reported to improve the mechanical properties of chitosan based films. Incorporation of only 0.8wt.% MWNTs, increased about 93% and 99% in the tensile

strength and modulus of the chitosan based nanocomposites, respectively however, carbon nanotube decreased strain at break (flexibility) of biocomposite (Wang et al., 2005b).

Tang et al. (2009a) have successfully prepared chitosan/clay–CNT ternary nanocomposites by a simple solution-intercalation/mixing method. They observed a great synergistic effect of clay platelets and CNTs (chitosan/2% clay/1% CNTs) on thermal stability, dynamic mechanical and barrier properties of chitosan matrix. They emphasized that a formation of 3D jammed and conjugated filler network with 1D CNTs inserted in the 2D clay platelet network, could explain the observed synergistic effect and probably resulted in higher improvement in the chitosan film properties (Fig. 13).

4. Organic nano-structured materials and their bionanocomposites

4-1. Cellulose-based nanoreinforcements

4-1-1. Structure and properties

Cellulose, the building material of long fibrous cells, is a highly strong natural polymer which is consisted from glucose by beta 1→4 linkages. Cellulose nanofibers which can be obtained from cellulose fibrils or microcrystalline cellulose have several advantages such as low in cost, widely available material (most abundant polysaccharide in the world), biodegradable, low density ($\sim 1.5 \text{ gcm}^{-3}$), high mechanical strength and special surface. These impotent and valuable properties makes cellulose nanofibers as an attractive class of nanomaterials for producing low in cost, lightweight, and high-strength nanocomposites (Podsiadlo et al., 2005). Basically two types of nanoreinforcements can be obtained from cellulose –microfibrils and whiskers (Azizi Samir et al., 2005). In plants, the cellulose chains are synthesized to form elementary microfibrils (or

nanofibers), which are bundles of molecules that are elongated and stabilized through hydrogen bonding (Azizi Samir et al., 2005; Wang and Sain, 2007) and macrofibrils are formed by aggregation of elementary microfibrils (Figs. 14,15). The microfibrils have nanosized diameters (2–20 nm, depending on the origin), and lengths in the micrometer range (Azizi Samir et al., 2005; Oksman et al., 2006), and are made up of crystalline and amorphous parts (Fig. 16). The size, shape and orderliness of the crystallite regions play a predominant role as far as such fiber properties as tensile strength, density, rigidity; swelling and heat-sensitivity are concerned. The less ordered areas (amorphous region) and the ratio of such amorphous areas to the crystalline regions are more influential in controlling extensibility. With hydrolysis of amorphous regions and isolation of crystalline parts by several treatments, nanowhiskers (also known as nanocrystals), are produced with lengths ranging from 500 nm up to 1–2 μm , and about 2–20 nm in diameter resulting in high aspect ratios (Azizi Samir et al., 2004; Lima and Borsali, 2004). Each microfibril can be considered as a string of whiskers, linked along it by amorphous domains (which act as structural defects), and having a modulus close to that of a crystal of native cellulose (about 150 GPa) and a strength of about 10 GPa (Helbert et al., 1996) which are only about seven times lower than those of single-walled carbon nanotubes (Podsiadlo et al., 2005).

The main method used to obtain cellulose whiskers has been basically acid hydrolysis which in this method acid removes the amorphous regions in the microfibrils and leaves the crystalline regions intact (Fig. 17); the dimensions of the whiskers after hydrolysis depend on the percentage of amorphous regions in the bulk fibrils, which varies for each organism (Gardner et al., 2008). Cellulose nanowiskers can be produced from microcrystalline cellulose (MCC) (Fig.

18). Microcrystalline cellulose is formed by particles of hydrolyzed cellulose consisting of a very large amount of cellulose microcrystals together with amorphous areas (Petersson and Oksman, 2006). MCC is prepared by removing part of the amorphous regions by acid degradation leaving the less accessible crystalline regions as fine crystals of typically 200–400 nm in length and an aspect ratio of about 10. Degree of polymerization (DP) is about 140–400, depending on the cellulose source and treatment procedure (Wu et al., 2007). Subsequent hydrolysis breaks down those portions of the long glucose chains in accessible, noncrystalline regions. A leveling-off degree of polymerization is achieved: this corresponds to the residual highly crystalline regions of the original cellulose fiber. When this level is reached, hydrolysis is terminated by rapid dilution of the acid. A combination of centrifugation and extensive dialysis is then employed to fully remove the acid, and a brief sonication completes the process to disperse the individual particles of cellulose and yield an aqueous suspension (Fig. 18)(Hamad, 2006). The cellulose rods that remain after this treatment are almost entirely crystalline and named cellulose nanocrystallites (Fig. 19).

The precise physical dimensions of the crystallites depend on several factors, including the source of the cellulose, the exact hydrolysis conditions, and ionic strength (Fleming et al., 2001). Bondeson et al., (2006) investigate the effect of reaction conditions on the acid hydrolysis processing of MCC. The factors that varied during the process were the concentration of MCC and sulfuric acid, the hydrolysis time and temperature, and the ultrasonic treatment time. Optimized treatment conditions proposed to achieve the best results of isolation of nanocrystallites from MCC (derived from Norway spruce (*Picea abies*)) includes: Temperature: 44 °C; H₂SO₄ concentration: 63.5 % (w/w); time: 130.3 min; MCC concentration: 10.2 g/100ml and sonication

time: 29.6 min (Bondeson et al., 2006). They noted that optimized process parameters would most probably have been different if cellulose from other sources had been used.

Table 1 shows properties of nanocrystals obtained from cotton linters (Oksman et al., 2006). Structural dimensions of whiskers obtained from different sources are given in Table 2 (Azizi Samir et al., 2005).

4-1-2. Applications and effects on biopolymers matrices

Cellulose nanocrystals have been reported to have considerable improving effects on physicochemical properties of biopolymer matrices. Cao et al., (2008a) showed that the hemp cellulose nanocrystal (HCN) content had a profound effect on the mechanical properties of the starch films. The tensile strength increased from 3.9 to 11.5 MPa and Young's modulus increased significantly from 31.9 to 823.9 MPa with increasing filler content from 0 to 30 wt %. This can probably be explained by the reinforcement effect from the homogeneously dispersed high-performance HCN fillers in the starch matrix and strong hydrogen bonding interaction between the HCNs and starch molecules. Meanwhile, the strain at break decreased from 68.2 to 7.5%, which indicated that the incorporation of HCNs restricted the motion of the starch chains due to the formation of strong interactions between the fillers and matrix. These results conformed to Angles and Dufrence (2001) work which carried out by using Tunicin whiskers in starch matrix. The same results have been reported about improving mechanical properties of hydroxypropyl cellulose (Zimmermann et al., 2005), cellulose acetate butyrate (Grunert and Winter, 2002), polylactic acid (Oksman et al., 2006) and Carboxymethyl Cellulose (Choi and Simonsen, 2006) films by addition of cellulose nanofillers.

Moisture barrier of biopolymer films has been observed to be improved by cellulose nanoreinforcements (Cao et al., 2008a; Cao et al., 2008b; Svagan et al., 2009; Choi and Simonsen, 2006). On one hand, the presence of crystalline fibers is thought to increase the tortuosity in the materials leading to slower diffusion processes and, hence, to lower permeability (Sanchez- Garcia et al., 2008). On the other hand, cellulose nanocrystal has lower hydrophilicity in comparison to most biopolymer based matrixes such as plasticized starch which in turn decrease total solubility of water molecules in composite matrixes. Meanwhile, strong hydrogen interaction between starch and cellulose nanocrystal decreases OH group in matrix. The barrier properties are enhanced if the filler be less permeable, have good dispersion in the matrix and high aspect ratio (Lagaron et al., 2004).

Nanosized cellulose fibrils have been also reported to improve thermal properties of biocomposite (Cao et al., 2008a; Cao et al., 2008b; Zimmermann et al., 2005; Choi and Simonsen, 2006). On the other hand, their effects on T_g of polymers have been controversial. Mathew and Dufresne (2002) observed that T_g of a sorbitol-plasticized starch nanocomposite with tunicin whiskers first increased up to a whisker content around 10–15 wt.% and then decreased at higher concentration. The increase of T_g , up to 15 wt.% whiskers, was attributed to the increase in the crystallinity of the starch matrix with enhancing nanowiskers content which restrict mobility of amorphous amylopectin chains (due to the physical cross-links induced by the crystalline region). The decrease of T_g at higher concentration of nanocrystal, was attributed to partially ejection of plasticizer (sorbitol) from crystalline domains during crystallization and inclusion of it in the amorphous domains of the matrix.

This phenomenon should compete with the increase of T_g (due to increase of crystallinity) and becomes predominant at high loading level. However, Cao et al., (2008b) reported that the T_g of starch films increases by increasing flax cellulose nanocrystal content, up to 30% wt. Choi and Simonsen, (2006) showed the same results about the use of cellulose nanocrystals in carboxymethyl cellulose matrix.

4-2. Starch nanocrystals

4-2-1. Structure and properties

Starch is a semicrystalline biopolymer and when native starch granules are submitted to an extended-time hydrolysis at temperatures below the gelatinization temperature, the amorphous regions are hydrolyzed allowing separation of crystalline lamellae, which are more resistant to hydrolysis. The starch crystalline particles (crystallites) show platelet morphology with thickness of 6–8 nm, length of 20–40 nm and width of 15–30 nm. However, individual starch crystallites could hardly be obtained since the starch platelets flocculate and form aggregates. Nevertheless, since at least one of the dimensions of aggregates is at the nanometer scale, the term ‘nanoparticle’ is applicable for starch crystalline particles derived by acid etching of granular starch (Kristo and Biliaderis, 2007).

4-2-2. Applications and effects on biopolymers matrices

It was shown that the reinforcing effect of the starch nanocrystals can be attributed to strong filler/filler and filler/matrix interactions due to the establishment of hydrogen bonding. The

presence of starch nanocrystals also led to slow down the recrystallization of the matrix during aging in humid atmosphere (Viguie' et al., 2007).

Kristo and Biliaderis (2007) reported that the addition of starch nanocrystals improved tensile strength and modulus of pullulan films, but decreased their elongation. The T_g values shifted to higher temperatures with increasing starch nanocrystals content, which was attributed to a restricted mobility of pullulan chains due to the formation of strong interactions between starch nanocrystals as well as between filler and matrix. The water vapor permeability of the pullulan films was decreased by addition of 20% or more starch nanocrystals. The same results were observed by Viguie' et al., (2007) for reinforcing sorbitol plasticized waxy maize starch films by starch nanocrystals.

Zheng et al., (2009) investigated the effect of the starch nanocrystals on the physical properties of the soy protein isolate (SPI) films. The SPI films containing 2wt% starch nanocrystal showed an ultimate tensile strength (UTS) about 10.39 MPa (6.51 MPa for control sample). However, when the starch nanocrystal loading was higher than 2 wt%, the UTS gradually decreased with increasing of the starch nanocrystal content. On the other hand, by addition of 1 wt% starch nanocrystal, strain at break (ϵ_b) of films sharply decreased from 171.5 to 64.4%. The reinforcement of low- starch nanocrystal loading level (lower than 2 wt%) was attributed to uniform distribution of starch nanocrystal in SPI matrix which in turn increased matrix–filler interactions and decreased SPI chain mobility. However, with increasing of the starch nanocrystal content, the nanocrystals probably self-aggregated as large domains which in turn decreased the starch nanocrystal surface for interacting with the SPI matrix. The T_g values also increased with increasing starch nanocrystals content. However, unlike the results obtained by

Kristo and Biliaderis (2007) and Viguie' et al., (2007) about the effects of starch nanocrystals on starch films, Zheng et al., (2009) showed that water uptake of SPI films containing starch nanocrystals was slightly higher than those in pure SPI films which was attributed to higher hydrophilic nature of the starch nanocrystal than SPI matrix.

4-3. Chitin/chitosan nanoparticles

4-3-1. Structure and properties

Chitin, poly β -(1-4)-N-acetyl-d-glucosamine, is a second most abundant polysaccharide in the world (cellulose is first abundant) which is synthesized by an enormous number of living organisms; It is extracted from crab and shrimp shells as a byproduct of the seafood industry (Jayakumar et al., 2010).

The most important derivative of chitin is chitosan which obtained by (partial) deacetylation of chitin in the solid state under alkaline conditions (concentrated NaOH) or by enzymatic hydrolysis in the presence of chitin deacetylase. Because of the semicrystalline morphology of chitin, chitosan obtained by solid-state reaction has a heterogeneous distribution of acetyl groups along the chains. Chitin and chitosan are biocompatible, biodegradable and non-toxic polymers (Ravi Kumar, 2000).

Chitin is known to form microfibrillar arrangements in living organisms. These fibrils are usually embedded in a protein matrix and their diameters usually range from 2.5 to 2.8 nm, with chitin microfibrils from cuticles of crustaceans being found to be as large as 25 nm (Wathanaphanit et al., 2008). Under hydrolytic conditions of boiling HCl and vigorous stirring, chitin whiskers of slender parallelepiped rods have been successfully prepared from different chitin sources such as

crab shells (Nair and Dufresne, 2003), shrimp shells (Sriupayo et al., 2005), squid pens (Paillet and Dufresne, 2001), and tubes of *Tevnia jerichonana* (Saito et al., 1997) and *Riftia pachyptila* tubeworms (Morin and Dufresne, 2002).

Chitosan nanoparticles can be obtained by ionic gelation, where the positively charged amino groups of chitosan form electrostatic interactions with polyanions employed as cross-linkers, such as tripolyphosphate (Lopez-Leon et al., 2005).

4-3-2. Applications and effects on biopolymers matrices

Chitin and chitosan whiskers were used as reinforcing fillers in both synthetic and natural polymeric matrices (Ravi Kumar, 2000). Lu et al. (2004) added chitin whiskers to soy protein isolate (SPI) thermoplastics and reported that the whiskers greatly improved not only the tensile properties (tensile strength and elastic modulus) of the matrix, but also its water resistance.

Watthanaphanit et al., (2008) investigated the thermal stability, mechanical behavior, and biodegradability of the chitin whisker-reinforced alginate nanocomposite fibers. Incorporation of a low amount of the whiskers in the nanocomposite fibers improved both the mechanical and the thermal properties of the fibers significantly, possibly a result of the specific interactions, i.e., hydrogen bonding and electrostatic interactions, between the alginate molecules and the homogeneously dispersed chitin whiskers. The addition of the chitin whiskers in the nanocomposites fibers accelerated the biodegradation process of the fibers.

Sriupayo et al., (2005) added chitin whiskers to chitosan films and observed that the whiskers improving chitosan tensile strength up to 2.96% whisker content while higher content of whiskers resulted in decreasing strength. The strain at break of the films was diminished by

addition of whiskers up to 2.96%, and then it leveled off at higher whiskers contents. They also showed the addition of α -chitin whiskers improved water resistance of the nanocomposite films.

Chang et al., (2010a) studied the effect of chitin nanoparticles on the morphology, structural, thermal and mechanical properties of the starch-based nanocomposites. At low chitin nanoparticles concentration (2 wt.%), most chitin nanoparticles are dispersed uniformly in the glycerol plasticized starch matrix without obvious aggregation which is ascribed to strong interaction because of the similar polysaccharide structures of chitin nanoparticles and potato starch in the glycerol plasticized starch matrix. However, at a high filler content (5 wt.%) conglomeration of chitin nanoparticles was obvious. When the chitin nanoparticles content varied from 0 to 5 wt.%, the UTS increased from 2.84 to 7.79 MPa while as, the ϵ_b decreased from 59.3% to 19.3%. Increasing chitin nanoparticles content from 1 to 3 wt.% increased and decreased T_g and WVP values of the starch based nanocomposite, respectively. However, the slightly decrease in WVP subsequently observed at concentration of 3 to 5 wt.% chitin nanoparticles.

The water resistance of chitin nanoparticles was better than that of the GPS matrix on the other hand; the addition of chitin nanoparticles introduced a tortuous path for water molecules to pass through the composites. Chitin nanoparticles dispersed well in the matrix at low chitin nanoparticles concentrations and so there were fewer paths for water molecules to pass through the composite matrix; however, superfluous chitin nanoparticles caused to aggregation of particles which in turn facilitated water vapor permeation.

Chang et al., (2010b) prepared chitosan nanoparticles, by physical crosslinking between tripolyphosphate and protonised chitosan and used as filler in a glycerol plasticised-starch

matrix. It was also shown that the obvious improved effect on the tensile strength, storage modulus, glass transition temperature, water vapour barrier and thermal stability which could be attributed to the filler/matrix interactions and it occurred when chitosan nanoparticle was dispersed uniformly in the glycerol plasticized-starch matrix at low content. However, higher chitosan nanoparticle loads (8 wt %) resulted in the aggregation of chitosan nanoparticle in the composites. The significant improves in mechanical and barrier properties of the hydroxypropyl methylcellulose (HPMC) films by addition of chitosan–tripolyphosphate (CS-TPP) nanoparticles also reported (De Moura et al. 2009).

Conclusion

This review illustrated the potential of nano- scale fillers in improvement of biopolymer based composites for food packaging purposes. Unfortunately for certain applications, biopolymer based packaging materials cannot be fully competitive with conventional thermoplastics since some of their properties are too weak. Therefore, to extend their applications, these biopolymers have been formulated and associated with nano-sized fillers, which could bring a large range of improved properties. Nanobiocomposites technology is still in its early stages and is a new strategy to improve physical properties of biopolymers, including mechanical strength, thermal stability, antimicrobial activity and gas barrier properties. In food packaging, a major emphasis is on the development of high barrier properties against the migration of water vapor, oxygen, carbon dioxide and flavor compounds. Decreasing water vapor permeability is a critical issue in the development of bioplastics as sustainable packaging materials and nanofillers could be

potentially improved water vapour barrier properties of biopolymer based packaging which in turn may advance the utilization of biopolymers in food packaging.

References

- Abbasi, Z. (2011). Water resistance, weight loss and enzymatic degradation of blends starch/polyvinyl alcohol containing SiO₂ nanoparticle. *Taiwan Institute of Chemical Engineers*. In Press Paper.
- Adame, D., and Beall, G.W. (2009). Direct measurement of the constrained polymer region in polyamide/clay nanocomposites and the implications for gas diffusion. *Applied Clay Science*. **42**: 545–552.
- Akhavan, O. (2009). Lasting antibacterial activities of Ag–TiO₂/Ag/a-TiO₂ nanocomposite thin film photocatalysts under solar light irradiation. *Journal of Colloid and Interface Science*. **336**: 117–124.
- Alexandre, M., and Dubois, P. (2000). Polymer-layered silicate nanocomposites: preparation, properties and uses of a new class of materials. *Materials Science and Engineering*. **28**: 1–63.
- Almasi, H., Ghanbarzadeh, B., and Entezami, A.A. (2010). Physicochemical properties of starch–CMC–nanoclay biodegradable films. *International Journal of Biological Macromolecules*. **46**(1): 1-5.
- Altinisik, A., Seki, Y., and Yurdakoc, K. (2009). Preparation and Characterization of Chitosan/KSF Biocomposite Film. *Polymer Composites*. **77**: 1035-1042.
- Alves, V.D., Costa, N., and Coelho, I.S. (2010). Barrier properties of biodegradable composite films based on kappa-carrageenan/pectin blends and mica flakes. *Carbohydrate Polymers*. **79**: 269-276.

- Amin, S.A., Pazouki, M., and Hosseinnia, A. (2009). Synthesis of TiO₂-Ag nanocomposite with sol-gel method and investigation of its antibacterial activity against E. coli. *Powder Technology*. **196**: 241–245.
- Angle`s M.N., and Dufresne, A., (2001). Plasticized starch/tunicin whiskers nanocomposite materials, 2: mechanical behavior. *Macromolecules*. **34**(9): 2921-2931.
- Anwar, N.S., Kassim, A., Lim, H.N., Zakarya, S.A., and Huang, N.M. (2010). Synthesis of titanium dioxide nanoparticles via sucrose ester micelle-mediated hydrothermal processing route. *Sains Malaysiana*. **39**(2): 261-265.
- Aouada, F.A., Mattoso, L.H.C., and Elson, L. (2011). New strategies in the preparation of exfoliated thermoplastic starch-montmorillonite nanocomposites. *Industrial Crops and Products*. **34**: 1502–1508.
- Armellao, L., Barreca, D., Bottaro, G., Gasparotto, A., Maccato, C., Maragno, C., Tondello, E., Stangar, U.L., Bergant, M., and Mahne, D. (2007). Photocatalytic and antibacterial activity of TiO₂ and Au/TiO₂ nanosystems. *Nanotechnology*. **18**: 1-7.
- Arora, A., and Padua, G.W. (2010). Review: nanocomposites in food packaging. *Journal of Food Science*. **75**: 1, 43-49.
- Asahara, T., Koseki, H., Tsurumoto, T., Shiraishi, k., Shindo, H., Baba, k., Taoda, H., and Terasaki, N. (2008). The bactericidal efficacy of a photocatalytic TiO₂ particle mixture with oxidizer against staphylococcus aureus. *Japanese Journal of Infectious Diseases*. **62**: 378-380.
- Avella, M., Errico, M.E., and Gentile, C. (2005). Nylon 6/calcium carbonate nanocomposites: characterization and properties. *Macromolecular Symposia*. **243**: 170-175.

- Avérous, L., and Halley, P.J. (2009). Biocomposites based on plasticized starch. *Biofuels, Bioproducts and Biorefining*. **3**(3): 329-343.
- Azeredo, H.M.C. (2009). Nanocomposites for food packaging applications. *Food Research International*. **42**: 1240-1253.
- Azeredo, H.M.C., Mattoso, L.H.C., Wood, D., Williams, T.G., Avena-Bustillos, R.J., and Mughch, T.H. (2009). Nanocomposite edible films from mango puree reinforced with cellulose nanofibers. *Journal of Food Science*. **74**: 5, 31-35.
- Azizi Samir, M.A.S., Alloin, F., Sanchez, J.Y., and Dufresne, A. (2004). Cellulose nanocrystals reinforced poly(oxyethylene). *Polymer*. **45**: 4149–4157.
- Azizi Samir, M. A. S., Alloin, F., and Dufresne, A. (2005). Review of recent research into cellulosic whiskers, their properties and their application in nanocomposite field. *Biomacromolecules*. **6**: 612–626.
- Bae, H.J., Park, H.J., Darby, D.O., Kimmel, R.M., and Whiteside, W.S. (2009). Development and characterization of PET/fish gelatin–nanoclay composite/LDPE laminate. *Packaging Technology and Science*. **22**: 371–383.
- Bae, H.J., Park, H.J., Hong, S.I., Byun, Y.J., Darby, D.O., Kimmel, R.M., and Whiteside, W.S. (2009). Effect of clay content, homogenization RPM, pH, and ultrasonication on mechanical and barrier properties of fish gelatin/montmorillonite nanocomposite films. *LWT- Food Science and Technology*. **42**: 1179–1186.
- Banerjee, S., Gopal, J., Muraleedharan, P., Tyagi, A.K. and Raj, B. (2006). Physics and chemistry of photocatalytic titanium dioxide: Visualization of bactericidal activity using atomic force microscopy. *Current Science*. **90**: 10-15.

- Barlow, S., Chesson, A., Collins, J.D., Flynn, A., Hardy, A., Jany, K., Knaap, A., Kuiper, H., Larsen, J.C., Neindre, P., Schans, J., Schlatter, J., Silano, V., Skerfving, S., and Vannier, P. (2009). The potential risks arising from nanoscience and nanotechnologies on food and feed safety. *The European Food Safety Authority Journal*. **958**: 1-39.
- Battista, O. A. (1975). Microcrystal polymer science. *McGraw-Hill*.
- Benli, B., Boylu, F., Can, M.F., Karakas, F., Cinku, K., and Ersever, G. (2011). Rheological, electrokinetic, and morphological characterization of alginate–bentonite biocomposites. *Journal of Applied Polymer Science*. **122**: 19–28.
- Bharadwaj, R.K. (2001). Modeling the barrier properties of polymer-layered silicate nanocomposites. *Macromolecules*. **34**: 9189-9192.
- Bigdeli, F., Morsali, A., and Retailleau, P. (2010). Syntheses and characterization of different zinc (II) oxide nano-structures from direct thermal decomposition of 1D coordination polymers. *Polyhedron*. **29**: 801–806.
- Bondeson, D., Mathew, A., and Oksman, K. (2006). Optimization of the isolation of nanocrystals from microcrystalline cellulose by acid hydrolysis. *Cellulose*. **13**:171 –180.
- Boo, W.J. (2007). Structured-property relationship of nanoplatelet reinforced polymer nanocomposites. *Thesis for degree of doctor of philosophy*.
- Bordes, P., Pollet, E., and Averous, L. (2009). Nano-biocomposites: Biodegradable polyester/nanoclay systems. *Progress in Polymer Science*. **34**: 125–155.
- Bouwmeester, H., Dekkers, S., Noordam, M.Y., Hagens, W.I., Bulder, A.S., de Heer, C., ten Voorde, S.E.C.G., Wijnhoven, S.W.P., Marvin, H.J.P., and Sips, A.J.A.M. (2009). Review

of health safety aspects of nanotechnologies in food production. *Regulatory Toxicology and Pharmacology*. **53**: 52-62.

Bradley, E.L., Castle, L., and Chaudhry, Q. (2011). Applications of nanomaterials in food packaging with a consideration of opportunities for developing countries. *Trends in Food Science & Technology*. In Press Paper.

Brody, A.L., Bugusu, B., Han, J.H., Sand, C.K., and Mchugh, T.H. (2008). Innovative food packaging solutions. *Journal of Food Science*. **73**(8):107-116.

Cao, X., Chen, Y., Chang, P.R., and Huneault, M.A. (2007). Preparation and properties of plasticized starch/multiwalled carbon nanotubes composites. *Journal of Applied Polymer Science*. **106**: 1431–1437.

Cao, X., Chen, Y., Chang, P.R., Stumborg, M., and Huneault, M.A. (2008a). Green composites reinforced with hemp nanocrystals in plasticized starch. *Journal of Applied Polymer Science*. **109**: 3804–3810.

Cao, X., Chen, Y., Chang, P.R., Muir, A.D., and Falk, G. (2008b). Starch-based nanocomposites reinforced with flax cellulose nanocrystals. *Express Polymer Letters*. **2**(7): 502–510.

Casariello, A., Souza, B.W.S., Cerqueira, M.A., Teixeira, J.A., Cruz, L., Diaz, R. and Vicente, A.A. (2009). Chitosan/clay films' properties as affected by biopolymer and clay micro/nanoparticles' concentrations. *Food Hydrocolloids*. **23**: 1895–1902.

Casciola, M., Donnadio, A., Pica, M., Valentini, V., and Piaggio, P. (2005). Characterization of Zr phosphate/PVDF nanocomposites by vibrational spectroscopy. *Macromolecular Symposia*. **230**: 95–104.

- Cerrada, M.L., Cristina Serrano, C., Chaves, M.S., Marta Fernandez-Garcia, M.F., Martin, F.F., de Andres, A., Rioboo, R.J.J., Kubacka, A., Ferrer, M., and Garcia, M.F. (2008). Self-sterilized EVOH-TiO₂ nanocomposites: Interface effects on biocidal properties. *Advanced Functional Materials*. **18**: 1949–1960.
- Chan, C.M., Wu, J., Li, J.X., and Chung, Y.K. (2002). Polypropylene/calcium carbonate nanocomposites. *Polymer*. **43**: 2981-2992.
- Chang, P.R., Jian, R., Yu, J., and Ma, X. (2010a). Starch-based composites reinforced with novel chitin nanoparticles. *Carbohydrate Polymers*. **80**: 420–425.
- Chang, P.R., Jian, R., Yu, J., and Ma, X. (2010b). Fabrication and characterisation of chitosan nanoparticles/plasticised-starch composites. *Food Chemistry*. **120**: 736–740.
- Chaudhry, Q., Aitken, R., Scotter, M., Blackburn, J., Ross, B., Boxall, A., Castle, L., and Watkins, R. (2008). Applications and implications of nanotechnologies for the food sector. *Food Additive and Contaminants*. **25**: 242-258.
- Chawengkijwanich, C., and Hayata, Y. (2008). Development of TiO₂ powder-coated food packaging film and its ability to inactivate Escherichia coli in vitro and in actual tests. *International Journal of Food Microbiology*. **123**: 288–292.
- Chen, P., and Zhang, L. (2006). Interaction and properties of highly exfoliated soy protein/montmorillonite nanocomposites. *Biomacromolecules*. **7**(6): 1700–1706.
- Chen, W., Tao, X., Xue, P., and Cheng, X. (2005). Enhanced mechanical properties and morphological characterizations of poly(vinyl alcohol)–carbon nanotube composite films. *Applied Surface Science*. **252**: 1404–1409.

- Cheng, Q., Li, C., Pavlinek, V., Saha, P., and Wang, H. (2006). Surface-modified antibacterial TiO₂/Ag⁺ nanoparticles: Preparation and properties. *Applied Surface Science*. **252**: 4154–4160.
- Chiu, C.W., and Lin, J.J. (2011). Self-assembly behavior of polymer-assisted clays. *Progress in Polymer Science*. In Press Paper.
- Chivrac, F., Pollet, E., and Averous, L. (2009). Progress in nano-biocomposites based on polysaccharides and nanoclays. *Materials Science and Engineering*. **67**: 1–17.
- Chivrac, F., Coussy, H.A., Guillard, V., Pollet, E., and Avérous, L. (2010a). How does water diffuse in starch/montmorillonite nano-biocomposite materials? *Carbohydrate Polymers*. **82**: 128–135.
- Chivrac, F., Pollet, E., Schmutz, M., and Averous, L. (2010b). Starch nano-biocomposites based on needle-like sepiolite clays. *Carbohydrate Polymers*. **80**: 145-153.
- Choi, Y., and Simonsen, J. (2006). Cellulose nanocrystal-filled carboxymethyl cellulose nanocomposites. *Journal of Nanoscience and Nanotechnology*. **6**: 633–639.
- Chorianopoulos, N.G., Tsoukleris, D.S., Panagou, E.Z., Falaras, P., and Nychas, G.J.E. (2011). Use of titanium dioxide (TiO₂) photocatalysts as alternative means for *Listeria monocytogenes* biofilm disinfection in food processing. *Food Microbiology*. **28**(1): 164-170.
- Choudalakis, G., and Gotsis, A.D. (2009). Permeability of polymer/clay nanocomposites: A review. *European Polymer Journal*. **45**: 967-984.
- Chung, Y.L., Ansari, S., Estevez, L., Hayrapetyan, S., Giannelis, E.P., and Lai, H.M. (2010). Preparation and properties of biodegradable starch–clay nanocomposites. *Carbohydrate Polymers*. **79**: 391–396.

- Costa, C., Conte, A., Buonocore, G.G., and Del Nobile M.A. (2011). Antimicrobial silver-montmorillonite nanoparticles to prolong the shelf life of fresh fruit salad. *International Journal of Food Microbiology*. **148**(3): 164-167.
- Cushen, M., Kerry, J., Morris, M., Cruz-Romero, M., and Cummins, E. (2011). Nanotechnologies in the food industry - Recent developments, risks and regulation. *Trends in Food Science and Technology*. In Press Paper.
- Dai, H. (2002). Carbon nanotubes: synthesis, integration, and properties. *Accounts Of Chemical Research*. **35**: 1035-1044.
- Denice S. Vicentini, D.S., Smania, A., and Laranjeira, M.C.M. (2010). Chitosan/poly(vinyl alcohol) films containing ZnO nanoparticles and plasticizers. *Materials Science and Engineering*. **30**: 503–508.
- De Moura, M. R., Aouada, F. A., Avena-Bustillos, R. J., McHugh, T. H., Krochta, J. M., and Mattoso, L. H. C. (2009). Improved barrier and mechanical properties of novel hydroxypropyl methylcellulose edible films with chitosan/tripolyphosphate nanoparticles. *Journal of Food Engineering*. **92**: 448–453.
- dePaiva, L. B., Morales, A.M., and Valenzuela Diaz, F.R. (2008). Organoclays: Properties, preparation and applications. *Applied Clay Science*. **42**: 8–24.
- Drozdzov, A.D., Christiansen, J., Gupta, R.K., and Shah, A.P. (2003). Model for anomalous moisture diffusion through a polymer–clay nanocomposite. *Journal of Polymer Science, Part B, Polymer Physics*. **41**: 476–492.

- Duan, Y., Jia, J., Wang, S., Yan, W., Jin, L., and Wang, Z. (2007). Preparation of antimicrobial poly (ϵ -caprolactone) electrospun nanofibers containing silver-loaded zirconium phosphate nanoparticles. *Journal of Applied Polymer Science*. **106**: 1208–1214.
- Duncan, T.V. (2011). Applications of nanotechnology in food packaging and food safety: Barrier materials, antimicrobials and sensors. *Journal of Colloid and Interface Science*. **363**: 1–24.
- Elashmawi, I.S., Hakeem, N.A., Marei, L.K., and Hanna, F.F. (2010). Structure and performance of ZnO/PVC nanocomposites. *Physica B: Condensed Matter*. **405**(19): 4163-4169.
- Emamifar, A., Kadivar, M., Shahedi, M., & Soleimani-Zad, S. (2010). Evaluation of nanocomposite packaging containing Ag and ZnO on shelf life of fresh orange juice. *Innovative Food Science and Emerging Technologies*. **11**(4): 742-748.
- Emamifar, A., Kadivar, M., Shahedi, M., & Soleimani-Zad, S. (2011). Effect of nanocomposite packaging containing Ag and ZnO on inactivation of *Lactobacillus plantarum* in orange juice. *Food Control*. **22**: 408-413.
- Falguera, V., Quintero, J.P., Jimenez, A., Munoz, J.A., and Ibarz, A. (2011). Edible films and coatings: Structures, active functions and trends in their use. *Trends in Food Science and Technology*. **22**: 292-303.
- Fama, L.M., Pettarin, V., Goyanes, S.N., and Bernal, C.R. (2011). Starch/multi-walled carbon nanotubes composites with improved mechanical properties. *Carbohydrate Polymers*. **83**: 1226–1231.
- Feng, F., He, W., Zhang, X., Jia, X., and Zhao, H. (2007). The preparation of nanoparticle zirconium phosphate. *Materials Letters*. **61**: 3258–3261.

- Fleming, K., Gray, D.G., and Matthews, S. (2001). Cellulose crystallites. *Chemical European Journal*. **7**(9): 1831-1835.
- Frey-Wyssling, A. and K. Mühlethaler. (1965). Ultrastructure plant cytology. *Elsevier*. pp. 34-40.
- Fu, G., Vary, P.S., and Lin, C.T. (2005). Anatase TiO₂ nanocomposites for antimicrobial coatings. *Journal of Physical Chemistry, B*. **109**: 8889-8898.
- Furman, B.R., Wellinghoff, S.T., Thompson, P.M., Beall, G.W., Laine, R.M., and Rawls, H.R. (2008). Preparation, characterization, and modeling of α -Zirconium phosphonates with ether-functional surfaces. *Chemistry of Materials*. **20**: 5491–5499.
- Gacitua, W.E., Ballerini A.A., and Zhang, J. (2005). Polymer nanocomposites: synthetic and natural fillers: A review. *Ciencia y tecnología*. **7**(3): 159-178.
- Gamage, J., and Zhang, Z. (2010). Applications of photocatalytic disinfection: A review. *International Journal of Photoenergy*. In Press Paper.
- Gang, L., Zhongqing, L., Zhao, Z., and Xin, Y. (2009). Preparation of Titania Nanotube Arrays by the Hydrothermal Method. *Chinese Journal of Catalysis*. **30**(1): 37–42.
- Gao, W., Dong, H., Hou, H., and Zhang, H. (2011). Effects of clays with various hydrophilicities on properties of starch–clay nanocomposites by film blowing. *Carbohydrate Polymers*. In Press Paper.
- García-Gutiérrez, M. C., Nogales, A., Hernández, J.J., Rueda, D.R., and Ezquerro, T.A. (2007). X-ray scattering applied to the analysis of carbon nanotubes, polymers and nanocomposites. *Optica Pura Y Aplicada*. **40**(2): 195-205.

- Gardner, D. J., Oporto, G. S., Mills, R., and Azizi Samir, M. A. S. (2008). Adhesion and surface issues in cellulose and nanocellulose. *Journal of Adhesion Science and Technology*. **22**: 545–567.
- Geng, L.N., Wang, X., Li, N., Xiang, M.H., and Li, K. (2004). Characterization of hemoglobin immobilized on γ -zirconium phosphate. *Colloids and Surfaces B: Biointerfaces*. **34**: 231–238.
- Ghanbarzadeh, B., and Oromiehi, A.R. (2009). Thermal and mechanical behavior of laminated protein films. *Journal of Food Engineering*. **90**: 517-524.
- Gibson, R.F., Ayorinde, E.O., and Wen, Y.F. (2007). Vibrations of carbon nanotubes and their composites: A review. *Composites Science and Technology*. **67**: 1–28.
- Grunert, M., and Winter, W. (2002). Nanocomposites of cellulose acetate butyrate reinforced with cellulose nanocrystals. *Journal of Polymers and the Environment*. **10**: 27-30.
- Guigo, N., Vincent, L., Mija, A., Naegel, H. and Sbirrazzuoli, N. (2009). Innovative green nanocomposites based on silicate clays/lignin/natural fibres. *Composites Science and Technology*. **69**: 1979–1984.
- Guilherme, M.R., Mattoso, L.H.C., Gontard, N., Guilbert, S., and Gastaldi, E. (2010). Synthesis of nanocomposite films from wheat gluten matrix and MMT intercalated with different quaternary ammonium salts by way of hydroalcoholic solvent casting. *Composites, Part A*. **41**: 375–382.
- Hamad, W. (2006) On the development and applications of cellulosic nanofibrillar and nanocrystalline materials. *The Canadian Journal of Chemical Engineering*. **84**: 513-519.

- Han, Y.S., Lee, S.H., Choi, K.H., and Park, I. (2010). Preparation and characterization of chitosan–clay nanocomposites with antimicrobial activity. *Journal of Physics and Chemistry of Solids*. **71**: 464–467.
- Hassan Nejad, M., Ganster, J., and Volkert, B. (2010). Starch esters with improved mechanical properties through melt compounding with nanoclays. *Journal of Applied Polymer Science*. **118**: 503–510.
- He, L., Liu, Y., Mustapha, A., and Lin, M. (2011). Antifungal activity of zinc oxide nanoparticles against *Botrytis cinerea* and *Penicillium expansum*. *Microbiological Research*. **166**(3): 207-215.
- Helbert, W., Cavaille, C. Y., and Dufresne, A. (1996). Thermoplastic nanocomposites filled with wheat straw cellulose whiskers. Part I: processing and mechanical behaviour. *Polymer Composites*. **17**(4): 604–611.
- Hsu, S.H., Wang, M.C., and Lin, J.J. (2011). Biocompatibility and antimicrobial evaluation of montmorillonite/chitosan nanocomposites. *Applied Clay Science*. In Press Paper.
- Hussain, F., Hojjati, M., Okaamoto, M., and Gorg, R.E. (2006). Polymer-matrix nanocomposites, processing, manufacturing, and application: An overview. *Journal of Composite Materials*. **40**(17): 1511-1575.
- Jang, S.A., Lim, G.O., and Song, K.B. (2010). Use of nano-clay (Cloisite Na+) improves tensile strength and vapour permeability in agar rich red algae (*Gelidium corneum*)–gelatin composite films. *International Journal of Food Science and Technology*. **45**: 1883–1888.

- Jang, S.A., Shin, Y.J., Seo, Y.B., and Song, K.B. (2011). Effects of various plasticizers and nanoclays on the mechanical properties of red algae film. *Journal of Food Science*. **76**(3): 30-34.
- Jayakumar, R., Menon, D., Manzoor, K., Nair, S.V., and Tamura, H. (2010). Biomedical applications of chitin and chitosan based nanomaterials: A short review. *Carbohydrate Polymers*. **82**: 227–232.
- Jha, A.K., Prasad, K., and Kulkarni, A.R. (2009). Synthesis of TiO₂ nanoparticles using microorganisms. *Colloids and Surfaces B: Biointerfaces*. **71**: 226–229.
- Jiang, W., Mashayekhi, H., and Xing, B. (2009). Bacterial toxicity comparison between nano- and micro-scaled oxide particles. *Environmental Pollution*. **157**: 1619–1625.
- John, A. K., and Surender, G. D. (2005). Low temperature process for the synthesis of rutile phase titania through vapor phase hydrolysis. *Journal of Materials Science*. **40**: 2999-3001.
- Jones, N., Ray, B., Ranjit, K.T., and Manna, A.C. (2008). Antibacterial activity of ZnO nanoparticle suspensions on abroad spectrum of microorganisms. *FEMS Microbiology Letters*. **279**: 71–76.
- Jordan, J., Jacob, K.I., Tannenbaum, R., Sharaf, M.A., and Jasiuk, I. (2005). Experimental trends in polymer nanocomposites: a review. *Materials Science and Engineering A*. **393**: 1-11.
- Kanade, K.G., Kale, B.B., Aiyer, R.C., and Das, B.K. (2006). Effect of solvents on the synthesis of nano-size zinc oxideand its properties. *Materials Research Bulletin*. **41**: 590–600
- Kang, S., Herzberg, M., Rodrigues, D.F., and Elimelech, M. (2008). Antibacterial effects of carbon nanotubes: size does matter. *Langmuir*. **24**, 6409–6413.

- Kang, S., Pinault, M., Pfefferle, L.D., and Elimelech, M. (2007). Single-walled carbon nanotubes exhibit strong antimicrobial activity. *Langmuir*. **23**: 8670–8673.
- Karami, A. (2010). Synthesis of TiO₂ nano powder by the sol-gel method and its use as a photocatalyst. *Journal of the Iranian Chemical Society*. **7**: 154-160.
- Khataee, A.R., and Kasiri, M.B. (2010). Photocatalytic degradation of organic dyes in the presence of nanostructured titanium dioxide: Influence of the chemical structure of dyes. *Journal of molecular catalysis A: Chemical*. **328**: 8–26.
- Kim, B., Kim, D., Cho, D., and Cho, S. (2003). Bactericidal effect of TiO₂ photocatalyst on selected food-borne pathogenic bacteria. *Chemosphere*. **52**: 277–281.
- Kontos, A.G., Katsanaki, A., Maggos, T., Likodimos, V., Ghicov, A., Kim, D., Kunze, J., Vasilakos, C., Schmuki, P., and Falaras, P. (2010). Photocatalytic degradation of gas pollutants on self-assembled titania nanotubes. *Chemical Physics Letters*. **490**: 58–62.
- Kreyling, W.G., Semmler-Behnke, M., and Chaudhry, Q. (2010). A complementary definition of nanomaterial. *Nano Today*. **5**: 165-168.
- Kristo, E., and Biliaderis, C.G. (2007). Physical properties of starch nanocrystal-reinforced pullulan films. *Carbohydrate Polymers*. **68**: 146-158.
- Kumar, A.P., Depan, D., Tomer, N.S., and Singh, R.P. (2009). Nanoscale particles for polymer degradation and stabilization: Trends and future perspectives. *Progress in Polymer Science*. **34**: 479-515.
- Kumar, P., Sandeep, K.P., Alavi, S., and Truong, V.D. (2011). A Review of experimental and modeling techniques to determine properties of biopolymer-based nanocomposites. *Journal of Food Science*. **76**(1): 1-13.

- Kumar, P., Sandeep, K.P., Alavi, S., Truong, V.D., and Gorga, R.E. (2010a). Preparation and characterization of bio-nanocomposite films based on soy protein isolate and montmorillonite using melt extrusion. *Journal of Food Engineering*. **100**: 480–489.
- Kumar, P., Sandeep, K.P., Alavi, S., Truong, V.D. and Gorga, R.E. (2010b). Effect of type and content of modified montmorillonite on the structure and properties of bio-nanocomposite films based on soy protein isolate and montmorillonite. *Journal of Food Science*. **75**(5): 46-56.
- Kuo, C.L., Wang, C.L., Ko, H.H., Hwang, W.S., Chang, K.M., Li, W.L., Huang, H.H., Chang, Y.H., and Wang, M.C. (2010). Synthesis of zinc oxide nanocrystalline powders for cosmetic applications. *Ceramics International*. **36**: 693–698.
- Lagaron, J.M., Catala, R., and Gavara, R. (2004). Structural characteristics defining high barrier polymeric materials. *Materials Science and Technology*. **20**: 1–7.
- Lagaron, J.M., and Lopez-Rubio, A. (2011). Nanotechnology for bioplastics: Opportunities, challenges and strategies. *Trends in Food Science & Technology*. In Press Paper.
- Lanao, M., Ormad, M.P., Goni, P., Miguel, N., Mosteo, R., and Ovelleiro, J.L. (2010). Inactivation of *Clostridium perfringens* spores and vegetative cells by photolysis and TiO₂ photocatalysis with H₂O₂. *Solar Energy*. **84**: 703–709.
- Lavorgna, M., Piscitelli, F., Mangiacapra, P., and Buonocore, G.G. (2010). Study of the combined effect of both clay and glycerol plasticizer on the properties of chitosan films. *Carbohydrate Polymers*. **82**(2): 291-298.
- Lee, J.E., and Kim, K.M. (2010). Characteristics of soy protein isolate-montmorillonite composite films. *Journal of Applied Polymer science*. **118**: 2257-2263.

- Lee, S.H. (2004). Photocatalytic nanocomposites based on TiO₂ and carbon nanotubes. *Thesis for degree of doctor of philosophy*.
- Li, L.H., Deng, J.C., Deng, H.R., Liu, Z.L., and Li, X.L. (2010). Preparation, characterization and antimicrobial activities of chitosan/Ag/ZnO blend films. *Chemical Engineering Journal*. **160**: 378–382.
- Li, Y., Jiang, Y., Liu, F., Ren, F., Zhao, G., and Leng, X. (2011). Fabrication and characterization of TiO₂/whey protein isolate nanocomposite film. *Food Hydrocolloids*. **25**: 6, 1-7.
- Lim, S.H., Lee, M.W. and Tay, Y.C. (2009). Development of biopolymeric nanocomposites for sustainable packaging. *SIMTech technical reports*. **10**(4): 191- 196.
- Lima, M. M. D., and Borsali, R. (2004). Rodlike cellulose microcrystals: structure, properties, and applications. *Macromolecular Rapid Communications*. **25**(7): 771–787.
- Lin, F. (2006). Preparation and characterization of polymer TiO₂ nanocomposites via in-situ polymerization. *Thesis of the degree of Master of Applied Science*.
- Liu, C., and Yang, Y. (2009). Effects of α -zirconium phosphate aspect ratio on the properties of polyvinyl alcohol nanocomposites. *Polymer Testing*. **28**: 801–807.
- Liu, D., Zhong, T., Chang, P.R., Li, K., and Wu, Q. (2009). Starch composites reinforced by bamboo cellulosic crystals. *Bioresource Technology*. **101**: 2529-2536.
- Liu, H., Chaudhary, D., Yusa, S. and Tadé, M.O. (2010). Glycerol/starch/Na⁺-montmorillonite nanocomposites: A XRD, FTIR, DSC and ¹H NMR study. *Carbohydrate Polymers*. In Press Paper.

- Llorens, A., Lloret, E., Picouet, P.A., Trbojevič, R., and Fernandez, A. (2011). Metallic-based micro and nanocomposites in food contact materials and active food packaging. *Trends in Food Science & Technology*. In Press Paper.
- Lopez-Leon, T., Carvalho, E. L. S., Seijo, B., Ortega-Vinuesa, J. L., and Bastos-Gonzalez, D. (2005). Physicochemical characterization of chitosan nanoparticles: electrokinetic and stability behavior. *Journal of Colloid Interface Science*. **283**: 344–351.
- Lu, Y., Weng, L., Zhang, L. (2004). Morphology and properties of soy protein isolate thermoplastics reinforced with chitin whiskers. *Biomacromolecules*. **5**: 1046–1051.
- Lu, C., and Mai, Y.W. (2007). Permeability modelling of polymer-layered silicate nanocomposites. *Composites Science and Technology*. **67**: 2895–2902.
- Lu, D.R., Xiao, C.M., and Xu, S.J. (2009). Starch-based completely biodegradable polymer materials. *Express Polymer Letters*. **3**(6): 366–375.
- Luecha, J., Sozer, N., and Kokini, J.L. (2010). Synthesis and properties of corn zein/montmorillonite nanocomposite films. *Journal of Mater Science*. **45**: 3529–3537.
- Ma, X., Chang, P. R., Yu, J., and Lu, P. (2008). Characterizations of glycerol plasticized starch (GPS)/carbon black (CB) membranes prepared by melt extrusion and microwave radiation. *Carbohydrate Polymers*. **74**: 895–900.
- Ma, X., Chang, P.R., Yang, J., and Yu, J. (2009). Preparation and properties of glycerol plasticized-peastarch/zinc oxide-starch bionanocomposites. *Carbohydrate Polymers*. **75**: 472–478.
- Magalhães, N.F., and Andrade, C.T. (2009). Thermoplastic corn starch/clay hybrids: Effect of clay type and content on physical properties. *Carbohydrate Polymers*. **75**: 712–718.

- Mahalik, N.P., and Nambiar, A.N. (2010). Trends in food packaging and manufacturing systems and technology. *Trends in Food Science & Technology*. **21**: 117-128.
- Mahshid, S., Sasani Ghamsari, M., Askari, M., Afshar, N., and Lahuti, S. (2006). Synthesis of TiO₂ nanoparticles by hydrolysis and peptization of titanium isopropoxide solution. *Semiconductor Physics, Quantum Electronics & Optoelectronics*. **9**(2): 65-68.
- Maneerat, C., and Hayata, Y. (2006). Antifungal activity of TiO₂ photocatalysis against *Penicillium expansum* in vitro and in fruit tests. *International Journal of Food Microbiology*. **107**: 99–103.
- Maness, P.C., Smolinski, S., Blake, D.M., Huang, Z., Wolfrum, E.J., and Jacoby, W.A. (1999). Bactericidal activity of photocatalytic TiO₂ reaction: toward an understanding of its killing mechanism. *Applied and Environmental Microbiology*. **65**(9): 4094–4098.
- Mangiacapra, P., Gorrasi, G., Sorrentino, A., and Vittoria, V. (2006). Biodegradable nanocomposites obtained by ball milling of pectin and montmorillonites. *Carbohydrate Polymers*. **64**: 516-523.
- Mathew, A.P., and Dufresne, A. (2002). Morphological investigation of nanocomposites from sorbitol plasticized starch and tunicin whiskers. *Biomacromolecules*. **3**(3): 609–617.
- Mbey, J.A., Hoppe, S., and Thomas, F. (2011). Cassava starch–kaolinite composite film: effect of clay content and clay modification on film properties. *Carbohydrate Polymers*. In Press Paper.
- Mills, A., Doyle, G., Piero, A.M., and Durrant, J.R. (2006). Demonstration of a novel, flexible, photocatalytic. *Journal of Photochemistry and Photobiology A: Chemistry*. **177**: 328–331.

- Moghbelli, E., Sun, L., Jiang, H., Boo, W.J., and Sue, H.J. (2009). Scratch behavior of epoxy nanocomposites containing α -Zirconium phosphate and core-shell rubber particles. *Polymer Engineering and Science*. **62**: 483-490.
- Morin, A., and Dufresne, A. (2002). Nanocomposites of chitin whiskers from Riftia tubes and Poly(caprolactone). *Macromolecules*. **35**: 2190–2199.
- Nadtochenko, V.A., Sarkisov, O.M., Nikandrov, V.V., Chubukov, P.A., and Denisov, N. N. (2008). Inactivation of pathogenic microorganisms in the photocatalytic process on nanosized TiO₂ crystals. *Russian Journal of Physical Chemistry B*. **2**(1): 105–114.
- Nair, K. G., and Dufresne, A. (2003). Crab shell chitin whisker reinforced natural rubber Nanocomposites, 1: Processing and swelling behavior. *Biomacromolecules*. **4**: 657–665.
- Nakayama, N., and Hayashi, T., (2007). Preparation and characterization of poly(L-lactic acid)/TiO₂ nanoparticle nanocomposite films with high transparency and efficient photodegradability. *Polymer Degradation and Stability*. **92**: 1255-1264.
- Neethirajan, S., and Jayas, D. S. (2011). Nanotechnology for the Food and Bioprocessing Industries. *Food Bioprocess Technolgy*. **4**: 39-47.
- Nepal, D., Balasubramanian, S., Simonian, A.L., and Davis, V.A. (2008). Strong antimicrobial coatings: single walled carbon nanotubes armored with biopolymers. *Nano letters*. **8**(7): 1896-1901.
- Oksman, K., Mathew, A. P., Bondeson, D., and Kvien, I. (2006). Manufacturing process of cellulose whiskers/poly(lactic acid) nanocomposites. *Composites Science and Technology*. **66**(15): 2776–2784.

- Ozerin, A.N., Perov, N.S., Zelenetskii, A.N., Akopova, T.A., Ozerina, L.A., Kecheqyan, A. S., Surin, N.M., Vladimirov, L.V., and Yulovskaya, V.D. (2009). Hybrid nanocomposites based on graft copolymer of chitosan with poly(vinyl alcohol) and titanium oxide. *Nanotechnologies in Russia*. **4**: 331-339.
- Padmavathy, N., and Vijayaraghavan, R. (2008). Enhanced bioactivity of ZnO nanoparticles-an antimicrobial study. *Science and Technology Advanced Materials*. **9**: 134-140.
- Paillet, M., and Dufresne, A. (2001). Chitin whisker reinforced thermoplastic nanocomposites. *Macromolecules*. **34**: 6527–6530.
- Pan, B., Pan, B., Chen, X., Zhang, W., Zhang, X., Zhang, Q., Zhang, Q., and Chen, J. (2006). Preparation and preliminary assessment of polymer supported zirconium phosphate for selective lead removal from contaminated water. *Water Research*. **40**: 2938–2946.
- Pan, B., Zhang, Q., Du, W., Zhang, W., Pan, B., Zhang, Q., Xu, Z., and Zhang, Q. (2007). Selective heavy metals removal from waters by amorphous zirconium phosphate: Behavior and mechanism. *Water Research*. **41**: 3103–3111.
- Pandey, J.K., and Singh, R.P. (2005). Green nanocomposites from renewable resources: effect of plasticizer on the structure and material properties of clay-filled starch. *Starch/Stärke*. **57**: 8–15.
- Park, N.K., Lee, Y.J., Han, G.B., Ryua, S.O., Lee, T.J., Chang, C.H., and Han, G.Y. (2007). Synthesis of various zinc oxide nanostructures with zinc acetate and activated carbon by a matrix-assisted method. *Colloids and Surfaces A: Physicochemical Engineering Aspects*. **122**: 66–71.

- Pastor, P.O., Torres, P.M., Castellon, E.R., and Lopez, A.J. (1996). Nanostructured Inorganically Pillared Layered Metal (IV) Phosphates. *Chemistry of Materials*. **8**: 1758-1769.
- Paul, D.R., and Robeson, L.M. (2008). Polymer nanotechnology: Nanocomposites. *Polymer*. **49**: 3187–3204.
- Pavlidoua, S., and Papaspyrides C.D. (2008). A review on polymer–layered silicate nanocomposites. *Progress in Polymer Science*. **33**: 1119–1198.
- Peng, H., Li, G., and Zhang, Z. (2005). Synthesis of bundle-like structure of titania nanotubes. *Materials Letters*. **59**: 1142–1145.
- Petersson, L., and Oksman, K. (2006). Biopolymer based nanocomposites: comparing layered silicates and microcrystalline cellulose as nanoreinforcement. *Composites Science and Technology*. **66**: 2187–2196.
- Piero, A.M., Doyle, G., Mills, A., and Durrant, J.R. (2005). Freestanding polymer-metal oxide nanocomposite films for light-driven oxygen scavenging. *Advanced Materials*. **17**: 2365-2368.
- Podsiadlo, P., Choi, S.Y., Shim, B., Lee, J., Cuddihy, M., and Kotov, N. A. (2005). Molecularly engineered nanocomposites: layer-by-layer assembly of cellulose nanocrystals. *Biomacromolecules*. **6**: 2914–2918.
- Polizos, G., Tuncer, E., Sauers, I., and More, K.L. (2010). Physical properties of epoxy resin/titanium dioxide nanocomposites. *Polymer engineering and science*. **102**: 87-93.
- Prasad, K., Pinjari, D.V., Pandit, A.B., and Mhaske, S.T. (2010). Phase transformation of nanostructured titanium dioxide from anatase-to-rutile via combined ultrasound assisted sol–gel technique. *Ultrasonics Sonochemistry*. **17**: 409–415.

- Puppi, D., Chiellini, F., Piras, A.M., and Chiellini, E. (2010). Polymeric materials for bone and cartilage repair. *Progress in Polymer Science*. **35**: 403-440.
- Qiu, Y., and Yu, J. (2008). Synthesis of titanium dioxide nanotubes from electrospun fiber templates. *Solid State Communications*. **148**: 556-558.
- Ramos, L. P. (2003). The chemistry involved in the stream treatment of lignocellulosic materials. *Química Nova*. **26**(6): 863–871.
- Ravi Kumar, M.N.V. (2000). A review of chitin and chitosan applications. *Reactive & Functional Polymers*. **46**: 1–27.
- Ray, S., Quek, S.Y., Easteal, A., and Chen, X.D. (2006). The potential use of polymer-clay nanocomposites in food packaging. *International Journal of Food Engineering*. **2**(4): 1-13.
- Ray, S.S., and Okamoto, M. (2003). Polymer/layered silicate nanocomposites: a review from preparation to processing. *Progress in Polymer Science*. **28**: 1539–1641.
- Rhim, J.W. (2011). Effect of clay contents on mechanical and water vapor barrier properties of agar-based nanocomposite films. *Carbohydrate Polymers*. **86**: 691– 699.
- Rhim, J.W., and Perry, P.K.W. (2007). Natural biopolymer-based nanocomposite films for packaging applications. *Critical Reviews in Food Science and Nutrition*. **47**: 4, 411-433.
- Rhim, J.W., Hong, S.I., Park, H.M., and Ng, P.K.W. (2006). Preparation and characterization of chitosan-based nanocomposite films with antimicrobial activity. *Journal of Agriculture and Food Chemistry*. **54**: 5814–5822.
- Rhim, J.W., Lee, S.B. and Hong, S.I. (2011). Preparation and characterization of agar/clay nanocomposite films: the effect of clay type. *Journal of Food Science*. **76**(3): 40-48.

- Rimdusit, S., Jingjid, S., Damrongsakkul, S., Tiptipakorn, S. and Takeichi, T., (2008). Biodegradability and property characterizations of Methyl cellulose: effect of nanocompositing and chemical crosslinking. *Carbohydrate Polymers*. **72**: 444–455.
- Robert, D., and Weber, J. V. (1999). Titanium dioxide synthesis by sol gel methods and evaluation of their photocatalytic activity. *Journal of Materials Science Letters*. **18**: 97-98.
- Robinson, D.K.R., and Morrison M.J. (2010). Nanotechnologies for food packaging: Reporting the science and technology research trends: Report for the Observatory NANO.
- Rodriguez, F.J., Galotto, M.J., Guarda, A., and Bruna, J.E. (2011). Modification of cellulose acetate films using nanofillers based on organoclays. *Journal of Food Engineering*. In Press Paper.
- Rozenberg, B.A., and Tenne, R. (2008). Polymer-assisted fabrication of nanoparticles and nanocomposites. *Progress in Polymer Science*. **33**: 40–112.
- Saito, Y., Putaux, J. L., Okano, T., Gaill, F., and Chanzy, H. (1997). Structural aspects of the swelling of β chitin in HCl and its conversion into α chitin. *Macromolecules*. **30**: 3867–3873.
- Salehi, R., Arami, M., Mahmoodi, N.M., Bahrami, H., and Khorramfar, S. (2010). Novel biocompatible composite (Chitosan–zinc oxide nanoparticle): Preparation, characterization and dye adsorption properties. *Colloids and Surfaces B: Biointerfaces*. **80**: 86–93.
- Sanchez-Garcia, M.D., Gimenez, E., and Lagaron, J.M. (2008). Morphology and barrier properties of solvent cast composites of thermoplastic biopolymers and purified cellulose fibers. *Carbohydrate Polymers*. **71**: 235–244.

- Sanchez-Garcia, M.D., Lagaron, J.M., and Hoa, S.V. (2010). Effect of addition of carbon nanofibers and carbon nanotubes on properties of thermoplastic biopolymers. *Composites Science and Technology*. **70**: 1095–1105.
- Sanguansri, P., and Augustin, M.A. (2006). Nanoscale materials development- a food industry perspective. *Trends in Food Science & Technology*. **17**: 547-556.
- Sekhon, B.S. (2010). Food nanotechnology – an overview. *Nanotechnology, Science and Applications*. **3**: 1–15.
- Sheikh, F.A., Kanjwal, M.A., Kim, H.Y., and Kim, H. (2010). Fabrication of titanium dioxide nanofibers containing hydroxyapatite nanoparticles. *Applied Surface Science*. **257**(1): 296-301.
- Sikong, L., Kongreong, B., Kantachote, D., and Sutthisripok, W. (2010). Photocatalytic activity and antibacterial behavior of Fe³⁺-doped TiO₂/SnO₂ nanoparticles. *Energy Research Journal*. **1**(2): 120-125.
- Silvestre, C., Duraccio, D., and Cimmino, S. (2011). Food packaging based on polymer nanomaterials. *Progress in Polymer Science*. **67**: 156-161.
- Sjorgren, J.C., and Sierka, R.A. (1994). Inactivation of Phage MS2 by Iron-Aided Titanium Dioxide Photocatalysis. *Applied and Environmental Microbiology*. **60**(1): 344–347.
- Sorrentino, A., Gorrasi, G., and Vittoria, V. (2007). Potential perspectives of bionanocomposites for food packaging applications. *Trends in Food Science & Technology*. **18**: 84-95.
- Sothornvit, R., Hong, S.I., An, D.J., and Rhim, J.W., (2010). Effect of clay content on the physical and antimicrobial properties of whey protein isolate/organo-clay composite films. *LWT-Food Science and Technology*. **43**: 279–284.

- Sothornvit, R., Rhim, J.W., and Hong, S.I. (2009). Effect of nano-clay type on the physical and antimicrobial properties of whey protein isolate/clay composite films. *Journal of Food Engineering*. **91**: 468–473.
- Souza, A.C., Benze, R., Ferrão, E.S., Ditchfield, C., Coelho, A.C.V., and Tadini, C.C. (2011). Cassava starch biodegradable films: Influence of glycerol and clay nanoparticles content on tensile and barrier properties and glass transition temperature. *LWT - Food Science and Technology*. In Press Paper.
- Sozer, N., and Kokini, J.L. (2008). Nanotechnology and its applications in the food sector. *Trends in Biotechnology*. **2**: 27, 82-89.
- Sriupayo, J., Supaphol, P., Blackwell, J., and Rujiravanit, R. (2005). Preparation and characterization of α -chitin whisker-reinforced chitosan nanocomposite films with or without heat treatment. *Carbohydrate Polymers*. **62**: 130–136.
- Sue, H.J., and Gam, K.T. (2004). Epoxy nanocomposites based on the synthetic α -Zirconium phosphate layer structure. *Chemistry of Materials*. **16**: 242-249.
- Sun, L., Boo, W.J., Browning, R.L., Sue, H.J., and Clearfield, A. (2005). Effect of crystallinity on the intercalation of monoamine in α -Zirconium phosphate layer structure. *Chemistry of Materials*. **17**: 5606-5609.
- Sun, L., Boo, W.J., Sue, H.J., and Clearfield, A., (2007a). Preparation of α -zirconium phosphate nanoplatelets with wide variations in aspect ratios. *New Journal of Chemistry*. **31**: 39–43.
- Sun, L., Boo, W.J., Sun, D., Clearfield, A., and Sue, H.J. (2007b). Preparation of exfoliated epoxy/ α -Zirconium phosphate nanocomposites containing high aspect ratio nanoplatelets. *Chemistry of Materials*. **19**: 1749-1754.

- Svagan, A.J., Hedenqvist, M.S., and Berglund, L. (2009). Reduced water vapour sorption in cellulose nanocomposites with starch matrix. *Composites Science and Technology*. **69**: 500–506.
- Tai, Q., Kan, Y., Chen, L., Xing, W., Hu, Y., and Song, L. (2010). Morphologies and thermal properties of flame-retardant polystyrene/ α -zirconium phosphate nanocomposites. *Reactive and Functional Polymers*. **70**: 340–345.
- Tam, K.H., Djurišić, A.B., Chan, C.M.N., Xi, Y.Y., Tse, C.W., Leung, Y.H., Chan, W.K., Leung, F.C.C., and Au, D.W.T. (2008). Antibacterial activity of ZnO nanorods prepared by a hydrothermal method. *Thin Solid Films*. **516**: 6167–6174.
- Tanc, S., Angellier, H., Cahyana, Y., Chailier, P., Gontard, N., and Gastaldi, E. (2007). Functional properties of wheat gluten/montmorillonite nanocomposite films processed by casting. *Journal of Membrane Science*. **289**: 1-2, 159-168.
- Tang, C., Chen, N., Zhang, Q., Wang, K., Fu, Q., and Zhang, X. (2009a). Preparation and properties of chitosan nanocomposites with nanofillers of different dimensions. *Polymer Degradation and Stability*. **94**: 124–131.
- Tang, H., Xiong, H., Tang, S., and Zou, P. (2009b). A starch-based biodegradable film modified by nano silicon dioxide. *Journal of Applied Polymer Science*. **113**: 34–40.
- Tang, X., Alavi, S., and Herald, T.J. (2008a). Effects of plasticizers on the structure and properties of starch–clay nanocomposite films. *Carbohydrate Polymers*. **74**: 552–558.
- Tang, S., Zou, P., Xiong, H., & Tang, H. (2008b). Effect of nano-SiO₂ on the performance of starch/polyvinyl alcohol blend films. *Carbohydrate Polymers*. **72**: 521–526.

- Thostenson, E.T., Ren, Z., and Chou, T.W. (2001). Advances in the science and technology of carbon nanotubes and their composites: a review. *Composites Science and Technology*. **61**: 1899–1912.
- Tongpool, R., umpon, S.C., and Yoriya, S. (2007). Synthesis of Titanium Dioxide Nanotubes from Titanium Dioxide Nanoparticles and Their Photocatalytic Activities. *Ciang Mai University Jornal Natural Sciences*. **6**(2): 287-299.
- Trobajo, C., Khainakov, S.A., Espina, A., and Garcia, J.R. (2000). On the Synthesis of α -Zirconium Phosphate. *Chemistry of Materials*. **12**: 1787-1790.
- Tsai, T.M., Chang, H.H., Chang, K.C., Liu, Y.L., and Tseng, C.C. (2010). A comparative study of the bactericidal effect of photocatalytic oxidation by TiO_2 on antibiotic-resistant and antibiotic-sensitive bacteria. *Journal of Chemical Technolgy and Biotechnolgy*. **85**: 1642-1653.
- Tunç, S., and Duman, O. (2011). Preparation of active antimicrobial methyl cellulose/carvacrol/montmorillonite nanocomposite films and investigation of carvacrol release. *LWT - Food Science and Technology*. **44**: 465-472.
- Tunc, S., Angellier, H., Cahyana, Y., Chaliier, P., Gontard, N., and Gastaldi, E. (2007). Functional properties of wheat gluten/montmorillonite nanocomposite films processed by casting. *Journal of Membrane Science*. **289**: 159–168.
- Tunç, S., and Duman, O. (2010). Preparation and characterization of biodegradable methyl cellulose/montmorillonite nanocomposite films. *Applied Clay Science*. **48**: 414-424.

- Upadhyayula, V.K.K., Deng, S., Mitchell, M.C., and Smith, G.B. (2009). Application of carbon nanotube technology for removal of contaminants in drinking water: A review. *Science of the Total Environment*. **408**: 1–13.L
- Utracki, L. A., Sepehr, M., and Boccaleri, E. (2007). Synthetic, layered nanoparticles for polymeric nanocomposites (PNCs). *Polymers for Advanced Technologies*. **18**: 1–37.
- Vaivars, G., Furlani, M., Mellander, B.E, and Granqvist, C. G. (2003). Proton-conducting zirconium phosphate/poly(vinyl acetate)/glycerinegel electrolytes. *Journal of Solid State Electrochemistry*. **7**: 724–728.
- Vartiainen, J., Tammelin, T., Pere, J., Tapper, U., and Harlin, A. (2010). Biohybrid barrier films from fluidized pectin and nanoclay. *Carbohydrate Polymers*. **82**(3): 989-996.
- Vercelheze, A.E.S., Fakhouri, F.M., Dall’Antonia, L.H., Urbano,A., Youssef, E.Y., Yamashita, F., and Mali, S. (2102). Properties of baked foams based on cassava starch, sugarcane bagasse fibers and montmorillonite. *Carbohydrate Polymers*. **87**: 1302– 1310.
- Viguie´, J., Molina-Boisseau, S., and Dufresne, A. (2007). Processing and characterization of waxy maize starch films plasticized by sorbitol and reinforced with starch nanocrystals. *Macromolecular Bioscience*. **7**: 1206–1216.
- Vigneshwaran, N., Kumar, S., and Kathe, A.A. (2006). Functional finishing of cottonfabrics using zinc oxide-soluble starch nanocomposites. *Nanotechnology*. **17**: 5087–5095.
- Visurraga, J.D., Melendrez, M.F., Garcia, A., Paulraj, M., and Cardenas, G. (2010). Semitransparent chitosan-TiO₂ nanotubes composite film for food package applications. *Journal of Applied Polymer Science*. **116**: 3503–3515.

- Vivani, R., Alberti, G., Costantino, F., and Nocchetti, M. (2008). New advances in zirconium phosphate and phosphonate chemistry: Structural archetypes. *Microporous and Mesoporous Materials*. **107**: 58–70.
- Vohra, A., Goswami, D.Y., Deshpande, D.A., and Block, S.S. (2005). Enhanced photocatalytic inactivation of bacterial spores on surfaces in air. *Journal of Industrial Microbiology Biotechnology*. **32**: 364–370.
- Wang, D.Y., Liu, X.Q., Wang, J.S., Wang, Y.Z., Stec, A.A., and Hull, T.R. (2009a). Preparation and characterisation of a novel fire retardant PET/ α -zirconium phosphate nanocomposite. *Polymer Degradation and Stability*. **94**: 544–549.
- Wang, B., and Sain, M. (2007). Isolation of nanofibers from soybean source and their reinforcing capability on synthetic polymers. *Composites Science and Technology*. **67**: 2521–2527.
- Wang, S.F., Shen, L., Tong, Y.J., Chen, L., Phang, I.Y., Lim, P.Q. and Liu, T.X. (2005a). Biopolymer chitosan/montmorillonite nanocomposites: preparation and characterization. *Polymer Degradation and Stability*. **90**: 123–131.
- Wang, S.F., Shen, L., Zhang, W.D., and Tong, Y.J. (2005b). Preparation and mechanical properties of chitosan/carbon nanotubes composites. *Biomacromolecules*. **6**: 3067–3072.
- Wang, W., and Wang, A. (2009). Preparation, characterization and properties of superabsorbent nanocomposites based on natural guar gum and modified rectorite. *Carbohydrate Polymers*. **77**: 891–897.
- Wang, W., Zhai, N. and Wang, A. (2011). Preparation and swelling characteristics of a superabsorbent nanocomposite based on natural guar gum and cation-modified vermiculite. *Journal of Applied Polymer Science*. **119**: 3675–3686.

- Wang, X., Zhang, X., Liu, H., and Wang, N. (2009b). Impact of pre-processing of montmorillonite on the properties of melt-extruded thermoplastic starch/montmorillonite nanocomposites. *Starch/Stärke*. **61**: 489–494.
- Watson, S., Beydoun, D., Scott, J., and Amal, R. (2004). Preparation of nanosized crystalline TiO₂ particles at lowtemperature for photocatalysis. *Journal of Nanoparticle Research*. **6**: 193-207.
- Wathanaphanit, A., Supaphol, P., Tamura, H., Tokura, S., and Rujiravanit, R. (2008). Fabrication, structure, and properties of chitin whisker-reinforced alginate nanocomposite fibers. *Journal of Applied Polymer Science*. **110**: 890–899.
- Wei, H., YanJun, Y., NingTao, L., and LiBing, W. (2011). Application and safety assessment for nano-composite materials in food packaging. *Chinese Science Bulletin*. **56**(12): 1216–1225.
- Wei, Y.L., and Chang, P.C. (2008). Characteristics of nano zinc oxide synthesized under ultrasonic condition. *Journal of Physics and Chemistry of Solids*. **69**: 688–692.
- Weiss, J., Takhistov, P., and McClements, D.J. (2006). Functional Materials in Food Nanotechnology. *Journal of Food Science*. **71**(9): 107-116.
- Wilson, M.J. (2003). Clay mineralogy and related characteristics of geophagic materials. *Journal of Chemical Ecology*. **29**(7): 1525–1547.
- Wodka, D., Bielanska, E., Socha, R.P., Wodka, M.E., Gurgul, J., Nowak, P., Warszynski, P., and Kumakiri, I. (2010). Photocatalytic activity of titanium dioxide modified by silver nanoparticles. *Applied Materials & Interfaces*. **2**(7): 1945–1953.

- Wong, M.S., Chu, W.C., Sun, D.S., Huang, H.S., Chen, J.H., Tsai, P.J., Lin, N.T., Yu, M.S., Hsu, S.F., Wang, S.L., and Chang, H.H. (2010). Visible-light-induced bactericidal activity of a nitrogen-doped titanium photocatalyst against human pathogens. *Applied and Environmental Microbiology*. **72**(9): 6111–6116.
- Wongkaew, A., Jansome, W., and Khemchan, S. (2010). Synthesis of Nanoparticles of Mixed Oxides Containing Titanium Cerium Silver and Silicon: Phase Transformation. *Energy Research Journal*. **1**(2): 73-77.
- Wu, Q., Henriksson, M., Liu, X., and Berglund, L. A. (2007). A high strength nanocomposite based on microcrystalline cellulose and polyurethane. *Biomacromolecules*. **8**: 3687–3692.
- Wu, C.I., Huang, J.W., Wen, Y.L., Wen, S.B., Shen, Y.H., and Yeh, M.Y. (2008). Preparation of TiO₂ nanoparticles by supercritical carbon dioxide. *Materials Letters*. **62**: 1923-1926.
- Wu, H., Liu, C., Chen, J., Chang, P.R., Chen, Y., and Anderson, D.P. (2009). Structure and properties of starch/ α -zirconium phosphate nanocomposite films. *Carbohydrate Polymers*. **77**: 358–364.
- Wu, H., Liu, C., Yang, Y., Chen, J., Chang, P.R., Chen, Y., and Chen, Y. (2010a). Starch-based nanocomposites reinforced with layered zirconium phosphonate. *Polymer Composites*. **43**: 1-9.
- Wu, H., Liu, C., Chen, J., Yang, Y., and Chen, Y. (2010b). Preparation and characterization of chitosan/ α -zirconium phosphate nanocomposite films. *Polymer International*. **59**: 923–930.
- Xiao, X., Ouyang, K., Liu, R., and Liang, J. (2009). Anatase type titania nanotube arrays direct fabricated by anodization without annealing. *Applied Surface Science*. **255**: 3659–3663.

- Xiaobo, C. (2009). Titanium dioxide nanomaterials and their energy applications. *Chinese Journal of Catalysis*. **30**(8): 839-851.
- Xiao-e, L., Green, A.N.M., Haque, S.A., Mills, A., and Durrant, J.R. (2004). Light-driven oxygen scavenging by titania/polymer nanocomposite films. *Journal of Photochemistry and Photobiology A: Chemistry*. **162**: 253–259.
- Xiong, H., Tang, S., Tang, H., and Zou, P. (2008). The structure and properties of a starch-based biodegradable film. *Carbohydrate Polymers*. **71**: 263–268.
- Xu, M.F., Lin, S., Chen, X.M., and Peng, Y.Z. (2006a). Studies on characteristics of nanostructure of N-TiO₂ thin films and photo-bactericidal action. *Journal of Zhejiang University Science B*. **7**(7): 586-590.
- Xu, Y., Ren, X., and Hanna, M.A. (2006b). Chitosan/clay nanocomposite film preparation and characterization. *Journal of Applied Polymer Science*. **99**: 1684–1691.
- Yang, H., and Pan, C. (2010). Diameter-controlled growth of TiO₂ nanotube arrays by anodization and its photoelectric property. *Journal of Alloys and Compounds*. **492**: 133–135.
- Yang, X., Chen, X., Yang, L., and Yang, W. (2008). Direct electrochemistry and electrocatalysis of horseradish peroxidase in α -zirconium phosphate nanosheet film. *Bioelectrochemistry*. **74**: 90–95.
- Yang, Y., Liu, C., Chang, P.R., Chen, Y., Anderson, D.P., and Stumborg, M. (2010). Properties and structural characterization of oxidized starch/PVA/ α -Zirconium phosphate composites. *Journal of Applied Polymer Science*. **115**: 1089–1097.
- Yao, K., Cai, J., Liu, M., Yu, Y., Xiong, H., Tang, S., and Ding, S. (2011). Structure and properties of starch/PVA/nano-SiO₂ hybrid films. *Carbohydrate Polymers*. **86**: 1784–1789.

- Yeung, K.L., Leung, W.K., Yao, N., and Cao, S. (2009). Reactivity and antimicrobial properties of nanostructured titanium dioxide. *Catalysis Today*. **143**: 218-224.
- Yu, J., Yang, J., Liu, B., and Ma, X. (2009). Preparation and characterization of glycerol plasticized pea starch/ZnO–carboxymethylcellulose sodium nanocomposites. *Bioresource Technology*. **100**: 2832–2841.
- Yuan, J.Y., and Su, B.L. (2004). Titanium oxide nanotubes, nanofibers and nanowires. *Colloids and Surfaces A: Physicochem. Eng. Aspects*. **241**: 173-183.
- Zan, L., Tian, L., Liu, Z., and Peng, Z. (2004). A new polystyrene–TiO₂ nanocomposite film and its photocatalytic degradation. *Applied Catalysis A: General*. **264**: 237-242.
- Zenkiewicz, M., and Richert, J. (2008). Permeability of polylactide nanocomposite films for water vapour, oxygen and carbon dioxide. *Polymer Testing*. **27**: 835–840.
- Zeppa, C., Gouanve, F., and Espuche, E. (2009). Effect of a plasticizer on the structure of biodegradable starch/clay nanocomposites: thermal, water-sorption, and oxygen-barrier properties. *Journal of Applied Polymer Science*. **112**: 2044–2056.
- Zhai, J., Tao, X., Pu, Y., Zeng, X.F., and Chen, J.F. (2010). Core/shell structured ZnO/SiO₂ nanoparticles: Preparation, characterization and photocatalytic property. *Applied Surface Science*. **257**(2): 393-397.
- Zhang, Q., Jiang, P., Pan, B., Zhang, W., and Lu, L. (2009). Impregnating Zirconium Phosphate onto Porous Polymers for Lead Removal from Waters: Effect of Nanosized Particles and Polymer Chemistry. *Industrial Engineering Chemistry Research*. **48**: 4495–4499.

Zhanjun, L., Lei, Z., Minnan, C., and Jiugao, Y. (2010). Effect of Carboxylate Multi-Walled Carbon Nanotubes on the Performance of Thermoplastic Starch Nanocomposites.

Carbohydrate Polymers. **83**: 2, 447-451.

Zhao, H., and Li, R.K.Y. (2006). A study on the photo-degradation of zinc oxide (ZnO) filled polypropylene nanocomposites. *Polymer*. **47**: 3207–3217.

Zhao, R., Torley, P., and Halley, P.J. (2008). Emerging biodegradable materials: starch and protein-based bionanocomposites. *Journal of Material Science*. **43**: 3058-3071.

Zhao, Y., Qiu, Z., Yan, S., and Yang, W. (2011). Crystallization behavior of biodegradable poly(L-lactide)/multiwalled carbon nanotubes nanocomposites from the amorphous State.

Polymer engineering and science. **78**: 1564-1573.

Zheng, H., Ai, F., Wei, M., Huang, J., and Chang, P.R. (2007). Thermoplastic soy protein nanocomposites reinforced by carbon nanotubes. *Macromolecular Materials and Engineering*. **292**: 780–788.

Zheng, H., Ai, F., Chang, P.R., Huang, J., and Dufresne, A. (2009). Structure and properties of starch nanocrystal-reinforced soy protein plastics. *Polymer Composites*. **1002**(10): 474-480.

Zhou, J.J., Wang, S.Y., and Gunasekaran, S. (2009). Preparation and characterization of whey protein film incorporated with TiO₂ nanoparticles. *Journal of Food Science*. **74**: 7, 50-56.

Zhu, Y., Buonocore, G.G., Lavorgna, M., and Ambrosio, L. (2011). Poly(lactic acid)/Titanium dioxide nanocomposite films: influence of processing procedure on dispersion of titanium dioxide and photocatalytic activity. *Polymer Composites*. **88**: 519-528.

Zimmermann, T., Pohler, E., and Schwaller, P. (2005). Mechanical and morphological properties of cellulose fibril reinforced nanocomposites. *Advanced engineering materials*. **7**(12): 1156-1161.

Captions

Fig. 1. Various types of nanoscale materials (Kumar et al., 2009).

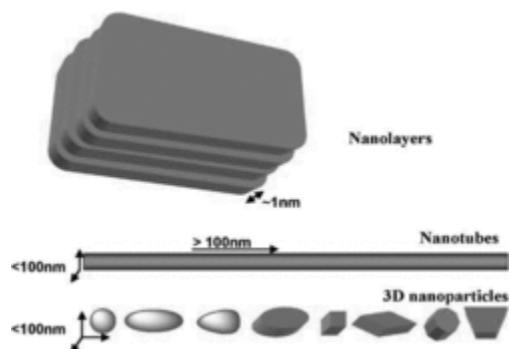


Fig. 2. Different forms and shapes of nano-structured particles (Bouwmeester et al., 2009).

Particle type and shape	Description
	Spherical or compact particles compositionally homogenous
	Tubular particles compositionally homogenous
	Complex non-spherical particles compositionally homogenous
	Compositionally heterogeneous particles compositional variation core-surface
	Compositionally heterogeneous particles distributed compositional variation
	Homogeneous aggregates/agglomerates Consisting of a single particle class
	Homogeneous aggregates/agglomerates Consisting of diverse particle types

Fig. 3. Crystalline structure of: (A) anatase, (B) brookite and (C) rutile (Khataee & Kasiri, 2010).

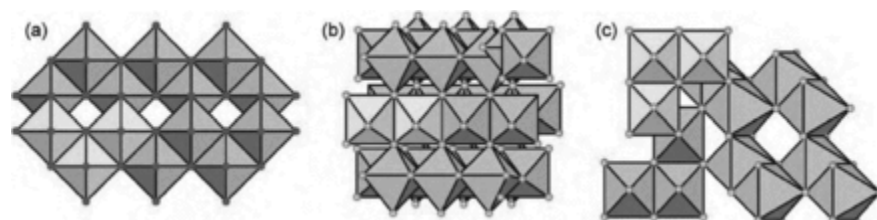


Fig. 4. (a) Schematic representation of a bacterial cell on the surface of porous TiO_2 film under exposure to UV_A light, (b) representation of TiO_2 nanoparticles agglomerate in contact with an E.coli cellular surface observed via transmission electronic microscopy, and (c) scheme of the photocatalytic act with TiO_2 nanoparticles

(Nadtochenko et al, 2010).

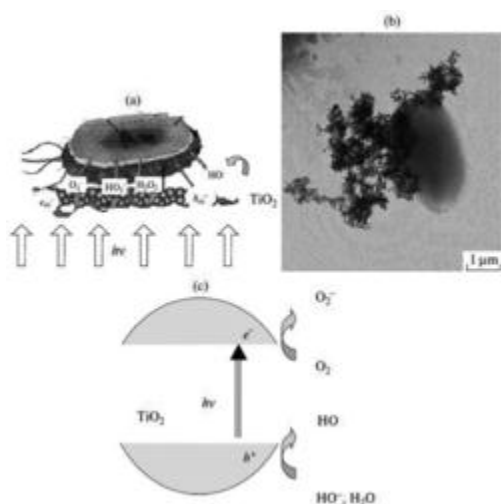


Fig. 5. Photographs of the pure WPI film (a) and TiO_2 /WPI composite films (b: 0.1% TiO_2 ; c: 2% TiO_2).

(Li et al. 2011).

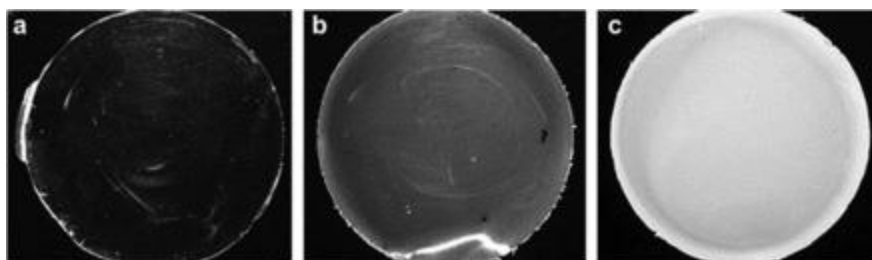


Fig. 6. TEM image of zinc oxide nanoparticle (ZnONP) suspension (Liu et al. 2009).

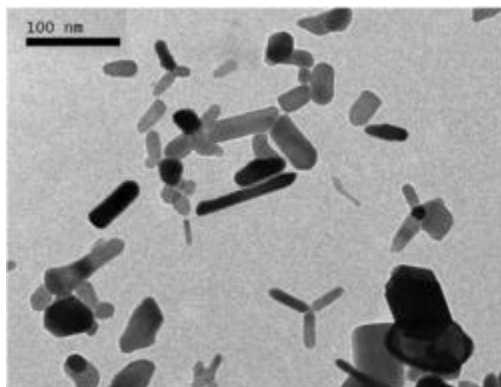


Fig. 7. SEM images of the α -ZrP (Wu et al., 2010) and Field emission scanning electronmicroscope (FESEM) image of precursor α -ZrP (Yang et al., 2008).

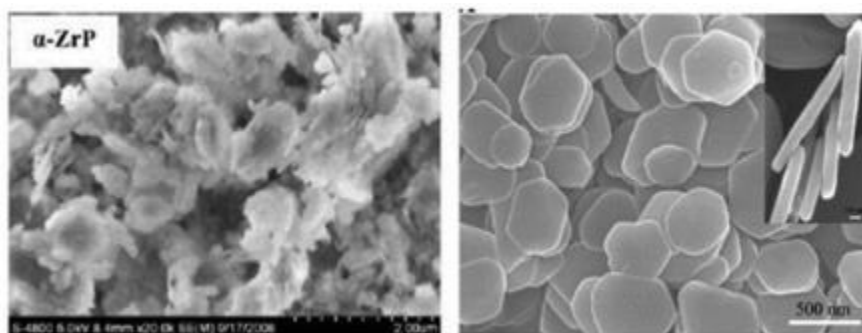


Fig. 8. The chemical general structures for: 2:1 phyllosilicates with the schematic representation of the tetrahedral (T) and octahedral (O) occupancies in natural and synthetic layered nano-fillers (Utracki et al., 2007).

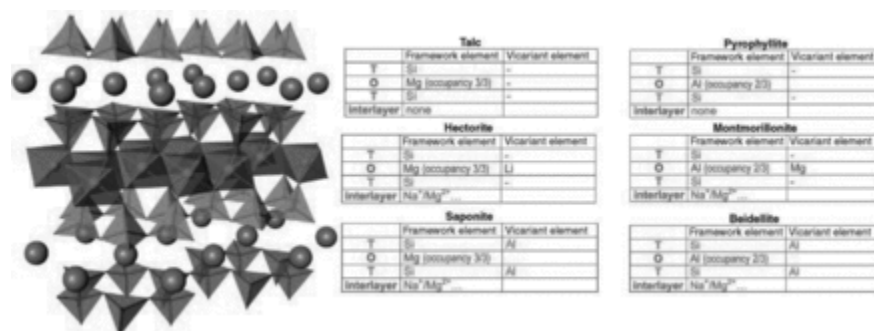


Fig. 9. Tactoid (a), intercalated (b) and exfoliated (c) polymer–clay nanocomposite morphologies (Duncan, 2011; Ray and Okamoto, 2003; Robinson and Morrison, 2010).

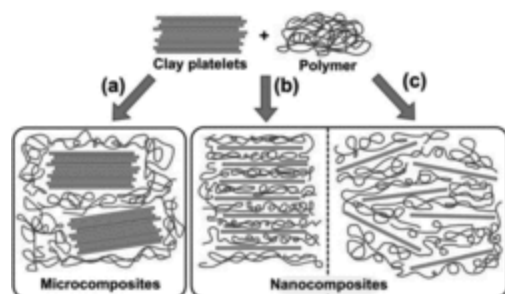


Fig.10. Diffusing gas molecules in a film composed only of polymer (a) and in a nanocomposite (b) (Duncan, 2011).

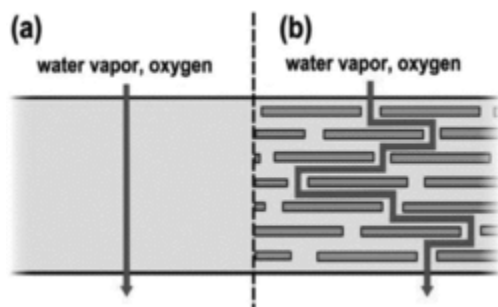


Fig. 11. Different structure of composites. Composite formed by the mixing of filler into plasticized starch (STN1), composite structure formed by the mixing of filler into starch followed by plasticization (STN2), composite structure formed by the together mixing of all components (clay / starch / plasticizer) (STN3) and composite structure formed when starch was mixed into slurry of plasticizer and clay (STN4). The thick bold rods indicate the silicate layers, whereas long and short chains denote starch and plasticizer, respectively (Pandey and Singh, 2005).

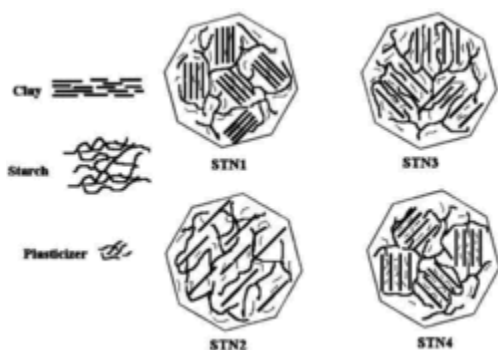


Fig.12. Molecular model of an ideal carbon nanotube (García-Gutiérrez et al., 2007).



Fig.13. Schematic illustration of morphology of clay and CNTs in chitosan membrane: (a) chitosan/3% clay and (b) chitosan/2% clay/1% CNTs (Tang et al. 2009a).

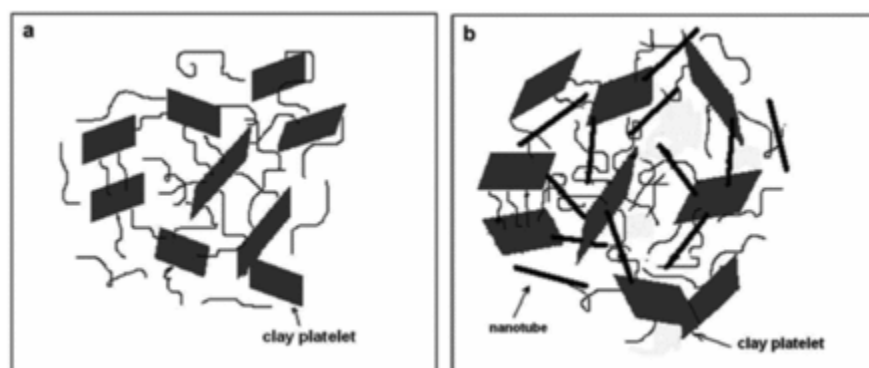


Fig. 14. The ultrastructure of lignocellulosic fibres (Frey-Wyssling and Mühlethaler, 1965).

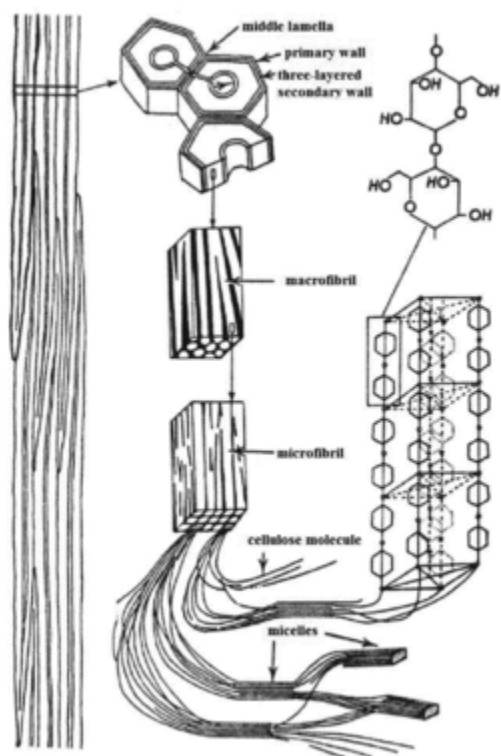


Fig. 15. Internal structure of a cellulose microfibril: (A) a cellulose chain; (B) an elementary fibril containing bundles of cellulose chains; (C) parallel elementary fibrils; (D) four microfibrils held together by hemicellulose and lignin (Ramos, 2003).

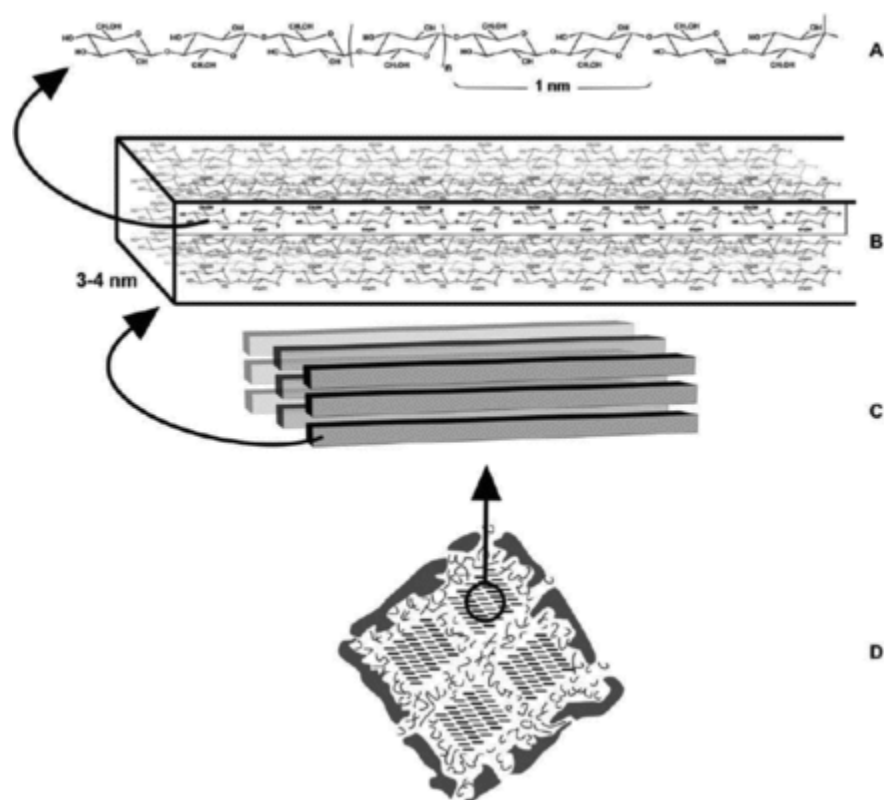


Fig. 16. Schematic presentation of the crystalline structure of cellulose (Battista, 1975).

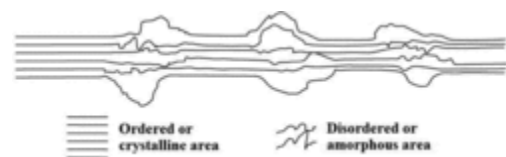


Fig. 17. Production of cellulose nanowhiskers from cellulose microfibrils by acid hydrolysis treatment (Gardner et al., 2008).

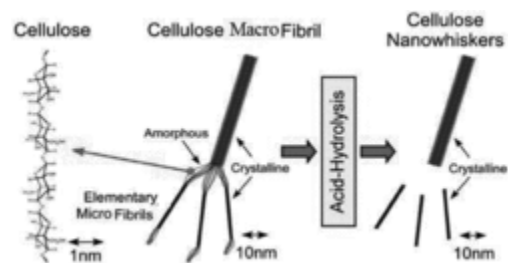


Fig. 18. The schematic illustration of production stages of cellulose nanocrystal from microcrystalline cellulose (MCC) (Hamad, 2006).



Fig. 19. AFM image of cellulose nanocrystals (Hamad, 2006).

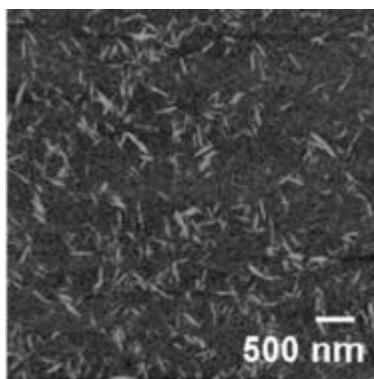


Table 1. Properties of cellulose crystallites obtained from cotton linter (Oksman et al., 2006).

Characteristics	Amount
Length (nm)	100-2000
Diameter (nm)	3-20
Aspect ratio	20-60
Tensile strength (MPa)	≈ 10000
Young modulus (GPa)	≈ 150

Table 2. Structural dimensions of whiskers obtained from different sources (Azizi Samir et al., 2005).

Source of cellulose	Diameter (nm)	Length (nm)
Wood	3-5	100-250
Cotton	5-15	100-250
Tunicate	10-20	100 to few micrometer
Valonia (alga)	10-20	> 1000
Bacteria	6-10	100 to few micrometer