Developments in Nano-particle Embedded Biodegradable Polymers for Packaging and Storage of Fruits and Vegetables

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Abstract
Nano-technology is the design, production, application of structures, devices and system through control of the size and shape of the material at 10^{-9} of a meter scale. This review summarises the development of nano-film from whey protein, corn zein protein and soy protein, and testing the mechanical, physical, rheological, chemical properties. The main factors include the origin of the extracts and the biopolymer carriers, polymer carriers/extracts composition and material-forming processes used. Interactions between polymer carriers and extracts have been well managed in explaining some of the above observations.

Key words: Nano-technology, Nano foods, Mechanical properties, Rheological properties.

1. Introduction
Fruits and vegetable are perishable in nature because of its high water content. Different types of techniques are applied for packaging and storage of fruits and vegetable. The material used in packaging is non-degradable. Packaging is the most important intervention for extending the effectiveness of food preservation and distribution chain. However, the environmental pollution caused by excessive use of plastic is a matter of great concern. Recently many state governments have banned use of petrochemical based non-degradable plastics. Therefore, there is a necessity to develop biodegradable films, coatings and bio-composite materials for this purpose. Bio-plastics development is just beginning; it covers approximately 5-10% of the current plastic market, about 50,000 ton in Europe (European Commission, 2004). The European countries with the highest utilization of bio-plastics are France, Germany, England, Netherland and Italy but in India it is yet to be introduced. The principal use of packaging films for food products are loose films used for transport packaging, service packaging like carry bags, cups, plates and cutlery, biowaste bags, in agricultural and horticultural fields in the form of bags and compostable articles.

Nanotechnology involves the characterization, fabrication and/or manipulation of structures, devices or materials that have least one dimension or contains component with at least one dimensions that is approximately 1-100 nm in the length (Duncan, 2011). In 2008, the nanotechnology field was so huge growing and over 400000 scientists, researchers have been working across the globe and the requirement of worker and research in this field is 6 million by end of this decade (Roco et al., 2011). The most active area of food nanoscience research and development is packaging and storage. The global and nano-embedded food and beverage system packaging market was 4.13 billion US dollars in 2008 and has been projected to grow upto 7.3 billion by the end of the year 2014 (Research Report, 2010). Now-a-days, the largest part of materials used in packaging industries are produced from fossil fuel and it is practically non-degradable that represents a serious global environment problem (Kirwan and Strawbridge, 2003). So use of protective and edible packaging by food industries has become an interesting topic because of their potential for increasing shelf life of various foods products (Ahvenainen, 2003; Coles et al., 2003; Giles and Bain, 2001; Hernandez et al., 2000) by maintaining the product quality, freshness and extending its shelf life during the time required for its commercialization and consumption (Brown, 1992; Stewart et al., 2002). The biological basis of the starting material provides the material engineer with a unique opportunity to incorporate a very appealing functionality in to materials that of comparability. Bio-based packaging materials have attached considerable research and development interest for the significant length of time (Coombs and Hall, 2000). The use of protective coating and suitable packaging material in food industries facilitates inducement in shelf life for many food items (Ahveninen, 2003; Coles et al., 2003; Giles and Bain,
2001; Hernandez et al., 2000). The application of nanotechnology to these polymers may open new possibilities not only for improving the properties but also to develop cost-effective technique. Huge efforts to extend the shelf life and maintain food quality while reducing packaging waste has encouraged the exploration of new bio-based packaging material, such as edible and bio-degradable films from renewable resources (Tharanathan, 2003).

Nano technology can possibly improve production process to provide products with better characteristics and new functionalities in the food and bio-processing industries (Roco, 2003). Total global investment in nanotechnology in the year 2004 was US $7 billion (European Commission, 2004). The annual values of nanotechnology related products for the years 2011-15 were estimated to near $ 1 trillion (Roco and Bain-Bridge, 2002). Recently, interest in composite manufacturing has shifted towards the use of natural fibres as reinforcement because of their environment benefits. The use of biodegradable matrix (film) is worth considering since this would result in a completely bio-degradable composite (Van de Velde and Kiekens, 2002).

Nowadays, efforts are being made to find new uses for proteins and starches, e.g. production of edible films (Anker et al., 1998; Kokoszka et al., 2010), or films with antimicrobial functionality (nanoparticle) for more effective protection of food products. The increased interest in ‘ready to eat’ and easy to consume products enhances the obligation for greater control on food quality and safety. Outbreaks of food borne diseases brought the necessity for alternative methods in controlling microbial growth in food products (Appendini and Hotchkiss, 2002). Unlike chitosan film, whey protein films themselves have not shown any antimicrobial activity; therefore, incorporation of antimicrobial agent such as sorbic acid, p-amino benzoic acid (Cagri et al., 2001), and lysozyme is required to impart this property (Kristo et al., 2008). Another potential route to impart antimicrobial functionality to packaging films is through the utilization of antimicrobial nanoparticles such as titanium dioxide (TiO$_2$) nanocomposites. Titanium dioxide (TiO$_2$) or titania is a nontoxic and inexpensive material exhibiting bactericidal activity against a wide variety of microbes due to its photocatalytic activity. Under UV, TiO$_2$ catalyses the oxidation of H$_2$O and O$_2$ to generate free hydroxyl and oxygen radicals that can effectively kill microorganisms. When TiO$_2$ is incorporated into a polymer matrix then this type of packaging material will provide protection against food borne microorganisms as well as odour, staining, deterioration, and allergens on the presence of radiation of relatively low wavelength near the ultraviolet region (Rajh et al., 1999; Zhou et al., 2009). However, TiO$_2$ particles easily aggregate and deteriorates the properties of the film (Zhou et al., 2009). Besides, the direct contact between TiO$_2$ and the polymer matrix may lead to quick degradation of the polymer films themselves. To maintain the integrity of the polymer film, the TiO$_2$ nanoparticles need to be sealed inside shells to prevent direct contact between the TiO$_2$ and the polymer molecules. To maintain the functionality of the TiO$_2$ particles, which relies on the exchange of free radicals generated by photoreaction on the TiO$_2$ surface and the surrounding environment, the shells must be porous to allow fast in/out diffusion of free radicals.

Thus biopolymers fulfil the environmental concerns but they show some limitations in terms of performance like thermal resistance, barrier and mechanical properties, associated with the costs. Moreover, this kind of packaging materials, needs more research in the form of value addition like the introduction of smart and intelligent molecules (which is the nanotechnology field) that provides information about the properties of the food inside the package (quality, shelf-life, microbiological safety) and nutritional values (Siracusa et al., 2008).

The food and bio-processing industries are facing different kinds of problems for designing, developing and implementing efficient system that can prepare high quality, safe food as well as feeds. Nano-technology is improving its fame and gaining momentum, also becoming a worldwide important tool for food and bio-processing due to world’s demand that will result from population growth and increasing incomes in developing countries. Nano-technology can possibly improve production process to provide products with better characteristics and new functionalities in food and bio-processing industries (Roco, 2010). Application of nano-technology to food processing industry will have a positive impact on consumers according to market analysis personnel.

Food nano-technology is still a lesser known subfield of the greater nano-technology spectrum, even among professional nano-technology deficits. By providing a comprehensive review of current developments in nano-technology applied to food and food-related systems, provides a special focus on applications that are most likely to enjoy consumer acceptance and regulatory attention in the intermediate future. This review covers wide topic of nano-technology in food packaging including polymer nano-composite for stronger, high barrier packaging materials. Also, nanoparticle based anti-microbial and sensor/assays that detect contaminants in food is also discussed (Duncan, 2011).
2. Materials for Nano-particle Films/ Biopolymers Based Packaging Materials

The research has focused on certain physico-chemical properties including mechanical properties (TS, EAB and puncture strength (PS)), water related properties (WVP and water solubility), rheological properties (viscous, Bingham, Newtonian and non-Newtonian), optical properties (colour, transparency and organoleptic). For example, it has been reported that the addition of components such as anti-oxidant extract, oregano and rosemary extract to tuna-skin gelatine brought a pronounced increase in film solubility, which is in agreement with other researcher, who also reported the increase in solubility of soy protein film with addition of green tea extract (GTE, comellascienensis) (Gómez-Estaca et al., 2009; Kim et al., 2006). There are thousands of scientists working on nano-technology and successfully produce natural biopolymers (1) polysaccharides like starch, cellulose derivatives, pectin, alginate, carrageenan, natural gums, chitosan and pullulan, (2) Proteins derived from plants legumes, grains and vegetable such as soy, wheat gluten, rice bran, peanut, pea and cottonseed. Dinkel et al. (1996) has compared products (films and injection-moulded article) made from starch and starch containing plastic with conventional plastic products. Bio-based packaging materials and bio-degradable materials currently available in the market are based on natural renewable sources of bio-polymers (A European Concerted Action, 2000).

2.1 Natural Polymers

2.1.1 Collagen

Collagen is the major natural protein component in mammals that is fabricated from glycine-proline-hydroxyproline, repeats to form a triple helix molecular structure (Kojima et al., 2009). So far, nineteen types of collagen molecules have been isolated, characterized and reported in both medical and pharmaceutical applications (Parenteau-Bareil et al., 2010; Chen et al., 2010; Holladay et al., 2009). Collagen has been widely used in pharmaceutical applications due to the fulfillment of various requirements of a drug delivery system such as good biocompatibility, low antigenicity and degradability upon implantation (Yang et al., 2004). Furthermore, collagen gels are one of the first natural polymers to be used as a promising matrix for drug delivery and tissue engineering (Weiner et al., 1985). Biodegradable collagen-based systems have served as 3D scaffold for cell culture, survival of transfected fibroblasts and gene therapy (Holladay et al., 2009). As mentioned the impact of various plastics extracts physico-chemical attributes of various edible bio-polymers bond films are presented in Table 1.

Table 1: Impact of various plastics extracts on physico-chemical attributes of various edible bio-polymers bond films

<table>
<thead>
<tr>
<th>A. Natural Polymers</th>
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<tbody>
<tr>
<td>a. Protein based polymers</td>
<td>Collasan, albumin and gelatin</td>
<td></td>
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<tr>
<td>b. Polysaccharides</td>
<td>Alginate, Cydodextrin, Chitosan, Dextrin Agarose, Hyaluronic acid, Starch and Cellulose</td>
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<th>B. Synthatic Polymers</th>
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<td>a. Bio-degradable polymers</td>
<td></td>
<td></td>
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<tr>
<td>i. Polyster</td>
<td>Polylectic acid Poly glycolic acid polyHydroxyle butyrate, polyester polycaprplactone PLGA Poliodoxanase</td>
<td></td>
</tr>
<tr>
<td>ii. Poly anhydride</td>
<td>Poly adipic acid Poly sebaic acid Poly tethalic acid Various copolymers</td>
<td></td>
</tr>
<tr>
<td>iii. Polyamides</td>
<td>Poly amino acid Polyiminino-carbohydres</td>
<td></td>
</tr>
<tr>
<td>iv. Phosphoras based polymers</td>
<td>Poly phosphate Poly phosphonate Polyphosphozenes</td>
<td></td>
</tr>
<tr>
<td>v. Others</td>
<td>Poly cryanonycarlates Polyeuarthanes Poly ortho ester Poly acetales</td>
<td></td>
</tr>
<tr>
<td>b. Non-degradable</td>
<td></td>
<td></td>
</tr>
<tr>
<td>i. Silicones</td>
<td>Polymidimethyl siloxane Coloidal silica Polymethacrylates</td>
<td></td>
</tr>
<tr>
<td>ii. Cellulose derivatives</td>
<td>Carboy ethyle cellulose Methyle cellulose Cellulose acetate Hydroxyl propyl methyle cellulose</td>
<td></td>
</tr>
<tr>
<td>iii. Others</td>
<td>Poly vinylypyrrolidone Poly viny acetate Poloxamines</td>
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</table>

2.1.2 Gelatin

Gelatin is a common natural polymer (water soluble polymer) or protein which is normally
produced by denaturing collagen (Hao et al., 2009). It has been used in pharmaceutical and medical applications due to its outstanding properties such as biodegradability, biocompatibility and low antigenicity (Narita et al., 2009). In addition, gelatin can be easy to manipulate due to its isoelectric point that allows it to change from negative to positive charge in an appropriate physiological environment or during the fabrication, a property that has found to be very attractive to many pharmaceutical researchers (Young et al., 2005).

Gelatin is one of the natural polymers used as support material for gene delivery, cell culture and more recently developed tissue engineering. Gelatin-based systems have the ability to control release of bioactive agents such as drugs, protein, and dual growth factors (Ofokansi et al., 2010). It has been reported that it is possible to incorporate liposome loaded bioactive compounds into PEG gelatin gel which function as porous scaffold gelatine based temporary depots with controlled drug release over prolonged periods of time (Burke et al., 2007). However, some setbacks have been identified and they are said to be associated with the use of gelatin-based systems in pharmaceutical applications. These setbacks include poor mechanical strength and ineffectiveness in the management of infected sites (Parenteau-Bareil et al., 2010).

### 2.1.3 Albumin

Serum albumin was conjugated to poly-ethylene glycol (PEG) and cross-linked to form mono-PEGylatedalbumin hydrogels. These hydrogels were used as a basis for drug carrying tissue engineering scaffold materials, based on the natural affinity of various drugs and compounds for the tethered albumin in the polymer network.

### 2.1.4 Alginate

Alginate also serves as an example of a naturally occurring linear polysaccharide. It is extracted from seaweed, algae and bacteria (Gombotz et al., 1998). The fundamental chemical structure of alginate is composed of 1–4-b-D-mannuronic acid (M) and 1–4-a-L-guluronic acid (G) units in the form of homo polymeric (MM- or GG-blocks) and hetero polymeric sequences (MG or GM-) blocks (Gao et al., 2009). Alginate and their derivatives are widely used by many pharmaceutical scientists for drug delivery and tissue engineering applications due to its many unique properties such as biocompatibility, biodegradability, low toxicity, non-immunogenicity, water solubility, relatively low cost, gelling ability, stabilizing properties and high viscosity in aqueous solutions (Li et al., 2006). Since alginate is anionic, fabrication of alginate hydrogels has successively been achieved through a reaction with cross-linking agents such as divalent or trivalent cations mainly calcium ions, water-soluble carbodiimide, and/or glutaraldehyde (Xu et al., 2003). The cross-linking methodology was conducted at room temperature and physiological pH (Jeon et al., 2009).

The success in fabricating highly porous 3D alginate scaffolds is possible through lyophilisation (Mohan and Nair, 2005). So far, alginate based systems have been successfully used as a matrix for the encapsulation of stem cells and for controlled release of proteins, genes and drugs (Khanna et al., 2010; Kong et al., 2008). In addition, alginate based systems have been used as depots for bioactive agent loaded liposomes, for slow drug release (Monshipouri and Rudolph, 1995). Highly increased efficacy has been reported from these integrated delivery systems when compared to polymeric-based systems or liposome-based systems alone (Dhoot et al., 2006; Dai et al., 2003). Dextran is a natural linear polymer of glucose linked by a 1–6 linked-glucopyranoside, and some branching of 1, 3 linked side-chains (Mehvar, 2000).

Dextran is synthesized from sucrose by certain lactic acid bacteria, the best-known being Leuconostoc mesenteroides and Streptococcus mutans. There are two commercial preparations available, namely dextran 40 kilodaltons (kDa) (Rheomacrodex) and dextran 70 Kilodaltons (kDa) (Macrodex) (Sun et al., 2010; Hornig et al., 2009). In pharmaceutics, dextran has been used as model of drug delivery due to its unique characteristics that differentiate it from other types of polysaccharide. This includes water solubility, biocompatibility and biodegradability (Shrivastava and Shrivastava, 2010). In recent studies, dextran has been regarded as a potential polysaccharide polymer that can sustain the delivery of proteins, vaccines, and drugs (Qi et al., 2010; Bachelder et al., 2010). Interleukin-2, highly effective anticancer drug is among the success obtained in delivering a combination of drug-loaded liposome and injectable dextran hydrogel (Groot et al., 2002). Injectable and degradable dextran-based systems for drug delivery were generated by a cross-linking reaction with photo-polymerization or free radical polymerization. Stenekes et al. (2000) demonstrated the successive encapsulation of a drug-loaded liposome depot into a dextran polymer-based material. The polymeric-based materials are fabricated using a two phase system, the first phase is water and poly(ethylene glycol) and the second one water methacrylated dextran. The slower degradation of dextran polymeric material resulted in sustained liposome release over a period of 100 days. Liposomes released from depot were reported to be intact and there is no significant change in liposomal size. In a gene
therapy study, Liptay et al. (1998) reported that recombinant DNA (which contains chloramphenicol acetyltransferase) is successively encapsulated in cationic liposomes and then integrated within dextran. This system is reported to be a suitable delivery system since it could stop transfection efficiency within the colon epithelium wall in vivo (Liptay et al., 1998).

2.1.5 Chitosan

Chitosan is a natural polycationic copolymer consisting of glucosamine and N-acetyl glucosamine units. It is mainly obtained by deacetylation of chitin derived from the exoskeleton of crustaceans. Chitosan has valuable properties as biomaterials because it is considered to be biocompatible, biodegradable, nontoxic (Singla et al., 2001). The cationic character and the potential functional group make it an attractive biopolymer for many biomedical and pharmaceutical applications. As a pharmaceutical excipient, chitosan has been used in many formulations such as powders, tablets, emulsions and gels. Furthermore, a controlled release of incorporated drugs can be guaranteed. Chitosan also shows mucoadhesive properties and antimicrobial properties. The bitter taste of natural extracts such as caffeine has been masked using chitosan. Chitosan can potentially be used as a drug carrier, a tablet excipient, delivery platform for parenteral formulations, disintegrant and tablet coating. From toxicity and safety point, lower molecular weight chitosan (as an oligosaccharide) has been shown to be safer with negligible cytotoxicity on coca-2-cell. During the encapsulation process using synthetic polymers, the protein is exposed to the conditions that might cause their denaturation or deactivation. Therefore, a biocompatible and biodegradable alternative such as chitosan is desirable for such applications. Gels based on chitosan and ovalbumin protein have been applicable for pharmaceutical and cosmetic. Chitosan can also be mixed with anionic surfactant such as sorbitan ester to make emulsions like solutions or creams (Prabaharan et al., 2008). It is a promising bio-adhesive material at physiological pHs. This polymer possesses OH and NH2 group that can give rise to hydrogen bonding. These properties are considered essential for muco-adhesion (Peppas et al., 1985; Robinson, 1995). One study accounts for the possible use of chitosan in mixtures of different ratios with anionic polymers for the preparation of mucoadhesive tablets to be used as a vaginal delivery system for metronidazole (El-Kamel et al., 2002). By the introduction of thiol groups to chitosan, the muco-adhesive properties could be strongly improved while maintaining its biodegradability (Bernkop-Schnürch et al., 2004). Chitosan was thereby modified by attaching thioglycolic acid (TGA) onto the primary amino groups of the polymer via an amide bond formation (Kast et al., 2002). The excellent bioadhesion could result in an increased residence time of a drug at the site of absorption by interacting with the mucosa (Duchêne et al., 1992; Khanvilkar et al., 2001). As chitosan is also known to exhibit antimicrobial activity, the chitosan-TGA conjugate would be ideal as a matrix for the cationic anti-mycotics for treating mycotic infections in the vagina. A common microbial problem in the vulvovaginal tract is the infection with C. Albicans. Approximately 75% of women will have a vaginal infection with a Candida strain during their life and about 40–50% of them will suffer a second one and a small percentage will show a chronic course. By the introduction of thiogroups the bioadhesive properties of chitosan could be significantly improved.

2.1.6 Cellulose Derivatives

Cellulose is the most abundant naturally occurring biopolymer (Hinterstoisser and Salmén, 2000). Various natural fibers such as cotton and higher plants have cellulose as their main constituent (Myasoedova, 2000; Gross and Scholz, 2000). It consists of long chains of anhydro-D-glucopyranose units (AGU) with each cellulose molecule having three hydroxy groups per AGU, with the exception of the terminal ends. Cellulose is insoluble in water and most common solvents (Bochek et al., 2003). The poor solubility is attributed primarily to the strong intramolecular and intermolecular hydrogen bonding between the individual chains (Hinterstoisser and Salmén, 2000). In spite of its poor solubility characteristics, cellulose is used in a wide range of applications including composites, netting, upholstery, coatings, packing, paper, etc. Chemical modification of cellulose is performed to improve process ability and to produce cellulose derivatives (cellulosics) which can be tailored for specific industrial applications (Akira, 1997). Large scale commercial cellulose ethers include carboxymethyl cellulose (CMC), methyl cellulose (MC), hydroxyethylcellulose (HEC), hydroxypropyl methyl cellulose (HPMC), hydroxypropyl cellulose (HFC), ethyl hydroxyethyl cellulose (EHEC), and methyl hydroxyethyl cellulose (MHEC).

2.1.7 Starch

Plants synthesize and store starch in their structure as an energy reserve. It is generally deposited in the form of small granules or cells with diameters between 1-100 μm. After cellulose, starch is the most abundant carbohydrate available from plant kingdom as raw material. The estimated world production of starch amounts to 58 million tonnes, extracted from maize (46 million), wheat (4.6 million), potatoes (3.5 million) and the remainder coming from rice and cassava roots.
(tapioca). Starch is the main carbohydrate in plants and acts as a reserve food supply for periods of growth, dormancy and germination. Being a biodegradable polymer with well-defined chemical properties, it has a huge potential as a versatile renewable resource for various material applications in food and non-food areas. The composition and properties of commercial available starches have been studied extensively. The properties of each starch are strongly dependent on their plant source. Starch is a heterogeneous polymer of α-D-glucose units. The anhydrous glucose units (AGUs) are mainly linked by α-(1, 4)-bonds and to some extent by α-(1, 6)-linkages. The biopolymer consists of two distinguished structural forms: amylose and amylopectin. Amylose is mainly found as a long linear polymer containing about several hundred α-(1, 4)-linked glucose units (up to 6000 AGUs), with a molecular weight of 105-106 g mol\(^{-1}\). In the solid state, the chains very easily form single or double helices. In contrast, amylopectin is a highly branched molecule with a molecular weight of 107-109 g mol\(^{-1}\). The branched polymer contains α-(1,4)-linked glucose units but has additional α-(1,6)-glucosidic branching points which are believed to occur every 10 to 60 glucose units, i.e. 5% of the glucose moieties are branched.

2.1.8 Hyaluronic Acid

Hyaluronic acid (also called as Hyaluronan and Hyaluronate (HA) and Sodium Hyaluronate (SA) is sodium salt form of hyaluronic acid) is a biodegradable, biocompatible and viscoelastic linear polysaccharide of a wide molecular weight range (1000 to 10,000,000 Da). It is a naturally occurring biopolymer, which serves important biological functions in bacteria and higher animals including humans. Naturally occurring hyaluronic acid may be found in the tissue of higher animals, particularly as intercellular space filler. It is found in greatest concentrations in the vitreous humor of the eye and in the synovial fluid of articular joints (O’Regan et al., 1994). Hyaluronic acid comprises linear, unbranching, polyanionic disaccharide units consisting of glucuronic acid (GlcUA), an N-acetyl glucosamine (GlcNAc) joined alternately by β-1-3 and β-1-4glycosidic bonds. Hyaluronic acid solutions are characteristically viscoelastic and pseudo-plastic. The viscoelastic property of hyaluronic acid solutions is that important in its use as a biomaterial is controlled by the concentration and molecular weight of the hyaluronic acid chains. As a microcapsule, it can be used for targeted drug delivery (Fraser et al., 1998).

2.1.9 Cyclodextrin

They are cyclic oligosaccharides consisting of six to eight glucose units joined through α-1, 4 glucosidic bonds. Cyclodextrins remains intact during their passage throughout the stomach and small intestine of the GI tract. However, in colon, they undergo fermentation in the presence of vast colonic microfloras into small monosaccharide and thus absorbed from these regions (Gerloczy et al., 1985). β-cyclodextrins are degraded to a very small extent in the small intestine but are completely digested in the large intestine. Most bacterial strains found abundantly in human beings are capable of degrading cyclodextrins polysaccharide.

2.1.10 Biodegradable Polymer

Biodegradation is a natural process by which organic chemicals in the environment are converted to simpler compounds, mineralized and redistributed through elemental cycles such as carbon, nitrogen and sulphur cycles. Biodegradable polymers have been widely used in biomedical applications because of their known biocompatibility and biodegradability. Biodegradable polymers are intended for temporary aids, such as sutures, tissue-supporting scaffolds and drug delivery devices. Polymers within this group retain their properties for alimited period of time and then gradually degrade into soluble molecules that can be excreted from the body (Vainionpää et al., 1979).

2.2 Synthetic Polymers

2.2.1 Polyester

2.2.1.1 Polylactic Acid (PLA)

PLA is thermoplastic biodegradable polymer produced synthetically by polymerization of lactic acid monomers or cyclic lactide dimmers. Fig 1 shows the structure of PLA. Lactic acid is produced by fermentation of natural carbohydrates for example, maize or wheat or waste products from the agricultural or food industry. Commercial quantities of PLA for packaging applications are produced through ring opening polymerization of lactide, a reaction favoring the formation of high molecular polymers. The final crystallinity and mechanical properties of the polymer depends on the stereochemistry of polymer backbone. PLA is degraded by hydrolysis (the breaking of a chemical bond by adding water to it) of the backbone esters of the polymer. The esters are broken at random, so that the PLA chains in the material get shorter and shorter until monomers of lactic acid start to come loose and the plastic essentially dissolves. This process is called ‘bulk degradation’. PLA does not degrade by microbial attack and is currently used in loose fill packaging, food packaging films, thermoformed containers and short shelf life bottles. PLA can be laminated to paper and paperboard by extrusion coating
for further use as packaging material. Drinking cups and food containers for short shelf life products are other application areas. Fabrics produced from PLA provide a silky feel, durability and moisture management properties. PLA is useful for producing compost bags and disposable tableware also. It has number of biomedical applications, such as sutures, stents, dialysis media and drug delivery devices.

![Fig1: General structure of PLA.](image)

### 2.2.1.2 Polyglycolic Acid (PGA)

PGA is commonly obtained by ring-opening polymerization of the cyclic diester of glycolic acid, glycolide (Frazza and Schmitt, 1971; Benicewicz and Hopper, 1991). PGA is a hard, tough, crystalline polymer with a melting temperature of 225 °C and a glass transition temperature, Tg, of 36 °C (Frazza and Schmitt, 1971). Unlike closely related polymers such as PL, PGA is insoluble in most common polymer solvents. PGA has excellent fiber-forming properties and was commercially introduced in 1970 as the first synthetic absorbable suture under the trade name Dexon™ (Frazza and Schmitt, 1971). The low solubility and high melting point of PGA limits its use for drug delivery applications, since it cannot be made into films, rods, capsules or microspheres using solvent or melt techniques.

### 2.2.1.3 Polyhydroxy butyrate (PHB)

PHB is a biopolymer, which is present in all living organisms. Many bacteria produce PHB in large quantities as storage material. It is non toxic and is totally biodegradable. The polymer is primarily a product of carbon assimilation (from glucose or starch) and is employed by microorganisms as a form of energy storage molecule to be metabolized when other common energy sources are not available. PHB and its copolymers have attracted much attention because they are produced biosynthetically from renewable resources. Microcapsules from PHB has been prepared by various techniques and investigated for the release of bovine serum albumin.

According to Atkins and Peacock (1996) PHB has also been suggested as a suitable matrix for drug delivery in veterinary medicine, for instance in the rumen of cattle (Holmes, 1985).

### 2.2.1.4 Poly (lactide-co-glycolide), PLGA

Among the co-polymers investigated, extensive research has been performed in developing a full range of PLGA polymers. Both L- and DL-lactides have been used for co-polymerization. The ratio of glycolide to lactide at different compositions allows control of the degree of crystallinity of the polymers (Cohn et al., 1987). When the crystalline PGA is co-polymerized with PL, the degree of crystallinity is reduced and as a result this leads to increases in rates of hydration and hydrolysis. It can therefore be concluded that the degradation time of the copolymer is related to the ratio of monomers used in synthesis. In general, the higher the content of glycolide, the quicker the rate of degradation exception to this rule is the 50:50 ratio of PGA: PL, which exhibits the fastest degradation (Park et al., 1995; Miller et al., 1977). PLGA is used in drug delivery applications. Non-steroidal anti-inflammatory drugs, e.g., diflunisal (Castelli et al., 2000) and diclofenac sodium (Chandrashekar and Udupa, 1996; Tuncay et al., 2000), have been incorporated into PLGA microspheres and investigated for the treatment of rheumatoid arthritis, osteoarthritis and related diseases. The encapsulation of bio macromolecules, e.g., proteins and vaccines, into polymeric microspheres presents a formidable problem because of the delicacy of these agents; bioactivity might be lost during preparation, and the release may be poor due to adsorption and/or aggregation. For instance, the release of recombinant human interferon-g from PLGA microspheres was incomplete and the instability of the system limited its use to 7 days or less (Yang et al., 1997). Similarly, incomplete release of lysozyme, recombinant human growth hormone and a nerve growth factor from PLGA microspheres is reported (Park et al., 1998; Kim and Park, 1999). Hence, much effort has been spent in evaluating PLGA delivery systems with special regard to microsphere preparation, protein stability and release characteristics. Model proteins studied include bovine serum albumin, lysozyme, transferrin, and trypsin (Crotts and Park, 1998; Sah et al., 1995). Several peptides, including vapreotide and rismorelin porcine, have been successfully incorporated and released from PLGA microspheres (Blanco-Prieto et al., 2000; Thompson et al., 1997). Systems for the controlled release of antigens have a great potential as vaccine adjuvants (O’Hagan, 1998; Sturesson et al., 1999). Recently, several studies of controlled release systems for DNA have been presented. DNA of different sizes has successfully been incorporated into PLGA microspheres but the loss of DNA integrity and activity still remains an important issue to be solved for these systems (Luo et al., 1999; Walter et al., 1999).
2.2.1.5 Poly (ε-caprolactone), PCL

PCL is obtained by ring-opening polymerization of the 6-membered lactone, ε-caprolactone (ε-CL). Anionic, cationic, coordination, or radical polymerization routes are all applicable (Pitt, 1990). Recently, enzymatic catalyzed polymerization of ε-CL has been reported (Dong et al., 1999; Henderson et al., 1996). PCL crystallizes readily due to the regular structure and has a melting temperature of 61 °C. It is tough and flexible and the Tg of PCL is low (–60 °C) (Pitt, 1990). Thus, PCL is in the rubbery state and exhibits high permeability to low molecular species at body temperature. These properties, combined with documented biocompatibility, make PCL a promising candidate for controlled release applications as by enzymatic attack (Dubernet et al., 1987). Hence, PCL degrades under a range of conditions, biotically in soil, lake waters, sewage sludge, in vivo, and in compost, and abiotically in phosphate buffer solutions (Benedict et al., 1983; Chen et al., 2000). Hydrolysis of PCL yields 6-hydroxyhexanoic acid, an intermediate of the w-oxidation, which enters the citric acid cycle and is completely metabolized. Hydrolysis, however, proceeds by homogeneous erosion at a much slower rate than PLA and PLGA (Chen et al., 2000). Hydrolysis of PCL is faster at basic pH and higher temperatures (Pitt, 1990).

2.2.1.6 Polydioxanone (PDS)

Although biodegradable polylactides and glycolides have been used to develop versatile resorbable multi-filament structures, there is growing research involved in the development of materials that form monofilament sutures. Multifilament sutures have a higher risk of infection associated with their use and cause a greater amount of friction when penetrating tissues (Krukowski et al., 1987; Schoetz et al., 1988). Polydioxanone (referred to as PDS) is made by a ring-opening polymerization of the p-dioxanone monomer. It is characterized by a glass transition temperature in the range of –10 to 0°C and a degree of crystallinity of about 55%. Materials prepared with PDS show enhanced flexibility due to the presence of an ether oxygen within the backbone of the polymer chain. When used in vivo, it degrades into monomers with low toxicity and also has a lower modulus than PLA or PGA. For the production of sutures, PDS is generally extruded into fibers at the lowest possible temperature, in order to avoid its spontaneous depolymerisation back to the monomer.

2.2.1.7 Polyanhydrides

Poly anhydrides are class of biodegradable polymer characterized by anhydride bonds that connect repeat unit of polymers backbone chain. Poly (anhydride-esters) is polymeric compounds consisting of salicylic acid moieties bridged by linker structures. An example of the polymer structure is shown in Fig 2. These compounds contain two types of important bonds - anhydride and ester bonds and red respectively. In the presence of water, both bonds may degrade hydrolytically, releasing salicylic acid (B) and sebacic acid (C). Salicylic acid (B) is the active form of aspirin, an anti-inflammatory agent, and sebacic acid is currently used in drug delivery systems (Brem et al., 1995). In vivo mice studies have indicated that this polymer assists in wound healing and thus it promotes bone growth (Macedo et al., 1999).

![Fig 2: Poly (anhydride-esters), a polymeric compounds consisting of salicylic acid moieties bridged by linker structures](Image)

The release of salicylic acid (B) via bond hydrolysis opens up a variety of possibilities for creating drug delivery systems. Potential applications include treatment of inflammatory bowel disease, dental implants and tissue scaffolding. The studies on the degradation rate, the rate of release of salicylic acid as a function of pH, have shown that this polymer takes three months to degrade in acidic and neutral environment, but at basic pH it degrades in 19-40 hours (Erdmann and Uhrich, 2000). Since the upper gastrointestinal tract is acidic or neutral, this polymeric drug can reach the intestines undamaged, and release salicylic acid directly to the lower intestinal tract to treat the disease. Aspirin is also used in dentistry, for example, in cases of tooth breakage when there cannot be an immediate operation. In this procedure, the fast influx of salicylic acid irritates the surrounding tissue. Slower release of the medication, provided by the poly(anhydride-esters) would be a gentler solution. A drawback to the poly(anhydride-ester) structure shown in Fig 2 is its low Tg (glass transition temperature). This is a temperature at which a polymer goes from a solid into a rubbery state. The Tg of this polymer is several degrees below body temperature (37 °C), which means that it becomes a soft, sticky material when...
placed in the body. Because the polymer is being developed for use as a suture material, it is undesirable for the polymer to become soft during the sutureing process. Therefore, poly(anhydride-esters) with Tgs higher than body temperature need to be developed (Erdmann et al., 1998; Macedo et al., 1999).

2.2.1.8 Polyamide

The synthetic aliphatic polyamides are polymeric compounds frequently referred to as Nylons which form an important group of poly condensation polymers. They are linear molecules (i.e. aliphatic) that are semi-crystalline and thermoplastic in nature (Kiely et al., 1994; Hopf, 2001). A typical polyamide chain consists of amide groups separated by alkane segments and the number of carbon atoms separating the nitrogen atoms which defines the particular polyamide type. The aliphatic polyamides are very useful and versatile material that are valuable because of their superior physico-chemical and physico-mechanical properties such as abrasion resistance, chemical inertness, relatively high modulus, minimal degradation, ease of processing, thermo plasticity, higher melting points and heat resistance than many other semi-crystalline polymers such as polyethylene (Makino et al., 1990; Kiely et al., 1994; Chattaraj et al., 1995; Jones et al., 1997; Murthy, 1999; Ostad and Gard, 2000; Hopf, 2001; Li et al., 2001; Sikorski et al., 2001; Ostad et al., 2002; Fornes et al., 2003; Cui and Yan, 2005).

2.2.2 Phosphorous Based Derivatives

2.2.2.1 Polyphosphazenes

It consists of phosphorous atoms attached to either carbon or oxygen. Polyphosphazenes, another new class of polymer are being investigated for delivery of proteins (Andrianov et al., 1998). The uniqueness of this class of polymer lies in the chemical reactivity of phosphorous which enables a wide range of side chains to be attached for manipulating the biodegradation rates and the molecular weight of polymer.

2.2.3 Others

2.2.3.1 Polyorthoester

![Fig 3: Structure of poly (orthoester) s (POE) degradable polymers suitable](image)

Poly (orthoester)s (POE) are another family of polymers identified as degradable polymers suitable for orthopaedic applications. Heller and co-workers reported on the synthesis of a family of polyorthoesters (Fig 3) that degrades by surface erosion (Ng et al., 1997). With the addition of lactide segments as part of the polymer structure, tunable degradation times ranging from 15 to hundreds of days can be achieved. The degradation of the lactide segments produces carboxylic acids, which catalyze the degradation of the orthoester (Ng et al., 1997). Preliminary in-vivo studies have shown that POE to increase bone growth in comparison with poly (dilactide-co-glycolide) (Andriano et al., 1999).

In recent years, investigators have focussed on the incorporation of plant extract in to a certain dietary biopolymer based films and found such incorporations were able to modify the physico-chemical quality of these bio-polymers, green tea extract (20%) provide chitosan films with increase TS (16%), opacity (11%) and decreased WVP, whereas 80% ethanol clove extract decreases elongation at break (EAB) by 15% of fish skin gelatin films e.g. soy protein), animal protein e.g. skin gelatine from cuttle fish (sepia pharaonis) (Hoque and Chuan, 2011). The Table 2 provides legislative status of some starting substances for bio-based materials.

3. Development of Nano-particle Films

Engineering of a bio-based package or packaging material requires knowledge of the processing and material properties of the polymers. If the properties of the native biopolymer are not identical to the required one, or if the polymer by nature is not thermoplastic, a certain modification of the polymer must take place. For very specific requirements (very low gas permeability or high water resistance) it is unlikely that one polymer will be able to provide all required properties even after modifications. Hence, it is necessary to use multiple materials in a composite, a laminate or co-extruded material.

The development of bio-degradable nano-particle embedded polymer film can be done by different methods like as casting method/ extrusion blowing/ extrusion sheet making/ compression molding. The following instruments are mandatory used for film making for getting good strength: extruder, hot plate, characterisation instruments, digital micrometer, chroma meter and viscometer are used for formation of bio-degradable polymer films.

Kester and Fennema (1986) discussed edible films derived from several poly-saccharides, lipids, and proteins. Formation and properties of films from proteins such as casein, whey protein, corn zein, wheat gluten and soy protein. Stuchell and Krochta (1994)
reported that pieces of glycerol plasticized films from commercial soy protein isolate maintained their integrity after incubation in water for 24 hours with occasional gentle agitation. It was suggested that only monomers, small peptides, and non-protein materials solubilised in water. Film pieces immersed in water in the present study were not broken apart and the film network remained intact. Most likely, the hydrophilic glycerol constituted a large part of the film TSM.

Table 2: Legislative status of some starting substances for bio-based materials

<table>
<thead>
<tr>
<th>Substance</th>
<th>Status</th>
</tr>
</thead>
<tbody>
<tr>
<td>Albumin</td>
<td>Starting substance list</td>
</tr>
<tr>
<td>Cellulose</td>
<td>Starting substance list</td>
</tr>
<tr>
<td>Glucose</td>
<td>Starting substance list</td>
</tr>
<tr>
<td>3-Hydroxybutanoic acid-3-</td>
<td>Starting substance list</td>
</tr>
<tr>
<td>hydroxypentanoic acid, copolymer1</td>
<td></td>
</tr>
<tr>
<td>Lactic acid</td>
<td>Starting substance list</td>
</tr>
<tr>
<td>Lignocellulose</td>
<td>Starting substance list</td>
</tr>
<tr>
<td>Starch, edible</td>
<td>Starting substance list</td>
</tr>
<tr>
<td>Sucrose</td>
<td>Starting substance list</td>
</tr>
<tr>
<td>Alginic acid</td>
<td>Additive list</td>
</tr>
<tr>
<td>Casein Cellulose</td>
<td>Additive list</td>
</tr>
<tr>
<td>Cellulose acetate butyrate</td>
<td>Additive list</td>
</tr>
<tr>
<td>Cellulose derivatives, various</td>
<td>Additive list</td>
</tr>
<tr>
<td>Cellulose, regenerated</td>
<td>Additive list</td>
</tr>
<tr>
<td>Dextrin</td>
<td>Additive list</td>
</tr>
<tr>
<td>Glycerol and various derivatives</td>
<td>Additive list</td>
</tr>
<tr>
<td>Gelatin</td>
<td>Additive list</td>
</tr>
<tr>
<td>Hydroxyethyl starch</td>
<td>Additive list</td>
</tr>
<tr>
<td>Hydroxypropylstarch</td>
<td>Additive list</td>
</tr>
<tr>
<td>Lactic acid</td>
<td>Additive list</td>
</tr>
<tr>
<td>Lactic acid, butyl ester</td>
<td>Additive list</td>
</tr>
<tr>
<td>Pectin</td>
<td>Additive list</td>
</tr>
<tr>
<td>1,2-propylene glycolalgin</td>
<td>Additive list</td>
</tr>
<tr>
<td>Starch, edible</td>
<td>Additive list</td>
</tr>
<tr>
<td>Starch, hydrolysed</td>
<td>Additive list</td>
</tr>
<tr>
<td>Alginate</td>
<td>No classification2</td>
</tr>
<tr>
<td>Carrageenan</td>
<td>SCF list 1 and list 92</td>
</tr>
<tr>
<td>Cellulose acetate</td>
<td>SCF list 3, inert material,</td>
</tr>
<tr>
<td></td>
<td>modified natural cellulose2</td>
</tr>
<tr>
<td>Chitin, chitosan</td>
<td>No classification2</td>
</tr>
<tr>
<td>Gluten</td>
<td>No classification2</td>
</tr>
<tr>
<td>1,3-propylene glycolalgin</td>
<td>SCF list 82</td>
</tr>
<tr>
<td>Zein</td>
<td>SCF list 02</td>
</tr>
</tbody>
</table>

Soliman et al. (2007) studied various factors affecting the formation of bio-polymer films by measuring the physical (thickness and surface density), chemical (moisture content and water solubility), optical (light transmission and color), mechanical (tensile strength and elongation at break) and barrier (water vapour and oxygen permeability) properties.

The pH value for preparing soy protein film with good mechanical and barrier properties was 10. Cross-linking of soy protein film by adding formaldehyde or glutaraldehyde at different level into film forming solution improves the tensile and barrier properties of the obtained film. The optimum amount of formaldehyde gives good mechanical and barrier properties (0.3 mg/100ml). Soy proteins isolate (SPI) based films are prepared. Nano-structured calcium silicate (NCS) was used by Johnston et al. (2008) to adsorb Ag+ from solution down to the 1 mg kg⁻¹ level. The resulting NCS–Ag composite exhibited effective antimicrobial activity at desirably low levels of silver down to 10 mg kg⁻¹, and could be incorporated into food packaging as an antimicrobial agent. Titanium dioxide (TiO2) is widely used as a photo-catalytic disinfecting material for surface coatings. Kim et al. (2008) modified CNTs by introducing carboxylic acid groups on their surfaces in order to enhance their intermolecular interactions with the poly(ethylene-2,6-naphthalene) (PEN) matrix. CNTs, even in concentrations as low as 0.1 wt. %, greatly improve thermal stability as well as tensile strength and modulus of PEN. Chitosan triply-phosphate nanoparticle (C,N) were incorporated into hydroxypropyl methyl cellulose (HPMC) films and observed improvement in mechanical properties and water vapour barrier of films were observed (deMoura et al., 2009). Soy protein isolates (SPI) based films are environmentally friendly because of their biodegradability. Different ratios of plasticizer incorporated into SPI-based films helped to improve mechanical properties (Guerrero et al., 2010). Glycerol in the range of 30-40% has a plasticizing effect on the films. Apart from the plasticizer, the processing method employed to prepare films also influenced on the mechanical properties. Films processed by compression showed much better mechanical properties, higher tensile strength and elongation at break, than the ones processed by casting. It is concluded that the denaturation temperatures of the two main globulin fractions present in SPI were influenced by the moisture content of the sample but not by the processing method employed.

3.1 Biopolymer Formation

Soy protein isolates (SPI)/corn zein protein and WPI. Protein (5%, w/v) and glycerol (1.5%, w/v) heated in distilled water at 90°C for 15 min. Two to three pH levels of the solutions has been used. The temperature of the solution will be measured by a standard thermometer. The viscometer is used for
measuring the viscosity of biopolymer solution. Electronic balance will take the weight of solution. Chromameter is used for measuring the color of a biopolymer. The area of the film will be measured by taking length and breadth of the solution as well as the film. For measuring the thickness of film digital micrometer will be used (Kadam et al., 2013).

The fundamental repeating chemical units of the bio-based materials described so far are identical to those of a significant body of the conventional plastics. Thus in the broad sense, poly-34 saccharides possessing repeating acetal functionality can be regarded as the naturally occurring analogues of the synthetic polyacetal. Proteins (repeating peptide functionality) can be compared to the synthetic polyamides while polyactic acid is merely an example of the diverse group of polyesters. However, the gross physical and chemical properties of native biobased materials and their synthetic counterparts are quite different, and this is a feature of additional chemical functionality inherent in biobased materials. It should be expected that the following requisite processing and product development of biobased materials resulting properties should be equal or better than those of the conventional alternatives. However, such processing and product development is not always trivial and is unlikely to be cost-effective in all cases. The current applications of bio-based materials seek not to emulate the properties of conventional plastics but to capitalize on inherent biodegradability and other unique properties of these polymers. Bio-based plastic applications are currently targeted towards single-use, disposable, short-life packaging materials, service ware items, disposable non-wovens and coatings for paper and paperboard applications. However, the possible products made from bio-based resources cover a broader range. In general, the same shapes and types of food packaging can be made from synthetic and bio-based resources. The question is whether the same performance can be achieved by using the bio-based materials as with the synthetic ones.

Edible coatings and films comprise a unique category of packaging materials differing from other bio-based packaging materials and conventional packaging by being edible. Films and coatings differ in their mode of formation and application to foods. Edible coatings are applied and formed directly on the food product either by the addition of a liquid film-forming solution or molten compounds. They may be applied with a paint brush, by spraying, dipping or fluidising (Cuq et al., 1995). Edible coatings form an integral part of the food product, and hence should not impact on the sensory characteristics of the food (Guilbert et al., 1997). Edible films, on the other hand, are free standing structures formed and later applied to foods. They are formed by casting and drying film-forming solutions on a levelled surface, drying a film-forming solution on a drum drier, or using traditional plastic processing techniques, such as extrusion. Edible films and coatings may provide barriers towards moisture, oxygen (O₂), carbon dioxide (CO₂), aromas, lipids, etc., and carry food ingredients (e.g. antimicrobials, antioxidants, and flavour components), also improve the mechanical integrity or handling of the food product. Edible films and coatings may be used to separate different components in multi-component foods thereby improving the quality of the product (Krochta and De Mulder-Johnston, 1997). Starch and protein can be used as edible, biodegradable film and coating for packaging application (Pan and Caballero, 2011). The major processing routes and products are given in Table 3.

Table 3: Major Processing Routes to Potential Biobased Products

<table>
<thead>
<tr>
<th>Processing route</th>
<th>Product examples</th>
</tr>
</thead>
<tbody>
<tr>
<td>(Co-)Extruded film</td>
<td>Packaging film</td>
</tr>
<tr>
<td>Cast film</td>
<td>Packaging film</td>
</tr>
<tr>
<td>Thermoformed sheets</td>
<td>Trays, cups</td>
</tr>
<tr>
<td>Blown films</td>
<td>Packaging film</td>
</tr>
<tr>
<td>Injection (blow-)moulding</td>
<td>Salad pots, cutlery, drink</td>
</tr>
<tr>
<td></td>
<td>beakers, cups, plates, drinks</td>
</tr>
<tr>
<td>Fibres and non-wovens</td>
<td>Agricultural products, diapers,</td>
</tr>
<tr>
<td></td>
<td>feminine hygiene products,</td>
</tr>
<tr>
<td></td>
<td>certain medical plastics, clothing</td>
</tr>
</tbody>
</table>

These films protect fruit and nuts during export from physical damage, to reduce shrivelling of fruits. Layered double (LDHs) represent another interesting class of capable nano-filter for polymers (Fischer et al., 1999; Wei et al., 2004). LDH particle are constituted by magnesium aluminium hydroxide layers. In contrast to layered silicates the hydroxide layer display a positive surface charge that is counter balanced by anion located in domains between adjacent layers (Ray, 1998; Labajos et al., 1992). In Sandia Multinational Laboratory, Sandia has developed a sample preparation system, 2011 that enables reproducible deposition of cross-linked nano-particle film on a variety of substrate. Use of such sample preparation system is vital for developing mass-produced sensors from nanoparticle film and also for gathering statics on devices performance data collected for several nanoparticle film depositions demonstrate Sandia’s ability to vary the conduction of the organic molecule and thus the total conduction of the film by the judicious selection of Nano-particle, size, composition and the cross-linking ligand. By preparing the Nano particles films using a robot. This sample preparation system is
designed with the capability to measure the resistivity of the nanoparticle film after assembly of each layer.

Strawberries coated with dipping method, stored at 5±1°C and 70±5 % RH. The effectiveness of the coating treatment is evaluated in terms of weight loss, fungal growth and fruit decay, firmness, sensory qualities and microbial assay to determine extending shelf life. Coated samples have superior sensory acceptability in comparison with uncoated fruits, from which formulation containing 0.75% and 1% chitosan exhibited similar effect on the samples but higher than that of 0.5 %, conferred the great protective value with low concentration (Hazarika and Jana, 2012). According to Helbert et al. (2001) this reinforcing effect depends strongly on the formation of a cellulose micro-fibrils network within the matrix, resulting from hydrogen bonds that can be formed during the evaporation step.

Moisture barrier of polymers films has been observed to be improved by cellulose nano reinforcement (Paralikar et al., 2008; Sanchez-Garcia et al., 2008; Svagan et al., 2009). The thermal stability of polymers in nano-composites with cellulose whiskers was reported to be improved when compared to those of the corresponding bulk polymers (Helbert et al., 1996; Oksman et al., 2006).

De Moura et al. (2009) incorporated chitosan/tripolyphosphateno-particle (CsN) to hydroxyl propyl methyl cellulose (HPMC) films and observed improvement in mechanical properties and water vapour barrier of films. The water vapour permeability lowers if the particle of CsN is small.

4. Testing of Mechanical Properties of Nano-particle Films

The thermal and mechanical properties of the materials are both important for processing. Most bio-based polymer materials perform in a similar fashion to conventional polymers. This indicates that both polystyrene-like polymers (relatively stiff materials with intermediate service temperatures), polyethylene-like polymers (relatively flexible polymers with intermediate service temperatures) and PET-like materials (relatively stiff materials with higher service temperatures) can be found among the available bio-based polymers. The mechanical properties in terms of modulus and stiffness are not very different compared to conventional polymers. The modulus of bio-based materials ranges from 2500-3000 MPa and lowers for stiff polymers like thermoplastic starches to 50 MPa and lower for rubbery materials like medium chain poly-hydroxalkanoates. Furthermore, the modulus of most bio-based and petroleum-derived polymers can be tailored to meet the required mechanical properties by means of plasticizing, blending with other polymers or fillers, crosslinking or by the addition of fibres. A polymer like bacterial cellulose could, for instance, be used in materials that require special mechanical properties. In theory, bio-based materials can be made having similar strength to the ones we use today (Iguchi et al., 2000). Bio-polymer and composite mechanical test do include tensile, flexural, shear, compressive and more include peel, tear, poisson's ratio, bearing bypass, fracture toughness, ASTM testing for plastic and bio-polymers. Siripatrawan and Harte (2010) successfully prepared chitosan-based films incorporated with chitosan powder (deacetylation degree 95%) and glycerol plasticizer. They reported that the mechanical properties of the resulting film is not significantly different (P<0.05). However, both the addition of GTC at low concentration (0-5%) however, both TS and EBA significantly increase up to 16 % and 11% as compared to the unfortified control respectively, upon the incorporation of GTE from up to 20%. Siracusa et al. (2008) review that tensile test analysis are made to determine the tensile strength (MPa), the percent elongation at yield (%), the percent elongation at break (%) and elastic modulus (GPa) of the food polymer packaging material. These values are important to get mechanical information of the bio-materials to be compared with the commercial non-biodegradable ones (ASTM D 882-02, standard test methods for tensile properties of the thin plastic sheeting). Impact properties test is a method utilized to determine the energy that causes the plastic to fail under specific impact conditions conducting following the ASTM D1709-03 standard test methods for impact resistance of the plastic films by the free falling dart method. The compression test is normally conducted on thermoformed sample. According to ASTM D642 standard test method for determining the compressive resistance of shipping containers, components an unit loads the compression strength is function to the material land of design (shape and size). According to Daniels et al. (2004), the mechanical properties of biodegradable polymers and composites proposed for use in the internal fixation (in place of stainless steel) are crucial to the performance of the devices made from them for support of healing bone. Kohn (2004) studied the degradable polymers for medical application and the tensile properties (young’s modulus, tensile strength and elongation at yield and break) were determined by an instron stress-stress tester. The flexural storage modulus as a function of temperature was determined by dynamic mechanical analysis.

Van de Velde and Kiekens (2001) describe that flexural and tensile properties are mostly correlated and the tendencies found are probably the same as found when comparing flexural properties. Tensile properties
are clearly best for the densest reported polymers especially for PGA, PCL on the other hand, seems to be the weakest polymer with remarkable high strain at failure. It has to be remarked that molecular mass can play a very important role in the obtained mechanical properties. Varying the molecular mass from 50,000 over 150000 to 200000 will yield tensile strength for L-PLA (3) of 15.5, 80 and 150 MPa respectively.

Mechanical properties of biopolymer-based films as the consequence of adding plant extracts such as plasticizer or extract solvents used for plant extract, as well as film forming processing, such as adding extracts before or after thermal treatment of the film forming solution. A 2% sucrose (0.72 ± 0.11 MPa TS; 12.35 ± 3.17% EAB) and fructose (0.94 ± 0.09 MPa TS; 25.54 ± 3.28% EAB) addition result in a significant difference in TS and EAB of 4% RBP protein films (Shin et al., 2011), as compared to controls. Also, as raspberry extract solvent (lactic acids only) is able to significantly increase EBA by 39% of an SPI film (Wei et al., 2012). However, discussions regarding the impact of other variables on the outcome of the research are limited.

5. Contribution of Plant Extracts to Bioactive Properties of Dietary Biopolymer-Based Films

Incorporating plant extracts (such as antimicrobial agents) into starch or protein based edible films could create an antimicrobial packaging material (Campos et al., 2011). This can be used to inhibit or reduce the growth of pathogens and spoilage microorganisms in packaged foods and prolong shelf life and safety. Methods applied to evaluate antimicrobial activates, include disc diffusion testing and agar dilution assay. This can be used to evaluate with edible coatings enriched with natural oleoresins on selected microbial indicators (Ponce et al., 2008). Most recently, Campos et al. (2011) summarized antimicrobial activities found in edible films including soy protein films containing combinations of grape seed extract or green tea extracts and nisin, which could inhibit the growth of L. monocytogenes (Theivendran et al., 2006). Similarly, when GTE is added, SPI film exhibit promising antimicrobial activity against Streptococcus mutans (dental caries inducer) and Staphylococcus aureus (food pathogen) (Kim et al., 2006). The addition of GSE causes SPI films to exhibit bactericidal activity against food pathogens, such as L. monocytogenes, E. coli O157:H7 and S. Typhimurium. With the addition of 1% GSE, SPI films show reductions of L. Monocytogenes, E. coli and S. Typhimurium by 1.0, 0.1 and 0.2 log CFU/mL respectively (Sivarooban et al., 2008). The susceptibility of the native micro-flora of butternut squash to L. monocytogenes is analyzed by the in vitro agar diffusion assay using various film-forming solutions (chitosan, CMC, and casein) enriched with various oleoresins (olive, rosemary, onion, capsicum, cranberry, garlic, oreganum and oreganum + carvacrol 5%) (Ponce et al., 2008). Incorporating plant extracts (as antioxidant agents) into starch or protein based edible films could also create packaging with antioxidant-like properties (Gómez-Estaca et al., 2009b; Gómez-Guillén et al., 2007; Siripatrawan and Harte, 2010). Such a package can be used to inhibit or reduce oxidative degradation of the food inside. For example, it is found that the total phenolic content and free radical scavenging ability of chitosan films increased from 0-15% when GTE concentration increased from 0 to 20% (Siripatrawan and Harte, 2010). Other researchers reported that the incorporation of extracts from two ectotypes of murta leaves SG and SC are able to increase antioxidant capacity of tunfish gelatine film by 5-fold based on the ferric reducing antioxidant power (FRAP) assay (Gómez--Guillén et al., 2007). Adding oregano or rosemary extracts significantly increase antioxidant (Gómez-Estaca, 2009b) capacity of either the bovine-hide or the tunaskin gelatin films (Gómez-Estaca, 2009b). The incorporation of the borage extract into the films result into bothsole (Solea spp.) skin gelatin and commercial catfish skin gelatine films having higher antioxidant properties than those of films incorporated with alpha-tocopherol and butylated hydroxytoluene (BHT). This is shown by total phenolics, reducing ability by the FRAP assay, radical scavenging capacity by the ABTS assay, iron (II) chelation activity (Gómez-Estaca et al., 2009a).

6. Conclusions

Biological derived polymers might be used for the production of all types of packaging (trays, cups, bottles, films, etc.) using the same equipment and technology used for conventional materials. However, these materials have to be well performing in order to compete with the highly developed and sophisticated materials used today. Comparing the properties of bio-based polymeric materials with the conventional synthetic petroleum-derived polymers shows a major potential of these polymers for the production of well-performing food packaging. However, when using proteins or polysaccharides in the materials, their sensitivity towards relative humidity must overcome. The bio-based materials have an inherent potential of being compostable which may help the commercialization of these materials. Similar to the synthetic materials used today it will be necessary to use several polymeric materials in multi-layers or
composites, tailoring the properties of the packaging to meet the demands of specific foodstuffs. In general, the more diverse side chains and functional groups of bio-based polymers, compared to conventional plastics derived from mineral oil gives the resin and material manufacturer unique possibilities to tailor the properties of the finished package. This advantage should be used further to produce materials with even better properties than the ones we know today. Biopolymers fulfil the environmental concerns but they show some limitations in terms of performance like thermal resistance, barrier and mechanical properties, associated with the costs.

References


Gautam and Kumar... Nano-particle Embedded Biodegradable Polymers for Packaging of Fruits and Vegetable


