

Development of Protein Based Films with Nanoparticle as Strengthening Material for Biodegradable Packaging - A Review

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Abstract — The aim of this review is to reveal the most appropriate biopolymers are available for new research, which can be used and may have been great potential application in food and processing industries/sectors. Most of works that we categorised in to four sections, namely: soy protein Isolate films, whey protein Isolate films, characterization of films and antimicrobial properties of film.

Keywords — Soy Protein Isolates, Whey Protein Isolate, TiO₂, Biopolymeric and Packaging Films

I. INTRODUCTION

Fruits and vegetable are perishable in nature because of high water content. Different types of techniques are applied for packaging and storage of fruits and vegetables. 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 banned use of petrochemical based non-degradable plastics. The necessity of the day is therefore to develop bio-degradable films, coatings and bio-composite materials for the purpose. Bio-plastics development is just beginning; until now it covered approximately 5-10% of the current plastic market, about 50,000 ton in Europe (Anonymous 2004). The European countries with the highest utilization of bio-plastics are France, Germany, England, Netherland and Italy. In India it is yet to be introduced, the principal field of use of packaging films for food products are loose film used for transport packaging, service packaging like carry bags, cups, plates and cutlery, bio-waste bags, in agri- and horticultural fields like bags and compostable articles.

In past two decades, the use and production of plastic (non-biodegradable) in the world have been tremendously increased (Avella *et al.*, 2005). Plastic production has increased from 0.5 to 260 million tons per year since 1950. Forty percent of plastics produced every year is discarded into landfill. Every year, more than 500 billion plastic bags are distributed and less than 3% bags are recycled. They are typically made of polyethylene and can take up to 1000 years to degrade in landfills that emit harmful greenhouse gases (Heap, 2009). The solution to protect the environment from plastics may be bio-degradable polymers. The term “bio-degradable” material is used to describe those materials which can be degraded by the enzyme action of living organisms, such as bacteria, yeast,

fungi and the ultimate product of the degradation process, being CO₂, H₂O and bio-mass under aerobic conditions and hydrocarbons, methane and biomass under anaerobic conditions (Kuorwel *et al.*, 2011).

Development of a new type of bio-packaging materials to replace petroleum-based non-biodegradable plastics has become a growing field of interest since synthetic plastics lead to serious environmental concerns as a result of their non-biodegradability and depletion of natural resources. The packaging requirements of biological systems, including foodstuffs, are more diverse and complex than those for other products. In recent years, edible films and coating materials are being increasingly used for food packaging to improve the food quality by serving as mass transfer barriers between food components and the surrounding environment (Ashley, 1994; Cha and Chinnan, 2004). Food package should protect the products against physical hazards and environmental elements such as water vapour, gases, and odours; a combination of structural design and material selection should meet the requirements. An adequate selection of packaging materials can prevent food quality loss by providing barrier, or otherwise protective features (Campos *et al.*, 2011), and enhancing food quality and shelf life (Gennadios, 2002).

Nanotechnology provides a potential optimistic approach to deal with this growing environmental concern. The technique provides a way not only to incorporate the active agent in the structure of the existing materials, but also to develop novel biodegradable packaging films, composites using agricultural and food industries waste. Nanotechnology involves the characterization fabrication and/or manipulation of structures, devices or materials that have at least one dimension or contains component with at least one dimension that is approximately 1-1000nm in the length (Duncun, 2011). The applicability of polymer nanotechnology and nano composites to emerging biomedical/biotechnological applications is a rapidly emerging area of development. One area of intense research involves electro spinning for producing bio-resorbable nanofibers scaffolds for tissue engineering applications. This might be construed as a nano composite as the resultant scaffold allows for cell growth yielding a unique composite system. Another area also involving nanofibers is the utilization of electrically conducting nanofibers based on conjugated polymers for regeneration of nerve growth in a biological living system.

Titanium dioxide (TiO₂) can provide protection against food borne micro-organisms as well as odour, staining,

deterioration, and allergens in the presence of relatively low wavelength radiation near the ultraviolet region. However, TiO_2 particle easily aggregate and thus deteriorate the properties of the film. In addition, the direct contact between TiO_2 and the polymer matrix may lead to rapid degradation of polymer films themselves (Kadam *et al.*, 2013). The Titanium dioxide (TiO_2), due to the advantages of high chemical stability, high photo catalytic activity, relative low cost and non-toxicity, is one of the most important photo active reagents which is widely used for degradation (Ali *et al.*, 2011). The addition of nano-reinforcements has been related to improvement in overall performance of biopolymers, enhancing their mechanical, thermal and barrier properties, usually even at very low contents. Thus nano-particles have an important role to improve feasibility of use of biopolymers for food packaging (Azeredo, 2009)

Whey protein isolate (WPI), which is an abundant by-products in the cheese industry, is a biopolymer that has received much attention for use as a potential edible or biodegradable food packaging material because it has been shown to produce transparent films and coatings that can act as an excellent oxygen barrier properties (Sothornvit and Krochta 2000, Sothornvit and Krochta 2005). The ability of WPI-based edible films to act as barriers to solute and gas and enhance food quality and shelf-life has been previously demonstrated (Krochta and De Mulder-Johnston, 1997; Pe' rez-Gago and Krochta, 2002). However, these films do not have good mechanical and water vapor barrier properties because they are intrinsically hydrophilic (Krochta & De Mulder-Johnston, 1997). As a result of this property, they cannot be used for wide spread applications in the food industry.

Soy protein isolate (SPI) has been regarded as a viable alternative to the petroleum polymers in the manufacture of adhesives, plastics, and packaging materials (Lu *et al.*, 2004; Mohanty *et al.*, 2005; Liu *et al.*, 2010). Soy protein is the major co-product of soybean oil and is readily available and renewable. The commercial raw material of soy protein is soy protein isolate (SPI) with more than 90% protein and 18 diverse amino acids. Usually, the poor mechanical performance as well as the water sensitivity of soy protein materials limits their applications (Tian *et al.*, 2009).

Films produced with biopolymers from renewable sources have the ability to carry active compounds (Muñoz-Bonilla and Fernández- García, 2012); thus, they can be used as active packaging for food.

Active packages may contain substances that interact with the packaged product (Pereira-de-Abreu, Cruz, and Paseiro-Losada, 2012; Suppakul, Miltz, Sonneveld, and Bigger, 2003) such as antioxidants. In active packages, the active compounds may be incorporated into the films rather than directly adding the compounds to foods, providing functional effects at the food surface (Coma, 2008), which is where the oxidation process is mostly found.

Bioactive packaging materials need to be able to keep bioactive compounds, such as prebiotics, probiotics, encapsulated vitamins or bioavailable flavonoids, in

optimum condition until they are released in a controllable manner into the food product (Brody, 2005; Guerra, and N P, 2005 and Lopez-Rubio, 2006)) Bioactive-packaging materials can help to control oxidation of food stuffs and to prevent the formation of off-flavors and undesirable textures of food. Bioactive compounds that are encapsulated into the packaging itself are a promising approach because this would allow the release of the active compounds in a controllable manner.

Improvement in technologies for preservation of food from microbial spoilage is essential to ensure food safety and quality. The functional ingredients commonly used in packages for antioxidant and antimicrobial purposes are certain organic compounds (butylatedhydroxytoluene, nisin, benzoate, organic acids, and enzymes). These active packaging materials have been shown to suppress oxidation in model systems of meat or oil products, as well as to inhibit microbial growth in food products. The use of nisin as a surface coating material on packaging film can inhibit bacterial growth and extend shelf-life of foods. Polylactic acid (PLA) is another growing alternative as a green food-packaging material. Researchers have demonstrated the effectiveness of antimicrobial PLA film/coating to inhibit/control pathogens in juices, liquid egg, and milk. Chitosan is a well-known film-forming biopolymer. It has shown antimicrobial activities against different groups of microorganisms. Chitosan films and coatings have been applied as a microbial hurdle in a variety of fruits and vegetables, such as strawberries, longan, litchi, peaches, lettuces, cucumbers, bell peppers, and tomatoes. Whey protein isolates has also been successfully employed as a raw material for preparation of biodegradable polymers. Its film forming and barrier properties are comparable to petro-based products. However, low tensile strength and high water vapour permeability are considered as weaknesses of the films made of whey protein. (Heneriette *et al.* 2010).

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 (nano particle) 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 agents, such as sorbic acid, p-amino benzoic acid (Cagri *et al.*, 2001), and lysozyme is needed 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 catalyzes the oxidation of H_2O and O_2 to generate free hydroxyl and

oxygen radicals that can effectively kill microorganisms. When TiO₂ is incorporated into a polymer matrix such as packaging material, it will provide protection against foodborne microorganisms as well as odor, 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, TiO₂ particles easily aggregate and thus deteriorate the properties of the film (Zhou *et al.*, 2009). Besides, the direct contact between TiO₂ and the polymer matrix may lead to quick degradation of the polymer films themselves. To maintain the integrity of the polymer film, the TiO₂ nanoparticles need to be sealed inside shells to prevent direct contact between the TiO₂ and the polymer molecules. To maintain the functionality of the TiO₂ particles, which relies on the exchange of free radicals generated by photoreaction on the TiO₂ surface and the surrounding environment, the shells must be porous to allow fast in/out diffusion of free radicals.

Thus biopolymers fulfil the environment concerns but they show some limitations in terms of performance like thermal resistance, barrier and mechanical properties, associated with costs. Moreover, this kind of packaging materials needs more research in the form of value addition like the introduction of smart and intelligent molecules (Valentina *et al.* 2008).

II. PROTEINS

There are different proteins are available, some of them are described as below and whey and soy protein have been taken for experiments.

Collagen

Collagen is the primary protein component of animal connective tissues. It contains many types of collagen (over twenty types). Collagen is composed of different polypeptides, which contain mostly glycine, proline, hydroxyproline and lysine. Some differences in amino acid composition are apparent across collagens derived from different sources. There are certain features that are common to and uniquely characteristic of all collagens (Karim and Bhat, 2009) (Vroman and Tighzert, 2009).

Gelatin

Gelatin is a protein obtained by hydrolyzing the collagen contained in bones and skin (Gómez-Guillén *et al.*, 2009). Gelatin obtained from mammalian sources (porcine and bovine), is the most important and most used (Karim and Bhat, 2009). His structure is determined by the properties of collagen from which gelatin is obtained (Staroszczyk *et al.*, 2012). In the last years, in the food industry, the number of new applications for gelatine has increased. The new applications found for gelatin in food products are very diverse, from emulsifiers and foaming agents to stabilizers, and biodegradable films. All this applications are given by the growing demand to replace synthetic agents with natural and biodegradable ones (Gómez-Guillén *et al.*, 2011).

Soy protein

Soy protein has been used since the 19th in a variety of foods. The main characteristics of soy proteins that are

useful in food industry are emulsification and texturizing (Vroman and Tighzert, 2009). Soy protein exists as soy flour (SF) which requires less purification, soy protein isolate (SPI) and soy protein concentrate (SPC). Chemically, SPI contains 90% proteins and 4% carbohydrates, SPC contains 70% proteins and 18% carbohydrates, SF contains about 52% proteins and 32% carbohydrates. SF is the least expensive variety of these three forms (Giancone *et al.*, 2009). Soy protein can be used in the manufacture of adhesives, plastics, and packaging materials and can be a good alternative to the petroleum polymers (Tian *et al.*, 2011).

Whey protein

Whey proteins are a by-product from the cheese industry, and consist of whey protein isolates (WPI) which represent the purer form of such proteins. Another form of whey proteins are whey protein concentrate (WPC) (Ramos *et al.*, 2012). Whey proteins are capable to form elastic films (Wang *et al.*, 2013), and they have been employed as raw material for biodegradable packaging because they have good oxygen barrier and moderate moisture permeability (Ramos *et al.*, 2012) (Popović *et al.*, 2012).

Zein

Zein, is the major storage protein of corn (*Zea mays L.*) and is a naturally occurring protein polymer obtained as a product of industrial corn processing that has been used to develop various types of thermoplastic products (Biswas *et al.*, 2006) (Del Nobile *et al.*, 2008) (Reddy and Yang, 2011). The high content of non-polar amino acids gives corn zein a relatively hydrophobic nature and this feature lead to obtaining excellent barrier tooxygen but instead lead to poor mechanical properties (Ozcalik and Tihminlioglu, 2013)

2.1 Soy protein Isolate and their characterization

Soy protein isolate (SPI) has been regarded as a viable alternative to the petroleum polymers in the manufacture of adhesives, plastics, and packaging materials (Lu *et al.* 2004, Mohanty *et al.* 2005 and Liu *et al.* 2010). Soy protein a major co-product of soybean oil and was readily available and renewable. The commercial raw material of soy protein named as soy protein isolate (SPI) with more than 90% protein and 18 diverse amino acids. Usually, the poor mechanical performance as well as the water sensitivity of soy protein materials was observed and found limited their applications (Tian *et al.*, 2009). Soy protein could be used in the manufacturing of adhesive, plastic and packaging material and could be a good alternative to the petroleum polymers (Tian *et al.*, 2011).

Pierre *et al.* (1995) developed TiO₂ (titanium dioxide) polymer nanocomposite by sol-gel. Sol-gel processes make it possible to develop new hybrid electrolyte materials of the type ceramic polymer, known as Nano crystallite-Insetion-Material (NCIM). TiO₂ polyethylene oxide hybrid materials were synthesized from TiCl₄ and from Ti ethoxide. Their structure was analysed in relation with the processing parameters. A primary evaluation of the nano-scale composite material for reversible Li insertion was performed. Hybrid PEO-TiO₂ material with a range of structures from completely x-rays amorphous

and SEM homogeneous to completely phase separated were synthesized. This could be achieved by controlling the hydrolysis process and the nature of the precursor. Nanoscale TiO₂ gel PEO composites were obtained by hydrolysis with excess water.

Kunte *et al* (1997) prepared films from soy protein isolate and fractions by casting method. The glycerol-plasticised soy protein films were cast from alkaline aqueous film-forming solution of laboratory-prepared 7S,11S soy isolate fraction and from commercial soy isolate (CSI). Tensile strength (TS), elongation at break (E), water vapour, water vapour permeability (WVP), total soluble matter (TSM), protein solubility (PS), and Hunter L, a and b color values were determined. The 11S films had greater TS than 7S films ($p < 0.05$), while LSI films had greater TS than CSI films ($P < 0.05$). No significant differences were detected among mean E values and among mean WVP values of all films ($p > 0.05$). The 7S films had higher TSM and PS values than 11S films ($p < 0.05$), CSI films were significantly darker (Lower L value) and more yellow (greater positive b value) than LSI films ($p < 0.05$).

Zhong and Sun (2001) investigated blend of soy protein isolate with 10, 20, 30, 40 and 50 percent polycaprolactone (SPI/PCL) alone or with addition of 0.5, 1.0, 2.0 and 5.0 percent methyl di-phenyl di-isocyanate (MDI). Thermal, mechanical properties and water absorption of the blend were studied. It was reported that the glass transition temp (T_g) of SPI was found to decrease with increasing PCL contents in the blend containing 2% wt MDI. For 50/50 (SPI/PCL) blends, the T_g of SPI decreased with increases in MDI content. Both DSC and DMA results showed that compatibility between SPI and PCL improved with the addition of MDI. Mechanical properties of the 50/50 (SPI/PCL) blends increased with increasing MDI concentrations. Water resistance of the blends was improved significantly by increasing PCL concentration and incorporating MDI.

Liyange *et al* (2002) studied preparation and characterization of edible soy protein isolate of edible soy protein film. Soybean had more protein (about 38-44%) than the protein content (8-15%) of cereals grains. Water was used as the solvent to make casting solutions and glycerol was used as the plasticiser. The pH of the casting solution was adjusted by adding 2M HCL. Similar to other gain protein film, the properties of the soy protein isolate film largely depend on the relative humidity of environment. Tensile strength of soy protein films was found to be comparable with those of conventional packaging materials such as low density polyethelene. Moisture absorption isotherms were found to be similar in behaviour to other protein such as zein, wheat and gluten etc.

Xiaoqun and Xiuzhi (2002) studied plasticization of soy protein polymer by polyol-based plasticisers. Soy protein isolate (SPI) was mixed with four polyol-based plasticizers and molded into plastics using a hot press. Thermal properties of the SPI plastics with propylene glycol were depressed to the largest degree and the plastics with glycerol showed the largest strain at break whereas

plastics with 1, 3-butanediol gave the highest tensile strength. The morphology of the fractured surfaced of the SPI plastics changed from brittle fracture for the unplasticized SPI to ductile fracture for the plasticized SPI. Water absorption of all the plastics was lower than that of the unplasticized SPI plastics.

Avella *et al* (2005) studied biodegradable starch /clay nano-composite films for food packaging applications. Structural and mechanical characterization on the nano-composite films was performed. The result showed that in case of starch/clay material, a good intercalation of the polymeric phase into clay interlayer galleries, together with an increase of mechanical parameters, such as modulus and tensile strength. Finally the conformity of samples with actual regulation and European directives on bio-degradable materials was assessed and demonstrating that these materials could be utilised in the food packaging sector owing to their low overall migration limits.

Cao *et al* (2007) studied the preparation and physical properties of soy protein isolate and gelatin composite films. Mechanical swelling and optic properties of composite film prepared from soy protein isolate (SPI) and gelatine were investigated. With increasing gelatin ratio in composite films, TS, elongation at break (E), elastic modulus (EM) and swelling properties of gelatin composite films increased. The film was more transparent and easier to handle. When the ratio of SPI : gelatine was 4:6:2:8, the TS, EB and other properties of composite films approached those of gelatine film and were better than those of SPI films. The composite film was more economized than the gelatine film, so it could be used as edible film instead of gelatine film for packaging. When the ratio of gelatine was 4:6, adding 0.1g glycerine/g protein the films appeared transparent and could be easily handled. The TS, EB, and EM of the film were 33.65MPa, 3.19 percent, 1540.61MPa. At this ratio, increase of concentration of glycerine and NaCl, EB and water content of composite films increased, while TS, EM decreased. The appropriate amount of glycerine for the SPI/gelatin composite films was 0.1-0.2g glycerine /g protein, which could break the brittleness of film, improve flexibility and toughness. When the pH of SPI film – forming solution was 8-9, the properties of composite films were better. Thermal treatment (50-90°C) of SPI film forming solution could produce excellent mechanical and homogeneous film.

Nakayami and Hayashi (2007) studied the preparation and characterization of the poly (L-lactic acid)/ TiO₂ nano particle nano-composite films, with high transparency and efficient photo degradability. In the process of preparing nano composite films severe aggregation of TiO₂ nanoparticles could be reduced by surface modification using carboxylic acid and long chain alkayl amine. As a result nanocomposite films with high transparency, similar to pure PLA films were obtained without depending on the amount of added TiO₂ nano particles. ATEM micrograph of the nanocomposite films suggested that the TiO₂ nanoparticles of 3-6nm in diameter were uniformly dispersed in polymer matrices, photo degradation of PLA-TiO₂ nanoparticle nano-composite films was also

investigated. The results showed that nano-composite films could be efficiently photo degraded by UV irradiation in comparison with pure PLA.

Rhim *et al* (2007) studied the mechanical and barrier properties of biodegradable soy protein isolate based film coated with polyactic acid (PLA). TS of SPI films increased from 2.870 upto the 17.472 MPa depending on the PLA concentration of coating solution without sacrificing the film's extensibility. In contrast, the extensibility of SPI films coated with solution more than 2 g PLA/100 ml solvent caused increased WVP of PLA coating solution. Water resistance of SPI films was greatly improved as demonstrated by dramatic decrease. Mechanical and water vapour properties of PLA coated SPI films were greatly improved up to the levels of LDPE and cellulose acetate films respectively.

Soliman *et al* (2007) studied soy protein isolate (SPI) based film and various factors affecting the formation of these film by measuring the physical (thickness and surface density), chemical (moisture content and water solubility), optical (light transmission and color), mechanical (tensile and elongation at break) and barrier (water vapour and oxygen permeability) properties. The pH value for preparing soy protein film was adjusted by adding formaldehyde or glutaraldehyde at different level into film forming solution improving the tensile and barrier properties of the obtained films. The appropriate amount of formaldehyde (0.3mg/100 ml) gave good mechanical and barrier properties.

Yen *et al* (2007) investigated the effect of processing parameters including amount of microbial transglutaminase (MTgase), the pH of film forming solution, air drying temperature as well as pre incubation on the properties of MTgase-treated soy protein isolate (SPI) films. The treatment with low concentration of MTgase (4-10 units per gram of SPI, $U\ g^{-1}$) significantly increased the tensile strength (TS) values of SPI films, while high concentration of MTgase (over $20\ U\ g^{-1}$) resulted in significantly decrease in the TS values ($p \leq 0.05$). The elongation at break (EB) values of MTgase-treated SPI films were significantly higher than that at pH 7.0 ($p \leq 0.05$). The TS, EB and contact angle values significantly decreased with increasing the air drying temperature from 18 to $50^{\circ}C$ ($PN\ 0.05$). The properties of MTgase-treated films were also affected by the additional pre-incubation of film-forming solution with MTgase before casting.

Bourtoom (2008) studied the properties of biodegradable blend from rich starch-chitosan with different plasticizers. Three plasticizers comprised sorbitol (SOR), glycerol (GLY) and polyethylene glycol having concentration range from 20 to 60%. Increasing concentration of these plasticizers resulted in decrease in tensile strength, increase in elongation at break (E), water vapour permeability (WVP), and film solubility (FS). SOR plasticized films were most brittle, with the highest tensile strength (TS, 26.06 MPa). The color of biodegradable blend films from rice starch-chitosan was more affected by the concentration of plasticizer used than by its type. Nine moisture sorption models were applied to experimental data. Moisture content of the film resulted in increased

and elevated water activity. The time to reach equilibrium moisture content (EMC) was about 20-24 days at lower humidity and 13-16 days at higher humidities.

Johnson *et al* (2008) prepared soy proteins Isolate (SPI) based film. Nano-structured calcium silicate (NSS) was used to absorb Ag^{+} from solution down to the $1\ mg\ kg/1$ level. The results showed that NCS-Ag composite exhibit effective antimicrobial activity at desirably low level of silver down to $10\ mg\ kg^{-1}$ and could be incorporated into food packaging as an antimicrobial agent. Titanium dioxide (TiO_2) is widely used as photo-catalytic disinfecting material for surface coatings

Lee *et al* (2008) prepared characterization of protein coated polypropylene as novel composite structure for active food packaging, application. Plasticized protein coatings on polypropylene (PP) films were prepared and examined for their optical and tensile properties as affected by protein and plasticizer types in order to exploit a novel composite film for the food packaging applications. Protein as well as plasticizers exerted a noticeable effect on colour of the coated films. Whey Protein Isolate coated films also showed greater transparency and tensile strength than the other coated films. Nisin incorporated WPI coating on PP films exhibits significant bacterial growth inhibition against lactobacillus plant arum. The results suggested that WVI coatings with a proper plasticizer process excellent visual and mechanical characterization and had great potential for application in food packaging.

Sivarooaban *et al* (2008) evaluated the physical and antimicrobial properties of soy protein isolate (SPI) films containing grape seed extract (GSE 1 percent w/w), nisin (10,000 IU/g), ethylenediamine tetra acetic acid (EDTA 0.16% w/w), and their combinations. The incorporation of GSE significantly increased the thickness, puncture, and tensile strengths compared to control film. The SPI film containing combinations of GSE, nisin, and EDTA had a thickness of 61.81 μm and demonstrated 3.3 N puncture strength while the control film had 33.0 μm thicknesses and 2.5 N puncture strength. Furthermore, the darkness of the film increased in the presence of GSE as indicated by the lower L^* (Lightness) values. The SPI film incorporated with the combined GSE, nisin, and EDTA demonstrated the greatest inhibitory activity against *Listeria monocytogenes*. The results showed that the SPI film containing GSE 1 percent, nisin 10,000 IU/g, and EDTA 0.16 percent was able to reduce *Listeria monocytogenes* populations by 2.9 log CFU/ml, while the population of *Escherichia coli* O157:H7 and *Salmonella typhimurium* were reduced by 1.8 and 0.6 log CFU/ml, respectively. This finding has great applications to maintain shelf life, and improve safety of ready-to-eat food products.

Zhong and Xia (2008) determined the physio-chemical properties of edible and preservatives films from chitosan/Cassava, cassava starch and gelatine plasticised with glycerol. Edible films from chitosan, cassava starch, and gelatin plasticized with glycerol have been developed by casting methods, and effect of cassava starch (50,100, and 150 g per 100 g of chitosan) glycerol (21,42 and 63 g

per 100g of chitosan) from the film solution of various properties of chitosans based films were studied using response surface methodology (RSM). The possible interaction between the major components were evaluated by x-rays diffraction (XRD) and Fourier transforms infrared spectroscopy (FTIR). The introduction of gelatine and gelatinised cassava starch suppressed the semi crystalline peak of chitosan films.

Goh *et al* (2009) investigated edible soy protein isolate (SPI) based film prepared using hot film forming solutions containing SPI, glycerol and either glucose or sucrose. As a result of the Maillard reaction SPI/ glucose films were darker, higher in tensile strength, lower in water vapour transmission rate, oxygen gas transmission rate, and solubility in disruptive solvents (sodium dodecyl sulphate protective effects on fish oil oxidation during storage. Result indicated a higher oxidative stability of oil covered with SPI/ glucose films. This protection was attributed mainly to additional protein cross-linking with in SPI/glucose films that had affected their physical properties and to a lesser extent on the oxygen scavenging activities of maillard products within the films.

Lu *et al* (2009) studied that the structure and characterization of starch and some synthetic degradable polymers were briefly introduced. Then preparation of SCBP via physical blending and chemical modification was reviewed and discussed. Finally it was concluded that different physical and chemical approaches were effective to develop starch based completely biodegradable polymers of appropriate biocompatibility, degradation rate and physical properties for various applications and their development was a good solution for reducing the consumption of petroleum resources and environmental problem.

Qing *et al* (2009) developed soy protein isolate (SPI) edible film that could be used as food refreshing materials. The SPI edible films modified by different concentrations of glycerol and oleic acid (OA) were prepared. The film-forming dispersions were characterized in terms of group changes by FT-IR analysis. The appearance, tension strength (TS), WVP, optical properties, peroxide values (POV) and contact angle of different films were evaluated. The addition of OA promoted changes in the arrangement of groups on the surfaces of film-forming dispersion (FFD) particle. Microstructure analysis indicated that the OA-treated SPI films had rougher surface. The addition of OA caused a decrease in TS and WVP. The mechanical and optical properties of the films were closely related with their microstructure. In addition, both pH value and temperature had direct effects on the film forming feature of FFD.

Kaur and Gautam (2010) studied on the synthesis and characterization of soy protein grafted polyethylene modification of polyethylene (PE) through graft copolymerization of naturally occurring biodegradable polymer, soy protein into PE. Maximum grafting percentage (115 percent) was obtained at $(BPO) = 2.15 \times 10^{-2}$ mol/ L in 40ml of water at 70°C within 150 minutes. Physical characterization of pristine PE and PE grafted with soy protein was carried out by infrared (IR)

spectroscopy, thermo gravimetric analysis (TGA) and scanning electron microscopy (SEM). Swelling behaviour in binary and ternary solvent system comprising of water, ethanol and water, ethanol, dimethyl sulphoxide respectively of PE grafted with soy protein was compared to the respective data of pristine PE. The thermal and swelling behaviour of grafted PE showed much improvement over that of pristine PE.

Chao *et al* (2010) prepared an edible oxygen barrier film pouch which was fabricated from a heat sealable corn zien (CZ) layer laminated on soy protein isolate (SPI) film to pack olive oil condiments for use with instant noodles. The mechanical, barrier, and physical properties of the CZ/SPI bilayer films were investigated and the oxidative stability of olive oil in the pouches was measured during storage under dry and intermediate relative humidity conditions. SPI film lamination with an additional layer of the CZ film increased tensile strength and water barrier properties, while it had a lower elongation at break and decreased oxygen barrier properties. The oxygen permeability of CZ/SPI film was lower than that of nylon-metalocene catalysed linear low-density polyethylene film. The CZ/SPI bilayer film generated were heat sealable at 120-130°C and produced a seal strength greater than 300N/m. The higher oxygen barrier property of the CZ/SPI bilayer films resulted in reduced oxidative rancidity of olive oil packaged in the CZ/SPI film when compared to olive packaged in nylon-etalocene /linear low density ethylene (NY/m LLDPE) films.

Emamifar *et al* (2010) developed nano-composite LDPE films containing Ag and ZNO nano-particles by melt mixing in a twin-screw extruder. Microbial stability, ascorbic acid (AA) content, browning index, color value, and sensory attributes were evaluated after 7, 28, and 56 days of storage. The results showed that such packages the limited the microbial shelf life (6 log cfu/ml) up to 28 days. Packages containing nano-silver increased shelf life of fresh juice although parts of its sensory attributes were lost.

Guerrero *et al* (2010) studied soy protein isolate (SPI) based films that are environmentally friendly because of their biodegradability. Different ratios of plasticizer were incorporated into SPI-based films to improve mechanical properties. Glycerol had a plasticizing effect on the films in the range of 30-40 percent. Moreover, 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 was concluded that the denaturation temperature of the two main globulin fractions present in SPI were influenced by the moisture content of the sample but not with the processing method employed.

Kokoszka *et al* (2010) determined the effect of protein and glycerol contents on physio-chemical properties soy protein isolate based edible films casted from heated (70°C for 20 min) alkaline (pH 10) aqueous solution of SPI a 6,7, 8 and 9 (w/w percent) glycerol (50 percent w/w percent) and SPI 7at (w/w percent), glycerol (40,60,70 percent of w/w of SPI). WVP was measured at 25°C and four

relative humidities (30-100 percent, 30-84 percent, 30-75 percent and 30-53 percent. Varying the proportion of SPI and GLY had an effect on water vapour permeability, wetting and thermal properties of SPI films. A synergistic effect on glycerol and protein was observed on the WVP. Glycerol and RH gradient strongly enhanced the moisture absorption rates and permeability of SPI based films. SPI content weakly increased the WVP and did not modify the surface properties. The temperature of denaturation of soy protein decreased glycerol content except for the higher concentration whereas it increased with protein ratios

Gonzalez *et al* (2011) developed bio-degradable film by modifying soy protein isolate (SPI) with different amounts of naturally occurring cross-linking agent (genipin, Gen) with glycerol as plasticiser. The films yield were cast from heated and alkaline aqueous solution of SPI, glycerol and Gen and then dried in an oven. Total soluble matter, WVP and mechanical properties were improved by adding small amount of Gen. These properties were not significantly affected ($p \geq 0.05$) by additions exceeding 205% (w/w of SPI). The opacity and cross linking degree were linearly increased with the addition of Gen, where as the swelling ratios in water were decreased. All the films were submitted to degradation under indoor soil burial conditions and the weight loss of films was measured at different times. This study revealed that the film biodegradation time could be controlled or modified from at least 14 to 33 days. The tests performed showed the potential of Gen to improve the SPI film properties.

Kaleel *et al* (2011) studied on thermal and mechanical properties of polyethylene/doped-TiO₂ nano-composite synthesized in situ- polymerization. Ethylene polymerization was carried out using highly active metallocene catalysts in combination with methyl aluminoxane. Titanium dioxide containing 1percent Manganese (Mn) as dopant was used as nano-fillers. The thermal properties were analysed using differential scanning calorimetry (DSC) and thermo gravimetric analysis (TGA). The ash content was also analysed for each nano-composites and found to be in line with the activity of the catalyst. There was a significant increased in mechanical properties of the polyethylene by addition of filler

Nayak *et al* (2011) studied that synthesis and characterization of soy protein isolate/MMT nano-composite film for the control release of drug of loxacin. Nano composite were prepared by blending soy protein isolate with different percentage of MMT by melt extrusion techniques. The nano-composite was characterized by using XRD, TEM, SEM, and TGA methods. The XRD studies indicated that absence of diffraction peak for bio-nano-composites. From TEM studies it was ascertained that the degree of exfoliation increased with increase in MMT content. The morphology of the nano-composite was ascertained from the SEM studies. The degradation pattern of the nano-composites was evaluated from the TG analysis. The drug delivery system of the nano-composite was investigated by blending the nano-composite with ofloxacin at different pH media. The various kinetics parameters were evaluated

and the mechanism of drug delivery has been postulated based on the kinetics of data.

Tian *et al* (2011) prepared a series of soy protein isolate/agar blend films containing 33% glycerol as plasticizer by solution casting and thermo-moulding methods. The micro-structure and mechanical properties of the blend films were evaluated in relation to the agar/protein ratio as well as the processing methods.. The casting films possessed more homogeneous interfaces compared with the molding films, leading to the superior mechanical properties than those molding films. Owing to the rigid 3-dimensional network formed by the agar, the tensile strength of casting blend films was enhanced. With the increase of agar in the casting blend films, the cross-linking density increased and was responsible for the variations in tensile strength. Microstructure and mechanical properties of soy protein/agar blend films has been affected by composition and processing methods.

Liorens *et al* (2012) studied the biocide capacity of TiO₂ nano composites with typical packaging materials. EVOH (copolymer of ethylene and vinyl alcohol) and TiO₂ nano materials with 2-5 percent TiO₂ were acceptably well dispersed and adhered and mechanical properties were enhanced. They were efficient against gram positive and gram negative micro-organisms and kept self sterility.

Olad *et al* (2012) prepared polyaniline/ TiO₂(PANI TiO₂) nano-composite with core shell structure as photo catalyst, Titanium dioxide nano-particle with an average crystal size 21nm were encapsulated by PANI via the in situ polymerization on aniline on the surface of Ti O₂ nano-particle. XRD, TEM, and TEM techniques were used to characterize the PANI/TiO₂ nano composite was investigated under both UN and visible light irradiation and compared with unmodified TiO₂ nano-particles. The results indicated that deposition of PANI on the surface of TiO₂ nano-particle with improved the photocatalyst active of pristine TiO₂ nanoparticles.

Galus *et al* (2013) studied the influence of oxidised starch on the physic-chemical of cast soy protein isolate films. Films were cast from heated (70°C for 20 min) alkaline (pH=10) aqueous solutions of 7% soy protein isolate containing 50 percent (by mass) glycerol as a plasticizer and different levels of added oxidized starch (0, 5, 10, 15 and 20 by mass). For all type of films, opacity, contact angle, tensile strength, elongation at break and WVP were measured at 25°C for four relative humidity (30-53, 30-75, 30-84 and 30-100 percent). Differential scanning calorimetry and micro-structure were determined after conditioning film specimens at 25°C and 30% relative humidity for 48 h. Oxidised starch content significantly affecting ($p < 0.05$) tensile strength from 0.95 to 1.51 MPa temperature at maximum degradation rate from 64.8 to 74.2°C water permeability from 1.08/10-10 to 3.89/10-10g (m.pas) at relative humidity differentials of 30-50 and 30-100% respectively. Various internal arrangements were observed as a function of film composition (percentage of oxidized starch).

Garrido *et al* (2013) prepared thin film based soy protein and polyols by using two different processing methods. The effect of preparation process, casting or compression

was analysed in order to explain the differences observed in the functional properties of the films, mainly in optical, barrier, and mechanical properties. These differences were related to the changes in the structure during the film forming. Results indicated that casting films showed better properties than the film prepared by the hot pressing. Films prepared by casting were flexible and transparent and showed less yellowish color, lower gloss and much higher resistance against water.

Rouhi *et al* (2013) studied the physical properties of fish gelatine-based bio nano-composite films incorporated with zinc oxide (ZnO) nano-rods. The effects of ZnO NR fillers on the mechanical, optical and electrical properties of fish gelatine bio nanocomposite films were investigated. Results showed an increased in Young's modulus and tensile strength of 42 percent and 25percent for nano-composite with 5% ZnO NRs respectively, compared with unfilled gelatine based films. UV transmission decreased to zero with addition of small amount of ZnO NRs in the biopolymer matrix. X-rays diffractions showed an increase in intensity of the crystal facets of (10¹¹) and (0002) with addition ZnO NRs in the bio-composite matrix. The surface topography of the gelatine films indicated an increase in surface roughness with increasing ZnO NR concentrations. These results indicated that bio-nano composite based on zinc oxide (ZnO) NRs had great potentials for applications in packaging technology, food preservation, and UV shielding system

Tanima *et al* (2013) developed a special protein isolate (Aggregates is 396 nm in size) by lazer granulomerty based film from soya bean that showed good thermo stability as it started degradation beyond 50°C where as film blended with chitosan an antimicrobial agent. Incorporated with chitosan, protein isolate film further laminated with palm stearin showed even greater thermo stability as it started degrading from 60⁰ C. Soya protein isolate control film do not show so much thermo stability as it started degradation at much lower temperature like 35°C as compared to chitosan incorporated protein isolate films laminated with palm stearin . Micro structural study reported that edible films made from special protein isolate gives a homogeneous and uniform pattern, along with compact structure, upper surface shows globular arrangement. The films when incorporated with chitosan also revealed homogeneity and compactness but at higher concentration (> 50%) roughness was observed. When the concentration of the chitosan was increase beyond 15-20%, water vapour permeability rate and total soluble matter was decreased, thus resulting in good moisture barrier properties. The films incorporated with chitosan showed good inhibition against pathogenic bacteria.

Humairah *et al* (2014) characterized the thermoplastic starch and starch reinforced montmorillonite (MMT) clay nano composite. The thermoplastic starch Montmorillonite (TPS-MMT) nano composite was produced by plasticizing with glycerol through melt blending before being compression moulded. The TPS and nano-composite were prepared with starch /glycerol weight fraction of 70:30 with 3, 6, and 12 percent of MMT content. The degree of crystallinity of the TPS-MMT was analysed by the x-rays

diffraction (XRD) which showed that TPS crystalline structure was affected by MMT integration while both XRD and fourier transform intercalation scanning electron microscope (SEM) presented micrograph of continuous phase and good adhesion of TPS-MMT nano composite at lower clay concentration. Thus, the findings proved the addition of MMT posed favourable interaction with TPS from sago starch plasticized glycerol.

2.2 Whey protein Isolate based films and their characterization.

Whey protein isolate (WPI), which is an abundant by-products in the cheese industry, is a biopolymer that has received much attention for use as a potential edible or biodegradable food packaging material because it had been shown to produce transparent films and coatings that can act as an excellent oxygen barrier and provide certain mechanical properties (Sothornvit & Krochta, 2000, 2005). The ability of WPI-based edible films to act as barriers to solute and gas and enhance food quality and shelf-life has been previously demonstrated (Krochta & De Mulder-Johnston, 1997). However, these films do not have good mechanical and water vapor barrier properties because they are intrinsically hydrophilic (Krochta & De Mulder-Johnston, 1997). As a result of this property, they cannot be used for wide spread applications in the food industry. Whey proteins are capable to form elastic films (Wang *et al*, 2013). They have been employed as raw material for bio-degradable packaging because they have good oxygen and moderate permeability (Ramos *et al*, 2012)

Kester and Fennema (1986) discussed edible films derived from several polysaccharides, lipids and proteins. Formation and properties of films from proteins such as casein, whey protein, corn zein, wheat gluten and soy protein were also discussed.

Seydim and Sarikus (2006) analysed the use of edible films to release antimicrobial constituents in food packaging as a form of active packaging. Antimicrobial properties of whey protein isolate (WPI) films containing 1.0–4.0% (wt/v) ratios of oregano, rosemary and garlic essential oils were tested against *Escherichia coli* O157:H7 (ATCC 35218), *Staphylococcus aureus* (ATCC 43300), *Salmonella enteritidis* (ATCC 13076), *Listeria monocytogenes* (NCTC 2167) and *Lactobacillus plantarum* (DSM 20174). Ten millilitres of molten hard agar was inoculated by 200 μ l of bacterial cultures (colony count of 1.108 CFU/ml) grown overnight in appropriate medium. Circular discs of WPI films containing spice extracts, prepared by casting method were placed on a bacterial lawn. Zones of inhibition were measured after an incubation period. The film containing oregano essential oil was the most effective against these bacteria at 2 percent level than those containing garlic and rosemary extracts ($P < 0.05$). The use of rosemary essential oil incorporated into WPI films did not exhibit any antimicrobial activity whereas inhibitory effect of WPI film containing garlic essential oil was observed only at 3% and 4% level ($P < 0.05$). The results suggested that the antimicrobial activity of some spice extracts were expressed in a WPI based edible film.

Ferreira *et al* (2009) produced blended chitosan–whey protein films at acidic pH, carrying a high amount of protein, even though under these conditions a pure whey protein film could not be obtained. The films were biphasic and characterized by a compositional gradient, with the downward film surface containing a lower amount of protein than the upward surface. The surface richer in protein was more hydrophobic than that richer in chitosan. The difference in composition and hydrophilicity between both surfaces increased with the amount of protein incorporated in the film. Increasing the protein amount decreased elongation at break and tensile strength they had little effect on water vapour permeability. Although some of the film functionality might be compromised due to the incompatibility between the polysaccharide and protein components within the film matrix, the blended films especially those with intermediated protein amount may have useful applications on those food systems where the edible films should break up during the cooking or mastication process.

Sothornvit *et al* (2010) studied whey protein isolate (WPI)/Cloisite 30B organo-clay composite films with different amounts of the clay (0, 5, 10, and 20 g/100 g WPI). Films were prepared using a solution casting method and their properties were determined to assess the effects of clay content on film properties. The resulting films had an opaque appearance, which depended on the amount of clay added, and a similar gloss. However, the composite films were slightly less transparent compared to the transparent neat WPI films. Film properties such as surface color and optical properties varied depending on clay content. The haze index of the WPI/clay composite films as assessed by surface reflectance decreased indicating that the surface of the films was more smooth and homogeneous. The tensile and water vapor barrier properties of the composite films were also influenced by the amount of incorporated clay. In addition WPI/Cloisite 30B composite films showed a beneficially bacteriostatic effect against *Listeria monocytogenes*.

Kadam *et al* (2013) prepared whey protein isolate (WPI) films embedded with TiO₂ and SiO₂ (porous silica (SiO₂) coated titania (TiO₂)) nano-particles for improved mechanical properties using solution casting. A WPI solution of 1.5 percent TiO₂ and SiO₂ nano-particles was subjected to sonication at amplitudes of 0, 16, 80 and 160 % prior to casting in order to improve the film forming properties of protein and obtained a uniform distribution of nano-particles in the WPI films. The results showed that high sonication levels caused addition of nano-particles preventing protein agglomeration. The thermal stability of the materials revealed the presence of 3–4 degradation stages in oxidizing the protein films. The addition of nano-particles strengthens the WPI film, as evidenced by tensile stress analysis. Sonication improved nano-particle distribution in film matrix; such films can potentially become effective packaging materials to enhance food quality and safety.

Zolfi *et al* (2014) developed and characterized biodegradable kefiran-whey protein isolate (WPI)-titanium dioxide (TiO₂) blend films as a function of incorporating

amount of TiO₂ nanoparticles (1, 3 and 5% wt.). Results showed that the water vapor permeability, moisture content, moisture absorption and water solubility decreased by increasing the nano-TiO₂ content. Mechanical tests revealed the plasticizing effect of TiO₂ nanoparticles on the kefiran-WPI-TiO₂ film. Addition of TiO₂ nanoparticles to kefiran-WPI films significantly decreased tensile strength and Young's modulus, while increased its elongation at break. Differential scanning calorimetry data indicated that the glass transition temperature significantly changed by adding nano-TiO₂. X-ray diffraction analysis also demonstrated that crystal type in kefiran-WPI was not affected by incorporation of TiO₂ nanoparticles. A uniform distribution at 1 and 3% wt. loading levels of TiO₂ nanoparticles was observed using scanning electron microscopy (SEM) micrographs.

III. OTHER MATERIALS BASED BIO-DEGRADABLE FILMS AND THEIR CHARACTERIZATION

Shukla and Cheryan (2001) studied that Zein is the major storage protein of corn and comprises: 45–50 percent of the protein in corn. Zein isolate are not used directly for human consumption due to its negative nitrogen balance and poor solubility in water. Current zein manufacture is limited to: 500 tonnes per year from corn gluten meal. The ability of zein and its resins to form tough, glossy, hydrophobic grease-proof coatings and their resistance to microbial attack have been of commercial interest. Potential applications of zein include use in fibre, adhesive, coating, ceramic, ink, cosmetic, textile, chewing gum and biodegradable plastics. These new applications of zein appear promising, but require the development of low-cost manufacturing methods. The characteristics of zein were discussed in terms of its composition, structure, solubility in various solvents and gelation properties.

Velde and Kiekens (2001) found that flectural and tensile properties are mostly correlated and the tendencies found here were probably the same as found when comparing flectural properties. Tensile properties were clearly best for the densest reported polymers especially for PGA and PCL on the other hand, seems to be the weakest polymer with remarkable high strain at failure. It was concluded that molecular mass can play a very important role in the obtained mechanical properties

Al-kaysi *et al* (2005) studied nanoparticles of a novel organic zwitterionic meisenheimer complex, synthesized by reprecipitation in water under different conditions. While reprecipitation alone resulted in a suspension of amorphous particles that fell out of solution within hours, sonication for different periods of time resulted in the formation of crystalline particles that were stable in solution over the course of weeks. The disk shaped particles had an average diameter of 140 nm and a thickness of 70nm. Comparison of the optical spectroscopy of these particles with the monomer indicates that they possess delocalized excitonic states and enhanced radiative decay rates. The use of zwitterionic molecules in conjunction with sonication provides a way to exert some

level of control over particle size and morphology, as well as increased colloidal stability.

Nikolova *et al* (2005) investigated biopolymer films from pectin with different degree of esterification and gelatin. The effect of film thickness upon the spectral and refractometric film characteristics with different weight contents were obtained. A comparative analysis of pectin films with a gelatin film were carried out. The refractometric data are made for liquid phases with 1, 0.5 and 0.25 % at 633 and 790 nm, using He-Ne and semiconductor lasers. On the base of the measured refractive index the Sellmeier's relation was obtained.

Khan *et al* (2006) prepared polymer films of sago starch/polyvinyl alcohol (PVA) by casting and cured under ultra violet (UV) radiation. Different blends were made varying the concentration of sago starch and PVA. Tensile strength (TS) and elongation at break (Eb) of the prepared films were studied. Films made up of sago starch and PVA with a ratio of 1:2 showed the highest TS and Eb. The physico-mechanical properties of prepared films were improved by grafting with acrylic monomers with the aid of UV radiation. A series of formulations was prepared with two monomers 2-ethyl 2-hydroxymethyl 1, 3 methacrylate (EHMPTMA) and 2-ethylhexylacrylate (EHA) and a photo-initiator. Monomer concentration, soaking time and radiation dose were optimized in terms of grafting and mechanical properties. The highest TS was at 50 percent EHMPTMA and 48 percent EHA and 2% photo initiator at 5 min soaking time and recorded value was 6.58 MPa. The prepared films were further characterized with NMR spectroscopy and scanning electron microscope (SEM).

Bondson and Oksman (2007) investigated that possibility to use of PVOH to improve dispersion of cellulose whiskers in a PLA matrix. However, PLA and PVOH formed two immiscible phases with a continuous PLA phase and a discontinuous PVOH phase, most whiskers having located in the PVOH phase. As result, the thermal stability and the mechanical properties of the nano-composite were not improved compared to its unreinforced counterpart. Several composite were developed by adding reinforcing compound to polymers to enhance their thermal, mechanical and barrier properties.

Silva *et al* (2007) investigated the structural features of chitosan/soy blended membranes by means of solid state carbon nuclear magnetic resonance (NMR), infrared spectroscopy (FTIR), contact angle, and atomic force microscopy. Physico-chemical characterization of blended membranes composed by chitosan and soy protein has been carried out in order to probe the interactions that allow membranes to be formed from these biopolymer mixtures. These membranes were developed aiming at applications in wound healing and skin tissue engineering scaffolding FTIR investigations suggested that chitosan and soy may have participated in a specific intermolecular interaction. The proton spin-lattice relaxation experiments in the rotating frame on blended membranes indicated that independently of the preparation conditions, the blend components are not completely miscible possibly due to a weak polymer-protein interaction. It was also shown that

the blended systems showed a rougher surface morphology which was dependent of soy content in the blend system

Soliman *et al* (2007) studied that the various factors affecting the formation of bio-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 improved the tensile and barrier properties of the obtained film. The optimum amount of formaldehyde gave good mechanical and barrier properties (0.3 mg/100ml).

Kim *et al* (2008) studied the modified CNTs by introducing carboxylic acid groups on their surfaces in order to enhance their inter-molecular interaction with the poly(ethylene-2,6-naphthlene) (PEN) matrix. The CNTs even in the concentration as low as 0.1 percent, greatly improved thermal stability as well as tensile strength and module of PEN. Chitogen tripoly-phosphate Nano particle(CsN) were incorporate to hydroxyl propyl methyl cellulose (HPMC) films and observed improvement in mechanical properties and water vapour barrier of films

Talja *et al* (2008) investigated effects of binary mixtures (1:1) of glycerol, xylitol and sorbitol at various concentrations on physical and mechanical properties of potato starch-based edible films stored at various relative vapor pressures (RVP). Edible films were prepared by casting using suspension of binary polyol mixtures (20–50 percent of solids), potato starch (50–80% of solids) and distilled water which was heated to gelatinize starch. Water sorption of films was affected by the type and content of binary polyol mixture. Water vapour permeability (WVP) of films was found to increase as the content and plasticization effect of binary polyol mixture as well as RVP gradient increased. Young's modulus of films was observed to decrease with the concurrent increase of elongation at break as the plasticization and the content of binary polyol mixture increased at RVP of 33%. Both tensile strength and elongation at break decreased when films were plasticized at the high content of binary polyol mixtures and stored at the RVP of 54 and 76 percent. Crystallization of polyols was not observed when binary polyol mixtures were used as plasticizers

Tang *et al* (2008) investigated enhancement of poor barrier and mechanical properties of biopolymer-based food packaging by the use of layered silicates (nanoclay) to produce nanocomposites. Films were made through casting using granulate produced by a twin-screw extruder. Natural (MMT) and organically modified (I30E) montmorillonite clays were chosen for the nanocomposite preparation. The structures of the hybrids were characterized by X-ray diffraction (XRD) and transmission electron microscopy (TEM). Starch/MMT composite films showed higher tensile strength and better water vapor barrier properties than films from starch/I30E

composites, as well as pristine starch, due to formation of intercalated nanostructure. To find the best combinations of raw materials, the effects of clay content (0–21 wt% MMT), starch sources (corn, wheat, and potato), and amylose content (\approx 0, 28, 55, 70, 100percent) on barrier and mechanical properties of the nano-composite films were investigated. With increase in clay content, significantly higher (15–92 percent) tensile strength (TS), and lower (22–67percent) water vapor permeability (WVP) were obtained. The barrier and mechanical properties of nano-composite films did not vary significantly with different starch sources. Nano-composite films from regular corn starch had better barrier and mechanical properties than either high amylopectin or high-amylose-based nano-composite films. WVP, TS, and elongation at break (percent E) of the films did not change significantly as amylose content increased beyond 50 percent.

Cao *et al* (2009) studied the effects of plasticizer composition, size and shape on the mechanical properties and water vapor permeability (WVP) of gelatin films. Firstly, oligosaccharides – sucrose, and some organic acids such as oleic acid, citric acid, tartaric acid, malic acid (MA) were added to gelatin. It was found that only MA could improve the ductility of gelatin film, and the visual appearance of MA modified gelatin film was better. Secondly, polyethylene glycols (PEG) with different molecular weights (300, 400, 600, 800, 1500, 4000, 10 000, 20 000) were used to plasticize gelatin films. This showed that PEG of lower molecular weights exhibited better plasticizing effect for gelatin films, and such films had better visual properties. This shows that mannitol (Man) and sorbitol (Sor) could make gelatin films flexible, whereas Man could crystallize from gelatin film. Following this the plasticization of ethylene glycol (EG), diethylene glycol (DEG), triethylene glycol (TEG) series and ethanolamine (EA), triethanolamine (TEA) series was studied. Suitable plasticizers (MA, PEG300, sorbitol, EG, DEG, TEG, EA, DEA, and TEA) for gelatin were selected to investigate the WVP and water content of these plasticized gelatin films. The mechanical properties of these films were also compared

Silver nanoparticles were formed in fluff pulp and nano structured Lyocell fibres by immersion in silver nitrate, (Fernandez *et al*, 2009) and a subsequent transformation of the adsorbed silver ions into elementary silver nanoparticles by physical (thermal/UV) or chemical (sodium borohydride) methods. Microscopy revealed that nanoparticles generated by physical methods were regular in shape and efficiently dispersed, while the chemical reduction produced highly aggregated nanoparticles. Nanoparticle size has been found relevant to guarantee high antimicrobial activity, being the samples with big aggregated silver nanoparticles almost inefficient. Indeed a satisfactory correlation between silver ion release and the antimicrobial efficiency against *Escherichia coli* and *Staphylococcus aureus* could be confirmed and furthermore, the highest concentrations tested were efficient to reduce the microbial load in poultry exudates.

This work demonstrates that especially designed absorbent materials could be optimised to preserve aseptic conditions during manipulation, leading to feasible applications of a silver based nano-technology in food technology.

Rhim *et al* (2009) prepared PLA-based composite films with different types of nanoclays such as Cloisite Nap, Cloisite 30B and Cloisite 20A, using a solvent casting method and their tensile, water vapor barrier and antimicrobial properties were tested. Tensile strength (TS), elongation at break (E), and water vapour permeability (WVP) of control PLA film were 50.45 /0.75 MPa, 3.0/0.1 % and 1.8 /10/11 g m/m² s Pa, respectively. TS and E of nano-composite films prepared with 5 g of clay/100 g of PLA decreased 10–20 and 11–17 %, respectively depending on the clays used. On the contrary, WVP of the nano-composite films decreased 6–33 % through nano-clay compounding. Among the clay types used, Cloisite 20A was the most effective in improving the water vapour barrier property while sacrificing tensile properties the least. The effect of clay concentration tested using Cloisite 20A showed a significant decrease in TS and WVP, with increases in clay content. Among the PLA/clay composite films tested, only PLA/Cloisite 30B composite film showed a bacteriostatic function against *Listeria monocytogenes*.

The *et al* (2009) studied regarding to their microstructure, moisture barrier and mechanical properties. Edible films based on the binary combination of agar (AG), cassava starch (CAS) and arabinosylan (AX). Though the films appear macroscopically homogeneous, electron microscopy observations reveal a phase separation and dispersion respectively in AG–CAS and AG–AX blend film structures, whereas the structure of CAS–AX blend films seems homogeneous. In case high moisture (84% and 99% RH), neither the combination of AG and CAS nor the addition of AX into CAS can improve film moisture barrier properties, except at a lower RH (57 percent). Blending AG with CAS increased the surface wet ability of AG films but not that of CAS films. Adding AG into CAS induces an improvement in elongation and tensile strength of CAS based films. Mechanical properties of agar based films degraded when CAS or AX was added. The results suggested that AG was found able to provide a very good cohesive matrix, which contributes to enhance the mechanical properties of other polysaccharide based films.

Cho *et al* (2010) prepared an edible oxygen barrier film Pouch fabricated from a heat sealable corn zein (CZ) layer laminated on soy protein isolate (SPI) film to olive oil condiments for use with instant noodles. The mechanical, barrier, and physical properties of the CZ/SPI bilayer films were then investigated and the oxidative stability of olive oil in the pouches was measured during storage under dry and intermediate relative humidity conditions. SPI film lamination with an additional layer of CZ film increased tensile strength and water barrier properties, while it had a lower elongation at break and decreased oxygen barrier properties. The oxygen permeability of the CZ/SPI film was lower than that of nylon-metalocene catalyzed linear low-density polyethylene film. The CZ/SPI bi-layer films

were heat sealable at 120-130°C and produced seal strength greater than 300 N/m. The higher oxygen barrier property of the CZ/SPI bilayer films resulted in reduced oxidative rancidity of olive oil packaged in NY/m LLDPE films. Soy protein isolate (SPI) could be subjected to modification with different amounts of a naturally occurring cross-linking agent (genipin, Gen) and glycerol used as plasticizer was carried out in this work.

Akbari *et al* (2011) found that most of the properties of nano particles are size-dependent. The particle size and size distribution of alumina nanoparticle, as critical properties, have been determined by transmission electron microscopy (TEM), photon correlation spectroscopy (PCS), surface area analysis (BET) and x-ray diffraction peak broadening analysis. The particle size was found to be in the range of 5-95nm. Cumulative percentage frequency plot of the data extracted from TEM images indicates that particle size distribution obeys the log-normal function. The TEM images also revealed that particles are spherical in shape and loosely agglomerated. Comparing of the XRD and TEM results shows that the particles are single-crystal. The HRTEM images also verify that the particles have a single-crystal nature. In comparison, there was a good correlation between the BET, XRD and TEM measurements other than PCS that was sensitive to the presence of the agglomerates

Iskender Arcan and Ahmet Yemencioğlu (2011) investigated effect of plasticization on elimination brittleness and flexibility problems zein films were plasticized by incorporation of different phenolic acids (gallic acid (GA), p-hydroxyl benzoic acid (HBA) or ferulic acids (FA)) or flavonoids (catechin (CAT), flavone (FLA) or quercetin (QU)). The use of GA, CAT, FA and HBA at 3 mg/cm² eliminated the brittleness of films and gave highly flexible films showed elongations between 135 and 189%, while FLA and QU caused no considerable effect on film elongation. The films containing FA and HBA showed extreme swelling and lost their structural integrity when hydrated in distilled water. In contrast, CAT and GA containing films maintained their integrity following hydration. Most of the GA (up to 93%) and a considerable portion of CAT (up to 60 %) in the films existed in soluble form. The films showed antioxidant and/or antimicrobial activity. The TEACs of soluble phenolic compounds in 3 mg/cm² CAT and GA containing films were 21.0 and 86.2 µm of trolox/cm², respectively. The GA containing films showed antimicrobial activity on *Listeria monocytogenes* and *Campylobacter jejuni*, while CAT showed no antimicrobial activity on these bacteria at the studied concentration. This work opened a new perspective for using zein in flexible bioactive packaging.

Chauhan (2012) studied that polymers are inseparable part of our life. In recent years, there has been a tremendous increase in interest of scientist for biodegradable polymers. Polymers form the backbones of plastic materials that are continually being employed in diversified areas. As a result, stress was imposed to modifying traditional materials to make them more user and environment – friendly by employing naturally occurring materials. A number of biological materials

might be incorporated into the biodegradable polymer materials like cellulose, hemp, flax, starch and fiber extracted from various types of plants. These help in decreasing the need for synthetic polymer production that ultimately reduces pollution and expense

Gumiero *et al* (2013) prepared a high density polyethylene (HDPE)/calcium carbonate (CaCO₃) film containing TiO₂ via blown film extrusion process. The photocatalytic properties of this film were evaluated by voltammetric, UV-Vis spectrophotometric and gas chromatographic measurements following the decomposition rate of suitably selected molecular probes, such as 4-hydroxybenzoic acid and methylene blue. The film containing 1 percent w/w of TiO₂ displayed a profitable and reproducible photo induced degradation activity towards target organic compounds. The effect of packaging photo catalytic activity on the structural and microbiological stability of a short-ripened cheese was studied. Cheese structure was assessed by dynamic, small deformation rheological tests. A container consisting of a multilayer material, made from the HDPE + CaCO₃ + TiO₂ composite matrix, was able to provide a greater maintenance of the original cheese structure than a rigid container currently used, mainly due to the inhibition of lactic acid bacteria and coliforms.

Zainal *et al* (2013) studied development of composite films using various gelatin sources with corn oil (CO) incorporation (55.18 percent) and to investigate the mechanical and physical properties of these films. There were increased ($p < 0.05$) in the tensile strength (TS) and puncture strength (PS) of films when the concentration of gelatin increased. The mechanical properties of these films also improved when compared with films produced without CO. Conversely, the water barrier properties of composite films decreased ($p < 0.05$) when the concentration of gelatin in composite films increased. Comparing with pure gelatin films, water and oxygen barrier properties of gelatin films caused decreased when manufactured with the inclusion of CO.

IV. ANTIMICROBIAL PROPERTIES OF FILMS

Antimicrobial packaging is a promising form of active packaging to improve safety and shelf-life of food products. In antimicrobial packaging, agents may be coated, incorporated, immobilized, or surface modified onto packaging materials. Many compounds such as organic acids, bacteriocins, enzymes, spices and polysaccharides (chitosan) have been tried in antimicrobial packaging with varying degree of success.

Carballo *et al* (2008) developed an antimicrobial photo sensitizer-containing edible films and coatings based on gelatin as the polymer matrix, incorporating sodium magnesium chlorophyllin (E-140) and sodium copper chlorophyllin (E-141). Chlorophyllins were incorporated into the gelatin film-forming solution and the inhibiting effect of the cast films was tested against *Staphylococcus aureus* and *Listeria monocytogenes*. The results demonstrated that water soluble sodium magnesium chlorophyllin and water soluble sodium copper

chlorophyllin reduced the growth of *S. aureus* and *L. monocytogenes* by 5 logs and 4 log respectively. Subsequently, the activity of self-standing films and coatings containing E-140 was assessed on cooked frankfurters inoculated with *S. aureus* and *L. monocytogenes*. These tests showed that it was possible to reduce microorganism growth in cooked frankfurters inoculated with *S. aureus* and *L. monocytogenes* by covering them with sodium magnesium chlorophyllin-gelatin films and coatings

Li *et al* (2008) studied about TiO₂ and its properties. Titanium dioxide (TiO₂) was considered as non-toxic mineral particles widely used in the fields like cosmetics, food and drug. When the scale come to nanometer, TiO₂ nanoparticles (nano-TiO₂) exhibits multiple specific characteristics coupled with unknown risks on health.. The results indicated that the erythrocytes treated with nano-TiO₂ underwent abnormal sedimentation, hemagglutination and dose dependent hemolysis, totally differing from those treated with micro-TiO₂. The ghost cells were investigated using ultra-thin cell section in the case under nano-TiO₂. The mechanism of such adverse effects is (1) the attachment around erythrocyte, change the surface native properties and ultimately lead to hemoagglutination; (2) the content leak to the outside of erythrocyte through the breakage induced by both the nano-TiO₂ trans-membrane and the oxidative stress under nano-TiO₂. Our findings imply that nano-TiO₂ may have potential toxicity to human being health.

Fernández *et al* (2009) formed silver nanoparticles in fluff pulp and nano structured Lyocell fibres by immersion in silver nitrate, and a subsequent transformation of the adsorbed silver ions into elementary silver nanoparticles by physical (thermal/UV) or chemical (sodium borohydride) methods. Microscopy revealed that nanoparticles generated by physical methods were regular in shape and efficiently dispersed, while the chemical reduction produced highly aggregated nanoparticles. Nanoparticle sizes were found relevant to guarantee high antimicrobial activity. The samples with big aggregated silver nanoparticles almost inefficient. Indeed a satisfactory correlation between silver ion release and the antimicrobial efficiency against *Escherichia coli* and *Staphylococcus aureus* could be confirmed, and furthermore, the highest concentrations tested were efficient to reduce the microbial load in poultry exudates. This work demonstrated that especially designed absorbent materials could be optimised to preserve aseptic conditions during manipulation, leading to feasible applications of a silver based nanotechnology in food technology.

Kim *et al* (2011) examined antimicrobial activity against *Listeria monocytogenes*, *Escherichia coli* 0157:H7 and *Salmonella typhimurium* of chitosan biopolymer films (CBFs) prepared with four different viscosities of chitosans (10, 40, 100 and 200 mPa s). Films were investigated by agar diffusion assay. The films were also characterized with measurements of color, tensile strength (TS), percent elongation (EL), water vapor permeability and oxygen permeability. CBFs prepared with 100 mPa s

chitosan showed an antimicrobial effect only on 10⁴ cfu/mL inoculations of *L. monocytogenes* while other viscosities showed an anti-listerial effect on all concentrations (10⁴e10⁶ cfu/mL) of *L. monocytogenes*. CBFs prepared with 10 mPa s (CBF-10) and 40 mPa s (CBF-40) chitosans showed an inhibitory effect against *E. coli* 0157:H7 and *S. typhimurium* only at the 10⁴ cfu/mL concentrations. CBFs prepared with the two higher viscosity chitosans did not show any effect regardless of bacterial level. TS and EL of the CBFs increased with increasing viscosity up to 100 mPa s. Molecular weight distribution was found to be positively correlated with viscosity. The oxygen permeability of the CBFs increased with increasing viscosity of chitosans, but water vapor transmission rate was not similarly affected. In conclusion, CBFs were more effective at inhibition of *L. monocytogenes* than *S. Typhimurium* and *E. Coli* O157:H7. Molecular weight of chitosan must be chosen selectively to control the target foodborne pathogens

In recent year's edible films and coating materials are increasingly used for food packaging to maintain the quality by serving as mass transfer barrier between food components and the surrounding environments. Biodegradable packaging material has been developed to replace petroleum based non bio-degradable plastics. Utilization of antimicrobial nano-particle, incorporated into polymer matrix such as packaging material will protect against food borne micro-organism as well as odour. The literature about that potential of nanotechnology (biopolymers) in current and the future application of biopolymers has been reviewed. Now a days efforts are being made to elaborate new uses for proteins and starches i.e production of edible film with antimicrobial functionality (nanoparticle) for effecting protection of food products.

V. CONCLUSION

In recent year's edible films and coating materials are increasingly used for food packaging to maintain the quality by serving as mass transfer barrier between food components and the surrounding environments. Biodegradable packaging material has been developed to replace petroleum based non bio-degradable plastics. Utilization of antimicrobial nano-particle, incorporated into polymer matrix such as packaging material will protection against food borne micro-organism as well as odour. The literature about that potential of nanotechnology (biopolymers) in current and the future application of biopolymers has been reviewed. Now a days efforts are being made to elaborate new uses for proteins and starches i.e production of edible film with antimicrobial functionality (nanoparticle) for effecting protection of food products

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