DEVELOPMENT OF PHOTODEGRADABLE POLYETHYLENE FILMS FOR FOOD PACKAGING WITH SHELF LIFE IMPROVEMENT

A thesis submitted in partial fulfilment of the requirements for the degree

of

Master of Science

In

Environmental Sciences

By

Nazish Iftikhar
(NUST201463486MSCEE65214F)

Institute of Environmental Sciences & Engineering (IESE)
School of Civil and Environmental Engineering (SCEE)
National University of Sciences and Technology (NUST)
Islamabad, Pakistan

APPROVAL SHEET

It is certified that the contents and forms of the thesis entitled

DEVELOPMENT OF POLYETHYLENE PHOTODEGRADABLE FILMS FOR FOOD PACKAGING WITH SHELF LIFE IMPROVEMENT

Submitted by

Nazish Iftikhar

Has been found satisfactory for the requirements of the degree of

Master in Environmental Science

Supervisor: _______________
Dr. Ishtiaq A. Qazi
Professor
IESE, SCEE, NUST

Member:________________
Dr. Muhammad Arshad
Associate Professor
IESE, SCEE, NUST

Member:________________
Dr. Zeshan
Assistant Professor
IESE, SCEE, NUST

This thesis is dedicated to my Parents

who have meant and continue to mean so much to me,

who have been so close to me that I found them with

me whenever I needed

ACKNOWLEDGEMENTS

All acclamations and appreciations are for **Almighty Allah**, who bestowed mankind with knowledge and wisdom, and granted him vigilance on earth. All the respect and honours to **Hazrat Mohammad (P.B.U.H)**, a star brightening in the path of faith and knowledge, and luminary to truth and justice who enabled us to recognize our creator and declared it to be obligatory duty of every Muslim to acquire knowledge.

It would not have been possible to write this MS thesis without the help and support of the kind people around me, to only some of whom, were possible to give particular mention here.

Sincere gratitude for my supervisor ***Dr. Ishtiaq A. Qazi*** for believing in me to complete my research work. His important guidance, innovative suggestions and kind behavior were source of motivation during the study. I am grateful to all my teachers who taught me throughout my academic career and for their kind support. I am grateful to ***Dr. Zeshan and Dr. Muhammad Arshad*** in particular for their kind help and facilitation throughout the project.

I would thank all the laboratory staff and technicians for their help, support and cooperation.

Further, above all, my parents, brother and sister have given me their unequivocal support throughout, as always, for which my mere expression of thanks likewise does not suffice. Last, but by no means least, I thank my friends in NUST and elsewhere for their support and encouragement throughout my course work and research.

Nazish Iftikhar

TABLE OF CONTENTS

LIST OF ABBREVATIONS

Ag-TiO_2	Silver Doped Titanium Dioxide
CFU/ml	Colony Forming Unit per Millilitre
e-	Electron
eV	Electron Volt
TiO_2	Titanium Dioxide
UN	United Nations
UNFAO	United Nations Food and Agriculture Organization
WHO	World Health Organization
λ	Wavelength
PE	Polyethylene
LDPE	Low-density polyethylene
HDPE	High-density polyethylene
SEM	Scannig Electron Microscope
EDS	Energy Dispersive spectroscopy
XRD	X-Ray Diffraction
TNPs	Titania Nano Particles

LIST OF FIGURES

LIST OF TABLES

Abstract

Titania and 1% Ag-doped Titania nanoparticles prepared by liquid impregnation method were embedded in polyethylene packagings. Prepared films and nano particles were then characterized through SEM, XRD and EDS analysis. The effect of nano-packings on preservation quality of Lettuce (*Lactuca sativa*) and Spinach (*Spinacia oleracea*) during room temperature storage was investigated. Quality indices of both vegetables; Weight loss, chlorophyll content, moisture content, ascorbic acid, browning index, sensory evaluation and microbial count of packaging materials were determined after 4 days of storage. The results showed that the nano-packing materials containing Ag-Ti had a quite beneficial effect on physicochemical and sensory quality of both vegetables followed by Titania embedded packaging. Moreover weight loss data along with SEM results confirmed photo degradation of nano packagings under artificial light (90days period). Therefore, the photodegradable nano-packagings could be applied as sustainable solution to the plastic waste along with shelf life and quality improvement of food.

Chapter 1

INTRODUCTION

1.1. Background

The global food consumption and supply situation is very alarming. UN FAO estimates that each year about one third of all the food produced for human consumption is wasted in the world. The global food wastage has an environmental perspective as well; grown but not eaten food has significant environmental and economical concern.. There are many reasons for food wastage like inefficiencies in food supply chains, such as poor transportation and logistics, lack of technology, insufficient skills, awareness and management. But most prominent one is microbial attack on food that decreases the shelf life of food (FAO, 2013).

Food losses cause an astounding financial concern towards the food industry while food borne outbreaks signify a noteworthy danger to public health. The occurrence of spoilage microorganisms on crude materials and on handled foodstuffs due to cross contamination may be pointed out as a main reason for food loss. This results in changes of nutritious and sensory qualities of food, for example, oxidation, generation of off-flavors and off-odors and also undesirable changes in composition and color. Around 1.3 billion tons of foods are lost each year. Also, human ailments brought about by the utilization of tainted food stuff result in overwhelming costs in medicinal care and decreased profitability, which, among different inconveniences, represent more than $77.1 billion every year, just in the USA. (Othoni, 2016)

Food borne ailments are the main cause of morbidity and mortality all around the world. The world is becoming more prone to outbreaks of disease caused by infected food because of growing worldwide trade (Kuchenmüller et al., 2013). Food borne diseases associated with leafy greens have shown an increase of 38.6% since 1996-2005(Crandall et al., 2011).

Leafy greens is a term given to vegetables including lettuce, cabbage, collard green, mustard green, endive, spinach, turnip greens, kale, broccoli, escarole, and spinach (Economic Research Service, 1998). These are considered to be ready to eat after minimal processing (Sandeep et al., 2013) and providing a diversified flavored, low caloric and micro nutrient rich diet. Leafy greens are perceived to be of optimum quality within 24 hours of harvesting. Consumer's preference is linked to them because of their sufficient nutrient content and freshness (Gomez- Govea et al., 2012).

1.2. Nanotechnology in Food Industry

Applications of nanotechnology in each section of the food industry have been identified by different scientists as shown in fig 1. from farming (e.g., pesticide, compost or antibody conveyance; animal and plant pathogen identification; and focused on hereditary designing) to edibles handling (e.g., exemplification of flavor or scent enhancers; nourishment textural or quality change; new gelation or viscosifying operators) to food packaging(e.g., pathogen, gas or manhandle sensors; anticounterfeiting gadgets, UV-security, and more grounded, more impermeable polymer movies) to nutritional supplements (e.g., nutraceuticals with higher dependability and bioavailability). Irrefutably, the most dynamic territory of food nanoscience innovative work is packaging: the worldwide nano-empowered diet and refreshment packaging business sector was 4.13 billion US dollars in 2008 and developed to 7.3 billion by 2014, speaking to a yearly development rate of 11.65% .This is associated with the fact that the buyer is all the more eager to accept nanotechnology in "out of food" applications than those where nanoparticles are straightforwardly added to food (Duncan, 2011).

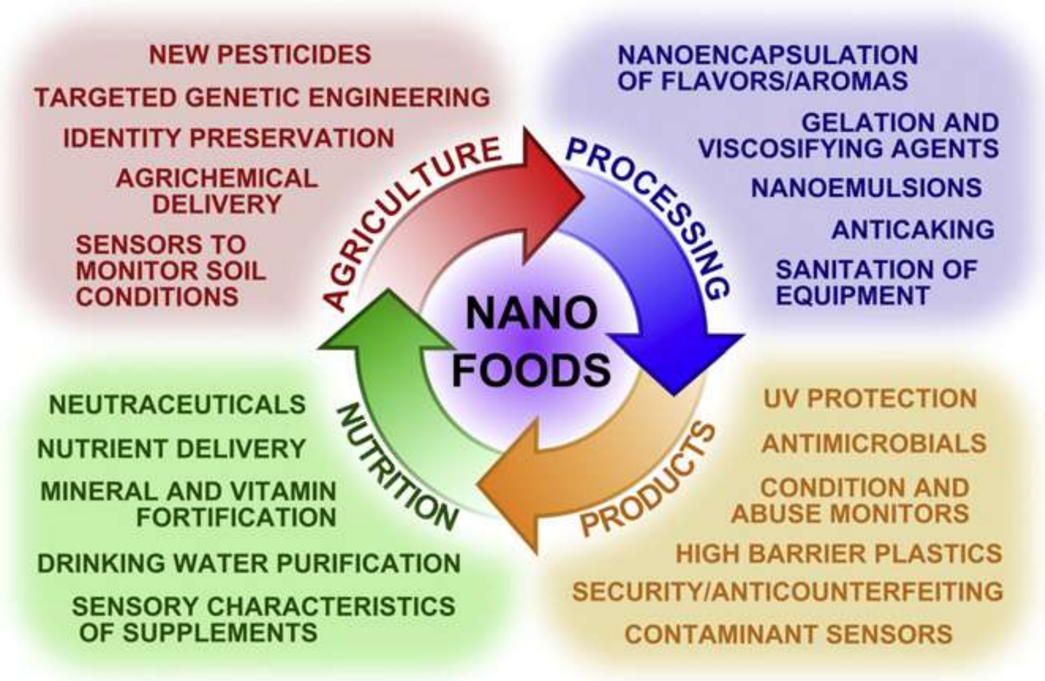


Figure 1.1 Application of Nanotechnology in Food sector (Duncan, 2011)

1.3. Shelf Life of Food

Shelf-life is an important characteristic of any food item and it is of significance to everyone in the food chain, from producers to customers. Foods are varied, complex and dynamic systems, in which different reactions including; microbiological, enzymatic, chemical and physicochemical can take place at the same time. We need to preserve the food in order to increase its shelf life .To preserve food different packaging materials are used and the use of polyethylene as packaging material is very common (Ansorena, 2012).

1.4. Plastic and the Modern World

The word plastic originates from greek word “plastikos’’, which means capable of being molded into different shapes .Plastics noticeably make up an important part of the range of materials used in modern world. Plastic industry has developed endlessly over 50 years. There are approximately 20 different groups of plastics, each with several grades available to bring specific properties for each different function. There are five high volume plastic families and these are the five main plastics in use: Low-density Polyethylene, High-density Polyethylene, Polyethylene Terepthalate , Polypropylene and PVC (Andrady & Neal, 2011).

1.5. Plastics in Packaging Industry

A number of polymer types are presently used for foodstuff packaging. Plastics are considered as the most favorite choice of packaging materials for different products (food beverages and chemicals). They offer unique advantages over common materials.

- Safety: They serve as safer materials for packaging of food products like polyolefin that do not react with food. And protect from contamination.

- Shelf Life: Plastics packaging l results in increased shelf life of food.
- Cost: Plastics art cost effective packaging material as compared to other packagings moreover the cost of haulage is reduced significantly because of lower weight and less spoilage.
- Convenience: Plastics can be transformed in any shape with various processing techniques, thus can pack any sort of substances like liquids, powders, flakes, or solids.
- Waste: They reduce the depletion of diverse food products, usual example is potatoes or onions packed in leno.
- Aesthetics: A right choice of plastics wrapping improved the visual value of products and helps in brand uniqueness
- Handling and Storage: Products filled in plastics are very easy to hold and store up as well as transport.

There is a very extensive option of plastic films made from different types of plastic polymer. Each type can have broad spectrum of mechanical, visual, thermal and humidity/gas barrier properties. These are formed by changing film thickness and the quantity and type of additives that are used in their fabrication. Some films (e.g. polyester, polyethylene, polypropylene) can be 'oriented' by stretching the material to line up the molecules in either one direction (uniaxial orientation) or two directions (biaxial orientation) to enhance their strength, transparency elasticity and moisture/gas barrier properties. Plastics based on polyethylene (PE), Polypropylene (PP), Polyvinylchloride (PVC) and Cellophane is mainly used for food packaging (Odian, 2004).

1.6. Polyethylene as Packaging Polymer

Low-density polyethylene (LDPE) is warmth resistant, sealable, non reactive, odor free polymer for food packaging. It is a good moisture barricade but is relatively porous to oxygen and is a poor odor blockade. It is less pricey than most films and is thus widely used for bags, for coating papers or boards and as a component in laminate sheets. LDPE is also used for shrink or stretch covering. High-density polyethylene (HDPE) is more stronger, thicker, less elastic and more fragile than LDPE and a improved barrier to gases and humidity. Bags made from HDPE have high rip and puncture resistance and have good seal power. They are water and chemicals resistant and are increasingly used in place of paper or sisal sacks (Allahvaisi, 2010).

1.7. Plastic – The White Pollution

As plastic applications in several field is increasing worldwide so is becoming a threat to the environment. Use of plastic shopping bags is widespread. About 1 trillion plastic bags are used every year (Miller, 2012). Hazard of discarding waste plastic, so called white plastic is becoming more and more severe.

1.8. Methods to Reduce the White Pollution

Plastic forms 5-8 percent of municipal solid waste. Though it can be recycled, most of the commercial plastics end up in landfills, in the ocean or in open dumps. Because the majority plastics are non-degradable, they take a very extensive time to break down, probably up to hundreds of years .Various techniques are proposed to reduce plastic waste

- Landfills
- Incineration
- Pyrolysis
- Thermal/Catalytic degradation
- Gasification, Bio-degradation
- Photocatalysis

1.9. Photo-Catalysis

Photocatalysis is composed of two Gree; the word photo is from ‘photos’ which means light and catalysis is from ‘katalyo’ which means to break apart or decompose. Photocataysis, therefore, is a process whereby we use light to turn on a photo catalyst which changes the speed of the chemical process while not getting involved in the reaction itself.

1.10. The Present Study

In the present study, it was intended to enhance the shelf life of food by incorporating titania and silver doped titania nanoparticles in the polyethylene packaging .The efficiency of nano-packagings as antimicrobial agents for improving the quality attributes like weight, chlorophyll content, moisture content, ascorbic acid, browning index and sensory evaluation which were determined after 4 days of storage at room temperature. Study was also focused on determining the photo degradability of these nano-packagings under artificial light as an alternative option for plastic waste disposal.

1.11. Objectives of the Study

The research had the following objectives:

a) To Develop Titania and doped Titania embedded polyethylene films

b) To Test effectiveness of films for food packaging

c) To Test photo degradation of films under artificial light

Chapter 2

Literature Review

2.1. What is Food?

The term food refers to materials, crude, prepared, or figured, that are expended orally by people or other living creatures for development, wellbeing, fulfillment, joy, and fulfilling the social needs. By and large, there is no confinement on the measure of food that might be consumed at a time (as there is for a medication as dose) (Rahman, 2007).

2.2. Why Preservation?

The primary purposes behind food preservation are to overcome wrong planning in farming, produce good quality items, and give variety in food items. Insufficient administration or inappropriate planning in farming can be overcome by staying away from wrong ranges, times, and measures of crude food materials and also by expanding shelf life utilizing different storage strategies for protection. Good quality diet items can give better-quality sustenances as far as enhanced dietary, practical, accommodation, and physical properties. In food preservation following points should be considered.

- Quality level
- Total time period for storage
- Targeted customers

After storing sealed food for a definite time, its quality characteristics (Table 2.1) may reach an undesirable state. Quality is a broader and dynamic concept.food has spoiled to such a level that it is found to be inappropriate for utilization, it is said to have reached the ending of its shelf life. In shelf life study of food, it is vital to assess the rate of change of a given quality attribute. Safety always comes at first priority followed by other quality procedures. Food quality attributes can be quite diverse, such as appearance, sensory, or microbial characteristics.

Different factors like type of food stored, its composition, packaging type used, and storage conditions contribute to the quality loss This quality deterioration can be controlled at any step of food harvesting, dispensation, supply and storage. (Rahman, 2007).

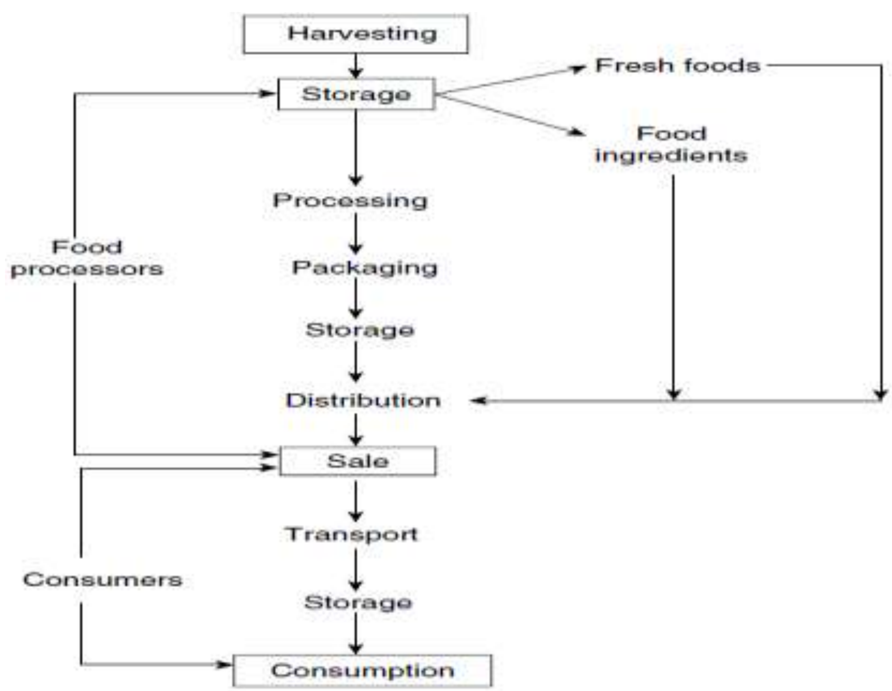
Table 2.1 Major Quality-Loss Mechanisms

Sr. No.	Chemical	Microbiological	Physical	Mechanical	Enzymatic
1	Color Change	Microorganism Growth	Collapse	Bruising	Browning
2	Non Enzymatic Browning	Off Flavor	Crystallization	Cracking	Off Flavor
3	Off Flavor	Toxin Production	Shrinkage	Damage due to Pressure	Color Change

Source: *Miller, 2012*

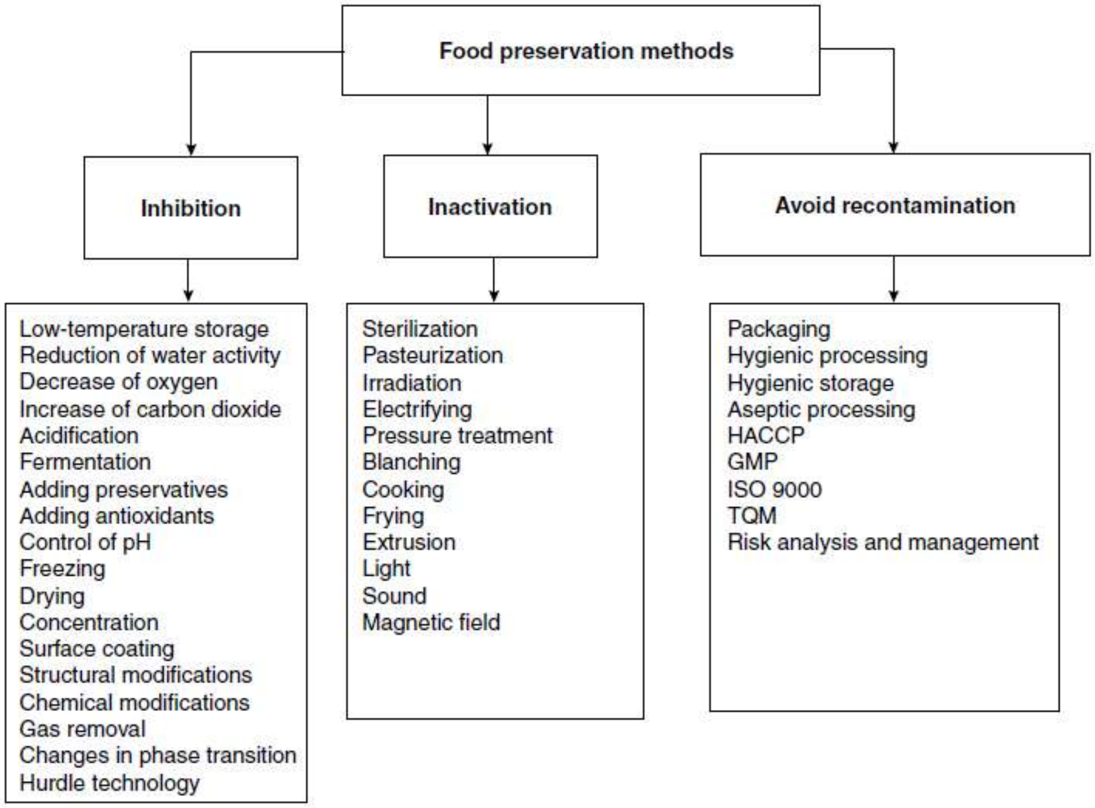
2.3. How Long to Preserve?

Prolonged storage of food leads to deterioration of various quality attributes of food. Food in this state is considered un edible and hence the end of its shelf life is reached. The rate of change of a given quality attribute is an important factor when studying the shelf life of food. Product quality is defined using many factors which include; appearance, yield, eating and microbial characteristics but the most important factor is the pleasure of the consumer. The many stages of food production are shown in Figure 2.1. Maintenance of the processing chain is therefore important and can lead to a reduction in quality loss because quality can be controlled at every step.



Source: *Crandall et al.*, 2011

Fig.2.1. Various stages of food production, manufacture, storage, manufacture and sale



Source: *Crandall et al.*, 2011

Figure 2.2 Methods for Preservation of Food

2.4. Food Preservation Methods

Food preservation methods can be divided into three main categories as following:

- Slowing down or inhibition of growth rate of microorganisms
- Directly killing bacteria, yeasts or enzymes, and

- To stop contamination during processing and storage (packaging)

A number of techniques from the above classes are shown in Figure 2.2. Preservation should be started immediately after harvesting of foods from their grown media (plant, soil, or water). Post-harvest technology includes management, protection, storage, and maintaining food originality and quality.

2.5. The Role of Packaging Technology

Proper packaging has a crucial role in preserving the quality and delivery of fresh, wholesome and safe food products to the end user. Packaging has three functions, containment, information and protection. In case of fresh vegetables, the packaging should be carefully selected to deal with the moisture, a condition that results in breakdown of the paper-based packaging as well as accelerated microbial contamination. Packaging must also be devised to protect against harsh and detrimental environmental and atmospheric conditions as well as threat of physical and chemical hazards. To facilitate the supply chain management and marketing operations there should be adequate labeling of the package. It is also essential to inform and educate the end user about the content and feasibility (Rehman et al., 2005).

2.6. Nanotechnology application in foodstuffs packaging polymers

Recently a number of applications of nanotechnology in food packaging and food safety have been studied. Clay nanocomposites have been identified as good moisture barrier packaging materials. Silver nanoparticles are effective antimicrobial agents that save food from spoilage and nanosensors have been evaluated as assays for the identification of food related analytes (gasses, small organic molecules and microorganisms,) (Duncan, 2011).

Packaging material prepared by mixing polyethylene and nano-powder has resulted in increased shelf life of Chinese jujube with better quality attributes (Li *et al*., 2011). Xing and his coworkers in 2011 studied the bactericidal effects of ZnO nanoparticles coated on PVC films and found that the ZnO-coated films showed very high antibacterial activity against two bacterial species(*E. coli* and *S. aureus)*. Also these nano-ZnO particles resulted in slight effects on the strength and elasticity of the film and decreased water loss rate.

Espitia *et al*. (2012) studied the dispersion of titanium nano particles in polypropylene (PP) film by scanning electron microscopy (SEM). They reported that titanium photo catalyst killed *E. coli* in presence of light because hydroxyl radicals and reactive oxygen species (ROS) produced by the illuminated titanium surface played key function in killing microorganisms by the oxidation of phospholipids component of the cell membrane of microorganisms. OH radicals are about thousand to ten thousand times extra efficient for *E. coli* control than other common disinfectants such as chlorine and ozone (Hur *et al.,* 2005).

2.7. Photocatalysis

The term photocatalysis comprises of the combination of photochemistry and catalysis. Photocatalysis can be defined as a process that accelerates the rate of a chemical reaction in the presence of a substance (photocatalyst) that absorbs UV, visible or infrared light (Al-Bastaki, 2003; Braslavsky, 2007). Photo catalysts are usually solid and not consumed or used during a reaction. They only tend to enhance the reaction kinetics. Photo catalysts are semiconductor in nature for example CeO_2, Fe_2O_3, TiO_2, WO_3, ZrO_2, and ZnO etc. (Herrmann, 2005; Benabbou et al., 2007).

2.7.1. Factors affecting the Photocatalysis

A photo catalytic process is a result of very complex reactions and its reaction rate may get affected due to the following factors (Rincón and Pulgarin, 2003):

- Oxygen Pressure
- Catalyst loading
- Water
- Concentration of substrate
- Light intensity
- pH of medium
- Temperature

Photocatalytic activities are further affected by physical properties i.e. microstructure and morphology and chemical properties of the employed photo catalyst, that could be improved by varying the morphologies like nano crystals, porous micro cubes, microsphere, concave micro crystals, tetra pods and flower like microspheres (Wang et al., 2002; Herrmann, 2005; Anpo and Kamat, 2010; Lou et al., 2013).

2.7.2 An ideal Photo catalyst

Photo activity, inertness (biologically and chemically), non toxicity, cost and photo stability are the properties considered while selecting a suitable photocatalyst (Bhatkhande et al., 2002).

2.7.3. TiO_2 as a Photo catalyst

TiO_2 is a semiconductor having a band structure with energy gap extending from the apex of the occupied valence band to the base of the empty conduction band (Leong *et al*., 2014). As a photo catalyst, when TiO_2 is exposed to Ultraviolet light having higher energy than the band gap energy of titanium, electrons get excited at the valance band and move to the conduction band, leaving positive holes in the valance band. The electron and hole pairs then move around to the surface of titanium to contribute in redox reactions and produce reactive oxygen species (ROS). Ti (IV) into Ti (III) are reduced by electrons and subsequently these electrons react with the absorbed oxygen (O_2) on titanium surface to create superoxide radical anions ($O_2^{\bullet -}$). At the same time, the holes react with water molecules (H_2O) to generate hydroxyl radicals ($OH^{\bullet}$). These ROS result in degradation of organic compounds and antibacterial activity (Latif *et al*., 2014).

As discussed above, a wide range of products is available which can be used in photocatalysis for water and environmental purification that have been used in fields like housing, agriculture, water treatment, clothes, living ware, and medicine. Among these photocatalysts, TiO2 has attracted the researchers due to its (Fujishima and Honda, 1972):

 Strong oxidation ability

 Super hydrophilicity

 Chemical stability

 Non toxicity and low cost

 Transparency to visible light

2.7.4. Polymorphs of TiO_2

Titanium dioxide generally exists in three polymorphs i.e.

 Anatase

 Rutile

 Brookite (Carp et al., 2004).

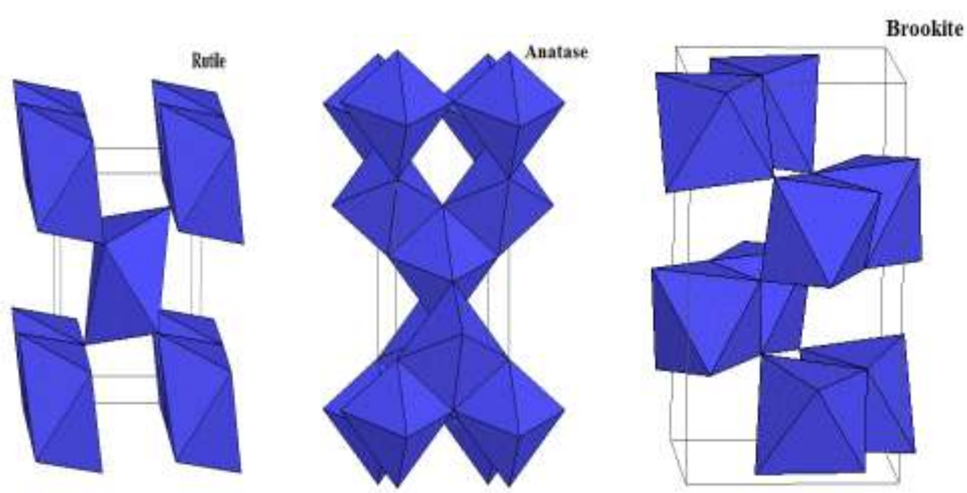


Fig. 2.2: Polymorphic forms of Titanium dioxide (TiO_2)

Among these, anatase is preferred to the rest for better photo catalytic performance (Beydoun et al., 1999). However research has proved that the photo catalytic degradation rate of organic pollutants could be enhanced using composites of anatse and rutile phase (Giolli et al., 2007).

2.8. Drawback of Titania and Metal Doping

TiO_2 suffers from the fact that it only functions well in the UV range of the spectrum which is only 3-5% of the solar irradiation. Shifting of photo excitation range to longer wavelengths has now-a-days become an active area of research as the material could response to visible light (constituting half of the solar light spectra). Metal doping of TiO2 narrows down the band gap and Photocatalysis can occur even under fluorescent light (Homola et al., 1999; Haes et al., 2004; Miller and Lazarides, 2005; Eustis and El-Sayed, 2006).

2.9. Photo catalytic Activity of TiO_2

The capacity of photo catalytic materials, such as titanium dioxide (TiO_2), to degrade organic contaminants in the air and water has been studied for more than 20 years (McCullagh et al. 2007). Photocatalytic activity of TiO_2 was first discovered by Fujishima and Honda in 1972 (Fujishima *et al*., 1972). They discovered that in the presence of light, electrons from valence band of TiO_2 are promoted to conduction band. This movement of electrons creates an electron-hole pair (e^- - h^+).

$TiO_2 + h_v \rightarrow e^- + h^+$ (Tan *et al*., 2011)

This electron-hole (e^- - h^+) pair can recombine or interact with other molecules (Behnajady *et al.*, 2008). Holes created in the valance band take part in oxidation reactions while electrons in the conduction band take part in reduction reactions of interacting molecules (Stamate *et al*., 2007).

Oxidation reaction;

$h^+ + H_2O \rightarrow {}^{\bullet}OH + H^+$ (Tan *et al*., 2011)

Reduction reaction;

$e^- + O_2 \rightarrow O_2^{\bullet -}$ (Tan *et al*., 2011)

Holes created in the valence band can interact with water molecules and hydroxyl ions (OH^-) and other Reactive Oxygen Species (ROS) can be generated. These hydroxyl (OH^-) or Reactive Oxygen Species (ROS) interact with any organic molecule present at or near the surface of TiO_2 and oxidize it leaving behind CO_2 and H_2O as an end product (Osburn, 2008).

${}^{\bullet}OH$ + Pollutant + $O_2^- \rightarrow CO_2 + H_2O$ (Tan *et al.*, 2011)

2.10. Photocatalytic Activity of Ag-TiO_2

Chances exist for the recombination of the electron-hole (e^- - h^+) pair which may reduce the photocatalytic activity of TiO_2. Metal (Ag, Pt, Fe, etc.) doping of semiconductor (TiO_2) reduces recombination of these electron-hole (e^- - h^+) pair. Studies have shown that doping of silver metal with TiO_2 has reduced recombination of electron-hole (e^- - h^+) pair significantly and Ag doping of TiO_2 nanoparticles increases photocatalytic ability (Behnajady *et al.*, 2008).

Photocatalytic activity only triggers when incident light has energy greater than band gap of the semiconductor (Fujishima *et al*., 2000; Qureshi, 2012). TiO_2 has band gap of 3.2 electron volts (E = 3.2eV) which requires incident light having wavelength of lower than 388 nm for photocatalytic activity (Stamate *et al*., 2007; Blake *et al*., 1999). In ordinary circumstances, photocatalytic activity of TiO_2 begins when UV radiation falls on it while sunlight has only 5 % UV radiation (Osburn, 2008). So, band gap of TiO_2 has to be reduced to start photocatalytic activity even in ordinary sunlight. For this purpose, doping of TiO_2 is done with some suitable metal which ultimately narrow downs the band gap.

Chapter 3

Materials and Methods

3.1 Reagents and Materials

LDPE (Low Density Polyethylene) beads of commercial grade with melting point 115 ˚C and density of 0.94 g / cm^3 for formation of films were obtained from the local market. Cyclohexane (Merck, Germany) was used as a solvent to dissolve LDPE beads for polymer formation. Titanium Dioxide (GPR, BDH Chemicals Ltd. England) was used as a source for the synthesis of pure TiO_2 nanoparticles while Silver Nitrate (Merck, Germany) was used for the synthesis of Ag doped TiO_2 nanoparticles. Solidified agar petri plates were prepared with the help of Nutrient Agar (Merck, VM 100650 943).

3.2 Plant Material

Lettuce (lactuca sativa) and Spinach (Spinacia oleracea) were grown in the green house at IESE NUST and harvested at mature-green stage in the morning and then transported to the laboratory. Leaves were selected immediately after transporting to laboratory by their shape, size and color and the physically damaged ones were removed. About 2g of selected leaves were randomly packed with 1% Ag doped titania nano-packing, 5% titania nano-packing and normal polyethylene packing which were then sealed and stored at room temperature for four days. Five replicates of each packing were used to analyze each index on the fourth day of storage.

3.3 Synthesis of Pure TiO_2 Nanoparticles

Pure Titania nanoparticles were prepared by Liquid Impregnation (LI) method (Mehmood et al. 2015). 50g Titanium in 300 ml water was stirred on a magnetic stirrer for 24 hours at a rate of 300 rpm. The solution was then allowed to settle for 12 hours. Then the supernatant was removed and the resulting material was dried in an oven at 105^{o}C for 12 hours to remove the moisture. The dried solids were crushed and mixed with mortar and pestle and calcined at 400°C for 6 hours in a muffle furnace (NEY-525 SRIESII) to obtain pure TiO_2 nanoparticles.

3.4 Synthesis of Ag doped TiO_2 Nanoparticles

Liquid Impregnation (LI) method was used for the synthesis of Ag - TiO_2 nanoparticles. It involves the following major steps:

Mixing: Slurry of 1 % Ag - TiO_2 nanoparticles was prepared in water by mixing 48.95g of TiO_2 GPR and 1.05 g of $AgNO_3$ in a beaker and continuous stirring was done for 24 hours for proper mixing of TiO_2 GPR and $AgNO_3$.

Settling: These solutions were allowed to settle for another 24 hours in separate beakers for proper settling of the solution.

Drying: After removing the supernatant the solid material was placed in an oven for 12 hours at 105 ^{0}C for proper drying purpose.

Calcination: After drying, the material was crushed properly in mortar and pestle and placed in china dishes separately. These china dishes were placed in the muffle furnace for 6 hours at 400 ^{0}C (Sahoo et al., 2005).

3.5 Preparation of PE Films

Polymer Stock solution was prepared by dissolving 0.5g of PE beads in 50 ml of Cyclohexane at 70˚C temperature and stirring rate of 300rpm on magnetic hot plate.10 ml aliquot was then measured in a graduated cylinder and poured into petri plate of 4 cm radius and allowed to cool for 24 hours at room temperature and then separated from petri plates using water bath at 65 ˚C.

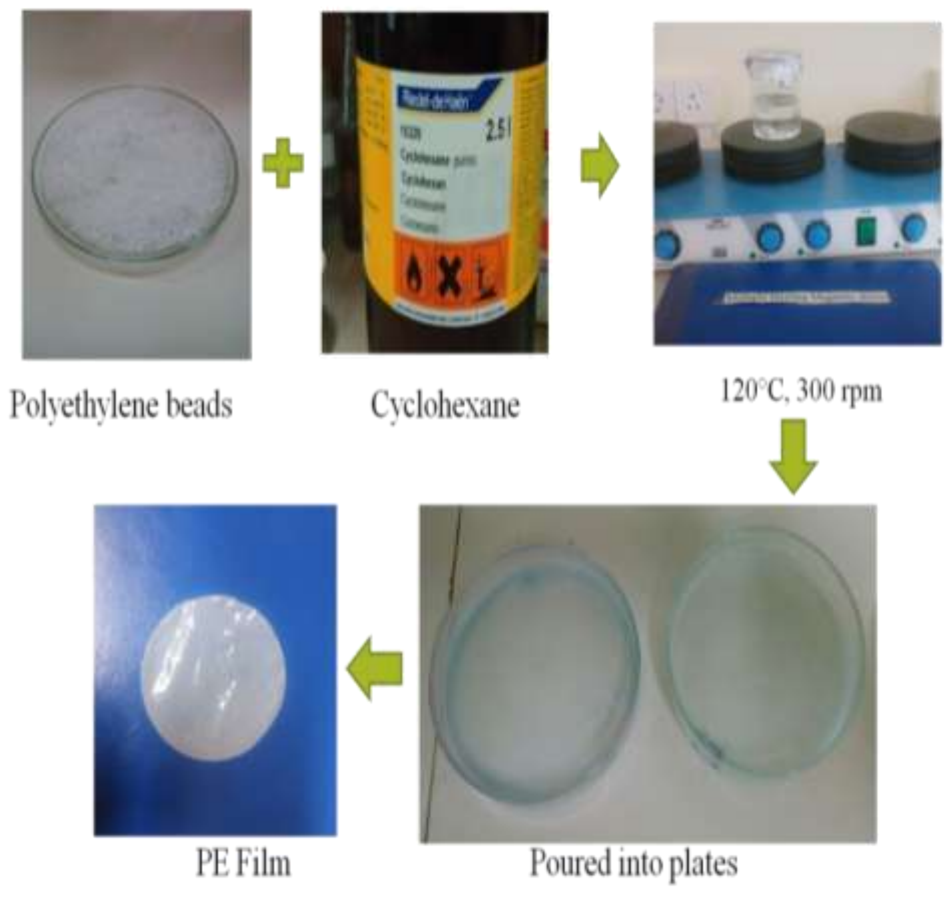


Figure 3.1: Preparation of Polyethylene Films

3.6 Preparation of Nanoparticles (TiO_2, 1% Ag - TiO_2) Embedded PE Films

An optimized quantity of nanoparticles (TiO_2, 1% Ag - TiO_2) was added in the above mentioned solution of PE polymer and Cyclohexane. Stirring of 30 minutes at 70°C was allowed and the solution was placed in a sonicator for 15 minutes, so that the nanoparticles could spread uniformly in the said solution. Finally, this solution was poured into the petri plate and the solvent was allowed to evaporate for 24 hours.

3.7 Preparation of Nutrient Agar Plates

14 g of Nutrient Agar (Merck) mixed in 1 liter distilled water with gradual mixing by glass rod. When the molten nutrient Agar was completely dissolved, the flask containing the agar solution was transferred to the autoclave for sterilization at 121^{o}C for 15 minutes. After sterilization, the flask was placed in hot water bath at 47^{o}C to stop the Agar solution from solidification. Finally, molten nutrient Agar solution was poured into petri plates (autoclaved at 121^{o}C for 15 minutes) under Laminar Flow Hood cabinet and allowed to cool down. Prepared petri plates, after solidification, were transferred to the incubator to check their sterility.

3.8 Characterization and Analysis of Nano particles and Polyethylene Packagings

Particle size and crystalline phase of the nanoparticles were identified with the help of X-Ray Diffraction (XRD). The morphology of the nanoparticles and films were observed using Scanning Electron Microscopy (SEM) whereas the elemental analysis of the material was carried out using Energy Dispersive Spectroscopy (EDS).

3.8.1. Morphology of TNPs and Films (SEM)

Scanning Electron Microscopy (SEM) is a powerful tool, being used now-a-days, in place of optical microscope. An electron beam is produced from the electron gun, and accelerated by high voltage in a vacuum. The electron beam then strikes the sample and signals are generated. These signals are detected by an electron collector and the image of the illuminated sample is formed by magnetic lenses.

SEM has a wide range of resolution ranging from 10X to 300,000X and may resolve even a few nanometers. In the present study, morphology of the samples was observed by using JEOL JSM 6460 SEM. SEM examined the prepared samples of pure and silver doped TNPs at an acceleration voltage of 20 kV.

3.8.2. Elemental Analysis of TNPs and Films (EDS)

In order to determine the chemical composition (in percentage) of the prepared pure and doped TNPs, Energy Dispersive Spectroscopy (EDS) coupled with SEM was used. Electron beam generated for the purpose of SEM, is also used for EDS. When electron beam strikes the sample, different elements present in the sample produce characteristic X-rays having different energies. Composition of different elements is found out by collecting and analyzing these characteristics X-rays. In the present study, Elemental Analysis of prepared TNPs and films was done by using EDS Oxford INCA X-sight 200.

3.8.3. Structure Analysis of TNPs (XRD)

X-Ray Diffraction (XRD) is a renowned and simple technique to determine the crystalline phase of any powdered sample. In XRD, a coherent X-Ray beam strikes the compact sample. After striking some of the X-rays will diffract at different angles. X-rays diffracting from a specific plane at the same angle will reinforce each other giving a high peaks indicating the crystallinity of the sample. In the present study, JEOL JDX-II X-ray diffractometer was used to analyze the crystalline phase or prepared pure and silver doped Titania Nanoparticles.

3.9 Quality assessment of Lettuce (*Lactuca Sativa*) and Spinach (*Spinacia Oleracea*)

3.9.1. Weight Loss Rate

Weight loss was measured using a weighing balance which could accurately measure up to 0.01 mg. Reduction in weight of the Lettuce stored in Ti-PE, Ag-Ti-PE and untreated PE was measured on the fourth day of storage at room temperature. Following formula was used to calculate weight loss rate:

$$\text{Weight Loss } = \frac{W_i - W_s}{W_i} \times 100$$

Where: W_i = Initial weight

W_s = Weight after storage

3.9.2. Chlorophyll Content

The chlorophyll content was measured using chlorophyll meter- CCM 200 Plus. 30 readings per leaf were taken in each packaging and Chlorophyll content was expressed as CCI unit.

3.9.3. Sensory Evaluation

At the end of storage (4 days), differences among sensory quality of vegetables stored in different packagings were evaluated using a preference sensory test. 10 untrained judges were consulted to evaluate the appearance, texture, and overall acceptance on a five point scale. The judges ranked the samples according to their preferences. The scale comprised the expressions ‘extremely liked’ to ‘extremely disliked’ corresponding to the highest and lowest scores of 5 and 1 respectively.

3.9.4. Moisture Content

The moisture content was determined by (AOAC, 1999) method. Briefly petri plate (4 inches diameter) was dried in oven at 105°C for 3 hours and transferred to a desiccator to cool and then weighed. Samples from all packagings (stored for four days) were uniformly spread into the dish and placed in the oven for 3 hours at 105°C. After drying, dish and its dried sample were reweighed.

Formula used to calculate Moisture (%)

$$\text{Moisture (\%)} = \frac{W_1 - W_2}{W_i} \times 100$$

Where: W_1 = weight (g) of sample before drying

W_2 = weight (g) of sample after drying

3.9.5. Browning Index Measurement

To assay the browning rate, spectrophotometric method described by Li et al. (2008) was followed.

3.9.5.1. Spectrophotometer

Spectrophotometer was used as a quantitative analytical technique by measuring the absorbance of sample solution before and after storage in different packagings.

3.9.5.2. Principal of UV/Vis Spectrophotometer

Spectrophotometer is widely used for the quantitative analysis of organic compounds. The molecules after exposure to UV-light, absorb it. Due to absorption of light, electrons become excited and move to high energy orbitals. The instrument basically measures transmitted light which is commonly known as transmittance is inverse of absorbance. The absorbance is recorded by taking the difference of light transmitted before and after the sample solution is being exposed to light. (Burgess, 2007).

3.9.5.3. Beer-Lambert law

According to Beer-Lambert law, absorbance is directly proportional to the concentration of the sample and path length of the cell in which sample is taken.

$$A = \varepsilon.c.L$$

Where

A = absorbance noted

ε = absorption coefficient, specific to sample solution

c = concentration of sample solution

L = path length of cell

3.9.5.4. Spectrophotometric Analysis of Samples

Briefly, 2 g sample from each packaging was homogenized in 5 ml of ethanol (95%). The homogenate was centrifuged at 4000rpm for 20 min to collect the supernatant and its absorbance was measured at 420 nm using UV-Visible Spectrophotometer (T-60U PG Instruments, UK) to assess the browning rate.

3.10. Ascorbic acid measurement

Ascorbic acid content of both vegetables was determined by the Iodometric method. In brief, a 4g sample was blended with 4ml of distilled water in mortar and pestle to extract ascorbic acid. The mixture was centrifuged at 4000 rpm for 10min, and then the supernatant was rapidly titrated with iodine solution using starch indicator until dark blue-black color persisted for more than 3s.

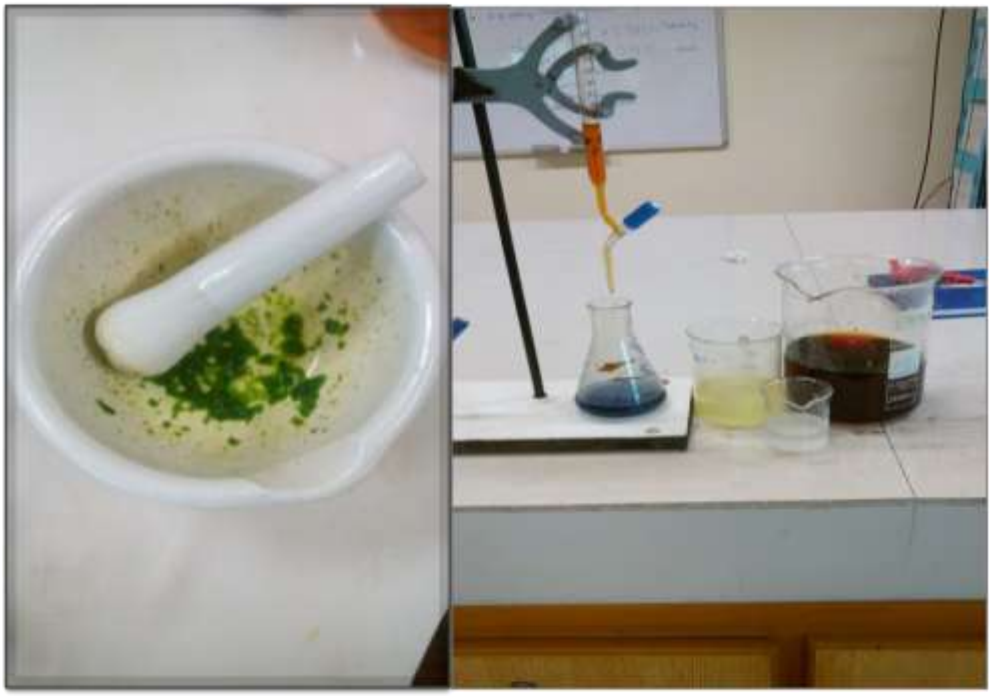


Figure 3.2: Determination of Ascorbic Acid Content by Iodometric method

3.11. Microbial Analysis of packaging films

Sterilized cotton swabs were used to draw samples from the inner surface of the packaging films for control and treated PE. Drawn samples were then streaked at the prepared agar media plates in laminar flow hood to ensure sterilized conditions. Agar plates were then incubated at 37 °C for 24 hours.

3.12. Photocatalysis of Polyethylene Films

Photocatalytic degradation of all types of prepared films was carried out in a chamber having 85 watt fluorescent bulb (Philips-china) as source of artificial light mounted at 5cm above the films. Weight loss of the films was measured using digital balance and morphology of films, before and after irradiation, was observed using SEM (JEOL JSM-6460) instrument.

Chapter 4

RESULTS AND DISCUSSION

4.1 Characterization Results

4.1.1 X - Ray Diffraction (XRD) Analysis

XRD identifies crystalline phase of the nanoparticles by measuring diffraction of X-rays. This also helps to find out particle size of TiO_2 nanoparticles. TiO_2 nanoparticles used in this study were **53.1 nm in** size whereas Ag-TiO_2 nanoparticles were 73 nm in size. Peaks of XRD results reveal that nanoparticles have crystalline structure. Also it was found that TiO_2 nanoparticles prepared are of anatase form. This crystalline form plays a key role in enhanced photocatalytic activity. It has been reported that the photocatalytic activity of anatase is much higher than rutile or brookite (Wold, 1993; Kawasaki, 2010; Yao, 2006). Moreover anatase has strong oxidizing power, non-toxicity and long-term photostability (Hoffmann et al., 1995). Therefore anatase was the most suitable crystalline form of titania to work with. Average crystalline size of nanoparticles was determined by using Scherer formula (Younas, 2011)

$$D = \frac{K\lambda}{\beta \text{Cos}\theta}$$

Where

D = Average particle size

k = 0.891, a shape factor of spherical particles

λ = 0.1542, wavelength of X-Rays

β = Full width of a diffraction line at half of maximum intensity (FWHM)

θ = Diffraction angle of crystal phase

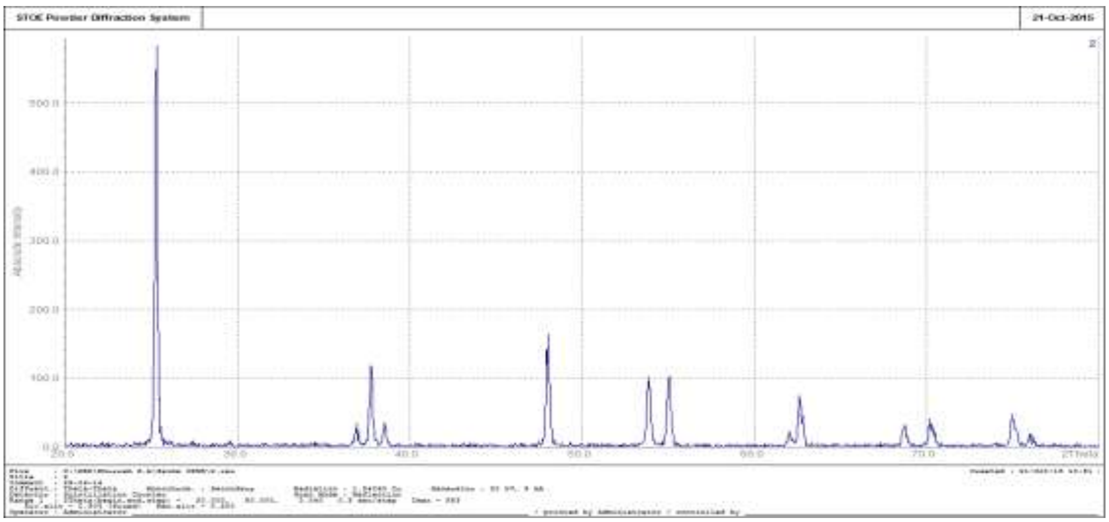


Fig. 4.1: XRD Pattern of Pure TiO_2 Nanoparticles

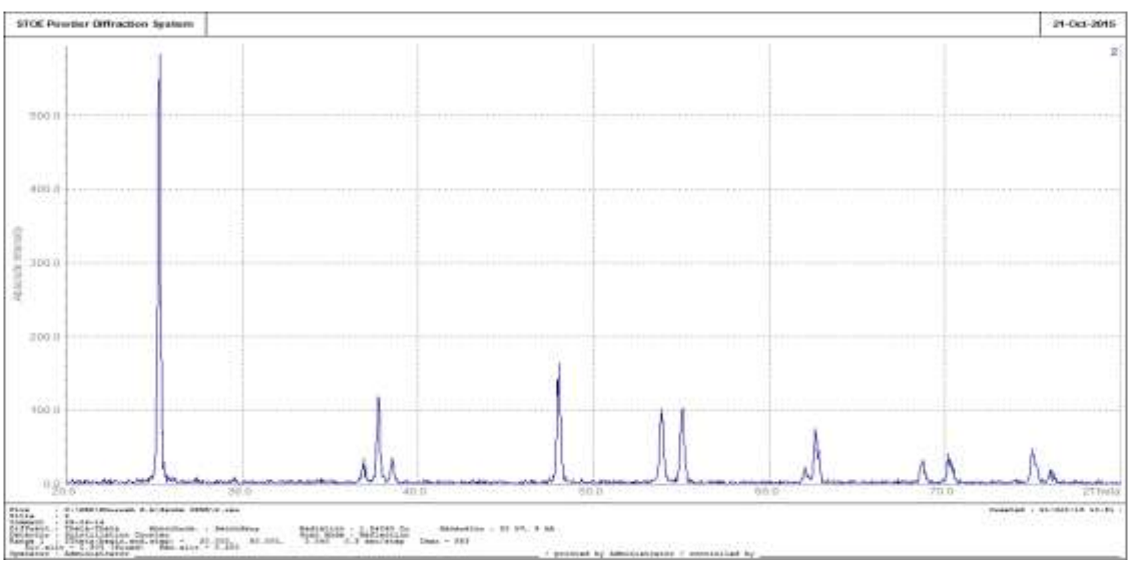


Fig. 4.2: XRD Pattern of Ag-TiO_2 Nanoparticles

4.1.2 Scanning Electron Microscopy (SEM)

The SEM images of pure and Ag-TiO_2 nanoparticles were obtained, at the magnification of 10,000, and are shown in Figures 4.3 and 4.4. Images of pure and Ag TiO_2 nanoparticles confirmed the presence of porous, sponge like structure, of high roughness and complexity. Such structure indicates the high surface area which has been proven to be efficient for photo catalytic degradation purposes. Fig 4.5 and 4.6 are showing Polyethylene films before and after irradiation. Nanoparticles have been successfully embedded over the surface of films and under the light theses particles have resulted in degradation of films showing large cavities on the surface.

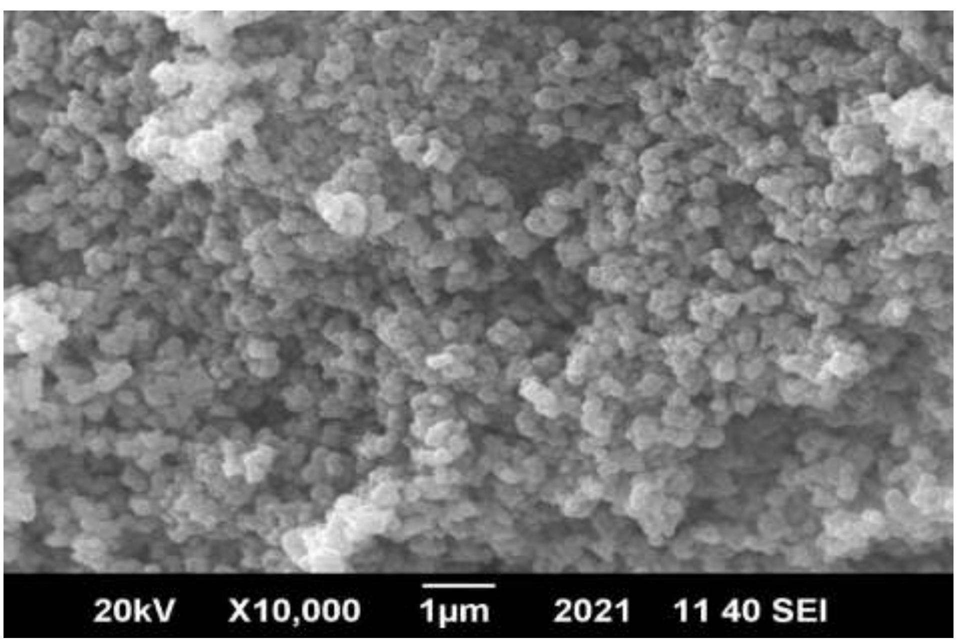


Fig. 4.3: SEM Image of Pure TiO_2 Nanoparticles at X 10,000

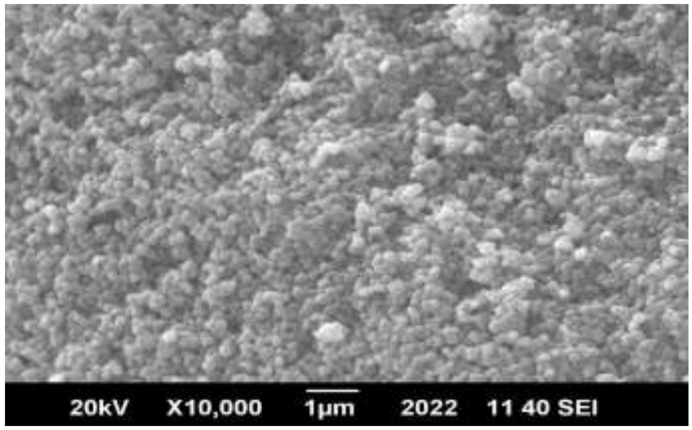
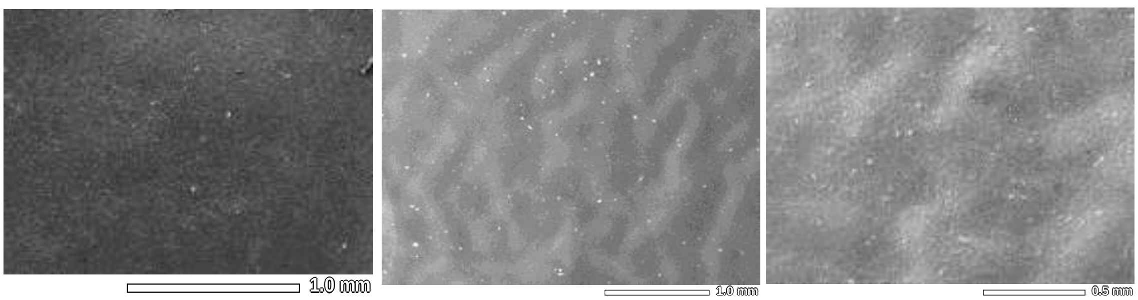
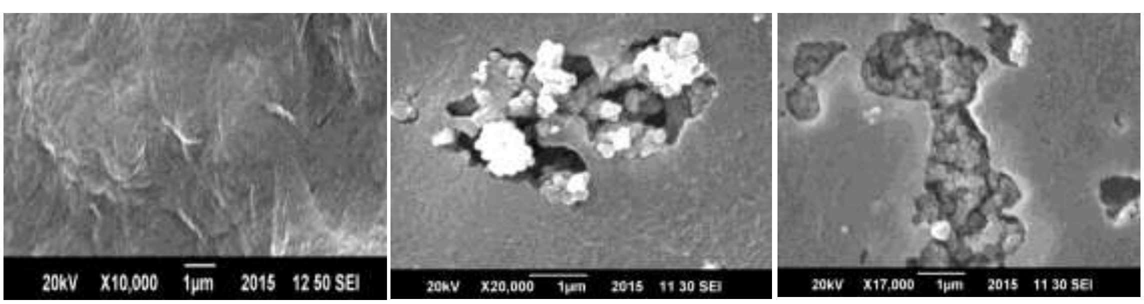


Fig. 4.4: SEM Image of Ag-TiO_2 Nanoparticles at X 10, 000



(a) Pure PE (b) TiO_2-PE (c) Ag-TiO_2-PE

Fig.4.5. SEM images of PE films before irradiation



(a) Pure PE (b) TiO_2-PE (c) Ag-TiO_2-PE

Fig.4.6. SEM images of PE films after irradiation

4.1.3 Energy Dispersive Spectroscopy (EDS) Analysis

EDS examines elemental composition of pure TiO_2, 1% Ag - TiO_2 and all three types of films. Figures 4.7- 4.10 and Table 1 show relative elemental mass composition of each category of nanoparticles and films (TiO_2, 1 % Ag - TiO_2 and films). This also confirms that nanoparticles contain silver and titania only while no alien element or impurity is introduced in the synthesis process.

Sr. no.	**Sample name**	**Elements in percent ratio**			
		Ti	Ag	C	0
1	Undoped TiO_2	55.95	-	-	44.05
2	Ag doped TiO_2	60.14	1.29	-	38.57
3	PE+TiO_2	5		74.3	19.7
4	PE+Ag dopedTiO_2	6.4	1	67.7	24.2

Table 4.1: EDS analysis of doped and undoped TiO_2 nanoparticles and Films

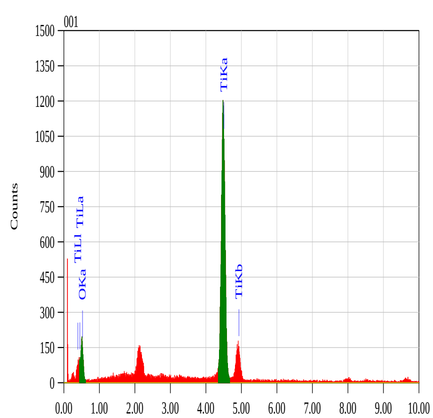


Fig 4.7 EDS pattern of TiO_2 nanoparticles

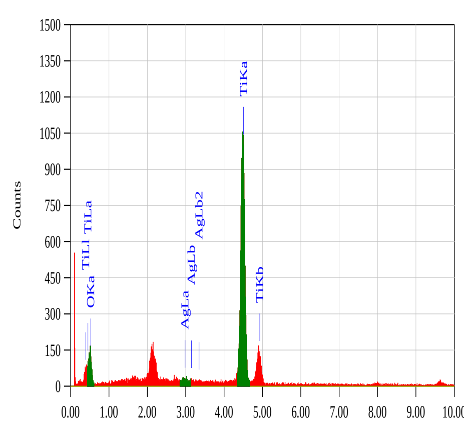


Fig 4.8 EDS pattern of Ag-TiO_2 nanoparticles

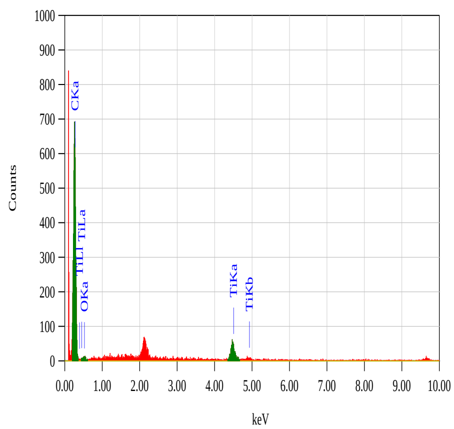


Fig 4.9 EDS pattern of Ag-TiO_2 PE film

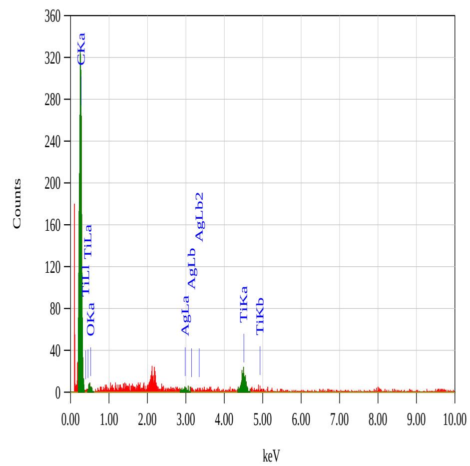


Fig 4.10 EDS pattern of TiO_2 -PE film

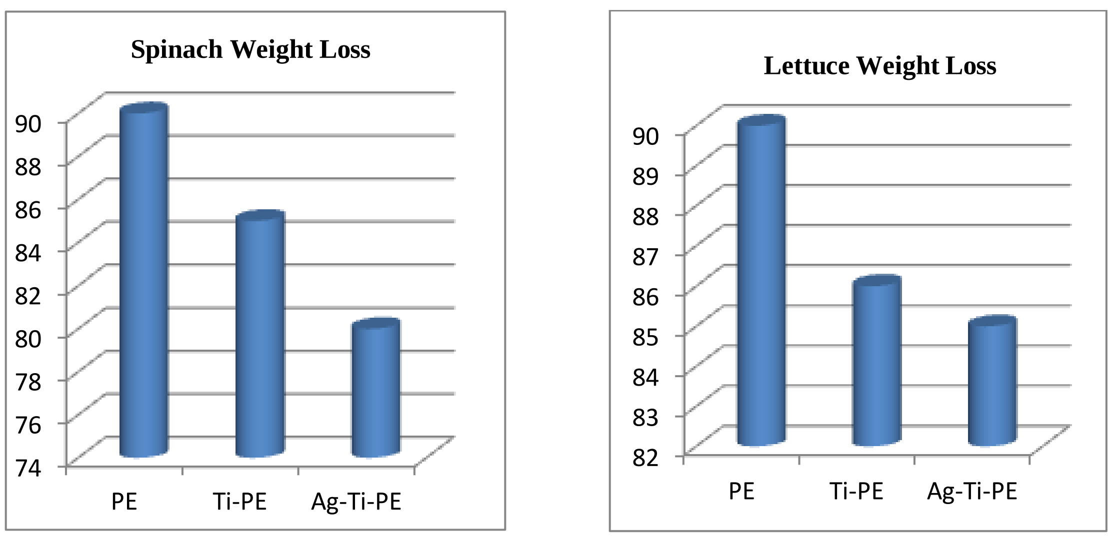


Fig. 4.11. Effect of nano-packagings and normal packaging on weight loss of Lettuce and Spinach during room temperature storage.

4.2. Weight Loss

One of the main indices used to determine food quality and post-harvest shelf life is the rate and extent of weight loss during storage. Due to transpiration, weight loss during storage was observed for all treatments. Compared to the control, lettuce and spinach stored with nano-packing with titania exhibited a significantly lower weight loss of 87% and 85% respectively. On day 4, weight loss of the both controls reached upto 90% of its original mass whereas that of composite packaging it was observed to be as low as 82% for spinach and 80% for lettuce. This result indicated that the nano-packing had a greater effect in preventing weight loss of food, which could be attributed to its better barrier properties against H_2O.

This weight loss reduction was previously reported for silver nanoparticles-PVP packaging on Asparagus as compared to control packaging (Jianshen et.al. 2007). Same results were also reported for nano Ag and Titania incorporated polyethylene packagings for Chinese jujube by Li.et.al. in 2008.

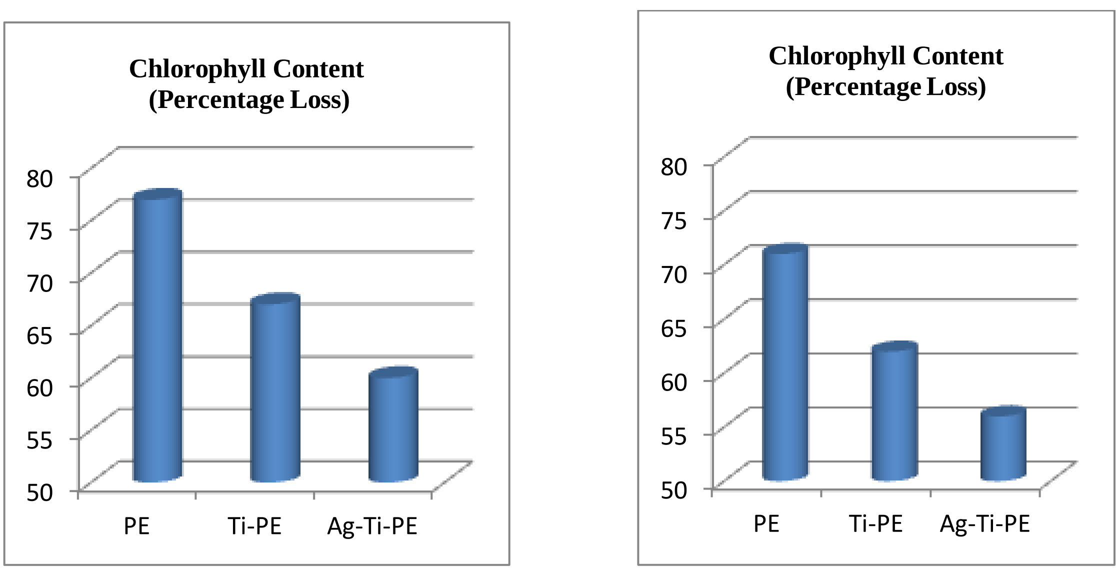


Fig.4.12 Effects of nano-packagings and normal packaging on chlorophyll content of Lettuce and Spinach during room temperature storage.

4.3. Chlorophyll Content

Chlorophyll content is another major quality index for the assessment of self life of green leafy vegetables. Results showed a same trend as that of weight loss. However the controls showed variation in the percentage loss based on chlorophyll content that is as followed 77 and 71 for lettuce and spinach respectively. On the other hand titania embedded packaging accounted for 67% and 62% of reduction. The effectiveness of composite packaging was much significant by the lowest reduction in chlorophyll content of lettuce at 60% and spinach at 57%. Positive effect on chlorophyll content of asparagus with silver nanoparticles-PVP packaging has been previously demonstrated by Jianshen et.al. in 2007.

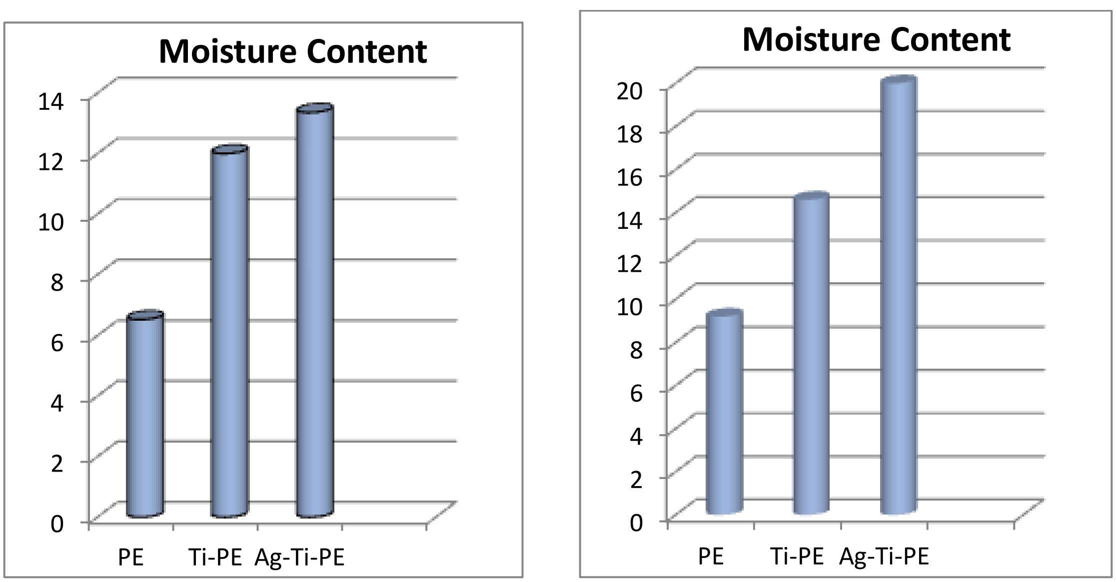


Fig. 4.13. Effects of nano-packings and normal packing on Moisture content of Lettuce and Spinach during room temperature storage.

4.4. Moisture Content

Retention of moisture within the leaves of both vegetables was used as a physiological index for the shelf life assessment. With simple polyethylene (control) packaging of lettuce water retention was recorded to be 6.53% whereas that of spinach it was 9.2%. Packaging containing titania was 12% and 14.6% for lettuce and spinach respectively. Maximum moisture is retained through the use of composite packaging as the results showed, 13.36% for lettuce and a much higher value for spinach that is 20%.

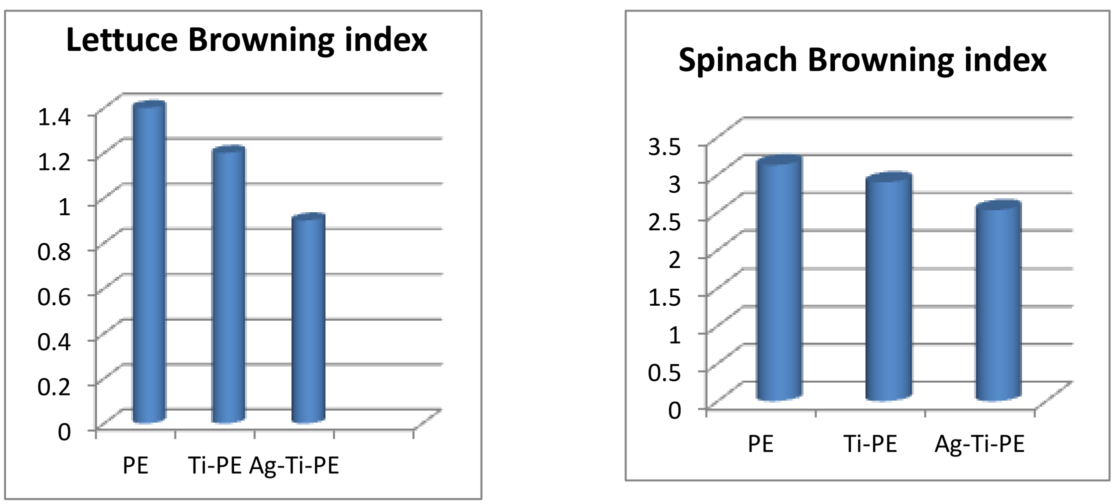
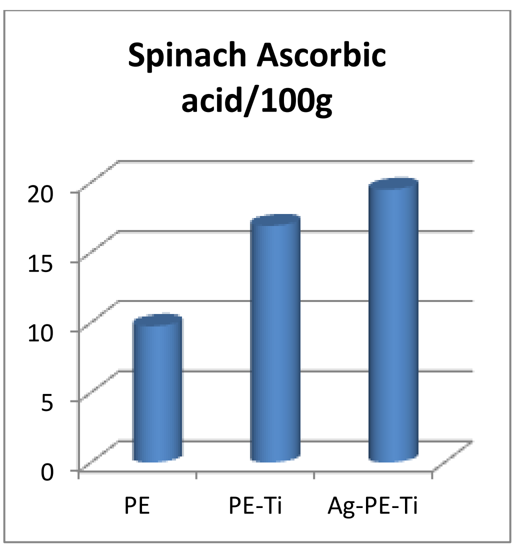


Fig. 4.14. Effects of nano-packings and normal packing on Browning index of Lettuce and Spinach during room temperature storage.

4.5. Browning Index

Enzymatic browning of leafy vegetables is the main factor responsible for quality during storage. It is the second most important cause of food deterioration after microbiological contamination. Enzymatic browning involves two oxidoreductases enzymes: polyphenoloxidase (PPO) and peroxydase (POD) which lead to the starting of browning reactions and ultimately results in losses or changes of flavor odor and nutritional value of food(Irina &Ghoul). With simple polyethylene (control) packaging of lettuce enzymatic browning was recorded to be 1.4 whereas that of spinach it was 3.1. Packaging containing titania was 1.2 and 2.9 for lettuce and spinach respectively. Lowest rate of browning i.e.0.9 for lettuce and is 2.5 for spinach were recorded for Ag-Ti-PE packagings.



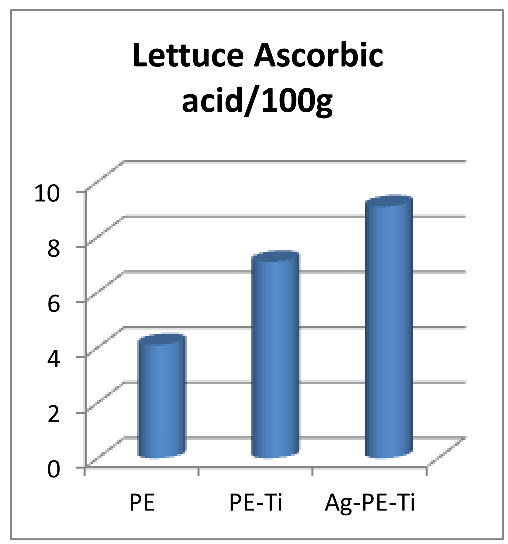


Fig. 4.15. Effects of nano-packings and normal packing on Ascorbic acid content of Lettuce and Spinach during room temperature storage.

4.6. Ascorbic acid

Ascorbic acid is one of the important nutritional index for leafy vegetables. The changes of ascorbic acid contents in the Lettuce and Spinach samples stored at room temperature are shown in Tables 10 and 11. A significant decrease is observed in the ascorbic acid content of all the experimental packages during storage . The reduction in controlled samples was larger than that of samples stored in nano-packagings. With simple polyethylene (control) packaging of lettuce ascorbic acid was recorded to be 4.5mg/100g whereas that of spinach it was 9.75mg/100 Packaging containing titania was 7.1mg/100g and 16.9mg/100g for lettuce and spinach respectively. Maximum ascorbic acid content is retained through the use of composite packaging as the results showed, 9.1mg/100g for lettuce and a much higher value for spinach that is 19.5mg/100g.

4.7. Sensory Evaluation

Results from the sensory evaluation ranked the Ag-Ti doped packaging at the top using the scale of 1 to 3, 1 being the most acceptable followed by Titania packaging. A clear reduction in visual quality was observed for the vegetables in polyethylene packaging. These results are consistent with the values of chlorophyll content and browning index presented above .Higher Chlorophyll content and lower browning rate along with low microbial count in nano packagings have lead to the above mentioned deductions. Overall sensory survey demonstrated panel consistency and adequacy in level of acceptance.

4.8. Microbial Count of Packaging Films

Polyethylene gave too numerous to count colony number, whereas the colonies for both nano packagings were too few to count. Thus a significant difference was recorded for the control and nano packagings in terms of microbial analysis. This may be due to the fact that Ag and Ti nanoparticles can damage cell membranes of microorganisms and penetrate into the cells resulting in DNA damage (Morones et al. 2005). Silver ions from the surface of these nanoparticles embedded films can interact with thiol groups in protein to cause bacterial inactivation, and loss of their reproduction capability (Feng et al., 2000). Ag/TiO_2 shows great potential as a photo catalytic material due to its photo reactivity and response in visible light. According to research work of Damm, Münstedt, and Rösch (2008) nano silver was found to be effective against E.coli polyamide even after being immersed in water for 100 days.

4.9. Surface Morphology and Weight loss studies of PE Films

All the films were prepared and irradiated under visible light for the period of three months. Higher weight loss was observed in Ag-Ti-PE films followed by Titania embedded films. On the other hand, no weight loss was observed in pure PE films .Over 8.2% weight loss was recorded in Ag- Titania composite PE films followed by 4% weight loss in Titania embedded films. Both cases confirmed the hypothesis that such weight reduction, in the PE films, is associated with the loss of volatile products formed by the photo catalytic degradation of the polymer. Same trend in weight loss of titania and silver titania embedded films have been previously demonstrated by Asghar et.al. (2010). SEM analysis was carried out to observe changes in surface morphology of the films. SEM images showed cracks and large cavities in the Ag-Ti-PE and Ti-PE matrix under the visible light exposure as compared to simple PE films. These effects are possibly due to the scissoring of the long chain polymer and the evolution of the volatile products from the PE surface (Roy et al., 2007; Zhao et al., 2007; Mumtaz et al., 2010).It is confirmed that development of this kind of composite polymer can lead to an environmental friendly polythene product.

Chapter 5

Conclusions and Recommendations

5.1 Conclusion

In this study Titania and silver doped Ttitania embedded polyethylene packaging was synthesized and applied to preserve quality of food during storage at room temperature. Results have shown quality maintenance in terms of physicochemical and sensory attributes of food during storage. Along with shelf life extension of food these nano packagings are photodegradable and can be used as environment friendly alternative for waste management. These packagings could be considered for commercial application during storage and marketing of food.

5.2 Recommendations

Following recommendations are proposed on the basis of current research;

- Nanoparticles embedded Polyethylene packaging should be used in local market to save food from deterioration and increase shelf life of food during storage and marketing.
- Research study may be extended by using different metal (Fe, Pt, Cu, etc.) doped nanomaterials.

- As one percent Ag doped TiO_2 is giving higher efficiency in both quality maintenance of food and photo degradation of packaging so the effect of variation in Ag percentage should be looked at.
- Incorporation of nano particles in plastic packagings other than polyethylene should be checked for the same purpose.

REFERENCES

Ahmad, A., Awan, G. H. and Aziz, S. (1994). Synthesis and applications of TiO_2 nanoparticles. Pakistan Engineering Congress, 70th Annual Session Proceedings, 676: 404 - 411.

Akarsu, M., Asilturk, M., Sayilkan, F., Kiraz, N., Arpac, E. and Sayilkan, H. (2006). A novel approach to the hydrothermal synthesis of anatase titania nanoparticles and the photocatalytic degradation of Rhodamine B. Turk Journal of Chemistry., 30(3): 333-343.

Angela, A. and Naomi, N.(2010).Nosocomial infections transmitted via computers: a literature review. Degree programme in nursing thesis, Laurea University of Applied Sciences, Finland, 16 - 18.

Andrady, M., & Neal, K. (2011). Environmentally benign photocatalysts: Applications of titanium oxide-based materials: *LWT - Food Science and Technology, 30*(6), 987-1012.

Allahvaisi, S. (2010). Polypropylene in the Industry of Food Packaging, Polypropylene, Dr. Fatih Dogan (Ed.), ISBN: 978-953-51-0636-4

An,J., Zhang, M., Wang, S., & Tang, J. (2008). Physical, chemical and microbiological changes in stored green asparagus spears as affected by coating of silver nanoparticles-PVP. *LWT - Food Science and Technology*, *41*(6), 1100-1107.

Ansorena, M., M., Roura S., Ponce, A., Moreira, M., & Di Scala, K. (2012). Assessment of lettuce quality during storage at low relative humidity using Global Stability Index methodology. *Food Science And Technology (Campinas)*, *32*(2), 366-373.

Asghar, W.,Qazi, I., Ilyas, H., Khan, A., Awan, M., & Rizwan Aslam, M. (2011). Comparative Solid Phase Photocatalytic Degradation of Polythene Films with Doped and Undoped TiO_2Nanoparticles. *Journal of Nanomaterials*, *2011*, 1-8.

AOAC (1999) Official Method of Analysis. 16th Edition, Association of Official Analytical Chemists, Maryland.

Braslavsky SE. 2007. Glossary of terms used in photochemistry, (IUPAC Recommendations 2006). Pure and Applied Chemistry 79:293-465.

Blake D.M., Huang Z., Wolfrum E. J., Huang J., Jacoby W. A. (1999) Application of the photocatalytic chemistry of titanium dioxide to disinfection and the killing of cancer cells. Sep. Purif. Methods 28 (1): 1-50.

Barry-Ryan, C., Devereux, M., & Lonchamp, J. (2009). Identification of volatile quality markers of ready-to-use lettuce and cabbage. *LWT - Food Science and Technology*, *41*(6), 1100-1107.

Chorianopoulos. N.G, Tsoukleris. D.S, Panagou. E.Z, Falaras. P, and Nychas G.J.E., (2011). Use of titanium dioxide (TiO2) photocatalysts as alternative means for Listeria monocytogenes biofilm disinfection in food processing. Food Microbiology 3:164–170.

Chen, S.C., Chang, C.F. and Liao, C.M. (2006). Predictive models of control strategies involved in containing indoor airborne infections. Indoor Air. 16(6): 469–481.

Choi, O. and Hu, Z. (2008). Size dependent and reactive oxygen species related nanosilver toxicity to nitrifying bacteria. *Materials Chemistry And Physics*., 42 (12): 4583–4588.

Carp, O., Huisman, C. L., & Reller, A. (2004). Photo induced reactivity of titanium dioxide. *Progress in Solid State Chemistry, 32*(1-2), 33-177.

Crandall, Neal, J. A. J., O.,Bryan, C. A., Murphy, C. A., Marks, B. P., & Ricke, S. C. (2011). Minimizing the risk of Listeria monocytogenes in Retail Delis by developing employee focused, cost effective training, *Journal Of Colloid And Interface Science* 1(2), 159–164.

Devleesschauwer, B., Haagsma, J. A., Angulo, F. J., Bellinger, D. C., Cole, D., Döpfer, D., Praet, N. (2015). Methodological Framework for World Health Organization Estimates of the Global Burden of Foodborne Disease. PloS One, 10(12).

Damm, C., Munstedt, H., & Rosch, A. (2008). The antimicrobial efficacy of polyamide 6/silver-nano- and microcomposites. *Materials Chemistry And Physics, 108*(1), 61-66. http://dx.doi.org/10.1016/j.matchemphys.2007.09.002

Duncan, T. (2011). Applications of nanotechnology in food packaging and food safety: Barrier materials, antimicrobials and sensors. *Journal Of Colloid And Interface Science, 363*(1), 1-24. http://dx.doi.org/10.1016/j.jcis.2011.07.017

Espitia, P., Soares, N., Coimbra, J., de Andrade, N., Cruz, R., & Medeiros, E. (2012). Zinc Oxide Nanoparticles: Synthesis, Antimicrobial Activity and Food Packaging Applications. *Food Bioprocess Technol*, *5*(5), 1447-1464.

Fujishima A. And Zhang. X. (2006) Titanium dioxide photocatalysis: present situation and future approaches. Comptes Rendus Chimie. 9(5-6): 750–60.

FAO(2013).Food wastage footprints, Impacts on natural resources. (/http://www.fao.org/docrep/018/i3347e/i3347e.pdf)

Gomez-Govea, M., Solis-Soto, L., Heredia. N., Garcia, S., Moreno, G. and Tovar, O.(2012). Analysis of microbial contamination levels of fruits and vegetables in Monterrey, Mexico. Journal of Food Agriculture and Environment.10(1): 152-154

Helrich, K., Horwitz, W., & Williams, S. (1991). *Official methods of analysis of the Association of Official Analytical Chemists*. Arlington, Va: AOAC.

Hur, J., Oh, S., Lim, K., Jung, J., Kim, J., & Koh, Y. (2005). Novel effects of TiO_2 photocatalytic ozonation on control of postharvest fungal spoilage of kiwifruit. *Postharvest Biology And Technology*, *35*(1), 109-113.

Hamal, D. B. and Klabunde, K. J. (2007). Synthesis, characterization, and visible light activity of new nanoparticle photocatalysts based on silver, carbon, and sulfur-doped TiO_2. Journal of Colloid and Interface Science. 311(2): 514-522.

Hui, Y. H, Sattar, S. A, Murrell, K. D., Nip, W.K, Stanfield, P.S. (2001), Food borne disease handbook. Viruses, parasites, pathogens and HACCP. 2nd edition.

Hoffmann, M.R., Martin, S.T., Choi, W. and Bahnemann, D.W. (1995). Environmental applications of semiconductor photocatalysis. Chemical Reviews. 95(1): 69-96.

Huang, N., Xiao, Z., Huang, D. and Yuan, C. (1988). Photochemical disinfection of Escherichia coli with a TiO_2 colloid solution and a self-assembled TiO_2 thin film. Supramolecular Science. 5(5-6): 559-564.

Ioannou,I & Ghoul(2013) .Prevention of enzymatic browning in fruit and vegetables. *European Scientific Journal*,30(9), 1857 – 7881.

Jeddi, M. Z., Yunesian, M., Gorji, M. E., Noori, N., Pourmand, M. R., & Khaniki, G. R. J. (2014). Microbial evaluation of fresh, minimally-processed vegetables and bagged sprouts from chain supermarkets. Journal of Health, Population, and Nutrition,32(3),391–9.

Kuchenmuller, A. R. (2013).Photocatalytic removal of C.I. Basic Red 46 on immobilized TiO2 nanoparticles: Artificial neural network modeling, *Environmental Technology*, 30: 11, 1155 — 1168

Li,H., Li, F., Wang, L., Sheng, J., Xin, Z., & Zhao (2011). Effect of nano-packing on preservation quality of Chinese jujube (Ziziphus jujuba Mill. var. inermis (Bunge) Rehd).*FoodChemistry*,*114*(2),547-552.

Xing, Y., Li, W., Jiang, Y., & Ding, Y. (2011). Antibacterial and Physical Properties of Poly(vinyl chloride)-based Film Coated with ZnO Nanoparticles. *Food Science And TechnologyInternational*,*16*(3),225-232.

Mehmood, C., Qazi, I., Baig, M., Arshad, M., & Quddos, A. (2015). Application of photodegraded polythene films for the treatment of Drimarene Brilliant Red (DBR) dye. *International Biodeterioration & Biodegradation*, *102*, 31-39.

Morones, J., Elechiguerra, J., Camacho, A., Holt, K., Kouri, J., RamÃ-rez, J., & Yacaman, M. (2005). The bactericidal effect of silver nanoparticles. *Nanotechnology*, *16*(10), 2346-2353. http://dx.doi.org/10.1088/0957-4484/16/10/059

Miller, R. (2012, August 28). Plastic Shopping Bags: An Analysis of Policy Instruments for Plastic Bag Reduction. Retrieved from http://dspace.library.uu.nl/handle/1874/253904

McHugh, T. H. (2016). Trends in antimicrobial food packaging systems: Emitting sachets and absorbent pads.FoodResearchInternational,83,60–73.

Othoni, V. Aggarwal, V, Bansal, S. Garg, S.P, and Chowdhary N (2016). Telephone mouthpiece as a possible source of hospital infection. J Assoc Physicians India. 46:372-373.

Odian, M.J., Fromm, K.M., Ashkarran, A.A., Jimenez de Aberasturi, D., Ruiz de Larramendi, I., Rojo, T., Serpooshan, V., Parak, W.J. and Mahmoudi, M.(2004). Antibacterial properties of nanoparticles. Trends in Biotechnology. 30(10): 499–511.

Rahman, M. S. (2007). Handbook of Food Preservation, Second Edition. (M. Shafiur Rahman, Ed.) (Vol. 20070849). CRC Press.

Rahman, M. S., Salman, Z., Kadim, I. T., Mothershaw, A., Al-Riziqi, M. H., Guizani, N., … Ali, A. (2005). Microbial and Physico-Chemical Characteristics of Dried Meat

Processed by Different Methods. International Journal of Food Engineering, 1(2) 499–511

Sachdeva, S., Sachdev, T. R., & Sachdeva, R. (2013). Increasing fruit and vegetable consumption: challenges and opportunities. Indian Journal of Community Medicine : Official Publication of Indian Association of Preventive & Social Medicine, 38(4), 192–7.

Sandeep, D., Kaur H, Gardner WG, and Treen LB, (2013). Bacterial contamination of hospital pagers. Infect. Control Hosp. Epidemiol :39 (4), 182–7.

Srikanth, P., Rajaram, E., Sudharsanam. S, Lakshmanam, A, Umamaheswari, S.S., and Kalyani,J., (2009). The mobile phone in a tropical setting- emergining threat for infection control. Sri Ram. *Journal of Medicine,* 2, 18-20.

Strini A, and Schiavi L. (2011). Low irradiance toluene degradation activity of a cementitious photocatalytic material measured at constant pollutant concentration by a successive approximation method. Appl Catal B Environ; 3:226–231.

Shahaby, A., Awad, N., El-Tarras, S. A. E, and Bahobial, A.S, (2012). African Journal of Biotechnology, 15896-15904.

Younas, H. (2011). Water disinfection using metal doped titania nanoparticles. MS Thesis, Institute of Environmental Sciences and Engineering, National University of Sciences and Technology, Islamabad, Pakistan.

Yao BD, Chan YF, Zhang XY, Zhang WF, Yan ZT, Wang N. (2003). Applied Physics Letters 82:281.