CHAPTER 1

INTRODUCTION

Packaging is an essential component in the complex distribution system which moves agricultural products from their point of origin to their point of consumption. Along with our culture, our packaging of food has become increasingly specialized and complex [1-4]. Food packaging has several functions other than its primary one of protection. Packaging protects food from microbial and other environmental contaminants and from damage during distribution. It also offers the consumer nutrition and ingredient information, cooking instructions, product weight, brand identification, and pricing. Packaging is the largest single market for plastics, amounting to over 12 million tons per year, about a quarter of the total U.S. plastics production. As per a report, the global food packaging market will attain sales of \$251.8bn in 2013 (http://www.marketwatch.com/story/global-food-packaging-market-2013-2023-2013-05- 08). With this huge market, the problem of its waste management is the need of the hour.

1.1 Types of polymer used in Packaging

The food packaging industry comprises almost a fifth of the net revenue of the plastic industry with the use of polyethylene terephthalate (PET), high-density polyethylene (HDPE), polyvinyl chloride (PVC), low-density polyethylene (LDPE), polypropylene (PP), and polystyrene (PS) as the main components of common food packaging plastics. These are synthetic polymers with hydrolysable functions, such as ester, amide and urethane, or polymers with carbon backbones, in which additives like antioxidants are added. A list of selected polymers used in food packaging is given in table 1.1.

Table 1.1: List of acceptable polymers for use in food packaging

1.2 Types of plastic degradation

Changes in polymer properties due to chemical, physical or biological reactions resulting in bond scissions and subsequent chemical transformations are known as polymer degradation [5-7]. Degradation reflects changes in material properties such as mechanical, optical or electrical characteristics in crazing, cracking, erosion, discoloration and phase separation [8]. Depending upon the nature of the process employed, polymer degradations have been classified as:

- \triangleright Photo-oxidative degradation,
- \triangleright Thermal degradation,
- \triangleright Ozone-induced degradation,
- \triangleright Mechanochemical degradation,
- \triangleright Catalytic degradation, and
- \triangleright Biodegradation.

1.2.1 Photo-oxidative degradation

Photo-oxidative degradation is the process of decomposition of the material by the action of light which is considered as one of the primary sources of damage exerted upon polymeric substrates at ambient conditions. Most of the synthetic polymers are susceptible to degradation initiated by UV and visible light. Normally the near-UV radiations (290-400 nm) in the sunlight determine the lifetime of polymeric materials in outdoor applications [9]. Polymer degradation occurs mainly in the ether parts of the softsegments, where photo-irradiation generates ester, aldehyde, formate and propyl end groups [10]. UV radiations have sufficient energy to cleave C-C bond [9]. The most damaging UV wavelength for a specific plastic depends on the bonds present and the maximum degradation therefore occurs at different wavelengths for different types of plastics, e.g. it is around 300 nm for polyethylene (PE) and around 370 nm for polypropylene (PP). Photodegradation changes the physical and optical properties of the plastic. The most damaging effects are:

- \triangleright Visual effect (yellowing),
- \triangleright Loss of mechanical properties of the polymers,
- \triangleright Changes in molecular weight, and
- \triangleright Molecular weight distribution.

PE and PP films when exposed to solar UV radiation readily lose their extensibility, mechanical integrity and strength along with decrease in their average molecular weight. Mechanical integrity of polystyrene (PS) is diminished through extensive chain scission during photo degradation. At any given temperature and moisture content the rate of weathering increases with an increase in UV flux. Tensile stressing of stabilized types of PP in thermo-oxidative and photo-oxidative environment has accelerated embrittlement of the polymers [9]. In one study, tensile stress has been applied at constant load (in the range of 0 to 6.86 MN/m²) to observe the behavior of stabilized and unstabilized types of isotactic PP in the course of thermo-oxidative aging at 80-130 $^{\circ}$ C, photooxidative aging at 45 \degree C and relative humidity of 65%. From kinetic evaluation of the temperaturedependence of weight changes of unstabilized PP during thermo-oxidative aging, it has been found that the weight losses of unstressed and tension-stressed specimens have obeyed the kinetic equations for a reaction of the first order [11]. Along with stress,

introduction of carbonyl group on polymeric backbone has also accelerated photochemical degradation. PS undergoes photochemical ring-opening reactions, which leads to backbone cleavage by subsequent Norrish Type II reactivity.

(a) Mechanism of photo degradation

The mechanisms of the degradation and oxidation reactions are determined by the extraneous groups and/or impurities in the polymer, which absorb light quanta and form excited states. Initially short-lived singlet state is transformed to long-lived triplet state [12]. Excited triplet states may cleave the polymer chains and form radical pairs (Norrish Type I reaction) or form pairs of saturated and unsaturated chain ends by hydrogen transfer (Norrish Type II reaction) [13]. The polymer radicals thus formed may add molecular oxygen (in triplet ground state) to peroxy radicals, which abstract hydrogen and form hydro peroxide groups, which absorb UV light or become excited by energy transfer, the weak O-O bonds break and pairs of alkoxy and hydroxyl radicals are formed which may react in various ways, e.g. by hydrogen abstraction, chain scission, rearrangement, etc. and accelerate photo degradation [14]. Double bonds may add excited oxygen molecules in singlet state. In this reaction, the double bond is shifted to an adjacent C-C bond and a hydro peroxide group is formed. Some synthetic polymers, e.g. aromatic polyesters and polyamides, have inherent absorption of UV light, causing excitation, radical formation, oxygen addition, splitting off small molecules, chain scission, etc. Some of these polymers are auto-stabilized towards photo degradation by formation of an oxidized surface layer with high absorption of near UV and visible light of short wavelengths, preventing further penetration of light into deeper layers. In photooxidative degradation, mechanism involves auto oxidation cycle comprising various steps shown in Scheme 1.1

Scheme 1.1

Initiation

The absorption of UV light that has sufficient energy to break the chemical bonds in the main polymer chain leads to the initiation of mechanism responsible for polymer degradation. It involves a radical chain mechanism for the formation of initial radical. Different initiation steps under varied conditions have been undertaken in different polymers. Bond dissociation energy of C-C bond (375 kJ/mol) and C-H bond (420 kJ/mol) is equivalent to UV radiation of 320 nm and 290 nm. Thus, direct photolysis of C-C and C-H bond is possible and the radical formed in these reactions become a source of initiation radicals as shown in Scheme 1.2 [15].

Scheme 1.2

Catalyst residues as source of generation of radicals

Some metal salts and oxidation products of such residues when added to the polymers act as catalysts to generate initiation radicals [16]. Polymerization catalysts such as transition metals (Ti) may remain in polyolefins at 2-100 ppm, depending on workup and catalyst efficiency. These residues have been implicated in both photo- and thermal stability problems. For example, $TiO₂$ is a well-known photo sensitizer for polyamide and polyolefin degradation and absorbs at 480 nm. Photosensitization involves the formation of highly reactive species including atomic oxygen, -OH , -OOH and O_2 . The primary process involves the promotion of the Ti electron to the conduction band of the semiconductor to form an electron-positive hole pair. The relative proportions of the reactive species depend on the presence of water. No $TiO₂$ sensitization will be observed unless both oxygen and water are present.

Incorporation of carbonyl groups

Carbonyl groups formed by mild oxidation of polymer during synthesis or processing act as chromophores and become source of the initiation radicals. Carbonyl chromophore absorbs near-UV radiations and subsequently forms radicals following Norrish Type I, Norrish Type II and H-atom abstraction processes (Scheme 1.3) [17].

Scheme 1.3

Introduction of peroxides or site of unsaturation

The peroxides or C=C sites become source of initiation radicals as shown in Scheme 1.4 [18]. The near UV component of sunlight (280-390 nm) is energetic enough to cleave C-C bond and C-heteroatom bonds provided that light of the appropriate wavelength is absorbed. Chain oxidation occurs in most of the polymers because of the labile O-O bond present in the macrohydroperoxide C-OOH, the macroalkoxyl and hydroxyl radicals thus formed may abstract hydrogen from the surrounding polymer matrix to generate alcohol, water and new macroalkyl radicals which can then take part in many cycles of the chain-initiation reactions. In the case of unsaturated polymers, light generated singlet oxygen ${}^{1}O_{2}$ reacts with an unsaturated site by way of an "ene" reaction and starts chain oxidation [17].

Scheme 1.4

Propagation

The propagating reactions of auto-oxidation cycle are common to all carbon backbone polymers. These reactions lead to generation of hydro peroxide species and are not directly led to backbone cleavage but are the key intermediates to further reactions as shown in Scheme 1.1. Hydro peroxide species generated in propagating step lead to backbone degradation through cleavage of hydro peroxide O-O bond followed by βscission (Scheme 1.5). Polymer backbone cleavage occurs through Norrish Type I and II reactions of chromophores (carbonyl) following β-scission route, which is a prevailing route for photo-oxidative degradation. In semi-crystalline polymers, this scission occurs in the amorphous domains. The scission process generates two chain ends that are free to restructure, and can often lead to increase in crystallinity as oxidative degradation proceeds [9, 17]. PS undergoes photo-oxidative bulk degradation *via* two steps:

- a) Formation of hydro peroxide and
- b) Decomposition of these hydro peroxides

Such oxidative reactions are initiated when hydrogen is removed through a photoreaction.

The free radical formed on polystyrene reacts with oxygen to form proxy radical, which can abstract a proton from some other labile positions, thereby forming hydro peroxides and a new radical site. The newly formed hydro peroxide group is subjected to decomposition and resulting ultimately in chain cleavage into ketones and olefins [19].

Scheme 1.5

Termination

The termination of photo degradation is achieved by 'mopping up' the free radicals to create inert products. This occurs naturally by combining free radicals or assisted by using stabilizers in the plastic Macro alkyl radicals may combine to give a cross linked, branched or disproportionate product. Peroxyl radicals eventually terminate by reaction with other radicals to give dialkyl peroxides, carbonyl species or alcohols [8, 17].

(b) Methods for photo degradation

Natural weathering method

Outdoor exposure can be performed on samples mounted on testing racks, oriented under standard conditions to expose the material to the full radiation spectrum besides the temperature and humidity of that location [12]. In order to observe the aging of the material, it is characterized with respect to mechanical properties (elongation at break, tensile properties or impact strength) and visible characteristics, such as crack formation, chalking, and changes in color [18]. The alterations in the polymeric materials on exposure can be characterized with FTIR spectroscopy and ultra violet/visible (UV/vis) spectroscopy [9].

Artificial weathering method/laboratory test

Pure laboratory testing involves using environmental chambers and artificial light sources to approximately replicate outdoor conditions but with a greatly reduced test time under highly controlled conditions. Laboratory testing can quickly assess the relative stability of plastics but has the major disadvantage that the quicker the test lowers is the correlation to real behavior in the field [20, 21].

1.2.2 Biodegradation

Biodegradation is a biochemical transformation of compounds in mineralization by microorganisms [22, 23]. Abiotic hydrolysis, photo-oxidation and physical disintegration of polymers may enhance biodegradation of polymers by increasing their surface area for microbial colonization or by reducing molecular weight [24]. According to ASTM standard D-5488-94d biodegradation is defined as ''process which is capable of decomposition of materials into carbon dioxide, methane, water, inorganic compounds, or biomass in which the predominant mechanism is the enzymatic action of microorganisms, that can be measured by standard tests, in a specified period of time, reflecting available disposal conditions'' [23]. This method is governed by different factors:

- \triangleright Characteristics of polymer,
- \triangleright Type of organism, and
- \triangleright Nature of pretreatment.

Biodegradation can occur at different structural levels, i.e. molecular, macromolecular, microscopic and macroscopic depending upon the mechanism [25]. It has been argued that the phenomenon of degradation *in vivo* might not be equated with the term biodegradation, since biodegradation implies the active participation of biological entities such as enzymes or organisms in the degradation process [23]. It is, however, difficult to identify the involvement and the role of biological species *in vivo* degradation. Polymer molecules may, but not necessarily breakdown to produce fragments in this process, but the integrity of the material decreases in this type of process [26]. A general mechanism for polymer degradation is given in figure 1[27, 28].

Figure 1 A general mechanism for polymer degradation

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1.2.3 Methods for Biodegradation

There are wide varieties of methods currently available for biodegradation of polymers. Some are well developed and some are at the initial research stages.

1.2.3.1 Soil burial method

Soil burial method is one of the frequently used methods for the determination of biodegradability of plastic [29]. In this method, biodegradation test is performed under natural conditions or laboratory conditions. Sample with definite weight and dimension is buried in specific depth in the soil for different time intervals. After a specified time, sample is taken out of soil, thoroughly rinsed with distilled water following immersion in distilled water and after that dried at 50 $^{\circ}$ C, for 24 h in a vacuum oven. Sample is allowed to equilibrate to ambient temperature and humidity for at least 24 h before measurement. In one study starche plastic films buried in a forest soil have developed rapid colonization (15 days later) by fungal hyphae and showed degradation of the starch granules on the films [9].

1.2.3.2 Pure culture method.

In pure culture method, specific bacteria and fungi can be applied for degradation of polymers [30]. In laboratory conditions, isolated microorganism strain has been allowed for sufficient growth in different nutrient media. In pure culture method, preweighed disinfected films are aseptically added to sterilized culture medium and films in culture medium are incubated with shaking for 24 h before inoculation to ensure asepsis. Culture medium is inoculated with spores from a specific microorganism and is incubated with shaking at 125 rpm for 4 weeks at optimal growth temperature for the selected microorganism. Four replicates are prepared for each different pretreated film. The sample is weighed after washing with 70% ethanol and drying at 45 \degree C until equilibrated. Each of the different films is then compared with the corresponding uncultured material. The presence of microbes can be confirmed by using a microscope.

1.2.3.3 Compost method

In this method, the definite weight of the dry plastic is subjected to the mixture of definite amount of mature compost and then incubated at $58\,^{\circ}$ C, with maintained moisture content at 65% [31]. Biodegradation is measured based on the amount of material carbon converted to gaseous carbon dioxide. Nature of compost affects the degree of degradation.

1.2.4 Factors affecting Polymer Degradation

In general, the degradation process affects the thermal stability, mechanical properties, crystallinity and lamellar thickness distribution and begins in the amorphous/crystalline interface. Degradations of plastic are affected by various factors.

(i) Chemical composition

Chemical composition of the polymers plays a very important role in their degradation. Presence of only long carbon chains in the thermoplastic polyolefins makes these polymers non-susceptible to degradation by microorganisms. By the incorporation of the heterogroups such as oxygen in polymer chain makes polymers labile for thermal degradation and biodegradation [32].

(ii) Molecular weight

Increase in molecular weight of the plastic decreases the rate of plastic degradation [33]. It has been reported that some microorganisms utilize polyolefins with low molecular weight faster as compared to high molecular weight polyolefins.

(iii) Hydrophobic character

Petrochemical-based plastic materials are not easily degraded in the environment because of their hydrophobic character and three-dimensional structure. Hydrophobicity of PE interferes with the formation of a microbial bio-film, thus decreases the extent of biodegradation [34].

(iv) Size of the molecules

Size of the molecules in the polymers affects their mechanical degradation, thermal degradation and biodegradation. These degradations increase as the size of the molecule decreases [32].

(v) Introduction of functionality

Introduction of carbonyl groups in polyolefins makes these polymers susceptible to photo degradation. As the number of chromophores increases the rate of photo degradation increases due to the more sites, which are available to absorb more photons and to initiate the reaction for degradation [35].

(vi) Additives

Non-polymeric impurities such as residues of polymerization catalysts, transformation products of additives, fillers or pigments affect the resistance to degradation [36]. It reported that the thermal stability slightly decreases and the ash content increases when the ligno-cellulosic filler loading increases in the sample.

(vii) Chemical bonding

Linkage affects the degree of degradation in plastic. In thermoplastic, head-tohead addition of monomer units and tail-to-tail addition of monomer units during addition polymerization create weak points which make the plastic susceptible for degradation [37].

(viii) Methods of synthesis

Methods of synthesis show the noteworthy effect on the stability of the polymers [38]. For example, anionic polymerized PS showed more photo-stability than free radically formed polymer due to the presence of peroxide residue in the latter, which is labile for photo degradation.

(ix) Effect of stress

Stress has significant effect on polymer degradation. Tensile stress increases the rate of photo degradation whereas compressive stress retards the photo degradation rate [38].

CHAPTER 2

EXPERIMENTAL

2.1 Materials

The plastic used in this study was collected from the local milk vendors. As per literature, the sample was a thin clear film of LDPE (Low density polyethylene). The physical properties of LDPE are given in table 2.1.

| S. No. | Properties | Value | Units |
|---------------|--------------------|-------------|------------------------|
| | Tensile strength | 18 | MPa (Psi) |
| \mathcal{D} | Density | 0.920-0.922 | g/cm ³ |
| 3 | Melt index | $1.8 - 2.4$ | G 10 min^{-1} |
| 4 | Avg. molecular wt. | 80,000 | Dalton |

Table 2.1: Physical properties of LDPE packaged film

The milk packets were cut into required shape and were thoroughly washed with water. The sample was dried at normal room temperature and subjected to various degradation processes.

2.2 Methodology

2.2.1 Photo degradation method

In this method, samples were put on the clear glass tightly clamped with cello tape and put them in sun light. Outdoor exposure can be performed on samples mounted on testing racks, oriented under standard conditions to expose the material to the full radiation spectrum besides the temperature and humidity of that location. In order to observe the aging of the material, it is characterized with respect to mechanical properties (elongation at break, tensile properties or impact strength) and visible characteristics, such as crack formation, chalking, and changes in color.

2.2.2 Soil Burial method

Soil burial method is one of the frequently used methods for the determination of biodegradability of plastic. In this method, biodegradation test is performed under natural conditions or laboratory conditions. Sample with definite weight and dimension is buried in specific depth in the soil for different time intervals. After a specified time, sample is taken out of soil, thoroughly rinsed with distilled water following immersion in distilled water and after that dried at 50 $^{\circ}$ C for 24 h in a vacuum oven. Sample is allowed to equilibrate to ambient temperature and humidity for at least 24 h before measurement.

2.2.3 Compost method

The composting was done under controlled conditions in thermal insulated composting chamber using a standard mixture of manure obtained from local villagers. The packaging film was taken in small stainless steel container and buried in compost pile for 2 weeks; 4 weeks and 6 weeks. During the initial days, the pile temperature was around $55-60$ °C.

CHAPTER 3

RESULTS AND DISCUSSION

The boom in the organized retail is going to be a sea change in the way milk is sold in India. With milk consumption increasing, the increase in waste packaging films also alarming. The degradation of these waste milk packaging films has been done by three methods:

- (i) Photo degradation method
- (ii) Soil Burial method
- (iii) Compost method

In this study, we choose the LDPE milk polymeric films for study. The study was carried out for 6 weeks. Figure $2(a)$ shows the degradation process under light (photo degradation) and figure 2(b) shows the degradation process by soil burial method. Figure 3 shows the compost method of polymer degradation. As a result of this there was a change in the mechanical properties of the films due to degradation which can be seen from the analytical data.

3.1 Mechanical Properties of films

The mechanical properties of thin polymer films are of primary importance. In the present study, the effect of soil and photo degradation on the mechanical properties of the films like - Tensile strength, Elongation at break and tensile modulus etc. are studied. The tensile tests were performed on LDPE films according to ASTM 882-85 using a materials testing machine (Model JRI-TT25). Films of 100 mm length and 10 mm width were cut out from the exposed films and subjected to a crosshead speed of 100 mm/min.

 Figure 2 (a) Photographs showing the pre-cut LDPE samples as used in the photo degradation experiment; (b) LDPE samples as used in the soil Burial method (arrow).

Figure 3 Compost degraded polymeric films

The tests were undertaken in an air-conditioned environment at 20 $\,^{\circ}\text{C}$ and a relative humidity of 65%. Different samples were tested for each experiment and the average value has been reported (Figure 3). The comparative studies of these samples are summarized in table 3.1 and figure 8. From the values obtained we conclude that the mechanical properties of the samples changes. We can observe that there is a sharp decreases in the Tensile strength in the photo-degraded film as compared to soil degraded film.

Figure 4 Stress-strain curve for Virgin LDPE (Milk packaging) film

Figure 5 Stress-Strain curve for soil Bio-degraded LDPE Milk packaging film

Figure 6 Stress-Strain curve for Photo-degraded LDPE Milk packaging film

Figure 7 Stress-Strain curve for Compost LDPE Milk packaging film

Table 3.1: Comparison between various Mechanical Properties of different LDPE Milk

packaging films

Figure 8 Comparison of Mechanical Properties

3.2 Scanning electron microscopy

A scanning electron microscope (SEM) is a type of electron microscope that produces images of a sample by scanning it with a focused beam of electron. The electrons interact with atoms in the sample, producing various signals that can be detected and that contain information about the sample's surface topography and composition. The electron beam is generally scanned in a raster scan pattern, and the beam's position is combined with the detected signal to produce an image. SEM can achieve resolution better than 1 nanometer. Specimens can be observed in high vacuum, in low vacuum, and (in environmental SEM) in wet conditions.

Figure 9 (a & b): Micrographs showing the surface morphology of soil degraded films after 6 weeks of exposure

Figure 10(a & b): Micrographs showing the surface morphology of compost degraded

films after 6 weeks of exposure

The SEM micrographs of the samples exposed in soil for 6 weeks and samples exposed in compost for 6 weeks are shown in Figures 9 and 10. In case of soil degrade films, the surface of the sample was found to be finely granular and homogenous sheet in appearance as compared to compost method at 40μ magnification. After 6 weeks, exfoliation, peeling and holes in the film structure were observed. Peeling and loosening of the film were more pronounced in films exposed *via* Compost method (Figure 10). After 6 weeks, fractures on the surface are seen even though a considerable portion of the film was found to be unaffected. At the end of the study the clusters and formation of cracks were evident. Longer soil exposure of this sample would lead to its further deterioration into disintegration. The destructive process of degradation was very prominent in compost degraded films. Loss of integrity of LDPE network after 6 weeks resulted into very rough and fragile surface. Figure 10(b) reveals complete destruction of film caused by microbial erosion. Compared to the soil burial film exposed for 6 weeks in soil showed non-preferential colonization and perforations, which progress with time and loosen the network as seen after 6 weeks.

CHAPTER 4

CONCLUSION AND FUTURE PROSPECTS

4.1 Conclusion

Food safety including milk is a growing concern among consumers. Standards and specifications for milk packaging have played a vital role in putting the milk packaging industry on a sound footing in globalised markets. Plastics have been the ideal material for milk packaging. Concerns on environmental waste problems caused by nonbiodegradable petrochemical-based plastic packaging materials as well as the consumer's demand for high quality food products has caused an increasing interest in developing degradation process.

- a. The present study deals with the various degradation methods of milk packet LDPE films. Plastic sample was collected from retail market and dumped in soil of hostel garden for soil burial test, Tin plates were used for natural weathering method and manure were used for compost method.
- b. When the total biodegradation process of any organic substrate is considered the formation of microbial colony is critical to the initiation of biodegradation. Thus, the duration of the microbial colonization is an important factor that effects total degradation period as shown in SEM micrographs.
- c. Compost method is more efficient method of polymer degradation compare to natural weathering and soil burial as shown in the mechanical properties graphs.

4.2 Future Prospects

The status of polythene pollution is increasing worldwide. The awareness campaign of the polythene pollution is the need of the hour and also development of industrial viable process for their degradation.

The present study must be continued keeping the focus on following points.

- \triangleright The microbes responsible for the degradation of polythene should be isolated from all the sources, screened to know the efficient isolates. The efficient microbes are needed to characterize at molecular level.
- \triangleright Once the genes responsible for the degradation of polythene would be known, the genes would be used to enhance the polythene degrading capacity of the other easily available microbes. After field trials, the most efficient polythene degrading microbes should be multiplied at large scale to decompose the polythene at commercial level.
- \triangleright Other studies like-XRD Analysis, FTIR & TGA must be conducted further.

CHAPTER 5

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