EFFECT OF IONIZING IRRADIATION TECHNIQUES ON BIODEGRADABLE PACKAGING MATERIALS

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ABSTRACT

EFFECT OF IONIZING IRRADIATION TECHNIQUES ON BIODEGRADABLE PACKAGING MATERIALS

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Ionizing irradiation has developed as a package sterilization technology, which may be an alternative to other current sterilization methods. This is because of its efficiency in reducing foodborne pathogen levels without leaving residual chemicals. In the use of irradiation sterilization either prior to or after filling, the packaging material is directly exposed to radiation. Irradiation has been known to alter the properties of polymeric packaging materials. The exposure causes changes in material properties and may produce by-products.

Biodegradable packaging materials have received more attention in the current marketplace in order to reduce the packaging waste in the landfill. Polylactic acid (PLA) and cellophane, derived from renewable sources, have become well-known as green packaging materials in today's markets for foods and pharmaceuticals. However, knowledge about the effects of ionizing radiation on these biodegradable materials is still scarce and. In this study, the effects of three common irradiation types (X-ray, gamma, and electron beam irradiation) on properties of PLA and cellophane were studied. The physical, chemical, thermal, mechanical, and barrier properties of irradiated samples at absorbed doses of 1 to 30 kGy after storage times of up to 9 months were determined and compared to non-irradiated samples. The effect of irradiation on the migration from PLA and cellophane films into liquid food simulants was

also investigated. Furthermore, the biodegradation of irradiated biomaterials also was investigated.

The physical, chemical, thermal, and mechanical properties were affected by X-ray, gamma and electron beam irradiation as a function of irradiation dose and storage time. A significant decrease in molecular weight of PLA indicated the degradation of the polymer by irradiation. Irradiation induced a change in polymer properties due to the predominance of chain scission. Ionizing radiation decreased the water vapor permeability of PLA and nitrocellulose-coated cellophane, while PVdC-coated cellophane was not sensitive to irradiation. In the study of food and packaging interaction, overall migration of PLA into food simulants increased with absorbed dose. but remained below the limit set by EU regulations. Overall migration from nitrocellulose-coated cellophane and PVdC-coated cellophane was higher in 95% ethanol. Biodegradation of PLA was influenced by ionizing radiation. Aging irradiated PLA had some potential to increase the biodegradation rate. Non-irradiated and irradiated PLA films can be considered as biodegradable plastics with greater than 60% mineralization as required by ASTM D6400 and ISO 14855-1. The results of the biodegradation study showed that the non-irradiated and irradiated uncoated cellophane qualified as a biodegradable plastic while nitrocellulose-coated cellophane and PVdC-coated cellophane films with and without irradiation treatments showed potential to be considered biodegradable. The results from this dissertation indicated that commercial PLA and three cellophane films were suitable for packaging applications after irradiation treatment.

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Chapter 1

Introduction

1.1 Introduction and rationale

Plastics are a primary packaging material for food and pharmaceutical products. Most plastics currently used are non-renewable packaging materials (petroleum-based materials), which remain as packaging waste in the landfill as the most common end of lifetime scenario. Bio-based biodegradable materials have been developed in order to reduce the use of non-renewable materials, and to save the limited landfill space, which is gradually decreasing. Polylactic acid (PLA) and cellophane are two of the most well known biodegradable materials used as “green” packaging and a sustainable alternative to petroleum-based polymers.

Polylactic acid (PLA) is a biodegradable polymer that is also biocompatible. PLA is a linear aliphatic thermoplastic polyester obtained by ring-opening polymerization of lactic acid, a fermentation product available from the conversion of dextrose, which is derived from renewable resources such as corn, sugar beets, rice, sugarcane, wheat and sweet potato (Auras et al., 2004; Vink et al., 2003). The fermentation of carbohydrates can produce lactic acid, which is a basic constituent of PLA. Lactide dimers exist in three different forms: L,L-lactide (called L-lactide), D,D-lactide (called D-lactide) and L,D-lactide or D,L-lactide (called meso-lactide) (Kim-Kang & Gilbert, 1991). PLA properties depend on the ratio of the L- to the D-isomer of lactic acid (Auras et al., 2003). Commercial PLA grades are generally copolymers of PLLA and PDLA (Martin &

Averous, 2001). PLA is a unique polymer since it behaves like both polyethylene terephthalate (PET) and polypropylene (PP). Moreover, its ability to be stress crystallized, thermally crystallized, impact modified, filled, copolymerized and processed in many types of polymer processing equipment allow PLA to have a broad range of applications (Henton et al., 2005; Mahalik & Nambiar, 2010).

Cellophane or regenerated cellulose film (RCF) is another well-known biodegradable material. Cellulose films are produced from sustainable wood pulp, which is converted to a thick liquid (called viscose). The viscose is converted back to smaller cellulose molecules, which restores its biodegradability. Celluloid was developed as the first thermoplastic polymer material and later it was transformed into a commercial form as cellophane® or Transparit® which was the first transparent packaging material (Brydson, 1989; Simon et al., 1998). PLA and cellophane are currently used in applications such as packages for fresh produce, snacks, and several food and pharmaceutical products, which might use irradiation for treatment.

Ionizing radiation was discovered by a French scientist and began to be used for food preservation in the early 1920s. However, the radiation technology was not accepted in the United States until World War II (Andress et al., 1998). In the 1950-1960s, the United States Army became interested in the feasibility of food irradiation and conducted research with fruits, vegetables, dairy products, fish and meats (Diehl, 1995). This technology was continuously viewed with suspicion and there were concerns from public health organizations about the safety of products (WHO, 2007; WHO, 1997). As outbreaks of foodborne pathogens and diseases continue to increase

and become major public health problems worldwide, effective novel strategies are being developed to prevent foodborne illness. Radiation has been considered as a sterilization method to ensure the hygienic quality of food products. Irradiation of fruits, vegetables and grains was approved in the U.S. in 1986 (Ozen & Floros, 2001). In 1997, the use of ionizing radiation was approved by the U.S. Food and Drug Administration (FDA) to inactivate pathogenic bacteria in red meat (Sommers & Fan, 2006). This regulation increased interest and led to several research studies on a variety of food irradiation applications (Morehouse & Komolprasert, 2004). The use of irradiation for foods and pharmaceuticals is increasing in the United States and more than 40 other countries (Ozen & Floros, 2001).

At present, radiation has been used in two different ways: 1) sterilization of packaging materials for aseptic and pharmaceutical products (Demertzis et al., 1999) such as an aseptic bag-in-box packaging system (Ansari & Datta, 2003; Nelson, 1984), and 2) radiation processing for pre-packed food. In aseptic packaging, a sterile product is filled in a sterile package under a microbiologically controlled environment. For food irradiation, the packaging material and the food, which is prepackaged to avoid recontamination from microorganisms, are irradiated simultaneously (Chuaqui-Offermanns, 1989). During either process, packaging materials are exposed to radiation. The interaction between irradiated materials and products as well as the integrity of the packaging materials, hence, leads to a safety concern.

Gamma (γ) radiation (including Cobalt-60 (^{60}Co) and Cesium -137 (^{137}Cs)), electron beam (E-beam) and X-ray are types of ionizing radiation that have been

authorized by the US Food and Drug Administration (FDA) to be used in sterilization processes for food and pharmaceutical packaging materials (FDA, 2001). Guidelines on maximum irradiation dose, an important factor to achieve sterility, are defined for various categories of foods by FDA regulations under Title 21 of Code of Federal Regulations (CFR) 179.26 (FDA, 2005).

Even though irradiation is a very effective sterilizing method, ionizing radiation is known to cause ionization, which is a process in which one or more orbital electrons are removed from a neutral atom (Urbain, 1986). Ionizing radiation leads to two competing reactions in polymers: chain scission and cross-linking, which can cause the formation of low-molecular weight radiolysis products (RPs) and a decrease in residual oligomers, respectively. These reactions can also cause changes in polymer properties (Buchalla et al., 1993a; Goldman et al., 1996; Gorna & Gogolewski, 2003; Goulas et al., 2002). Irradiation-induced changes in polymers depend on the type of irradiation, radiation energy level, irradiation dose, irradiation conditions, chemical structure of the polymer and polymer additives (Buchalla et al., 1993a; Clough, 2001; Clough & Shalaby, 1991). Due to the public heath significance of products such as food and pharmaceuticals, it is important to understand the influence of irradiation on packaging materials and their migration behavior. The determination of migration from food contact materials for each food type is difficult to conduct due to the complexity of food matrices and the low concentration of substances migrating into foods (McCort-Tipton & Pesselman, 2000). The United States (US) and the European Union (EU) regulations have established the use of food-simulating liquids (FSL) for migration tests (Jeanfils, 1996). Food-simulating solvents, test media imitating food, for a packaging material test are selected to be

representative of the enormous range of food products (Thompson et al., 1997) and are based on regulations of each country (McCort-Tipton & Pesselman, 2000). For the EU, the lists of food simulants and specific test conditions to be applied to migration experiments for each simulant are described in detail in Directive 93/8/EEC (EEC, 1993). The U S congress granted authority to the FDA to regulate the components of food contact materials with two acts: Food Additives Amendment to the Federal Food, Drug, and Cosmetic Act (FFDCA) and National Environmental Policy Act (NEPA). Food simulants, which are recommended for migration tests, are defined in Title 21 CFR 176.170 (FDA, 2002). In addition, the articles of food contact substances (FCS) is codified in Title 21 CFR 171 for the food additive petition (FAP) process, 21 CFR 170.39 for threshold of regulation (TOR) exemption and 21 CFR 170.100 for and effective food contact notification (FCN) (Bailey et al., 2008).

When irradiating biodegradable packages, it is important to understand the effects of ionizing radiation on the materials. Numerous studies on irradiation of polymeric packaging materials, however, have been mostly performed on non-biodegradable materials (Clough & Shalaby, 1991; Goulas et al., 2004; Pentimalli et al., 2000; Rojas De Gante & Pascat, 1990; Varsanyi, 1975; Woo & Sandford, 2002; Zhang et al., 1992). Knowledge about the effects of irradiation on these biodegradable materials, including physical, chemical, and toxicological properties after treatment, is much needed.

Hence, the overall goal of this research was to study the effects of different sources of commercial ionizing radiation (gamma, E-beam irradiation and X-ray) on PLA

and three different types of cellophane films including uncoated cellophane, nitrocellulose-coated cellophane and polyvinylidene chloride (PVdC)-coated cellophane, as a function of irradiation dose and storage time. This dissertation is divided into 4 studies. In study 1 (chapter 4), the effect of gamma and electron beam irradiation on the property changes of PLA and cellophane films was investigated. The food safety concerns from irradiated polymeric packaging materials directly contacting foods led to the migration study. Study 2 (chapter 5) examines the overall migration from commercial PLA and cellophane films, irradiated by gamma and electron beam irradiation, into liquid food simulants. This work helped to understand migration behavior from packaging material into foods. The goal of study 3 (chapter 6) was to evaluate the biodegradation of irradiated PLA and cellophane films. Lastly, the properties of X-ray irradiated PLA and cellophane films with different radiation intensities and as a function of storage time were assessed in chapter 7.

Chapter 2

Literature Review

2.1 Plastic sterilization

Increasingly, plastics are the main packaging material for numerous applications, especially in food and medical packaging, due to their light weight and performance characteristics which meet the demands in many applications (Selke et al., 2004). Foodborne disease is a serious worldwide public health problem. The major cause of foodborne illness is from foodborne pathogens in various foods such as Salmonella (eggs, poultry and other meats, raw milk and chocolate), Campylobacter (raw milk, raw or undercooked poultry and drinking water), enterohaemorrhagic *Escherichia coli*, especially *E. coli* O157:H7 (beef, fresh fruits, and vegetables) and cholera (water, rice, vegetables, and seafood) (WHO, 2007). To ensure food safety, proper pasteurization or sterilization of foods and packaging materials is needed. In the field of medicine, plastics are used as materials for medical devices or carriers for pharmaceutical products and hence they must also be sterilized for safety.

Microbial contamination of packaging materials is usually low. This might be because of the protection of layers in the roll stock. Also, there is seasonal variation of the microbial load in packaging material (Buchner, 1993). To reduce the risk of pathogenic microorganisms such as bacteria and fungi, sterilization has been used as a process to eliminate the harmful microorganisms. The most important characteristics for sterilization of packaging material are the ability to inactivate microorganisms rapidly on a high speed packaging line, ease of removal of the sterilization agent from treated

material surfaces, ease of operation and control, and no adverse influence on product quality (Toledo, 1988; Wakabayashi, 1993). Another challenge for packaging sterilization is maintaining the stability of packaging materials in order to protect the product during and after the sterilization process (Massey, 2005).

In packaging sterilization for aseptic packaging, the decimal reduction time (D-value), which is the time required to kill 90% of the microbial population at a constant temperature and under specified conditions (Devidson & Weiss, 2003), is important for the process design. To achieve successful sterilization for aseptic packaging of aseptic products, low D-values are required due to continuous processing, which means there is not much time available for sterilization (Reuter, 1993).

The required lethality for commercial sterility is determined by the type of product. For low acid products (pH > 4.5), a minimum of six decimal reductions (6D) in bacterial spores is required. For high acid products (pH < 4.5), a four decimal reduction (4D) is required. If there is the possibility of the growth of *Clostridium botulinum* (C. botulinum) in products, a 12 decimal reduction process (12 D-value) is required (Buchner, 1993; Robertson, 2006 ; Sandeep & Simunovic, 2006). Commercial sterilization processes for packaging are summarized in Table 2.1.

Table 2.1 Commercial sterilization processes for packaging materials adapted from Reuter (1993)

Sterilization process	Decimal reduction (D-value)
Thermal sterilization	
Heating with saturated steam (plastic cup)	6
Heating with over-heated steam (tin cans)	5-6
Heating with hot air	3
Heating with mixtures of hot air or steam (plastic cups)	3-4
Heating by extrusion	4
Chemical sterilization	
Hydrogen peroxide (20-35% solution)	5-6
- Dipping bath process	
- Spraying process	
- Rinsing process	
Peracetic Acid (PAA) (0.1-1%)	n/a
Irradiation sterilization	
Gamma (γ) irradiation (big bag)	6
UV-irradiation (wave length λ = 254 nm)	2-3
Infrared irradiation (wave length λ = 0.8-15 $\times$ 10^{-6} nm)	2-3

2.2 Sterilization techniques

Sterilization of packaging materials is an important concern especially for aseptic foods and pharmaceuticals. The three main sterilization techniques for packaging materials commonly used for foods and pharmaceuticals involve heat, chemical, or irradiation sterilization (Robertson, 2006).

2.2.1. Heat sterilization

Heat sterilization is the traditional process used to inactivate microorganisms. Sterilization by heat can involve either moist heat (steam) or dry heat. In general, the time for heat sterilization will depend on the resistance of the target microorganism.

2.2.1.1 Moist heat/steam

Moist heat (steam) sterilization uses water or saturated steam with no air or other gases present. This process can be applied to sterilize packaging materials used for low acid foods since steam is sporicidal at temperatures above the boiling point of water. Moist heat sterilization is generally conducted in a pressurized chamber or autoclave at a temperature of 121ºC. Moist heat is more effective compared to dry heat; however, it is not a suitable sterilant when paper-based packaging materials are used (Toledo, 1988). The target microorganism in this environment is *Bacillus stearothermophilus* (1518) as presented in Table 2.2.

2.2.1.2 Dry heat

Dry heat sterilization uses superheated steam or hot air (Robertson, 2006 ; Toledo, 1988). This technique requires higher temperatures (160ºC-170ºC) and longer exposure than moist heat. This is because moist heat has higher sporicidal properties than dry heat. The thermal transfer rate is faster in moist heat due to the presence of water molecules, whereas dry hot air is not as conductive as moist steam. The slower heat transfer rate in dry hot air requires more time for microbial kill as compared to moist heat. For example, at the same level of sporicidal effectiveness (microbial reduction), moist heat sterilization requires 121°C for 20 min while dry heat sterilization requires 170°C for 60 min (Buchner, 1993; Massey, 2005; Robertson, 2006). *Bacillus polymyxa* is a test organism for dry heat sterilization (Table 2.2).

Due to its operation without water, hot air is preferred over superheated steam for sterilization of paper-based packaging materials (Toledo, 1988). The main limitation of hot air is the high temperature needed to sterilize, especially for aseptic packaging materials and low acid foods. The temperature required may be beyond the capability of most polymeric packaging materials to withstand and can damage the properties of heat-sensitive materials.

Table 2.2 Indicator organisms most commonly used for verification of sterilization (Bernard et al., 1990; Gill, 1990)

Sterilization medium	**Organism**
Superheated steam	*Bacillus stearothermophilus* (strain1518)
Dry heat	*Bacillus polymyxa* (PSO)
H_2O_2 + heat (steam, extrusion)	*Bacillus stearothermophilus (*strain 1518), *Bacillus subtilis* A or B or *var. globigii*
H_2O_2 + UV radiation	*Bacillus subtilis* A
Ethylene oxide	*Clostridium sporogenes* (PA 3679)
Gamma irradiation	*Bacillus pumilus*

2.2.2 Chemical sterilization

2.2.2.1 Ethylene oxide

Ethylene oxide (EtO or EO, C_2H_4O) is an alkylating agent which is used for sterilizing packaging materials in the form of a gaseous chemical sterilant (Joslyn, 2001). The effectiveness of ethylene oxide sterilization is temperature-dependent. Conditions for ethylene oxide sterilization are generally 40ºC-60ºC and 45-75% relative humidity (Massey, 2005). *Clostridium sporogenes* (PA 3679) is usually used to test ethylene sterilization (Table 2.2). Ethylene oxide is commonly used for sterilization of medical devices as well as paper-based packaging materials (Sandeep & Simunovic, 2006). However, it has adverse effects, as ethylene oxide is a flammable and toxic

chemical in both the liquid and vapor phases. It has been listed as a mutagen and human carcinogen by the Occupational Safety and Health Administration (OSHA). Short-term exposure can cause irritation of the skin, eyes, or nose and can cause acute pulmonary edema at high concentrations. Chronic exposure can cause nerve damage, chromosomal damage and cancer. The use of ethylene oxide, therefore, is a concern due to its potential for toxic residues in products and/or packaging materials (CDPH, 1991; Freeman, 1960; Joslyn, 2001; OSHA, 1988; Sexton & Henson, 1949).

2.2.2.2 Hydrogen peroxide

Hydrogen peroxide (H_2O_2) is an oxidizing agent which is widely used as a chemical sterilant (Baldry, 1983; Sandeep & Simunovic, 2006). Hydrogen peroxide has good sporicidal activity at concentrations of 10 to 30% (Stevenson & Shafer, 1983; Turner, 1983). *Bacillus subtilis* is generally used as an indicator microorganism for testing hydrogen peroxide sterilization (Table 2.2).

The use of hydrogen peroxide sterilization for packaging materials that directly contact food was first approved by FDA for polyethylene (PE) in 1981. Approval was later extended to include all polyolefins in 1984. In 1985, hydrogen peroxide was approved as a sterilant for polystyrene (PS), modified polystyrene, ionomeric resins, ethylene methyl acrylate copolymer resin, ethylene vinyl acetate copolymer resin, and polyethylene terephthalate (PET). Ethylene acrylic acid copolymers were also approved in 1987.

Hydrogen peroxide is extensively used in both liquid and vapor phases. For sterilization of packaging material surfaces, hydrogen peroxide can be applied in

several ways such as bathing, spraying, or rinsing, or it can be combined with other sterilization methods such as heat or irradiation. Hot-air drying is used to remove peroxide from material surfaces and to ensure sterility of the entire package (Cerny, 1989). There are some challenges in the use of hydrogen peroxide for sterilization of packaging material surfaces since sterilization is based on its concentration, the quantity applied to packaging materials per unit area, and the temperature and quality of the drying air and exposure time to dry the materials. The effectiveness of hydrogen peroxide increases with temperature. The critical controlling factor for sterilization is wetting of the packaging materials with a uniform fluid film on the material surface (Toledo, 1988).

Hydrogen peroxide is not considered a mutagen or carcinogen (OSHA). Since it is a nontoxic gas sterilant, it has become a substitute for ethylene oxide. However, residual hydrogen peroxide can be trapped inside packaging materials after sterilization (Stannard & Wood, 1983; Toledo, 1986). FDA regulations limit the levels of residual hydrogen peroxide to less than 0.5 µg/mL (0.5 ppm). The test must be determined in distilled water immediately after packaging under production conditions (Code of Federal Regulations 2000). The residual hydrogen peroxide left on packaging materials has been shown to affect the degradation of ascorbic acid in fruit juices, and anthocyanin pigment in cherries, thereby decreasing the product's stability (Özkan et al., 2004; Özkan et al., 2000; Toledo, 1986).

Rolled paper is bathed in 35% hydrogen peroxide at a temperature of 75˚C, normally for 7 seconds or more for sterilization and then hot air is applied to remove the

peroxide residue (Wakabayashi, 1993). During sterilization of plastic cups, preformed cups are sprayed or atomized with hydrogen peroxide for 3 seconds and then dried with compressed hot air at approximately 400˚C, with the inside surface of the package reaching a temperature of 70˚C. Form-fill-seal cups are sterilized using a hydrogen peroxide bath and thermoformed at 130-150˚C (Sandeep & Simunovic, 2006).

Vapor hydrogen peroxide (VHP) can be produced by mixing hydrogen peroxide with air in order to allow recycling, which minimizes the amount of hydrogen peroxide in the environment. Lower concentrations of VHP such as 7.6 mg/L at 70˚C can be used to obtain a 6 decimal reduction of spores of *B. subtilis var. niger* in 1.2 minutes, compared to hot air at 150˚C which induces only a 1 log reduction in the same time (Toledo, 1988; Wang & Toledo, 1986). Less residual hydrogen peroxide is left on the packaging material using vapor phase (VHP) as compared to liquid phase hydrogen peroxide. Low temperature sterile air can also be used to remove residual hydrogen peroxide from the package.

2.2.2.3 Peracetic acid (PAA)

Peracetic acid (CH_3COOOH) is another chemical agent used in packaging sterilization in both liquid and vapor phases (Joyce, 1993). It is sporicidal in the vapor phase at 80% RH (Hoffman, 1971). PAA is highly effective against microorganisms at low concentrations. Both the concentration of peracetic acid and exposure time dictates the microbial kill. It is very unstable in diluted form and generally used in specially designed sterilizers (APIC, 2002). Higher concentrations of PAA used in processing systems can cause damage to the equipment as PAA is corrosive. Another drawback of

PAA is that it is toxic (at 40% concentration or more) and can cause skin damage, and eye and respiratory irritation (Joslyn, 2001; Joyce, 1993).

2.2.3 Irradiation sterilization

2.2.3.1 Ionizing radiation

Ionizing radiation is used in many applications for sterilizing food, medical and pharmaceutical products. In the field of packaging, ionizing radiation is used to sterilize packaging materials that cannot withstand the high temperatures used for thermal sterilization. Radiation sterilization is currently accepted for aseptic products (Joyce, 1993; Robertson, 2006). Ionizing radiation will be discussed in detail later in this chapter.

2.2.3.2 Ultraviolet irradiation

Ultraviolet (UV) light is electromagnetic radiation, which has wavelengths between 210 and 328 nm. UV radiation has been used as a sterilization method in several applications such as for water, air, food and packaging materials. The antimicrobial effectiveness of UV radiation is greatest between wavelengths 250 to 280 nm. The DNA of microorganisms absorbs UV light and then leading to the formation of various photoproducts that result in DNA damage, mutations, and cell death. The use of UV radiation has several limitations. UV light has poor penetration power. It can penetrate liquids at a limited level. Dust particles and microcolonies also limit the depth of its penetration. Moreover, UV light is not very effective in the shade and therefore any

kind of shading due to the package can affect penetration (Joyce, 1993; Robertson, 2006). Limitations of different sterilization processes are summarized in Table 2.3.

Table 2.3 Limitations of sterilization methods

Sterilization Techniques	Limitation
Moist/dry heat	• Not suitable for materials which cannot withstand the heat or moisture of steam sterilization. • Contamination if steam is not pure • Thermal tolerance of microorganisms
Ethylene oxide (EtO, EO)	• Highly flammable, toxic and carcinogenic • Operator exposure risk and training costs
Hydrogen peroxide (H_2O_2)	• Absorption into resin e.g. PET • Chemical handling and supply logistics • Operating costs • Complexity of process control
Peracetic acid (PAA)	• Corrosive on metal • Toxic chemical
UV light	• Sterilization efficacy • Slow line speed • Shadowing issues limit to direct line of site applications • Very limited penetration

2.3 Irradiation

Irradiation is a process utilizing ionizing radiation, which is radiant energy that has the potential to penetrate and break strong chemical bonds in microorganisms and pathogens in order to sterilize (Graham, 1992). Ionizing radiation has sufficient energy to split a molecule, resulting in the creation of positive and negative charges (Graham, 1992; Olson, 1998). This spatially random process leads to the production of free radicals or ionic species (Reichmanis et al., 1993). Generally, electron irradiation uses

electron accelerators to provide beams with energies in the million-electron volts (MeV) range (Reichmanis et al., 1993; Urbain, 1986).

2.3.1 Radiation sources

Ionizing radiation is a non-thermal process commonly used to sterilize foods, medicals, pharmaceuticals and packages by exposing the products for a limited time (Murano, 1995). In order to use as a treatment for food, radiation must have the ability to penetrate into the food. Not all types of ionizing radiation are suitable for food applications (Urbain, 1986).

The three ionizing radiation sources allowed for pasteurization and sterilization by the U.S. Food and Drug Administration (FDA) are gamma (γ) rays, X-rays, and electron beams (e-beam) (Komolprasert, 2007). High-energy Gamma radiation is most often produced off by radioactive substance such as Cobalt-60, ^{60}CO (1.17 and 1.33 MeV) and Cesium-137, ^{137}Cs (0.662 MeV). They can penetrate food to a depth of several feet. X-rays are produced by electron bombardment of appropriate metal targets with electron beams and can pass through thick foods. They are generated at energies not to exceed 5 MeV. Electron beams (E-beam) are highly charged energetic electron streams which are generated by the acceleration and conversion of electricity, not to exceed 10 MeV (Diehl, 1995; Molins, 2001; O'Donnell, 1989; O'Donnell & Sangster, 1970; Olson, 1998).

2.3.2 Absorbed dose

The dose (absorbed dose) of irradiation, which is the amount of energy transferred to a mass of food or material within a set time period, is normally measured in SI units (International System Unit) called gray, Gy. One gray is equal to one joule of energy absorbed per kilogram of material. This SI unit has superseded the traditional unit, which was expressed in rads, corresponding to 10^{-2} joule/kg (1Gy = 100 rad = 1 joule/kg). As a quantitative basis for radiation chemical yields, another unit, the G value, has been used. The G value is the number of molecules changed or new substance formed per 100 eV of energy absorbed (Cleland, 2006; McLaughlin et al., 1989; O'Donnell, 1989; Urbain, 1986).

2.3.3 Temperature

The irradiation temperature does not affect the amount of ionizing radiation or electronic excitation. However, there may be subsequent effects of temperature. The activation energy of chemical reactions differs with temperature. The mobility of free radicals and other reactants can be altered. At adequately low temperature, effective immobility can occur, resulting in reduction of the capacity for interaction. Free radicals, thus, can persist for relatively long periods without reacting (Urbain, 1986).

When a packaging material is irradiated below its glass transition temperature (T_g), the irradiation temperature does not have any influence on radiolysis products (RPs), the result of dissociation of molecules, from irradiated polymeric materials. However, temperatures above T_g may increase the concentration of RPs (Helmroth et al., 2002).

2.4 Effect of irradiation on microorganisms

Unlike other non-ionizing radiation and/or heating radiation processing such as cooking, microwaving or canning, ionizing radiation is more damaging to living tissues due to its high penetrating power. Damage occurring from ionizing radiation is extensive, resulting in the inability of microorganisms to repair (Graham, 1992; Smith & Pillai, 2004). Ionizing radiation inactivates microorganisms by damaging genetic materials such as chromosomal DNA, which is a primary target of ionizing radiation, (Grecz et al., 1983) and cytoplasmic membranes, enzymes and plasmids (Mahapatra et al., 2005; Smith & Pillai, 2004). The effect of ionizing radiation on DNA can occur either directly, by energy deposition at a DNA target, or indirectly, by the interaction of radiation with other atoms and/or molecules in or around the cell (Figure 2-1), resulting in 90% of DNA damage which inactivates the microbes (Yarmonenko, 1988).

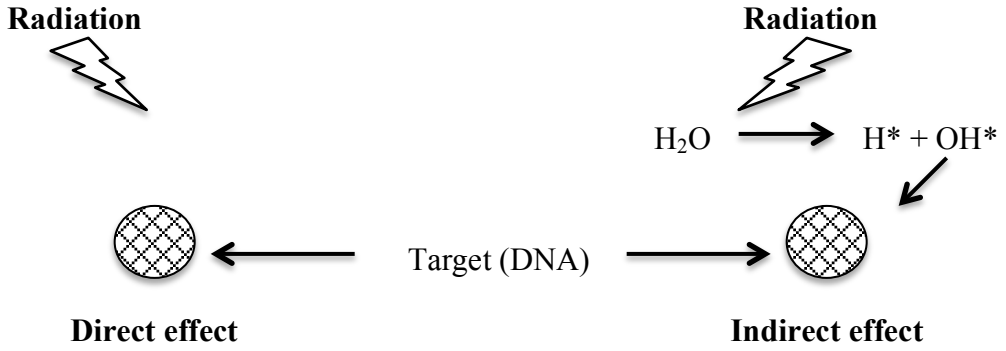

Figure 2.1 Mechanism of cell damage by ionizing radiation

In order to determine the appropriate irradiation treatment, the D_{10}-value of the target microorganisms is required. The D_{10}-value is defined as the absorbed irradiation

dose required to reduce the number of target microorganisms by 90%. It is used as a measure of radiation resistance (Moreira et al., 2010). To eliminate bacteria, high doses of irradiation with D_{10}-values of 0.3 to 0.7 kGy are required. Bacterial spores are more difficult to destroy. They require higher doses, with D_{10}-values of 2.8 kGy (Molins, 2001; Satin, 1996). It has been reported that Gram-negative bacteria are more sensitive to irradiation than Gram-positive bacteria (Monk et al., 1995; Thayer et al., 1993). Viruses have nucleic acids, consisting of either DNA or RNA. They have a less complex structure and are smaller than bacteria. This makes viruses generally resistant to approved irradiation dosages for foods, with D_{10}-values of 10 kGy or higher.

Parasites and insects can also be killed by radiation. Since they have large amounts of DNA and a more complex cellular structure, parasites and insects are rapidly killed by low doses of irradiation, with D_{10}-value of 0.1 kGy or less (Molins, 2001; Satin, 1996). Consequently, the more complex an organism, the more sensitive it is to irradiation. The general guideline for microbial inactivation is shown in Table 2.4 and Table 2.5.

Table 2.4 Inactivation of microbes by gamma irradiation (Kučera, 1988; Marciniec & Dettlaff, 2008)

Type of microbe	D_{10} (kGy)
Balantidium coli, Aerobacter acrogens, Salmonella, Shigella	1.0
B. proteus	1.2
Pseudomonas	2.5
Pasteurella, Brucella	1.8
Staphylococcus aureus, Corynebacterium diphtheriae	4.5
Streptococcus, Neisseria, Haemophillius	5.5
B. brevis, Subtillis mesentericus	10.0
Clostridium sporogenes	20.0
Clostridium botulinum	10.0
Micrococcus R	40.0
Aspergillius niger	4.0
Penicillium	5.7
Neurospora	6.0
Saccharomyces	5.2
Bacteriophagy	4.0
Herpes virus, tobacco mosaic virus	5.5
Foot-and-mouth disease virus (FMDV)	2.8
Tobacco necrosis virus	6.7

The D_{10} value represents the irradiation dose required to reduce the microbial population by 90%.

Table 2.5 Inactivation of pathogenic and spoilage bacteria in foods (Monk et al., 1995)

Type of microbe	Medium	D_{10} (kGy)	Reference
A. hydrophila	Beef	0.17	Palumbo et al. 1986
B.cereus (vegetative)	Beef	0.14-0.19	Grant et al. 1993
C. jejuni	Beef	0.18	Clavero et al. 1994
E. coli O157:H7	Beef	0.25	Clavero et al. 1994
L. monocytogenes	Chicken	0.42-0.55	Huhtanen et al. 1989
	Pork	0.57-0.65	Grant and Patterson 1991
	Beef	0.51-0.59	Monk et al 1994
Salmonella spp.	Chicken	0.38-0.50	Thayer et al. 1990
Staph. aureus	Chicken	0.42	Thayer et al. 1992
	Roast beef	0.39	Patterson 1988
Y.enterocolitica	Beef	0.11	El-Zawahry et al. 1979
Cl. botulinum (spore)	Chicken	3.56	Anellis et al 1977
C. sporogenes (spore)	Beef fat	6.3	Shamsuzzaman and Luct 1993
M. phenylpyruvica	Chicken	0.63-0.88	Patterson 1988
P. putida	Chicken	0.88-0.11	Patterson 1988
S. faecalis	Chicken	0.67-0.7	Patterson 1988

The D_{10} value represents the irradiation dose required to reduce the microbial population by 90%.

2.5 Radiation for food and pharmaceutical applications

The advantage of irradiation is not only to eliminate and/ or reduce harmful human pathogens, which helps to ensure food safety, but also to improve the quality and extend the storage life of foods (Komolprasert, 2007). Sterilization of the packaging materials by ionizing radiation, hence, has become a more common treatment especially for aseptic and pharmaceutical products (Ozen & Floros, 2001).

Irradiation has been widely recognized and successfully used to commercially sterilize various products including medical devices, pharmaceuticals and foods (Table

2.6). This is because of its potential to provide benefits over other traditional methods such as heat and chemical treatments which ordinarily cause nutritional loss in foods, damage heat-sensitive products and some plastics, or leave a chemical residue (Brennand, 2011; Haji-Saeid et al., 2007).

Table 2.6 Items sterilized with ionizing radiation (Berejka & Kaluska, 2008; Thayer & Boyd, 1999)

Medical/Pharmaceutical Products	
Absorbents	Instruments
Airways and tubes	Intravenous administration sets
Alcohol wipes	Liquid detergents
Bandages	Lubrication gels
Blood	Operating room towels
Contact lenses	Petri dishes
Cotton balls	Prostheses (arterial, vascular, orthopedic)
Dental anchors, burrs, and sponges	Surgical gloves
Drain pouches	Surgical drapes and gowns
Drug products	Sutures
Drug mixing/dispensing systems	Syringes and needles
Enzymes	Thermometers/covers
Eye droppers and ointments	Tongue depressors
Fetal probes	Topical ointments
Hand towels	Urine bags

Consumer Products	
Adhesive bandages	Disposable nursery bottles
Animal vaccines	Food packaging
Baby bottle nipples	Pacifiers and teething rings
Contact lens cleaning solutions	Pet food
Cosmetics	Rawhide dog toys
Dairy and juice containers	Tampons

It is necessary to choose suitable sterilization doses for products. In order to achieve the required or desired sterility assurance level (SAL), determination of the sterilization dose is based on 1) the level of viable microorganisms on the product before sterilization, 2) the relative mix of various microorganisms with different D_{10} values and 3) the sterility required for that product (Hammad, 2008).

In food radiation, dose is the most important factor. Particular applications require specific doses in order to achieve the desired objective (Urbain, 1986). Doses can be classified as low, medium, or high (Table 2.7). A low dose irradiation (<1kGy) is used to delay sprouting and aging of fresh fruits and vegetables. A medium dose (between 1 to 10 kGy) is applied to eliminate and/or control pathogenic microorganisms such as in pasteurization. To achieve sterility of the product, a high dose (>10 kGy) is required (Burg & Shalaby, 1996; McLaughlin et al., 1989; Morehouse & Komolprasert, 2004).

Table 2.7 The radiation dose-range needed for food irradiation applications (IAEA, 2000)

Benefit	Dose (kGy)	Products
Low-dose (up to 1 kGy)		
Inhibition of sprouting	0.05 - 0.15	Potatoes, onions, garlic, root ginger, yam
Insect disinfestation and parasite disinfection	0.15 - 0.5	Cereals and pulses, fresh and dried fruits, dried fish and meat, fresh pork
Delay of physiological processes (e.g. ripening)	0.25 - 1.0	Fresh fruits and vegetables
Medium-dose (1-10 kGy)		
Extension of shelf-life	1.0 - 3.0	Fresh fish, strawberries, mushrooms
Elimination of spoilage and pathogenic microorganisms	1.0 - 7.0	Fresh and frozen seafood, raw or frozen poultry and meat
Improving technological properties of food	2.0 - 7.0	Grapes (increasing juice yield), dehydrated vegetables (reduced cooking time)
High-dose (10-50 kGy)		
Industrial sterilization (in combination with mild heat)	30 – 50	Meat, poultry, seafood, prepared foods, sterilized hospital diets.
Decontamination of certain food additives and ingredients	10 – 50	Spices, enzyme preparations, natural gum

In commercial sterilization of foods, the overall average dose of food irradiation is usually less than 10 kGy, which has been recognized by the Joint Food and Agriculture Organization (FAO), the International Atomic Energy Agency (IAEA) and the World Health Organization (WHO) expert committees on the wholesomeness of irradiated food since 1980 to ensure safety (or not produce a toxicological, nutritional or microbiological issue in foods) (Wholesomeness of irradiated food, 1981).

The dose of 10 kGy, however, is not sufficient to sterilize or produce shelf-stable foods. The use of high-dose radiation for sterilization of products such as meat, poultry, and fish is now of much interest (van Kooij, 1981). In 1995, high-dose irradiation was approved for frozen and packaged meats; however, this application is for NASA only. Currently, high irradiation doses have been approved for spice in the United States (30 kGy) and France (11 kGy) (WHO, 1997). Information including nutrition, microbiology and toxicology is needed for approving the use of high dose radiation for processing of food (van Kooij, 1984).

Irradiation has been considered by the World Health Organization (WHO) as an important process for helping to ensure food safety (Diehl, 1995). Irradiation of foods has been extensively used in the United States (Ozen & Floros, 2001). The current approval of radiation doses and foods for processing by food irradiation are listed under U.S. quarantine regulations (Table 2.8).

For pharmaceuticals and medical devices, a radiation dose of 25 kGy is commonly used for sterilization (Burg & Shalaby, 1996). In the European standard (EN552), the use of gamma rays and electron beams (<10 MeV) for medical devices to ensure the sterilization assurance level (SAL) of 10^{-6} is also at a minimum dose of 25 kGy (European Pharmacopoeia Commission, 1980; Marciniec & Dettlaff, 2008). In some countries such as those in Scandinavia, doses of 32-50 kGy are required for this application (Goulas et al., 2004). According to international standards (ISO 11137), the irradiation dose for gamma rays, X-rays and e-beams for medical instruments, devices and products such as drugs, vaccines, and health care products depends on the types

and levels of microbiological contamination and sterility requirement (Marciniec & Dettlaff, 2008).

Table 2.8 Foods approved for irradiation under FDA's regulations (FAD, 1986)

Food	Purpose	Dose
White potatoes	Sprout inhibition	0.05- 0.15 kGy max
Wheat, wheat flour	Insect disinfection	0.2-0.5 kGy max
Fresh pork	Control Trichinella spiralis	0.3 kGy min-1 kGy max
Fresh foods (fruits, vegetables)	Growth and maturation inhibition	1 kGy max
Foods	Arthropod disinfection	1 kGy max
Dry or dehydrated enzyme preparations	Microbial disinfection	10 kGy max
Dry or dehydrated spices/seasonings	Microbial disinfection	30 kGy max
Fresh or frozen, uncooked poultry products	Pathogen control	3 kGy max
Frozen meats NASA	Sterilization	44 kGy min
Refrigerated, uncooked meat	Pathogen control	4.5 kGy max
Frozen uncooked meats	Pathogen control	7 kGy max
Shell eggs	Pathogen control (Salmonella)	3 kGy max
Seeds for sprouting	Pathogen control	8 kGy max
Fresh or frozen molluscan shellfish	Control Vibrio species and other foodborne pathogens	5.5 kGy max
Animal and pet food	Microbial disinfection	25 kGy max

2.6 Advantages of irradiation sterilization

Irradiation is a very effective process which has the ability to eliminate and/or reduce contaminating microorganisms and pathogens without leaving residues or radioactivity in the products. Furthermore, high-energy radiation can be used to sterilize many packaging materials for pharmaceuticals and foods due to its high penetrating power (Hammad, 2008; Komolprasert, 2007; Neijssen, 1993).

Irradiation sterilization is simple and easy to control automated process, which is continuous with few processing variables (dose, dose rate, and exposure time). Other sterilization processes such as ethylene oxide are batch processes and require several processing variables (time, temperature, pressure, vacuum, gas concentration) (Hammad, 2008). The use of irradiation combined with other techniques such as heat treatment or modified atmosphere packaging (MAP) can be advantageous to preserve and prolong the shelf life of products (Chuaqui-Offermanns, 1989; Crawford et al., 1996; Farkas, 1990; Grant & Patterson, 1991; Lafortune et al., 2005; Lee et al., 1996).

Irradiation, however, has its drawbacks. The effect of high-energy radiation on polymers is a concern and has been investigated in many published scientific papers. It also becomes a main concern in terms of acceptance by consumers.

2.7 Influence of radiation on polymeric packaging materials

Polymers have become a major category of packaging materials. Most packaging materials for food and pharmaceutical products are made of polymers (Brown, 1992; Goulas et al., 2004; Selke et al., 2004). In irradiation sterilization of foods,

pharmaceuticals and medical disposables, packaging materials are directly exposed to ionizing radiation. As organic materials, polymeric packaging materials are affected by irradiation (Chuaqui-Offermanns, 1989).

2.7.1 Chemical change in polymers

2.7.1.1 Primary interaction process

During the irradiation process, high-energy radiation is absorbed by polymeric materials, causing excitation and ionization. This reaction creates excited and ionized species which are the initial chemical reactants (O'Donnell & Sangster, 1970).

When macromolecules of polymers are excited by ionizing radiation, free radicals are formed (Mark et al., 1986). These free radicals react with one another and initiate further reactions among the polymeric chains (Miao et al., 2009; Selke et al., 2004). The formation of free radicals can occur in plastics in both amorphous and crystalline regions (Buchalla et al., 1993b; Ozen & Floros, 2001) leading to changes in the material properties and shelf life of the plastics.

The combination of two radicals leads to cross-linking or recombination in the amorphous and crystalline regions, whereas chain transfer and subsequent splitting results in chain scission and lowers the molecular weight of polymers (Pionteck et al., 2000).

2.7.1.2 Secondary effects

The predominant effects of ionizing radiation on polymeric materials are cross-linking and chain scission (Charlesby, 1987). Cross-linking is the combination of two polymer chains via a bridge-type chemical bond, leading to an increase in molecular weight or polymerization (Figure 2-2). In many plastics and rubbers, cross-linking is a curing process that can affect the physical and mechanical properties of the polymer (Morehouse & Komolprasert, 2004). It can increase the mechanical strength but decrease elongation, crystallinity and solubility of the plastic material (Ozen & Floros, 2001). Cross-linking dominates during irradiation under vacuum or in an inert atmosphere such as nitrogen (Morehouse & Komolprasert, 2004; Streicher, 1988). Cross-linking is the principal result in most plastics used for pharmaceutical and food packaging including polyethylene (PE), polypropylene (PP), and polystyrene (PS) (Haji-Saeid et al., 2007).

Conversely, chain scission is a fragmentation of the polymer chains. When energy from ionizing radiation exceeds the attractive forces between the atoms, the chemical bonds are disrupted causing chain scission (Carlsson & Chmela, 1990), which reduces the molecular weight by a degradation process (Charlesby, 1987; Lovinger, 1990; Morehouse & Komolprasert, 2004). This decrease of polymer chain length increases the free volume in the polymer. Chain scission dominates in the presence of oxygen or air (Morehouse & Komolprasert, 2004; Streicher, 1988). In the presence of oxygen, peroxide, alcohol and various low-molecular-weight oxygen-containing compounds are also formed by additional reactions. In contrast, chain scission

produces hydrogen, methane, and hydrogen chloride in chloride-containing polymers under vacuum (Ozen & Floros, 2001).

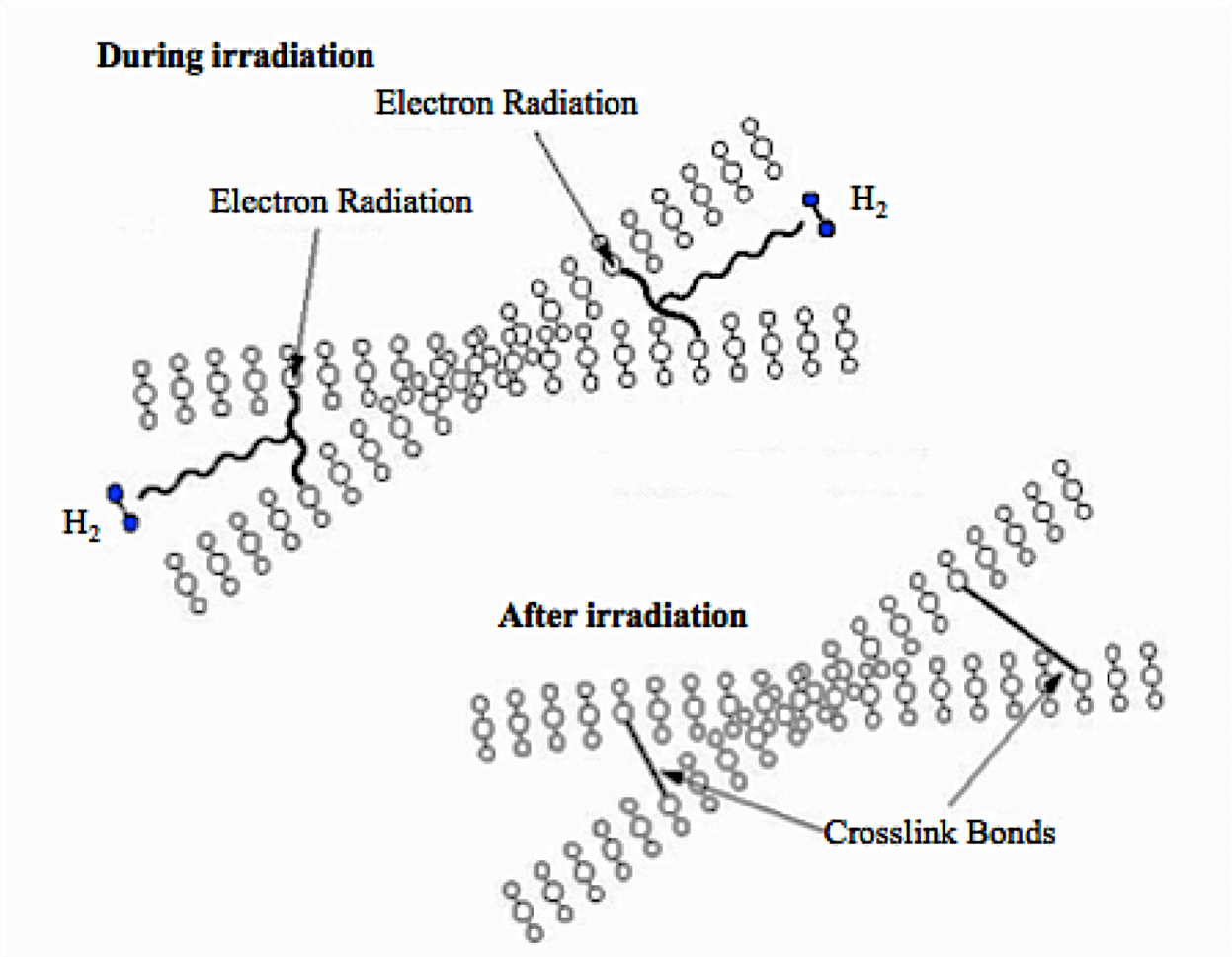

Figure 2.2 Mechanism of cross-linking in polyethylene molecules by irradiation (RSCC, 2010)

In general, these phenomena, polymerization and degradation, will occur simultaneously for many polymers (Bovey, 1958; Loo et al., 2005a) depending upon the chemical structure of the polymer, degree of crystallinity, thickness of the packaging material, irradiation conditions, irradiation dose, and the irradiation environment during exposure (e.g. level of oxygen in the atmosphere during irradiation) (Buchalla et al.,

1993a; Burg & Shalaby, 1996; Crook & Boylston, 2004; Dole, 1991; Goldman et al., 1996; Goulas et al., 2002; Killoran, 1972; Pionteck et al., 2000; Riganakos et al., 1999).

Increasing the radiation dose will cause cross-linking up to an optimum point; when the dose is increased beyond that optimum point, chain scission occurs. In the absence of oxygen during irradiation, an increase in absorbed dose causes a linear rise in radiolysis products (RPs) (Dawes & Glover, 1996; El Makhzoumi, 1994). Aromatic polymers are normally more resistant to ionizing radiation than aliphatic polymers because the phenyl rings provide both intramolecular and intermolecular protection, whereas the presence of impurities and additives may promote degradation and/or cross-linking (Gorna & Gogolewski, 2003; Grassie & Scott, 1985; Kamiga & Niki, 1979).

Many tests are performed to determine the effect of ionizing radiation on properties of packaging materials. Radiation-induced chemical changes in molecular weight may be used to investigate the presence of scission and cross-linking in irradiated polymers. Average molecular weights can be determined by several methods such as viscometry, osmometry, light scattering, gel permeation chromatography and sedimentation equilibrium (Drobny, 2003; O'Donnell, 1989).

2.7.1.3 Post-irradiation effects

In most irradiated polymers, changes in properties can occur due to long term reactions after irradiation (O'Donnell, 1989). This is because of the presence of free radicals. Post-irradiation reactions are commonly observed as a result of high-energy radiation polymer exposure and can be attributed to 1) trapped radicals that react with oxygen which diffuses into the polymer, 2) peroxides formed by irradiation in air or a

vacuum, and 3) trapped gases in glassy crystalline polymers that cause localized stress concentrations. Free radicals trapped in amorphous polymers can survive for days to months in glassy and crystalline structures. Free radicals may migrate to certain reaction centers during storage. The reaction of free radicals probably occurs at or near chain ends in the polymer (O'Donnell, 1989; Sandler, 2004; Urbain, 1986).

Due to post-irradiation effects, polymer materials might have reduced strength and increased cracking and brittleness, which can be reduced by addition of appropriate scavengers (O'Donnell, 1989). For example, free radicals in ethylene vinyl alcohol (EVOH) result in bond scission, cross-linking, water production and production of oxygenated polymer fragments including alcohols, aldehydes, and acids (Sandler, 2004).

One should also evaluate the impact of packaging materials on the safety and quality of products. Materials should not have significant changes in physical and chemical properties, or transmit any toxic substances from the packaging materials to foods (Barbosa-Canovas et al., 1998).

The packaging materials and all adjuvants used in irradiation for foods, thus, must meet all specifications and limitations of the applicable FDA regulations and must be authorized by FDA in order to be marketed in the U.S. for food contact (Komolprasert, 2007; Paquette, 2004). The packaging materials that are currently approved by FDA under 21 CFR 179.45 for use with irradiated prepackaged food are listed in Table 2.9.

Table 2.9 Packaging materials and maximum irradiation doses permitted by the U.S. Food and Drug Administration for prepackaged foods (Komolprasert, 2007; Paquette, 2004)

Year	Material	Requester	Max. Dose (kGy)
1964	Nitrocellulose-coated cellophane	AEC	10
	Glassine paper	AEC	10
	Wax-coated paperboard	AEC	10
	Polyolefin film*	AEC	10
	Polystyrene film*	AEC	10
	Rubber hydrochloride film*	AEC	10
	Vinylidene chloride-vinyl chloride copolymer film*	AEC	10
1965	Vinylidene chloride copolymer-coated cellophane	AEC	10
	Vegetable parchments	U.S. Army	60
1967	Kraft paper to contain only flour	U.S. Army	0.5
	Polyethylene film*	U.S. Army	60
	Polyethylene terephthalate (PET) film*	U.S. Army	60
	Nylon 6 film*	U.S. Army	60
	Vinyl chloride-vinyl acetate copolymer film*	U.S. Army	60
1968	Optional adjuvants for polyolefin films plus optional vinylidene chloride copolymer coating	AEC	10
	PET film plus optional adjuvants, vinylidene chloride copolymer and polyethylene coatings	AEC	10
	Nylon 11	AEC	10
1989	Ethylene-vinyl acetate copolymers	Cryovac	30
1996	Polystyrene foam tray	Amoco	7.2

The U.S. Atomic Energy Commission (AEC)

* plus limited optional adjuvants

Presently, numerous new polymeric materials have been developed to provide specific requirements to prolong the shelf life of food and pharmaceutical products and to meet industry needs. These new materials, nevertheless, might not be approved by FDA for irradiation treatment (Komolprasert, 2007). In addition, the packaging materials approved by FDA are all single films which do not necessarily satisfy modern packaging needs. Single-layer films are not suitable for aseptic packaging. Multilayer packaging materials, complex structures using two or more film-layers commonly formed by coextrusion, are often needed to improve gas barrier, moisture barrier, aroma or flavor barrier properties and product shelf life (Chuaqui-Offermanns, 1989). All food packaging materials need to be tested to prove that ionizing radiation does not significantly alter the physical and chemical properties of the materials (Komolprasert, 2007; Paquette, 2004).

2.7.2 Changes in properties of irradiated polymeric materials

Radiation-induced changes in the structure of polymers can affect the physical and chemical properties of packaging materials such as strength, seal integrity, brittleness, color, opacity, barrier, and emission of volatile compounds (Ozen & Floros, 2001). Even if irradiation is performed at doses approved for food products and packaging material use, high-energy radiation has shown significant effects on material behavior (Skiens, 1980). The formation of gases (hydrogen), low-molecular-weight hydrocarbons and halogenated polymers can occur and these have a potential to migrate into foods (Kilcast, 1990; Lee et al., 1996; Olson, 1998). The changes can affect the functionality and safety, which are of prime importance in food and pharmaceutical packaging applications.

Radiation, however, does not cause changes in all properties of polymeric materials to the same degree. To select a polymer for a particular application and to avoid a health hazard from polymeric chemical compounds, the effect of ionizing radiation on the overall stability of the materials must be considered (Morehouse & Komolprasert, 2004).

2.7.2.1 Non-renewable packaging materials

Most current polymeric packaging materials used for foods and pharmaceuticals are petroleum-based polymers. In the food and pharmaceutical industry, multilayer materials, and combinations of various types of polymeric materials (normally 3, 5, or 7 layer structures), are increasingly used to improve film barrier properties and provide adequate mechanical protection (Twede & Goddard, 1998). The effect of ionizing radiation on properties of monolayer and/or multilayer nonrenewable packaging materials has been studied (Table 2.10); however, the information is still limited for the numerous new materials in today's market.

The chemical and physical changes in polymeric packaging materials affected by ionizing radiation depend on irradiation conditions and oxygen content, and on the type of polymer and polymer structure such as antioxidants, stabilizers, and other additives (Crook & Boylston, 2004; Kim-Kang & Gilbert, 1991). Irradiation at doses between 0 to 8 kGy did not affect the crystallinity of low-density polyethylene (LDPE), high-density polyethylene (HDPE), polypropylene (PP), polyethylene terephthalate (PET), polyvinyl chloride (PVC) and polyvinylidene chloride (PVDC) (Varsanyi, 1975). No significant changes were detected in the molecular structure of LDPE and oriented polypropylene

Table 2.10 Effect of irradiation on mechanical and barrier properties of packaging materials (modified from Ozen and Floros (2001))

Material	Dose (kGy)	Effect	Reference
Mechanical properties			
EVA	50 kGy γ irradiation	Decrease in heat seal strength	Matsui et al., 1991
Surlyn	< 50 kGy E-beam	No significant change in tensile strength, elongation, Young's modulus, tear strength and heat seal strength	Hoh and Cumberbatch, 1991
PS	100 kGy γ irradiation	No significant change	Pentimalli et al., 2000
PP, LDPE, PLA	0.5-2.0 kGy ^{60}Co γ irradiation	No significant change	Krishnamurthy et al. 2004
EVA, HDPE, PS, BOPP, LDPE	5, 10 kGy	No significant change in tensile strength, % elongation, Young's modulus	Goulas et al. 2002
HDPE, BOPP	30 kGy	Tensile strength decreased	Goulas et al. 2002
LDPE	30 kGy	% elongation at break decreased	Goulas et al. 2002

Table 2.10 (cont'd)

Material	Dose (kGy)	Effect	Reference
Barrier properties			
LDPE, OPP	25 kGy E-beam	No change in oxygen permeability	Rojas De Gante and Pascat, 1990
PE pouch	25 kGy ^{60}Co γ irradiation	No change in oxygen and water vapor permeability	Pilette, 1990
PET/PVdC/PE	^{60}Co γ irradiation	Decrease in oxygen permeability	Kim-Kang and Gilbert, 1991
EVA, HDPE, PS, BOPP, LDPE	5, 10, 30 kGy γ irradiation	No significant changes in oxygen, carbon dioxide, and water vapor permeability	Goulas et al, 2003
LDPE, HDPE, PET, PVC	8 kGy	No significant changes in gas permeability	Crook and Boylston 2004
LDPE, EVA, PET/PE/EVOH/PE	5,20,100 kGy E-beam	No significant changes in gas (O_2, CO_2) and moisture permeability	Riganakos et al. 1999
EVA	50 kGy γ irradiation	Increase in diffusivity and decrease in solubility to volatile compounds	Matsui et al., 1991

Table 2.10 (cont'd)

Material	Dose (kGy)	Effect	Reference
Volatile formation			
LDPE, OPP	<25 kGy	H_2O_2, carbonyl compounds (ketones and aldehydes)	Rojas De Gante and Pascat, 1990
PP	40 kGy	Alkyl radicals	Marque et al. 1995
PET	25 kGy (Cesium 137)	Formic acid, acetic acid, 1,3-dioxolane, and 2-methyl-1,3 dioxolane	Komolprasert et al. 2001

EVA = Ethylene vinyl acetate

HDPE = High density polyethylene

LDPE = Low density polyethylene

PE = Polyethylene

PS = Polystyrene

PET = Polyethylene terephthalate

PVC = Polyvinyl chloride

PVDC = Polyvinylidene chloride

PLA = Polylactic acid

PP = Polypropylene

OPP = Oriented polypropylene

BOPP = Biaxially-oriented polypropylene

(OPP) at ionization doses of 10 to 50 kGy with electron beams. However, at doses of 100 kGy and higher an increase in the number of double bonds in ionized materials was observed (Rojas De Gante & Pascat, 1990).

Hon and Cumberbatch (1991) reported that the mechanical strength of Surlyn (ethylene/methacrylic acid copolymer) did not significantly change after exposure to an electron beam at doses up to 50 kGy. Changes in mechanical properties of irradiated PS at 100 kGy were not detected (Pentimalli et al., 2000). Tensile strength, percent elongation at break and Young's modulus of HDPE, LDPE, ethylene vinyl acetate (EVA), polystyrene (PS), and biaxially-oriented polypropylene (BOPP) did not change at doses of 5 or 10 kGy but their mechanical properties decreased at a dose of 30 kGy (Goulas et al., 2002). Another study of radiation-induced effects on material mechanical properties, however, showed that heat-seal strength of ionized EVA film exposed to electron beam radiation decreased with increasing dose (Matsui et al., 1991).

The change in barrier properties due to irradiation of plastic packaging materials has been investigated (Table 2.10). Irradiation did not cause any significant changes in gas permeability of LDPE, HDPE, PET and PVC (Crook & Boylston, 2004). Oxygen (O_2), carbon dioxide (CO_2), and water vapor permeability of EVA, HDPE, PS, BOPP, LDPE and ionomer were not affected by gamma irradiation at doses of 5, 10, and 30 kGy (Goulas et al., 2004). Oxygen permeability of irradiated LDPE and OPP films by electron beam irradiation at doses up to 25 kGy also did not change significantly (Rojas De Gante & Pascat, 1990). Water vapor permeability and stiffness were not affected by irradiation of LDPE film (Han et al., 2004). There was also no significant change in

oxygen and water vapor permeability after treating PE with ^{60}Co gamma irradiation and accelerated electrons (Pilette, 1990). However, a decrease in oxygen permeability of glycol modified PET/PVDC/PE laminate was observed after exposure to ^{60}Co gamma irradiation (Kim-Kang & Gilbert, 1991). The influence of ionizing radiation (electron beam) on diffusion and sorption of octane, ethyl hexanoate, and D-limonene in EVA film was studied by Matsui et al. (1991). The diffusion coefficient through irradiated EVA increased with increasing absorbed dose and was related to chain scission.

2.7.2.2 Biodegradable packaging materials

Bio-based biodegradable packaging materials have been developed in an attempt to meet the growing demand for packaging waste reduction and to replace the use of petroleum-based polymers in order to protect the environment. Consequently polymeric biomaterials have received more attention in research, marketing and from consumers. Recently, biodegradable materials have been used in various applications including medical, drugs, and food (Chandra & Rustgi, 1998).

Biodegradable packaging materials include polymeric materials which are derived from renewable resources including agricultural or marine resources such as starch, cellulose, chitosan/chitin, protein from animals or plants, and lipids from animals or plants (Chan et al., 1978). Biopolymers can be classified into three principal categories based on the source or production of the polymers: 1) Polymers produced by direct extraction from biomass such as polysaccharides (e.g. starch, cellulose), chitosan/chitin and proteins like casein and gluten, 2) Polymers produced by chemical

synthesis from renewable bio-based monomers such as polylactic acid, and 3) Polymers produced by microorganisms or genetically modified bacteria which contain polyhydroxyalkonoates (Cutter, 2002; Kandemir et al., 2005; Ruban, 2009).

Polylactic acid (PLA) is a well-known biodegradable polymer. PLA is a linear aliphatic thermoplastic biopolyester derived from natural sources such as maize (corn), sugar beets, potatoes, and whey. Production of PLA is based on a basic carbohydrate fermentation, transforming starch into lactic acid and ultimately into bio-polymer pellets. Subsequently, the pellets are used to produce biodegradable plastic film (Figure 2-3). Lactic acid (2-hydroxypropionic acid) is the simplest hydroxyl acid with an asymmetric carbon atom which exits in two optically active configurations: the L(+) and D(-) isomers (Figure 2-4) which are produced by bacteria (lactobacilli) through the fermentation of carbohydrates. The fermentation processes used to produce lactic acid are classified by the type of bacteria (Auras et al., 2004; Kharas et al., 1994; Krishnamurthy et al., 2004). The glass transition temperature (T_g) of PLA ranges from 50ºC-80ºC, and the melting temperature (T_m) ranges from 130ºC-180ºC. The glass transition temperature of poly (L-lactic acid) (PLLA) is greater than that of poly (D,L-lactic acid) (PDLA) (Auras et al., 2004; Ikada & Tsuji, 2000; Lunt, 1998; Witzke, 1997).

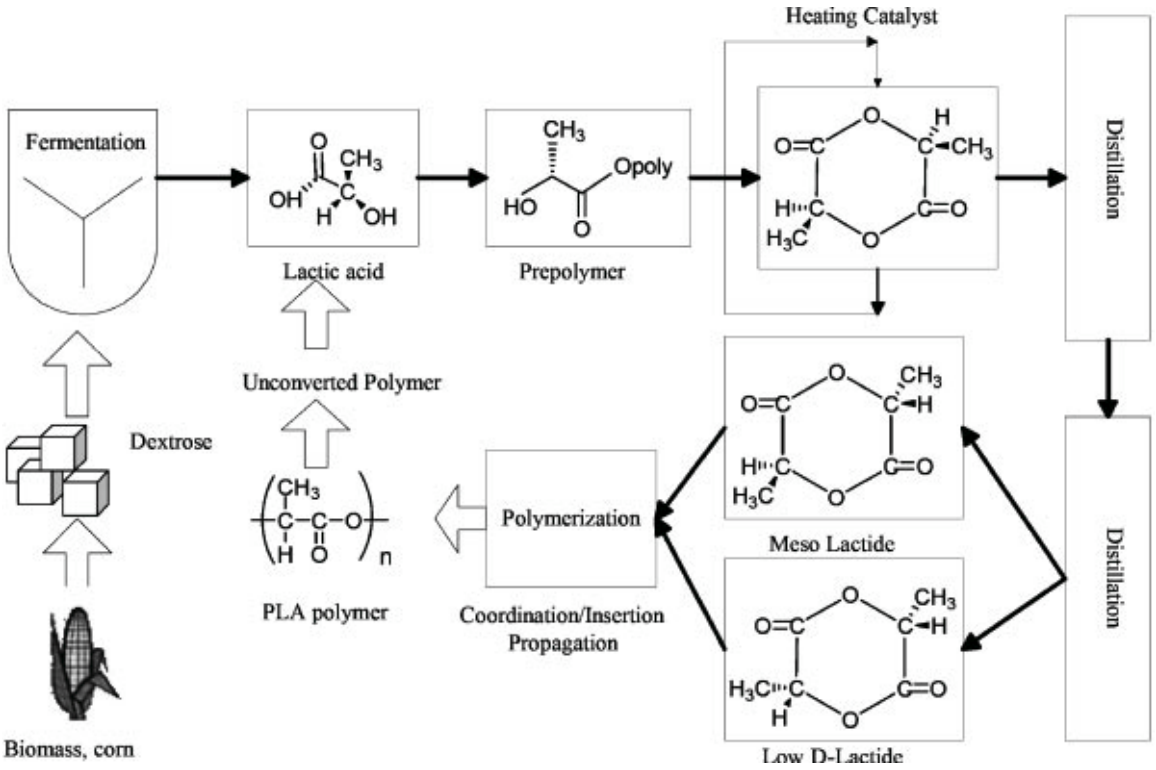

Figure 2.3 Production process of PLA (Auras et al., 2004; Gruber et al., 1992)

L-Lactic Acid
melting point 16.8°C

D-Lactic Acid
melting point 16.8°C

Figure 2.4 Chemical structure of L and D-lactic acid (Auras et al., 2004)

PLA has been approved by the FDA as a food contact surface for packaging materials. The use of PLA in food package applications is increasing for products such as snacks, beverages, meats, fruits and vegetables. In the medical field, as shown in Table 2.11, PLA is one of the most widely used biomaterial drug carriers. Two forms of

Table 2.11 Biodegradable polymers currently used for medical applications (Ikada & Tsuji, 2000)

Polymers	Structure	M_w/ kD	Degradation rate	Medical application
Poly(glycolide)	Crystalline	–	100% in 2–3 months	Suture, Soft issue anaplerosis
Poly(glycolic acid-co-L-lactic acid)	Amorphous	40 – 100	100% in 50–100 days	Suture, Fracture fixation, Oral implant, Drug delivery microsphere
Poly(L-lactide)	Semicrystalline	100 – 300	50% in 1–2 years	Fracture fixation, Ligament augmentation
Poly(L-lactic acid-co-e-caprolactone)	Amorphous	100 – 500	100% in 3–12 months	Suture, Dural substitute
Poly(e-caprolactone)	Semicrystalline	40 – 80	50% in 4 years	Contraceptive delivery implant,
Poly(p-dioxanone)	Semicrystalline	–	100% in 30 weeks	Suture, Fracture fixation
Poly(ortho ester)	Amorphous	100 – 150	60% in 50 weeks (saline, 37ºC)	Contraceptive delivery implant

polylactic acid are used in pharmaceutical manufacturing as drug carriers: poly (L-lactic acid) (PLLA) which is a semi-crystalline material, and poly(D,L-lactic acid) (PDLLA) which is an amorphous polymer (Razem & Katusin-Razem, 2008).

Regenerated cellulose film (RCF), commonly known as cellophane, is a polymeric cellulose film. The word cellophane was derived from the first syllable of cellulose and the last syllable of the French word diaphane, which means transparent, and has become a generic term for RCF and is also registered as a trademark of Innovia Films Ltd., United Kingdom (Robertson, 2013). Cellophane is derived from renewable resources including wood pulp, hemp and cotton (McKeen, 2012). It was first invented by J.F. Brandenberger of France in 1908 and introduced into the United States by E.I. Du Pont de Nemours & Company, Inc. in 1924 (Lancaster & Richards, 1996). Cellophane cannot be melted and hence numerous chemicals are usually used to dissolve it in order to modify its properties and in subsequent process these modifiers are taken out and the film is shaped in the desired form. In the manufacturing process, the pulp is dissolved in sodium hydroxide (alkali) using the mercerization process and aged for several days. The mercerized pulp then is treated with carbon disulfide to form sodium cellulose xanthate (viscose). Viscose is then extruded through a slit and shaped into film. An aqueous solution of glycerol or ethylene glycol, used as a plasticizer in order to confer flexibility on the film, comes into contact with the viscose during the extrusion process (McKeen, 2012; Robertson, 2013; Selke et al., 2004). The regeneration process is completed by passing it through a bath to remove carryover acid and remove any elemental sulfur, carbon disulfide or hydrogen sulfide. After this

the film goes through the bleaching process. The lack of crystallinity in cellophane makes it transparent.

Since cellophane cannot be melted, it cannot be heat-sealed. Cellophane contains many hydroxyl groups, which makes it sensitive to water. For these reasons, cellophane used for packaging is usually coated (Selke et al., 2004). Uncoated cellophane has good gas and aroma barrier properties but is highly moisture sensitive. It is normally, thus, applied with water-resistant coatings on one or both sides in order to improve the seal quality and water vapor barrier. Nitrocellulose (or cellulose nitrate, NC) and polyvinylidene chloride (PVdC) are primary coatings for cellophane (Robertson, 2013). Initially, cellophane film was used to package soaps and luxury goods. Uncoated and coated cellophane films have been used for candies, baked goods, cake mixes, cookies, biscuits, cheese, gum, nuts, dried fruits, spices, cooked meat, tobacco products, and pharmaceutical products (Lokensgard, 2008). Due to growing environmental consciousness, cellophane is expanding in use as a flexible packaging material. One unique advantage of cellophane is that it can be used with additional types of coatings, which allows it to have a wide temperature range and barrier properties to suit specific requirements (Buchner et al., 2003).

Research on irradiation of PLA has typically focused on improvement of polymer properties such as heat stability and mechanical properties by generating crosslinking. This may be beneficial to expand the application of PLA in several fields. Cellophane is irradiated to reduce the molecular weight of natural cellulose before making viscose, which reduces the production time (Cleland et al., 1998; Nagasawa et al., 2005;

Nugroho et al., 2001; Rytlewski et al., 2010; Stepanik et al., 1998; Ware et al., 2010). Research studies on the effect of irradiating these biomaterials in terms of packaging for foods and pharmaceuticals, nevertheless, are still limited.

Some research studies on the degradation of PLA by gamma and electron beam radiation were conducted with PLA reported to be highly sensitive to ionizing radiation. Irradiation decreases the thermal and mechanical properties of PLA due to chain scission (Babanalbandi et al., 1995; Ho & Pometto, 1999; Milicevic et al., 2007; Nugroho et al., 2001). The crosslinking to chain scission ratio for irradiating this aliphatic polyester increases as a function of increasing $–CH_2$ to –COO- ratio in the main chain (D'Alelio et al., 1968). Ho et al. (1999) found that electron-beam irradiation decreased the weight-average molecular weight (M_w), stress at break, percentage of elongation, and strain energy of PLA monolayer plastic films.

Poly($_{D,L}$-lactic acid)-b-poly(ethylene glycol)-b-poly($_{D,L}$-lactic acid) (PLA-b-PEG-b-PLA) irradiated with electron beam under a nitrogen atmosphere at doses from 0 to 100 kGy also degraded (Miao et al., 2009). Chain scission was the main effect; however, recombination reactions or fractional crosslinking was found to occur in addition to chain scission with increasing irradiation dose. A decrease in molecular weight, elongation at break, tensile strength, and thermal stability was found with increasing dose.

Irradiation sterilization (^{60}Co in air at room temperature) also negatively impacts the properties of hydroxy apatite/poly L-lactide (Hap/PLLA), which is widely used for

bone tissue reparation. The number average molecular weight (M_n), mechanical strength, and thermal stability of Hap/PLLA decreased with an increase in the absorbed dose, due to chain scission. However, the change in and damage to the material from the dose of irradiation required for sterilization were acceptable (Suljovrujic et al., 2007).

Electron beam radiation also affects poly(lactide-co-glycolide) (PLGA) and poly($_L$-lactide) (PLLA), which are widely used as a controlled release carrier for drug delivery. PLGA and PLA films were treated with electron beam at doses from 2.5 to 50 Mrad (25 kGy to 500 kGy) in the presence of air at room temperature. The mechanism of radiation-induced degradation was chain scission, which occurred first through scission of the polymer backbone main chain, followed by hydrogen abstraction. This change caused a decrease in molecular weights (M_n and M_w) and thermal properties (T_g, T_c, and T_m) of plastics. The greater stability of PLLA to electron beam is due to its higher crystallinity as compared to PLGA (Loo et al., 2005a). Another study of PLGA exposed to electron beam (50, 100 and 200 kGy) showed that PLGA films were hydrolytically degraded in phosphate-buffered saline solution at 37ºC with a higher irradiation dose (200 kGy), causing a faster mass loss and decrease in molecular weight (Loo et al., 2005a).

2.8 Migration of irradiated polymeric materials

The chemical changes in polymeric packaging materials by high-energy radiation cause secondary effects: polymerization and cross-linking. As a consequence, these predominant effects lead to the formation of gases, low-molecular weight radiolysis

products (RPs) and unsaturated bonds (Buchalla et al., 1993b; Gilbert et al., 1991). The amount of gases such as carbon monoxide, carbon dioxide, hydrogen, methane and hydrocarbons in irradiated packaging materials increases with the increase in absorbed dose. Formation of low-molecular-weight radiolysis products may induce off-odor and off-flavor and can lead to migration from packaging materials into products, which may affect the sensory characteristics of products (Buchalla et al., 1993b; Feazel et al., 1960; Killoran, 1972; Merritt, 1972).

Oxygen concentration, antioxidants, additives and stabilizers have been reported as the main factors which cause radiation-induced RPs development and migration (Franz & Welle, 2004). Irradiation in the presence of oxygen or air leads to radiation-induced chain scission. This phenomenon causes the formation of oxidative degradation products which are mainly volatile and semi-volatile organic compounds such as aldehydes, ketones, and carboxylic acids (Azuma et al., 1984; Bersch et al., 1959; Buchalla et al., 1993b; Dawes & Glover, 1996). After exposure in the presence of oxygen, the radiolysis product (RPs) concentrations from polymeric packaging materials increase and then become steady. This may happen due to the peroxy radicals being trapped in the polymer and reacting to form RPs until all of the free radicals are consumed (Paquette, 2004). The effect of irradiation atmosphere on development of RPs was also investigated. Polymer samples irradiated in air (presence of oxygen) had higher levels of oxygenated volatile and semi-volatile organic compounds than those irradiated in a vacuum. However, the irradiation environment did not affect the level of formation of hydrocarbons. The levels of hydrocarbons from irradiated polymers in the presence or absence of oxygen were the same (Azuma et al., 1984).

Higher irradiation doses may also destroy polymer additives, which can affect the specific migration behavior of polymer additives and their degradation compounds. In general, the concentration of particular radiolysis products increases linearly with absorbed dose. However it might deviate from linearity at some time. This depends on the range of the doses used (Franz & Welle, 2004).

Several new antioxidants and stabilizers have been created in order to improve the performance of plastic packaging materials. Studies on the effect of irradiation on volatile compounds and migration behavior are still limited. Also, these new polymer composites may not be approved by FDA for use in packaging intended for exposure to ionizing radiation (McNeal et al., 2004). Consequently, interaction between irradiated packaging materials and products, especially foods, must be a concern and must be evaluated.

Some studies from the literature related to RPs from ionized packaging materials including PS, PET, LDPE, PP, EVA, Nylon 6 and PVC by Paquett (2004) are listed in Table 2.12. The polymer samples were irradiated at 10-50 kGy with gamma or electron beam sources in the presence of oxygen at room temperature and then analyzed within one day of irradiation. According to FDA regulations, the dietary concentration (DCs) for RPs formed in packaging materials must not exceed 0.5 ppb (parts-per-billion), which is the safe level stated by FDA. It was observed that polymer adjuvants, EVA copolymer, GRAS (generally recognized as safe) substances, and pentanamide from Nylon 6 formed RPs exceeding 0.5 ppb DC. Moreover, the formation of RPs depended on the absorbed dose, dose rate, atmosphere, temperature, time after irradiation and food

Table 2.12 Radiolysis products from polymers irradiated to 10 kGy (Paquette, 2004)

Polymer / RP	Concentration in polymer (mg/kg)	Concentration in food (µg/kg)	DC (ppb)	Ref.
Polystyrene (PS) (density 1.06 g/cm^3)				
1-phenylethanol	3	8.2	0.41d	Buchalla et al. 1998
acetophenone	18	fresh: 7.8	0.39e	Buchalla et al. 1998
benzene	1	2.7 fresh: 0.53 froz.: 0.36	0.14j 0.02e	Buchalla et al. 1998
phenylacetaldehyde	3	8.2	0.41a	Buchalla et al. 1998
Benzaldehyde	18	fresh: 8.4	0.42e	Buchalla et al. 1998
Phenol	5	fresh: 2.5	0.12e	Buchalla et al. 1998
benzoic acid	4	fresh: 1.7	0.09e	Buchalla et al. 1998
unidentified carboxylic acid a	2.7	7.4	0.37d	Demertzis et al.1999
unidentified carboxylic acid b	2.7	7.4	0.37d	Demertzis et al.1999
Polyethylene terephthalate) (PET) (density 1.4 g/cm^3)				
diisopropyl ether	0.8	2.89 fresh: 0.11	0.14d 0.006e	Demertzis et al.1999
formic acid	0.297	1	0.05d	Komolprasert et al. 2001
acetic acid	0.369	1.3	0.06d	Komolprasert et al. 2001
1,3-dioxolane	0.384	1.4	0.07d	Komolprasert et al. 2001
2-methyl-1,3-dioxolane	3.7	fresh: 0.55	0.03e	Komolprasert et al. 2001
Acetone	0.086	0.3	0.02d	Komolprasert et al. 2001

Table 2.12 (cont'd)

Polymer / RP	Concentration in polymer (mg/kg)	Concentration in food (µg/kg)	DC (ppb)	Ref.
Low-Density Polyethylene (LDPE) (density 0.92 g/cm^3)				
acetic acid	8.5	8.5	1.0d,f	Azuma et al. 1984
propionic acid	5.1	12	0.6d,f	Azuma et al. 1984
n-butyric acid	1	2.4	0.12d	Azuma et al. 1984
n-valeric acid	0.4	0.95	0.05d	Azuma et al. 1984
butanoic acid vinylester or 2-furanmethanol	1.68	4	0.20d	Demertzis et al.1999
1,3-di-terf-butylbenzene from Irgafos 168	1.7	4	0.20d	Demertzis et al.1999
2,4-di-terr-butylphenol from Irgafos 168	30	71	3.6d,f	Bourges et al. 1992
2,6-di-tert-butyl-p-benzoquinone from Irganox 1010,1076	4	9.5	0.47d	Bourges et al. 1992
Polypropylene (PP) (density 0.90 g/cm^3)				
2,4-pentanedione	2.4	5.6	0.22d	El Makhzoumi 1994
1- dodecene	1.4	1.4	0.13d	El Makhzoumi 1994
acetone	2.6	6	0.24d	El Makhzoumi 1994
2- pentanone	0.75	1.7	0.07d	El Makhzoumi 1994
4-hydroxy-4-methyl-2-pentanol	1.9	4.4	0.18d	Demertzis et al.1999
3-methyi-2-butanone	1.5	3.5	0.14d	Demertzis et al.1999
acetic anhydride	7.4	17	0.69d,f	Demertzis et al.1999
3-methylbutanoic acid	2	4.6	0.19d	Demertzis et al.1999
acetic acid-(l-ethylhexyl)-ester	0.7	1.6	0.07d	Demertzis et al.1999

Table 2.12 (cont'd)

Polymer / RP	Concentration in polymer (mg/kg)	Concentration in food (µg/kg)	DC (ppb)	Ref.
Polypropylene (PP) (density 0.90 g/cm^3) [continued]				
octanoic acid	1.8	4.2	0.17d	Demertzis et al. 1999
3-methyl-4-methylene-hexane-2-one	0.9	2.1	0.08d	Demertzis et al. 1999
2,5-cyclohexadiene-1,4-dione	2.1	4.9	0.20d	Demertzis et al. 1999
hexadecanol or octadecanol	2	4.6	0.19d	Demertzis et al. 1999
4-methyl-2,3-pentanedione	1.1	2.6	0.10d	Demertzis et al. 1999
1,3-di-ferf-butylbenzene from Irgafos 168	17	39	1.6d,f	El Makhzoumi 1994
2,4-di-fert-butylphenol	75	174	7.0d,f	Bourges et al. 1992
from Irgafos 168	16g	28	1.1h	Bourges et al. 1993
l,3-di-re**-butyl-2-hydroxybenzene from Irgafos 168	14	33	1.3d,i	El Makhzoumi 1994
2,6-di-tert-butyl-p-benzoquinone from Irganox 1010,1076	14	33	1.3d,i	Bourges et al.1992
Ethylene-Vinyl Acetate Copolymers (EVA) (density 0.94 g/cm^3)				
Acetaldehyde	-	1600	32j	FDA 1986
n-propyl acetate	-	570	11j	FDA 1986
3-methylhexane	-	1000	20j	FDA 1986
n-heptane	-	430	8.6j	FDA 1986
tt-occane	-	67	1.3j	FDA 1986
Nylon 6 (density 1.1 g/cm^3) A				
Butanamide	2	5.7	0.11d	Selmi et al. 1999
pentanamide (PA6)	85	fresh: 42 fresh: 29	0.71e	Selmi et al. 1999

Table 2.12 (cont'd)

Polymer / RP	Concentration in polymer (mg/kg)	Concentration in food (µg/kg)	DC (ppb)	Ref.
Poly(vinyl chloride) (PVC) (density 1.3 g/cm^3)				
4- hydroxy-4-methyl-2-pentanone	6.2	21	1.0d,i	Demertzis et al.1999
5- hexen-2-one	3.8	13	0.64d,i	Demertzis et al.1999
l-ethoxy-2-heptanone	7.1	24	1.2d,i	Demertzis et al.1999
methoxyacetaldehyde diethyl acetal	15	50	2.5d,i	Demertzis et al.1999
diethoxy acetic acid ethylester	4	13	0.67d,i	Demertzis et al.1999
3-methylheptyl acetate	2.4	8	0.40d	Demertzis et al.1999
diethyl adipate	8.3	28	1.4d,i	Demertzis et al.1999
nonanoic acid ethylester	2.4	8	0.40d	Demertzis et al.1999
unidentified n-alkane acid ethylester a	34.5	116	5.8d,i	Demertzis et al.1999
unidentified n-alkane acid ethylester b	50.3	169	8.4d,i	Demertzis et al.1999

DC represents dietary concentration (DCs in bold exceed 0.5 ppb)

a = Concentrations determined at 20-50 kGy were extrapolated to 10 kGy, assuming a linear relationship between concentration and dose. Concentrations reported for unirradiated control samples were subtracted from those reported for irradiated test samples.

b = Only the highest concentration reported for each RP in the literature is included in this table.

c = Assuming a food mass-to-polymer surface area ratio of 10 g/in^2 (see text).

d = 100% migration calculation.

e = Modeled migration (see text).

f = Migration models failed to describe migration below 100% from thin films made of polymers that yield fast diffusion coefficients.

g = Migration to 10% ethanol food simulant expressed as mg/kg polymer tested.

h = Measured migration value into 10% ethanol after 10 d at 40° C.

i = Migration modeling not possible due to lack of diffusion coefficients for PVC films.

j = Measured migration value into 95% ethanol after 1 d at room temperature.

simulant. These RPs from packaging materials consisted of low-molecular weight aldehydes, acids and olefins (Paquette, 2004). El Makhzoumi (1994) investigated the formation of up to 63 volatile compounds in irradiated PET, PE, and OPP films. Some research studies that investigated the formation of volatiles in packaging materials are listed in Table 2.10.

At irradiation doses below 25 kGy, several volatile organic compounds were observed in irradiated LDPE and OPP films, such as ketones, aldehydes and carboxylic acids, which can affect the organoleptic properties of prepackaged foods and their shelf-life. However, no significant overall migration from ionized LDPE and PP was detected (Rojas De Gante & Pascat, 1990). Primary (methyl derivatives) and secondary compounds (ketones, aldehydes, alcohols, carboxylic acid) were formed in irradiated LDPE, EVA and PET/PE/EVOH, PE multilayer films with electron beam. These volatile compounds increased with increasing absorbed irradiation dose, and may affect the shelf life of packaging materials (Riganakos et al., 1999).

Irradiation causes the formation of hydrogen, carbon dioxide, carbon monoxide and methane gas and produces volatile oxidation products in LDPE, HDPE, PET and PVC (Crook & Boylston, 2004). LDPE irradiated with electron beam (20 kGy) produced several volatiles including aliphatic hydrocarbons, aldehydes, ketones and carboxylic acid (e.g. acetic acid, propionic acid, n-butyric acid, and n-valeric acid), which are the main causes of off-odor development. The formation of carboxylic acid depends on the processing history of the materials and on the presence of various additives. The intensity of off-odor is associated with the concentration of oxygen in the atmosphere

(Azuma et al., 1984). Tripp (1959) observed that irradiated LDPE developed more intense odors than irradiated HDPE. Also, irradiation of these polyethylenes produced a stronger off-odor than irradiation of polystyrene, polyamides and polyesters. Transfer of the off-odor from laminated LDPE/HDPE film to water occurred at low irradiation doses (10 kGy) and the intensity of the odor increased with increasing dose (up to 150 kGy) (Grünewald & Berger, 1961).

Marque (1995) detected alkyl radicals, which were oxidized to peroxyl radicals in the presence of air after ionization treatment of PP at 40 kGy under vacuum. The antioxidants in polyolefins, PVC and HDPE films irradiated with gamma and electron beam such as phenol antioxidants, Irganox 1076 and Irganox 1010 decreased as the absorbed dose increased. The antioxidant degradation rate depended on the polymer type and antioxidant investigated. Antioxidant degradation products in PP treated with electron beam at doses of 2 to 10 kGy were detected in food-simulating liquids; however, migration behavior of antioxidants was not affected by irradiation (Allen et al., 1987; Allen et al., 1990; Bourges et al., 1992). PP exposed to electron beam at 10 kGy in the presence of oxygen formed low-molecular-weight volatile RPs which became stable after 15 days, whereas the concentration of volatile higher-molecular-weight RPs of Irganox and Irgafos antioxidants used in the polymer increased by a factor of 2 to 5 during 1 to 60 days and then they leveled off (Bourges et al., 1992; El Makhzoumi, 1994).

Studies on the effects of ^{60}Co gamma irradiation at a dose of 44 kGy on food packaging polymers such as PE, PP, PET, PA, PS and PVC showed an increase in low

molecular weight volatile compounds from PE and PP, due to oxidative decomposition of the materials and polymer substances like oligomers and additives. PVC was not resistant to irradiation treatment and there was no significant change in volatile compounds from PET, PA and PS (Demertzis et al., 1999). Lox et al. (1986) found that the global migration from PVC exposed to gamma and electron beam increased at a low dose of 3-15 kGy, but decreased at a dose higher than 15 kGy.

When volatile compounds from two semi-rigid amorphous PET and copolymer materials irradiated with ^{60}Co and electron beam at doses of 5, 25 and 50 kGy were investigated, no differences in volatiles were seen compared to non-irradiated samples. Even if the acetaldehyde levels increased after irradiation, the treatment had no influence on non-volatile compounds migrating into food simulants (Komolprasert et al., 2003). Cesium-137 (^{137}Cs) gamma irradiation at a dose of 25 kGy significantly increased the level of volatile compounds in crystalline and oriented semi-rigid PET homopolymer (Komolprasert et al., 2001). Komolprasert et al. (2001) reported that the major volatile compounds of irradiated PET were formic acid, acetic acid, 1,3-dioxolane, and 2-methyl-1,3 dioxolane.

There was no significant difference in the formation of radiolysis products and sensory changes between the multilayers which contained a middle buried layer of recycled LDPE and 100% virgin LDPE treated with gamma irradiation at doses ranging from 5-60 kGy (Chytiri et al., 2005). Goulas et al. (2003b) reported that an irradiation dose of 30 kGy induced a decrease in overall migration from Ionomer/EVOH/LDPE and LDPE/PA/Ionomer films into 3% acetic acid and iso-octane but an increase in overall

migration from PP/EVOH/LDPE-LLDPE into iso-octane compared with the non-irradiated samples.

The comparison between the effects of irradiation sources on the formation of oxygenated volatiles was also investigated. Amounts of oxygenated volatiles and volatile profiles created by electron beam irradiation were less than that after gamma irradiation (Buchalla et al., 1993a; Deschenes et al., 1995).

2.9 Mathematical modeling of food migration

The migration of chemical components from packaging materials into food products has become an important safety aspect. The amount of migrants transferring from plastic packaging materials to foods or simulants depends on the characteristics of the packaging materials, migrant, food/food simulant and temperature (Helmroth et al., 2002; Riquet & Feigenbaum, 1997). Migration from polymeric materials to food occurs when migrants from the polymer transfer through voids or gaps between the polymer molecules. The rate of migration, thus, depends on the size and shape of the migrants as well as on the size and number of gaps between the polymer molecules, which are based on polymer properties such as density, crystallinity, crosslinking and branching.

The glass transition temperature (T_g) is also an important factor in the migration rate. At temperatures below T_g, an amorphous polymer is glassy and brittle (called the glassy state), decreasing the extent of migration while at temperature above T_g, the polymer molecules become rubbery and elastic (rubber state) which results in a higher

probability for migrants to transfer through the matrix of the polymer. Therefore, the lower the T_g of a polymer, the greater migration rate. Irrespective of T_g, the higher the temperature, the higher the migration rate (Brydson, 1995; Crank & Park, 1968 ; Helmroth et al., 2002; Selke et al., 2004; Stannett et al., 1979). In addition, polarity and solubility affect the migration rate due to interactions between the polymer, migrant and food simulant. A list of food-simulating solvents is provided in Table 2.13. The migration rate is generally higher in fatty food simulants (e.g. olive oil, 95% ethanol or isooctane) than in aqueous food simulants such as water (Riquet & Feigenbaum, 1997; Till et al., 1987.).

In general, the level of migration in food can be determined by different methods: 1) accelerated migration studies which are conducted with food simulating solvents under the most severe conditions of use; 2) migration studies assuming 100% migration from the packaging to food with actual use or residue levels; 3) mathematical modeling of mass transfer from packaging materials to food (Bailey et al., 2008).

Mathematical modeling is popularly used to predict the mass transfer from plastic packaging materials into food products as it can help to reduce the need for migration experiments, which are often expensive and time-consuming. In general, Fick's Second Law of Diffusion is used in most studies of mass transfer (Brandsch et al., 2002; Helmroth et al., 2002; Manzoli et al., 2008; Selke et al., 2004).

The Fickian diffusion equation is:

$$\frac{\partial C}{\partial t} = D\frac{\partial^2 C}{\partial x^2} \tag{2.1a}$$

where C is the concentration of the migrating substance in the polymeric material at time, t, x is the distance (in the diffusion direction), and D is the diffusion coefficient.

$$K_{p,f} = \frac{C_{p,\infty}}{C_{f,\infty}} \tag{2.1b}$$

where $K_{p,f}$ is partition coefficient, $C_{p,\infty}$ is the concentration of migrant in the sample at equilibrium (g/cm^3), $C_{f,\infty}$ is the concentration of migrant in the food or simulant at equilibrium (g/cm^3).

Table 2.13 Food simulants and their characteristics

Simulant	Water content (%)	A_w	pH	Viscosity (cSt) at 40°C
Official simulants				
• Distilled water	100	1.00	6.5	0.73
• Acetic acid (3% w/v in water)	97	0.99	2.5	0.78
• Rectified olive oil	-	-	-	42.57
Substitute fatty food simulants				
• Isooctane	-	-	-	0.67
• Ethanol (95% v/v in water)	6	0.96	5.2	1.01
Alternative simulants				
• Glycerol (16.7% w/w in water)	83	0.96	3.5	0.92
• Glycerol (33.5% w/w in water)	66	0.90	3.6	1.59
• Glycerol (51.0% w/w in water)	49	0.80	3.7	3.30
• NaNO3 (46% w/w in water)	54	0.74	4.8	1.34
• Aqueous agar gel (1.5% w/v)	98	0.99	5.5	-

cSt (centiStokes) represents kinematic viscosity

The two model parameters used in the main models for migration prediction are 1) the diffusion coefficient (D); and 2) the partition coefficient (K) representing the ratio of the migration concentration in the package to the migrant concentration in the food simulant at equilibrium. The effect of the model parameters on the migrant concentration in the food simulant as a function of time is based on Fick's law of diffusion as shown in Figure 2.5 (Helmroth et al., 2002).

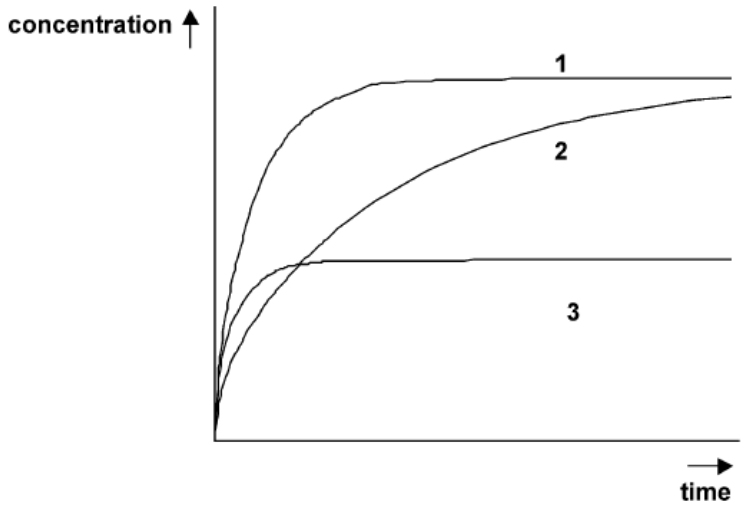

Figure 2.5 The effect of model parameters D and K on additive concentration in a food simulant caused by migration from a plastic material as a function of time. Curve 1 represents D = D_1, K = K_1; Curve 2 represents D < D_1, K = K_1; Curve 3 represents D =D_1, K > K_1

Common assumptions in migration modeling are 1) a uniform distribution of the migrant in the packaging material; 2) migration from one side of the packaging material to the liquid food; 3) a well mixed liquid food with no gradient of migrant concentration, which gives a very large surface mass transfer coefficient (k_m); 4) the surface mass transfer coefficient is much larger and Biot number [Bi] = $K_{FP}k_mL_P/D \approx \infty$ (where K_{FP} is

partition coefficient of migration between food and packaging film, L_p is thickness of packaging film), which means that migration is controlled by Fick's Law of diffusion in the packaging material and the effect of mixing is negligible; 5) a constant value for the diffusion and partition coefficients, varying only with temperature; 6) an equilibrium state exists at the interface of the food and the packaging material; and 7) edge effects are negligible (Chung, 2000; Chung et al., 2001; Crank, 1975; Crawford et al., 1996; Gandek et al., 1989; Reid et al., 1980).

Migration can be modeled in two ways based on Fick's Second Law: limited packaging and infinite food as shown in equations (2.2) and (2.3), and limited packaging and limited food, equation (2.6) (Chung et al., 2002). The analytical solution to Ficks' law in infinite food can be given by;

$$\frac{M_{F,t}}{M_{F,L}} = 2\left(\frac{Dt}{{L_P}^2}\right)^{0.5}\left\{\frac{1}{\pi^{0.5}} + 2\sum_{n=1}^{\infty}(-1)\,ierfc\left[\frac{nL_P}{(Dt)^{0.5}}\right]\right\} \tag{2.2}$$

For large migration times, the solution can be given as:

$$\frac{M_{F,t}}{M_{F,L}} = 1 - \sum_{n=0}^{\infty}\frac{8}{(2n+1)^2\pi^2}\,exp\left[\frac{-D(2n+1)^2\pi^2 t}{4{L_P}^2}\right] \tag{2.3}$$

where $M_{F,t}$ is the amount of migrant transferred from the packaging film to the food from time zero to time t; $M_{F,L}$ is the amount of migrant in food at the end of migration for limited packaging, infinite food; D is the diffusion coefficient of migrant in the packaging material and L_p is the thickness of the packaging material.

The following equations (equation (2.4) and (2.5)) are the simplified version of equation (2.2), which is used extensively to predict the diffusion coefficient. This simplification is based on the assumption of a short migration time when ierfc[nL$_p$/(Dt)$^{0.5}$] $\rightarrow$ 0. However these equations are not accurate for determining the diffusion coefficient for partition migration (i.e. when $M_{P,0} > M_{F,\infty}$).

$$\frac{M_{F,t}}{M_{P,0}} = \frac{2}{L_P}\left(\frac{Dt}{\pi}\right)^{0.5} \tag{2.4}$$

$$\frac{M_{F,t}}{M_{F,\infty}} = \frac{2}{L_P}\left(\frac{Dt}{\pi}\right)^{0.5} \tag{2.5}$$

where $M_{p,0}$ is the amount of initial migrant in the packaging film; $M_{F,\infty}$ is the total amount of migrant transferred from the packaging film to the food until equilibrium

In the case of limited packaging and limited food, (Chung et al., 2002) proposed a modified boundary condition at x = L_P in the migration model as shown in equation (2.6). The equation (2.6) assumes that there is no migrant concentration initially and as migration occurs the migrant concentration in the food reaches equilibrium (Chung et al., 2001; Gandek et al., 1989).

$$K_{FP}\left(\frac{V_{\mathrm{F}}}{A}\right)\frac{\partial C_P}{\partial t} = -D\frac{\partial C_P}{\partial x}\, at\, x = L_P,\ t > 0 \tag{2.6}$$

where V_F is the volume of food; K_{FP} is the partition coefficient; A is the area of the packaging film; C_p is the concentration of migrating substance in the polymeric material; D is the diffusion coefficient; and x is the distance of diffusion. The initial condition is $C_p = C_0$ (Crank, 1975).

The solution of equation (2.1) using equation (2.6) as a boundary condition can be given by equation (2.7) below (Crank, 1975):

$$\frac{M_{F,t}}{M_{F,\infty}} = 1 - \sum_{n=1}^{\infty}\frac{2\alpha(1+\alpha)}{1+\alpha+\alpha^2 q_n^2}\, exp\left[\frac{-Dq_n^2 t}{L_p^2}\right] \tag{2.7}$$

where, q_n are the non-zero positive roots of $\tan q_n = -\alpha q_n$, and α is the mass ratio of migrant in the food to that in the packaging film at equilibrium ($\alpha = K_{FP}V_F/V_P$).

The numerical solution of Fick's law can also be used to estimate the diffusion parameter. Equation (2.1) has been discretized using a finite difference numerical scheme (Manzoli et al., 2008).

$$\frac{d}{dx}D(x)\frac{d}{dx}C(x) \cong \frac{d}{dx}D(x)\left[\frac{C_{i+1/2} - C_{i-1/2}}{\Delta_i + \Delta_{i-1}}2\right]$$

$$= \left(D_{i+1/2} \frac{C_{i+1} - C_i}{\Delta_i} - D_{i-1/2} \frac{C_i - C_{i-1}}{\Delta_{i-1}} \right) \frac{2}{\Delta_i + \Delta_{i-1}}$$

$$= \left(\frac{2D_{i+1/2}}{\Delta_i (\Delta_i + \Delta_{i-1})} \right) C_{i+1} - \left(\frac{2D_{i+1/2}}{\Delta_i (\Delta_i + \Delta_{i-1})} \right) + \left(\frac{2D_{i-1/2}}{\Delta_{i-1} (\Delta_i + \Delta_{i-1})} \right) C_i + \left(\frac{2D_{i-1/2}}{\Delta_{i-1} (\Delta_i + \Delta_{i-1})} \right) C_{i-1} \quad (2.8)$$

where Δ_i is the non-constant distance between successive points i and D is the diffusion coefficient. This numerical solution of the diffusion model provides flexibility for modeling irregularly shaped packages.

The diffusion coefficient for a plasticizer in PVC film was studied and the kinetics of migration of di-2-ethylhexyl phthalate (DEHP) from PVC film into solid cheese were measured by total immersion and gas chromatography. Fick's law model as shown in equation (2.1) was solved by a finite difference scheme as shown above. The diffusion coefficient of DEHP inside PVC was 14 $\mu m^2/s$. The diffusion coefficient of the UV absorber in PET was also determined using n-heptane as a food simulant. The diffusion coefficient for Tinuvin P, which is an additive substance inside PET, was 4.3×10^2 μm^2/day and diffusion of Tinuvin P inside n-heptane was 5×10^5 μm^2/day (Manzoli et al., 2008).

The above migration models are used to study the diffusion process in packaging and food/pharmaceutical systems (Brandsch et al., 2002; Chan et al., 1978; Piringer et al., 1998). These models are useful in estimating the migration of various compounds through different packaging materials. However, there are some challenges to the

migration model as it requires systematic experiments to obtain good data (Manzoli et al., 2008; Mercea & Piringer, 2008). The model assumption laboratory results need to be completely understood in order to use the models as predictive models.

Chapter 3

Materials and Methods

3.1 Materials

The bio-based film materials used in this study included a commercial polylactic acid (PLA) film with thickness of 0.0229 mm purchased from BI-AX International Inc. (Ontario, Canada) and three types of cellophane films including uncoated cellophane (CP), nitrocellulose two-side coated cellophane (CM) and polyvinylidene chloride (PVdC) two-side coated cellophane (CK)) with 0.0229 mm thickness supplied by Innovia. The film samples were cut into three different sizes: 1) 203.2 mm × 25.4 mm for mechanical tests, 2) 50.8 mm × 50.8 mm for physical properties, thermal analysis, permeability (of PLA) and migration test, and 3) a hexagonal shape (area of 50 cm^2) for barrier analysis of cellophane films.

3.2. Irradiation

3.2.1 Gamma irradiation

Film samples were irradiated with a ^{60}Co gamma irradiation source of 1.3 million curies at absorbed doses of 1, 5, 10 and 30 kGy at Food Technology Service, Inc. (FTSI), FL, USA. The average dose rate was 3200 kilogray per seconds (kGy/sec). Irradiation treatment was carried out at room temperature and in the presence of air. Irradiation doses were measured using Alanine film dosimeters (Kodak, USA) with a Bruker-Biospin dosimeter reader.

3.2.2 Electron beam (E-beam) irradiation

For E-beam irradiation, film samples were irradiated with electron beam at irradiation doses of 1, 5, 10 and 30 kGy, at an electron beam energy level of 4.5 MeV and beam currents of 1.5 and 15 mA, at room temperature and in the presence of air. The electron beam irradiation was performed at NEO Beam Alliance Ltd, OH. Irradiation doses were measured using Alanine film dosimeters (Kodak, USA) with a Bruker-Biospin dosimeter reader.

3.2.3 X-ray irradiation

PLA and cellophane films were treated at 10 kGy using a low-energy X-ray irradiator (Rainbow™ II, Rayfresh Foods Inc., Ann Arbor, MI) at Michigan State University. The X-ray tube operates at a maximum constant potential of 70 kV and a filament current of 57 mA, which gives 4 kW of maximum allowable input power, which was applied in this study. Irradiation was carried out in air at room temperature and at the typical dose rate of 20 Gy/s. The standard spectrophotometric method (Spectronic Genesys 20, Thermo Fisher Scientific, Inc., Waltham, Massachusetts, USA) based on calibration curves at 500/550 nm was used to measure the irradiation dose.

3.3 Stability Study

Stability studies were performed after 3, 6 and 9 months of storage on samples irradiated at 1, 5, 10 and 30 kGy. Non-irradiated film samples were used as controls. All samples were kept in plastic containers to avoid influence from other light sources and stored at 25 ± 1ºC, 60% RH. The different sample codes used in this dissertation are

presented in Table 3.1. To represent the sample codes at different storage times, 3M (3month), 6M (6 month) and 9M (9 month) were used as an extension to the codes presented in Table 3.1.

Table 3.1 The acronyms for samples used in this dissertation

Acronyms	Description
PA	Polylactic acid
CP	Uncoated cellophane
CM	Nitrocellulose coated cellophane
CK	PVdC coated cellophane
CoPA	Non-irradiated polylactic acid
CoCP	Non-irradiated uncoated cellophane
CoCM	Non-irradiated nitrocellulose coated cellophane
CoCK	Non-irradiated PVdC coated cellophane
GMPA	Gamma irradiated polylactic acid
GMCP	Gamma irradiated uncoated cellophane
GMCM	Gamma irradiated nitrocellulose coated cellophane
GMCK	Gamma irradiated PVdC coated cellophane
EBPA	E-beam irradiated polylactic acid
EBCP	E-beam irradiated uncoated cellophane
EBCM	E-beam irradiated nitrocellulose coated cellophane
EBCK	E-beam irradiated PVdC coated cellophane
XPA	X-ray irradiated polylactic acid
XCP	X-ray irradiated uncoated cellophane
XCM	X-ray irradiated nitrocellulose coated cellophane
XCK	X-ray irradiated PVdC coated cellophane

3.4 Property tests

3.4.1 Color measurement

Changes in film color were measured using a Hunter colorimeter (LabScan, model LSXE, Hunter Laboratory, Inc., VA, USA). An aperture size of 25.4 mm was used as a test area. Hunter color L*, a* and b* values were determined. The instrument was calibrated to standard black and white tiles. Average values from triplicate samples were reported.

3.4.2 Surface Tension

The surface tension of film samples was measured using the wetting tension test (Jemmco, LLC, WI, USA) in accordance with ASTM D2578. The surface tension was reported as dynes/cm, which is compliant with dyne test inks. If the liquid spreads out over the material surface, adhesive forces dominate (Figure 3.1-A). If cohesive forces dominate, then the liquid forms droplets on the material surface (Figure 3.1-B).

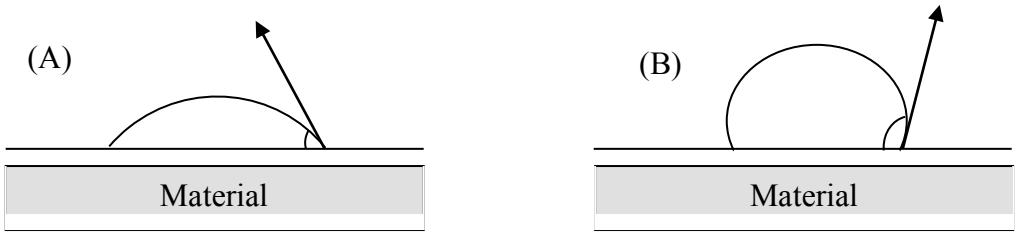

Figure 3.1 Surface energy of polymeric materials: adhesive forces (A) and cohesive forces (B)

3.4.3 Fourier transform infrared (FTIR) spectroscopy

FTIR spectra of non-irradiated and irradiated samples were obtained using a Shimadzu IR-Prestige 21 spectrophotometer (Columbia, MD, USA) with an Attenuated Total Reflectance (ATR) attachment from PIKE Technologies (Madison, WI, USA). Spectrometric measurements were performed at room temperature with 40 scans and a resolution of 40 cm^{-1}. The spectra were determined in absorbance mode for wave numbers ranging from 650 to 4000 cm^{-1}.

3.4.4 Thermal properties

Thermal analyses including glass transition temperature (T_g), crystallization temperature (T_c), and melting temperature (T_m) were performed using a differential scanning calorimeter (DSC) from TA Instruments model Q200 (New Castle, DE, USA) equipped with a refrigerated cooling system. Film samples (6 - 8 mg) were placed in aluminum DSC pans (non-hermetic aluminum pan for PLA samples and hermetic aluminum pan for cellophane samples) and encapsulated using a sample press. An empty pan was used as reference. The samples were heated from -50ºC to 185ºC at a heating rating of 10ºC/min in accordance with ASTM D3418-03 (ASTM, 2003a). Thermograms were analyzed with TA Instruments Universal Analysis 2000 software. The instrument calibration was performed using sapphire as a standard.

The properties were measured from the second heating scan since the first scan was meant to discard the thermal history of the material. However, for cellophane samples, the values from the first cycle were reported because there were no peaks observed in the second cycle. The exothermic and endothermic peaks, for T_c and T_m, respectively, were not determined for cellophane since these peaks were not observed.

3.4.5 Molecular weight

Gel permeation chromatography (GPC) was employed to analyze the weight average molecular weight (M_w) and number average molecular weight (M_n) of PLA. A Waters GPC chromatograph with refractive index (RI) detector, a series of 3 columns

(HR4, HR3, HR2) and Waters Breeze software (Waters Inc., Milford, MA, USA) was used. Twenty milligrams of sample was dissolved in 10 ml of tetrahydrofuran (THF). The solution was filtered through a polytetrafluoroethylene (PTFE) disk filter (0.45 µm). An injected volume of 100 µl was used for analysis. GPC was performed at 35ºC with a flow rate of 1 ml/min and a runtime of 45 min. The calibration was done using polystyrene molecular weight standards (M_W range of $1.20x10^3$ to $3.64x10^6$ Da).

3.4.6 Mechanical properties

Film tensile strength, elastic modulus (Young's modulus) and elongation at break were analyzed using an Instron testing machine (Instron Inc., Norwood, MA, USA), equipped with Bluehill v.2.21 software. The strip-shaped samples (152.4 mm × 25.4 mm) in the machine direction (MD) and cross-machine direction (CD) were tested according to the standard ASTM 882-02 method (ASTM, 2002). The initial grip distance was 50.8 mm. The grip separation rate was set at 25.4 mm/min. Five replicates were tested for each treatment.

3.4.7 Barrier properties

Permeability of non-irradiated and irradiated PLA and cellophane films (except uncoated cellophane, CP) was measured using Mocon instruments (Mocon®, Minneapolis, MN, USA). Permeability to oxygen, carbon dioxide and water vapor was measured for PLA samples. Due to the high permeability of PLA film, which was beyond the machine testing range, a 3.14 cm^3 mask was used as the test area for all permeability tests by placing the specimen on a cut masking film. Oxygen and carbon

dioxide permeability of coated cellophane samples were determined using a sample area of 50 cm^3. Three specimens per sample set were measured and the mean values of triplicates were reported as $Kg.m.m^{-2}.s^{-1}.Pa^{-1}$.

3.4.7.1 Oxygen barrier properties

The oxygen transmission rates (OTR) were measured using an oxygen permeability analyzer (Oxtran® Model 2/21, Mocon, MN, USA) in accordance with ASTM D3985-05 (ASTM, 2005a). Analysis occurred at 23 ± 1ºC, and 0% relative humidity. The analyzer was calibrated using certified films from Mocon labeled as having transmission rates of 0.2514 and 0.2453 cc/pkg/day.

3.4.7.2 Carbon dioxide barrier properties

The carbon dioxide transmission rates (COTR) were determined using a carbon dioxide permeability analyzer (Permatran-C® Model 4/41, Mocon, MN, USA) following ASTM F2476-05 (ASTM, 2005c). The COTR tests were performed at 23 ± 1ºC, and 0% relative humidity. The calibration was done using a certified film from Mocon labeled as having a transmission rate of 1.40 cc/pkg/day.

3.4.7.3 Water vapor barrier properties

The water vapor transmission rates (WVTR) were evaluated using a water vapor permeability analyzer (PermatranTM-W® Model 3/33, Mocon, MN, USA) in accordance with ASTM F1249-05 (ASTM, 2005b). WVTR measurements were carried out at 23 ±

1ºC and 100% relative humidity. The nitrogen flow rate was 100 standard cubic centimeters per minute (SCCM). The calibration was done using a certified film from Mocon labeled as having a transmission rate of 0.01689 gm/pkg/day.

3.5 Migration test

3.5.1 Food and packaging interaction

Films were cut into square pieces measuring 50.8 mm x 50.8 mm and then threaded onto a stainless steel wire with alternating glass beads used as specimen supports, in accordance with ASTM D 4754 (ASTM, 2003b). Samples in glass beakers were directly exposed on two sides (total two-side contact surface area 200 cm^2) to 100 ml of four different food simulants (distilled water, 3% acetic acid, 15% ethanol and 95% ethanol), in accordance with the CEN standard EN 1186-1 (EN, 2002a) (Figure 3.2). Beakers were covered by glass watch glasses and parafilm to avoid evaporation of the simulant during the contact period. Samples were kept in a thermostatically controlled incubator at 40 ± 1ºC for 10 days.

One hundred ml of food simulant was placed in beakers containing only the support stand and glass beads, as a blank. The beakers containing blank samples were also covered with glass watch glasses and parafilm, and kept in a thermostatically controlled incubator at 40 ± 1ºC for 10 days. After treatment, film samples were removed from the beakers. Two ml of simulant was removed by pipet and transferred to an HPLC vial for the specific migration test (this will be future work and hence the

results of this test are not included in this dissertation). The remaining simulant in the beaker was used for the overall migration test.

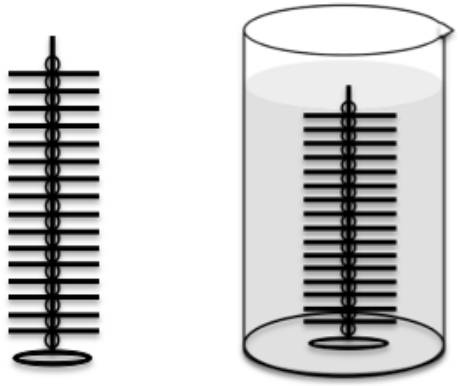

Figure 3.2 Film specimen threaded on sample support for total immersion testing in a food simulant, in accordance with FDA (ASTM, 2003b)

3.5.2 Overall migration

Testing of overall migration was performed in accordance with the European regulation (EC, 1997; EEC, 1990; EN, 2002a; EN, 2002b). The food simulant was placed in a pre-weighed evaporating flask (OHAUS, Pleasant Prairie, WI, USA), which was dried in an oven at 105ºC for 1 hour and then placed in a desiccator for 1 hour before use. The simulant in the flask was evaporated to dryness using a rotary evaporator (BUCHI Rotavapor R-3, New Castle, DE, USA) with distilled water in the thermostatic bath, depending on the boiling point of the simulant (water at 55ºC, acetic acid at 54ºC, 15% ethanol at 50ºC and 95% ethanol at 48ºC). After evaporation, the evaporating flask was kept in an oven at 105ºC for 1 hour and in a desiccator for 1 hour before weighing. The mass of non-volatiles was calculated as the overall migration in

milligrams per square decimeter of surface area of test sample (mg/dm^2) as shown in Eq. 3.1.

$$M = \frac{(m_a - m_b)}{S} \times 1000 \tag{3.1}$$

where M is the overall migration from the polymeric material into the food simulant, in milligrams per square decimeter of surface area of test materials (mg/dm^2), m_a is the mass of the residue from the polymer after evaporation of food simulant in grams (g), m_b is the mass of residue from only the food simulant (blank), in grams (g), and S is the surface area of the test material that came into contact with the food simulant (dm^2).

3.6 Compostability test

3.6.1 Compost preparation

Two types of compost were used in this test: 1) commercial organic manure compost from Earthgro (Hyponex Corporation, OH, USA) (commercial compost) was used for non-irradiated and gamma irradiated samples after 3 months of storage, and 2) mature manure compost from the Michigan State University composting facility (MSU compost), East Lansing, MI., USA, was used for the 6 and 9 months of storage.

The moisture content of the compost was determined using a moisture analyzer (AD MX-50 moisture analyzer, IL, USA) and pH was measured (Omega pH meter, Omega Engineering Inc., CT, USA). The carbon to nitrogen (C/N) ratio was measured using a PerkinElmer CHN analyzer (Waltham, Mass., USA). The composts were screened to separate pieces of rock, wood and other residuals and then stored in

closed opaque containers in a dark chamber at 50 ± 1ºC for activation for 2-3 days. The activated composts were mixed with vermiculite saturated with distilled water before use. Vermiculite, a clay mineral, is known to enhance microbial activity (Bellia et al., 2000; Bellia et al., 1999; Pesenti-Barili et al., 1991).

3.6.2 Sample preparation

Film samples were analyzed for carbon content (Perkin Elmer CHN analyzer, model 2400, Waltham, Mass., USA) to determine the percent of carbon in the polymer that was converted to carbon dioxide. These data were used to calculate the percent mineralization. Film samples were cut into 1 cm × 1 cm pieces as shown in Figure 3.3 for PLA and Figure 3.4 for cellophane.

Figure 3.3 Pieces of cut PLA samples (1 cm × 1 cm)

Figure 3.4 Three different cellophane samples measuring 1 cm × 1 cm: Left to right, uncoated cellophane (CP), nitrocellulose-coated cellophane (CM), PVdC-coated cellophane (CK)

3.6.3 Aerobic respirometic system

An in-house built direct measurement respirometric (DMR) system (Kijchavengkul et al., 2006) was used to determine biodegradability of the PLA and cellulose films in compost, in accordance with ASTM International - D5338 and ISO 14855-1. The respirometric test components included an air supply, airtight closed containers called bioreactors, and a device to measure the release of carbon dioxide (CO_2) (Figure 3.5). Bioreactors were constructed from 1.9 L (0.5 gallon) glass jars containing mesh screens inside for air ventilation and airtight closures (Figure 3.6). A hole was drilled in the jar 2.5 cm above the bottom and a plastic barb lure was attached to create an air inlet port. Two holes were drilled in the lid 3.81 cm apart, one connected to a tube fitting to create an air outlet port and the other fitted with a rubber septum for water injections. Humidified air was automatically pumped in to supply oxygen (O_2) to the bioreactors from the bottom port (inlet). The air was pretreated by passing through a

scrubbing system (a series of six 3.78 L canisters, each contained 3 L of soda lime ($Ca(OH)_2$) to generate CO_2-free air). All bioreactors were connected to manifolds with solenoid valves (Clippard Minimatics, Cincinnati, OH, USA). Exhaust air from the bioreactors was periodically sent to a detector. The data were recorded by a data acquisition system (DAQ).

There were three types of bioreactors: 1) blank controls (540 g of compost mixture only), 2) positive controls (540 g of compost mixture with 8 g of cellulose powder (Sigma Aldrich, St. Louis, Mo., USA), and 3) test samples (540 g of compost mixture with 8 g of test materials). The DRM chamber was maintained at a temperature of 58 ± 2ºC and humidity at 50–60% RH. The CO_2-free air, which was pretreated by passage through the scrubbing system, was supplied to the bioreactors through inlet ports at a flow rate of 40 scm^3/min. When operating the system, the total run time for each cycle (one bioreactor to another bioreactor) was 17 min. Measurement time for each bioreactor was 12 min and purge time was 5 min with CO_2-free air to clean the pathway and detector. The measurement time for CO_2 concentration, which was used for analysis, was the last 30 seconds at the steady state. LabView software (LabView™vi, National Instruments, TX, USA) was used to operate the instrument. The CO_2 gas evolved from aerobic biodegradation inside the bioreactors was carried through the outlet port to a CO_2 infrared gas analyzer (model LI-840 from LI-COR, Lincoln, Nebraska). The biodegradation experiment passed validation if the percentage of biodegradation of cellulose (positive control) approached 70 percent within 45 days

with the biodegradation of test materials then continued for not more than 180 days according to ASTM D5338 (ASTM, 2011a), ASTM D6400 (ASTM, 2012) and ISO 14855-1 (International Standard, 2005). The DMR system was calibrated by injecting known amounts of pure CO_2 (1, 2, 4, and 8 cm^3) into empty bioreactors at the operating conditions. A calibration curve was obtained by plotting the actual CO_2 concentration versus measured concentration.

For the duration of the experiment, the airflow, temperature, moisture content and pH were monitored. All bioreactors were shaken weekly to avoid clumps, channels and non-uniform distribution of samples. Compost moisture was partially maintained by the humid air flowing into the bioreactors. The moisture content of the compost in a separate bioreactor, used for this purpose only, was measured weekly and used to determine the required amount of water to inject into the bioreactors to maintain the desired moisture level during the incubation period. The pH of the compost was periodically measured after diluting the compost with distilled water, using a dilution ratio of 5:1 w/w and pH paper (Hydrion, Micro Essential, USA).

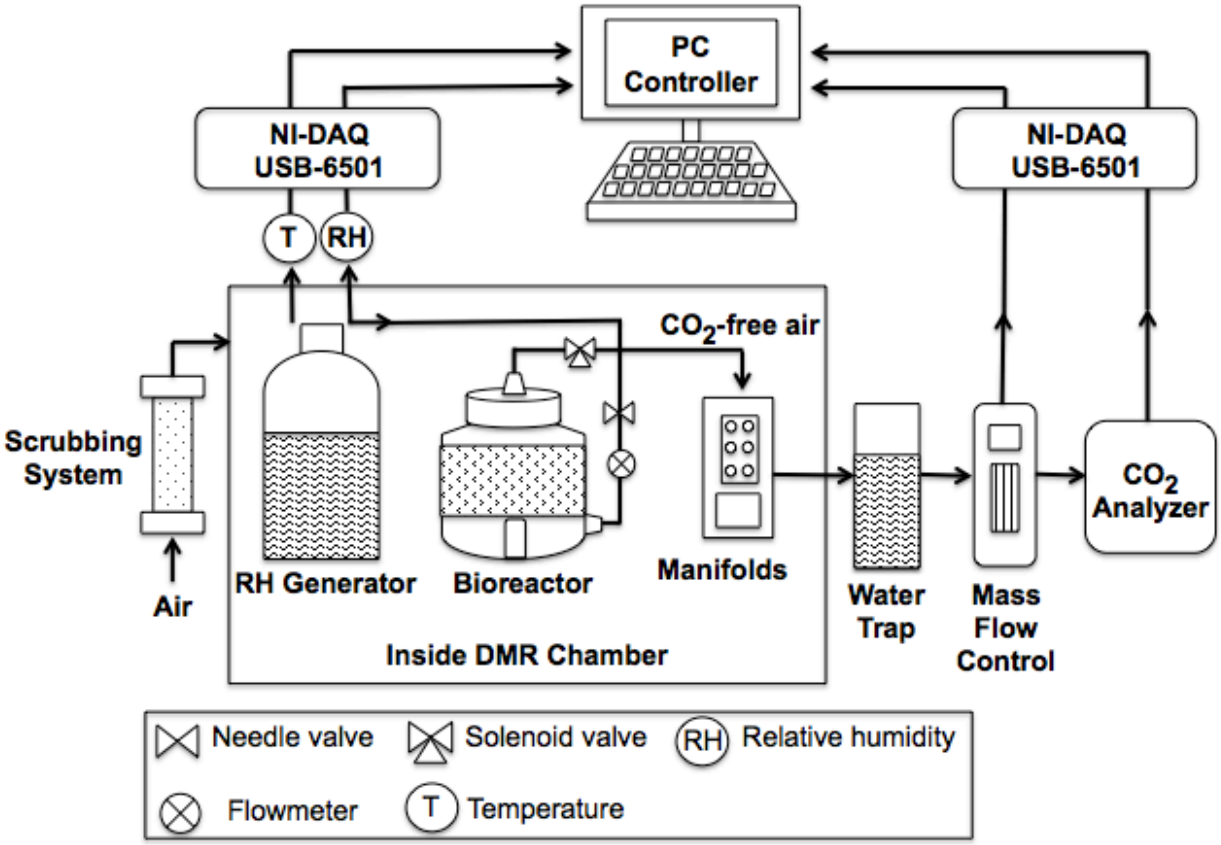

Figure 3.5 Schematic of the direct measurement respirometric (DMR) system adapted from Kijchavengkul et al. (2006)

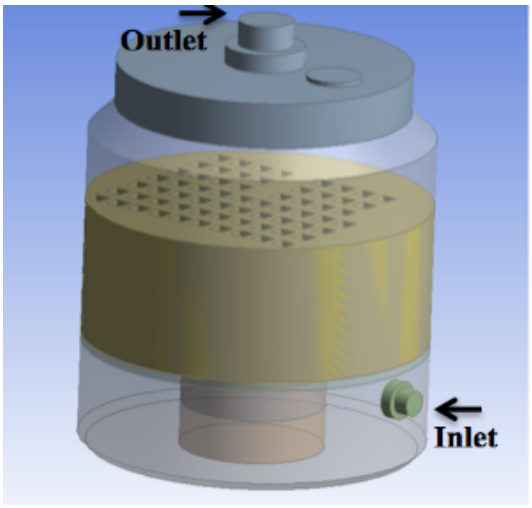

Figure 3.6 Aerobic bioreactor for the DMR system

3.6.4 Degradation calculation

The accumulated evolution of CO_2, in grams, was calculated using Eq. (3.2).

$$gCO_2 = \int_0^t \frac{C(t) \times F(t) \times 44}{22414 \times 10^6} dt \tag{3.2}$$

where gCO_2 is the accumulated mass of CO_2 evolution in grams, $C(t)$ is average CO_2 concentration (ppm) during the measurement time (30 sec), $F(t)$ is flow rate (scm^3/min), t is experimental time (days), 44 is the molecular weight of CO_2, 22414 is the standard gas volume in cubic centimeters per mole, and 10^6 is the conversion factor for ppm. The time integral to calculate accumulated CO_2 was evaluated using the trapezoidal method of numerical integration.

Percent mineralization of the cellophane films was calculated using Eq. (3.3), based on the carbon content of the materials

$$\%Mineralization = \frac{sCO_2 - bCO_2}{W \times \frac{\%C}{100} \times \frac{44}{12}} \times 100 \tag{3.3}$$

where sCO_2 is the amount of CO_2 from the sample reactor or from the cellulose reactor, bCO_2 is the amount of CO_2 from the compost reactor, W is the initial weight of samples or cellulose, and %C is the percent carbon in the sample or cellulose obtained from the CHN analyzer.

3.7 Statistical analysis

Statistical analyses were performed using SAS (version 9.4, SAS Institute Inc., NC, USA) based on Bonferroni adjustment for multiple comparisons based on 95% confidence level and MATLAB® (version12, MathWorks, MA, USA). The comparison was done between non-irradiated and irradiated samples of each film type and each irradiation source. The aging effect on property, migration and compostability of materials was also determined.

Chapter 4

Results of Property Study

4.1 Ionizing radiation effects on properties of poly(lactic) acid films

4.1.1 Color analysis

The Hunter color L*, a* and b* results are shown in Table 4.1. The change in brightness (L* = 100 bright/0 dark) of gamma irradiated PLA (GMPA) and E-beam irradiated PLA (EBPA) at absorbed doses of 1 to 30 kGy was not significant. Also, no significant difference in brightness of post-irradiated samples was seen during storage. This indicates that the transparency of PLA film was not affected by either gamma or E-beam irradiation. No significant changes in a*-values (a* = +red/-green) or b*-values (b* = +yellow/-blue) were found in GMPA and EBPA at any dose level (0 to 30 kGy) or storage time. After 9-month storage, there was also no significant difference in Hunter a*-values within the same irradiation dose.

Irradiation-induced color formation is associated with changes in the macromolecular structure of polymers (e.g. double bonds, aromatic rings, carbonyl groups). When irradiated in the presence of air, oxygen molecules can be absorbed by the polymer to quench the free radicals created by irradiation. Certain stabilizer additives also can attribute to radiation-induced color formation; for example phenols are additives that are prone to discoloration. For commercial polymers, which contain a variety of additives, the discoloration depends on the type of additives added (Clough et al., 1996).

Table 4.1 Color changes of non-irradiated (CoPA), gamma irradiated (GMPA) and E-beam irradiated (EBPA) PLA films at doses of 1, 5, 10 and 30 kGy after 9 months

Sample	Dose (kGy)	Time (month)	L^*	a^*	b^*
CoPA	0	0	92.74 ± 0.04^{A}	-1.02 ± 0.02^{A}	0.55 ± 0.03^{A}
GMPA	1	3	$92.76 \pm 0.03^{A,a,*}$	$-1.02 \pm 0.00^{A,a,*}$	$0.54 \pm 0.02^{A,a,*}$
		6	92.73 ± 0.02^{a}	-1.03 ± 0.00^{a}	0.56 ± 0.02^{a}
		9	92.71 ± 0.02^{a}	-1.01 ± 0.02^{a}	0.55 ± 0.01^{a}
	5	3	$92.77 \pm 0.01^{A,a,*}$	$-1.01 \pm 0.01^{A,a,*}$	$0.55 \pm 0.00^{A,a,*}$
		6	92.73 ± 0.03^{a}	-1.02 ± 0.01^{a}	0.54 ± 0.02^{a}
		9	92.72 ± 0.02^{a}	-1.01 ± 0.01^{a}	0.56 ± 0.02^{a}
	10	3	$92.77 \pm 0.04^{A,a,*}$	$-1.01 \pm 0.03^{A,a,*}$	$0.54 \pm 0.03^{A,a,*}$
		6	92.78 ± 0.02^{a}	-1.02 ± 0.01^{a}	0.54 ± 0.02^{a}
		9	92.72 ± 0.02^{a}	-1.02 ± 0.01^{a}	0.56 ± 0.01^{a}
	30	3	$92.78 \pm 0.03^{A,a,*}$	$-1.02 \pm 0.02^{A,a,*}$	$0.57 \pm 0.01^{A,a,*}$
		6	92.76 ± 0.01^{a}	-1.02 ± 0.01^{a}	0.56 ± 0.03^{a}
		9	92.75 ± 0.03^{a}	-1.00 ± 0.01^{a}	0.56 ± 0.02^{a}
EBPA	1	3	$92.74 \pm 0.08^{A,a,**}$	$-1.01 \pm 0.01^{A,a,*}$	$0.54 \pm 0.03^{A,a,*}$
		6	92.76 ± 0.03^{a}	-1.03 ± 0.01^{a}	0.56 ± 0.01^{a}
		9	92.75 ± 0.00^{a}	-1.02 ± 0.00^{a}	0.56 ± 0.01^{a}
	5	3	$92.76 \pm 0.01^{A,a,*}$	$-1.01 \pm 0.01^{A,a,*}$	$0.54 \pm 0.04^{A,a,*}$
		6	92.76 ± 0.02^{a}	-1.02 ± 0.01^{a}	0.56 ± 0.01^{a}
		9	92.74 ± 0.01^{a}	-1.01 ± 0.01^{a}	0.56 ± 0.01^{a}
	10	3	$92.77 \pm 0.05^{A,a,*}$	$-1.00 \pm 0.01^{A,a,*}$	$0.57 \pm 0.03^{A,a,*}$
		6	92.77 ± 0.02^{a}	-1.02 ± 0.01^{a}	0.56 ± 0.01^{a}
		9	92.72 ± 0.02^{a}	-1.01 ± 0.01^{a}	0.58 ± 0.01^{a}
	30	3	$92.77 \pm 0.02^{A,a,*}$	$-1.00 \pm 0.02^{A,a,**}$	$0.57 \pm 0.03^{A,a,*}$
		6	92.76 ± 0.03^{a}	-1.02 ± 0.01^{a}	0.56 ± 0.01^{a}
		9	92.75 ± 0.01^{a}	-1.03 ± 0.00^{a}	0.57 ± 0.00^{a}

L*=Lightness; a*=redness; b*=yellowness. Data are mean values (± standard deviations). Capital letters show the comparison between non-irradiated and irradiated samples at different dose levels after 3 months of storage, within the same irradiation type ($P < 0.05$). Lowercase letters show the comparison between storage times for the same dose and irradiation source ($P < 0.05$). Asterisks (*) indicate a comparison between irradiation sources at the same dose after 3 months of storage

4.1.2 Surface tension

Surface tension measured in units of mJ/m^2 or dynes/cm is a prime measurement to determine the surface and adhesion properties of polymers,. The free energy available at the surface of solids and liquids, called surface tension, occurs due to unbalanced molecular forces associated with molecules at the surface (Selke et al., 2004). If the intermolecular force is higher in the liquid than the surface tension of the polymeric material, the liquid forms droplets rather than spreading out, referred to as wet out.

The surface tension of PLA before and after gamma and E-beam irradiation and storage of up to 9 months is presented in Table 3.2. In this study, dyne test inks (30 to 70 dyne/cm) were used to determine the surface tension of PLA film. If the dyne level is equal to or greater than the material's surface tension, a droplet of liquid will form. If the dyne level is lower than the material's surface tension, the liquid will spread out. The dyne level of a material defines its surface tension. Before irradiation, the surface tension of PLA (CoPA) was 57 dyne/cm. After 3 months of storage after irradiation treatment, the surface tension of gamma irradiated PLA at absorbed doses of 1 to 10 kGy was lower than non-irradiated PLA, while samples gamma irradiated at 30 kGy had slightly higher surface tension than non-irradiated samples. This showed that gamma irradiation at doses up to 10 kGy decreased the surface tension of PLA. Additional storage time up to 9 months did not significantly change the surface tension.

The treated surface of E-beam irradiated PLA at doses of 1 and 5 kGy showed a reduction in surface tension (50 and 52 dyne/cm, respectively), compared to non-

irradiated PLA (57 dyne/cm). This indicated a decrease in surface wettability. Samples exposed to higher E-beam irradiation at 10 and 30 kGy showed a dyne level of 58 dyne/cm. As was the case for E-beam irradiated films, further storage up to 9 months did not significantly affect the surface tension.

Cairns et al. (2012) reported that contact angle values for E-beam irradiated PLLA (150 and 500 kGy) decreased and surface wettability increased after treatment. The authors suggested that PLA surfaces increased in hydrophilic groups after treatment; however, hydrophobic recovery may occur after 1 month of irradiation. When air is present during irradiation, the formed carbon radicals can react with oxygen, thereby increasing the surface oxygen content, resulting in an increase in surface wettability. This has been observed in O_2 and Ar-plasma treated PLLA (De Geyter et al., 2010; Inagaki et al., 2002; Khorasani et al., 2008).

Table 4.2 Surface tension of non-irradiated (CoPA), gamma irradiated (GMPA) and E-beam irradiated PLA (EBPA) films

Sample	Dose (kGy)	Time (month)	*Surface Tension* (dyne/cm)
CoPA	0	0	56-57
		3	57
		6	57
		9	57
GMPA	1	3	50
		6	50
		9	50
	5	3	50
		6	50
		9	49
	10	3	54
		6	55
		9	54
	30	3	58
		6	58
		9	59
EBPA	1	3	50
		6	50
		9	50
	5	3	52
		6	52
		9	52
	10	3	58
		6	58
		9	57
	30	3	58
		6	59
		9	59

4.1.3 Fourier transform infrared (FTIR) spectroscopy

The effect of gamma and E-beam irradiation on the chemical structure of PLA was determined using FTIR spectroscopy. The summary of PLA absorbance bands in

the infrared spectra is shown in Table 4.3. PLA is characterized by absorption bands for -CH- stretch, -C=O- carbonyl, -CH- deformation, -C-O- stretch, and -C-C- stretch. Figure 4.1 corresponds to the spectra of non-irradiated and gamma irradiated PLA, and Figure 4.2 corresponds to the spectra of non-irradiated and E-beam irradiated PLA. An absorption band at 1746 cm^{-1} attributed to C=O stretching in the ester groups of PLA decreased after exposure to gamma and E-beam irradiation for all dose levels. This peak value for gamma irradiated PLA at 30 kGy became stronger in intensity compared to other dose levels (1-10 kGy). Zaidi et al. (2013) reported that after gamma irradiation, C=O stretching of PLA decreased. Gamma irradiation leads to the oxidation of ester groups leading to the formation of hydroxyl groups. A decrease in the peak at 1078 cm^{-1}, associated with C-O-C stretching vibration of ester-like functional groups, was observed. The peak of -C-O- stretch at absorbance of 1180 cm^{-1} also decreased. The shoulder of the peak diminished at the higher dose rates of 10 and 30 kGy. The decrease in PLA bands at 1078 and 1043 cm^{-1} after irradiation is in agreement with the observations of Yotoriyama et al. (2005) and Zaidi et al. (2013).

Table 4.3 Peak band assignments for infrared spectra of PLA

Assignment	Wave number (cm^{-1})
-CH- stretch	2993 (asymmetric), 2943 (symmetric)
-C=O- carbonyl	1746
-CH- deformation (including asymmetric and symmetric bend)	1450, 1360, 1265
-C-O- stretch	1180, 1126, 1078, 1043
-C-C- stretch	866

Adapted from (Agarwal et al., 1998; Auras et al., 2004)

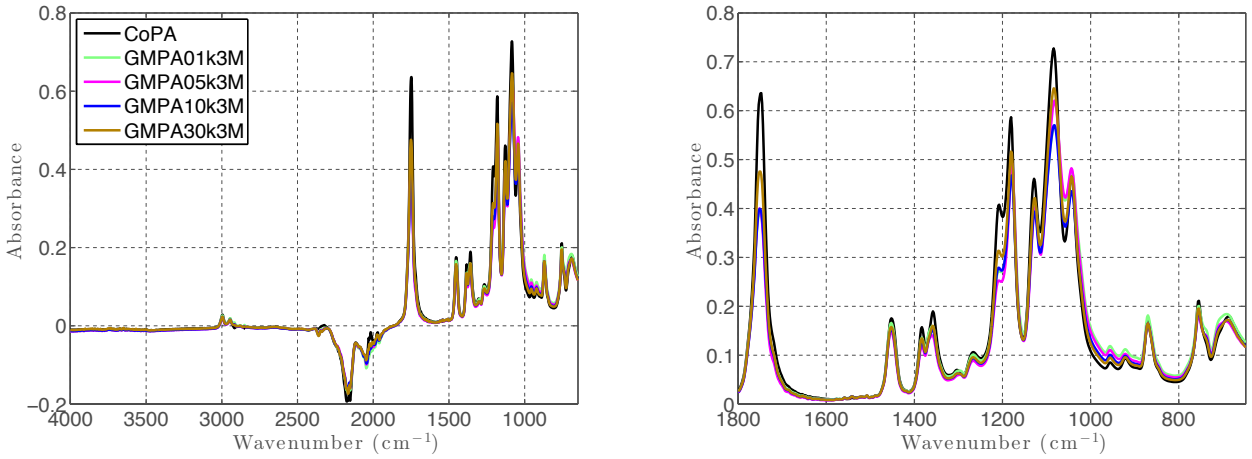

Figure 4.1 FTIR spectra of non-irradiated, and gamma irradiated PLA at absorbed doses of 0, 1, 5, 10 and 30 kGy after 9 months of storage

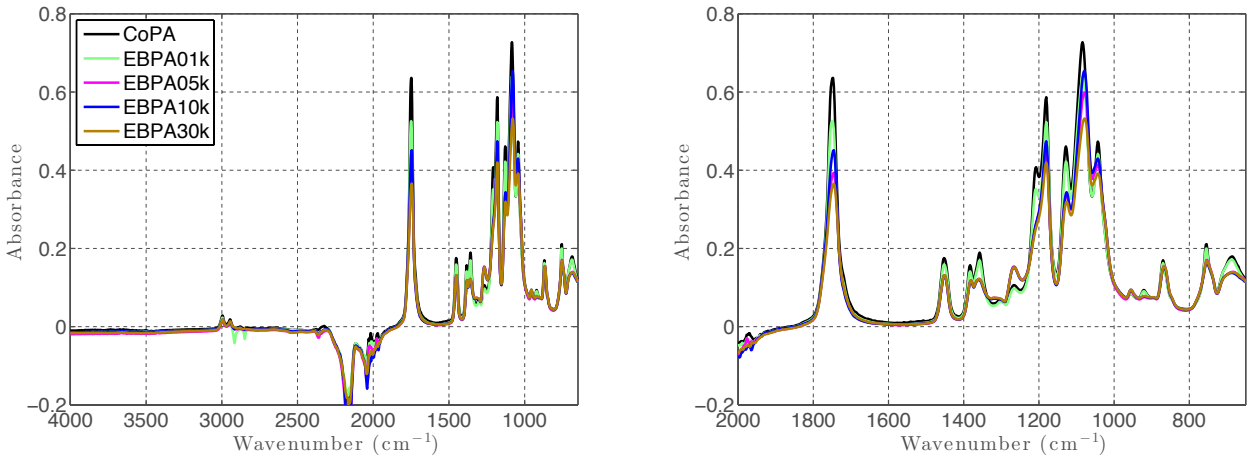

Figure 4.2 FTIR spectra of non-irradiated, and E-beam irradiated PLA at absorbed doses of 0, 1, 5, 10 and 30 kGy after 9 months of storage

4.1.4 Thermal properties

The results obtained from differential scanning calorimetry (DSC) of non-irradiated, gamma irradiated and E-beam irradiated PLA are shown in Table 4.4. Before irradiation, the DSC thermogram of non-irradiated PLA (CoPA) exhibited a glass

Table 4.4 Thermal properties of non-irradiated and irradiated polylactic acid by gamma (GM) and E-beam (EB) irradiation after 9 months of storage

Sample	Dose (kGy)	Time (month)	T_g (ºC)	T_c (ºC)	T_{m1} (ºC)	T_{m2} (ºC)
CoPA	0	0	61.21 ± 0.31^{A}	121.81 ± 0.43^{A}	163.75 ± 0.38^{A}	168.75 ± 0.36^{A}
GMPA	1	3	$61.18 \pm 0.71^{A,a,*}$	$120.98 \pm 0.68^{B,a*}$	$163.85 \pm 0.44^{A,a,*}$	$169.54 \pm 0.76^{A,a,*}$
		6	61.21 ± 0.39^{a}	120.61 ± 0.18^{a}	163.89 ± 0.12^{a}	169.23 ± 0.12^{a}
		9	61.54 ± 0.13^{a}	120.40 ± 0.10^{a}	163.82 ± 0.36^{a}	169.45 ± 0.64^{a}
	5	3	$61.06 \pm 0.55^{A,a,*}$	$118.88 \pm 0.23^{C,a*}$	$163.10 \pm 0.27^{B,a,*}$	$169.41 \pm 0.25^{A,a,*}$
		6	60.94 ± 0.60^{a}	119.36 ± 0.43^{a}	163.30 ± 0.55^{a}	169.51 ± 0.56^{a}
		9	60.85 ± 0.16^{a}	118.38 ± 0.19^{a}	162.67 ± 0.28^{a}	168.90 ± 0.09^{a}
	10	3	$61.01 \pm 0.43^{A,a,*}$	$117.02 \pm 0.27^{D,a*}$	$162.15 \pm 0.25^{C,a,*}$	$169.00 \pm 0.24^{A,a,*}$
		6	60.74 ± 0.84^{a}	117.04 ± 0.08^{a}	162.14 ± 0.12^{a}	169.02 ± 0.06^{a}
		9	60.64 ± 0.40^{a}	116.47 ± 0.22^{a}	161.86 ± 0.20^{a}	168.82 ± 0.32^{a}
	30	3	$59.79 \pm 0.39^{B,ab,*}$	$112.45 \pm 0.35^{E,a*}$	$159.65 \pm 0.36^{D,a,*}$	$167.48 \pm 0.51^{B,a,*}$
		6	60.06 ± 0.41^{a}	112.29 ± 0.23^{a}	159.54 ± 0.02^{a}	167.53 ± 0.12a
		9	58.80 ± 1.63^{b}	111.78 ± 0.19^{a}	159.35 ± 0.27^{a}	167.22 ± 0.43a
EBPA	1	3	$61.26 \pm 0.03^{A,a,*}$	$120.96 \pm 0.24^{B,a*}$	$163.89 \pm 0.32^{A,a,*}$	$169.20 \pm 0.34^{A,a,*}$
		6	61.09 ± 0.27^{a}	121.06 ± 0.18^{a}	163.78 ± 0.18^{a}	169.05 ± 0.10^{a}
		9	60.61 ± 0.17^{a}	120.34 ± 0.36^{a}	163.49 ± 0.44^{a}	169.01 ± 0.50^{a}
	5	3	$61.10 \pm 0.33^{A,a,*}$	$119.81 \pm 0.51^{C,a**}$	$163.36 \pm 0.47^{A,a,*}$	$169.19 \pm 0.42^{A,a,*}$
		6	61.19 ± 0.19^{a}	119.91 ± 0.40^{a}	163.49 ± 0.37^{a}	169.40 ± 0.34^{a}
		9	60.77 ± 0.37^{a}	119.41 ± 0.28^{a}	163.09 ± 0.34^{a}	169.12 ± 0.37^{a}

Table 4.4 (cont'd)

Sample	Dose (kGy)	Time (month)	T_g (ºC)	T_c (ºC)	T_{m1} (ºC)	T_{m2} (ºC)
EBPA	10	3	$61.19 \pm 0.42^{A,a,*}$	$118.54 \pm 0.19^{D,a**}$	$162.87 \pm 0.26^{B,a,**}$	$169.39 \pm 0.33^{A,a,*}$
		6	60.58 ± 0.09^{a}	117.53 ± 0.28^{b}	162.24 ± 0.24^{a}	168.82 ± 0.27^{a}
		9	60.73 ± 0.20^{a}	117.38 ± 0.29^{b}	162.28 ± 0.29^{a}	169.06 ± 0.43^{a}
	30	3	$60.46 \pm 0.29^{A,a,*}$	$114.51 \pm 0.05^{E,a,**}$	$160.69 \pm 0.04^{C,a,**}$	$168.11 \pm 0.02^{B,a,*}$
		6	60.20 ± 0.31^{a}	113.70 ± 0.11^{b}	160.31 ± 0.02^{a}	167.76 ± 0.05^{a}
		9	60.08 ± 0.23^{a}	113.79 ± 0.13^{b}	160.74 ± 0.08^{a}	168.04 ± 0.13^{a}

Data are mean values (± standard deviations). Capital letters show the comparison between non-irradiated and irradiated samples at different dose levels after 3 months of storage, within the same irradiation type ($P < 0.05$). Lowercase letters show the comparison between storage times for the same dose and irradiation source ($P < 0.05$). Asterisks (*) indicate a comparison between irradiation sources at the same dose after 3 months of storage

transition temperature (T_g) of 61.21ºC and crystallization temperature (T_c) of 121.81ºC. Two endothermic peaks appeared at 163.75ºC and 168.75ºC, which were related to the melting temperature (T_m) of PLA as shown in Figure 4.3.

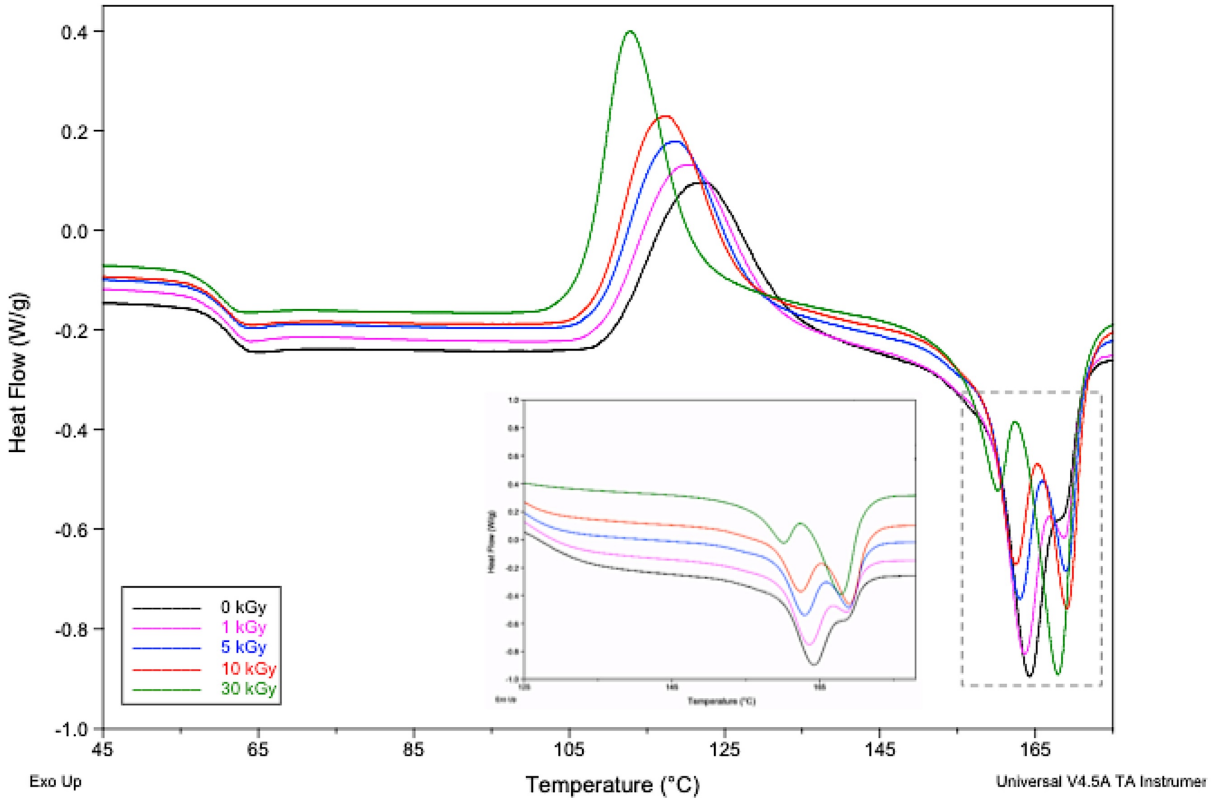

Figure 4.3 DSC thermogram for non-irradiated PLA and gamma irradiated PLA at absorbed doses of 0, 5, 10 and 30 kGy after 3 months of storage

There was no significant change in the glass transition temperature of gamma irradiated PLA (GMPA) and E-beam irradiated PLA (EBPA) at any of the absorbed doses, with the exception of GMPA at 30 kGy. During storage, a change in T_g of irradiated PLA was observed only in GMPA at 30 kGy between 6 and 9 months.

As mentioned earlier, two pronounced melting peaks were observed. Before irradiation the first peak (T_{m1}) was larger than second peak (T_{m2}). After irradiation T_{m1} decreased while there was an increase in T_{m2} (Figure 4.3). The rate of change in the second melting peak for PLA irradiated by either source decreased at a dose of 30 kGy. T_{m1} showed significant differences in GMPA at doses of 5 - 30 kGy and EBPA at doses of 10 and 30 kGy. T_{m2} showed a significant difference in GMPA and EBPA at an absorbed dose of 30 kGy as compared to non-irradiated PLA (CoPA). The change in T_{m2} for PLA exposed to either type of irradiation was insignificant. No change was seen in the melting peak during 9 months of storage, regardless of the irradiation dose level.

The crystallization temperature (T_c) of irradiated PLA significantly decreased as a function of irradiation dose. Significant differences in the effects of gamma and E-beam irradiation on the T_c of PLA were found at irradiation doses of 5, 10 and 30 kGy. Gamma irradiation resulted in larger changes in the T_c of PLA than did E-beam irradiation. The thermal characteristics of the PLA film showed significant differences in T_c of EBPA at 10 and 30 kGy between 3 months and 6 and 9 months. The reduction in the crystallization temperature can be explained by chain-scission in the amorphous regions of the polymer. The shorter chains are less entangled and have more mobility. Hence, less energy is required for re-orientation and re-crystallization of short amorphous chains than longer chains, resulting in the lower T_c (Loo et al., 2005b; Loo

et al., 2004).

Nugroho et al. (2001) reported that at low doses (up to 200 kGy), T_g and T_m of irradiated PLA decreased with increasing dose. The T_g of PLA exposed to gamma irradiation in air decreased sharply while that in vacuum decreased more slowly. Degradation of PLLA by E-beam irradiation (50-500 kGy) was reported by Loo et al. (2004). The decrease of T_g and T_m was investigated with increasing irradiation dose. The reduction in T_g and T_m of PLA is because of the dominant process of chain-scission; however, the chain-scission enhances its crystallization. T_g depends on the molecular weight of polymers. Hence, the greater the molecular weight, the greater the T_g (Sperling, 2005). Loo et al. (2004) also suggested that the decrease in T_g may be because the polymer chains have more mobility due to chain-scission. Moreover, recrystallization reduces the amount of amorphous material, resulting in an increase in brittleness of the irradiated PLLA. For irradiation carried out in the presence of air, peroxyl free radicals are formed (Montanari et al., 2001), which can lead to reaction with one another and further reactions among the polymeric chains. This reaction then causes chain-scission through chain transfer (Pionteck et al., 2000).

A decrease in T_m of PLA with increasing irradiation dose was found, suggesting that chain flexibility increased, which may be due to side chain branching, while the crystallinity decreased (Schnabel & Jellinek, 1978). Zaidi et al. (2013) also reported a decrease in T_m of gamma irradiated PLA with increasing irradiation dose (0-100 kGy).

This could be due to the formation of PLA chains with low molecular weight and the decrease in crystalline perfection, and the narrowing crystallite size distribution. The increase in irregularities after irradiation provides more mobility of macromolecules that induces the appearance of a disordered phase at low temperatures (Albano et al., 2003; Rabello & White, 1997).

4.1.5 Mechanical properties

The effects of irradiation on mechanical properties of PLA film are shown in Table 4.5. Tensile strength of PLA in the machine direction (MD) did not show any significant difference for gamma and E-beam irradiation as compared to non-irradiated PLA (CoPA). However, in the cross-machine direction (CD), irradiated PLA showed a significant decrease for the gamma-irradiated sample at dose levels of 5 - 30 kGy as compared to non-irradiated samples. For E-beam irradiated PLA, a significant decrease was found at all dose levels. Elongation at break of PLA in the MD significantly decreased at a dose level of 30 kGy using gamma and E-beam irradiation, and in the CD for gamma (GMPA) and E-beam irradiated PLA (EBPA) there were significant decreases at dose levels of 5 - 30 kGy. The effect of irradiation on the elastic modulus of PLA in the MD was not significant. However, EBPA in the CD showed a significant increase in elastic modulus as a function of dose. The irradiation source had no significant effect on mechanical properties. The increase in modulus implies an increase in the stiffness of PLA (Selke et al., 2004). Mechanical properties of PLA can be affected by gamma and E-beam irradiation (Rytlewski et al., 2010; Suljovrujic et al., 2007; Zaidi et al., 2013). Miao et al. (2009) reported a decrease in tensile strength and elongation of poly (D,L-Lactic acid) (PDLA) at break with increasing dose levels.

Table 4.5 Mechanical properties of non- irradiated (CoPA), gamma irradiated (GMPA) and E-beam irradiated PLA (EBPA) film after 9 months of storage

Sample	Dose (kGy)	Time (month)	Tensile strength (kpsi)	Elongation at break (%)	Elastic Modulus (kpsi)
			MD	MD	MD
CoPA	0	0	13.14 ± 0.46^{A}	11.00 ± 1.56^{A}	511.59 ± 24.94^{A}
GMPA	1	3	$13.79 \pm 0.60^{A,a,*}$	$10.28 \pm 3.72^{A,a,*}$	$507.03 \pm 38.49^{A,a,*}$
		6	13.06 ± 0.54^{a}	7.56 ± 1.90^{ab}	512.90 ± 31.92^{a}
		9	12.94 ± 0.96^{a}	6.73 ± 1.95^{b}	518.21 ± 32.32^{a}
	5	3	$13.58 \pm 1.14^{A,a,*}$	$9.67 \pm 3.76^{A,a,*}$	$475.59 \pm 26.57^{A,a,*}$
		6	12.81 ± 0.59^{a}	7.72 ± 2.30^{a}	482.86 ± 28.50^{ab}
		9	13.54 ± 0.90^{a}	6.49 ± 1.53^{a}	535.30 ± 21.11^{b}
	10	3	$13.18 \pm 1.43^{A,a,*}$	$8.60 \pm 3.60^{AB,a,*}$	$503.17 \pm 27.24^{A,a,*}$
		6	12.58 ± 1.01^{a}	7.58 ± 3.73^{a}	531.77 ± 28.59^{a}
		9	13.86 ± 0.63^{a}	7.60 ± 2.61^{a}	536.04 ± 20.40^{a}
	30	3	$13.40 \pm 1.07^{A,a,*}$	$5.78 \pm 1.09^{B,a,*}$	$477.83 \pm 15.87^{A,a,*}$
		6	13.45 ± 0.81^{a}	5.14 ± 0.83^{a}	532.20 ± 21.17^{b}
		9	13.77 ± 0.28^{a}	4.37 ± 0.81^{a}	545.37 ± 12.59^{b}
EBPA	1	3	$13.59 \pm 0.81^{A,a,*}$	$9.62 \pm 3.58^{AB,a,*}$	$522.53 \pm 25.67^{A,a,*}$
		6	13.72 ± 0.61^{a}	6.90 ± 3.82^{a}	542.48 ± 27.72^{a}
		9	13.22 ± 0.82^{a}	8.18 ± 1.71^{a}	529.22 ± 23.87^{a}
	5	3	$13.58 \pm 0.95^{A,a,*}$	$9.51 \pm 2.64^{AB,a,*}$	$492.60 \pm 39.78^{A,a,*}$
		6	14.18 ± 0.98^{b}	9.11 ± 3.90^{a}	534.83 ± 40.82^{b}
		9	13.67 ± 0.53^{b}	9.32 ± 5.17^{a}	538.22 ± 19.20^{b}
	10	3	$13.40 \pm 0.78^{A,a,*}$	$9.50 \pm 5.02^{AB,a,*}$	$497.19 \pm 24.84^{A,a,*}$
		6	13.87 ± 0.86^{a}	8.34 ± 3.22^{a}	502.86 ± 39.09^{a}
		9	12.45 ± 0.76^{a}	7.5 ± 1.838^{a}	517.45 ± 24.25^{a}
	30	3	$12.70 \pm 0.82^{A,a,*}$	$6.79 \pm 1.03^{B,a,*}$	$501.11 \pm 21.36^{A,a,*}$
		6	13.07 ± 1.03^{a}	6.07 ± 0.68^{a}	491.36 ± 46.61^{a}
		9	12.45 ± 0.83^{a}	5.99 ± 0.87^{a}	523.93 ± 20.08^{a}

Table 4.5 (cont'd)

Sample	Dose (kGy)	Time (month)	Tensile strength (kpsi)	Elongation at break (%)	Elastic Modulus (kpsi)
			CD	CD	CD
CoPA	0	0	24.06 ± 0.79^{A}	72.17 ± 3.78^{A}	718.98 ± 23.03^{A}
GMPA	1	3	$23.38 \pm 2.31^{A,a,*}$	$65.37 \pm 6.19^{AB,a,*}$	$761.25 \pm 75.68^{A,a,*}$
		6	21.65 ± 2.09^{ab}	65.57 ± 6.38^{a}	820.63 ± 47.38^{a}
		9	20.36 ± 1.71^{b}	53.84 ± 4.58^{b}	806.96 ± 41.81^{a}
	5	3	$20.33 \pm 3.23^{B,a,*}$	$62.96 \pm 8.64^{B,a,*}$	$772.39 \pm 16.55^{A,a,*}$
		6	19.07 ± 2.17^{a}	67.15 ± 3.97^{a}	778.20 ± 55.05^{a}
		9	20.05 ± 1.88^{a}	53.20 ± 3.96^{b}	831.60 ± 68.02^{b}
	10	3	$20.93 \pm 1.17^{B,a,*}$	$59.04 \pm 5.17^{B,a,*}$	$789.96 \pm 63.94^{A,a,*}$
		6	16.34 ± 1.16^{b}	51.24 ± 5.81^{a}	782.30 ± 99.83^{a}
		9	19.74 ± 1.70^{a}	51.77 ± 4.87^{a}	839.83 ± 38.01^{a}
	30	3	$16.85 \pm 1.05^{B,a,*}$	$46.89 \pm 6.75^{C,a,*}$	$759.30 \pm 70.55^{A,a,*}$
		6	16.17 ± 1.36^{a}	43.06 ± 5.53^{a}	800.92 ± 47.56^{ab}
		9	16.73 ± 1.08^{a}	45.22 ± 4.90^{a}	831.17 ± 31.77^{b}
EBPA	1	3	$21.20 \pm 3.25^{B,a,*}$	$64.54 \pm 6.14^{AB,a,*}$	$815.02 \pm 42.21^{B,a,*}$
		6	22.77 ± 2.03^{a}	63.12 ± 5.55^{a}	853.67 ± 54.22^{a}
		9	21.01 ± 1.80^{a}	54.58 ± 4.64^{b}	845.26 ± 42.16^{a}
	5	3	$20.23 \pm 2.23^{B,a,*}$	$57.23 \pm 9.74^{BC,a,*}$	$803.60 \pm 59.61^{B,a,*}$
		6	20.88 ± 1.99^{ab}	57.28 ± 7.57^{a}	844.72 ± 30.16^{a}
		9	23.02 ± 2.03^{b}	62.51 ± 4.15^{a}	843.92 ± 52.77^{a}
	10	3	$20.49 \pm 2.48^{B,a,*}$	$64.09 \pm 8.10^{B,a,*}$	$800.11 \pm 41.39^{B,a,*}$
		6	17.73 ± 2.48^{b}	52.48 ± 12.32^{b}	780.24 ± 39.23a
		9	21.74 ± 1.83^{a}	60.33 ± 2.24^{ab}	892.69 ± 48.87^{a}
	30	3	$17.45 \pm 1.40^{C,a,*}$	$51.09 \pm 9.22^{C,a,*}$	$822.50 \pm 50.96^{B,a,*}$
		6	18.03 ± 2.07^{a}	48.84 ± 7.39^{a}	810.66 ± 35.71^{a}
		9	18.62 ± 1.88^{a}	55.05 ± 9.13^{a}	835.82 ± 36.63^{a}

Data are mean values (± standard deviations). Capital letters show the comparison between non-irradiated and irradiated samples at different dose levels after 3 months of storage, within the same irradiation type ($P < 0.05$). Lowercase letters show the comparison between storage times for the same dose and irradiation source ($P < 0.05$). Asterisks (*) indicate a comparison between irradiation sources at the same dose after 3 months of storage

4.1.6 Molecular weight

The mechanism for irradiation-induced changes in PLA exposed to various doses was investigated using DSC. The molecular weight of non-irradiated PLA (CoPA), gamma irradiated PLA (GMPA) and E-beam irradiated PLA (EBPA) samples obtained by average values of triplicate samples after 3, 6, and 9 months of storage are shown in Table 4.6. After irradiation, the number average molecular weight (M_n) and weight average molecular weight (M_w) of gamma irradiated and E-beam irradiated PLA clearly decreased with increasing irradiation dose, with the exception of EBPA at 1 kGy, compared to non-irradiated samples, indicating degradation of PLA by ionizing irradiation. The decrease in M_w with increasing dose of EBPA was slower than for GMPA. A significant difference in the effects of gamma and E-beam on M_n at the same dose level was found at irradiation doses of 1, 5 and 30 kGy. The observed change in M_w after 9 months of storage showed a significant difference between GMPA and EBPA at 1, 5 and 10 kGy. There was significant difference for the 30 kGy sample during storage. The change in M_n, however, did not seem to depend on the storage time. The decrease in M_n and M_w of irradiated PLA suggests random chain scission. Post-irradiation ageing of PLA at 20.5-100 kGy over 336 days by Birkinshaw (1992) showed no changes in molecular weight with time.

The polydispersity index (PI = M_w/M_n) increased for GMPA and EBPA at absorbed doses of 5 - 30 kGy. There was no significant difference in the change of

Table 4.6 Molecular weight of non-irradiated (CoPA), gamma irradiated (GMPA) and E-beam irradiated PLA (EBPA) film after 9 months of storage

Sample	Dose (kGy)	Time (month)	$M_n \times 10^4$ ($gmol^{-1}$)	$M_w \times 10^4$ ($gmol^{-1}$)	PI
CoPA	0	0	6.86 ± 0.04^{A}	9.75 ± 0.03^{A}	1.42 ± 0.01^{A}
GMPA	1	3	$6.54 \pm 0.10^{B,a,*}$	$9.53 \pm 0.05^{B,a,*}$	$1.46 \pm 0.02^{AB,a,*}$
		6	6.24 ± 0.08^{b}	9.49 ± 0.03^{a}	1.52 ± 0.02^{b}
		9	6.09 ± 0.05^{b}	10.35 ± 0.08^{b}	1.70 ± 0.01^{c}
	5	3	$5.76 \pm 0.08^{C,a,*}$	$8.66 \pm 0.03^{C,a,*}$	$1.50 \pm 0.02^{BC,a,*}$
		6	5.68 ± 0.03^{a}	8.64 ± 0.01^{a}	1.52 ± 0.00^{a}
		9	5.62 ± 0.08^{a}	9.45 ± 0.03^{b}	1.68 ± 0.02^{b}
	10	3	$5.27 \pm 0.07^{D,a,*}$	$7.95 \pm 0.05^{D,a,*}$	$1.51 \pm 0.01^{C,a,*}$
		6	5.19 ± 0.03^{ab}	7.93 ± 0.02^{a}	1.53 ± 0.01^{a}
		9	5.04 ± 0.08^{b}	8.59 ± 0.02^{b}	1.71 ± 0.02^{b}
	30	3	$3.33 \pm 0.02^{E,a,*}$	$5.31 \pm 0.01^{E,a,*}$	$1.59 \pm 0.01^{D,a,*}$
		6	3.14 ± 0.06^{ab}	5.09 ± 0.04^{b}	1.62 ± 0.02^{a}
		9	3.01 ± 0.11^{b}	5.42 ± 0.05^{c}	1.80 ± 0.05^{b}
EBPA	1	3	$6.84 \pm 0.23^{A,a,**}$	$9.77 \pm 0.10^{A,a,**}$	$1.43 \pm 0.03^{A,a,*}$
		6	6.89 ± 0.24^{a}	9.81 ± 0.13^{a}	1.42 ± 0.03^{a}
		9	6.89 ± 0.05^{a}	10.69 ± 0.02^{b}	1.55 ± 0.01^{b}
	5	3	$6.26 \pm 0.07^{B,a,**}$	$9.25 \pm 0.03^{B,a,**}$	$1.48 \pm 0.01^{B,a,*}$
		6	6.18 ± 0.06^{a}	9.19 ± 0.03^{a}	1.49 ± 0.01^{a}
		9	6.18 ± 0.04^{a}	10.04 ± 0.03^{b}	1.63 ± 0.01^{b}
	10	3	$5.46 \pm 0.04^{C,a,*}$	$8.36 \pm 0.01^{C,a,**}$	$1.53 \pm 0.01^{C,a,*}$
		6	5.18 ± 0.05^{b}	8.34 ± 0.02^{a}	1.61 ± 0.02^{b}
		9	5.18 ± 0.18^{b}	8.95 ± 0.06^{b}	1.73 ± 0.05^{c}
	30	3	$4.13 \pm 0.06^{D,a,**}$	$6.60 \pm 0.03^{D,a,**}$	$1.60 \pm 0.02^{D,a,*}$
		6	3.82 ± 0.03^{b}	6.40 ± 0.03^{b}	1.68 ± 0.01^{b}
		9	3.90 ± 0.03^{b}	7.15 ± 0.05^{c}	1.83 ± 0.00^{c}

Data are mean values (± standard deviations). Capital letters show the comparison between non-irradiated and irradiated samples at different dose levels after 3 months of storage, within the same irradiation type ($P < 0.05$). Lowercase letters show the comparison between storage times for the same dose and irradiation source ($P < 0.05$). Asterisks (*) indicate a comparison between irradiation sources at the same dose after 3 months of storage

polydispersity index at any dose level due to the irradiation type. The PI was not significantly affected by storage time. Loo et al. (2005a) explained that the increase in polydispersity index (PI) occurs because the free radicals within the crystalline regions are encouraged to recombine, which results in more branched and non-uniform chains of PLA. A decrease in T_m along with an increase in PI was found by Loo et al. (2004), indicating possible branching of the chains through the recombination of free radicals.

A decrease in M_n of PLA with gamma irradiation was observed by Nugroho et al. (2001). Zaidi et al. (Zaidi et al., 2013) also reported a significant decrease in M_n and M_w of gamma irradiated PLA with increasing irradiation dose. Dorati et al. (2008) reported that gamma irradiation at doses above and below 25 kGy caused a reduction in M_w of PLA. The decrease in M_w by irradiation doses below 25 kGy was due to breaks in the polymer backbone, while irradiation doses above 25 kGy caused scission mainly by hydrogen abstraction. For E-beam irradiation, the degradation of PLLA was studied by Loo et al. (2004). The authors reported that E-beam irradiation (20.5 - 500 kGy) decreased M_n of PLLA with increasing absorbed doses and then remained relatively unchanged at irradiation doses above 200 kGy (200 Mrad) with the dominance of chain-scission likely responsible. Ho and Pometto (1999) also reported a decrease of 35% in M_w of PLA using E-beam irradiation at 33 kGy. Gilding and Reed (1979) suggested that the dramatic decrease in M_n rather than M_w at a very low dose (10 kGy) occurred not because of random chain-scission as a primary mechanism of degradation but because

of the production of a large number of acid end groups by an unzipping mechanism. Gupta and Deshmukh (1983) concluded that PLA undergoes chain scission and crosslinking simultaneously during gamma irradiation in the presence of air and nitrogen at room temperature. These phenomena decreased the crystallinity of PLA.

The decrease in molecular weight of irradiated PLA was caused by chain scission, which occurs because of radical formation (Babanalbandi et al., 1995; Charlesby, 1987; Loo et al., 2005a; Montanari et al., 1998). During treatment, high-energy irradiation is absorbed by the irradiated polymeric material, causing excitation and ionization of macromolecules. Chain scission, a common phenomenon during irradiation of polymers, occurs by chain transfer and subsequent splitting at weaker bonds in the polymer chain (Carlsson & Chmela, 1990; O'Donnell & Sangster, 1970; Pionteck et al., 2000). Chain scission predominates in the amorphous phases of polymeric materials (Buchalla et al., 1993a; Nijsen et al., 2002; Streicher, 1988). Gupta and Deshmukh (1983) suggest that chain scission and crosslinking in PLA occur because of the cleavage of the ester linkage by increasing COOH end groups and hydrogen abstraction at the quaternary carbon atom sites. Using electron spin resonance (ESR), Nugroho et al. (2001) found that five types of free radicals were formed by chain-scission in PLA after exposure. These free radicals were produced by H abstraction from methine groups in the backbone of the polymer chain and from cleavage at C-C bonds in the main polymer chain and might decay by chain transfer and recombination. Dorati et al. (2008) studied the stability of gamma irradiated PLA (5 - 50 kGy) for 4 months and indicated that M_w decayed along with storage time and was not affected by the initial irradiation dose applied to the sample.

4.1.7 Barrier properties

Barrier properties of polymeric materials are very important for sensitive and perishable products such as foods and pharmaceuticals. Different food types need differing amounts of gases in order to prolong their quality and shelf life (Hedenqvist, 2005). Similarly, pharmaceutical products often need to be protected from moisture and oxygen to preserve the drug properties. Table 4.7 presents the oxygen, water vapor and carbon dioxide permeability values for non-irradiated, gamma irradiated and E-beam irradiated PLA after different storage times. No statistically significant differences in oxygen permeability values were evident between irradiated PLA and non-irradiated PLA (CoPA) at any irradiation doses or storage times.

Water vapor permeability of GMPA and EBPA significantly decreased after exposure, compared with non-irradiated PLA. However, there was no significant effect of increasing dose on water vapor permeability of irradiated PLA. The effect of E-beam irradiation on water vapor permeability of PLA was greater than that of gamma irradiation at all irradiation doses. After the 9 months of stability study, no additional irradiation-induced changes in water vapor permeability of EBPA were seen at any dose levels.

Permeability to CO_2 of PLA was not significantly affected by gamma or E-beam irradiation at absorbed doses of 1-10 kGy but E-beam irradiation at 30 kGy resulted in a significant difference compared to non-irradiated PLA. As a comparison between irradiation sources, there was no significant difference in CO_2 values for GMPA and

Table 4.7 Permeation properties of non-irradiated, gamma irradiated and electron irradiated PLA films after 9 months of storage

Sample	Doses (kGy)	Time (month)	$P_{O_2} \times 10^{-18}$ (Kg-m/m^2-sec-Pa)	$P_{H_2O} \times 10^{-14}$ (Kg-m/m^2-sec-Pa)	$P_{CO_2} \times 10^{-18}$ (Kg-m/m^2-sec-Pa)
CoPA	0	0	3.28 ± 0.06^{A}	1.87 ± 0.01^{A}	25.95 ± 0.53^{A}
GMPA	1	3	2.95 ± 0.18^{A,a,*}	1.76 ± 0.08^{B,a,*}	25.40 ± 2.03^{A,a,*}
		6	3.21 ± 0.09^{a}	1.60 ± 0.02^{b}	24.08 ± 0.81^{a}
		9	3.12 ± 0.04^{a}	1.65 ± 0.01^{b}	27.33 ± 1.85^{a}
	5	3	3.10 ± 0.15^{A,a,*}	1.71 ± 0.04^{B,a,*}	26.87 ± 3.44^{A,a,*}
		6	3.10 ± 0.21^{a}	1.40 ± 0.05^{b}	23.05 ± 0.37^{b}
		9	3.16 ± 0.06^{a}	1.62 ± 0.04^{b}	25.52 ± 0.81^{ab}
	10	3	3.37 ± 0.09^{A,a,*}	1.78 ± 0.10^{B,a,*}	24.96 ± 2.08^{A,a,*}
		6	3.31 ± 0.04^{a}	1.52 ± 0.02^{b}	21.89 ± 0.38^{a}
		9	3.14 ± 0.18^{a}	1.68 ± 0.03^{ab}	22.82 ± 1.29^{a}
	30	3	3.09 ± 0.05^{A,a,*}	1.74 ± 0.02^{B,a,*}	25.02 ± 0.41^{A,ab,*}
		6	2.98 ± 0.07^{a}	1.42 ± 0.02^{b}	21.88 ± 1.35^{a}
		9	3.02 ± 0.04^{a}	1.52 ± 0.06^{b}	25.51 ± 3.52^{b}
EBPA	1	3	3.27 ± 0.16$^{A, a,*}$	1.61 ± 0.09^{B,a,**}	26.31 ± 1.18^{A,a,*}
		6	3.09 ± 0.10^{a}	1.56 ± 0.09^{a}	23.88 ± 1.58^{a}
		9	3.29 ± 0.08^{a}	1.69 ± 0.03^{a}	26.66 ± 1.19^{a}
	5	3	2.96 ± 0.13^{A,a,*}	1.59 ± 0.09^{B,a,**}	23.17 ± 0.59^{AB,a,*}
		6	3.21 ± 0.62^{a}	1.60 ± 0.06^{a}	22.71 ± 1.21^{a}
		9	3.39 ± 0.08^{a}	1.63 ± 0.05^{a}	25.37 ± 0.16^{a}
	10	3	3.34 ± 0.47$^{A, a,*}$	1.53 ± 0.10^{B,a,**}	23.03 ± 0.07^{AB,a,*}
		6	3.08 ± 0.20^{a}	1.72 ± 0.21^{a}	23.73 ± 3.06^{a}
		9	3.08 ± 0.20^{a}	1.71 ± 0.08^{a}	25.07 ± 2.08^{a}
	30	3	3.17 ± 0.23^{A,a,*}	1.62 ± 0.08^{B,a,**}	22.54 ± 1.00^{B,ab,*}
		6	3.13 ± 0.24^{a}	1.67 ± 0.11^{a}	21.95 ± 2.15^{a}
		9	3.30 ± 0.07^{a}	1.69 ± 0.07^{a}	25.88 ± 1.13^{b}

Data are mean values (± standard deviations). Capital letters show the comparison between non-irradiated and irradiated samples at different dose levels after 3 months of storage, within the same irradiation type ($P < 0.05$). Lowercase letters show the comparison between storage times for the same dose and irradiation source ($P < 0.05$). Asterisks (*) indicate a comparison between irradiation sources at the same dose after 3 months of storage

EBPA at any of the doses. Storage time of irradiated PLA did not have an effect on CO_2 permeability.

Other authors reported no significant effects of ionizing irradiation on barrier properties of polymeric packaging to oxygen, water vapor and CO_2 (1-25 kGy) (Buchalla et al., 1993a; Deschenes et al., 1995). Riganokos et al. (1999) also observed no significant difference in gas and water vapor permeability for electron beam irradiated multi-layer (PET/PE/EVOH/PE) at 100 kGy.

4.1.8 Conclusion

In conclusion, this study including exposure of commercial PLA film to two ionizing irradiation sources at irradiation doses of 1 to 30 kGy found no significant color changes (Hunter color L*, a* and b*). The surface tension of PLA decreased after gamma irradiation of doses of 1 to 10 kGy and E-beam irradiation of doses of 1 to 5 kGy. The number average molecular weight (M_n) and weight average molecular weight (M_w) of PLA decreased markedly after gamma and E-beam irradiation. The polydispersity index (PI) increased due to the dominance of chain-scission. The thermal properties of PLA were also affected by ionizing irradiation, as evidenced by the decrease in T_c and T_m. A decrease was found in tensile strength, elongation at break and elastic modulus. O_2 permeability of PLA was not affected by gamma or E-beam ionizing irradiation at doses of 1 - 30 kGy or by storage time. Gamma and E-beam irradiation (1 - 30 kGy) resulted in a reduction in water vapor permeability of PLA. A

significant reduction in CO_2 permeability was observed only for E-beam irradiated PLA at 30 kGy. There was no consistent trend in changes during post-irradiation aging up to 9 months.

4.2 Ionizing radiation effects on properties of cellophane films

4.2.1 Color

The effect of irradiation on the color of cellophane films is shown in Table 4.8-4.10. Hunter colorimeter L*-values, which are a function of brightness (L*, 100 = bright, 0= dark) significantly decreased in E-beam irradiated uncoated cellophane (EBCP), compared to non-irradiated uncoated cellophane (CoCP). There was no significant difference in the brightness values of gamma irradiated uncoated cellophane (GMCP). The brightness value of EBCP at all dose levels was significantly lower than that of GMCP after 3 months of storage. The GMCP samples showed a significant decrease during storage. The Hunter a* value (+ red/- green) for EBCP and GMCP at all dose levels showed a significant decrease as compared to CoCP. After 9 months of storage, GMCP showed a significant decrease while EBCP showed a significant decrease at doses of 10 and 30 kGy. The Hunter b* values (+ yellow/-blue) decreased significantly for GMCP at all dose levels, whereas EBCP showed a significant decrease at a dose of 30 kGy, as compared to CoCP. Gamma irradiated samples showed significantly lower b* values compared to E-beam irradiated samples at all dose levels, indicating that the degree of yellowness decreased in samples irradiated by gamma. Both irradiation sources induced a change in yellowness over time.

Table 4.8 Color changes for non-irradiated (CoCP), gamma irradiated (GMCP) and E-beam irradiated (EBCP) uncoated cellophane films at doses of 1, 5, 10 and 30 kGy after 9 months of storage

Samples	Dose (kGy)	Time (month)	L*	a*	b*
ConCP	0	0	91.83 ± 0.02^{A}	-1.05 ± 0.01^{A}	1.08 ± 0.04^{A}
GMCP	1	3	$91.87 \pm 0.02^{A,a,*}$	$-1.08 \pm 0.01^{B,a,*}$	$1.00 \pm 0.03^{B,a,*}$
		6	91.78 ± 0.02^{b}	-1.10 ± 0.01^{b}	1.10 ± 0.01^{b}
		9	91.60 ± 0.02^{c}	-1.08 ± 0.01^{a}	1.21 ± 0.02^{c}
	5	3	$91.87 \pm 0.07^{A,a,*}$	$-1.09 \pm 0.01^{B,a,*}$	$0.96 \pm 0.02^{B,a,*}$
		6	91.87 ± 0.04^{a}	-1.12 ± 0.01^{b}	0.99 ± 0.02^{a}
		9	91.74 ± 0.01^{b}	-1.13 ± 0.01^{b}	1.07 ± 0.02^{b}
	10	3	$91.88 \pm 0.03^{A,a,*}$	$-1.11 \pm 0.01^{C,a,*}$	$0.95 \pm 0.02^{B,a,*}$
		6	91.77 ± 0.02^{b}	-1.13 ± 0.01^{b}	0.96 ± 0.01^{a}
		9	91.65 ± 0.02^{c}	-1.12 ± 0.01^{b}	1.06 ± 0.01^{b}
	30	3	$91.89 \pm 0.01^{A,a,*}$	$-1.10 \pm 0.01^{C,a,*}$	$0.80 \pm 0.03^{C,a,*}$
		6	91.89 ± 0.00^{a}	-1.12 ± 0.01^{b}	0.84 ± 0.02^{a}
		9	91.76 ± 0.02^{b}	-1.13 ± 0.01^{b}	0.92 ± 0.01^{b}
EBCP	1	3	$91.48 \pm 0.09^{B,a,**}$	$-1.08 \pm 0.01^{B,a,*}$	$1.11 \pm 0.01^{A,a,**}$
		6	91.44 ± 0.01^{a}	-1.08 ± 0.01^{a}	1.23 ± 0.01^{b}
		9	91.47 ± 0.05^{a}	-1.09 ± 0.01^{a}	1.34 ± 0.02^{c}
	5	3	$91.65 \pm 0.06^{C,a,**}$	$-1.09 \pm 0.01^{B,a,*}$	$1.10 \pm 0.01^{A,a,**}$
		6	91.60 ± 0.01^{a}	-1.10 ± 0.01^{a}	1.21 ± 0.01^{b}
		9	91.55 ± 0.02^{a}	-1.11 ± 0.01^{a}	1.34 ± 0.01^{c}
	10	3	$91.60 \pm 0.01^{C,a,**}$	$-1.09 \pm 0.01^{B,a,*}$	$1.08 \pm 0.01^{A,a,**}$
		6	91.60 ± 0.01^{a}	-1.12 ± 0.01^{b}	1.15 ± 0.01^{b}
		9	91.58 ± 0.01^{a}	-1.14 ± 0.01^{c}	1.30 ± 0.01^{c}
	30	3	$91.64 \pm 0.03^{C,a,**}$	$-1.09 \pm 0.01^{B,a,*}$	$1.01 \pm 0.02^{B,a,**}$
		6	91.63 ± 0.02^{a}	-1.13 ± 0.00^{b}	1.09 ± 0.01^{b}
		9	91.68 ± 0.03^{a}	-1.16 ± 0.01^{c}	1.21 ± 0.00^{c}

Data are mean values (± standard deviations). Capital letters show the comparison between non-irradiated and irradiated samples at different dose levels after 3 months of storage, within the same irradiation type ($P < 0.05$). Lowercase letters show the comparison between storage times for the same dose and irradiation source ($P < 0.05$). Asterisks (*) indicate a comparison between irradiation sources at the same dose after 3 months of storage

Table 4.9 Color changes for non-irradiated (CoCM), gamma irradiated (GMCM) and E-beam irradiated (EBCM) nitrocellulose-coated cellophane films at doses of 1, 5, 10 and 30 kGy after 9 months of storage

Samples	Dose (kGy)	Time (month)	L*	a*	b*
ConCM	0	0	92.17 ± 0.03^{A}	-1.17 ± 0.00^{A}	1.18 ± 0.03^{A}
GMCM	1	3	$92.17 \pm 0.05^{A,a,*}$	$-1.18 \pm 0.01^{A,a,*}$	$1.21 \pm 0.01^{AB,a,*}$
		6	92.08 ± 0.03^{b}	-1.20 ± 0.01^{ab}	1.24 ± 0.03^{ab}
		9	91.93 ± 0.01^{c}	-1.21 ± 0.00^{b}	1.28 ± 0.01^{b}
	5	3	$92.14 \pm 0.02^{AB,a,*}$	$-1.20 \pm 0.01^{B,a,*}$	$1.24 \pm 0.02^{B,a,*}$
		6	92.07 ± 0.02^{b}	-1.22 ± 0.01^{a}	1.30 ± 0.03^{b}
		9	91.95 ± 0.03^{c}	-1.24 ± 0.01^{b}	1.38 ± 0.02^{c}
	10	3	$92.15 \pm 0.02^{AB,a,*}$	$-1.21 \pm 0.01^{B,a,*}$	$1.28 \pm 0.03^{C,a,*}$
		6	92.15 ± 0.06^{a}	-1.23 ± 0.01^{a}	1.33 ± 0.01^{b}
		9	91.88 ± 0.04^{b}	-1.26 ± 0.02^{b}	1.46 ± 0.02^{c}
	30	3	$92.10 \pm 0.01^{B,a,*}$	$-1.24 \pm 0.01^{C,a,*}$	$1.45 \pm 0.03^{D,a,*}$
		6	92.10 ± 0.02^{a}	-1.25 ± 0.01^{a}	1.53 ± 0.01^{b}
		9	91.83 ± 0.01^{b}	-1.28 ± 0.01^{b}	1.77 ± 0.01^{c}
EBCM	1	3	$92.05 \pm 0.02^{B,a,**}$	$-1.18 \pm 0.01^{AB,a,*}$	$1.20 \pm 0.01^{AB,a,*}$
		6	92.09 ± 0.01^{a}	-1.20 ± 0.01^{a}	1.23 ± 0.01^{a}
		9	91.82 ± 0.02^{b}	-1.19 ± 0.01^{a}	1.38 ± 0.01^{b}
	5	3	$92.08 \pm 0.01^{B,a,**}$	$-1.19 \pm 0.01^{B,a,*}$	$1.23 \pm 0.02^{B,a,*}$
		6	92.10 ± 0.02^{a}	-1.22 ± 0.00^{b}	1.33 ± 0.01^{b}
		9	91.87 ± 0.01^{b}	-1.21 ± 0.01^{ab}	1.42 ± 0.01^{c}
	10	3	$92.08 \pm 0.03^{B,a,**}$	$-1.19 \pm 0.01^{B,a,**}$	$1.28 \pm 0.01^{C,a,*}$
		6	92.07 ± 0.02^{a}	-1.23 ± 0.01^{b}	1.36 ± 0.02^{b}
		9	91.87 ± 0.02^{b}	-1.23 ± 0.01^{b}	1.49 ± 0.01^{c}
	30	3	$92.09 \pm 0.03^{B,a,*}$	$-1.21 \pm 0.02^{C,a,**}$	$1.33 \pm 0.02^{D,a,**}$
		6	92.07 ± 0.02^{a}	-1.20 ± 0.01^{a}	1.37 ± 0.02^{b}
		9	91.88 ± 0.04^{b}	-1.20 ± 0.01^{a}	1.40 ± 0.02^{c}

Data are mean values (± standard deviations). Capital letters show the comparison between non-irradiated and irradiated samples at different dose levels after 3 months of storage, within the same irradiation type ($P < 0.05$). Lowercase letters show the comparison between storage times for the same dose and irradiation source ($P < 0.05$). Asterisks (*) indicate a comparison between irradiation sources at the same dose after 3 months of storage

Table 4.10 Color changes for non-irradiated (CoCK), gamma irradiated (GMCK) and E-beam irradiated (EBCK) uncoated cellophane films at doses of 1, 5, 10 and 30 kGy after 9 months of storage

Samples	Dose (kGy)	Time (month)	L*	a*	b*
ConCK	0	0	91.21 ± 0.02^{A}	-1.18 ± 0.04^{A}	1.16 ± 0.02^{A}
GMCK	1	3	$91.22 \pm 0.02^{A,a,*}$	$-1.18 \pm 0.03^{A,a,*}$	$1.21 \pm 0.02^{B,a*}$
		6	91.21 ± 0.01^{a}	-1.14 ± 0.02^{a}	1.22 ± 0.01^{a}
		9	91.18 ± 0.02^{a}	-1.13 ± 0.02^{a}	1.30 ± 0.01^{b}
	5	3	$91.22 \pm 0.01^{A,a,*}$	$-1.19 \pm 0.02^{A,a,*}$	$1.23 \pm 0.03^{B,a,*}$
		6	91.23 ± 0.01^{a}	-1.17 ± 0.02^{a}	1.23 ± 0.02^{a}
		9	91.16 ± 0.02^{b}	-1.18 ± 0.01^{a}	1.39 ± 0.01^{b}
	10	3	$91.22 \pm 0.02^{A,a,*}$	$-1.19 \pm 0.03^{A,a,*}$	$1.26 \pm 0.01^{B,a,*}$
		6	91.20 ± 0.02^{a}	-1.18 ± 0.04^{a}	1.30 ± 0.02^{b}
		9	91.11 ± 0.01^{b}	-1.19 ± 0.04^{a}	1.46 ± 0.01^{c}
	30	3	$91.18 \pm 0.01^{A,a,*}$	$-1.17 \pm 0.05^{A,a,*}$	$1.38 \pm 0.03^{C,a,*}$
		6	91.19 ± 0.02^{a}	-1.21 ± 0.01^{a}	1.55 ± 0.03^{b}
		9	91.00 ± 0.02^{b}	-1.20 ± 0.02^{a}	1.75 ± 0.02^{c}
EBCK	1	3	$91.21 \pm 0.05^{A,a,*}$	$-1.16 \pm 0.05^{A,a,*}$	$1.21 \pm 0.02^{B,a,*}$
		6	91.22 ± 0.02^{a}	-1.18 ± 0.02^{a}	1.28 ± 0.01^{b}
		9	91.06 ± 0.01^{b}	-1.19 ± 0.02^{a}	1.34 ± 0.02^{c}
	5	3	$91.22 \pm 0.01^{A,a,*}$	$-1.16 \pm 0.01^{A,a,*}$	$1.30 \pm 0.01^{C,a,**}$
		6	91.22 ± 0.01^{a}	-1.17 ± 0.01^{a}	1.32 ± 0.01^{a}
		9	91.08 ± 0.02^{b}	-1.21 ± 0.01^{a}	1.40 ± 0.01^{b}
	10	3	$91.20 \pm 0.01^{A,a,*}$	$-1.16 \pm 0.02^{A,a,*}$	$1.37 \pm 0.02^{D,a,**}$
		6	91.22 ± 0.01^{a}	-1.21 ± 0.02^{a}	1.41 ± 0.01^{a}
		9	91.02 ± 0.02^{b}	-1.19 ± 0.02^{a}	1.49 ± 0.01^{b}
	30	3	$91.14 \pm 0.02^{B,a,**}$	$-1.16 \pm 0.05^{A,a,*}$	$1.51 \pm 0.03^{E,a,**}$
		6	91.15 ± 0.02^{a}	-1.17 ± 0.04^{a}	1.65 ± 0.02^{b}
		9	90.97 ± 0.01^{b}	-1.20 ± 0.02^{a}	1.71 ± 0.02^{c}

Data are mean values (± standard deviations). Capital letters show the comparison between non-irradiated and irradiated samples at different dose levels after 3 months of storage, within the same irradiation type ($P < 0.05$). Lowercase letters show the comparison between storage times for the same dose and irradiation source ($P < 0.05$). Asterisks (*) indicate a comparison between irradiation sources at the same dose after 3 months of storage

The brightness (L* value) of nitrocellulose-coated cellophane significantly decreased for E-beam irradiated nitrocellulose-coated cellophane (EBCM) samples at all dose levels, while it decreased only at 30 kGy for gamma irradiated nitrocellulose-coated cellophane GMCM as compared to non-irradiated nitrocellulose-coated cellophane (CoCM). The brightness of EBCM was significantly lower than that of GMCM at dose levels of 1 - 10 kGy after 3 months of storage. Over time there was a significant decrease in brightness for GMCM and EBCM. A significant decrease in the Hunter a* value was detected in GMCM and EBCM at doses of 5 - 30 kGy as compared to CoCM. Gamma irradiation decreased a* values more than E-beam irradiation. Also there was a significant decrease in a* values over the storage time with the exception of EBCM at 1 and 30 kGy. The Hunter b* values were significantly higher for EBCM and GMCM at doses of 5 - 30 kGy as compared to CoCM. The yellowish color of GMCM was significantly higher than that of EBCM at 30 kGy. An increase in yellowness was also seen for GMCM and EBCM during storage.

Irradiation of PVdC-coated cellophane changed the color of the films. Brightness (L*) values decreased significantly for E-beam irradiated PVdC-coated cellophane (EBCK) at an absorbed dose of 30 kGy compared to non-irradiated PVdC-coated cellophane (CoCK). At 30 kGy, the brightness of gamma irradiated PVdC-coated cellophane (GMCK) was higher than that of EBCK. After 9 months of storage, a significant decrease in L* values was observed for GMCK and EBCK samples, except for GMCK at a dose of 1 kGy. The Hunter b* values significantly increased for both irradiation sources as compared to CoCK. The yellowish color of EBCK at absorbed

doses of 5 - 30 kGy was significantly higher than that of GMCK. Storage time also resulted in a significant increase in yellowness for all GMCK and EBCK samples.

The yellowish coloration of E-beam irradiated PVdC-coated cellophane was reported by LeClair and Cobbs (1958). Clough et al. (1996) concluded that the irradiation source has an effect on the discoloration of different polymer types. Chapiro (1988) reported that the discoloration of polymeric materials can be caused by ions and radicals that are trapped after irradiation. Several other studies also reported a change in color after irradiation, depending on the types of polymeric materials (Jo et al., 2005; Kabeel et al., 1991).

4.2.2 Surface tension

The wettability of solid materials can be expressed by the balance between adhesive forces of the liquid on the solid and cohesive forces of the liquid. When the liquid's surface energy is lower than the material's surface energy, adhesive forces cause the liquid to spread over the material surface. In contrast, when the surface energy of the liquid is equal to or higher than the material's surface energy, cohesive forces tend to retain the liquid in a droplet form. Uncoated cellophane is highly sensitive to moisture due to its many hydroxyl groups, and can absorb its own weight in water (Robertson, 2013; Selke et al., 2004) eliminating droplet formation. Hence, the surface tension of uncoated cellophane could not be tested in this study.

The effect of irradiation on wettability was determined using dyne test inks. The surface tensions of nitrocellulose-coated cellophane (CoCM) and PVdC-coated cellophane (CoCK) were 55 and 58 dyne/cm, respectively as shown in Table 4.11.

Table 4.11 Surface tension of non-irradiated (Co), gamma irradiated (GM) and E-Beam irradiated (EB) of nitrocellulose-coated cellophane (CM) and PVdC-coated cellophane (CK) films after 9 months of storage

Samples	Dose (kGy)	Time (month)	Surface Tension (dyne/cm)	
			CM	CK
Co	0	0	55	58
GM	1	3	47	58
		6	47	58
		9	47	58
	5	3	43	57
		6	42	57
		9	42	57
	10	3	43	57
		6	43	57
		9	43	56
	30	3	44	58
		6	44	58
		9	44	58
EB	1	3	45	57
		6	44	58
		9	44	58
	5	3	42	57
		6	42	57
		9	42	56
	10	3	43	57
		6	43	58
		9	43	58
	30	3	44	58
		6	43	58
		9	43	58

There was no change in the surface tension of CoCM and CoCK during 9 months of storage. E-beam and gamma irradiation induced greater changes in the surface tension of CoCM than that of CoCK. The surface tension values for gamma-irradiated samples (GMCM) decreased from 55 dyne/cm for CoCM to 47 - 44 dyne/cm for GMCM

at dose levels of 1 - 30 kGy, respectively. The surface tension of GMCM at each dose level remained constant after 3, 6 and 9 months of storage. E-beam irradiated samples (EBCM) decreased in surface tension from 55 dyne/cm for CoCM to 45 dyne/cm for EBCM at 1 kGy and to 43 dyne/cm for EBCM at 30 kGy. Storage time did not seem to affect the surface tension of the E-beam irradiated nitrocellulose-coated cellophane films. Neither type of irradiation, E-beam or gamma, impacted the surface tension of PVdC-coated cellophane. The values for irradiated samples GMCK and EBCK ranged from 57 - 58 dyne/cm, which is close to the 58 dyne/cm for CoCK. Storage time also did not have any effect.

4.2.3 Fourier transform infrared (FTIR) spectroscopy

FTIR analyses, as shown in Table 4.12, Figure 4.4 for gamma and Figure 4.5 for E-beam irradiation of the uncoated cellophane (CP), showed an increase in -OH-stretching between 3000-3600 cm^{-1}. The peak intensity also increased after gamma and E-beam irradiation exposure for the antisymmetrical bridge C-O-C stretching and C-O-C pyranose ring skeletal vibration at 1155 and 1018 cm^{-1} as also reported by others (Higgins et al., 1961; Nelson & O'Connor, 1964; Zhu et al., 2013). The increase in peak intensity was higher at higher doses of gamma and E-beam irradiation. The small peak at absorbance band 893 cm^{-1}, which is associated with the vibration of glycosidic bonds (Higgins et al., 1961), showed a sharp and intense peak. In the region of 1313 -1363 and 1647 cm^{-1} attributed to -CH_2 and C=O stretching (Gong & Zhang, 1998),

respectively, an increase in intensity was observed after irradiation by gamma and E-beam.

The effect of gamma and E-beam irradiation on the FTIR peaks of nitrocellulose-coated cellophane is shown in Table 4.12, Figure 4.6 and Figure 4.7, respectively. The absorption band of the nitro group (NO_2) group at 1643, 1277, and 837 cm^{-1} showed a pronounced decrease after exposure to 30 kGy of gamma or E-beam irradiation. At lower doses of 1 - 10 kGy the NO_2 group showed a slight decrease in intensity. A decrease in the peak at absorption band 1009-1057, which is associated with the glucopyranose group (C-O) (Gong & Zhang, 1998), was detected for gamma and E-beam irradiated samples as a function of dose. Heppel-Masys et al. (1997) reported a similar effect of gamma irradiation on nitrocellulose.

Figure 4.8 and Figure 4.9 show the spectrum of gamma irradiated (GMCK) and E-beam irradiated PVdC-coated cellophane (EBCK) films, respectively. The C-Cl stretching vibration at 748 and 665 cm^{-1} for PVdC-coated cellophane decreased with increasing irradiation dose for both gamma and E-beam. The CH stretching and CH_2 stretching bands at 2916, 2848 and 1409, 1359 and 1311 cm^{-1} did not change after irradiation.

Table 4.12 Peak infrared spectra band assignments for uncoated cellophane, nitrocellulose-coated cellophane and PVdC-coated cellophane

Assignment	Wave number (cm^{-1})
Uncoated cellophane	
OH stretching	3600-3000
CH stretching	2887
C=O stretching	1647
CH_2 stretching	1313-1363
C-O-C antisymmetric bridge stretching	1155
C-O-C stretching	1018
β-anomer or *β*–linked glucose	893
Nitrocellulose-coated cellophane	
CH stretching	2916, 2848
C=O stretching (carboxylic group)	1720
NO_2 (antisymmetric stretching)	1643
NO_2 (symmetric stretching)	1276
C-O stretching	1057, 1009
NO_2 stretching	837
PVdC-coated cellophane	
CH stretching	2916, 2848
C=O stretching	1730
CH_2 stretching	1409, 1359, 1311
CH_2 stretching	893
C-Cl stretching	665, 748

Adapted from (Coleman & Painter, 1976; Costa et al., 2014; Krimm & Liang, 1956; Nelson & O'Connor, 1964; Zhu et al., 2013)

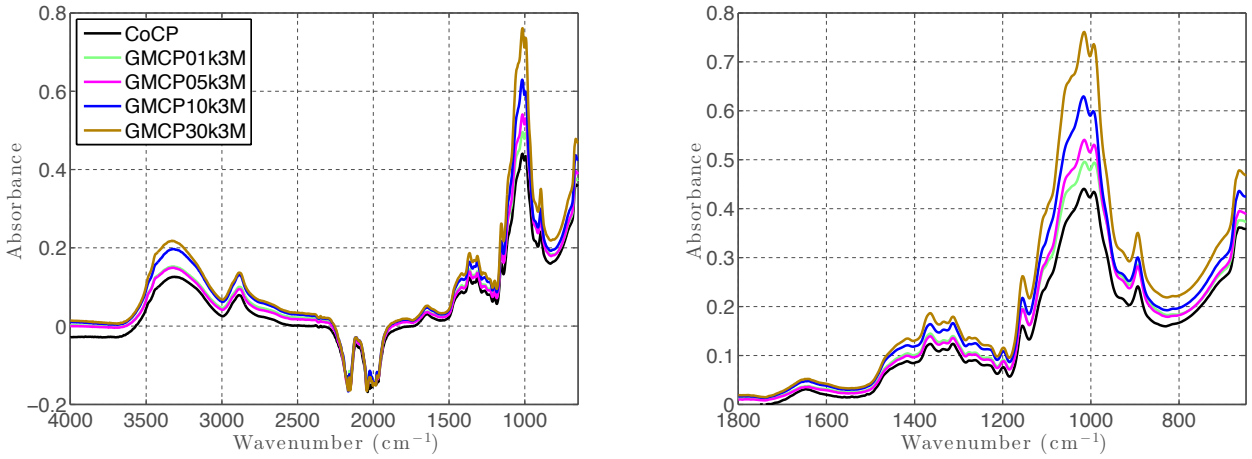

Figure 4.4 FTIR spectra of non-irradiated (CoCP) and gamma irradiated uncoated cellophane (GMCP) at absorbed doses of 0, 1, 5, 10 and 30 kGy after 9 months of storage.

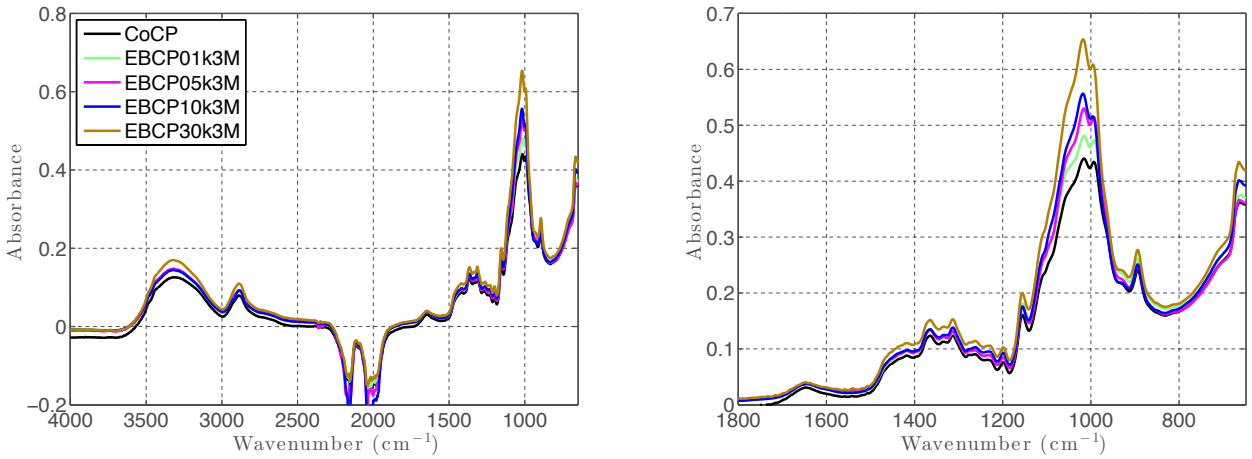

Figure 4.5 FTIR spectra of non-irradiated (CoCP) and E-beam irradiated uncoated cellophane (EBCP) at absorbed doses of 0, 1, 5, 10 and 30 kGy after 9 months of storage

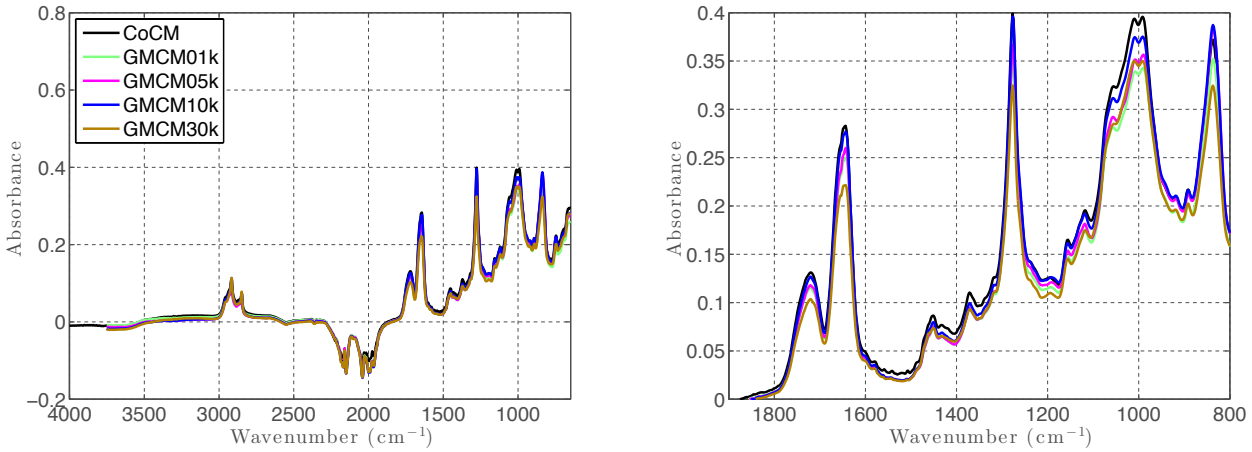

Figure 4.6 FTIR spectra of non-irradiated (CoCM) and gamma irradiated nitrocellulose-coated cellophane (GMCM) at absorbed doses of 0, 1, 5, 10 and 30 kGy after 9 months of storage

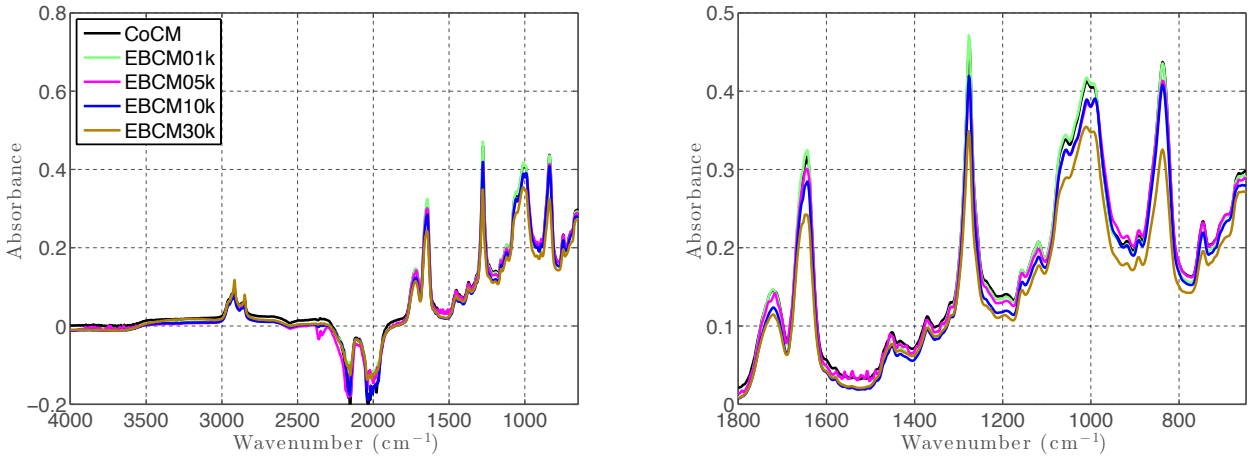

Figure 4.7 FTIR spectra of non-irradiated (CoCM) and E-beam irradiated nitrocellulose-coated cellophane (EBCM) at absorbed doses of 0, 1, 5, 10 and 30 kGy after 9 months of storage

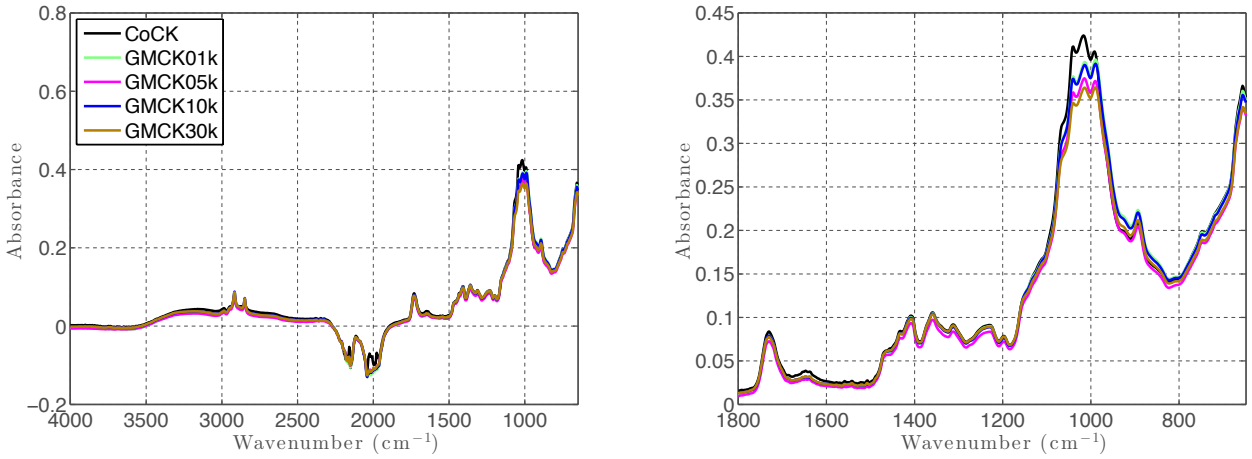

Figure 4.8 FTIR spectra of non-irradiated (CoCK) and gamma irradiated PVdC-coated cellophane (GMCK) at absorbed doses of 0, 1, 5, 10 and 30 kGy after 9 months of storage

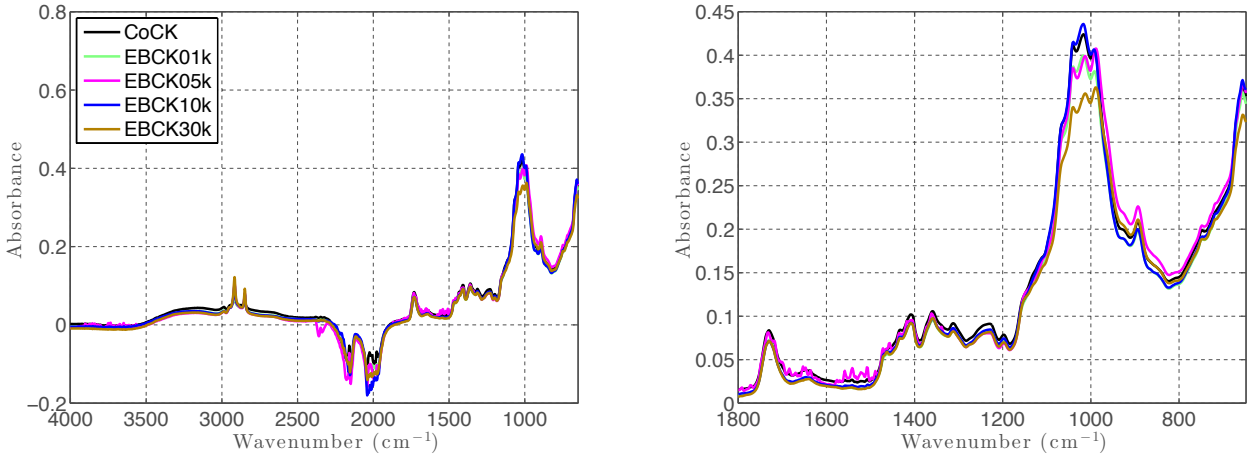

Figure 4.9 FTIR spectra of non-irradiated (CoCK) and E-beam irradiated PVdC-coated cellophane (EBCK) at absorbed doses of 0, 1, 5, 10 and 30 kGy after 9 months of storage

4.2.4 Thermal properties

The changes in glass transition temperature (T_g) of gamma and E-beam irradiated cellophane using a differential scanning calorimeter (DSC) are shown in Table 4.13. Gamma irradiation of the uncoated cellophane film (GMCP) resulted in a significant decrease in the glass transition temperature at all dose levels except at 1 kGy after 3 months of storage. A significant decrease was also observed for the E-beam irradiated uncoated cellophane samples (EBCP) at 1 and 5 kGy. No significant difference between gamma and E-beam irradiation was found. Significantly higher T_g values were seen in all GMCP samples irradiated at 10 and 30 kGy during storage whereas these values were significantly higher only after 9 months of storage at doses of 1 and 5 kGy as compared to 3 and 6 months. EBCP showed a significant increase during storage for only some of the comparisons, as shown in Table 4.13.

Gamma irradiated nitrocellulose-coated cellophane (GMCM) showed a significant decrease in T_g at a dose of 10 kGy after 3 months of storage. Increasing dose levels of E-beam (1-30 kGy) on nitrocellulose-coated cellophane film (EBCM) did not have an impact T_g. E-beam irradiated nitrocellulose-coated cellophane films had significantly higher T_g values as compared to the gamma irradiated nitrocellulose-coated cellophane after 3 months of storage. In general, GMCM samples increased in T_g after 9 months of storage, while EBCM samples decreased in T_g after 9 months of storage.

Table 4.13 Glass transition (T_g) of non-irradiated (Co), gamma irradiated (GM) and E-Beam irradiated (EB) of uncoated cellophane (CP), nitrocellulose-coated cellophane (CM), PVdC-coated cellophane (CK) after 9 months of storage

Sample	Dose (kGy)	Time (month)	T_g (˚C)		
			CP	CM	CK
Co	0	0	131.83 ± 3.39^{A}	131.95 ± 2.26^{A}	133.96 ± 0.66^{A}
GM	1	3	126.76 ± 0.64^{AB,a*,}	127.64 ± 1.01^{AB,a*}	125.83 ± 3.05^{B,a,*}
		6	128.06 ± 3.02^{a}	130.83 ± 1.11^{ab}	135.97 ± 2.88^{b}
		9	138.03 ± 1.97^{b}	135.31 ± 2.64^{b}	136.05 ± 0.68^{b}
	5	3	125.28 ± 2.88^{B,a,*}	127.12 ± 1.77^{AB,a*}	129.14 ±1.74^{A,a,*}
		6	128.09 ± 2.53^{a}	134.07 ± 1.58^{b}	134.16 ± 0.92^{ab}
		9	137.82 ± 0.84^{b}	137.72 ± 1.62^{b}	135.67 ± 2.20^{b}
	10	3	125.01 ± 1.78^{B,a,*}	124.18 ± 0.89^{B,a*}	130.17 ± 4.56^{A,a,*}
		6	130.99 ± 0.34^{b}	128.30 ± 1.32^{a}	137.11 ± 1.18^{b}
		9	137.78 ± 0.32^{c}	137.15 ± 0.88^{b}	136.91 ± 1.96^{b}
	30	3	123.11 ± 1.68^{B,a,*}	128.36 ± 1.20^{AB,a*}	131.41 ± 2.73^{A,a,*}
		6	130.91 ± 1.43^{b}	133.49 ± 1.57^{b}	135.51 ± 2.95^{a}
		9	136.93 ± 2.15^{c}	136.19 ± 0.52^{b}	136.45 ± 3.73^{a}
EB	1	3	126.32 ± 0.74^{B,a,*}	131.46 ± 0.16^{A,b,**}	129.63 ± 3.16^{A,a,*}
		6	134.79 ± 4.50^{b}	137.63 ± 0.31^{a}	136.53 ± 1.17^{b}
		9	131.56 ± 1.10^{ab}	130.74 ± 2.43^{b}	131.20 ± 0.88^{ab}
	5	3	125.88 ± 2.64^{B,a,*}	133.34 ± 3.43^{A,ab**}	136.43 ±2.94^{A,ab,**}
		6	133.98 ± 1.97^{b}	137.83 ± 0.68^{a}	138.39 ± 2.27^{a}
		9	132.45 ± 1.63^{b}	130.84 ± 0.45^{b}	130.22 ± 2.21^{b}
	10	3	128.42 ± 0.82^{AB,a,*}	134.74 ± 2.08^{A,a,**}	135.60 ± 2.20^{A,a,*}
		6	133.35 ± 0.70^{b}	135.51 ± 1.09^{a}	139.12 ±0.86^{a}
		9	134.39 ± 1.66^{b}	128.93 ± 1.91^{b}	129.92 ± 2.66^{b}
	30	3	134.39 ± 2.50^{A,a,**}	136.18 ± 1.89^{A,a,**}	137.47 ± 1.36^{A,a,*}
		6	134.29 ± 0.98^{a}	132.60 ± 0.51^{ab}	134.63 ± 2.42^{ab}
		9	130.12 ± 0.88^{a}	130.59 ± 0.39^{b}	132.53 ± 1.14^{b}

Data are mean values (± standard deviations). Capital letters show the comparison between non-irradiated and irradiated samples at different dose levels after 3 months of storage, within the same irradiation type ($P < 0.05$). Lowercase letters show the comparison between storage times for the same dose and irradiation source ($P < 0.05$). Asterisks (*) indicate a comparison between irradiation sources at the same dose after 3 months of storage

T_g values for gamma irradiated PVdC-coated cellophane (GMCK) at 1 kGy were significant lower than for non-irradiated PVdC-coated cellophane (CoCK) with T_g decreasing after 3 months of storage. E-beam irradiation (EBCK) did not no impact on the T_g at any dose level. The T_g of PVdC-coated cellophane was significantly lower for gamma than for E-beam irradiation at 5 kGy after 3 months of storage. A significant increase in T_g was found for GMCK during storage, while the EBCK samples showed a significant decrease during storage.

4.2.5 Mechanical properties

Results for tensile strength, elongation at break and elastic modulus of uncoated cellophane (CP), nitrocellulose-coated cellophane (CM) and PVdC-coated cellophane (CK) films before and after exposure to gamma and E-beam irradiation are summarized in Tables 4.14 - 4.16. The machine direction (MD) tensile strength of gamma irradiated uncoated cellophane (GMCP) significantly decreased at a dose level of 30 kGy as compared to non-irradiated uncoated cellophane (CoCP). Elongation at break in MD of GMCP at 10 and 30 kGy significantly decreased and also for E-beam irradiated uncoated cellophane (EBCP) at 30 kGy. The elastic modulus of uncoated cellophane was not affected by gamma or E-beam irradiation at any dose level.

The tensile strength of nitrocellulose-coated cellophane in MD significantly increased after gamma irradiation, whereas it was not affected by E-beam irradiation. Elongation at break of nitrocellulose-coated cellophane in MD at all dose levels and in CD except at a dose of 1 kGy, was significantly lower than non-irradiated nitrocellulose-

coated cellophane (CoCM). The elastic modulus of gamma irradiated (GMCM) and E-beam irradiated nitrocellulose-coated cellophane (EBCM) significantly increased in MD and in CD at all dose levels compared to CoCM. The elastic modulus of GMCM was significantly higher than that of EBCM at all dose levels.

The tensile strength in MD for gamma (GMCK) and E-beam irradiated PVdC-coated cellophane (EBCK) significantly decreased at 30 kGy. Tensile strength of GMCK and EBCK in the CD was significantly lower at all dose levels compared to CoCK. Gamma and E-beam irradiation decreased the elongation at break of PVdC-coated cellophane in MD at 30 kGy and in CD at all doses. A significant increase in elastic modulus in MD of GMCK at irradiation doses of 5 - 30 kGy and EBCK at 30 kGy was observed. Elongation at break in both MD and CD of GMCK at 30 kGy was higher than EBCK while the elastic modulus in MD of GMCK was lower than EBCK at 30 kGy. The mechanical properties for irradiated cellophane films during 9 months of storage did not show any clear trend. LeClair and Cobbs (1958) reported a significant decrease in mechanical properties (elongation at break, modulus, tear strength and impact strength) for uncoated and PVdC-coated cellophane (K-202) after E-beam irradiation at approximately 10 kGy. Goulus et al. (2003a) and (2004) studied the effect of irradiation on mechanical properties of various polymeric packaging materials including monolayer and multilayer structures and reported that gamma irradiation at doses up to 10 kGy induced no significant change in mechanical properties, while significant differences did occur at a dose of 30 kGy.

Table 4.14 Mechanical properties of non- irradiated (CoCP), gamma irradiated (GMCP) and electron beam irradiated uncoated cellophane (EBCP) film after 9 months of storage

Sample	Dose (kGy)	Time (month)	Tensile strength (kpsi)	Elongation at break (%)	Elastic Modulus (kpsi)
			MD	MD	MD
CoCP	0	0	21.34 ± 1.12^{A}	19.55 ± 2.19^{A}	408.84 ± 80.09^{A}
GMCP	1	3	$21.10 \pm 1.00^{A,a,*}$	$18.55 \pm 1.03^{A,a,*}$	$376.19 \pm 36.04^{A,a,*}$
		6	20.49 ± 0.56^{a}	18.65 ± 1.88^{a}	330.85 ± 61.74^{a}
		9	23.19 ± 1.38^{b}	16.45 ± 1.51^{b}	316.14 ± 91.52^{a}
	5	3	$21.15 \pm 0.54^{A,a,*}$	$18.61 \pm 1.58^{A,a,*}$	$403.01 \pm 63.24^{A,a,*}$
		6	19.31 ± 1.02^{b}	19.15 ± 1.03^{a}	281.71 ± 40.92^{b}
		9	22.58 ± 1.06^{a}	14.96 ± 1.15^{b}	404.00 ± 24.06^{a}
	10	3	$20.83 \pm 0.51^{A,a,*}$	$16.67 \pm 0.92^{B,a*}$	$425.03 \pm 35.86^{A,a,*}$
		6	19.08 ± 0.86^{b}	17.19 ± 1.88^{a}	254.72 ± 39.97^{b}
		9	22.57 ± 0.65^{c}	14.75 ± 0.88^{c}	377.49 ± 53.04^{c}
	30	3	$19.58 \pm 0.98^{B,a,*}$	$14.51 \pm 1.39^{C,ab,*}$	$488.70 \pm 65.30^{A,a,*}$
		6	20.52 ± 0.78^{ab}	15.54 ± 1.05^{a}	451.88 ± 32.89^{a}
		9	21.45 ± 0.90^{b}	12.82 ± 1.75^{b}	432.23 ± 28.03^{a}
EBCP	1	3	$21.23 \pm 0.80^{A,a,*}$	$18.12 \pm 1.43^{A,a,*}$	$403.80 \pm 85.40^{A,a,*}$
		6	21.84 ± 0.46^{a}	16.26 ± 0.99^{ab}	485.09 ± 68.98^{b}
		9	22.16 ± 0.67^{a}	15.82 ± 1.56^{a}	497.12 ± 65.25^{b}
	5	3	$21.19 \pm 0.92^{A,a,*}$	$18.88 \pm 1.30^{A,a,*}$	$378.13 \pm 57.87^{A,a,*}$
		6	21.97 ± 0.98^{a}	16.46 ± 1.21^{b}	458.98 ± 55.70^{b}
		9	23.69 ± 1.35^{b}	17.05 ± 2.31^{ab}	478.55 ± 73.83^{b}
	10	3	$21.60 \pm 1.11^{A,a,*}$	$17.99 \pm 2.30^{A,a,*}$	$436.25 \pm 72.94^{A,a,*}$
		6	20.77 ± 0.38^{b}	15.49 ± 0.56^{b}	502.02 ± 57.30^{ab}
		9	22.90 ± 0.98^{a}	15.46 ± 1.95^{b}	558.54 ± 75.01^{b}
	30	3	$20.54 \pm 0.55^{A,a,*}$	$16.20 \pm 1.79^{B,a,*}$	$360.09 \pm 55.86^{A,a,*}$
		6	20.99 ± 0.89^{a}	16.07 ± 1.33^{b}	458.72 ± 48.77^{b}
		9	23.35 ± 0.89^{b}	16.78 ± 1.36^{a}	420.70 ± 63.81^{ab}

Table 4.14 (cont'd)

Sample	Dose (kGy)	Time (month)	Tensile strength (kpsi)	Elongation at break (%)	Elastic Modulus (kpsi)
			CD	CD	CD
CoCP	0	0	10.33 ± 0.40^{A}	48.42 ± 4.25^{A}	77.17 ± 8.54^{A}
GMCP	1	3	$9.94 \pm 0.60^{A,a,*}$	$48.42 \pm 5.36^{A,a,*}$	$72.89 \pm 13.98^{A,a,*}$
		6	8.81 ± 0.35^{b}	44.53 ± 6.97^{a}	84.05 ± 16.83^{ab}
		9	12.23 ± 0.28^{c}	32.65 ± 2.04^{b}	141.94 ± 17.81^{b}
	5	3	$10.35 \pm 0.60^{A,a,*}$	$46.64 \pm 7.46^{A,a,*}$	$82.23 \pm 21.35^{A,a,*}$
		6	9.60 ± 0.51^{b}	49.16 ± 9.03^{a}	64.67 ± 19.68^{a}
		9	12.11 ± 1.08^{c}	38.30 ± 3.16^{b}	109.49 ± 30.97^{a}
	10	3	$10.54 \pm 0.46^{A,a,*}$	$45.67 \pm 7.52^{A,a,*}$	$105.28 \pm 93.00^{A,ab,*}$
		6	9.23 ± 0.71^{b}	45.52 ± 8.98^{a}	92.40 ± 29.18^{a}
		9	12.02 ± 0.65^{c}	35.00 ± 4.95^{a}	129.16 ± 35.42^{b}
	30	3	$10.15 \pm 0.38^{A,a,*}$	$42.17 \pm 5.10^{A,a,*}$	$97.29 \pm 28.68^{A,a,*}$
		6	10.03 ± 0.24^{a}	34.38 ± 3.35^{b}	110.83 ± 24.35^{a}
		9	11.46 ± 0.55^{b}	31.48 ± 4.75^{b}	110.56 ± 24.73^{a}
EBCP	1	3	$10.44 \pm 0.38^{A,a,*}$	$47.57 \pm 4.61^{A,a,*}$	$74.73 \pm 16.01^{A,a,*}$
		6	11.00 ± 0.61^{ab}	42.23 ± 6.54^{ab}	96.20 ± 28.51^{a}
		9	11.51 ± 0.32^{b}	40.30 ± 3.15^{b}	88.98 ± 12.37^{a}
	5	3	$10.42 \pm 0.24^{B,a,*}$	$43.71 \pm 2.82^{A,a,*}$	$99.29 \pm 8.42^{A,a,*}$
		6	10.67 ± 0.64^{b}	39.18 ± 7.24^{a}	106.43 ± 28.79^{a}
		9	11.58 ± 0.45^{a}	40.59 ± 5.36^{a}	86.67 ± 18.83^{a}
	10	3	$10.03 \pm 0.37^{A,a,*}$	$42.94 \pm 2.26^{B,a,*}$	$101.16 \pm 11.30^{A,a,*}$
		6	10.67 ± 0.75^{a}	42.69 ± 4.73^{a}	97.27 ± 13.91^{a}
		9	11.89 ± 0.73^{b}	38.52 ± 4.89^{a}	108.28 ± 33.82^{a}
	30	3	$10.34 \pm 0.86^{A,a,*}$	$41.61 \pm 7.99^{B,a,*}$	$84.65 \pm 22.87^{A,a,*}$
		6	10.54 ± 0.45^{a}	37.80 ± 5.26^{a}	117.10 ± 27.24^{a}
		9	10.91 ± 0.56^{a}	35.82 ± 4.75^{a}	108.49 ± 24.70^{a}

Data are mean values (± standard deviations). Capital letters show the comparison between non-irradiated and irradiated samples at different dose levels after 3 months of storage, within the same irradiation type ($P < 0.05$). Lowercase letters show the comparison between storage times for the same dose and irradiation source ($P < 0.05$). Asterisks (*) indicate a comparison between irradiation sources at the same dose after 3 months of storage

Table 4.15 Mechanical properties of non- irradiated (CoCM), gamma irradiated (GMCM) and electron beam irradiated nitrocellulose-coated cellophane (EBCM) film after 9 months of storage

Sample	Dose (kGy)	Time (month)	Tensile strength (kpsi)	Elongation at break (%)	Elastic Modulus (kpsi)
			MD	MD	MD
CoCM	0	0	20.03 ± 0.28^{A}	18.58 ± 1.03^{A}	367.84 ± 25.66^{A}
GMCM	1	3	$20.85 \pm 0.88^{B,a,*}$	$16.55 \pm 0.92^{B,a,*}$	$475.88 \pm 27.03^{B,a,*}$
		6	21.31 ± 0.30^{a}	15.45 ± 0.30^{b}	478.56 ± 28.01^{b}
		9	20.64 ± 0.34^{a}	16.62 ± 0.41^{a}	436.58 ± 14.70^{c}
	5	3	$21.69 \pm 1.06^{B,a}*,$	$16.01 \pm 0.46^{B,a,*}$	$513.17 \pm 35.28^{B,a,*}$
		6	18.51 ± 1.76^{b}	16.73 ± 1.06^{ab}	386.09 ± 43.98^{b}
		9	21.96 ± 0.32^{a}	17.48 ± 0.42^{b}	420.60 ± 19.35^{b}
	10	3	$21.06 \pm 0.95^{B,a,*}$	$14.84 \pm 0.37^{C,a,*}$	$531.93 \pm 56.17^{B,a,*}$
		6	20.58 ± 0.56^{a}	14.56 ± 0.45^{a}	479.64 ± 13.41^{b}
		9	21.31 ± 0.32^{a}	16.21 ± 0.28^{b}	462.44 ± 17.11^{b}
	30	3	$20.87 \pm 0.26^{B,a,*}$	$14.34 \pm 0.50^{C,a,*}$	$577.62 \pm 30.99^{C,a,*}$
		6	19.79 ± 0.44^{b}	13.88 ± 0.49^{a}	497.64 ± 28.15^{b}
		9	20.39 ± 0.36^{ab}	16.01 ± 0.64^{b}	462.64 ± 28.01^{b}
EBCM	1	3	$20.28 \pm 0.69^{A,a,*}$	$16.21 \pm 0.91^{B,a,**}$	$428.65 \pm 28.00^{B,a,**}$
		6	21.70 ± 0.42^{b}	16.14 ± 0.84^{a}	479.72 ± 27.52^{b}
		9	20.78 ± 0.35^{a}	15.77 ± 0.45^{a}	427.12 ± 17.14^{a}
	5	3	$21.04 \pm 0.73^{A,b,*}$	$16.23 \pm 0.62^{B,a,*}$	$442.95 \pm 39.62^{B,a,**}$
		6	22.27 ± 0.32^{a}	15.48 ± 0.27^{a}	412.16 ± 31.21^{a}
		9	21.24 ± 0.49^{b}	16.55 ± 0.91^{a}	424.03 ± 21.26^{a}
	10	3	$20.63 \pm 0.42^{A,a,*}$	$15.83 \pm 0.92^{B,a,**}$	$445.95 \pm 27.85^{B,a,**}$
		6	20.37 ± 0.50^{a}	14.12 ± 0.88^{b}	536.96 ± 37.93^{b}
		9	21.62 ± 0.54^{b}	16.53 ± 0.57^{a}	459.22 ± 30.02^{a}
	30	3	$19.69 \pm 0.78^{A,a,*}$	$15.39 \pm 1.36^{B,a,**}$	$440.96 \pm 78.50^{B,a,**}$
		6	19.93 ± 0.21^{a}	13.47 ± 0.40^{b}	556.53 ± 31.64^{b}
		9	19.92 ± 0.63^{a}	15.34 ± 0.60^{a}	447.55 ± 41.03^{a}

Table 4.15 (cont'd)

Sample	Dose (kGy)	Time (month)	Tensile strength (kpsi)	Elongation at break (%)	Elastic Modulus (kpsi)
			CD	CD	CD
CoCM	0	0	10.12 ± 0.32^{A}	66.48 ± 4.06^{A}	466.89 ± 9.70^{A}
GMCM	1	3	$10.09 \pm 0.99^{A,a,*}$	$55.94 \pm 17.18^{AB,a,*}$	$479.57 \pm 8.18^{B,a,*}$
		6	10.03 ± 0.55^{a}	49.92 ± 9.06^{a}	541.64 ± 9.36^{b}
		9	10.02 ± 0.59^{a}	50.39 ± 7.08^{a}	497.25 ± 3.48^{c}
	5	3	$10.26 \pm 1.53^{A,a}*$	$44.65 \pm 19.48^{BC,a,*}$	$479.26 \pm 5.91^{B,a,*}$
		6	8.55 ± 0.38^{b}	57.67 ± 5.79^{a}	460.41 ± 7.11^{b}
		9	9.77 ± 0.36^{a}	44.44 ± 5.40^{a}	478.93 ± 5.83^{a}
	10	3	$10.55 \pm 0.94^{A,a,*}$	$43.90 \pm 13.06^{BC,a,*}$	$473.44 \pm 10.10^{B,a,*}$
		6	8.60 ± 0.54^{b}	53.61 ± 6.95^{a}	492.04 ± 5.62^{a}
		9	8.86 ± 0.94^{b}	25.23 ± 11.00^{b}	521.11 ± 16.07^{b}
	30	3	$10.45 \pm 0.89^{A,a,*}$	$38.35 \pm 10.67^{C,ab,*}$	$495.98 \pm 13.40^{B,a,*}$
		6	10.12 ± 0.97^{a}	41.51 ± 11.96^{a}	543.96 ± 5.44^{b}
		9	9.04 ± 1.01^{b}	25.57 ± 11.65^{b}	501.13 ± 10.48^{c}
EBCM	1	3	$9.52 \pm 0.70^{A,a,*}$	$53.88 \pm 12.60^{AB,a,*}$	$488.43 \pm 19.80^{B,a,*}$
		6	9.78 ± 1.08^{a}	53.22 ± 12.25^{a}	489.21 ± 13.68^{a}
		9	9.61 ± 0.68^{a}	48.65 ± 10.84^{a}	509.46 ± 3.40^{b}
	5	3	$9.87 \pm 0.61^{A,a,*}$	$45.72 \pm 16.85^{B,a,*}$	$473.02 \pm 9.34^{B,a,*}$
		6	9.38 ± 0.59^{a}	31.31 ± 8.00^{b}	484.45 ± 4.03^{a}
		9	9.68 ± 0.86^{a}	43.91 ± 12.29^{ab}	506.27 ± 5.78^{b}
	10	3	$10.07 \pm 0.94^{A,a,*}$	$43.52 \pm 12.75^{B,a,*}$	$493.74 \pm 22.63^{B,a,*}$
		6	10.13 ± 1.27^{a}	44.53 ± 11.05^{a}	517.86 ± 5.12^{b}
		9	9.67 ± 0.68^{a}	38.09 ± 6.39^{a}	524.84 ± 3.64^{b}
	30	3	$9.75 \pm 1.15^{A,a,*}$	$48.14 \pm 17.35^{B,a,*}$	$496.66 \pm 29.94^{B,a,*}$
		6	10.96 ± 0.95^{b}	47.92 ± 11.39^{a}	513.79 ± 12.88^{b}
		9	10.32 ± 0.78^{ab}	44.14 ± 8.22^{a}	520.78 ± 5.38^{b}

Data are mean values (± standard deviations). Capital letters show the comparison between non-irradiated and irradiated samples at different dose levels after 3 months of storage, within the same irradiation type ($P < 0.05$). Lowercase letters show the comparison between storage times for the same dose and irradiation source ($P < 0.05$). Asterisks (*) indicate a comparison between irradiation sources at the same dose after 3 months of storage

Table 4.16 Mechanical properties of non- irradiated (CoCK), gamma irradiated (GMCK) and electron beam irradiated PVdC-coated cellophane (EBCK) film after 9 months of storage

Sample	Dose (kGy)	Time (month)	Tensile strength (kpsi)	Elongation at break (%)	Elastic Modulus (kpsi)
			MD	MD	MD
CoCK	0	0	24.37 ± 0.39^{A}	19.66 ± 1.06^{A}	421.74 ± 22.28^{A}
GMCK	1	3	$23.75 \pm 0.58^{A,a,*}$	$19.19 \pm 1.08^{A,ab,*}$	$402.78 \pm 33.38^{A,a,*}$
		6	24.48 ± 0.28^{a}	18.19 ± 0.53^{a}	472.99 ± 24.57^{b}
		9	22.76 ± 0.28^{b}	19.36 ± 0.78^{b}	395.23 ± 22.00^{a}
	5	3	$24.00 \pm 1.18^{A,a,*}$	$18.59 \pm 0.96^{A,a,*}$	$476.90 \pm 33.72^{B,a*}$
		6	22.49 ± 0.98^{b}	20.88 ± 1.47^{b}	361.72 ± 30.77^{b}
		9	23.39 ± 0.41^{a}	18.63 ± 1.08^{a}	439.96 ± 32.51^{c}
	10	3	$24.27 \pm 0.41^{A,a,*}$	$18.60 \pm 0.39^{A,a,*}$	$482.83 \pm 23.00^{B,a,*}$
		6	22.86 ± 0.75^{b}	20.24 ± 0.92^{b}	361.10 ± 23.46^{b}
		9	23.72 ± 0.24^{a}	18.79 ± 0.32^{a}	415.40 ± 15.39^{c}
	30	3	$22.77 \pm 0.73^{B,a,*}$	$14.27 \pm 0.65^{B,a,*}$	$650.73 \pm 43.23^{B,a,*}$
		6	21.45 ± 0.61^{b}	13.54 ± 0.98^{a}	648.91 ± 46.50^{a}
		9	20.23 ± 0.48^{c}	13.15 ± 0.94^{a}	629.13 ± 47.63^{a}
EBCK	1	3	$23.84 \pm 0.39^{A,a,*}$	$19.39 \pm 1.18^{A,a,*}$	$432.55 \pm 29.31^{A,a,*}$
		6	23.75 ± 0.63^{a}	17.34 ± 1.30^{b}	478.68 ± 35.10^{b}
		9	23.44 ± 0.45^{a}	18.56 ± 0.45^{a}	394.77 ± 20.54^{a}
	5	3	$24.43 \pm 0.97^{A,a,*}$	$18.64 \pm 0.44^{A,a,*}$	$440.88 \pm 35.16^{A,a,*}$
		6	24.07 ± 0.87^{a}	17.82 ± 0.54^{ab}	469.91 ± 36.34^{a}
		9	23.05 ± 0.33^{b}	17.24 ± 1.08^{b}	457.93 ± 41.81^{a}
	10	3	$24.39 \pm 0.45^{A,a,*}$	$18.63 \pm 1.02^{A,a,*}$	$458.53 \pm 31.18^{AB,a,*}$
		6	22.88 ± 0.59^{b}	16.53 ± 1.23^{b}	499.31 ± 39.25^{b}
		9	23.00 ± 0.50^{b}	18.05 ± 0.82^{a}	419.87 ± 27.55^{a}
	30	3	$22.02 \pm 1.35^{B,a,*}$	$16.53 \pm 0.71^{B,a,**}$	$483.38 \pm 27.51^{B,a,**}$
		6	21.70 ± 0.29^{a}	16.41 ± 0.52^{a}	482.42 ± 20.83^{a}
		9	21.87 ± 0.56^{a}	17.23 ± 0.93^{a}	425.14 ± 35.50^{c}

Table 4.16 (cont'd)

Sample	Dose (kGy)	Time (month)	Tensile strength (kpsi)	Elongation at break (%)	Elastic Modulus (kpsi)
			CD	CD	CD
CoCK	0	0	12.58 ± 0.42^{A}	52.23 ± 3.55^{A}	587.24 ± 17.40^{A}
GMCK	1	3	$11.31 \pm 0.68^{B,a,*}$	$41.12 \pm 6.25^{B,a,*}$	$564.06 \pm 14.94^{B,a,*}$
		6	11.61 ± 0.25^{a}	40.20 ± 2.16^{ab}	629.19 ± 13.04^{b}
		9	10.79 ± 0.38^{b}	39.26 ± 3.96^{a}	578.19 ± 22.54^{b}
	5	3	$11.68 \pm 0.36^{B,a,*}$	$40.09 \pm 3.90^{B,a,*}$	$582.47 \pm 13.55^{A,a,*}$
		6	10.76 ± 0.25^{b}	47.54 ± 2.92^{b}	603.27 ± 27.47^{b}
		9	10.84 ± 0.44^{b}	36.62 ± 3.36^{a}	594.05 ± 22.38^{b}
	10	3	$11.14 \pm 0.40^{B,a,*}$	$39.42 \pm 2.51^{B,a,*}$	$621.34 \pm 46.38^{A,a,*}$
		6	9.58 ± 0.42^{b}	38.84 ± 4.91^{ab}	615.19 ± 21.29^{a}
		9	9.97 ± 0.34^{b}	33.06 ± 3.70^{b}	594.61 ± 19.68^{a}
	30	3	$10.27 \pm 0.39^{C,a,*}$	$25.21 \pm 2.76^{C,ab,*}$	$601.95 \pm 52.02^{A,a,*}$
		6	10.25 ± 0.37^{a}	29.55 ± 4.88^{a}	599.49 ± 41.20^{a}
		9	9.51 ± 0.31^{b}	22.01 ± 3.40^{b}	558.16 ± 18.81^{a}
EBCK	1	3	$11.56 \pm 0.52^{B,a,*}$	$35.50 \pm 6.75^{B,a,*}$	$578.67 \pm 39.65^{A,a,*}$
		6	11.84 ± 0.46^{a}	48.17 ± 4.01^{b}	614.10 ± 25.21^{a}
		9	11.60 ± 0.25^{a}	47.09 ± 2.64^{b}	612.23 ± 7.95^{a}
	5	3	$11.93 \pm 0.84^{B,a,*}$	$38.94 \pm 7.07^{B,a,*}$	$631.78 \pm 24.55^{A,a,*}$
		6	11.51 ± 0.82^{ab}	46.55 ± 5.67^{b}	572.86 ± 41.09^{b}
		9	11.28 ± 0.32^{b}	48.29 ± 4.63^{b}	600.42 ± 17.81^{a}
	10	3	$11.35 \pm 0.58^{B,a,*}$	$40.91 \pm 6.55^{BC,a,*}$	$635.37 \pm 30.07^{A,a,*}$
		6	11.27 ± 0.89^{ab}	34.11 ± 10.08^{b}	572.76 ± 25.91^{b}
		9	11.11 ± 0.55^{b}	36.44 ± 6.62^{ab}	631.24 ± 5.83^{a}
	30	3	$10.36 \pm 0.64^{C,a,*}$	$35.88 \pm 9.11^{C,a,**}$	$600.46 \pm 27.01^{A,a,*}$
		6	10.23 ± 0.46^{ab}	36.06 ± 4.48^{a}	582.60 ± 10.72^{a}
		9	9.69 ± 0.32^{b}	34.22 ± 4.02^{a}	594.64 ± 7.81^{a}

Data are mean values (± standard deviations). Capital letters show the comparison between non-irradiated and irradiated samples at different dose levels after 3 months of storage, within the same irradiation type ($P < 0.05$). Lowercase letters show the comparison between storage times for the same dose and irradiation source ($P < 0.05$). Asterisks (*) indicate a comparison between irradiation sources at the same dose after 3 months of storage

4.2.6 Barrier properties

Oxygen, water vapor and carbon dioxide permeability coefficients for non-irradiated and irradiated nitrocellulose-coated cellophane and PVdC-coated cellophane films are presented in Tables 4.17 and 4.18. After irradiation exposure, the oxygen permeability of gamma (GMCM) and E-beam irradiated nitrocellulose-coated cellophane (EBCM) significantly decreased at all dose levels, compared to non-irradiated nitrocellulose-coated cellophane (CoCM). The aging study revealed that there was a significant decrease in oxygen permeability at all dose levels except GMCM at 1 and 30 kGy. Water vapor permeability, significantly decreased in the EBCM sample at a dose of 30 kGy as compared to CoCM after 3 months of storage. During storage, GMCM at 5 and 10 kGy and EBCM at 1 and 30 kGy showed significant differences but without any consistent trend.

The oxygen permeability of PVdC-coated cellophane showed a significant decrease for GMCK at 10 and 30 kGy and EBCK at 30 kGy. During storage, EBCK at 30 kGy showed an increase in oxygen permeability. E-beam and gamma irradiation did not affect the water vapor permeability of PVdC-coated cellophane at any dose level as compared to non-irradiated PVdC-coated cellophane (CoCK). The storage test indicated a rise in water vapor permeability for GMCK at dose levels of 5 and 10 kGy and for EBCK at doses of 10 and 30 kGy

Del Nobile et al. (2002) suggested that the barrier properties of polar packaging materials such as cellophane can be affected by the presence of moisture. Studies of irradiation effects on the barrier properties of cellophane film are scant. The effect of

irradiation on petroleum-based polymers, including monolayer and multilayer polymeric films, has been reported at irradiation doses of up to 25 kGy and it was found that irradiation did not affect the oxygen, carbon dioxide and water vapor permeability of plastic packaging materials (Buchalla et al., 1993a; Deschenes et al., 1995; Rojas De Gante & Pascat, 1990). Kang and Gilbert (1991) reported no change in water vapor permeability but a significant reduction in oxygen permeability for PE/polyvinylidene chloride/glycol modified polyethylene terephthalate (PETG) at gamma irradiation doses of 27 - 32 kGy.

Table 4.17 Permeation properties of non-irradiated (CoCM), gamma irradiated (GMCM) and electron irradiated cellophane nitrocellulose-coated cellophane (EBCM)

Sample	Doses (kGy)	Time (month)	$P_{O_2} \times 10^{-21}$ (Kg-m/m^2-sec-Pa)	$P_{H_2O} \times 10^{-15}$ (Kg-m/m^2-sec-Pa)
ConCM	0	0	4.68 ± 0.12^{A}	4.50 ± 0.16^{A}
GMCM	1	3	3.97 ± 0.16^{B,a,*}	3.98 ± 0.43^{A,a,*}
		6	3.95 ± 0.15^{a}	3.70 ± 0.04^{a}
		9	3.79 ± 0.27^{a}	2.84 ± 0.04^{a}
	5	3	4.07 ± 0.18^{B,a,*}	4.36 ± 0.71^{A,a,*}
		6	4.03 ± 0.01^{a}	3.17 ± 0.02^{b}
		9	3.06 ± 0.40^{b}	4.25 ± 0.13^{ab}
	10	3	4.02 ± 0.20^{B,a,*}	4.39 ± 0.97^{A,a,*}
		6	3.71 ± 0.68^{ab}	3.05 ± 0.38^{b}
		9	3.22 ± 0.18^{b}	3.67 ± 0.35^{ab}
	30	3	3.19 ± 0.27^{C,a,*}	3.96 ± 0.49^{A,a,*}
		6	3.18 ± 0.48^{a}	3.35 ± 0.32^{a}
		9	2.82 ± 0.37^{a}	3.34 ± 0.06^{a}
EBCM	1	3	3.93 ± 0.00^{B,a,*}	3.56 ± 0.01^{A,a,*}
		6	3.63 ± 0.03^{ab}	3.96 ± 0.24^{ab}
		9	2.99 ± 0.05^{b}	4.87 ± 0.44^{b}
	5	3	3.89 ± 0.09^{B,a,*}	3.95 ± 0.04^{A,a,*}
		6	3.29 ± 0.60^{a}	3.38 ± 0.50^{a}
		9	2.36 ± 0.28^{b}	3.47 ± 0.33^{a}
	10	3	3.90 ± 0.18^{B,a,*}	3.64 ± 0.17^{A,a,*}
		6	2.83 ± 0.39^{b}	2.67 ± 0.08^{a}
		9	3.08 ± 0.26^{b}	2.60 ± 0.12^{a}
	30	3	3.80 ± 0.06^{B,a,*}	3.35 ± 0.90^{B,ab,*}
		6	3.28 ± 0.50^{ab}	2.61 ± 0.24^{a}
		9	2.63 ± 0.04^{b}	3.84 ± 0.04^{b}

Data are mean values (± standard deviations). Capital letters show the comparison between non-irradiated and irradiated samples at different dose levels after 3 months of storage, within the same irradiation type ($P < 0.05$). Lowercase letters show the comparison between storage times for the same dose and irradiation source ($P < 0.05$). Asterisks (*) indicate a comparison between irradiation sources at the same dose after 3 months of storage

Table 4.18 Permeation properties of non-irradiated (CoCK), gamma irradiated (GMCK) and electron irradiated cellophane PVdC- coated cellophane (EBCK)

Sample	Doses (kGy)	Time (month)	$P_{O_2} \times 10^{-21}$ (Kg-m/m^2-sec-Pa)	$P_{H_2O} \times 10^{-15}$ (Kg-m/m^2-sec-Pa)
ConCK	0	0	0.53 ± 0.03^{A}	4.06 ± 0.09^{A}
GMCK	1	3	0.52 ± 0.02^{AB,a,*}	3.89 ± 0.11^{A,a,*}
		6	0.53 ± 0.02^{a}	4.91 ± 1.10^{a}
		9	0.45 ± 0.02^{a}	3.97 ± 0.08^{a}
	5	3	0.52 ± 0.05^{AB,a,*}	3.51 ± 0.35^{A,a,*}
		6	0.52 ± 0.0^{a}	3.54 ± 0.83^{a}
		9	0.42 ± 0.06^{a}	5.94 ± 0.06^{b}
	10	3	0.44 ± 0.01^{BC,a,*}	3.86 ± 0.10^{A,a,*}
		6	0.43 ± 0.06^{a}	4.49 ± 1.39^{a}
		9	0.41 ± 0.05^{a}	6.14 ± 0.22^{b}
	30	3	0.36 ± 0.05^{C,a,*}	3.47 ± 0.28^{A,a,*}
		6	0.43 ± 0.05^{a}	5.86 ± 0.04^{b}
		9	0.41 ± 0.01^{a}	4.84 ± 0.26^{ab}
EBCK	1	3	0.49 ± 0.03^{A,a,*}	3.22 ± 0.16^{A,a,*}
		6	0.45 ± 0.03^{a}	3.17 ± 0.04^{a}
		9	0.55 ± 0.06^{a}	4.98 ± 0.16^{a}
	5	3	0.46 ± 0.04^{A,a,*}	3.25 ± 0.10^{A,a,*}
		6	0.44 ± 0.00^{a}	4.28 ± 0.56^{a}
		9	0.45 ± 0.06^{a}	3.19 ± 0.26^{a}
	10	3	0.48 ± 0.01^{A,a,*}	3.47 ± 0.23^{A,a,*}
		6	0.44 ± 0.01^{a}	5.35 ± 0.01^{b}
		9	0.50 ± 0.05^{a}	5.24 ± 0.23^{b}
	30	3	0.38 ± 0.00^{B,a,*}	4.35 ± 1.16^{A,a,*}
		6	0.48 ± 0.03^{b}	5.97 ± 0.34^{b}
		9	0.51 ± 0.00^{b}	6.75 ± 0.11^{b}

Data are mean values (± standard deviations). Capital letters show the comparison between non-irradiated and irradiated samples at different dose levels after 3 months of storage, within the same irradiation type ($P < 0.05$). Lowercase letters show the comparison between storage times for the same dose and irradiation source ($P < 0.05$). Asterisks (*) indicate a comparison between irradiation sources at the same dose after 3 months of storage

4.2.7 Conclusions

Development of a yellow color occurred in all cellophane films as a result of irradiation by gamma and E-beam irradiation. The surface tension of gamma and E-beam irradiated nitrocellulose-coated cellophane decreased, while that of the PVdC-coated cellophane was not changed. Irradiation affected the thermal properties of the cellulose films. In general, the glass transition temperature (T_g) of cellophane films decreased after irradiation at all dose levels. The gas and water vapor barrier properties of PVdC-coated cellophane were higher than those of nitrocellulose-coated cellophane. The water vapor permeability of coated cellophane films was not affected by irradiation. However, oxygen permeability of gamma and E-beam irradiated nitrocellulose-coated cellophane and PVdC-coated cellophane decreased as a function of dose and storage time. No significant difference between the two irradiation sources for oxygen and water vapor permeability of nitrocellulose-coated cellophane and PVdC-coated cellophane were observed at any dose level.

Chapter 5

Results of Migration Study

5.1 Effect of ionizing radiation on overall migration from PLA films

5.1.1 Overall migration

The results of overall migration testing of non-irradiated, gamma irradiated and E-beam irradiated PLA film into aqueous food simulants are shown in Table 5.1. Food simulating solvents used in this experiment included distilled water, 3% acetic acid, 10% ethanol and 95% ethanol to represent the aqueous, acidic, alcohol and fat components of food, respectively (EEC 1990, 1997; López-Cervantesa et al. 2003; Thompson et al. 1997).

Overall migration of PLA film into distilled water before exposure was 0.12 mg/dm^2 as shown in Table 5.1. After gamma irradiation, overall migration increased with increasing irradiation dose with a significant change observed at an absorbed dose of 30 kGy as compared to non-irradiated PLA. The overall migration of E-beam irradiated PLA also significantly increased after exposure to 10 and 30 kGy, compared to non-irradiated PLA (CoPA). There was no statistically significant difference in the overall migration between PLA irradiated by gamma and E-beam. During the stability test, no significant differences were observed as a function of storage time up to 9 months under all test conditions.

Table 5.1 Overall migration mean values of non-irradiated (CoPA) and gamma irradiated (GMPA) and E-beam irradiated (EBPA) PLA into food simulants

Sample	Dose (kGy)	Time (month)	Distilled water (mg/dm^2)	3% Acetic acid (mg/dm^2)
CoPA	0	0	0.12 ± 0.08^{A}	0.36 ± 0.13^{A}
GMPA	1	3	$0.23 \pm 0.13^{A,a,*}$	$0.57 \pm 0.21^{AB,a,*}$
		6	0.20 ± 0.18^{a}	0.68 ± 0.15a
		9	0.27 ± 0.18^{a}	0.55 ± 0.10a
	5	3	$0.33 \pm 0.05^{A,a,*}$	$0.63 \pm 0.15^{B,a,*}$
		6	0.30 ± 0.13^{a}	0.55 ± 0.06^{a}
		9	0.22 ± 0.08^{a}	0.60 ± 0.08^{a}
	10	3	$0.37 \pm 0.07^{A,a,*}$	$0.68 \pm 0.13^{B,a,*}$
		6	0.32 ± 0.06^{a}	0.67 ± 0.08^{a}
		9	0.35 ± 0.15^{a}	0.55 ± 0.08^{a}
	30	3	$1.20 \pm 0.24^{B,a,*}$	$1.30 \pm 0.08^{C,a,*}$
		6	1.27 ± 0.24^{a}	1.22 ± 0.13^{a}
		9	1.23 ± 0.20^{a}	1.23 ± 0.13^{a}
EBPA	1	3	$0.13 \pm 0.17^{A,a,*}$	$0.58 \pm 0.13^{A,a,*}$
		6	0.10 ± 0.06^{a}	0.63 ± 0.15^{a}
		9	0.12 ± 0.10^{a}	0.57 ± 0.19^{a}
	5	3	$0.15 \pm 0.10^{A,a,*}$	$0.52 \pm 0.15^{A,a,*}$
		6	0.12 ± 0.23^{a}	0.67 ± 0.10^{a}
		9	0.18 ± 0.18^{a}	0.60 ± 0.21^{a}
	10	3	$0.48 \pm 0.13^{B,a,*}$	$0.58 \pm 0.09^{A,a,*}$
		6	0.53 ± 0.09^{a}	0.55 ± 0.20^{a}
		9	0.47 ± 0.06^{a}	0.60 ± 0.13^{a}
	30	3	$1.12 \pm 0.13^{C,a,*}$	$0.93 \pm 0.05^{B,a,**}$
		6	1.12 ± 0.08^{a}	1.03 ± 0.23^{a}
		9	1.18 ± 0.05^{a}	0.95 ± 0.13^{a}

Table 5.1 (cont'd)

Sample	Dose (kGy)	Time (month)	15% Ethanol (mg/dm^2)	95% Ethanol (mg/dm^2)
CoPA	0	0	0.55 ± 0.03^{A}	0.65 ± 0.10^{A}
GMPA	1	3	$0.58 \pm 0.19^{A,a,*}$	$0.58 \pm 0.10^{A,a,*}$
		6	0.55 ± 0.08^{a}	0.65 ± 0.08^{a}
		9	0.60 ± 0.13^{a}	0.57 ± 0.03^{a}
	5	3	$0.60 \pm 0.15^{A,a,*}$	$0.68 \pm 0.20^{A,a,*}$
		6	0.53 ± 0.06^{a}	0.60 ± 0.19^{a}
		9	0.58 ± 0.08^{a}	0.65 ± 0.15^{a}
	10	3	$0.70 \pm 0.26^{AB,a,*}$	$1.02 \pm 0.13^{B,a,*}$
		6	0.68 ± 0.18^{a}	0.97 ± 0.16^{a}
		9	0.75 ± 0.19^{a}	1.10 ± 0.12^{a}
	30	3	$0.97 \pm 0.09^{B,a,*}$	$1.43 \pm 0.10^{C,a*}$
		6	1.00 ± 0.23^{a}	1.32 ± 0.29^{a}
		9	0.93 ± 0.21^{a}	1.33 ± 0.10^{a}
EBPA	1	3	$0.60 \pm 0.13^{A,a,*}$	$0.48 \pm 0.30^{A,a,*}$
		6	0.52 ± 0.09^{a}	0.40 ± 0.03^{a}
		9	0.58 ± 0.14^{a}	0.45 ± 0.10^{a}
	5	3	$0.60 \pm 0.08^{A,a,*}$	$0.78 \pm 0.05^{AB,a,*}$
		6	0.57 ± 0.10^{a}	0.75 ± 0.03^{a}
		9	0.55 ± 0.03^{a}	0.80 ± 0.14^{a}
	10	3	$0.78 \pm 0.12^{AB,a,*}$	$1.02 \pm 0.15^{B,a,*}$
		6	0.70 ± 0.08^{a}	1.10 ± 0.23^{a}
		9	0.72 ± 0.10^{a}	1.13 ± 0.13^{a}
	30	3	$0.88 \pm 0.10^{B,a,*}$	$1.35 \pm 0.12^{C,a,*}$
		6	0.93 ± 0.06^{a}	1.40 ± 0.08^{a}
		9	0.90 ± 0.12^{a}	1.32 ± 0.08^{a}

Data are mean values (± standard deviations). Capital letters show the comparison between non-irradiated and irradiated samples at different dose levels after 3 months of storage, within the same irradiation type ($P < 0.05$). Lowercase letters show the comparison between storage times for the same dose and irradiation source ($P < 0.05$). Asterisks (*) indicate a comparison between irradiation sources at the same dose after 3 months of storage

For 3% acetic acid, non-irradiated PLA film yielded an overall migration of 0.36 mg/dm^2 (Table 5.1). The overall migration of PLA increased after irradiation exposure. Overall migration at a dose of 5 - 30 kGy was significantly higher for GMPA than CoPA (0.36 mg/dm^2). For E-beam irradiation, the overall migration for EBPA increased with increasing absorbed dose but the increase was significant only at a dose of 30 kGy. Overall migration of gamma irradiated PLA into 3% acetic acid was not significantly different than E-beam irradiated PLA, with the exception of an irradiation dose of 30 kGy. After 9 months of storage, the change in the overall migration of irradiated samples as compared within different dose levels was insignificant.

Migration from PLA into 15% ethanol indicated a significant increase only at the high dose of 30 kGy for both GMPA and EBPA. The overall migration of PLA into 95% ethanol, the fatty food simulant, before irradiation was 0.65 mg/dm^2. The overall migration of PLA into 95% ethanol significantly increased at a dose of 10 kGy for gamma and E-beam irradiation. The change in overall migration of irradiated PLA into both 15% ethanol and 95% ethanol was insignificant when compared between irradiation types and storage times. From visual observation, after an incubation time of 10 days at 40°C, the PLA film transformed from transparent to translucent. This change in appearance was similar to that found in a study by Fortunati et al. (2012). The change in PLA after contact with ethanol is because of the increased mobility induced by the food simulant leading to increased crystallinity. This also has been reported by Sodergård & Stolt (2002) to be an effect of accelerated spherulite formation.

The overall migration values from PLA into various food simulants were different. The migration of substances in polymeric packaging materials is restricted by their high molecular weight, low diffusivity (or inert) and the presence of a barrier layer (Castle, 2007). According to EU, Directive 2004/19/EC (EC, 2004), the overall migration into a foodstuff from food contact packaging material must not exceed 10 mg of migrants from plastic material per dm^2. Results of the overall migration from PLA films before and after irradiation at different doses into distilled water, acetic acid, 15% ethanol and 95% ethanol were below the current EU maximum of 10 mg/dm^2, suggesting that irradiated PLA film is safe to use as a food contact material.

Conn et al. (1995) studied the safety of PLA as a food contact polymer with 3% acetic acid and 8% ethanol and found potential migrants such as lactic acid, lactide and lactoyllactic acid (the linear dimer of lactic acid). They reported limited migration from PLA with the migrants expected to be converted to lactic acid, which is a safe food substance. The daily lactic acid intake from PLA is 0.054 mg/day/person, which is 0.25% of the current intake of lactic acid from all sources of lactic acid, added directly to foods. The authors concluded that PLA is safe and "Generally Recognized As Safe" (GRAS) for use as a polymeric packaging material for food products.

Mutsuga et al. (2008) studied the migration of lactic acid, lactide and oligomers from PLA, which was used in lunch boxes in Japan, with water, 4% acetic acid and 20% ethanol at temperatures of 40, 60, and 95ºC for different periods of time. They concluded that the rate of migration increased at high temperatures. The maximum amount of migrants was 49.63 $\mu g.cm^{-2}$ (Mutsuga et al., 2008). Mutsuga et al. (2007)

also assessed overall migration from a PLA sheet with water, 4% acetic acid, 20% ethanol, and heptane and reported overall migration values of less than 20 μg.cm^{-2}.

Fortunati et al. (2012) investigated the overall migration levels of PLA and PLA nano-biocomposites with 1 wt% cellulose, into ethanol 10% (v/v) for 10 days at 40ºC, and isooctane for 2 days at 20ºC. The level of PLA migration was 0.02 mg/kg in isooctane and 0.09 mg/kg in 10% ethanol, while the level of migration of PLA nano-biocomposites varied from 0.02 to 0.16 mg/kg in isooctane and 0.02 to 0.1 mg/kg in 10% ethanol. These migration levels were below the overall migration limits of 60 mg/kg required by the current legislation (EC, 2004).

5.1.2 Conclusions

Overall migration from PLA film before irradiation exposure into distilled water, 3% acetic acid, 15% ethanol and 95% ethanol was 0.12, 0.36, 0.55 and 0.65 mg/dm^2, respectively. After irradiation, the values of the overall migration from irradiated PLA by gamma and E-beam irradiation increased. This indicated that irradiation induced changes in the polymeric material and resulted in an increase in migrants from polymeric film into food simulants. At a high irradiation dose, there was an increase in diffusion of the migrants. No differences in overall migration were seen between gamma and E-beam irradiation, except for irradiated PLA at 30 kGy into 3% acetic acid.

Irradiated polymers may change in physical and chemical properties during storage after irradiation. Based on the stability study, irradiation-induced degradation in

post-irradiated PLA did not alter the amount of overall migration from PLA into the simulants. Overall migration from non-irradiated and irradiated PLA was lower than the maximum overall migration limit (10 mg/dm^2) as per the EU standard for food grade plastic packaging materials, suggesting that irradiated PLA is safe for food contact.

5.2 Ionizing radiation effect on overall migration from cellophane films

Table 5.2 presents the substances that migrated from non-irradiated uncoated cellophane (CoCP), nitrocellulose-coated cellophane (CoCM) and PVdC-coated cellophane (CoCK) into 95% ethanol after 10 days at 40ºC. The analysis was conducted using gas chromatography mass-spectrometry (GC-MS) and liquid chromatography mass-spectrometry (LC-MS). The GC-MS and LC-MS results for CoCP indicated the presence of glycerol (ethylene glycol), which is commonly used as a softening agent in cellophane films. In addition, triethylene glycol (TEG) and dodecyl acrylate were also found in CoCP. For nitrocellulose-coated cellophane, 1,2 benzenedicarboxylic acid and dicryclohexyl ester (known as dicyclohexyl phthalate, DCHP) were detected. Glycerol, dodecyl and acrylate acetyl tributyl citrate (ATBC) were found in PVdC-coated cellophane (CoCK). Results of the present work are in an agreement with those found in the literature (Castle et al., 1988; Goulas et al., 1998; Lancaster & Richards, 1996; Zygoura et al., 2011).

Table 5.2 Chemicals migrating from uncoated cellophane (CP), nitrocellulose-coated cellophane (CM) and PVdC-coated cellophane (CK) into 95% ethanol

Polymer	Compound	Mass to charge ratio (M/Z)
Uncoated cellophane	Glycerol	61
	Triethylene glycol (TEG)	89, 45
	Dodecyl acrylate (Lauryl acrylate)	55, 140.3
Nitrocellulose-coated cellophane	dicyclohexyl phthalate, (DCHP) (1,2 Benzenedicarboxylic acid, dicryclohexyl ester)	167.1, 149.1
PVdC-coated cellophane	Glycerol	61
	Dodecyl acrylate (Lausyl acrylate)	55, 140.3
	Acetyl tributyl citrate (ATBC)	259

5.2.1 Overall migration

According to EU, Directive 90/128/EEC (EEC, 1990), the overall migration limit (OML) should not exceed 10 mg/dm^2 for a contact area of 60 mg/L. In the case of regenerated cellulose films, the liquid migration technique has been considered unsuitable because the softening agents generally used with these materials are water-soluble, which can amount to a quarter of the film's weight when the initial and final weights of the film material are used to calculate overall migration (Figge, 1996; Lancaster & Richards, 1996). There is no clear guidance on the overall migration limit for RCF.

In this study, the test method used the weight of food simulants containing migrants from film materials into simulants. The residue after drying consisted of non-volatile compounds that migrated from the polymeric materials. Results from this study

might be a reference when regenerated cellulose films and irradiated regenerated cellulose films are applied as packaging materials for liquid or semi-liquid products.

The results of overall migration of non-irradiated, gamma irradiated and E-beam irradiated uncoated cellophane are presented in Table 5.3. Throughout this work, the statistical comparison of overall migration in non-irradiated and irradiated samples at different doses, the comparison of overall migration within irradiated samples at different doses and comparison of the effect of irradiation sources (gamma and E-beam radiation) were performed only after 3 months of storage. The effect of storage time was statistically evaluated only for the same irradiation dose and type.

Overall migration from non-irradiated uncoated cellophane (CoCP) into distilled water, 3% acetic acid, 15% ethanol, 95% ethanol was 31.22, 30.27, 31.57 and 32.77 mg/dm^2, respectively. As mentioned earlier, some softening agents such as glycerol, a common plasticizer used in regenerated cellulose film, are water-soluble and non-volatile (Lancaster & Richards, 1996). Uncoated cellophane film is also moisture sensitive. As expected, overall migration of uncoated cellophane into liquid simulant was higher than for coated films.

After 3 months of storage, the overall migration values for gamma irradiated uncoated cellophane (GMCP) at 1, 5, 10 and 30 kGy into distilled water decreased, with a significant decrease observed for GMCP at 5 and 10 kGy compared to the non-irradiated uncoated cellophane. Using E-beam irradiation overall migration significantly decreased between E-beam irradiated uncoated cellophane (EBCP) at 5, 10 and 30 kGy compared with non-irradiated samples. Overall migration of GMCP uncoated

Table 5.3 Overall migration values of non-irradiated (Co) and gamma irradiated (GM) and E-beam irradiated (EB) uncoated cellophane (CP) into food simulants

Sample	Dose (kGy)	Time (month)	Distilled water (mg/dm^2)	3% Acetic acid (mg/dm^2)
CoCP	0	0	31.22 ± 0.49^{A}	30.27 ± 0.35^{A}
GMCP	1	3	$30.73 \pm 0.49^{A, a,*}$	$28.25 \pm 0.62^{B,a,*}$
		6	31.30 ± 0.59^{a}	29.98 ± 0.93^{a}
		9	31.15 ± 0.64^{a}	29.40 ± 0.57^{a}
	5	3	$28.12 \pm 0.03^{B,a,*}$	$28.33 \pm 2.09^{B,a,*}$
		6	29.63 ± 1.00^{a}	31.03 ± 0.98^{b}
		9	28.05 ± 1.33^{a}	30.23 ± 1.13^{ab}
	10	3	$28.40 \pm 0.06^{BC,a,*}$	$29.25 \pm 0.89^{AB,a,*}$
		6	30.07 ± 1.81^{a}	31.00 ± 0.28^{ab}
		9	29.88 ± 1.20^{a}	31.35 ± 0.78^{b}
	30	3	$30.45 \pm 2.14^{AC,a,*}$	$30.32 \pm 0.98^{A,a,*}$
		6	31.98 ± 1.22^{a}	31.77 ± 0.76^{a}
		9	31.13 ± 0.95^{a}	31.40 ± 0.50^{a}
EBCP	1	3	$31.47 \pm 0.55^{A,a,*}$	$30.15 \pm 1.21^{A,a,*}$
		6	31.27 ± 1.46^{a}	30.17 ± 1.71^{a}
		9	30.87 ± 0.36^{a}	30.30 ± 0.93^{a}
	5	3	$29.08 \pm 0.52^{B,a,*}$	$30.88 \pm 0.61^{A,a,**}$
		6	30.93 ± 1.26^{a}	30.98 ± 0.20^{a}
		9	29.58 ± 0.41^{a}	31.12 ± 0.76^{a}
	10	3	$28.82 \pm 0.99^{B,a,*}$	$30.80 \pm 0.40^{A,a,*}$
		6	28.42 ± 1.28^{a}	30.87 ± 0.30^{a}
		9	29.93 ± 0.52^{a}	30.98 ± 0.35^{a}
	30	3	$28.20 \pm 0.35^{B,a,**}$	$30.93 \pm 0.15^{A,a,*}$
		6	29.97 ± 0.65^{a}	31.05 ± 1.36^{a}
		9	29.70 ± 0.91^{a}	30.87 ± 0.68^{a}

Table 5.3 (cont'd)

Sample	Dose (kGy)	Time (month)	15% Ethanol (mg/dm^2)	95% Ethanol (mg/dm^2)
CoCP	0	0	31.57 ± 0.61^{A}	32.77 ± 0.53^{A}
GMCP	1	3	$27.98 \pm 1.40^{B,a,*}$	$27.67 \pm 0.45^{B,a,*}$
		6	28.65 ± 0.58^{a}	28.67 ± 1.23^{a}
		9	27.47 ± 1.32^{a}	29.67 ± 2.59^{a}
	5	3	$28.28 \pm 0.77^{B,a,*}$	$27.90 \pm 1.32^{B,a,*}$
		6	30.65 ± 1.40^{b}	28.32 ± 1.14^{ab}
		9	30.75 ± 0.18^{b}	30.28 ± 0.39^{b}
	10	3	$29.02 \pm 1.30^{B,a,*}$	$28.27 \pm 1.16^{BC,a,*}$
		6	30.57 ± 0.84^{a}	29.32 ± 0.48^{a}
		9	30.88 ± 1.16^{a}	30.32 ± 0.73^{a}
	30	3	$29.10 \pm 0.20^{B,a,*}$	$30.15 \pm 0.44^{C,a,*}$
		6	30.05 ± 1.42^{ab}	31.08 ± 0.87^{a}
		9	31.95 ± 0.40^{b}	30.37 ± 0.83^{a}
EBCP	1	3	$28.28 \pm 0.88^{B,a,*}$	$27.53 \pm 0.35^{B,a,*}$
		6	29.18 ± 0.91^{a}	28.15 ± 0.64^{a}
		9	30.32 ± 0.58^{a}	28.40 ± 0.75^{a}
	5	3	$29.97 \pm 1.00^{AB,a,*}$	$28.58 \pm 0.65^{B,a,*}$
		6	30.18 ± 0.94^{a}	28.47 ± 0.60^{a}
		9	30.55 ± 1.02^{a}	28.77 ± 1.27^{a}
	10	3	$29.87 \pm 0.36^{AB,a,*}$	$28.68 \pm 1.21^{B,a,*}$
		6	30.93 ± 1.02^{a}	28.70 ± 0.23^{a}
		9	30.95 ± 0.68^{a}	28.83 ± 2.12^{a}
	30	3	$30.87 \pm 0.61^{A,a,*}$	$29.48 \pm 0.10^{B,a,*}$
		6	30.90 ± 0.58^{a}	29.15 ± 0.45^{a}
		9	31.17 ± 1.35^{a}	29.28 ± 0.52^{a}

Data are mean values (± standard deviations). Capital letters show the comparison between non-irradiated and irradiated samples at different dose levels after 3 months of storage, within the same irradiation type ($P < 0.05$). Lowercase letters show the comparison between storage times for the same dose and irradiation source ($P < 0.05$). Asterisks (*) indicate a comparison between irradiation sources at the same dose after 3 months of storage

cellophane at 30 kGy was significantly higher than for EBCP at 30 kGy. No significant effect of storage time after irradiation was found.

For 3% acetic acid, overall migration from CoCP was significantly higher than from GMCP at 1 and 5 kGy. No significant difference in overall migration between GMCP and EBCP after 3 months of storage was found, except for irradiated uncoated cellophane at a dose of 5 kGy. No statistically significant effects of storage time were found except for GMCP at 5 and 10 kGy between 3 and 6 months, and 3 and 9 months, respectively.

Overall migration of GMCP (all absorbed doses) into 15% ethanol was significantly lower than for CoCP. There was a significant decrease in EBCP at 1 kGy compared to CoCP. When storage time was examined, overall migration of GMCP at 5 kGy after 6 and 9 months was significantly higher than at 3 months, with a significant increase in GMCP at 30 kGy seen between 3 and 9 months of storage. The effect of gamma and E-beam irradiation on overall migration of uncoated cellophane was insignificant for all absorbed doses.

There was a significant decrease in overall migration of uncoated cellophane with 95% ethanol between non-irradiated and gamma irradiated and E-beam irradiated samples at all dose levels. A significant increase in overall migration was also seen for 30 kGy as compared to 1 and 5 kGy. Overall migration of GMCP increased significantly at an absorbed dose of 5 kGy (between 3 and 9 months). No significant changes were observed in EBCP at any of the doses during storage.

Overall migration values for nitrocellulose-coated cellophane are shown in Table 5.4. Overall migration of non-irradiated nitrocellulose-coated cellophane (CoCM) into distilled water, 3% acetic acid, 15% ethanol and 95% ethanol was 11.82, 11.98, 16.73 and 21.70 mg/dm^2, respectively. No significant difference in overall migration of gamma irradiated (GMCM) and E-beam irradiated nitrocellulose-coated cellophane (EBCM) into distilled water was found at different dose levels, and there was no significant effect of storage time.

For 3% acetic acid, there was also no statistically significant difference in overall migration values between different irradiation doses, irradiation types, or storage times. The only significant increase in overall migration was found in EBCM at 1 kGy after 9 months as compared to 3 and 6 months.

Overall migration of nitrocellulose-coated cellophane irradiated with gamma and E-beam radiation into 15% ethanol showed a significant decrease, compared to non-irradiated samples. The overall migration of GMCM was significantly higher than EBCM at a dose of 30 kGy after 3 months of storage. There was a significant decrease of migrants in GMCM at 30 kGy after 6 and 9 months as compared to 3 months. No significant differences were found for any other comparison group.

A significant increase in overall migration of GMCM was seen after exposure to 10 kGy, compared to the non-irradiated sample. Overall migration of GMCM at 1 kGy was significantly lower than that at 5, 10 and 30 kGy. For E-beam irradiation, overall migration of EBCM at 1 kGy was significantly higher than that of CoCM and EBCM at 5 kGy. At 1kGy, overall migration of GMCM was significantly lower than that of EBCM. As

a function of storage time, a significant decrease in overall migration of GMCM was observed at an absorbed dose of 10 kGy after 6 months with significant decrease in overall migration of EBCM at 5 kGy also seen after 9 months.

Table 5.4 Overall migration values of non-irradiated (Co) and gamma (GM) and E-beam irradiated (EB) nitrocellulose-coated cellophane (CM) into food simulants

Sample	Dose (kGy)	Time (month)	Distilled water (mg/dm^2)	3% Acetic acid (mg/dm^2)
CoCM	0	0	11.82 ± 0.51^{A}	11.98 ± 0.18^{A}
GMCM	1	3	$12.08 \pm 0.48^{A,a,*}$	$11.55 \pm 1.12^{A,a,*}$
		6	13.67 ± 1.25^{a}	11.63 ± 1.18^{a}
		9	13.95 ± 1.35^{a}	12.68 ± 1.31^{a}
	5	3	$11.70 \pm 0.89^{A,a,*}$	$11.98 \pm 0.91^{A,a,*}$
		6	11.23 ± 0.71^{a}	13.37 ± 0.53^{a}
		9	11.45 ± 0.83^{a}	13.28 ± 1.93^{a}
	10	3	$11.27 \pm 0.78^{A,a,*}$	$12.93 \pm 1.03^{A,a,*}$
		6	11.97 ± 0.67^{a}	13.75 ± 0.53^{a}
		9	11.37 ± 0.49^{a}	12.97 ± 0.58^{a}
	30	3	$12.85 \pm 0.56^{A,a,*}$	$11.20 \pm 0.85^{A,a,*}$
		6	12.55 ± 0.75^{a}	12.83 ± 0.70^{a}
		9	12.05 ± 0.88^{a}	13.12 ± 1.13^{a}
EBCM	1	3	$13.10 \pm 0.63^{A,a,*}$	$11.03 \pm 0.74^{A,a,*}$
		6	12.68 ± 0.30^{a}	12.05 ± 0.76^{a}
		9	12.48 ± 0.90^{a}	14.42 ± 1.19^{b}
	5	3	$11.10 \pm 0.81^{A,a,*}$	$11.05 \pm 0.55^{A,a,*}$
		6	12.47 ± 1.33^{a}	11.35 ± 1.01^{a}
		9	12.67 ± 0.52^{a}	12.73 ± 0.65^{a}
	10	3	$11.22 \pm 1.37^{A,a,*}$	$11.83 \pm 1.51^{A,a,*}$
		6	12.48 ± 2.15^{a}	12.60 ± 1.04^{a}
		9	12.05 ± 0.67^{a}	13.55 ± 1.59^{a}
	30	3	$12.42 \pm 1.45^{A,a,*}$	$12.05 \pm 1.04^{A,a,*}$
		6	12.08 ± 0.28^{a}	12.83 ± 0.52^{a}
		9	12.52 ± 0.48^{a}	12.53 ± 1.28^{a}

Table 5.4 (cont'd)

Sample	Dose (kGy)	Time (month)	15% Ethanol (mg/dm^2)	95% Ethanol (mg/dm^2)
CoCM	0	0	16.73 ± 0.68^{A}	21.70 ± 0.81AB
GMCM	1	3	$13.62 \pm 0.50^{B,a,*}$	20.18 ± 0.90A,a,*
		6	12.20 ± 0.79^{a}	19.58 ± 0.66a
		9	12.28 ± 0.81^{a}	19.27 ± 0.67a
	5	3	$14.48 \pm 1.55^{B,a,*}$	23.55 ± 0.60BC,a,*
		6	16.15 ± 0.75^{a}	21.07 ± 2.22a
		9	15.75 ± 1.48^{a}	22.85 ± 1.23a
	10	3	$13.17 \pm 0.78^{B,a,*}$	25.53 ± 1.10C,a,*
		6	13.12 ± 0.64^{a}	20.17 ± 2.72b
		9	14.37 ± 1.05^{a}	20.85 ± 1.74b
	30	3	$14.63 \pm 0.88^{B,a,*}$	24.33 ± 1.15BC,a,*
		6	12.42 ± 0.48^{b}	22.08 ± 0.48a
		9	12.70 ± 1.31^{b}	22.28 ± 2.21a
EBCM	1	3	$13.20 \pm 1.38^{B,a,*}$	24.60 ± 1.82C,a,**
		6	12.53 ± 0.34^{a}	25.05 ± 0.62a
		9	12.50 ± 0.13^{a}	25.22 ± 0.18a
	5	3	$13.80 \pm 0.55^{B,a,*}$	20.42 ± 0.77A,a,*
		6	13.00 ± 0.58^{a}	20.67 ± 1.66a
		9	13.72 ± 0.61^{a}	24.25 ± 1.25 b
	10	3	$13.63 \pm 0.08^{B,a,*}$	22.48 ± 0.91AC,a,*
		6	13.45 ± 1.05^{a}	22.80 ± 0.69 a
		9	12.65 ± 0.57^{a}	23.03 ± 0.39a
	30	3	$12.60 \pm 1.25^{B,a,**}$	22.70 ± 1.45AC,a,*
		6	12.85 ± 1.43^{a}	23.82 ± 3.41a
		9	12.72 ± 0.62^{a}	24.67 ± 1.51a

Data are mean values (± standard deviations). Capital letters show the comparison between non-irradiated and irradiated samples at different dose levels after 3 months of storage, within the same irradiation type ($P < 0.05$). Lowercase letters show the comparison between storage times for the same dose and irradiation source ($P < 0.05$). Asterisks (*) indicate a comparison between irradiation sources at the same dose after 3 months of storage

Table 5.5 shows the overall migration from PVdC-coated cellophane. Non-irradiated PVdC-coated cellophane (CoCK) with distilled water, 3% acetic acid, 15% ethanol and 95% ethanol showed overall migration of 20.63, 19.33, 21.02, and 21.73 mg/dm^2, respectively. After exposure, overall migration from gamma irradiated PVdC-coated cellophane (GMCK) at doses of 1 and 5 kGy into distilled water significantly decreased compared to CoCK. At 1 kGy, E-beam irradiated PVdC-coated cellophane (EBCK) yielded higher overall migration compared to GMCK. There were no significant differences among samples at particular doses during storage.

Overall migration of PVdC-coated cellophane into 3% acetic acid after exposure to gamma and E-beam irradiation was not significantly different at any dose level or storage time. For 15% ethanol, a significant decrease in overall migration of GMCK at all doses (1, 5, 10 and 30 kGy) was seen as compared to CoCK. The overall migration of EBCK at 1 kGy was significantly lower than CoCK. The overall migration of GMCK at higher doses was significantly lower than EBCK. There were significant increases for irradiated samples of GMCK at 10 and 30 kGy between the 3 and 9 months of storage. There was no significant change in EBCK at different storage times.

No significant differences were seen between irradiation types in overall migration from PVdC-coated cellophane into 95% ethanol. GMCK and EBCK yielded a significant decrease in overall migration as compared to CoCK. No significant difference was found between irradiated samples at 1, 5, 10 and 30 kGy. During 9 months of storage, overall migration of EBCK did not change significantly; however, a significant increase was found in GMCK at 10 kGy between 6 and 9 months.

The study of Lancaster & Richards (1996) on overall migration for regenerated cellulose films into noisettes showed that PVdC was a more effective barrier than nitrocellulose coating. Based on the results from this work, nitrocellulose-coated cellophane was a more effective barrier than PVdC-coated cellophane when exposed to water, 3% acetic acid and 15% ethanol.

Table 5.5 Overall migration values of non-irradiated (Co) and gamma (GM) and E-beam irradiated (EB) PVdC-coated cellophane (CK) into food simulants

Sample	Dose (kGy)	Time (month)	Distilled water (mg/dm^2)	3% Acetic acid (mg/dm^2)
CoCK	0	0	20.63 ± 0.18^{AC}	19.33 ± 0.36^{A}
GMCK	1	3	$18.53 \pm 0.74^{B,a,*}$	$20.42 \pm 0.58^{A,a,*}$
		6	19.12 ± 0.70^{a}	20.52 ± 0.69^{a}
		9	20.13 ± 0.61^{a}	20.37 ± 0.19^{a}
	5	3	$18.60 \pm 1.35^{B,a,*}$	$20.25 \pm 0.84^{A,a,*}$
		6	19.82 ± 0.49^{a}	20.43 ± 1.83^{a}
		9	20.05 ± 0.65^{a}	21.75 ± 0.33^{a}
	10	3	$19.40 \pm 0.90^{AB,a,*}$	$20.02 \pm 0.39^{A,a,*}$
		6	19.60 ± 0.78^{a}	20.60 ± 1.18^{a}
		9	20.05 ± 1.42^{a}	20.53 ± 0.72^{a}
	30	3	$19.92 \pm 0.08^{AB,a,*}$	$19.52 \pm 0.38^{A,a,*}$
		6	20.08 ± 0.48^{a}	21.13 ± 0.30^{a}
		9	20.28 ± 0.45^{a}	20.87 ± 1.25^{a}
EBCK	1	3	$21.60 \pm 1.63^{A,a,**}$	$18.53 \pm 1.10^{A,a,*}$
		6	21.72 ± 0.40^{a}	20.10 ± 1.15^{a}
		9	21.78 ± 1.36^{a}	19.30 ± 0.56^{a}
	5	3	$19.10 \pm 0.29^{C,a,*}$	$19.48 \pm 0.66^{A,a,*}$
		6	20.63 ± 0.25^{a}	20.82 ± 1.10^{a}
		9	19.92 ± 1.84^{a}	21.23 ± 1.19^{a}
	10	3	$19.40 \pm 0.92^{C,a,*}$	$20.50 \pm 0.65^{A,a,*}$
		6	21.15 ± 0.56^{a}	21.30 ± 2.63^{a}
		9	20.20 ± 1.32^{a}	21.13 ± 0.84^{a}
	30	3	$20.35 \pm 0.61^{AC,a,*}$	$18.80 \pm 1.38^{A,a,*}$
		6	21.87 ± 0.25^{a}	19.12 ± 1.55^{a}
		9	20.48 ± 0.95^{a}	18.90 ± 1.30^{a}

Table 5.5 (cont'd)

Sample	Dose (kGy)	Time (month)	15% Ethanol (mg/dm^2)	95% Ethanol (mg/dm^2)
CoCK	0	0	21.02 ± 0.71^{A}	21.73 ± 0.40^{A}
GMCK	1	3	$18.63 \pm 0.39^{B,a,*}$	$19.57 \pm 0.23^{B,a,*}$
		6	19.88 ± 0.64^{a}	20.13 ± 0.57^{a}
		9	19.92 ± 0.48^{a}	20.10 ± 0.75^{a}
	5	3	$18.85 \pm 1.19^{B,a,*}$	$18.27 \pm 0.94^{B,a,*}$
		6	19.85 ± 0.40^{a}	17.97 ± 0.23^{a}
		9	19.40 ± 1.09^{a}	18.88 ± 0.71^{a}
	10	3	$18.92 \pm 0.87^{B,a,*}$	$18.92 \pm 1.09^{B,ab,*}$
		6	19.92 ± 0.53^{ab}	16.95 ± 0.91^{a}
		9	20.88 ± 0.29^{b}	19.57 ± 2.01^{b}
	30	3	$19.47 \pm 0.43^{B,a,*}$	$18.33 \pm 0.93^{B,a,*}$
		6	20.20 ± 0.93^{ab}	19.05 ± 0.18^{a}
		9	21.48 ± 1.22^{b}	19.77 ± 0.56^{a}
EBCK	1	3	$19.30 \pm 0.19^{B,a,*}$	$19.53 \pm 1.28^{B,a,*}$
		6	19.70 ± 0.21^{a}	17.52 ± 0.98^{a}
		9	21.57 ± 1.05^{b}	18.42 ± 0.77^{a}
	5	3	$21.97 \pm 0.58^{A,a,**}$	$19.18 \pm 0.97^{B,a,*}$
		6	20.62 ± 0.22^{a}	19.38 ± 1.69^{a}
		9	21.97 ± 0.10^{a}	20.08 ± 1.65^{a}
	10	3	$21.53 \pm 0.55^{A,a,**}$	$19.93 \pm 0.31^{B,a,*}$
		6	21.90 ± 1.37^{a}	20.08 ± 0.13^{a}
		9	21.52 ± 1.08^{a}	20.70 ± 0.65^{a}
	30	3	$22.35 \pm 0.48^{A,a,**}$	$18.33 \pm 0.48^{B,a,*}$
		6	22.25 ± 0.78^{a}	17.87 ± 0.58^{a}
		9	22.20 ± 0.73^{a}	17.93 ± 1.13^{a}

Data are mean values (± standard deviations). Capital letters show the comparison between non-irradiated and irradiated samples at different dose levels after 3 months of storage, within the same irradiation type ($P < 0.05$). Lowercase letters show the comparison between storage times for the same dose and irradiation source ($P < 0.05$). Asterisks (*) indicate a comparison between irradiation sources at the same dose after 3 months of storage

5.2.2 Conclusions

The comparison of overall migration between non-irradiated and irradiated samples at different dose levels, and the comparison of irradiation effects between gamma and E-beam were carried out after 3 months of storage. The effect of post-irradiation aging was assessed within the same irradiation type and dose levels.

Overall migration from uncoated cellophane (CP) was greater than that from nitrocellulose-coated cellophane (CM) and PVdC-coated cellophane (CK). The coating not only helped to reduce migration from the polymeric materials to food but also provided better barrier properties. For use with semi-liquid or liquid products, the uncoated cellophane films might not be suitable. The effect of gamma and E-beam irradiation on overall migration of uncoated cellophane was similar for both 15% ethanol and 95% ethanol.

Ionizing radiation did not affect the overall migration of nitrocellulose-coated cellophane in contact with distilled water and 3% acetic acid. Both irradiation sources decreased overall migration from irradiated nitrocellulose-coated cellophane into 15% ethanol. Gamma irradiation at 5 - 30 kGy increased overall migration of nitrocellulose-coated cellophane into 95% ethanol while E-beam irradiation at 10 - 30 kGy did not show a significant increase even though there was a significant increase at a dose level of 1 kGy.

For PVdC-coated cellophane, overall migration from gamma irradiated samples at 1 - 5 kGy and E-beam irradiated samples at 5 - 10 kGy significantly decreased compared to the non-irradiated sample. There was no significant difference in overall

migration between irradiated and non-irradiated PVdC-coated cellophane into 3% acetic acid. Overall migration from PVdC-coated cellophane into 15% ethanol significantly decreased after gamma (at all absorbed doses) and E-beam irradiation at 1 kGy. Both types of irradiation significantly decreased overall migration from PVdC-coated cellophane into 95% ethanol. The effect of aging on migration was not consistent. Overall migration from all three cellophane films was greater than the upper limit set by the EU regulation (10 mg/dm^2).

Chapter 6

Results of Compostability Study

6.1 Effect of ionizing radiation on biodegradability of PLA films

6.1.1 Compostability

PLA is a biodegradable and compostable thermoplastic polymer. The results of this study agree. The biodegradation results of PLA using the direct measurement respirometric (DMR) system with aerobic composting conditions are presented as accumulated CO_2 (g) and percent mineralization. The results represent the averages of triplicate samples. Due to the long duration of the experiment at high temperature and high humidity (58°C, 60% RH), some technical problems can occur such as leaking/cracking of connections, manifold failure, and drying of the compost. These issues can cause low and high readings of evolved CO_2 from the bioreactors (Figure 6.1-A). For data analysis, the CO_2 raw evolution data were examined for out-of-range numbers. An issue with the gas flow in the bioreactor was encountered, causing a low reading of the evolved CO_2 since CO_2 from the bioreactor was not being carried to the detector in that measuring cycle. After the gas flow was restored to normal, the evolved CO_2 in the bioreactor in the next cycle showed much higher values after having accumulated from the previous cycle. For this reason, these data points were omitted for the test cycle in question and the next test cycle using the MATLAB program (Figure

6.1-B) before calculating the accumulated CO_2 (using Eq. (3.2)) and percentage of biodegradation (using Eq. (3.3)) as shown in Figure 6.1-C, D.

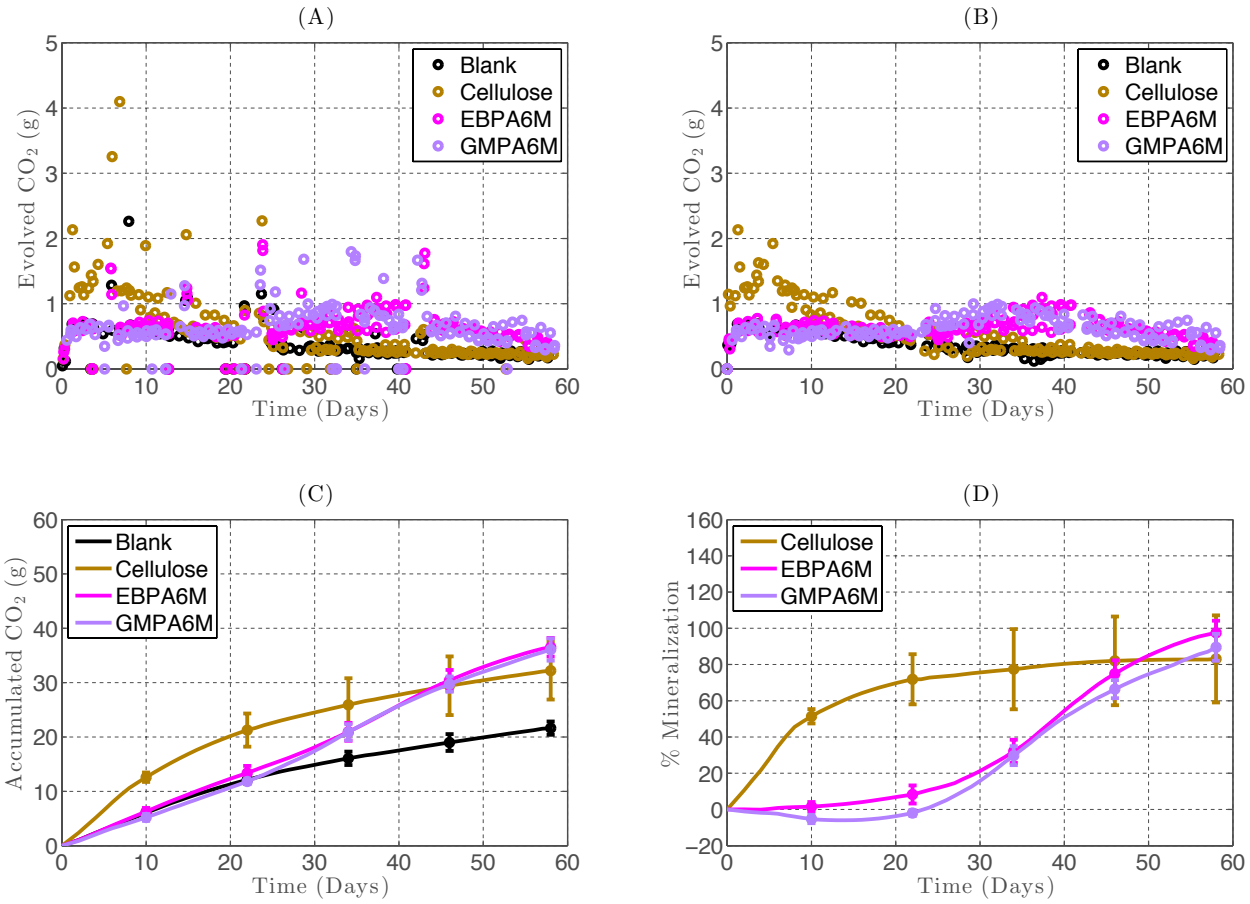

Figure 6.1 Evolution of carbon dioxide before (A) and after (B) removing the outliers. Carbon dioxide evolution (C) and percent of mineralization (D) after removing the outliers using MATLAB® program

Biodegradation of non-irradiated commercial PLA film (CoPA) in the two manure composts was analyzed to verify its biodegradability with results shown in Table 6.1. Tables 6.2 and 6.3 show the CO_2 evolution and percentage of mineralization, respectively, of PLA (PA) samples: non-irradiated (Co), gamma irradiated at 30k (GM) and E-beam irradiated at 30 kGy (EB) after 3, 6 and 9 months of storage. Commercial

compost was used to test non-irradiated (Co) and gamma irradiated PLA at 3 months (GMPA3M). The remaining tests were conducted using MSU compost.

Table 6.1 Carbon dioxide (CO_2) evolution and percent mineralization of cellulose (positive control) and non-irradiated PLA films in both composts

Samples	Experimental Time (Days)	CO_2 Evolution (g)		% Mineralization	
		Cellulose	CoPA	Cellulose	CoPA
Commercial compost	141	29.37 ± 2.34	33.50 ± 1.96	86.86 ± 10.99	96.42 ± 7.52
MSU compost	60	40.22 ± 1.43	94.33 ± 6.82	47.59 ± 7.18	117.11 ± 25.81

Table 6.2 Carbon dioxide (CO_2) evolution from cellulose (positive control) and non-irradiated, gamma irradiated and electron beam irradiated PLA films at 30 kGy

Irradiation	Storage Time (Mon)	Cellulose (g)	PA (g)
Co	0	29.37 ± 2.34	33.50 ± 1.96
GM	3	29.37 ± 2.34	29.35 ± 1.49
	6	32.21 ± 5.31	36.09 ± 2.05
	9	40.22 ± 1.43	49.39 ± 4.65
EB	3	32.21 ± 5.31	32.12 ± 5.27
	6	32.21 ± 5.31	36.50 ± 1.72
	9	40.22 ± 1.43	47.86 ± 2.46

Data represented are mean values (± standard error)

Table 6.3 Percent mineralization of cellulose (positive control), non-irradiated, gamma irradiated and electron beam irradiated PLA films at 30 kGy

Irradiation	Storage Time (Mon)	Cellulose (%)	PA (%)
Co	0	86.86 ± 10.99	96.42 ± 7.52
GM	3	86.86 ± 10.99	69.64 ± 5.95
	6	83.09 ± 24.07	89.50 ± 7.45
	9	94.33 ± 6.82	129.71 ± 16.96
EB	3	83.09 ± 24.07	67.48 ± 19.24
	6	83.09 ± 24.07	97.51 ± 6.69
	9	94.33 ± 6.82	119.92 ± 7.99

Data are mean values (± standard error)

The biodegradation results for CoPA using the DMR system are illustrated in Table 6.1 and Figure 6.2 for commercial compost and Figure 6.3 for MSU compost. The CoPA film tested with commercial compost was found to degrade with 96% mineralization after incubation for 141 days, while CoPA film examined with MSU compost was shown to degrade with 117% mineralization after incubation for 63 days. The percent mineralization of CoPA using MSU compost (Figure 6.3) was higher than 100%. This may occur due to the priming effect, which is an increase of the biodegradation of the compost itself in the biodegradation test due to the presence of glucose, starch and cellulose. The CO_2 evolved from the biodegradation process is a combination of CO_2 converted from the test substance and CO_2 converted from the compost. Some starch-based films such as PLA might stimulate the activity of compost-degrading microorganisms, thereby producing a percentage of mineralization greater than 100% (Bellia et al., 1999; Shen & Bartha, 1996). This PLA film, hence, can be classified as biodegradable plastic since the percentage of mineralization of PLA films

from those two tests was greater than 60% as required by ASTM D6400 and ISO 14855-1.

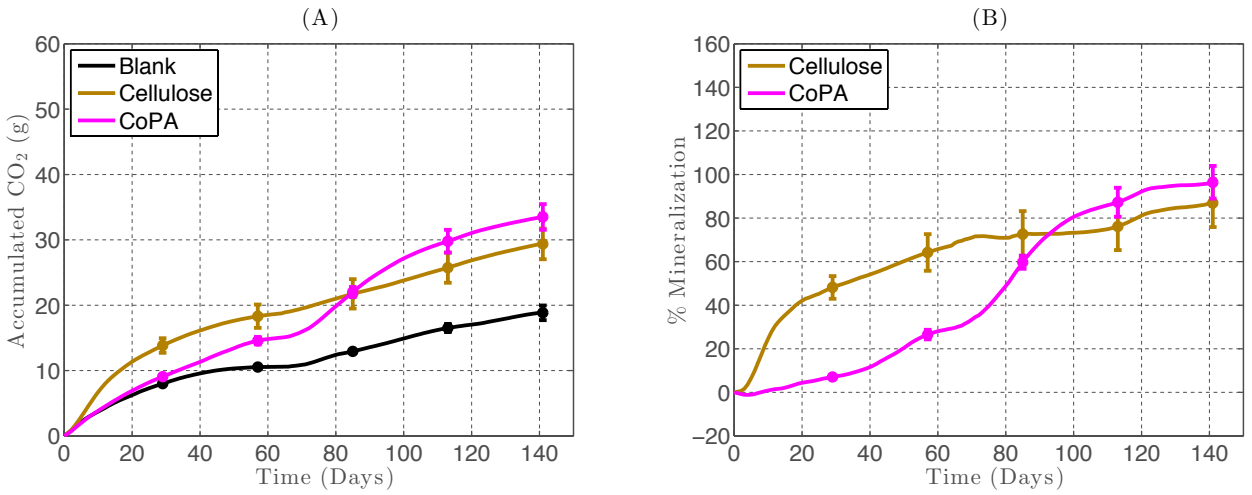

Figure 6.2 Carbon dioxide evolution (A) and percent mineralization (B) of cellulose (positive control) and non-irradiated PLA (CoPA) with standard error using commercial compost

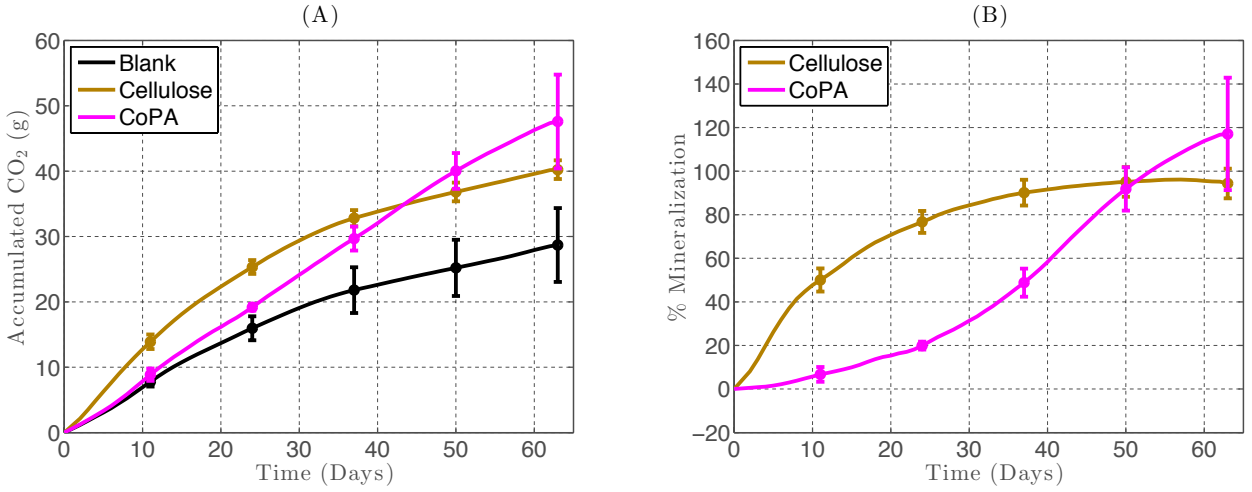

Figure 6.3 Carbon dioxide evolution (A) and percent mineralization (B) of cellulose (positive control) and non-irradiated PLA (CoPA) with standard error using MSU compost

For non-irradiated PLA (CoPA) in commercial compost (Figure 6.2) and gamma-irradiated PLA after 3 months of storage (GMPA3M) (Figure 6.4-A, B), some unexpected events happened during the test. The percent mineralization of cellulose (positive control) did not approach 70% after 45 days as the standard ASTM D5338 recommends. In addition, a decrease in CO_2 evolution was also observed around day 70 possibly due to the quality and dryness of the compost. As mentioned earlier, the compost used for these two experiments was commercial compost, which might have less activity than the MSU compost received directly from the compost pile at the MSU composting facility. Storing the commercial compost, in a sealed plastic bag under uncontrolled conditions, might also have affected the microbial activity. In addition, the age of the compost was unknown. Compost quality is correlated to its agronomic and commercial value as an organic solid conditioner such as formulation, pH, moisture, and microbial activity (Degli-Innocenti & Bastioli, 1997; Grima et al., 2002; Zee, 2005). Gu et al. (1994) reported that the physical form and nutritional components of compost affect the biodegradation rates of polymers using the gravity method; also, the weight loss of polymer films in aerobic thermophilic reactors does not directly correlate to the C/N ratios.

The MSU compost was taken directly from the manure compost pile. This compost pile had high moisture and temperature conditions suitable for the growth of a variety of microorganisms (Kijchavengkul & Auras, 2008). Based on visual observation, the commercial compost at the beginning of the test was lighter in color (light brown) and drier than the MSU compost. When looking at these two tests (non-irradiation test and gamma-irradiation after 3 months), carbon dioxide evolution and percent

mineralization decreased around day 70. This might have been due to the dryness of the compost, creating clumps that blocked the airflow and thus reduced microbial activity. The problem was solved by breaking the clumps and injecting water into the compost. The increase in biodegradation can be seen after day 80. Moisture is a key element for biodegradation. Inadequate water in the compost not only affects microbial growth but also reduces the biodegradation rates of some polymers degrading through hydrolysis (Grima et al., 2002; Kale et al., 2007; Stevens, 2003; Zee, 2005). The decrease in moisture content of the compost causes a change in degradation of polymers and a significant increase in time for test completion (Gu et al., 1994). For these reasons, the tests were extended to 141 days in order to allow the percent biodegradation of test materials to reach a plateau state. Sufficient oxygen supply is another important factor that also influences the biodegradability of polymers (Massardier-Nageotte et al., 2006).

The results of biodegradation of irradiated PLA films after 3, 6 and 9 months of storage are illustrated in Figures 6.4, 6.5, and 6.6, respectively. After testing PLA films that were irradiated with gamma irradiation and E-beam irradiation at 30 kGy (a typical irradiation dose in food and pharmaceutical applications) (Jay, 1996; Komolprasert, 2007), and stored for 3 months in a conditioned environment (25 ± 2°C, 40 ± 2% RH), GMPA-3M was degraded with 69.64% mineralization after 141 days and EBPA-3M was degraded with 67.48% mineralization after 60 days (Figure 6.4). Results of the biodegradation tests for both GMPA-3M and EBPA-3M also indicated that after 3 months of storage post-irradiation with gamma and E-beam, PLA films are still

considered as biodegradable polymers due to their percent mineralization above 60% based on the requirements of ASTM D6400 and ISO 14855-1.

Generally, irradiating polymers in the presence of air results in chain-scission reactions. Radiation energy absorbed by the exposed plastic material excites the macromolecules of the polymer causing scission of weaker bonds in those macromolecules. Irradiated PLA undergoes chain-scission at doses below 250 kGy (Gupta & Deshmukh, 1983; Nugroho et al., 2001) The decrease in molecular weight indicates the dominance of chain-scission after gamma and E-beam irradiation (Hamilton et al., 1996). A study on enzymatic degradation of irradiated PLA by Nugroho et.al. (2001) showed that the weight loss of irradiated PLA decreased (which means a slower degradation rate) even though the molecular weight was decreased, which might be due to crosslinking. Previous studies (chapter 4) on the effect of irradiation on PLA properties showed that the molecular weight of gamma and E-beam irradiated PLA significantly decreased compared to non-irradiated PLA. The result of Nugroho's study is similar to this biodegradation study. The mineralization result in this study showed decreased degradation after the irradiated PLA was stored to 3 months (both GMPA-3M and EBPA3M), compared to non-irradiated PLA (CoPA). The decrease in biodegradation rate of irradiated PLA might be because of the irradiation effect on the polymer and consequent creation of free radicals that may affect degradation of PLA polymers. Even though this difference was not statistically significant (Table 6.4), the potential to decrease further suggests that additional testing is needed.

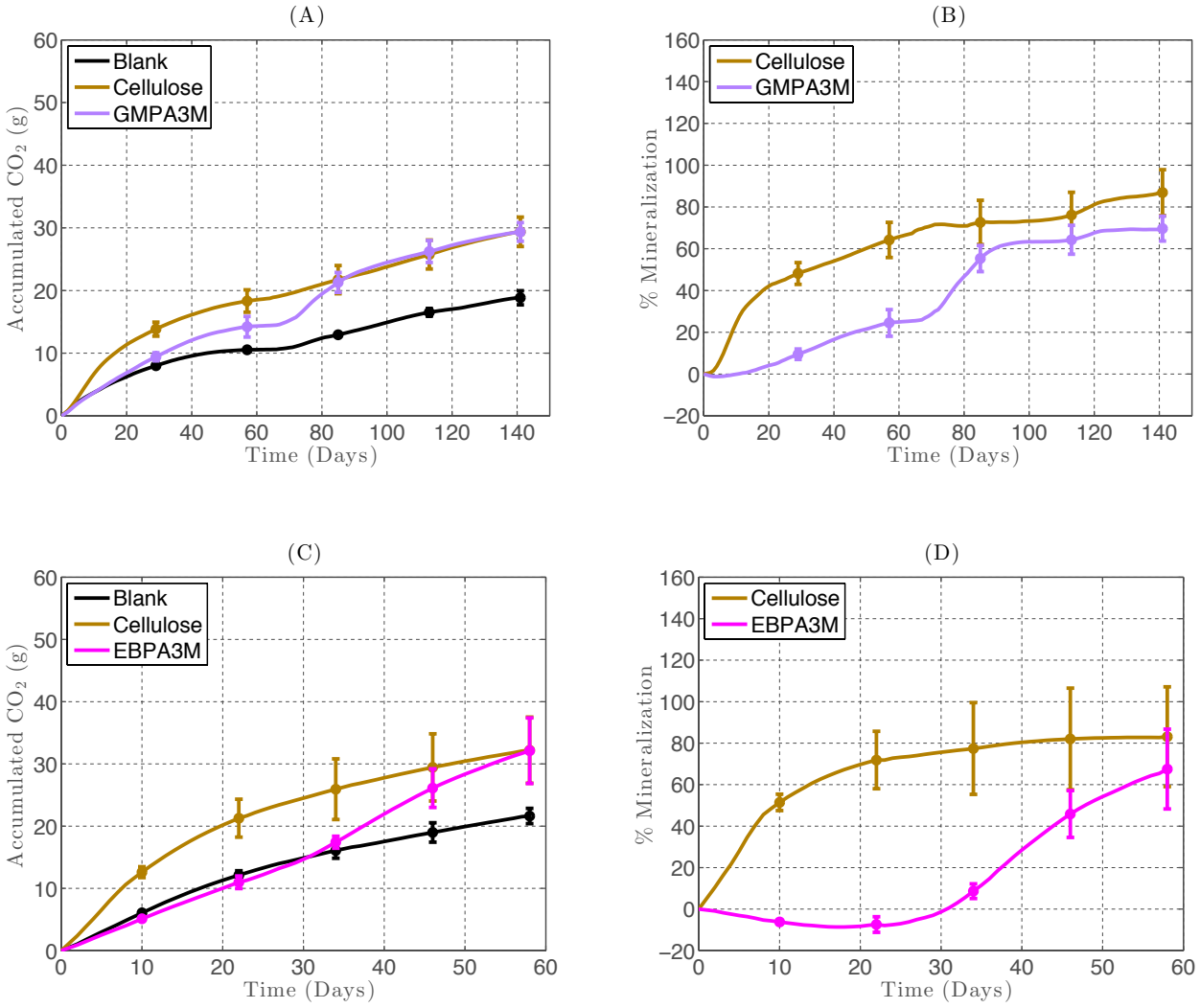

Figure 6.4 Carbon dioxide evolution (A, C) and percent mineralization (B, D) of gamma irradiated PLA (GMPA) and E-beam irradiated PLA (EBPA), respectively after 3 months of storage with standard error

Table 6.4 Comparison matrix of non-irradiated and irradiated PLA based films after Bonferroni adjustment

Sample	CoPA	EBPA3M	EBPA6M	EBPA9M	GMPA3M	GMPA6M	GMPA9M
CoPA		0.0476	0.9398	0.1058	0.0661	0.6301	0.0234
EBPA3M			0.0742	**0.0024**	0.8965	0.1878	**0.0004**
EBPA6M				0.18	0.0969	0.6295	0.0560
EBPA9M					**0.0035**	0.0705	0.5556
GMPA3M						0.2342	**0.0006**
GMPA6M							0.0179
GMPA9M							

Significant differences are indicated by bold type. Bonferroni adjusted alpha value is 0.05/3 = 0.0167 (based on planned comparisons)

Similarly, the results showed that gamma and E-beam irradiated PLA after 6 months of storage (Figure 6.5) are still considered biodegradable polymers since the percent mineralization of GMPA-6M (89.50% mineralization after 60 days) and EBPA-6M (97.51% mineralization after 60 days) was greater than 60%. Based on statistical analysis (Table 6.4), the biodegradation of GMPA-6M and EBPA-6M was not significantly different ($P > 0.05$) than CoPA, GMPA-3M and EBPA-3M.

After 9 months, the irradiated PLA films from both irradiation sources showed a percentage of biodegradation (129.71% for GMPA-9M and 119.92% for EBPA-9M, see Figure 6.6) greater than the required percentage to be considered as biodegradable film (60% mineralization). Similarly to the CoPA test using MSU compost, percent mineralization of GMPA-9M and EBPA-9M was greater than 100% due to the priming effect as discussed previously. The biodegradation of both GMPA-9M and EBPA-9M showed higher values, compared to non-irradiated PLA (CoPA), irradiated PLA after 3 months and irradiated PLA after 6 months. The biodegradation rates for GMPA-9M and EBPA-9M were not statistically significantly different from CoPA. For GMPA-6M and

EBPA-6M; however, this difference was significantly different as illustrated in Table 6.4. At the same storage times (e.g. EBPA-3M vs. GMPA-3M), there were no significant differences between PLA irradiated by gamma and E-beam (Table 6.4).

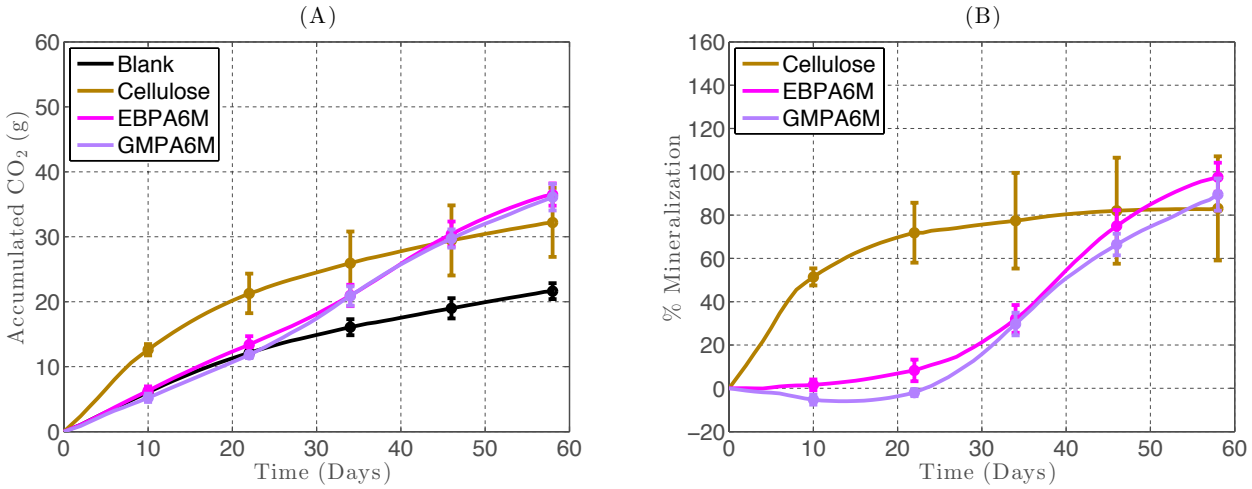

Figure 6.5 Carbon dioxide evolution (A) and percent mineralization (B) of cellulose (positive control) and gamma irradiated PLA (GMPA), and E-beam irradiated PLA (EBPA) after 6 months of storage with standard error

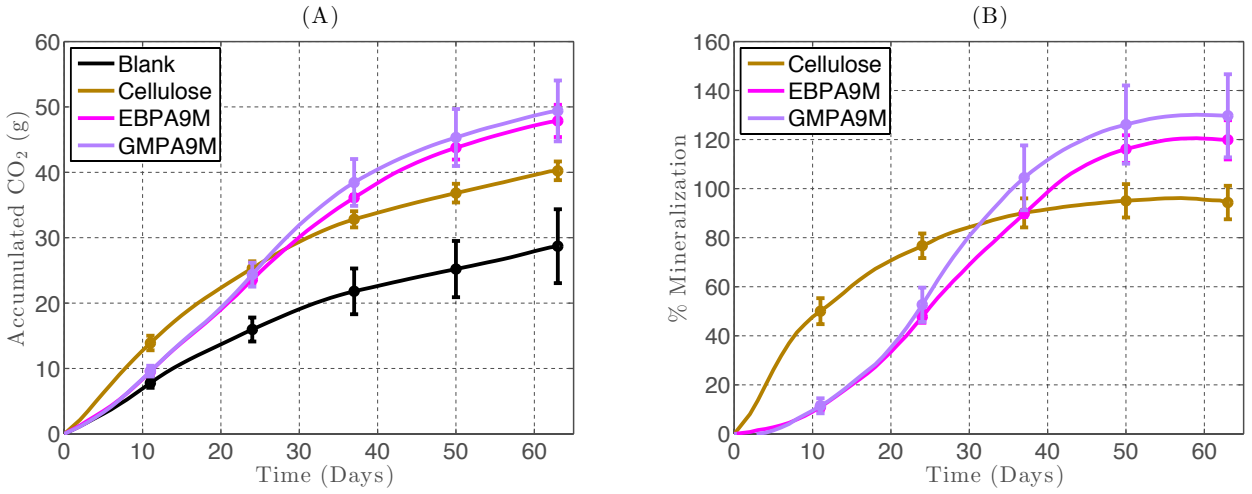

Figure 6.6 Carbon dioxide evolution (A) and percent mineralization (B) of cellulose (positive control) and gamma irradiated PLA (GMPA), and E-beam irradiated PLA (EBPA) after 9 months of storage with standard error

Negative PLA mineralization values were initially observed for EBPA-3M, GMPA-6M and EBPA-6M, see Figure 6.4-C, D and Figure 6.5-A, B. These occurrences might be due to the low amount of CO_2 released initially from the test material. The compost formulation might also contribute to this effect. It is also important to have good sensitivity of measurement by keeping the background CO_2 production in compost substantially lower than the CO_2 production of the test materials (Bellia et al., 1999). The main reason is likely the delayed biodegradation of PLA. As discussed previously, the PLA biodegradation process occurs after hydrolytic chain scission. For this reason, the amount of CO_2 produced by PLA was lower than that of the blank (compost only) in the initial phase, resulting in the negative percent mineralization.

In order to identify a plastic as compostable, the ecotoxicity of plastic materials must also be determined. In accordance with EN 13432 (EN, 2000) and ASTM D6868 (ASTM, 2011b), the concentration of heavy metals in plastic materials must be less than 50% of those listed in 40CFR Part 503.13 (EPA, 2007). Also, germination tests must be performed. The rate of germination of plants in test compost from the biodegradation test must not be less than 90% of that in the control compost (blank compost) (Kijchavengkul & Auras, 2008). In this study, an ecotoxicity evaluation of the final compost was not conducted. Therefore, it cannot be determined with certainly if these PLA films including non-irradiated PLA and irradiated PLA from both gamma and E-beam are compostable or not.

6.1.2 Conclusions

Compost consists of a complex biological environment due to different types of living organisms, organic and inorganic materials. The biodegradation rates of polymers, therefore, depend on the intrinsic properties of the compost including the nutritional content, moisture content, temperature, pH, oxygen availability, microbial types and microbial load. Moreover, the length of the polymer chain also affects the biodegradation rate. Biodegradation of commercial PLA films in a simulated aerobic composting environment using a direct measurement respirometric (DMR) system indicated that the non-irradiated PLA (CoPA) films tested in two different manure composts were biodegraded, reaching 96% mineralization in commercial compost and 117% mineralization in MSU compost. Even though the testing time for CoPA using commercial compost was longer than that of CoPA using MSU compost due to drying, the percentage of biodegradation from both tests was greater than 60% mineralization, in accordance with ASTM 6400 and ISO 14855.

The biodegradation rates for gamma irradiated and E-beam irradiated PLA after 3 and 6 months of storage were not significantly different from non-irradiated PLA. Moreover, no significant difference in biodegradability of PLA was found in irradiated PLA between the two different irradiation sources. The results from this study indicate that the free radicals formed during polymer irradiation might affect the chemical properties of irradiated PLA and afterward stimulate the biodegradation of aging irradiated PLA as shown by the increase in percent mineralization. There was a significant difference only between the 3 and 9 months of storage for gamma irradiated PLA. The result was also similar for E-beam irradiated PLA. In conclusion, all of the

gamma and E-beam irradiated PLA films were biodegraded aerobically in a composting environment and can still be considered as biodegradable plastics because they passed the minimum required degradation percentage of 60% mineralization. Since ecotoxicological analyses were not conducted in this work, the compostability of PLA films including non-irradiated PLA and irradiated PLA could not be confirmed.

6.2 Effect of ionizing radiation on biodegradability of cellophane films

6.2.1 Compostability

As discussed in section 6.1.1, the evolved CO_2 data of the test cycle showed low or high values due to the leakage and accumulation of CO_2 within the bioreactor. These extreme CO_2 values were not representative data for that particular cycle. Therefore, such suspect data points were removed from the analysis and replaced with linearly interpolated values from the previous and next cycle using the MATLAB® program as shown in Figure 6.7.

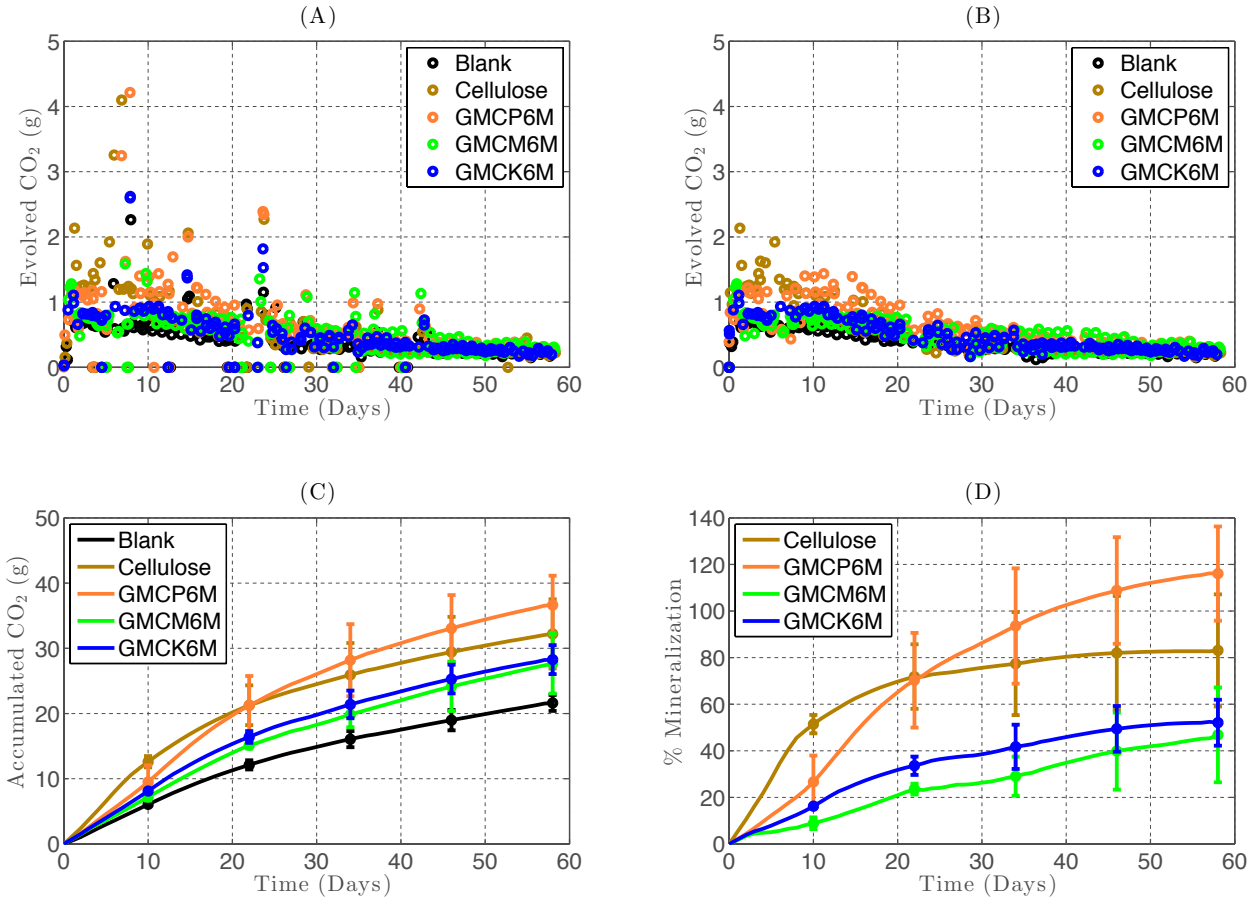

Figure 6.7 Evolution of carbon dioxide of raw data before (A) and after (B) removing the outliers. Carbon dioxide evolution (C) and percent of mineralization (D) after removing the outliers using MATLAB® program

The average concentration of cumulative carbon dioxide in each sample type was determined. Table 6.5 shows the carbon dioxide evolution of cellulose, non-irradiated (Co), gamma irradiated (GM) and E-beam irradiated (EB) cellophane films (uncoated (CP), nitrocellulose coated (CM) and PVdC coated (CK)) after 3, 6 and 9 months of storage, calculated by using Eq. (3.2). Percent mineralization of the cellulose (positive control) and cellophane films is presented in Table 6.6, using Eq. (3.3) for calculation.

Table 6.5 Carbon dioxide evolution (g) of cellulose (positive control), non-irradiated (Co), gamma-irradiated (GM) and electron beam-irradiated (EB) cellophane films: uncoated cellophane (CP), nitrocellulose-coated cellophane (CK), and PVdC-coated cellophane (CK) at 30 kGy

Irradiation	Storage Time (Mon)	Experimental Time (Days)	Cellulose (g)	CP (g)	CM (g)	CK (g)
Co	0	141	29.37 ± 2.34	27.57 ± 0.86	25.51 ± 1.21	26.18 ± 1.48
GM	3	141	29.37 ± 2.34	31.39 ± 2.96	27.90 ± 0.33	23.11± 0.86
	6	60	32.21 ± 5.31	36.64 ± 4.50	27.69 ± 4.62	28.27 ± 2.22
	9	63	40.22 ± 1.43	44.62 ± 2.28	40.66 ± 3.09	35.94 ± 5.11
EB	3	60	32.21 ± 5.31	33.02 ± 2.24	30.96 ± 1.27	27.84 ± 2.74
	6	60	32.21 ± 5.31	34.27 ± 3.90	28.24 ± 2.69	25.89 ± 0.97
	9	63	40.22 ± 1.43	46.00 ± 2.30	31.92±1.92	37.69 ± 4.82

Data represented are mean values (± standard error).

Table 6.6 Percent mineralization of cellulose (positive control), non-irradiated (Co), gamma-irradiated (GM) and electron beam-irradiated (EB) cellophane films: uncoated cellophane (CP), nitrocellulose-coated cellophane (CK), and PVdC-coated cellophane (CK) at 30 kGy

Irradiation	Storage Time (Mon)	Experimental Time (Days)	Cellulose (%)	CP (%)	CM (%)	CK (%)
Co	0	141	86.86 ± 10.99	70.52 ± 4.06	54.73 ± 5.87	63.13 ± 7.76
GM	3	141	86.86 ± 10.99	102.64 ± 13.75	73.88 ± 1.62	35.62 ± 4.08
	6	60	83.09 ± 24.07	116.10 ± 20.24	46.84 ± 20.36	52.05 ± 9.87
	9	63	94.33 ± 6.82	118.00 ± 10.10	88.29 ± 13.81	55.14 ± 24.17
EB	3	60	83.09 ± 24.07	87.60 ± 9.82	75.55 ± 5.72	49.82 ± 12.48
	6	60	83.09 ± 24.07	99.45 ± 18.36	50.19 ± 11.40	33.72 ± 3.96
	9	63	94.33 ± 6.82	127.85 ± 10.07	19.88 ± 8.22	64.89 ± 21.30

Data represented are mean values (± standard error)

Carbon dioxide evolution and percent mineralization of non-irradiated, gamma irradiated and E-beam irradiated cellophane films after 3, 6 and 9 months of storage were plotted in Figure 6.8, 6.9, 6.10 and 6.11, respectively. In all experiments, cellophane samples emitted more carbon dioxide than the blank compost, indicating that biodegradation had occurred (Grima et al., 2002). For non-irradiated cellophane, carbon dioxide evolution from cellulose (positive control) was higher than from cellophane. Carbon dioxide evolution of non-irradiated uncoated cellophane (CoCP), non-irradiated nitrocellulose-coated cellophane (CoCM) and non-irradiated PVdC-coated cellophane (CoCK) was comparable to each other (Figure 6.8-A). The percent mineralization of cellulose (Figure 6.8-B), CoCP, CoCM and CoCK at the end of the experiment was 87%, 71%, 55%, 63%, respectively. The percent mineralization of uncoated cellophane (CoCP) was greater than 60%, meeting the classification as a biodegradable plastic. Since the percent mineralization of PVdC-coated cellophane (CoCK, 63%) was also slightly above the standard (60%), this material has potential to be considered as a biodegradable polymer. The percent mineralization of nitrocellulose-coated cellophane (CoCM, 55%) was lower than the requirement. Considering the standard error for percent mineralization, CoCM has the potential to be a biodegradable film. Even though percent mineralization of CoCP was higher than CoCK and CoCM, the difference was not statistically significant based on the Bonferroni adjustment (Table A1). There was also no significant difference in biodegradation between CoCK and CoCM, as shown in Table A1.

Biodegradation of CoCK and CoCM was expected to be lower than CoCP due to the PVdC and nitrocellulose surface coating, respectively, which are known to be

resistant to microbial decomposition (Farajollahi et al., 2010). Uncoated cellophane and nitrocellulose coated cellophane films have been reported as biodegradable and intermediate biodegradable, respectively in compost (David et al., 1994). Studies of cellophane biodegradation in a soil environment indicated degradation with 100% mass loss in 2 years (Calmon et al., 1999). The authors also found that the biodegradation of two-sided nitrocellulose-coated cellophane and two-sided PVdC coated cellophane resulted in mass losses of approximately 85 and 80%, respectively, after 2 years, which was considered as “intermediary biodegradable”. When nitrocellulose-coated cellophane was buried in soil for 5 weeks, Monk (1972) showed that the one-sided nitrocellulose-coated cellophane degraded faster than two-sided nitrocellulose-coated cellophane. Zhang et al. (1999) observed that degradation of regenerated cellulose, regenerated cellulose coated with PU/nitrocellulose, and regenerated cellulose coated with PU/elaeostearin in soil resulted in a 90% mass loss in 30 days, 70% mass loss in 30 days, and 50% mass loss in 30 days, respectively. In the literature surveyed, the study of biodegradation of regenerated cellophane dealt with soil and was limited to a compost environment. The experimental results agreed with the literature reports in that the nitrocellulose-coated cellophane (CM) and PVdC-coated cellophane (CK) materials degraded more slowly than uncoated cellophane.

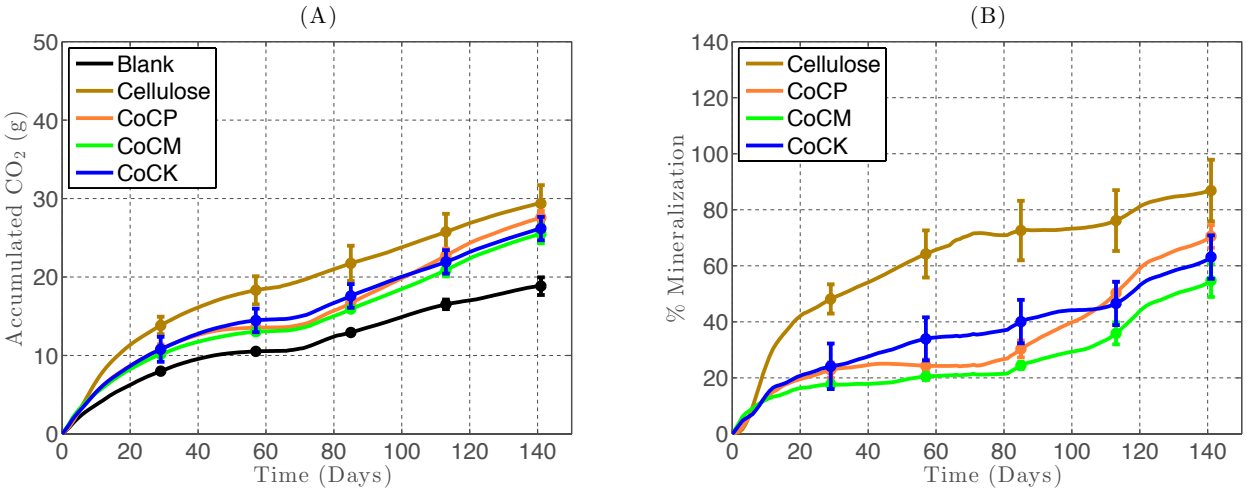

Figure 6.8 Carbon dioxide evolution (A) and percent mineralization (B) of non-irradiated (Co) uncoated cellophane (CP), nitrocellulose-coated cellophane (CM) and PVdC-coated cellophane (CK) with standard error

As is well known, irradiation affects the chemical structure (by cross-linking and/or chain scission mechanisms) and properties of polymers (Carlsson & Chmela, 1990; Charlesby, 1987; Ozen & Floros, 2001). The results for biodegradation of irradiated cellophane during composting are illustrated in Figures 6.9-6.11. After 3 months of storage (Figure 6.9), CO_2 evolution from gamma irradiated uncoated cellophane (GMCP3M) was comparable to cellulose, while the gamma irradiated nitrocellulose-coated cellophane (GMCM3M) and gamma irradiated PVdC-coated cellophane (GMCK3M) were slower (Figure 6.9-A). Gamma and E-beam irradiated samples behaved similarly (Figure 6.9-C). The biodegradation of irradiated uncoated cellophane films increased (103% for GMCP3M and 88% for EBCP3M) and was greater than that for CoCP (71%). There was no significant difference between CoCP and GMCP3M (Table A1) and EBCP3M (Table A2). There was also no significant difference in biodegradation between GMCP3M and EBCP3M (Table A3). The percent

mineralization of GMCP3M suggests a higher value than EBCP3M, but statistically it was not significant since the standard deviation for GMCP3M was too high. This could be because of the high penetration of gamma irradiation (IAEA, 2004), which affected biodegradation. The percent mineralization of GMCP3M (102%) was greater than 100%, and likely due to the priming effect (as discussed in section 6.1.1).

The biodegradation results for irradiated nitrocellulose-coated cellophane suggest an increase in biodegradation of GMCM3M and EBCM3M (73.88% and 75.55%, respectively), as compared to CoCM (54.73%), shown in Table 6.6 and Figure 6.9. However the increase for GMCM3M and EBCM3M was not significantly different than CoCM (Table A1 and Table A2). There was also no significant difference in biodegradation found between GMCM3M and EBCM3M (Table 6.6). In contrast, percent mineralization for both the gamma and E-beam irradiated PVdC-coated cellophane decreased (35.62% for GMCK3M and 49.82% for EBCK3M), as shown in Table 6.6 and Figure 6.9. Based on statistical analysis, there was no significant difference in biodegradation between any combination of GMCK3M, CoCK and EBCK3M (Table A1 and Table A2). The biodegradation of GMCK3M was not significantly different from that of EBCK3M (Table A3). After 3 months of storage, the comparison between irradiation sources and different film types (Table A3) showed significant differences in biodegradation between GMCP3M and GMCK3M, and between EBCP3M and EBCK3M.

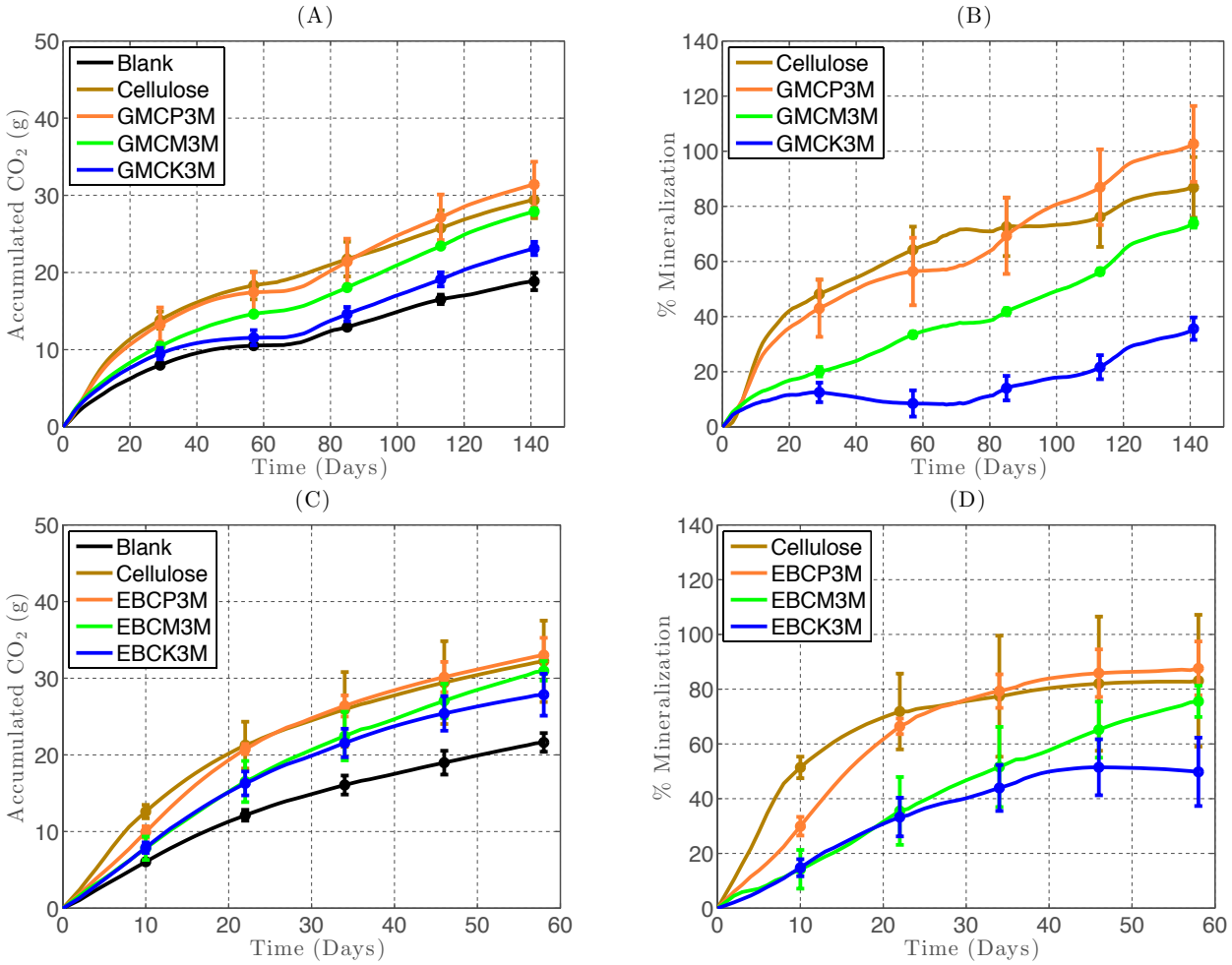

Figure 6.9 Carbon dioxide evolution (A, C) and percent mineralization (B, D) for gamma (GM) and E-beam (EB) irradiated uncoated cellophane (CP), nitrocellulose-coated cellophane (CM) and PVdC-coated cellophane (CK) after 3 months of storage with standard error

The experimental biodegradation time for non-irradiated (Figure 6.8) and gamma-irradiated samples after 3 months of storage (Figure 6.9-A, B) was longer than for the other tests. This might be because the commercial compost used in this experiment was less active than the MSU compost, used for the rest of the experiments as discussed in section 6.1.1. Due to the dryness issue, the percent mineralization for the cellulose (positive control) did not reach 70% within 45 days as ASTM D5338

(ASTM, 2011a) recommends, so the experimental time was extended to 141 days. For the remaining tests conducted using MSU compost, the compost activity and the biodegradation process met the standard for validity since percent mineralization for cellulose (positive control) reached 70% after 45 days.

The biodegradation results for post-irradiated cellophane after 6 months of storage (Figure 6.10) showed that the CO_2 evolution for cellulose and irradiated uncoated cellophane were comparable at the beginning and then started increasing above cellulose (around day 20). Biodegradation of both the gamma and E-beam irradiated uncoated cellophane (GMCP6M, 116.10% and EBCP6M, 99.45%) was greater than that of non-irradiated and irradiated uncoated cellophane after 3 months of storage. These results indicate that irradiation stimulated the biodegradability of uncoated cellophane. A significant increase in biodegradation was found only in GMCP6M and CoCP (not in EBCP6M and CoCP), as shown in Table A2). Percent mineralization of GMCP6M was not significantly different from GMCP3M. Similarly, there was no significant difference between EBCP6M and EBCP3M (Table A3). Biodegradation of GMCP6M and EBCP6M showed no significant difference, as illustrated in Table A3. Percent mineralization of GMCP6M (116%) was above 100%, similar to the GMCP3M result, which again is likely due to the priming effect discussed previously.

The biodegradation results for irradiated nitrocellulose-coated cellophane after 6 months of storage were opposite to those for irradiated uncoated cellophane (Figure 6.10). The percent mineralization of gamma (GMCM6M) and E-beam irradiated

nitrocellulose-coated cellophane (EBCM6M) were 46.84% and 50.19%, respectively, which were lower than CoCM (54.73%), GMCM3M (73.88 %) and EBCM3M (75.55%); however, this decrease was not statistically significant, as shown in Tables A1 and A2. The biodegradation of GMCM6M was not significantly different from that of EBCM6M (Table A3).

The percent mineralization of gamma irradiated PVdC-coated cellophane (GMCK6M) after 6 months of storage was 52.05%, 35.62% for GMCK3M and 63.13% for CoCK (Figure 6.10). E-beam irradiated PVdC-coated cellophane, EBCK6M and EBCK3M yielded values of 33.72% and 49.82%, respectively. Based on the statistical analysis (Table A2), significant differences in biodegradability of GMCK6M and GMCK3M, and CoCK were not found. Similarly, there was no significant difference in EBCK6M and EBCK6M, and CoCK (Table A2). Also, there was no significant difference between GMCK6M and EBCK6M (Table A3). There was a large variation in percent mineralization of GMCP6M and EBCP6M because the CO_2 evolution from one bioreactor in each set was lower than the other two. This may be attributed to 1) compost variation between the bioreactors during the mixing process and consequently different microbial activity in each jar, and 2) variation in the moisture content of the compost in each jar as a result of drying because of temperature differences between the upper and lower chambers of the DMR system.

Based on comparisons between material types for the same irradiation sources after 6 months (Table A3), there were significant differences in biodegradation of

GMCP6M as compared with GMCM6M and GMCK6M. For E-beam irradiation, biodegradation of EBCP6M was significantly different from EBCM6M and EBCK6M.

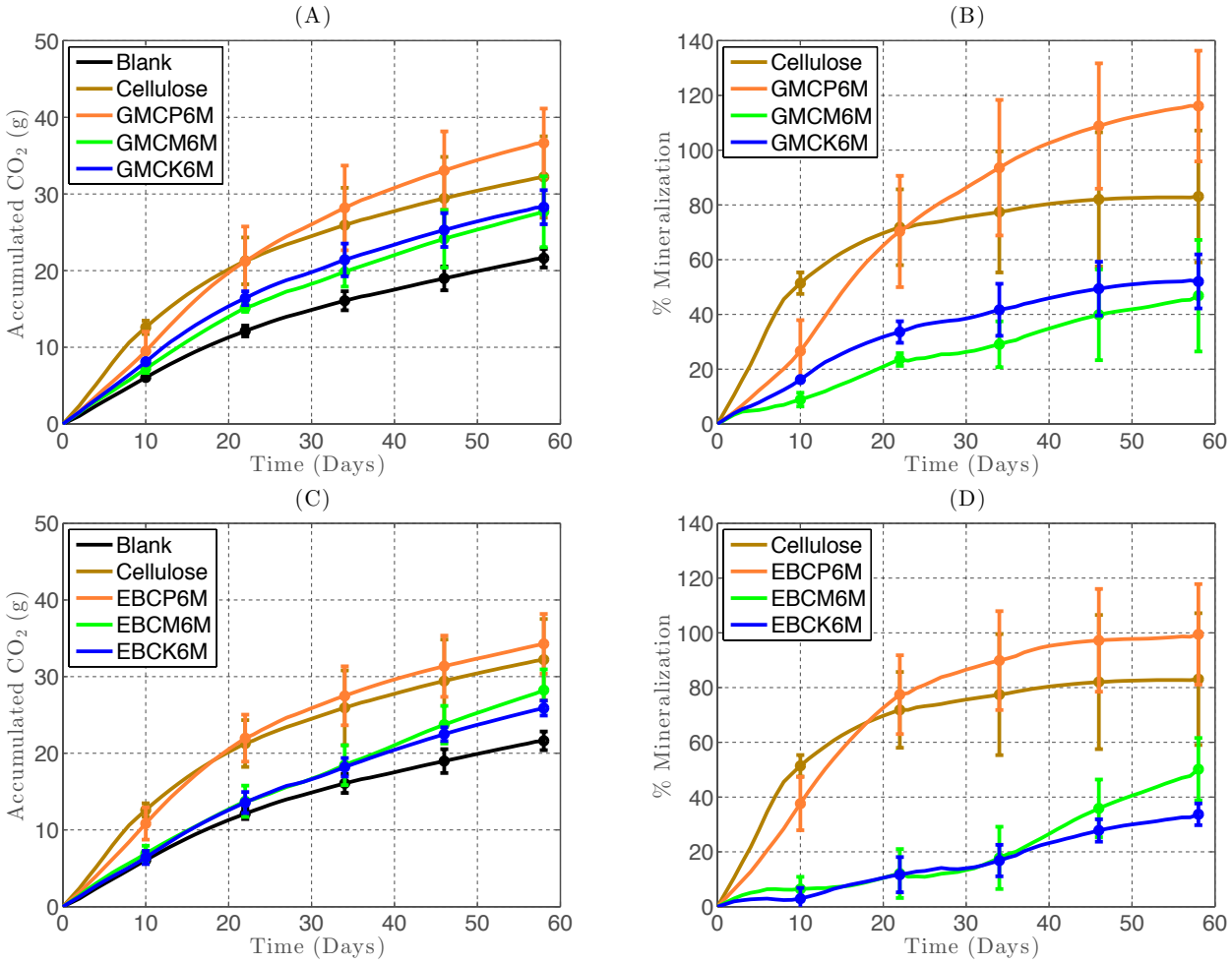

Figure 6.10 Carbon dioxide evolution (A, C) and percent mineralization (B, D) for gamma (GM) and E-beam (EB) irradiated uncoated cellophane (CP), nitrocellulose-coated cellophane (CM) and PVdC-coated cellophane (CK) after 6 months of storage with standard error

Figure 6.11 illustrates the biodegradability results for irradiated cellophane after 9 months of storage. The CO_2 evolution of gamma irradiated (GMCP9M) and E-beam irradiated uncoated cellophane (EBCP9M) increased above cellulose after day 12. The

CO_2 evolution of gamma irradiated nitrocellulose-coated cellophane (GMCM9M) was comparable to that of cellulose and greater than that of gamma irradiated PVdC-coated cellophane (GMCK9M). Conversely, CO_2 evolution from E-beam irradiated nitrocellulose-coated cellophane (EBCM9M) was lower than from E-beam irradiated PVdC-coated cellophane (EBCK9M).

Percent mineralization was 118% for GMCP9M and 128% for EBCP9M after 9 months of storage with these values not significantly different (Table A3). Biodegradation of GMCP9M was greater than that of CoCP (71%), GMCP3M (103%) and GMCP6M (116%). Percent mineralization of EBCP9M was also greater than that of CoCP and EBCP3M (88%) and EBCP6M (99%), as presented in Table 6.6. The biodegradation of GMCP9M and EBCP9M was significantly different from CoCP (Table A1 and A2). These results indicate that irradiation sterilization enhanced the biodegradability of uncoated cellophane (CP), likely due to the presence of irradiation-induced free radicals.

For irradiated nitrocellulose-coated cellophane after 9 months of storage, the percent mineralization of gamma irradiated nitrocellulose-coated cellophane (GMCM9M, 88.29%) was greater than CoCM (54.73%), GMCM3M (73.88%) and GMCM6M (46.84%). However, percent mineralization of E-beam irradiated nitrocellulose-coated cellophane (EBCM9M, 19.88%) was lower than CoCM, EBCM3M (75.55%) and EBCM6M (50.19%), as shown in Table 6.6. As seen in the graph in Figure 6.11, biodegradation of EBCM9M increased until day 20 to approximately 30%. However, percent mineralization started decreasing after day 25 and ended at 20% towards the

end of the experiment. Based on daily visual observation, no obvious problems were evident with the bioreactors for the EBCM9M samples. The standard error for triplicate samples was low. This might be due to the byproducts of the degradation process adversely affecting the microbial population. It is worthy of further investigation. Based on statistical analysis, no significant difference in the biodegradation was found for non-irradiated and gamma irradiated nitrocellulose-coated cellophane after 3, 6 and 9 months of storage as shown in Table A1. There was a significant difference between EBCM9M and EBCM3M, but not between EBCM9M and EBCM6M; and EBCM9M and CoCM (Table A2). The biodegradation of GMCM9M was significantly different from that of EBCM9M (Table A3).

The biodegradation results for gamma irradiated (GMCK9M) and E-beam irradiated PVdC-coated cellophane (EBCK9M) after 9 months were 55.14% and 64.89%, respectively. There was no statistically significant difference between GMCK9M and EBCK9M (Table A3). The biodegradation of GMCK9M was not significantly different from CoCK, GMCK3M and GMCK6M, as demonstrated in Table A1. Also, percent mineralization of EBCK9M was not significantly different from CoCK, EBCK3M and EBCK9M, as shown in Table A2. The biodegradation values for both GMCK9M and EBCK9M were highly variable, which could be due to differences in the compost and the microbial activity in each bioreactor.

The comparisons between material types for the same irradiation sources after 9 months of storage showed that the biodegradation of GMCK9M was significantly

different only from GMCP9M, while the biodegradation of EBCK9M was significantly different from EBCP9M and EBCM9M, as presented in Table A3.

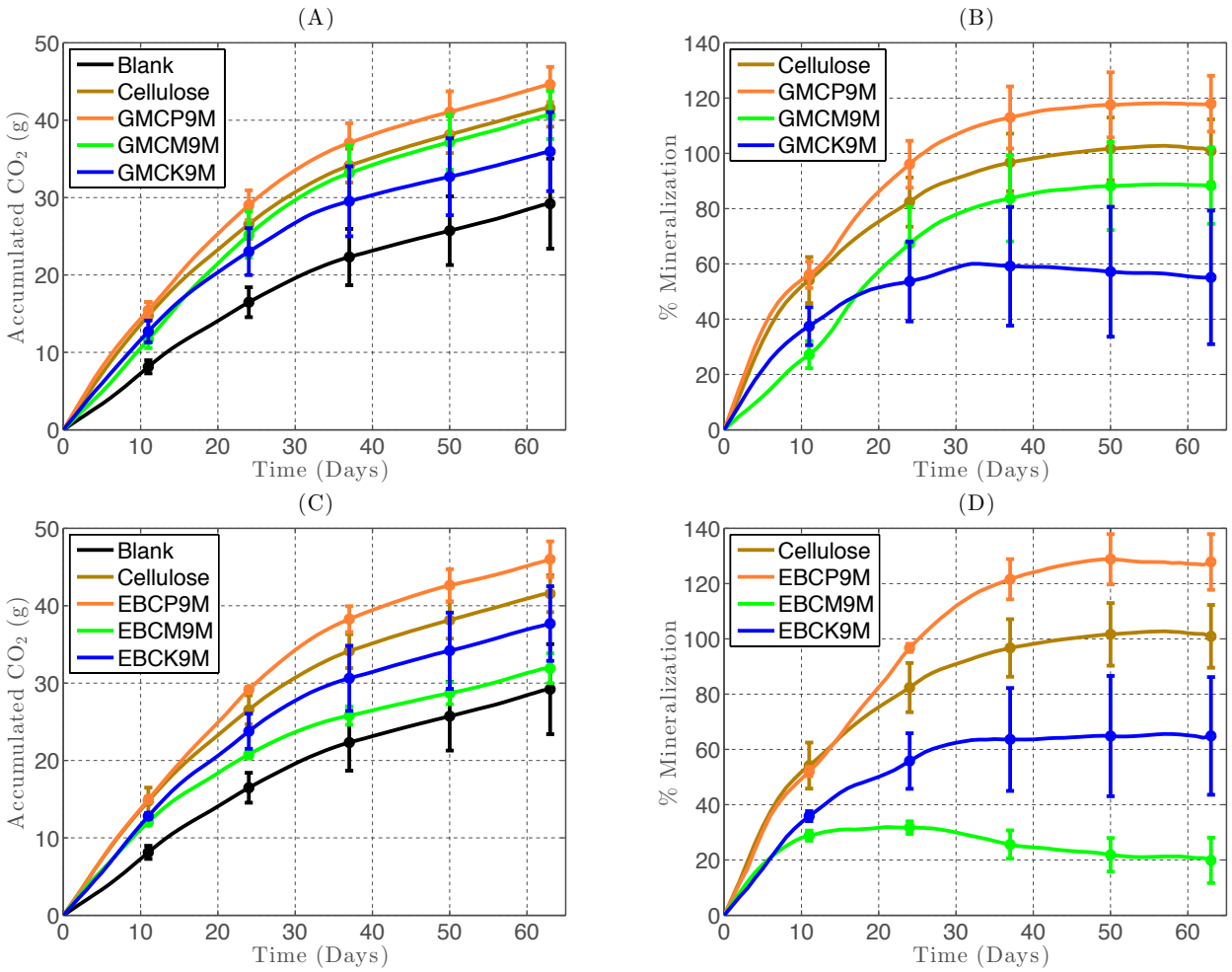

Figure 6.11 Carbon dioxide evolution (A, C) and percent mineralization (B, D) for gamma (GM) and E-beam (EB) irradiated uncoated cellophane (CP), nitrocellulose-coated cellophane (CM) and PVdC-coated cellophane (CK) after 9 months of storage with standard error

6.2.2 Conclusions

Polymer biodegradation depends on not only the properties of the polymer itself (chemical structure) but also the compost quality and types of microorganisms. Additionally, there are numerous key factors that affect biodegradation process such as moisture content, pH and temperature of compost. Oxygen availability is another key element for aerobic biodegradation. It is very important to monitor and maintain a suitable composting environment for microbial activity and growth. Based on the percent mineralization of non-irradiated uncoated cellophane (CoCP, 70.52%), nitrocellulose-coated cellophane (CoCM, 54.73%,) and PVdC-coated cellophane (CoCK, 63.13%) under composting conditions, CoCP qualified as a biodegradable plastic since its mineralization was greater than 60%, in accordance with ASTM D6400 and ISO 14855. However, CoCK and CoCM have the potential to be considered as biodegradable polymers since their biodegradation was around the standard threshold.

The effect of irradiation on the biodegradation of cellophane films was noticeable in uncoated cellophane. Percent mineralization of both gamma and E-beam irradiated uncoated cellophane after 3 months of storage (GMCP3M, 103% and EBCP3M, 88%) was greater than that of non-irradiated uncoated cellophane (CoCP, 70.52%). Due to its high penetration, gamma irradiation has a grater effect on mineralization (McKeen, 2012; O'Donnell & Sangster, 1970). Furthermore, the stability studies involving post-irradiated uncoated cellophane showed that biodegradation increased with the storage time. Therefore, aging of irradiated samples affected their biodegradation due to the presence of irradiation-induced-free radicals, which can create reactions that continue for long periods and cause changes in the material properties of the plastics (Urbain,

1986). Based on these results, uncoated cellophane (including non-irradiated, gamma irradiated and E-beam irradiated samples) can be considered as biodegradable. Irradiation also enhanced the biodegradation of two-side nitrocellulose-coated cellophane and two-side PVdC-coated cellophane. The mineralization of samples after storage did not show consistent upward or downward trends. Nitrocellulose and PVdC coatings are known to resist biodegradation but these regenerated cellophane films have a potential to be biodegradable.

Chapter 7

The effect of X-ray irradiation on properties of poly(lactic) acid and cellophane

The effect of X-ray irradiation on PLA and cellophane was limited in scope. Only one dose level (10 kGy) was examined due to equipment, cost, and time limitations. The aims of this study were to determine the effects of X-ray irradiation on physical, mechanical, thermal and permeability properties of PLA and cellophane films after storage for periods up to several months. Because of the more limited scope, these results are discussed separately from those of the main study.

7.1 Color analysis

The color changes of PLA and cellophane films after X-ray irradiation at 10 kGy during 9 months of storage are shown in Table 7.1. The change of brightness (Figure 7.1-A), represented in L* values (100 bright/0 dark) of X-ray irradiated PLA (XPA) was insignificant. X-ray irradiated uncoated cellophane (XCP), X-ray irradiated nitrocellulose-coated cellophane (XCM) and X-ray irradiated PVdC-coated cellophane (XCK) had a darker appearance than non-irradiated samples as indicated by the decreases in L* values. There was a significant increase in darkness of post-irradiated cellophane films with storage time (6 months for XCP, 3 months for XCM and 9 months for XCK). However, none of these films visually appeared darker. The a* values (+ red/-green) of the X-ray irradiation (Figure 7.1-B) did not significantly differ for XPA. A significant decrease in a* values occurred for XCP after 3 months and XCM after 9 months, while the a* values for XCK significantly increased after 3 months.

The development of a yellowish color, as indicated by the increase in Hunter b* values (+ yellow/– blue), occurred in irradiated cellophane samples and significantly increased for XCP at 9 months, XCM at 6 months, and XCK at 3 months, while no significant difference was noted in XPA samples during 9 months of storage (Figure 7.1-C). This study found irradiation-induced coloration in all three types of cellophane. Furthermore, cellophane is more sensitive to X-ray irradiation at 10 kGy than is PLA.

Table 7.1 Color changes of non-irradiated and X-ray irradiated PLA (PA), uncoated cellophane (CP), nitrocellulose-coated cellophane (CM), and PVdC-coated cellophane (CK) after 9 months of storage

Sample	Irradiation dose (kGy)	Time (month)	*L**	*a**	*b**
XPA	0	0	92.74 ± 0.04^{a}	-1.02 ± 0.02^{a}	0.55 ± 0.03^{a}
	10	3	92.74 ± 0.05^{a}	-1.02 ± 0.02^{a}	0.55 ± 0.01^{a}
		6	92.81 ± 0.02^{a}	-1.00 ± 0.02^{a}	0.57 ± 0.01^{a}
		9	92.78 ± 0.02^{a}	-1.02 ± 0.01^{a}	0.58 ± 0.01^{a}
XCP	0	0	91.83 ± 0.02^{a}	-1.05 ± 0.01^{a}	1.08 ± 0.04^{a}
	10	3	91.80 ± 0.09^{a}	-1.09 ± 0.01^{b}	1.10 ± 0.02^{a}
		6	91.62 ± 0.01^{b}	-1.11 ± 0.01^{b}	1.11 ± 0.01^{a}
		9	91.47 ± 0.06^{c}	-1.11 ± 0.01^{b}	1.23 ± 0.02^{b}
XCM	0	0	92.17 ± 0.03^{a}	-1.17 ± 0.00^{a}	1.18 ± 0.03^{a}
	10	3	91.96 ± 0.01^{b}	-1.18 ± 0.01^{a}	1.22 ± 0.01^{ab}
		6	91.97 ± 0.00^{b}	-1.19 ± 0.01^{ab}	1.24 ± 0.03^{b}
		9	91.91 ± 0.03^{b}	-1.22 ± 0.01^{b}	1.41 ± 0.01^{c}
XCK	0	0	91.21 ± 0.02^{a}	-1.18 ± 0.04^{a}	1.16 ± 0.02^{a}
	10	3	91.13 ± 0.02^{ab}	-1.14 ± 0.02^{b}	1.40 ± 0.03^{b}
		6	91.16 ± 0.02^{a}	-1.12 ± 0.00^{b}	1.50 ± 0.04^{c}
		9	91.07 ± 0.03^{b}	-1.12 ± 0.01^{b}	1.62 ± 0.02^{d}

Data represented are mean values (± standard deviation). Different superscript letter within the same column of each material type differ significantly ($p < 0.05$)

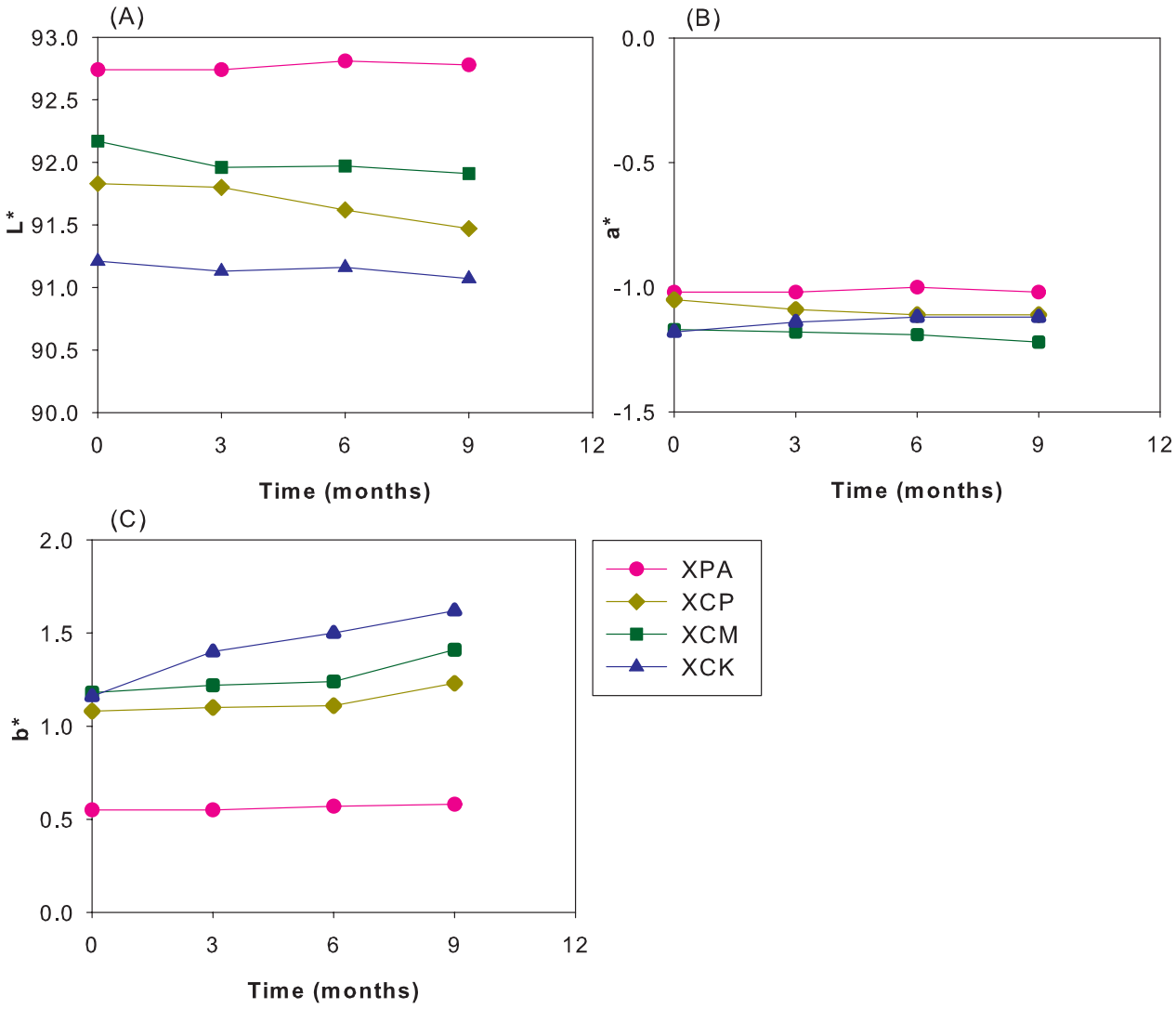

Figure 7.1 Changes in Hunter L*, a*, and b* values for X-ray irradiated PLA (XPA), uncoated cellophane (XCP), nitrocellulose-coated cellophane (XCM) and PVdC-coated cellophane (XCK) at 10 kGy during 9 months of storage

7.2 Surface tension

The effect of X-ray irradiation on the surface tension of PLA and cellophane films is shown in Table 7.2. The analysis of surface tension was conducted only for PLA, nitrocellulose-coated cellophane (CM) and PVdC-coated cellophane (CK). As stated before, uncoated cellophane could not be tested because of its moisture sensitivity. It was found that the surface tension of PLA was reduced after X-ray irradiation (from 57 to 54 dyne/cm). After exposure, a reduction in surface tension for X-ray irradiated nitrocellulose-coated cellophane (XCM) was observed (47 dyne/cm), compared to the non-irradiated sample (55 dyne/cm). In contrast, the surface tension of X-ray irradiated PVdC-coated cellophane (XCK) increased (62 dyne/cm), as compared to the non-irradiated sample (58 dyne/cm).

Table 7.2 Effect of X-ray irradiation on surface tension of PLA and cellophane after 9 months of storage

Sample	Dose (kGy)	Time (month)	Surface Tension (dyne/cm)
XPA	0	0	57
	10	3	54
		6	54
		9	54
XCM	0	0	55
	10	3	47
		6	47
		9	47
XCK	0	0	58
	10	3	61
		6	62
		9	62

7.3 Fourier transform infrared (FTIR) spectroscopy

X-ray induced changes in the chemical structure of PLA and cellophane films were determined using FTIR spectroscopy. Figures 7.2 - 7.5 show the FTIR spectra for non-irradiated and irradiated PLA (XPA), uncoated cellophane (XCP), irradiated nitrocellulose-coated cellophane (XCM) and irradiated PVdC-coated cellophane (XCK) at 10 kGy after 9 months of storage. As discussed in Chapter 4, PLA is characterized by absorption bands for -CH- stretch, -C=O- carbonyl, -CH- deformation, -C-O- stretch, and -C–C- stretch, as shown in Table 4.3 and Figure 7.2. An absorption band at 1746 cm^{-1} attributed to C=O stretching in the ester groups of PLA decreased after exposure to X-ray irradiation and its intensity decreased as a function of storage time. A decrease in the absorption band at 1180 and 1078 cm^{-1}, which is assigned to the C-O-C stretching vibration of ester-like functionality, was also observed, but the intensity of the peaks increased after 6 and 9 months of post-irradiation storage. The observed decrease in PLA bands at 1078 and 1043 after irradiation is in agreement with the findings of Yotoriyama et al. (2005) and Zaidi et al. (2013).

For uncoated cellophane (Table 4.12 and Figure 7.3), antisymmetrical bridge C-O-C stretching and C-O-C pyranose ring skeletal vibration at 1155 and 1018 cm^{-1} (Higgins et al., 1961; Nelson & O'Connor, 1964; Zhu et al., 2013) increased after X-ray irradiation exposure and during storage. A small band at 893 cm^{-1} attributed to the vibration of glycosidic bonds (Higgins et al., 1961) was strong and sharp after exposure to irradiation. The absorption band at 1647 cm^{-1} corresponding to glucose carbonyls

(C=O) of cellulose (Gong & Zhang, 1998) increased. There was also an increase in the intensity of bands 1313-1363 cm^{-1}, assigned to CH_2 stretching. The 3000-3600 cm^{-1} (-OH stretching) and 2887 cm^{-1} (-CH stretching) regions were more intense than in non-irradiated uncoated cellophane.

Nitrocellulose is characterized by vibrations from the nitro group (NO_2) at 1643 cm^{-1}, 1277 cm^{-1}, and 837 cm^{-1} (Table 4.12 and Figure 7.4). Those three bands of the nitrocellulose-coated cellophane decreased after X-ray irradiation. Heppel-Masys et al. (1997), who studied the effect of gamma irradiation on nitrocellulose, reported a similar trend. However, there was an increase in intensity of those peaks in the post-irradiated nitrocellulose-coated cellophane after storage for 6 and 9 months. A noticeable decrease in the absorption band at 1009-1057 cm^{-1} attributed to the glucopyranose group (C-O) (Gong & Zhang, 1998) occurred with increased storage time.

As a result of X-ray irradiation of PVdC-coated cellophane (Table 4.12 and Figure 7.5), the C-Cl stretching vibration at 748 and 665 cm^{-1} decreased during storage. The CH stretching and CH_2 stretching bands at 2916, 2848 and 1409, 1359 and 1311 cm^{-1} did not change after irradiation.

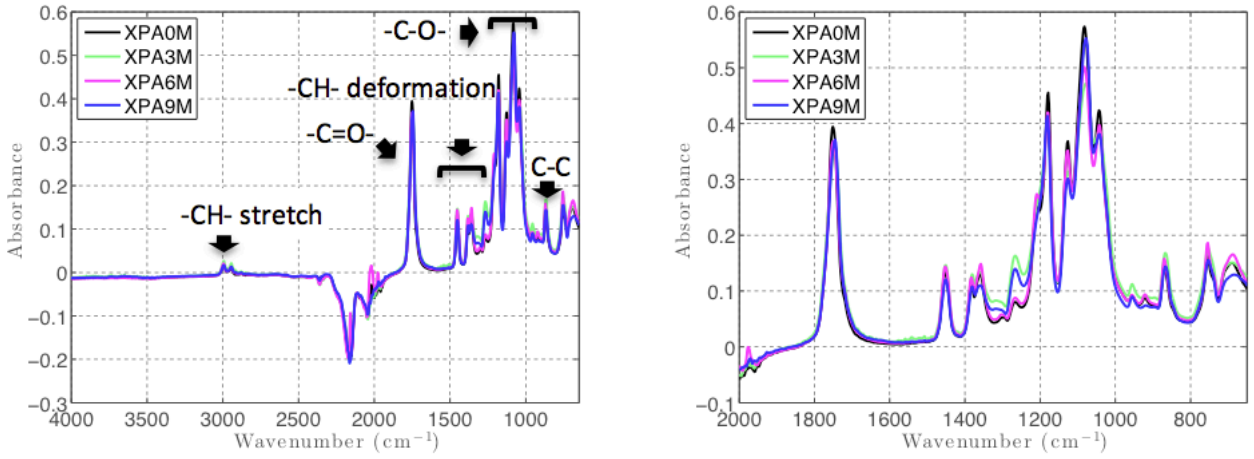

Figure 7.2 FITR spectra of non-irradiated and X-ray irradiated PLA (XPA) after 9 months of storage

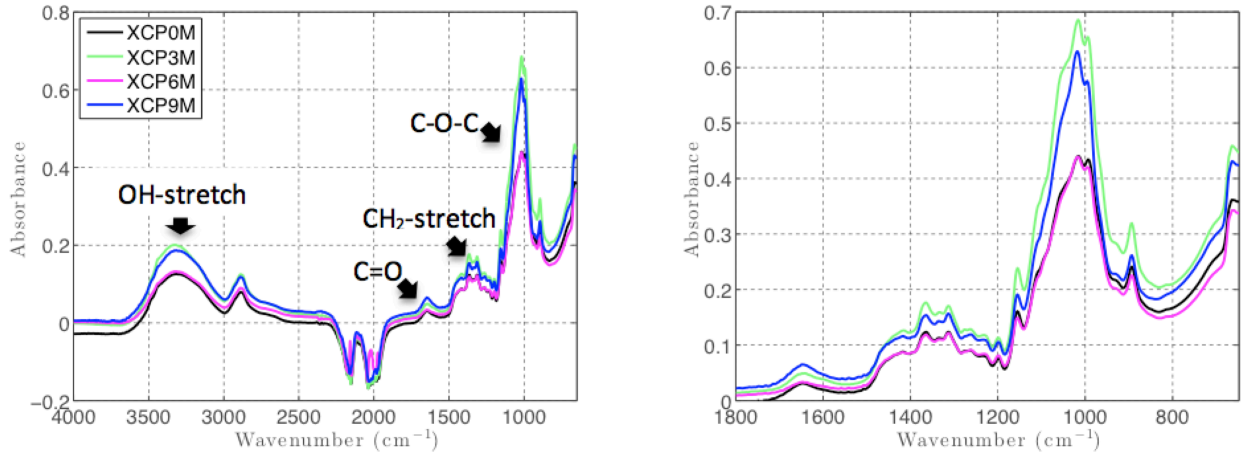

Figure 7.3 FITR spectra for non-irradiated and X-ray irradiated uncoated cellophane (XCP) after 9 months of storage

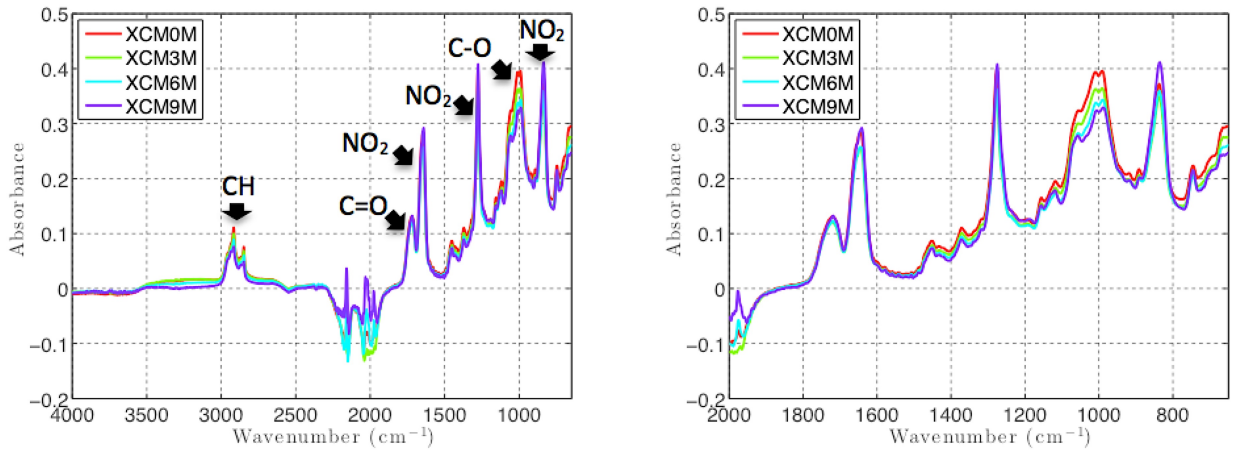

Figure 7.4 FITR spectra for non-irradiated and X-ray irradiated nitrocellulose-coated cellophane (XCM) after 9 months of storage

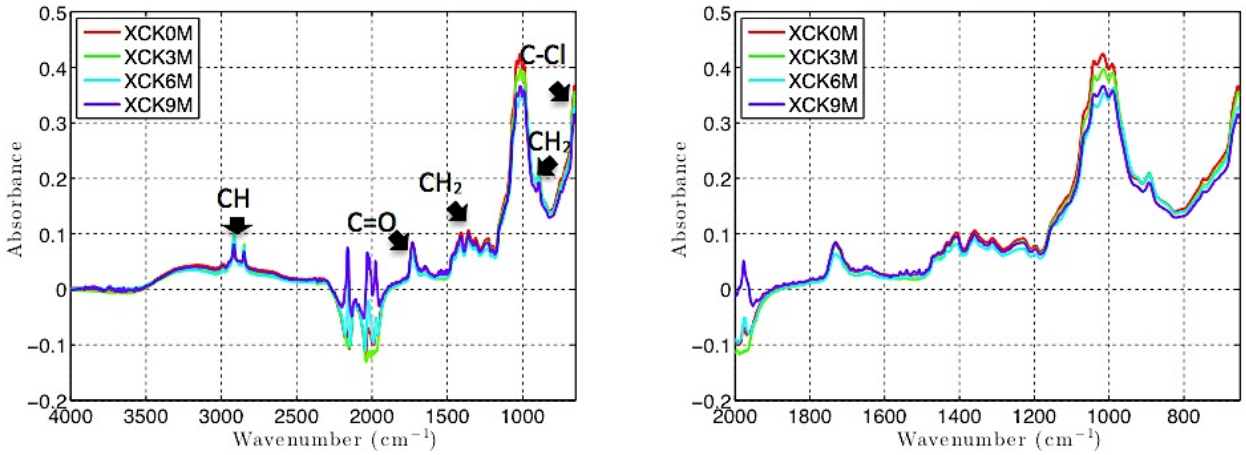

Figure 7.5 FITR spectra for non-irradiated and X-ray irradiated PVdC-coated cellophane (XCK) after 9 months of storage

7.4 Thermal properties

The influence of X-ray irradiation on the thermal properties of PLA and cellophane films, including glass transition temperature (T_g), crystallization temperature (T_c) and melting temperature (T_m), were determined using differential scanning calorimetry (DSC), as presented in Table 7.3. As found in the previous study (section

4.1.4), the DSC thermograms for PLA revealed two melting peaks (large peak, T_{m1} and small peak T_{m2}). The thermal properties of post-irradiated PLA (XPA) after 3 months of storage showed a significant decrease in T_c and T_{m1}, as compared to non-irradiated PLA. These changes were stable during 6 and 9 months of storage. X-ray irradiation caused a slight, but not significant decrease in the T_g of XCP, XCM and XCK after 3 months. A significant increase in T_g for XCP was seen after 6 and 9 months of storage compared to after 3 months. A similar result was found for XCM. A significant increase in T_g occurred with storage time. The T_g for XCK was also significantly higher after 6 and 9 months as compared to 3 months but was not significantly different than non-irradiated PVdC-coated cellophane (CK).

Table 7.3 Changes in thermal properties of irradiated PLA and cellophane by X-ray irradiation at 10 kGy after 9 months of storage

Sample	Dose (kGy)	Time (month)	T_g (ºC)	T_c (ºC)	T_{m1} (ºC)	T_{m2} (ºC)
XPA	0	0	61.21 ± 0.31^{a}	121.81 ± 0.43^{a}	163.75 ± 0.38^{a}	168.75 ± 0.36^{a}
	10	3	60.85 ± 0.24^{a}	118.51 ± 0.64^{b}	162.75 ± 0.46^{b}	169.06 ± 0.43^{a}
		6	60.83 ± 0.92^{a}	118.90 ± 0.12^{b}	162.95 ± 0.30^{ab}	169.35 ± 0.27^{a}
		9	60.54 ± 0.11^{a}	118.53 ± 0.27^{b}	162.45 ± 0.08^{ab}	169.21 ± 0.09^{a}
XCP	0	0	131.83 ± 3.39^{ab}	---	---	
	10	3	128.20 ± 2.83^{a}	---	---	
		6	134.83 ± 1.46^{b}	---	---	
		9	144.63 ± 0.87^{c}	---	---	
XCM	0	0	131.95 ± 2.26^{ab}	---	---	
	10	3	129.15 ± 2.66^{a}	---	---	
		6	136.50 ± 1.97^{bc}	---	---	
		9	140.65 ± 3.98^{c}	---	---	
XCK	0	0	133.96 ± 0.66^{ab}	---	---	
	10	3	128.76 ± 3.89^{b}	---	---	
		6	139.37 ± 0.77^{a}	---	---	
		9	139.12 ± 1.03^{a}	---	---	

Data represented are mean values (± standard deviation). Different superscript letters within the same column of each material type differ significantly ($p < 0.05$)

7.5 Molecular weight

The molecular weight values for PLA, as obtained by GPC analysis, before and after irradiation at 10 kGy are reported in Table 7.4. A significant decrease in the number average molecular weight (M_n) and weight average molecular weight (M_w) of X-ray irradiated PLA after 3 months of storage was observed. A slight increase in the M_n of XPA after 6 and 9 months was observed; however, it was not statistically significant. After 3 months, the M_w of XPA also increased with storage time and a significant increase was found for XPA after 9 months of storage. Figure 7.6 shows the number average molecular weight (M_n) and weight average molecular weight (M_w) of irradiated PLA plotted against storage time. The polydispersity (PI = M_w/M_n) of XPA increased after irradiation and a significant increase was found after 9 months of storage (Table 7.4). The increase in the polydispersity index (PI) occured since the free radicals within the crystalline regions are encouraged to experience recombination, resulting in more branched and non-uniform chains of PLA (Loo et al., 2005a).

Table 7.4 Molecular weights for non- irradiated and X-ray irradiated PLA (XPA) at 10 kGy after 9 months of storage

Sample	Time (month)	$M_n \times 10^4$ ($gmol^{-1}$)	$M_w \times 10^4$ ($gmol^{-1}$)	PI
CoPA	3	6.86 ± 0.04^a	9.75 ± 0.03^a	1.42 ± 0.01^a
XPA	3	5.53 ± 0.37^b	8.45 ± 0.07^b	1.53 ± 0.09^a
	6	5.51 ± 0.03^b	8.51 ± 0.04^b	1.54 ± 0.01^a
	9	5.57 ± 0.05^b	9.18 ± 0.04^c	1.68 ± 0.01^b

Data represented are mean values (± standard deviation). Different superscript letters within the same column differ significantly ($p < 0.05$)

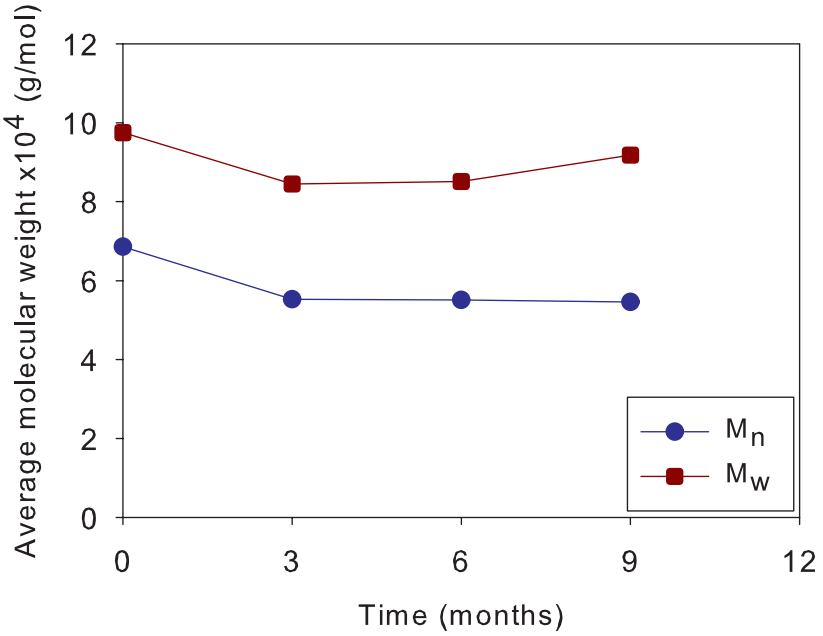

Figure 7.6 Number average molecular weight (M_n) and weight average molecular weight (M_w) of X-ray irradiated PLA (XPA) after 9 months of storage

Since the X-ray experiments were conducted only at 10 kGy, it was decided to further investigate the relationship between chain scission and cross-linking of materials. The changes in molecular weight are related to the radiation chemical yields: chain scission yield G_s and cross-linking yield G_x, which are important characteristics of

polymer radiation sensitivity. G_s and G_x are used to determine the dominance of chain scission or cross-linking during irradiation, as calculated from equations (7.1) and (7.2). A ratio of G_s/G_x greater than four would indicate that chain scission prevails, while a ratio of G_s/G_x lower than 4 indicates that cross-linking is more dominant (Devasahayam et al., 2003; Moad & Winzor, 1998; Sen et al., 2003).

$$1/M_{w,t} = 1/M_{w,0} + (G_s/2 - 2G_x)D \times 1.038 \times 10^{-6} \quad (7.1)$$

$$1/M_{n,t} = 1/M_{n,0} + (G_s - G_x)D \times 1.038 \times 10^{-6} \quad (7.2)$$

where $M_{w,0}$ and $M_{n,0}$ are the weight and number average molecular weight of non-irradiated polymers. $M_{w,t}$ and $M_{n,t}$ are the weight and number average molecular weight of irradiated polymer. D is irradiation dose (kGy).

The G_s and G_x values of XPA over 9 months are shown in Table 7.5. The G_s/G_x ratios for XPA after 3, 6 and 9 months of storage were 12.66, 62.76 and 5.81, respectively, which were all greater than 4. These results confirm the dominance of chain scission over cross-linking in irradiated PLA. Nugroho et al. (2001) , who studied the degradation of PLA by gamma irradiation in air and in vacuum, reported that the G_s of irradiated PLA in air (1.97) was greater than that in vacuum (0.83), and chain-scission was the main cause of degradation of PLA in both irradiation atmospheres (air and vacuum). The author suggested that it could be because the ester groups in the

structure of PLA are stable to oxidative reactions for irradiation in air, whereas the ester groups are sensitive to irradiation under vacuum. The result is a decrease in M_n due to oxidative chain scission.

Table 7.5 Chain scission yield G_S and cross-linking yield G_X of X-ray irradiated PLA at 10 kGy after 9 months of storage

Sample	Time (month)	G_S	G_X	G_S/G_X
XPA10k	3	0.3486	0.0115	30.1935
	6	0.3621	0.0187	19.3829
	9	0.4391	0.0793	5.5403

7.6 Mechanical properties

The tensile strength, elongation at break and elastic modulus of PLA (PA), uncoated cellophane (CP), nitrocellulose-coated cellophane (CM) and PVdC-coated cellophane (CK) before and after exposure to X-ray irradiation at 10kGy are shown in Table 7.6. Post-irradiated PLA (XPA) showed no statistically significant difference in tensile strength in the machine direction (MD) after 3, 6 and 9 months; however, a significant decrease occurred in the cross-machine direction (CD) of XPA after 9 months. Elongation at break for XPA in both MD and CD decreased after irradiation exposure and a significant decrease was found in CD for XPA after 3 months. The elastic modulus for XPA significantly increased in CD. Research on the effect of X-ray irradiation on mechanical properties of PLA and cellophane films is limited.

An increase in tensile strength was observed for X-ray irradiated uncoated cellophane (XCP) in MD after 3 months and in CD after 9 months. The elastic modulus

for XCP in MD also showed a significant increase. After irradiation exposure, tensile strength and elastic modulus of X-ray irradiated nitrocellulose-coated cellophane (XCM) both increased significantly while elongation at break in CD decreased. X-ray irradiation also altered the mechanical properties of PVdC-coated cellophane (XCK) film with elongation at break decreasing for CD and significantly increasing for elastic modulus (MD).

Table 7.6 Mechanical property changes for non-irradiated and irradiated PLA and cellophane by X-ray irradiation at 10 kGy during 9 months of storage

Sample	Time (month)	Tensile strength (kpsi)		Elongation at break (%)		Elastic Modulus (kpsi)	
		MD	CD	MD	CD	MD	CD
CoPA	3	13.14 ± 0.46^{a}	24.06 ± 0.79^{a}	11.00 ± 1.56^{a}	72.17 ± 3.78^{a}	511.59 ± 24.94^{a}	718.98 ± 23.03^{a}
XPA	3	13.63 ± 0.64^{a}	20.31 ± 0.22^{b}	8.24 ± 1.82^{a}	45.88 ± 2.57^{b}	502.71 ± 17.18^{a}	843.94 ± 23.35^{b}
	6	13.36 ± 0.60^{a}	21.89 ± 0.82^{b}	9.10 ± 2.90^{a}	59.10 ± 6.59^{c}	506.87 ± 14.19^{a}	836.17 ± 25.07^{b}
	9	13.82 ± 0.73^{a}	21.33 ± 1.25^{b}	9.07 ± 2.87^{a}	52.81 ± 4.63^{d}	516.79 ± 26.54^{a}	856.03 ± 41.34^{b}
CoCP	3	21.34 ± 1.12^{a}	10.33 ± 0.40^{a}	19.55 ± 2.19^{a}	48.42 ± 4.25^{ab}	408.84 ± 80.09^{a}	77.17 ± 8.54^{a}
XCP	3	22.90 ± 2.25^{b}	11.03 ± 0.74^{a}	17.61 ± 3.15^{a}	50.25 ± 5.96^{a}	502.87 ± 65.65^{b}	84.49 ± 11.92^{a}
	6	22.55 ± 1.50^{b}	10.51 ± 0.82^{a}	17.67 ± 3.03^{a}	52.47 ± 8.41^{a}	536.66 ± 61.66^{bc}	69.70 ± 22.38^{a}
	9	23.78 ± 1.82^{b}	12.54 ± 0.58^{b}	16.10 ± 1.93^{a}	46.30 ± 9.69^{b}	573.15 ± 76.79^{c}	62.33 ± 1.92^{a}
CoCM	3	20.03 ± 0.28^{a}	10.12 ± 0.32^{a}	18.58 ± 1.03^{a}	66.48 ± 4.06^{a}	367.84 ± 25.66^{a}	466.89 ± 9.70^{a}
XCM	3	22.70 ± 0.29^{b}	11.35 ± 0.54^{b}	15.79 ± 0.95^{a}	49.99 ± 9.29^{b}	560.92 ± 35.46^{b}	468.11 ± 10.48^{a}
	6	22.28 ± 0.91^{b}	10.21 ± 0.27^{ab}	16.75 ± 0.86^{a}	52.56 ± 3.62^{b}	464.58 ± 55.79^{c}	553.44 ± 7.20^{b}
	9	21.66 ± 0.79^{b}	9.03 ± 0.44^{c}	16.82 ± 1.43^{a}	35.67 ± 4.14^{c}	440.48 ± 39.89^{c}	517.13 ± 16.41^{ab}
CoCK	3	24.37 ± 0.39^{a}	12.58 ± 0.42^{a}	19.66 ± 1.06^{a}	52.23 ± 3.55^{a}	421.74 ± 22.28^{a}	587.24 ± 17.40^{a}
XCK	3	24.22 ± 0.84^{a}	12.05 ± 0.29^{a}	16.06 ± 1.94^{a}	40.41 ± 4.35^{b}	611.22 ± 72.08^{b}	551.30 ± 18.60^{a}
	6	23.56 ± 0.94^{a}	10.74 ± 0.92^{b}	17.03 ± 1.62^{a}	38.97 ± 4.31^{b}	502.93 ± 60.40^{c}	591.79 ± 70.16^{a}
	9	22.35 ± 0.43^{b}	10.05 ± 0.20^{b}	16.40 ± 0.72^{a}	30.47 ± 2.79^{c}	506.08 ± 23.30^{c}	572.86 ± 22.63^{a}

Data represented are mean values (± standard deviation). Different superscript letter within the same column of each material type differ significantly ($p < 0.05$)

7.7 Barrier properties

Barrier analysis was only conducted for PLA. The oxygen, water vapor, and carbon dioxide permeability results for non-irradiated and irradiated PLA (10kGy) during 9 months of storage are presented in Table 7.7. No significant differences in oxygen and carbon dioxide permeability were found. X-ray irradiation did not affect the water vapor permeability of PLA after 3 months of exposure; however, water vapor permeability decreased significantly after 6 and 9 months of storage.

Table 7.7 Permeability of non-irradiated (CoPA) and X-ray irradiated PLA (XPA) at 10 kGy after 9 months of storage

Sample	Time (months)	$P_{O_2} \times 10^{-18}$ (Kg-m/m^2-sec-Pa)	$P_{H_2O} \times 10^{-14}$ (Kg-m/m^2-sec-Pa)	$P_{CO_2} \times 10^{-18}$ (Kg-m/m^2-sec-Pa)
CoPA	3	3.28 ± 0.06^a	1.87 ± 0.01^a	25.95 ± 0.53^a
XPA	3	3.29 ± 0.18^a	1.83 ± 0.04^a	26.10 ± 2.70^a
	6	3.23 ± 0.12^a	1.65 ± 0.07^b	23.22 ± 0.39^a
	9	3.30 ± 0.19^a	1.57 ± 0.11^b	23.63 ± 2.85^a

Data represented are mean values (± standard deviation). Different superscript letters within the same column differ significantly ($p<0.05$)

7.8 Conclusion

Effects of X-ray irradiation on physical, chemical, mechanical, thermal and barrier properties of biomaterials including PLA, uncoated cellophane, nitrocellulose-coated cellophane and PVdC-coated cellophane were studied. Changes in physical properties included the development of a yellowish color in all cellophane films; however, the color of PLA was not affected by X-ray irradiation at 10 kGy. Surface tension after irradiation increased for PVdC-coated cellophane and decreased for nitrocellulose-coated

cellophane and PLA. Irradiation altered the thermal and mechanical properties of all polymeric materials. The crystallization temperature (T_c) and melting temperature (T_m) for irradiated PLA and the glass transition temperature (T_g) for PVdC-coated cellophane films decreased after 3 months of storage. The mechanical properties of PLA in the cross-machine direction (CD) decreased significantly. In cellophane films, X-ray irradiation also induced differences in mechanical properties. The decrease in molecular weight of PLA indicated that the degradation of PLA was primarily due to chain scission. Oxygen, water vapor and carbon dioxide permeability of PLA were not affected at the approved X-ray irradiation dose of 10 kGy. In general, some differences were observed during storage, indicating free radical induced progressive change.

Chapter 8

Conclusions and Recommendations for Future Work

8.1 Overall conclusions

The overall goal of this dissertation was to determine whether these biodegradable films had potential for packaging applications where irradiation sterilization was used. The results indicated that commercial PLA and three cellophane films were suitable for packaging applications after irradiation treatment.

Properties of commercial PLA and cellophane films were affected by ionizing radiation due to chain scission. Gamma, E-beam and X-ray irradiation of the PLA film resulted in a decrease in molecular weight, crystallization temperature and melting temperature, which suggested partial degradation of PLA by irradiation. There was also a decrease in surface tension, mechanical strength (including tensile strength, break elongation and elastic modulus), water vapor permeability and carbon dioxide permeability while there was no effect on oxygen permeability and color of PLA. However, the gas and water vapor permeability properties of PLA were not affected after X-ray irradiation. Gamma, E-beam and X-ray irradiation induced a color change in cellophane, but not in PLA. All irradiation sources led to a yellowing of coated cellophane and decreased the surface tension of nitrocellulose-coated cellophane, but the surface tension of PVdC-coated cellophane remained unchanged after irradiation over 9 months of storage. All three types of irradiation generally did not affect the glass transition temperature of nitrocellulose-coated cellophane or PVdC-coated cellophane. Gamma irradiation induced a significant decrease in the glass transition temperature of

uncoated cellophane. The FTIR results of X-ray irradiated PLA and three cellophane films showed similar changes in chemical structure as those of gamma and E-beam irradiated materials.

After exposure to gamma and E-beam irradiation, overall migration from PLA increased with irradiation dose. Irradiation-induced changes in overall migration during storage of post-irradiated PLA were not observed. Overall migration from non-irradiated and irradiated PLA films into all aqueous food simulants, representing aqueous, acetic acid, alcohol and fatty foods, was below the maximum overall migration limit (10 mg/dm^2) defined by the EEC Directive. This indicates that the irradiation sterilized PLA film is safe for food contact applications. Even though the migration study was not conducted for X-ray irradiated PLA, the reduction in molecular weight for X-ray irradiated PLA shows the potential for compounds to migrate from PLA to food simulants as indicated by gamma and E-beam results for irradiated PLA.

For cellophane, overall migration from non-irradiated nitrocellulose coated cellophane and non-irradiated PVdC coated cellophane was lower than for non-irradiated uncoated cellophane film. Thus, the coating helps to reduce overall migration of additives from the film into food simulants. Total overall migration was above the limit set by the EU regulation. Use of 95 % ethanol led to more overall migration in all cellophane films than the other simulants (32.77 mg/dm^2 for uncoated cellophane, 21.70 mg/dm^2 for nitrocellulose-coated cellophane, and 21.73 mg/dm^2 for PVdC-coated cellophane). The effect of irradiation on the overall migration depended on the type of

material and simulant. Irradiation decreased the overall migration in some cases such as nitrocellulose-coated cellophane into 15% ethanol and PVdC-coated cellophane into 95% ethanol. The irradiation effect on overall migration of post-irradiation aging of uncoated and coated cellophane films did not show a consistent trend.

Gamma and electron beam irradiation affected the biodegradation of post-irradiated PLA film. Aging irradiated PLA had some potential to increase the biodegradation rate, as the average mineralization value after 9 months was higher than the non-irradiated PLA. A comparison of the effect of storage time on PLA biodegradability showed a significant increase in biodegradation only between the gamma irradiated PLA at 3 and 9 months of storage. Similarly, there was a significant difference in the biodegradation of electron beam irradiated PLA between 3 and 9 months of storage. Due to the priming effect, the percent mineralization for gamma irradiated and E-beam irradiated PLA after 9 months of storage was greater than 100%. Based on the results from this study, both non-irradiated and irradiated PLA films can be considered as biodegradable plastics since they passed the minimum required degradation percentage of 60% mineralization.

In accordance with ASTM D6400 and ISO 14855, non-irradiated uncoated cellophane qualified as a biodegradable plastic, while non-irradiated nitrocellulose-coated cellophane and non-irradiated PVdC-coated cellophane have the potential to be considered as biodegradable polymers. The effect of irradiation-induced free radicals on the biodegradation of cellophane films was evident in uncoated cellophane. Irradiated uncoated cellophane degraded faster after 9 months of storage. Mineralization of the

post-irradiated nitrocellulose-coated and PVdC-coated cellophane was inconsistent for samples stored for 9 months. However, they also have the potential to be biodegradable.

8.2 Future recommendations

There are some recommendations for future work. In order to verify the performance of irradiated plastic materials, tests should be conducted with food and/or pharmaceutical products. To get more insight into the migrated compounds from materials before and after exposure to irradiation, specific migration should be conducted. Also, mathematical modeling of the diffusion process during migration can help to understand the migration behavior of the migrated compounds. Furthermore, modeling the biodegradation of polymeric materials will lead to a better understanding of the interactions between materials and composting conditions. Biodegradation of the coating materials used from cellophane should be studied separately to assess biodegradability for regulatory compliance purposes.

APPENDIX

Table A.1: The comparison matrix of non-irradiated and gamma irradiated cellophane films based on Bonferroni adjustment

Least Squares Means for effect Irr*Film*Time Pr > |t| for H0: LSMean(i)=LSMean(j) Dependent Variable: M												
Sample	CoCK	CoCM	CoCP	GMCK3M	GMCK6M	GMCK9M	GMCM3M	GMCM6M	GMCM9M	GMCP3M	GMCP6M	GMCP9M
CoCK		0.4838	0.5375	0.0651	0.4511	0.5863	0.4647	0.2695	0.0907	**0.0092**	**0.0007**	**0.0004**
CoCM			0.1907	0.1964	0.8552	0.9776	0.1952	0.5912	0.0256	**0.0019**	**0.0001**	**<0.0001**
CoCP				0.0205	0.2112	0.2966	0.8191	0.1107	0.2291	0.0323	**0.0029**	**0.0020**
GMCK3M					0.3343	0.2522	0.0274	0.5087	**0.0029**	**0.0002**	**<0.0001**	**<0.0001**
GMCK6M						0.8553	0.2010	0.7584	0.0363	**0.0041**	**0.0004**	**0.0003**
GMCK9M							0.2712	0.6244	0.0546	**0.0068**	**0.0007**	**0.0005**
GMCM3M								0.1147	0.3964	0.0939	**0.0154**	**0.0116**
GMCM6M									0.0173	**0.0017**	**0.0001**	**<0.0001**
GMCM9M										0.3984	0.1049	0.0839
GMCP3M											0.4279	0.3663
GMCP6M												0.9110
GMCP9M												

Significant differences are indicated by bold type. Bonferroni adjusted alpha value is 0.05/3 = 0.0167 (based on planned comparisons)
Co: non-irradiation
GM: gamma irradiation
EB: electron beam irradiation
CP: uncoated cellophane
CM: nitrocellulose coated cellophane
CK: PVdC coated cellophane

Table A.2: The comparison matrix of non-irradiated and E-beam irradiated cellophane films based on Bonferroni adjustment

Least Squares Means for effect Irr*Film*Time Pr > |t| for H0: LSMean(i)=LSMean(j) Dependent Variable: M												
Sample	CoCK	CoCM	CoCP	EBCK3M	EBCK6M	EBCK9M	EBCM3M	EBCM6M	EBCM9M	EBCP3M	EBCP6M	EBCP9M
CoCK		0.4838	0.5375	0.3661	0.0492	0.9045	0.3986	0.3795	**0.0046**	0.0997	**0.0161**	**<0.0001**
CoCM			0.1907	0.7383	0.1562	0.4893	0.1596	0.7574	0.0207	0.0286	**0.0035**	**<0.0001**
CoCP				0.1621	**0.0148**	0.7009	0.7319	0.1696	**0.0011**	0.2474	0.0529	**0.0003**
EBCK3M					0.3438	0.3754	0.1329	0.9825	0.0815	0.0293	**0.0049**	**<0.0001**
EBCK6M						0.0702	**0.0164**	0.3329	0.4152	**0.0024**	**0.0003**	**<0.0001**
EBCK9M							0.5297	0.3872	**0.0101**	0.1837	0.0454	**0.0005**
EBCM3M								0.1385	**0.0017**	0.4779	0.1622	**0.0031**
EBCM6M									0.0779	0.0309	**0.0052**	**<0.0001**
EBCM9M										**0.0002**	**<0.0001**	**<0.0001**
EBCP3M											0.4851	0.0206
EBCP6M												0.0980
EBCP9M												

Significant differences are indicated by bold type. Bonferroni adjusted alpha value is 0.05/3 = 0.0167 (based on planned comparisons)
Co: non-irradiation
GM: gamma irradiation
EB: electron beam irradiation
CP: uncoated cellophane
CM: nitrocellulose coated cellophane
CK: PVdC coated cellophane

Table A.3: The comparison matrix of gamma irradiated and E-beam irradiated cellophane films based on Bonferroni adjustment

Least Squares Means for effect Irr*Film*Time Pr > |t| for H0: LSMean(i)=LSMean(j) Dependent Variable: M																		
Sample	EBCK 3M	EBCK 6M	EBCK 9M	EBCM 3M	EBCM 6M	EBCM 9M	EBCP 3M	EBCP 6M	EBCP 9M	GMCK 3M	GMCK 6M	GMCK 9M	GMCM 3M	GMCM 6M	GMCM 9M	GMCP 3M	GMCP 6M	GMCP 9M
EBCK3M		0.3438	0.3754	0.1329	0.9825	0.0815	0.0293	**0.0049**	**<.0001**	0.4033	0.8954	0.7537	0.1595	0.8601	0.0266	**0.0029**	**0.0003**	**0.0002**
EBCK6M			0.0702	**0.0164**	0.3329	0.4152	**0.0024**	**0.0003**	**<.0001**	0.9106	0.2819	0.2095	0.0209	0.4399	**0.0021**	**0.0002**	**<.0001**	**<.0001**
EBCK9M				0.5297	0.3872	**0.0101**	0.1837	0.0454	**0.0005**	0.0885	0.4495	0.5653	0.5960	0.2891	0.1709	0.0295	**0.0037**	**0.0027**
EBCM3M					0.1385	**0.0017**	0.4779	0.1622	**0.0031**	0.0216	0.1691	0.2313	0.9213	0.0944	0.4532	0.1141	0.0198	**0.0149**
EBCM6M						0.0779	0.0309	**0.0052**	**<.0001**	0.3912	0.9128	0.7704	0.1659	0.8429	0.0281	**0.003**	**0.0003**	**0.0002**
EBCM9M							**0.0002**	**<.0001**	**<.0001**	0.3545	0.0619	0.0414	**0.0023**	0.1158	**0.0002**	**<.0001**	**<.0001**	**<.0001**
EBCP3M								0.4851	0.0206	**0.0033**	0.0398	0.0596	0.4193	0.0192	0.9675	0.3763	0.0968	0.0771
EBCP6M									0.098	**0.0004**	**0.0070**	**0.0113**	0.1353	**0.0030**	0.5108	0.8506	0.3276	0.2761
EBCP9M										**<.0001**	**<.0001**	**<.0001**	**0.0023**	**<.0001**	0.0228	0.1407	0.4889	0.5613
GMCK3M											0.3343	0.2522	0.0274	0.5087	**0.0029**	**0.0002**	**<.0001**	**<.0001**
GMCK6M												0.8553	0.2010	0.7584	0.0363	**0.0041**	**0.0004**	**0.0003**
GMCK9M													0.2712	0.6244	0.0546	**0.0068**	**0.0007**	**0.0005**
GMCM3M														0.1147	0.3964	0.0939	**0.0154**	**0.0116**
GMCM6M															0.0173	**0.0017**	**0.0001**	**<.0001**
GMCM9M																0.3984	0.1049	0.0839
GMCP3M																	0.4279	0.3663
GMCP6M																		0.9110

Significant differences are indicated by bold type. Bonferroni adjusted alpha value is 0.05/3 = 0.0167 (based on planned comparisons) Co: non-irradiation, GM: gamma irradiation, EB: electron beam irradiation, CP: uncoated cellophane, CM: nitrocellulose coated cellophane, CK: PVdC coated cellop

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