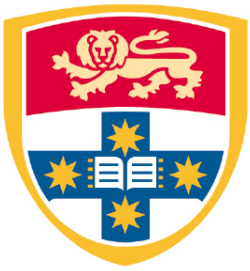

THE UNIVERSITY OF SYDNEY

Purification and Modification of a Biodegradable, Carbone Dioxide Based Polymer: A Sustainable Solution to Reduce Consumption of Non-degradable Plastics

By

Bahareh Bahramian

A DISSERTATION SUBMITTED IN FULFILMENT OF THE REQUIREMENTS FOR THE DEGREE OF DOCTOR OF PHILOSOPHY

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DECLERATION

I hereby declare that this submission is my own work and that, to the best of my knowledge and belief, it contains no material previously published or written by another person nor material which to a substantial extent has been accepted for the award of any other degree or diploma of the University or other institute of higher learning, except where due acknowledgment has been made in the text.

Bahareh Bahramian

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LIST OF PUBLICATIONS

Provisional Patent

1) F. Dehghani, **B. Bahramian**, Method of extracting impurities from plastic materials, Provisional Patent No. 2016901288.

Book chapter

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Journal Papers

1) **B. Bahramian**, Y. Ma, R. Rohanizadeh, W. Chrzanowski and F. Dehghani, "A New Solution for Removing Metal-Based Catalyst Residues from a Biodegradable Polymer" Green Chemistry, 2016 ,**18**, 3740-3748 (IF: 8.506)

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2) **B. Bahramian**, Y. Ma, F. Dehghani, "Development of an Antimicrobial and Biodegradable Polymer for Biomedical Applications" ICMAT2015, 28 Jun- 3 July 2015, Suntec, Singapore

3) **B. Bahramian**, Y. Ma, F. Dehghani, “Assessing the Properties of Poly(Propylene Carbonate) for Food Packaging Application” APSPIS2015, 20-22 Sep. 2015, Sydney, Australia
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ABSTRACT

The aim of this study was to develop a benign process for the removal of metal residue and other impurities from biodegradable poly(propylene carbonate) (PPC) to broaden its applications. This study demonstrated that the properties of PPC are favourable for fabrication of medical devices and food packaging products. For Instance, mechanical properties of PPC were either comparable or superior to commercial polymers such as low density polyethylene and polybutyrate adipate terephthalate (Eco-Flex). More importantly, permeability of PPC to oxygen and moisture was remarkably lower than these polymers. Furthermore, PPC was chemically stable in food simulated media such acidic or alkaline pH and fatty food.

The high level of zinc glutarate, a metal-based catalyst, in PPC was remarkably reduced by using a novel technique in which CO_2 laden water at high pressure and moderate temperature was used as a solvent. The extraction efficiency of this method at 45 ˚C and 70 bar was nearly 90% that was two-fold higher than using an acidic solvent for removing zinc residue. Additionally, at these conditions other impurities such as cyclic propylene carbonate were removed from PPC that further promoted the physico-mechanical properties of this polymer. For example, the thermal decomposition temperature of PPC was shifted from 124˚C to 214˚C and its mechanical strength was enhanced by 40%.

The results of this study showed that plasma surface modification was an efficient method for the chemical immobilization of thymol as an active, naturally derived, antimicrobial compound on the surface of PPC. The process parameters were optimized to achieve high loading efficiency. The results of bacterial counting and bacteria inhibition zone showed that the thymol immobilization was efficient when using plasma at high energy for a short period of 15 minutes.

In summary, this study led to design of two benign processes for removing zinc residues from PPC and surface modification to form an antimicrobial surface. Reduction of zinc residue in PPC below the acceptable range for composting

foster the application of this biodegradable polymer for a broader range of products. Antimicrobial and biodegradable plastics that eradicate the use of antibiotics, preservatives and metal nano-particles are attractive for manufacturing of biomedical devices and food packaging. Commercialization of the technology developed in this study will be of great value for reducing the disposal of non-degradable polymer in landfills that is one of the huge environmental issues.

Table of Content

Table of Figures

List of Tables

Chapter 1. Introduction

The growing application of synthetic plastics in recent decades has caused severe environmental issues. According to the United States Environmental Protection Agency, more than 12% of municipal solid waste (MSW) in 2012 were plastics [1]. Almost same share for plastics in MSW was reported for Australia [2]. Among this amount, 35-40% was used in packaging industry [3]. There is a shortage of space for landfills in many countries. Moreover, accumulation of a huge amount of wastes in landfills contributes in greenhouse gases (GHGs) emission and global warming [4]. Conventional plastics are mostly non-degradable and resistance to chemical and physical decomposition [5]. They usually remain in the environment for hundreds of years and accelerate landfilling problems. Replacing non-degradable conventional plastics with biodegradable plastics is a solution to tackle the issue of solid waste management. Particularly, biodegradable polymers synthesized from carbon dioxide as a renewable feedstock are promising materials to mitigate the growing environmental obstacle with the emission of carbon dioxide as one of the main green house gases [6].

Poly (propylene carbonate) (PPC) is a biodegradable polymer that is synthesized by copolymerization of CO_2 and propylene oxide (PO). In the presence of bioactive compounds such as enzymes, PPC degrades into water and CO_2 [7]. Therefore, the synthesis and application of PPC can have a significant impact on the environment by utilizing CO_2, a major green house gas, as a monomer and inhibiting its accumulation in the atmosphere.

The key criteria for selection of a polymer for packaging are transparency, biodegradability, and high resistivity to oxygen and water penetration. While PPC has favorable characteristics for packaging; it has not yet been accepted as a compostable polymer due to the presence of residues of by-product (cyclic propylene carbonate) and 2500 ppm of zinc glutarate catalyst [8]. Current methods for removing catalyst residue from PPC are not efficient and economically viable for large scale manufacturing due to the consumption of a high amount of organic solvent and acidic media, also multiple step operations.

Besides, these methods require further solvent recovery which is usually energy intensive.

It is critical to use plastics that are safe and preserve the quality of the product and prevent it from microbial contamination [9]. For example, the manufacturers nowadays seek more innovative approach such as smart or active packaging [10, 11]. This approach is more desirable when the active material is fabricated by natural based and non-toxic natural compounds such as essential oils [12, 13].

To avoid the concerns contributed by the migration of the antimicrobial agent to the product, the active compounds are immobilized and attached on the surface of packaging material [14]. Plasma treatment is commonly used for activation of inert surfaces of polymers and covalent bonding between some antimicrobial agents and a polymer [15, 16]. Therefore, the antimicrobial active compound is attached to the polymer surface with less risk of transfer to the food product.

The aim of the current research was to assess the potential of PPC for broad range of applications such as food packaging application. To this end, first, the physico-mechanical properties of PPC were measured and compared with commercial non-degradable and biodegradable polymers that are currently used in the market. In the second step, it was attempted to design a benign and low cost process for removing catalyst residue from PPC and improve its physico-chemical properties. Finally, antimicrobial films were fabricated from PPC by adding thymol as a benign, natural essential oil.

This dissertation is comprised of 10 chapters. In chapter 2 to chapter 4, an overview was provided about biodegradable polymers and the different techniques for their purification. In addition, examples of active packaging materials are discussed briefly. Following this, the research hypothesis and analytical methods were elaborated in chapter 5. The physico-mechanical properties of PPC were measured and compared with some commercially available polymers in food processing in chapter 6. Furthermore, a benign,

solvent-free method for purification of PPC and extraction of its metal-based catalyst residue was designed and established in chapter 7. In chapter 8, antimicrobial films of PPC were fabricated using direct incorporation and physical coating of thymol. Chapter 9 aimed to fabricate antimicrobial PPC films for food packaging by plasma treatment followed by thymol immobilization. Moreover, the migration of the thymol from the PPC surface into the food stimulated media and the biological activity of the PPC surface after thymol immobilization were assessed. Finally, in chapter 10, the overall conclusions and recommendations for future studies are presented.

Chapter 2. Biodegradable Polymers

2.1 Introduction

Disposal of non-degradable polymers that is 12% of municipal solid waste (MSW) is a major challenge due to the limited availability of landfill sites and their negative impacts on the environment and ecosystems [1]. Moreover, accumulation of a huge amount of wastes in landfills contributes in greenhouse gases (GHGs) emission and global warming [4]. It is estimated that 35-40% of plastics produced globally are consumed in the packaging industry, which is mostly for food products [3]. Conventional plastics are mostly non-degradable and resistance to chemical and physical decomposition [5]. Therefore, development of a new generation of eco-friendly plastics which are degradable can be a promising approach to address such an environmental issue. Biodegradable polymers are either synthetic or from natural sources such as plants or animals [17]. Synthetic biodegradable polymers such as poly(caprolactone) (PCL) are mainly made from fossil based monomers [18-20]. Therefore, mass production of these plastics results in depletion of natural resources. On the other hand, natural polymers are compostable and degrade simply by biological systems such as bacteria. Nevertheless, they usually have low mechanical properties and suffer from poor barrier properties [21]. Therefore, renewable, biodegradable polymers have attracted attention as an alternative to conventional non-degradable polymers. Poly(propylene carbonate) is an aliphatic polycarbonate synthesized from alternating copolymerization of carbon dioxide and propylene oxide (PO) [22]. In landfill condition, PPC is degraded into water and CO_2 via enzymatic degradation. In addition, its permeability to oxygen and water vapor, transparency and some other physical properties are comparable with polymers that are currently used in many industries for food packaging [23]. Consequently, it may be considered as an alternative polymer to reduce CO_2 emission via converting this gas to PPC and alleviate the problems exists with synthetic polymers. In this chapter, different categories of biodegradable polymers are reviewed. In addition, PPC as an alternative polymer for food packaging is introduced, and its physical and mechanical properties are evaluated.

2.2 Role of Plastics in Packaging Industry

Physico-chemical protection, seals appealing and recognition and extending the shelf life are the main roles of packaging materials [24]. Packaging has different functions for the end product [25].

- **Primary packaging:** It is closest part of packaging to the finished product and usually determine sales unit of the product (e.g. bottle of coke, can of sweet corn),
- **Secondary packaging:** This part of packaging is to assist carrying large quantity of the goods (e.g. Dozen boxes of packed biscuits),
- **Tertiary packaging:** Usually is used to facilitate transportation of the product (e.g. pallets and wraps).

Primary packaging that is taken with the product by the end user is usually contaminated with the product and mixed with a broad range of additives. Therefore, primary packaging should be designed for single use only and will be disposed of after a useful life time of the packed product [26].

Since the earliest usage of leaves, hollowed-out tree limb and skins as packaging materials, several attempts have been made to create more complex containers to protect food products [27]. Papers, glasses, metals and plastics are major categories of materials that have been applied for packaging of food products [28]. Low cost mass production of glassware dates back to early 20^{th} century [28]. Since then, glass bottles and containers have been counted as key products for food packaging. Due to its resistivity to water and chemical diffusion, glass can keep the packed food fresh for a long time. Nevertheless, heavy weight and low breakage resistivity limit its applications in the food industry [28]. Papers and paperboards also have been a major part of food packaging industry for a long period [28]. Paper-based packaging products are mostly low cost, light weight and printable. However, they are not resistance to the penetration and migration of water, oil and other food products [27]. Metals are also widely used to manufacture canned food products. Metals provide a good physical protection for

a food product. In addition, due to high heat transfer, canned food can be heat treated and sterilized in high temperatures that provide a long shelf life of up to 5 years for the food product [27]. However, corrosion is the major drawback of metal containers for food packaging applications. The presence of some acidic compounds in food products leads to oxidation of the metal packaging and contamination of the food which is harmful to human health. Plastics are the youngest group of material in this category. Owing to their desirable properties, plastics have been introduced as an alternative to conventional packaging materials including metals, glasses, papers, etc. They are cheap, light, soft, transparent and highly resistance to corrosion. Plastics are flexible, easy to be molded and formed into any shape using low energy intensive processes [29]. Moreover, their physico-mechanical properties can be tuned. For instance, they can be improved in term of mechanical properties to be applied as carrier bags or can be modified to reduce the oxygen or moisture permeability for food packaging [30].

2.3 Environmental Issues with Over-Consumption of Plastics

Around 50% of plastics are applied to manufacture single-used items, which are disposed after applications [31]. For instance, according to the Annual Report of Australian Packaging Covenant (APC) 514,000 tons of plastic materials are used for packaging application every year in Australia, out of which only 42% is recycled, and the rest 58% is disposed in the landfills [32]. Plastic materials are mostly non-degradable that have a long life-time. They do not degrade in the environment, instead, disintegrate into small pieces that can be carried to everywhere and contaminate water and soil. Moreover, a wide range of plastics are derived from non-renewable fossil fuel sources. Over-consumption of this materials leads to depletion of natural sources. [25]. Therefore, mitigating rules are created to minimize the consumption of plastics [33]. Re-use, energy recovery, recycling and composting are some of the strategies that can minimize the environmental impacts of plastic consumptions.

- **Re-use:** There was a conventional strategy in which the glass bottles were collected and refilled by manufacturers. This method still exists in some European countries which refill PET bottles. However, it can be only used for local markets and cannot be applied in large scale [26].

- **Energy recovery:** It is the process of incineration of the dry part of municipal waste to recover its energy content and apply this energy as an alternative to fossil fuels for power generation. The presence of hazardous additives and possibility of their release in the atmosphere are the limitations of this strategy for plastic materials.

- **Recycling:** Converting a waste material to a new applicable product is called recycling. This process consists of several steps including collection, sorting, size reduction, cleaning and re-processing [25]. Plastic goods are usually multi-component polymers, which are mixed with other additives such as adhesives, fillers, colors, metal and papers. At the first step, the plastic parts of a waste product are separated. Then, the polymeric parts are sorted according to their chemical composition, which is the most challenging part of the process. At this stage, the recycling resin needs to be completely separated from all additives and contaminants [24]. Inefficient separation leads to a significant decrease in the physico-mechanical properties of the recycled product. In the next stage, recycling polymers are washed and cleaned to remove all food residues and then are processed to fabricate new products. This process requires a huge amount of water (2-3 m^3 per ton of plastic material [25]). Furthermore, significant resources of fossil fuel are used to melt the polymeric materials during the recycling process. These issues limited the recycling rate of plastic materials to lower than 50% of total plastic waste production per annum.

- **Composting:** Replacing conventional, non-degradable plastics with biodegradable and compostable polymers is a new approach to mitigate the environmental impact of plastic wastes. These types of materials are mostly made of renewable and natural sources, which can be degraded in the environment after disposal [34]. The polymers are digested and degraded in soil into non-hazardous and safe by-products such as water, carbon dioxide and biomass.

2.4 Biodegradable or Compostable Polymers

The term biodegradability is the capability of organic materials to be decomposed by microorganisms and biological systems such as enzymes, bacteria, fungi [5]. Products of biodegradation are mostly water, carbon dioxide, and biomass [18]. According to British Standard, EN13432:2000 (Requirements for packaging recoverable through composting and biodegradation. Test scheme and evaluation criteria for the final acceptance of packaging) and Australian Standard, AS4736 (Biodegradable plastics suitable for composting and other microbial treatment) specifications for biodegradable plastics are [35]:

- Minimum of 90% biodegradation of plastic materials should be completed within 180 days in compost,
- Minimum of 90% of plastic materials should be disintegrated into less than 2mm pieces in compost within 12 weeks,
- There should be no toxic effect of the resulting compost on plants and earthworms,
- Hazardous substances such as heavy metals should not be presented above the maximum allowable levels as specified in Table 2.1,
- Plastic materials should contain more than 50% organic materials,

Table 2.1 Maximum element content of plastics according to EN13432:2000 [36]

Element	ppm on dry substance	Element	ppm on dry substance
Zn	150	Cr	50
Cu	50	Mo	1
Ni	25	Se	0.75
Cd	0.5	As	5
Pb	50	F	100
Hg	0.5		

Humidity, temperature and level of microorganism are the most important factors influencing the rate of biodegradation [29]. In the first step of biodegradation, polymeric materials break into smaller parts such as low molecular weight chains, oligomers and monomers. After which degradation process takes place either aerobic or anaerobic. The aerobic mechanism is degradation in the presence of oxygen that results in the formation of products including water, carbon dioxide and biomass [37]. However, in an anaerobic process that occurs in the absence of oxygen, methane is also one of the products of biodegradation [5]. The biomass produced from aerobic mechanism replaces other synthetic fertilizers from petrochemical sources. It helps plants growth and results in carbon dioxide consumption through photosynthesis [38]. During photosynthesis, renewable raw materials including starch, cellulose and oil are produced. The renewable raw materials are converted to degradable plastics and then recycled to nature during the composting process [29].

2.4.1 Classifications of Biodegradable Polymers

Biodegradable polymers are classified into two major categories, natural based biodegradable polymers and synthetic polymers from either petroleum or renewable sources [17].

2.4.1.1 Natural Based Biodegradable Polymers

These classes of polymers are made of natural macromolecules that are found in plants or animal bodies. Natural polymers are mostly compostable and are degraded simply by natural biological activities. The main categories of the natural polymers are including polysaccharides, proteins and lipids [39].

Polysaccharides are carbohydrates from the repetition of saccharin units. The molecular structure of polysaccharides is usually linear; however, different forms of branching are also detected. These types of material are mainly hydrophilic components and not resistance to water diffusion [21]. The most commercially used polysaccharides are starch, cellulose and their derivatives, which are commonly found in agricultural products such as corn, potato, rice and wheat. Starch derived from different resources may have different molecular structures and physico-mechanical properties. However, this natural polymer has low mechanical properties and is extremely hydrophilic that is not desirable for some applications such as packaging. Therefore, physical, chemical or mechanical modifications have been made to improve the properties of starch. For example, clay nanoparticles were mixed with starch to produce biodegradable nanocomposite films [40]. It was shown that starch phase and clay particles had a good interaction that led to the homogenous dispersion of nanoparticles in the polymer. As a result, starch was improved in term of mechanical properties. To modify starch, it is blended with different synthetic and natural, biodegradable polymers [41]. For example, starch was blended with low density polyethylene (50: 50 mass ratio) and the mechanical properties of this blend was two-fold higher than neat starch [42-44]. Chitosan as another example of polysaccharides has been used for food packaging. Cross-linked chitosan-polyvinyl alcohol was used for packaging of tomato [45].

Proteins and lipids have either agricultural or animal based origins. The most commercially used agricultural based proteins are soy and corn protein and wheat

gluten [38]. Moreover, gelatin is one of the most abundant animal based proteins that are industrially used as biodegradable polymers [21]. Lipids such as waxes, triglycerides, fatty acids, fatty alcohols and sucrose fatty acid esters are also used as edible, biodegradable polymers for many applications. For instance, lipid films have advantages in packaging material especially for food products due to their hydrophobic nature which makes them resistance to water diffusion. A layer of lipid film on the surface of food or pharmaceutical products acts as a moisture barrier. However, this class of biodegradable plastics have low resistivity to oxygen permeation and suffer from low mechanical properties [21].

Innovative natural polymers were applied for packaging of food products. For instance, edible coatings of natural polymers such as chitosan, lemon and orange extracts were applied as a barrier to protect the food from the environment and extend the shelf life [46, 47]. Chitosan-based edible coating was used to increase successfully the shelf life of strawberries from 10 days for the uncoated sample to 21 days [48]. These edible coatings inhibited the penetration of oxygen and humidity to the food and limited the microbial growth. The citral compound of lemon grass was used in combination of the alginate-based edible coating to coat the fresh-cut melon [49]. The incorporation of this active compound into the edible coating prolonged the shelf-life of the fruit by more than 20 days. Indeed, citral is the active antimicrobial compound of lemon grass essential oil that plays the main role in inhibition of bacteria growth. To conclude, despite their biodegradability, availability and low cost, natural polymers suffer from high permeability against water and gases such as air and oxygen. Moreover, they have poor mechanical properties that limit their applications for packaging of food products.

2.4.1.2 Synthetic Biodegradable Polymers

Synthetic biodegradable polymers are used in a broad range of applications such as packaging, agriculture, medicine, and biomedical. They are produced from the

polymerization of either synthetic, petroleum-based monomers or renewable, bio-based monomers.

- **Petroleum based biodegradable polymers** possess a wide variety of physical properties and are made of a large number of synthetic monomers based on fossil fuel sources [18]. Polycaprolactone (PCL) is one of the most widely used examples of nonrenewable based polymers. High mechanical properties, water resistivity, low viscosity and desirable processability are features that make PCL a favorable alternative to conventional polymers such as polyethylene, polypropylene and polystyrene [50, 51]. However, PCL suffers from low degradation rate [52]. Therefore, PCL was blended with a different type of natural polymers such as starch and chitosan to compensate this shortage. These resulted blends were applied for food packaging application [52]. Aliphatic copolyesters from copolymerization of diols, and dicarboxylic acids are other examples in this category. The combination of therphetalic acid with a broad range of aliphatic monomers leads to aliphatic-aromatic copolymers with different degree of degradability [19] [20]. The produced copolyesters showed physico-chemical advantages of polyethylene terephthalate together with biodegradation of polyesters. These features make them favorable for food and pharmaceutical packaging. However, production of these polymers in large scale leads to depletion of fossil fuel resources.

- **Renewable based biodegradable polymers:** The renewable sources of these biodegradable polymers are monomers derived from plants, animals or bacteria. Poly (lactic acid) (PLA) is the most common example in this group. It is synthesized by polymerization of lactic acid, a monomer derived from fermentation of carbohydrates such as corn [38]. PLA has outstanding physico-mechanical properties such as transparency, high mechanical properties, processability and water resistivity that make this polymer applicable in a wide range of application such as pharmaceutical and biomedical applications [29]. An advantage with this polymer is that the

degradation process can simply take place by hydrolysis reaction of the ester bond in the polymer structure [53]. The degradation period is between 6 to 24 months. Polyhydroxyalkanoates (PHAs) are another group of renewable based polymers which are synthesized by the fermentation process of sugars and lipids. A Large variety of PHAs is biosynthesized from different sugars, lipids and microorganism used for synthesis [38]. PHAs are completely degradable polymers and have been used as short term packaging products [29]. Brittleness is the major shortfall of these polymers that limits their application as packaging material [54].

CO_2 is one of the renewable sources of carbon for synthesizing of biodegradable polymers. It is an available, cheap, inert and non-toxic component that can be an alternative for fossil fuel source feedstock [55]. Furthermore, utilization and fixation of carbon dioxide into applicable and valuable products is a key to solve the issue of growing concentration of CO_2 in the atmosphere [6]. Direct copolymerization of CO_2 and epoxides such as propylene oxide, isobutylene oxide and cycloheptene oxide results in the formation of polyalkalene carbonates, which is a typical example of fixing CO_2 in polymers [55].

2.5 Poly (Propylene Carbonate)

Poly (propylene carbonate) is an aliphatic polycarbonate synthesized from alternative copolymerization of carbon dioxide and propylene oxide (PO). PPC was first synthesized in 1969 using a mixture of diethyl zinc and water as a catalyst [22]. Applying CO_2, a renewable, available and cheap component as feedstock to produce PPC is a key to meet sustainability requirements as it lowers reliance on fossil fuel based raw material. In addition, fixing CO_2 into useful polymers contributes in mitigating global warming effects [56]. Moreover, PPC, similar to other CO_2 based polymers is a biodegradable component.

Consequently, consumption of PPC as an alternative to conventional polymers addresses current issues of municipal waste management [56].

2.5.1 Physico-chemical Properties of PPC

PPC is a hydrophilic polymer, which is soluble in non-polar solvents like acetone, dichloromethane, tetrahydrofuran and chloroform, but is not soluble in polar solvents including water, methanol and ethanol. Its molecular structure is shown in Figure 2.1. This polymer has an amorphous structure with a glass transition temperature (T_g) of 25-40 ˚C [57].

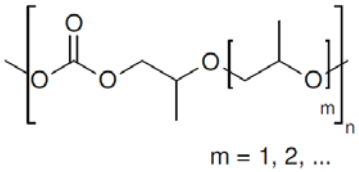


Figure 2.1. Molecular structure of PPC

The result of NMR tests illustrated that the backbone of the polymer chain mostly consists of carbonate linkages between PO and CO_2 molecules. In addition, there are ether linkages from the homopolymerization of PO molecules that are randomly distributed among the polymer chains (Figure 2.2) [58]. The percentage of ether linkages on the polymer backbone governs physical and mechanical properties of the polymer. For example, increasing the percentage of ether linkages in the polymer structure results in decreasing T_g and decomposition temperature of PPC [59]. With a completely alternated structure, it was proved that PPC can be treated and processed at a temperature above 160˚C [60]. CO_2 pressure, PO concentration and catalyst activity and selectivity play critical roles in the formation of polymer structure and percentage of the ether linkage [61].

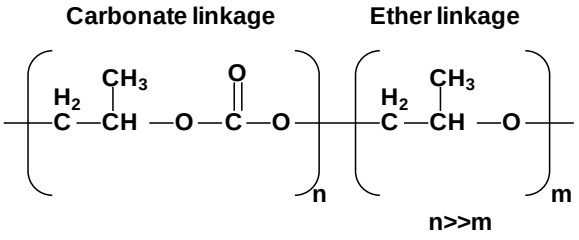


Figure 2.2. Schematic of carbonate and ether linkages of the PPC backbone

2.5.1.1 Thermal Behavior

Thermal degradation is an important factor that impacts the processability of PPC. Indeed, processing of PPC at high temperatures (above 200˚C) is not feasible due to its low degradation temperature that is within the range of 150 to 180˚C depending on the structure of the polymer backbone [62]. Thermal decomposition of PPC occurs following two main mechanisms. The first mechanism which usually takes place at lower temperatures of around 200˚C is attributed to chain unzipping reaction. At this step, the most reactive end groups in the polymer structure including hydroxyl groups disintegrate from the main chain [56]. Chain unzipping is followed by random chain scission mechanism at higher temperatures that result in scission of the main chain [59]. Chain unzipping is usually controlled effectively by increasing molecular weights and decreasing unstable end groups [59, 63]. With higher molecular weights, the amount of active terminal groups are reduced, which leads to bypass chain unzipping reaction. Several methods enhanced the thermal degradation temperature of PPC. For instance, Lai *et al.* synthesized maleic anhydrate (MA) end-capped PPC to improve its thermal degradation temperature. They demonstrated that, for MA-capped PPC, 95% mass loss temperature was 22.4˚C higher than neat PPC. Furthermore, the presence of metal residue affects its thermal degradation [8]. For example, the reduction of metal residue results in 85˚C shift in degradation temperature [8]. Therefore, thermal degradation of PPC is tuned by purification and removing metal residues.

2.5.1.2 Mechanical Properties

The amorphous structure of PPC leads to significant reduction in its mechanical performance around glass transition temperature [56, 64]. Furthermore, PPC has relatively poor mechanical properties at room temperature due to its low T_g that is in the range of 25 to 40˚C [65, 66].

Different methods have been used to improve mechanical properties of PPC such as chemical modification with end capping groups and physical blending with other polymers or fillers. Yao *et al.* used maleic acid (MA) as the end capped flexible end groups on the polymer structure and demonstrated that the tensile strength of PPC containing the optimum ratio of 0.5% of MA, increased 9-fold compared to neat PPC [67]. In the second approach, PPC was physically blended with polylactic acid (PLA), which resulted in higher Young's modulus of 32 times higher for PPC/PLA blend comparing to neat PPC [68]. Furthermore, exfoliated graphite (EFG) as inorganic filler was added to PPC structure by solvent casting method to prepare nanocomposites. It was shown that 2wt% of EFG could increase the tensile strength of PPC two-fold [66]. Degradable and natural polymers are the preferred types of fillers for PPC. The major advantages of natural fillers are their renewability and biodegradability. Therefore, the presence of these additives will not delay biodegradation of PPC. Moreover, natural fillers are usually abundant and cheap, with high specific strength and modulus and easy to be processed [69]. A wide range of natural fillers are used as reinforcing agents for plastics such as cotton, chitin, chitosan, wood derivatives, cellulose and starch [70]. For instance, cellulose and its derivatives that are used in a wide range of applications such as pharmaceutical, paper, wood manufacturing, clothing and packaging industry were used as filler for PPC [71]. Cellulose nanocrystals (CNCs) as novel bio-fillers were used to enhance mechanical properties of PPC [65]. CNCs are bio-based and biodegradable fillers with high mechanical properties, high surface area, low density and low thermal expansion coefficient. It was demonstrated that the presence of only 1 wt% of CNCs accelerated the tensile strength and Young's modulus of pure PPC from 1.8 and 2.1 to 19 MPa and 1414 MPa, respectively. Xing *et al.* showed that the addition of cellulose acetate butyrate (CAB) into PPC (PPC/CAB = 50/50 (wt%)) enhanced the tensile strength by 21-fold and modulus of PPC by 28-fold [72].

Starch as light weight natural filler was applied to reinforce PPC. Starch is a cheap, abundant, renewable and biodegradable polymer which can be derived from a wide range of crops including wheat, corn, and potato [73]. Starch was first used for modification of polyethylene in the 1970s [74]. Natural starch is a hydrophilic and water soluble compound. Therefore, as filler in PPC structure, presence of starch result in enhancing water sorption and hydrolysis [75]. The enhancement of mechanical properties of PPC by addition of starch is attributed to a hydrogen bond between hydroxyl groups of starch with carbonyl groups of the polymer [76]. In addition, the tensile strength of PPC/70 wt% starch composites increases 23% compared to neat PPC [74]. Starch acetate (SA) is less hydrophilic and can be used as an alternative additive to prepare more homogenous composite structure [75]. The tensile strength of PPC/ 20 wt% SA was shown to be 50% higher than neat PPC. Therefore, mechanical properties of PPC can be tuned by changing the type and concentration of fillers.

2.5.1.3 Biodegradation

The degradation of PPC at different conditions is examined [57]. The PPC's degradation rate depends on media, pH, temperature, moisture, and microorganism colony formation unit. The degradation of PPC in soil or composting condition is a critical factor to pass the standards of biodegradable plastics [35]. Du *et al.* 2003 studied soil burial and buffer solution immersion of PPC film with the molecular weight of 50-65 KDa the thickness of 40-50 μm [77]. They showed that within this range of molecular weight, the soil burial degradation of PPC was only 3.5 wt% within six months. However, degradation of PPC with same molecular weight in a buffered solution was 2-fold compared to the soil burial method, after a period of 6 months [77]. The result of another study in the standard composting condition for a 300 μm film of PPC with high molecular weight of 670 KDa demonstrated considerable decomposition of 38% after nearly 70 days [57]. It was demonstrated that the decomposition rate of the polymer increased with time and reached 63% after 95 days. However, this

degradation rate of PPC is still relatively lower than what is required by standards for compostable plastics which is 90% decomposition within 180 days [35]. Therefore, it was considered that the addition of starch as a hydrophilic filler helps PPC to degrade faster [78]. Lu *et al.* prepared different composition of PPC/starch with various polymer/filler weight percent and studied the effect of starch content on burial degradation of PPC [78]. They showed that, in the presence of 70% starch, up to 95% of PPC composite degraded after 180 days soil burial due to increase in hydrophilicity of the composite.

Enzymatic degradation is another crucial factor, particularly when applying a polymer for biomedical application. Enzymatic degradation of PPC in the solution of 18 different enzymes was the subject of a study carried out by Hwang *et al.*2006 [79]. They demonstrated over 9% degradation of PPC in the presence of 0.25 mg/1.0 ml of Esterase/lipase ColoneZyme after 10 days. Moreover, enzymatic decomposition of PPC was proved *in vivo* in mice body by surface erosion mechanism [80]. Altogether, it can be concluded that, in a potent condition, PPC can be degraded either in the composting environment or the presence of enzymes.

2.5.1.4 Barrier Properties

High barrier properties are key factors for a material when it is used for some applications such as packaging. Gas barrier properties of PPC comparing to conventional polymers used for packaging applications is shown in Table 2.2. As shown in Table 1-3, PPC not only has higher water and oxygen resistivity compared to PLA, a commonly used biodegradable plastic but also possesses comparable barrier properties to other non-degradable polymers such as polyethylene and nylons. Despite acceptable barrier properties of PPC, they are some methods that even improve them. Lee *et al.* showed that the water and oxygen permeability of PPC could be reduced by incorporating of exfoliated graphite nanocomposite nanoparticles as filler [66].

Table 2.2 Gas permeability data of common plastics for packaging applications

Polymer	H_2O ($g/m^2/day$)	O_2 ($cm^3/m^2/day/atm$)
Nylone 6 [81]	260	45
Nylone 66 [81]	180	80
High density polyethylene (HDPE) [81]	9	3000
Low density polyethylene (LDPE) [81]	18	8000
Polypropylene (PP) [82]	6	1150-2480
Polystyrene [82]	109-155	3100-4500
polyethylene terephthalate (PET) [82]	16-23	50-90
PPC [56]	40-60	10-20
Polylactic acid (PLA) [56]	325	550

2.5.2 PPC Synthesis

PPC is synthesized by copolymerization of CO_2 and PO. Since epoxies such as PO are extremely active components, the challenge in the synthesis of PPC is the activation of CO_2 as a thermodynamically stable molecule to initiate the polymerization. It is pivotal to select an active low-cost catalyst with low toxicity and high selectivity to minimize byproducts that are relatively more stable than PPC [57].

One common mechanism proposed for the copolymerization of CO_2 and epoxides is coordination-insertion mechanism catalyzed via metal compounds with Lewis acid and Lewis base active sites [83, 84]. In the coordination step, the epoxide molecule is coordinated by the metallic centre of a catalyst (Lewis acid active site) and then attacked by nucleophile site (Lewis base site) and undergone ring opening to form metal-bound alkoxide [83]. The nucleophilic attack can take place either by the nucleophile active site on the metal catalyst (bifunctional homogenous catalysts) or a separate compound (binary catalysts) and resulted in activation of alkoxide [85]. CO_2 molecule then inserts into the metal-oxygen bond and initiates the reaction by formation of metal carbonate. Up to this stage, all the steps are associated with the activity of the catalyst; however, the pathway of the reaction after this step relies on the selectivity of the catalyst. In fact, selectivity is

a function of the alkoxide type. Commonly, the metal carbonate goes towards its ring closure and forms propylene carbonate or propagates by multiple coordination and insertion of CO_2 and produces polycarbonate chain [86]. If the second pathway is followed by the alternative coordination-insertion mechanism, the resulted polycarbonate has 100% carbonate linkage in its structure; however, some catalysts can also homopolymerize epoxides and form ether linkages on the backbone of the polymer [83]. The schematic of suggested coordination-insertion mechanism for the copolymerization of epoxides and CO_2 is demonstrated in Figure 2.2.

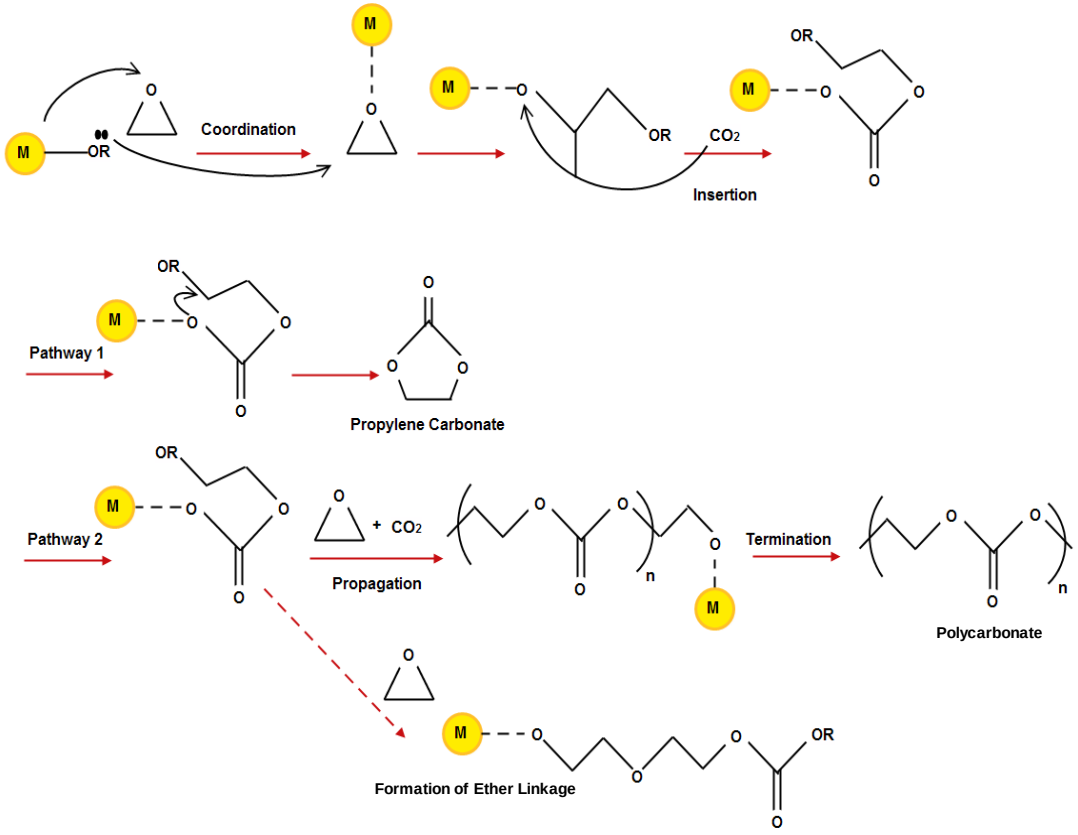


Figure 2.3. Coordination–insertion mechanism suggested for the copolymerization of epoxides with CO_2

2.5.2.1 Catalyst Systems for CO_2/PO Copolymerization

Since 1696 when PPC was first synthesized, many efforts carried out to find and improve several catalysts to enhance the yield of copolymerization and the quality

of the polymer. These systems can be mainly classified in two broad categories of homogeneous and heterogeneous catalysts. When the reaction takes place in the same phase with catalyst, the system is called homogenous. In contrast, when the phase of reaction and catalyst are different, the catalyst system is heterogeneous.

- **Homogeneous catalytic systems:** Triphenylposphate (TPP) compounds, metal complex catalytic systems and metal-salen complexes are different types of homogenous catalytic systems for copolymerization of CO_2 and PO. TPP compounds with a metal atom in the center were the first group of homogeneous catalytic systems reported for copolymerization of CO_2 and epoxies [87, 88]. These compounds are highly active catalysts; however, the copolymerization in the presence of TPPs is very slow, and it takes more than a week to accomplish the copolymerization. A number of other metal complexes catalytic systems such as Phenoxide [89-91] and β-Diiminate (BDI) [86, 92] were investigated regarding their activity for copolymerization of CO_2 and epoxies. They showed activity in the copolymerization of CO_2 and CHO. However, their selectivity for CO_2-PO copolymerization was relatively low. The early studies of metal-salen complexes were to create a catalytic system to synthesize poly(cyclohexen carbonate) [93]. After that, efforts carried out to develop more selective catalysts for PPC synthesis [94, 95]. Many research activities have focused on the area of homogeneous catalysts for CO_2-epoxide copolymerization. However, none of them have been well established so far. The reason is that most of these systems required complicated synthesis process and condition to be selective toward PO copolymerization with CO_2. Therefore, traditional catalysts have remained the topic of many studies.

- **Heterogeneous catalytic systems:** Organometallic compounds, double metal cyanide complexes (DMC) and rare earth metal catalysts are the main groups of heterogeneous catalysts that have been used to synthesis of PPC.

Organometallic catalysts were the first group of compounds that were recognized to facilitate copolymerization of CO_2 and PO. The combination of diethyl zinc ($ZnEt_2$) with water using dioxane as a solvent was used to catalyze PPC synthesis [22]. To address the issue of low catalyst activity, other hydrogen donor compounds rather than water have been used in combination with $ZnEt_2$ [96, 97]. It was found that hydrogen donor compounds with two or three active-hydrogen sites formed multi-site catalytic systems with higher activity and selectivity compared with mono-site components. Furthermore, a series of metal salts of acetic acid were applied to catalyze the copolymerization of carbon dioxide and PO [98, 99]. The combination of zinc hydroxide with dicarboxylic acids was investigated to have the potential to catalyze PPC synthesis [100]. Among all, catalyst system derived from zinc hydroxide and glutaric acid showed the highest activity. Ree *et al.* copolymerized PO and CO_2 using zinc glutarate (ZnGA) obtained from various zinc sources. As a result, zinc glutarate derived from zinc oxide and glutaric acid yielded the highest catalyst activity of 64 g /g of catalyst [101]. DMCs are the other group of catalytic components which efficiently catalyzed homopolymers of epoxides. $Zn_3[Co(CN)_6]_2$ was investigated as an active catalyst to promote copolymerization of CO_2 and PO [102, 103]. However, it was found that the system suffered from low selectivity at low temperatures and low activity at high temperatures [104]. Recently, Lee *et al.* reported a highly active and selective bimetallic cobalt-salen catalytic system [105]. The catalyst demonstrated an activity of 38,000 g PPC/ g metal, which is the highest activity reported so far. Rare earth metal catalysts showed an increase in selectivity and reduction in synthesis time for copolymerization of CO_2 with epoxides [106-108]. Yttrium carboxylate as a rare earth metal complex significantly improved carbonate linkage percentage on the PPC backbone [109]. A ternary catalytic system of rare earth complex, diethyl zinc and glycerin resulted in an extremely high molecular weight PPC [64].

Comparing all heterogeneous catalytic systems created so far, conventional zinc glutarate is the only catalyst that has been commercially used for alternative copolymerization of CO_2 and PO. Zinc glutarate appeared to be one of the most effective compounds regarding both catalyst activity and alteration selectivity [101, 110]. The optimum condition for the synthesis of PPC using this catalyst was 40-50 bar and nearly 60 ˚C [111]. ZnGA is cheap, non-toxic and easy to synthesize and yields PPC with relatively high molecular weight and carbonate linkage percentage [57]. This catalyst even is synthesized in high pressure CO_2 as benign and environmentally friendly reaction media [112]. However, its activity is still one or two orders of magnitude lower than the common catalysts used for the synthesis of conventional polymers [111]. Therefore, enhancement of catalytic activity of ZnGA was the topic of several studies [113-115].

2.5.2.2 Catalyst Activity of Zinc Glutarate

Particle size, crystallinity, microstructure and morphology are key factors influencing catalytic activity of zinc glutarate and yield of the final product. These characteristics are tuned by changing the source of zinc and glutarate in the synthesis process, particle size and purity of reactants, synthesis method, and process condition. Ree et al. studied the effect of various zinc sources on the catalyst activity of ZnGA [101]. Their results showed that the highest catalytic activity of ZnGA was achieved when zinc was derived from zinc oxide. Zinc glutarate from various sources of glutarate was synthesized in another study carried out with Ree *et al* [113]. Results of catalyst activity demonstrated that only ZnGA derived from zinc oxide, and glutaric acid yielded a considerable amount of PPC. Effect of zinc and glutarate source and synthesis media on the microstructure of ZnGA was also investigated in a study carried out by Kim *et al.*[114]. Zinc glutarate derived from the reaction of zinc oxide and glutaric acid synthesized in toluene showed the highest catalyst activity due to its lowest surface area with the best crystal perfection and highest crystallinity. It was

shown that crystal perfection and quality are more important factors than surface area to determine the activity of the catalyst.

Particle size and purity of reactants are other effective parameters on microstructure and activity of ZnGA [115]. It was shown that highly pure ZnO with largest particle size resulted in ZnGA with the best crystallinity but largest particle size. In addition, using the same grade of ZnO, catalyst synthesized via magnetic stirring method exhibited the best crystallinity and produced the highest yield of PPC with highest molecular weight. The effect of applying Pluronic PE6400 as an amphiphilic template in ZnGA synthesis to improve its microstructure was studied [116]. It was reported that in a mixture of ethanol/water as solvent using Pluronic PE6400, ZnGA with the highest crystallinity and surface area was prepared. The catalyst showed an activity of 83 g PPC/ g catalyst and improved PPC synthesis yield by 20%.

Optimization of the reaction condition was the subject of several studies with the aim of increasing of the polymerization yield. High yield of 126 g PPC/ g catalyst was reported for a zing glutarate supported on a perflourinated compound with PO/catalyst ratio of 200 ml/g under mechanical stirring [117]. An optimum PO/catalyst ratio of 312 ml/g resulted in PPC yield of 160 g PPC/ g catalyst for ZnGA prepared using ultrasonic stirring method [115]. The effect of pressure on copolymerization yield, product composition, molecular structure and thermal stability of PPC was investigated [118]. It was revealed that at lower pressures, increasing the reaction pressure led to accelerate copolymerization rate. However, at higher pressures, there was a decline in reaction yield by increasing the pressure. In addition, the structure of the polymer chain was not highly affected by reaction pressure [118]. To conclude, despite all efforts on increasing catalyst activity of ZnGA and optimization of the reaction condition, the yield of PPC production is still low (less than 300 g PPC/g catalyst). Accordingly, a high

concentration of the catalyst is required to accomplish an acceptable yield of PPC synthesis.

2.5.3 PPC Applications

PPC has attracted attention in recent years as an environmentally friendly polymer due to its biodegradability and ability to fix carbon dioxide. This polymer is commercially available for a variety of applications such as a binder, plasticizer, the raw material for polyurethane synthesis, and pharmaceutical dressing [56]. As a biodegradable polymer for biomedical applications, PPC is advantageous material comparing to common polyesters such as PLA. The reason is that the degradation products of PPC are only water and CO_2, which are non-toxic and cause no inflammation. However, pH reduction in surrounding organs as a result of degradation of PLA is a serious issue. Application of PPC as a potent polymer for biomedical applications has been the topic of several researches [76, 119-121].

Application of plastics in novel agriculture has been increased in recent years. Plastics are mainly used as mulches to protect plants, increase the soil temperature, maintain soil moisture and increase crop yield [122]. Plastic mulches aim to change microclimate of soil by increasing soil temperature, avoiding moisture fluctuations, and preventing evaporation of water [123]. Polyethylene films are the most commonly used polymer to produce agriculture mulches. However, environmental issues such as accumulation of plastic particles in agricultural spots, the high cost of collecting mulches after harvest season and contamination with soil and dirt limit application of non-degradable mulches [123]. Therefore, PPC can be considered as an alternative to polyethylene films to fabricate agricultural mulches according to its biodegradability, transparency, resistivity to moisture.

High transparency, biodegradability, high resistivity to oxygen and water penetration are factors that can introduce PPC as an alternative polymer to

conventional materials for food packaging [23]. Application of PPC as packaging material addresses the environmental issues of plastic accumulation in the environment. Cardia Bioplastic (CO_2starch Pty Ltd) developed a method for commercially manufacturing of PPC/starch composites [124]. The composite is applied to produce biodegradable shopping bags. However, for extending its application to food packaging, it should pass the some regulation of compostable polymers [36]. Lists of the companies that use PPC in commercial scale are listed in Table 2.3.

Table 2.3. List of some companies that use PPC in commercial scale

Name of Company	Country	Application	Website
Life Cycle Products	England	Plastic bag and waste management products	www.lifecycleproducts.co.uk
Nature Works Packaging	Australia	Shopping bag	www.natureworkspackaging.com
Drogaria Araujo	Brazil	Biohybrid™ bags	www.araujo.com.br
AZOmaterials	England	Organic binders for nanoparticles	www.azom.com
Novomer	USA	Adhesive for polyurethane hot-melt	www.novomer.com
Mengxi High-tech Group	China	Medical dressings, biodegradable packaging	www.mengxigroup.com
Jiangsu Jinlong-CAS Chemical Co., Ltd	China	Biodegradable packaging	www.zkjlchem.com
Cardia Bioplastics™	Australia	Shopping bag	www.cardiabioplastics.com

2.5.4 Limitations with PPC Application

PPC needs to meet the criteria of AS-4736 and EN13342 standards to be sorted among biodegradable plastics suitable for composting [35]. According to the abovementioned standards, the level of the zinc element in plastics should not

exceed 150 ppm. However, as it was discussed before, zinc glutarate is the most efficient catalytic system for commercial synthesis of PPC. Moreover, zinc glutarate should be introduced to the reaction as nano-size particles to have acceptable activity. Accordingly, high level of the catalyst remains among the polymer chains after synthesis [8]. On the other hand, the presence of catalyst residue affects thermal properties of PPC significantly. In fact, a small amount of metal residue plays the role of a catalyst to accelerate thermal degradation of PPC: hence has an adverse effect on the processability of the polymer. Reducing zinc residue in PPC below 1000 ppm led to 85˚C increase in decomposition temperature from 175˚C to 260˚C [8]. Thermogravimetric/infrared spectroscopy (TG/IR) analysis demonstrated slight improvement of PPC thermal degradation in the absence of catalyst residue [59]. Metal residue shows the same effect on poly(cyclohexene carbonate) (PCHC). Results of a study by Li *et al.* show that the thermal decomposition temperature of PHCH containing 4400 ppm zinc residue was 56˚C lower than purified polymer [125]. The reason is that presence of metal residue increases activation energy of the polymer, hence reduces its thermal stability.

2.5.5 PPC Purification Methods

Conventionally solvent-antisolvent method was applied for the purification of PPC. This method includes dissolving the polymer in an organic solvent, extracting the metal complex with an acidic solution and precipitating the polymer using an anti-solvent [57]. From an environmental point of view, the method is not sustainable due to the requirement of high level of organic solvents. On the other hand, it needs solvent recovery that makes the method energy intensive and economically inefficient. Recently, Fredriksen *et al.* reported a new method for removing zinc residue from PPC [8]. They used maleic acid solutions in different concentrations to extract zinc from the polymer. Using this method, no organic solvent was required. However, to have acceptable efficiency, PPC needed to be soft and plasticized. Therefore, the process was carried out at high

temperatures of up to 90˚C. At optimum condition, zinc residue of the purified polymer was still above 900 ppm. Due to the significant influence of impurity content on the final PPC's characteristics, more efficient and environmentally friendly method for PPC purification is required.

2.6 Summary

Replacement of non-degradable, petroleum-based plastics with biodegradable, renewable-based materials is in a great attention to overcome the current issues of overconsumption of plastics. PPC is a biodegradable polymer synthesized from renewable CO_2, one of the main GHGs. It has the potential to be used for a broad range of applications such as packaging industry due to its biodegradability, transparency and high resistivity to water and gases penetration. However, PPC has some drawbacks that limit its applications as a biodegradable plastic. Particularly, the presence of catalyst residue that is a metallic compound impedes the polymer to pass standards of biodegradable plastics. Besides, catalyst residue affects thermal properties and processability of the polymer. Conventional purification methods for PPC either were highly energy intensive or required a high amount of organic solvents. Therefore, an innovative benign method is required for removing the catalyst residue and other impurities from the polymer and broaden its applications for food packaging.

Chapter 3. Metal Extraction by High Pressure Carbone Dioxide

3.1 Introduction

High pressure CO_2 has been attempted to be used for the extraction of a broad range of non-polar, polar, and metallic compounds from liquid and solid matrices. Using this method, environmental and economic concerns with conventional solvent extraction methods are avoided. It also meets the criteria of recent environmental protocols limiting hazardous solvents. Supercritical fluid extraction (SFE) is the process of separation of chemical compounds from a solid matrix or liquid media using the solvent power of supercritical fluid. This method has been commercially established in the past three decades [126]. Separation of caffeine from coffee beans, extraction of flavors and spices from vegetables and oil extraction are some of the main commercial applications of high pressure CO_2 extraction [127]. In this chapter, the properties and application and requirement of high pressure CO_2 process for extraction of different types of non-metallic and metallic compounds are discussed

3.1.1 Applications of High Pressure CO_2 Extraction

The solvent power of CO_2 at elevated pressure and temperature, particularly above the critical conditions, remarkably enhanced [128]. In such a condition, the fluid has a density between a liquid and gas with a high dissolution power as a liquid solvent. Furthermore, any slight change in temperature and pressure leads to significant change in the fluid properties such as density. This facilitates the tuning of its dissolution power over a wide range of pressure and temperature. On the other hand, hydrodynamic properties including viscosity, surface tension and diffusivity, the fluid is comparable to a gas state phase [129]. This magnifies its mass transfer coefficient and assists it to diffuse easily in the structure of the solute [129]. Such features make this high pressure fluid as superior media for a range of applications including in the separation process, chemical reactions and polymer processing [127]. Characteristics of CO_2 in different states were compared in Table 3.1 to give an overview of physical properties of Supercritical Fluids (SCFs).

Table 3.1. Typical values for physical properties of carbon dioxide

Physical Properties	**Gas State (40˚C, 1 atm)**	**Supercritical Fluid (40˚C, 100 atm)**	**Liquid State (30˚C, 300 atm)**
Density (Kg/m^3) [130]	1.7201	638.10	949.83
Viscosity (Pa.s) [130]	1.5655e-05	4.8852e-05	1.0479e-04
Diffusion Coefficient (m^2/s^{-1}) [131]	5.1e-06	1.4e-08	8.1e-0.9

CO_2 has gained much attraction owing to its superior features comparing with other materials such as water, benzene, methanol, chloroform, propane, etc [132]. CO_2 is:

- cheap and accessible,
- non-flammable, non-oxidant, non-toxic and FDA approved,
- benign with a critical point of 31˚C and 71.8 bar, hence the operating condition at supercritical condition can be easily set up at moderate temperatures,
- suitable for separation and extraction of thermally unstable materials,
- easy to be separated and recovered from the solute or the product after the extraction or reaction,

Above-mentioned properties make high pressure CO_2 an excellent solvent for extraction of a broad range of compounds from a large number of matrices. As an example in the food industry, high pressure carbon dioxide has been broadly used to extract edible oils [133-135]. CO_2 also is effective to remove undesirable compounds from food products. For instance, it can be used to decaffeinate coffee beans and green tea [126, 136], refine vegetable oils to remove undesirable impurities without losing valuable compounds [137, 138] and selectively de-alcoholization of beer and wine to protect aroma compounds [139]. Furthermore, high pressure CO_2 is broadly applied to extract antioxidants from fruits and vegetable sources such as tomato, rosemary, grape and aloe-vera [127, 140]. CO_2 is successfully used for selective extraction of a number of bioactive compounds [141]. Essential oils [142, 143], phenolic antimicrobial compounds [144] and vitamin E [145] are some examples of bioactive materials that were successfully extracted using high pressure CO_2. High diffusivity of high pressure CO_2

compared to organic solvent promotes its penetration into the structure of polymers much easier [146]. This phenomenon can be used to extract impurities, which are entrapped in the structure of polymers such as un-reactant monomers and oligomers. In such cases, the first step is swelling of the polymer matrix by diffusion of the supercritical fluid. Subsequently, the trapped impurities can be dissolved in or bonded with supercritical fluid and leave the polymer matrix [147]. As an example, SFE was used as an alternative method to conventional aqueous or organic solvent extraction methods to remove volatile, low molecular weight impurities from polymeric pharmaceutical excipients [148].

3.1.2 Key Factors in High Pressure CO_2 Process

Temperature, pressure, co-solvent are the key factors that have an impact on a solvation power of high pressure CO_2. The solubility of a compound in high pressure CO_2 is also a function of the solute properties. As an example, high pressure CO_2 is a perfect solvent for organic and especially non-polar compounds, while polar or ionic solutes are hardly soluble in this solvent [149]. The solvation power of high pressure CO_2 for a soluble material is a function of its density. Therefore, at a constant temperature, the solubility increases upon elevating the pressure due to enhancing the CO_2 density [127]. However, at a set pressure when the temperature increases, while CO_2 density decreases, the vapor pressure of solute increases. Therefore, the effect of temperature on the solubility of depends on the dominant factors such as density and vapor pressure of CO_2 at each condition [150, 151]. The crossover point such as 130 bar in Figure 3.1 is a specific pressure for high pressure CO_2, as below that pressure the solubility of bisphenol depends on the density and decreases by elevating the temperature [152]. However, beyond crossover pressure, the viscosity is the dominant factor. Accordingly, increase in temperature at pressures higher than crossover point results in improving in solubility.

A number of mathematical models have been used to predict the solubility of different solids in high pressure CO_2. The majority of these models are empirical and semi-empirical based on the density of the CO_2 [150, 153, 154]. Furthermore, applying equations of states (EOSs) is another mathematical approach to correlate solubility data of different compounds in SCFs [155, 156].

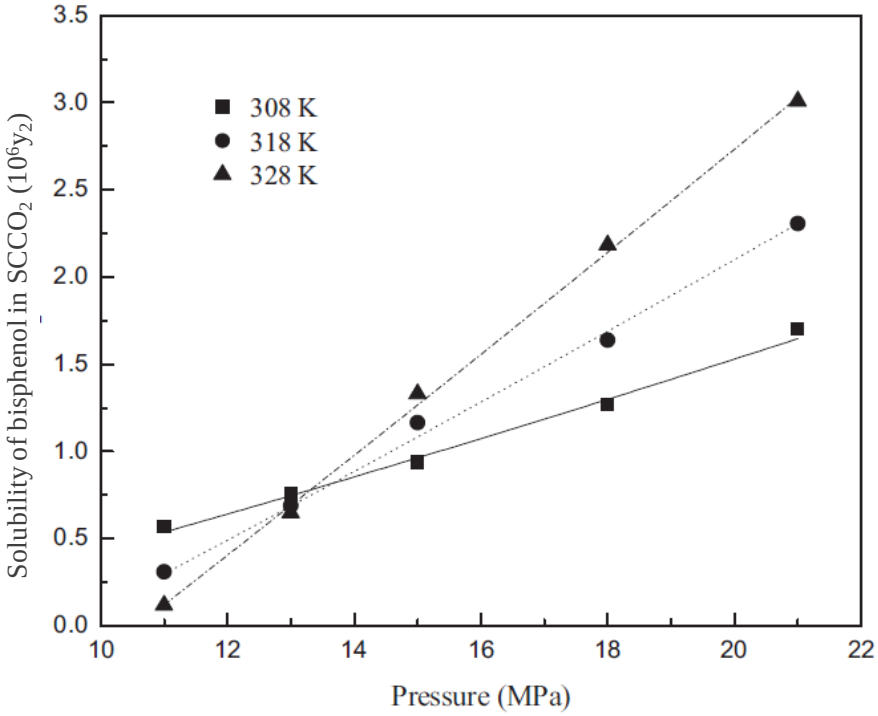


Figure 3.1 Effect of temperature on solubility of bisphenol A in pure supercritical CO_2 ($SCCO_2$)[150]

In any extraction process, it is important to increase the mass transfer rate. Therefore, particle size and the surface area of solid phase are factors that can have an impact on high pressure CO_2 extraction process [141]. As an example, by decreasing the particle size of pine kernel to half, the high pressure CO_2 extraction efficiency of lipid at 40˚C and 300 bar increased by two-fold [153]. It is also recommended to dry the plant or a solid phase prior to extraction by high pressure CO_2 as the presence of water as a polar compound decreases the diffusion of SCF into solid phase[153].

High pressure CO_2 is an ideal solvent for the extraction of many organic and especially non-polar compounds while polar or ionic solutes are hardly soluble in high pressure CO_2 [149]. The addition of polar liquids as co-solvent can significantly improve the solubility of the polar compound in high pressure CO_2 [127]. Indeed, the polar modifier solvent acts as an intermediate between the solute and high pressure CO_2 and enhances their interaction [141]. As an example, it was found that, at the same extraction condition, the solubility of gallic acid in high pressure CO_2 enhanced to four-fold by the addition of 6% ethanol [157]. Apart from ethanol, some other co-solvents such as methanol [158] and isopropyl alcohol [159] have been used to modify efficiency of high pressure CO_2 extraction [160-163].

3.1.3 Metal Recovery using SFE

The solubility of inorganic and especially metallic compounds in high pressure CO_2 is negligible due to its low dielectric constant (1.1-1.5 in the supercritical state) [164]. Consequently, direct extraction of metals using high pressure CO_2 is economically inefficient and unfavorable [164, 165]. However, complexing a heavy metal with an organic ligand increases the solubility in high pressure CO_2 [166]. Complexing or chelating agents that are used for conventional solvent extraction have been used for this purpose [132]. This method resulted in the production of neutralized metallic compounds that are efficiently extracted using high pressure CO_2 [166]. Type of the chelating agent and co-solvents play critical roles in the solubility of a metal in CO_2. Chelating agents consist of a CO_2-philic tail that is dissolved in CO_2 and an electron donating head that is bonded with metal ions to form the complex [167]. The CO_2-phile group can be fluorine-, hydrocarbon or phenyl-based [168]. It has been found that fluorine based complexing agents are most likely soluble in high pressure CO_2 [169]. For example, among Zn, Cu and Hg complexes with seven different complexing agents, the solubility of those bonded with the fluorine-based ligand (bis(trifluoroethyl) dithiocarbamate) in high pressure CO_2 were, at least, one order

of magnitude higher than hydrocarbon-based complexes [170]. Similarly, significantly higher solubility in high pressure CO_2 was obtained when fluorine-based complexes of Cu and Ni were compared to other hydrocarbon-based complexes [169]. It is due to more uniform electric charge distribution of fluorine-based complexes that leads to low polarity and subsequently high CO_2-philicity [168]. However, these ligands are not desirable in large-scale processes due to their adverse impact on the ozone layer and also high cost [171-173].

Chelating agents may have an affinity for bonding to a specific metal compound due to the charge or size of metal ion [174]. For example, aliquat 336 selectively extracts Hg from dry sand while no Cu was removed at similar condition[174]. Cyanex 302, Cyanex 923, TBP, D2EHPA, D2EHTPA, Aliquat 336, NaDDC and diisooctylphosphinic acid are examples of chelating agents that have been used for the extraction of zinc by high pressure CO_2 [168, 169]. The addition of a polar solvent can increase the solubility of a complexing agent in high pressure CO_2. For instance, the extraction efficiency of CO_2 modified with 5 mole% of ethanol was compared with pure CO_2 at 60˚C and 200 bar for removing Cr^{3+} and Cr^{6+} from sand using LiFDDC as a complexing agent. Addition of ethanol enhanced the extraction efficiency for Cr^{3+} and Cr^{6+} from 62% to 92% and from 70% to 94%, respectively [166].

Although high pressure CO_2 has been used in large scale for the extraction of many food products successfully, this technology has been mainly used in bench scale laboratory for extraction of metals. While it can be a solution for reducing the consumption of organic solvents, particularly in mining process for extraction of metals, it has not yet been broadly used in large scale, due to the high cost of chelating agents and their severe impacts on the ozone layer and environment [171-173]. Moreover, the recovery of metal after extraction still require a huge amount of organic solvent [168].

3.1.4 Water Laden CO_2

The addition of high pressure CO_2 to water decreases the pH due to the formation of carbonic acid [175]. The pH drops dramatically at below 50 bar and after which approaches a plateau. In fact, as CO_2 is injected in water, even at very low pressures of below 5 bar, pH remarkably decreaces to nearly 4. This pH drop continues by increasing the pressure and approaches to nearly 3 at 50 bar [176]. Temperature and pressure of CO_2 have negligible effect on the pH of water over 50 bar. As an illustration, pH of biphasic water-CO_2 system was measured using a pH detector equipped with a UV-vis spectrophotometer [177]. At different conditions of pressure (70-200 bar) and temperature (25-50˚C), an insignificant change in pH of the system from 2.80 to 2.95 was detected. The resulted pH data in various pressure and temperatures was shown in Table 3.2. The solubility of CO_2 in water was reported within the range of 3.91 to 4.20 g/100 g water at ambient temperature for pressure of 70 -130 bar and 4.40 to 5.25 g/100 g water at the same pressure range [178, 179]. By increasing the CO2 solubility in water, the pH decreases due to the formation of carbonic acid.

Table 3.2. pH of Water in Equilibrium with CO_2 at Different Pressure and Temperatures [177]

	Temperature (˚C)			
Pressure (bar)	25	40	50	70
70	2.83 ± 0.02	2.84 ± 0.02	2.90 ± 0.02	2.95 ± 0.02
80	2.82 ± 0.02	2.84 ± 0.02	2.88 ± 0.02	2.93 ± 0.04
100	2.83 ± 0.02	2.83 ± 0.02	2.88 ± 0.02	2.89 ± 0.03
150	2.82 ± 0.02	2.80 ± 0.01	2.85 ± 0.02	2.86 ± 0.03
200	2.80 ± 0.01	2.80 ± 0.01	2.84 ± 0.02	2.84 ± 0.03

Water laden carbon dioxide has been used as an alternative to conventional acids for the precipitation of proteins [180, 181]. As an example soy protein was precipitated by addition of CO_2 at 50 bar and ambient temperature to soy meal

extract dispersed in water and the efficiency of up to 80% recovery of the soy bean protein was obtained [176]. Similarly, more that 90% efficiency for precipitation of milk protein casein was accomplished using acidic water laden CO_2 at 40 bar and room temperature [182]. CO_2/water binary system has been used as green solvent for a wide range of applications. For instance, making porous structures of hydrogels and polymer composites using water in CO_2 as templateing media was the topic of some studies [183, 184].

3.2 Summary

High pressure CO_2 extraction is an environmentally friendly approach for extraction of organic compounds; however, it is not efficient for inorganic or metallic complexes. Chelating agents have been used to assist solubility of these compounds into high pressure CO_2. Nonetheless, high cost and the usage of organic solvents for their recovery are two major issues for their commercial applications in polymer purifications. On the other hand, the addition of high pressure CO_2 reduces the pH of the water to nearly 3. This acidic media has been used for the purification of proteins, extraction of compounds and many other applications; however, has not been applied for extraction of metallic compounds.

Chapter 4. Antimicrobial Plastics

4.1 Introduction

Antimicrobial plastics have found numerous applications in a broad range of industries. One of the largest markets for antimicrobial films is packaging industry particularly for sterile products such as syringes, biomedical implants, catheters and surgical devices [185]. Another example in this area is biomedical industry; fabrication of active films that inhibit the growth of bacteria on the surface of medical devices has been shown to be a promising method to mitigate the issues associated with microbial infections. In fact, medical devices are responsible for about 60-70% of hospital-acquired infections [186]. As an example, orthopedic implants have been reported to contribute in 800,000 infections per year in Europe [187]. Moreover, antimicrobial films can be used to inhibit the biofilm formation on the solid surfaces that are in long-term contact with water such as ships, bridges that are built on the rivers [182]. Antimicrobial surfaces even found applications in the fabrication of mold- free construction materials in humid countries such as Australia. However, one of the broadest applications of antimicrobial films in recent years was allocated for food packaging [14]. The consumers' concern about food safety and shelf life is an impetus for packaging industry to seek for innovative approaches that minimize microbial contamination [9]. Sterilization, pasteurization, irradiation, air removal, the addition of preservatives and oxygen scavengers have been used to reduce microbial growth in food [10]. However, some of these methods have a negative impact on the food texture and quality [188]. Antimicrobial food packaging can play a role in prolonging food shelf life [189]. Active packaging delineates a system in which shelf life enhances, or food safety is protected while maintaining its quality [11]. Application of packaging material that inhibits the microorganism growth is a strategy that is suggested for active packaging [14, 190].

This chapter focused on the application of the antimicrobial films in the food packaging area due to its huge market and demand for that. To this end, different antimicrobial agents that are utilized to fabricate active packaging surfaces are

reviewed. Moreover, the most common methodologies that are applied to add antimicrobial agents to the packaging material are discussed.

4.1.1 Antimicrobial Agents

It is important to note that antimicrobial agents that are approved by regulatory authorities such as Food Drug Administration (FDA) can be used for the fabrication of active food packaging [191]. Generally, these organizations assess the toxicity, mutagenic/carcinogenic, interaction of these compounds with food, also their impact on taste, smell and food texture to assure the consumer safety and concerns [192]. Finally, the antimicrobial agent has to comply with the limitations on the migration of packaging materials into the food [82]. To this end, the most common antimicrobial agents are antimicrobial polymers, metallic particles, organic acids, and herbal extracts.

Some natural polymers such as chitosan and poly-L-lysine are inherently antimicrobial due to the particular structure of their molecular backbone [193]. Polymeric antimicrobials are chemically stable, so have minimum interaction with the food. In addition, they are non-volatile and do not affect the food quality. For instance, edible coatings of natural polymers such as chitosan, lemon and orange extracts were applied as a barrier to protect the food from the environment and extend the shelf life [46, 47]. Chitosan-based edible coating was used to successfully increase the shelf life of strawberries from 10 days for uncoated sample to 21 days [48]. The citral compound of lemon grass was used in combination of the alginate-based edible coating to coat the fresh-cut melon [49]. The incorporation of this active compound into the edible coating prolonged the shelf-life of the fruit by more than 20 days. Moreover, modification of the polymer films to contain slippery, low surface energy surfaces is another approach to fabricate antimicrobial films. For instance, slippery polyurethane films reduced the bacteria growth to one tenth comparing to the unmodified surface [185].

Metallic particles are a family of antimicrobials includes metallic and metal oxide nanoparticles. Owing to the recent advances in synthesis of ionic metal oxide nanoparticulates with tunable size, shape and surface area, it is possible to design high performance antimicrobial agents [189]. Nanocomposites of metal and polymer are commonly used as a film for the fabrication of antimicrobial material. Silver (Ag), gold (Au), zinc oxide (ZnO), titanium dioxide (TiO_2), alumina (Al_2O_3) and iron oxides (Fe_3O_4, Fe_2O_3) are the most commonly used nanoparticles [194]. Despite their significant impact, their application in food packaging may not follow FDA and other food safety authorities due to recent studies that show the health concern of using nanoparticles in food [195]. Moreover, the presence of more than 150 ppm metallic particles is not in agreement with the regulation of compostable and biodegradable polymers [36].

Organic acids that are either synthetic or chemically modified natural acids are the other category of antimicrobial agents that have been conventionally used as food preservatives [196]. Benzoic acid, sorbic acid, sorbates, propionic acid, and lactic acid are some of the most frequently used organic acids used for active packaging [191]. However, application of these compounds has harmful effects such as increasing the risk of cancer or allergic reactions on human health [197, 198]. Therefore, there are strict regulations on the maximum levels of these compounds in food. For example, according to the Australia and New Zealand Food Standards, the maximum allowable concentration of benzoate in different type of food products is 3000 ppm.

Extracts from herbs have been used more widespread in antimicrobial packaging to avoid the side effects associated with chemical based antimicrobial agents and preservatives and due to the customers' desire for natural compounds in contact with food products. Essential oils are complex natural extracted from the herbs and plants with antibacterial properties [12]. Since the 1840s, when the antimicrobial activity of the essential oils was first discovered, numerous studies have proved their antibacterial, antioxidant, antifungal and antiviral activities

[199-201]. From the mechanistic view, constituent molecules of the essential oils disrupt and expand the cell membrane of the microorganism and as a result, inhibit the respiration and alteration of ion transport processes [13]. The most famous essential oils extracted from natural herbs and plants are thyme oil [202], oregano oil [203], lime oil [204], cinnamon oil [205], garlic oil [206], basil oil [207], rosemary oil [203], lavender oil [208], and coriander oil [209]. As an example, media containing 500 ppm lemon grass essential oil was efficient in inhibition of the colony formation of five different types of microorganism such as *Colletotrichum coccodes*, *Botrytis cinerea*, *Cladosporium herbarum*, *Rhizopus stolonifer* and *Aspergillus niger* [204]. 300 ppm of basil essential oil entitled as Ocimum sanctum oil was shown to have 95-100% efficiency in inhibition of the growth of a diverse range of microorganisms [207]. 1-4 wt% of garlic, rosemary and oregano essential oils were added to the edible films and their antimicrobial properties were assessed via bacteria inhibition zone. The results showed that the inhibitory effect of oregano oil against *E-coli* was 3-4 fold higher than garlic oil while no antimicrobial effect was observed for rosemary oil within the measured range [203].

4.1.2 Thymol

Thymol, one of the major components of oregano and thyme essential oils, is a phenolic monoterpene which is wieldy used as antimicrobial as well as antifungal and antioxidant agent [210-212].Thymol is stable at elevated temperatures and can be used in melt-blending processes below 190 ˚C.

Thymol has been used for coating the surface of various polymers and effectively reduced microbial contamination [213]. For example, Del Nobile et al. studied the antimicrobial effect of zein films that contained 5-35 wt% thymol [213]. The results of this study exhibited that a minimum concentration of 20% of thymol was required to inhibit the growth of bacteria, whereas the thymol concentration of up to 10% only slowed down their growth. Hot melt extrusion at 80˚C was

used to incorporate 7% to 15 wt% thymol in PCL matrix [214]. The results suggested that presence of 10% thymol in PCL film reduced the bacteria growth by 30%. Guarda et al. determined the antimicrobial properties of bi-axially oriented polypropylene films coated with microcapsules containing thymol [215]. Microencapsulation allowed the controlled release of thymol and inhibited the growth of a range of microorganisms such as *Escherichia coli, Staphylococcus aureus, Listeria innocua, Saccharomyces cerevisiae and Aspergillus niger*. The minimum inhibitory concentration of thymol was 125 ppm for *Saccharomyces cerevisiae* and 250 ppm for the other microorganisms. However, around 50 ppm of the thymol was released from the films within two days. In yet another study, Hu at al. investigated the release of thymol (6% w/w) from soy protein isolate films into olive oil at temperatures of 5°C to 60°C [216]. It was observed that by elevating the temperature the amount of thymol released from the polymer matrix was increased. Indeed, the release of thymol at 60˚C was three-folds higher than t ambient temperature. Kerddonfag et al. studied the antimicrobial activity of ethylene-vinyl acetate (EVA)/LDPE films incorporated with thymol and/or eugenol [217]. For the EVA/LDPE film containing 2% of thymol they found zones of inhibition of 15.0 ± 0.0, 15.4 ± 0.6 and 16.1 ± 1.5 mm for *E. coli*, *S. aureus* and *L.monocytogenes*, respectively. The concentration of thymol for inhibiting microbial growth was varied from ppm level to more than one third of the polymer weight in different studies. This variation may be attributed to its antimicrobial effect on different microorganism, fabrication process and the interaction of thymol with the polymer matrices.

4.1.3 Methods for Fabrication of Antimicrobial Polymers

The selection of an antimicrobial agent, its stability during the fabrication process, its short or long-term activity, and their effect on packaging material are critical parameters for the preparation of active packaging. For instance in food packaging, it is critical to choose the method and material that have minimal impact on food quality and safety [218]. Moreover, the migration of the

antimicrobial agent to the food should be controlled to prevent any change in its quality and safety [82]. Besides, the antimicrobial agent should not cause any adverse effect on the physical properties of the packaging material [218]. In this section, different techniques that have been used for the fabrication of antimicrobial films are discussed.

4.1.3.1 Direct Incorporation of a Compound into a Polymer

The antimicrobial agent is incorporated into a polymer either by solvent compounding or hot melt extrusion processes [190]. The former method is commonly used for the addition of heat labile compounds such as enzymes, peptides and proteins [14]. Using this technique, the efficiency of the antimicrobial agent is governed and restricted by its diffusion through the polymer packaging films [218]. As an example, hot melt extrusion was used to prepare antimicrobial polypropylene/montmorillonite films by addition of nisin (1-5 wt%), which was effective in inhibiting the growth of gram-positive bacteria such as *listeria monocytogenes*, *staphylococcus aureus*, and *clostridium perfringens* [219]. Poly(methyl methacrylate)/polyvinyl alcohol fibers were incorporated with silver nanoparticles for clinical wound dressing [220]. Hinoki oil was incorporated into the wall, floor and ceiling construction materials from epoxy to prevent microbial growth and mould formation [221]. In another study 10-25 wt% bergamot and lemongrass was incorporated into gelatin films using solvent casting method to prepare antimicrobial films [222]. However, only the film containing above 10 wt% of lemongrass oil exhibited the antimicrobial effect. It also found that incorporation of these oils in the bulk of the polymer lessened the tensile strength remarkably. In yet another study, thymol and carvacrol were added to LDPE, PLA, and PCL films by hot melt extrusion method [223]. It was found that the processing temperature has an impact on the antimicrobial activity of these active packaging as there is a risk of losing activity at a higher temperature. In addition, the presence of an antimicrobial agent reduces the polypropylene (PP) crystallinity and oxygen barrier properties [210].

It is, therefore, suggested that for addition of essential oil it is better to use alternative method rather than direct incorporation of the essential oils.

4.1.3.2 Coating of the Polymer Surface

In this method, the packaging film is first processed and then a biologically active compound is casted on its surface [14]. The advantages of this method include the direct interaction of the antimicrobial agent with the microorganisms on the surface, minimal impacts on both polymer physicochemical properties and stability of active reagents [218]. As an example, by the addition of cinnamon essential oil on the surface of polyethylene terephthalate (PET), the shelf-life of peach fruit was dramatically improved seven folds [224]. In another study nisin coated cellophane-based packaging showed significant impact on decreasing the microbial growth rate of chopped meat [225]. Fabric facial masks coated with silver nanoparticles were produced in pilot scale. The coated mask inhibited the growth of *E-coli* in the media whereas the number of bacteria cells increased 10 fold in the media containing uncoated mask [226]. The release profile of the antimicrobial agent is critical in determining the shelf life of a product [227]. A burst release is commonly observed when using surface coating; therefore, the antimicrobial properties might be only for a short-term [10]. In addition, care must be taken for the migration of these antimicrobial compounds and their adverse impact on the product such as food [228].

4.1.3.3 Chemical Immobilization of Antimicrobial Agents

Chemical immobilization of the antimicrobial agent on the surface of a polymer is another strategy to tackle the issues with direct coating [14]. It is, therefore, pivotal to have an active functional group on the inert surface of polymers [229]. Several methods have been developed for the functionalization of polymer surface prior to immobilization of antimicrobial agents [218]. Wet chemical activation [230, 231], self assembled monolayers formation [232], UV irradiation [233], are commonly used techniques for functionalisation of polymer surfaces. As an

example, the surface of LDPE was oxidized by soaking in the concentrated chromic acid solution at 25-75˚C followed by further treatment with 70% aqueous nitric acid at 50˚C [230]. As a result of chemical treatment carboxylic, ketone or aldehyde groups were formed on the surface of LDPE. Self-assembled monolayer functional groups were formed on the surface of elastomeric poly(dimethylsiloxane) (PDMS) by wetting with alkanethiol [232]. Polymethyl methacrylate surfaces were activated by exposure to UV light (254 nm) and then functionalized by amide solutions [233]. These common methods involve using organic solvents, toxic chemicals or may affect the physical properties of the polymer. Plasma treatment is another commercially available technique for the surface activation that tunes the properties of polymer surfaces within a thin layer on the surface (10 nm) [15, 16, 234].

4.1.3.4 Plasma Surface Modification

Plasma is a high energy stream of a single gas or a combination of different gases that are partially ionized into charged particles or electrons [235]. This method has been commercially used for sterilization in large scale, for coating the surface of metals for biomedical applications and treatment of polymer surfaces [234].When a polymeric surface is exposed to the plasma, some of its covalent bonds are broken, and free radicals of different functional groups are created on its top monolayer [236]. The type of the functional groups depends on the gas. For instance, oxygen containing active groups are introduced on the polymer surface when oxygen or air is used in plasma treatment [15]. Plasma coating is a solvent and waste-free process with minimal impact on the bulk polymer properties as it only diffuses to the top layer within 10 nm thickness [228]. Time of exposure, temperature, and plasma intensity are other crucial factors that can be optimized to tune the surface chemistry of a polymer [229]. PCL [15], polyethylene terephthalate (PET) [16], polystyrene (PS) [237], poly methyl methacrylate (PMMA) [238], and polytetrafluoroethylene (PTFE) [239] are examples of polymers that have been successfully activated via plasma modification.

Plasma has been used for the fabrication of antimicrobial surfaces for both biomedical and food packaging applications [240]. For instance, nitrogen and argon plasma treatment were used to activate the surface of non-degradable polymers such as polyether ether ketone, and poly(methyl methacrylate) for biomedical applications [238, 241]. In yet another study, glucose oxidase was coated on the surface of non-degradable polypropylene films to prepare antimicrobial product for food packaging application. However, even at room temperature, the films lost their anti-microbial activity within 30 days due to the heat sensitivity of the enzyme [240]. In addition, polyethylene films were modified by water vapour plasma and immobilized by antimicrobial enzyme [242]. Besides, the plasma-treated films coated with enzymes showed antimicrobial activity against *Micrococcus lysodeikticus*. In summary, plasma surface modification has been found to be useful in activation of a broad range of inert polymer surfaces and immobilization of the biologically active compounds on them. This technique is a potent method for fabrication of robust and long lasting antimicrobial packaging materials. Although this method is a promising approach for activation of polymer surfaces and immobilization of different active compound, it has not been used for chemical bonding of the essential oils, particularly thymol, on the polymeric materials.

4.2 Summary

Nowadays, antimicrobial films found a broad applications in different area from biomedical devices to marine ships and mold-free construction materials. In particular, fabrication of antimicrobial films for packaging of food and biomedical products is of great interest due to the fact that consumers are nowadays more concerned about the safety and quality of the food and biomedical products and preventing microbial contamination. Nanoparticles, organic acids, antimicrobial polymers, and essential oils are the most widespread agents that are used to fabricate packaging materials. Among all, essential oils are more desirable due to

their natural origin. Antimicrobial agents are either incorporated into the polymer bulk or coated on their surfaces. In both methods, migration of the biologically active compounds into the food product is a limiting hurdle. Immobilization of the packaging surfaces with the active compounds to increase their attachment is a promising method to avoid the antimicrobial agent migration. To achieve this purpose, the inert surface of the polymer needs to be first activated and then immersed into the antibacterial solution. Plasma treatment is a promising, solvent-free technique that has been successfully used to activate different polymer surfaces and is applicable for fabrication of antimicrobial polymer films.

Chapter 5. Research Hypothesis and Methodology

5.1 Introduction

The huge consumption of non-degradable fossil-based polymers is one of the emerging issues, particularly for countries that have limited land space for waste disposal. PPC that is a biodegradable plastic synthesised from CO_2 with favorable barrier and mechanical properties may be an option to tackle these environmental issues.However, the broad application of PPC in commercial scale impedes due to the presence of metal based catalyst residue in PPC that is far beyond the acceptable level for compostable, biodegradable materials. The catalyst residue also affects thermal properties and processability of PPC. Consequently, it is critical to develop a novel low-cost process for removing catalyst residue and other impurities from PPC and open a new avenue for its application, particularly for food packaging.

Removing microbial contamination is a major concern in many applications, particularly in food and medical device for consumer safety. Incorporation or coating of various antimicrobial agents such as nanoparticles, organic acids, volatile gases, antimicrobial polymers, and essential oils are reported to fabricate antimicrobial films. However, in both methods, migration of the biologically active compounds into the food product is a hurdle. Chemical immobilization of polymer surfaces with the active compounds and chemical bonding is a promising approach to reduce the antimicrobial agent migration. Among the methods used for surface activation of polymers, plasma treatment is one the promising solvent-free technique that has been successfully used to activate different polymer surfaces.

The aim of this project was to develop a safe, biodegradable polymer that can be used for food packaging to tackle the major environmental issue. This aim was achieved through several hypotheses. In this chapter, the main hypotheses of the project are elaborated. In addition, the materials, sample preparation

methodologies and analytical techniques that have been developed and used in this study are described in detail in this chapter.

5.2 Hypotheses

The hypotheses of this project were three folds:

(a) PPC can be an alternative polymer to none-degradable polymers, particularly for food packaging due to its superior barrier properties.

(b) High pressure CO_2-water system can be used as an alternative to the purification of polymer and removal of the metal-based catalyst.

(c) It is viable to develop a low cost and safe antimicrobial PPC by using an essential oil.

To assess the first hypothesis, the physico-mechanical prosperities of PPC such as mechanical strength, barrier properties, chemical resistance and biodegradability were measured and compared with commonly used polymers for food packaging such as LDPE, Ecoflex and polyethylene/starch blend. Particularly, the mechanism of biodegradation in soil was examined to determine their compostability. Finally, the effect of blending this partially renewable polymer with natural polymers such as starch and cellulose was assessed.

It was hypothesized that high pressure CO_2/water binary system can be contemplated as a benign solvent for the removal of metal-based catalyst from a polymer matrix. The pH drops by dissolving high pressure CO_2 in water and this acidic media could be used to extract metallic-based catalysts such as zinc glutrate (ZnGA), zinc adipate (ZnAA) and zinc methyl glutarate (ZnMGA) from PPC. The operating conditions for the solubility of these compounds and their extraction from PPC were determined. Furthermore, the effect of purification on the physico-chemical properties of PPC such as tensile strength, molecular weight, chemical structure, and thermal decomposition temperature was investigated.

Finally, it was hypothesized that thymol coated PPC films could show antimicrobial properties. PPC/thymol films were fabricated by physical and chemical immobilization methods. The effect of the fabrication method and thymol concentration on the growth of *Escherichia coli* (E-*Coli)* as a model gram-negative bacterial was determined. In addition, the physical properties of modified PPC films were compared with neat PPC.

5.3 Materials

Poly(propylene carbonate) (molecular weight of 463KDa and poly disparity of 3.26) was supplied by Cardia Bioplastics Pty Ltd. Food grade CO_2 (>0.99 purity) was purchased from BOC Company. Zinc oxide (ZnO) (<100 nm Particle size) and glutaric acid (GA) (99% Purity) were bought from Sigma-Aldrich. GA was grinded to produce a fine powder prior to synthesis. Maleic acid powder (99.5%) was bought from Fluka. 1-Methyl-2-pyrrolidinone (NMP) (99% purity), adipic acid (99.5%) and 2-methyl glutaric acid (98%), were also purchased from Sigma-Aldrich Company. Dichloromethane (DCM), acetone and 32% hydrochloric acid were supplied from Merck. Absolute ethanol was purchased from Chem-Supply. Dimethylacetamide (DMAc) was supplied form Sigma-Aldrich. LDPE was purchased from Sigma-Aldrich. Eco-Flex and PE/Starch blend (~70% starch) with the commercial name of BLFO2 were also supplied by Cardia Bioplastics Ltd. Buffer solutions of pH 4, pH 7 and pH 10 were purchased from Ajax Finechem. Edible olive oil was used as fatty food stimulated media. Cellulose powder (~50 μm) and soluble starch powder (~200 μm) were purchased from Sigma-Aldrich. Sodium chloride was bought form Merck. The mature compost soil was supplied by Landtasia Organic Farms. Thymol (>99.5% purity) was purchased from Sigma-Aldrich. The indicator culture for antimicrobial assessment was Escherichia coli (ATCC 25922). Nutrient Agar was supplied by Sigma-Aldrich. Antibiotic-antimycotic (100x) (Anti-Anti) were purchased from Invitrogen™. Peptone and Yeast Extract were supplied by Sigma-Aldrich and glycerol was

bought form Merck. All the solvents were analytical grade, and all materials were used as received. MilliQ water was used for all the experiments that required water.

5.4 Preparation of Polymer Films

Thin films of each polymer (thickness 500-1000 μm) were prepared by hot melt compression above their melting temperature. The conditions were applied for each polymer was written in Table 5.1.

Table 5.1. The hot melt compression condition for different polymer films.

Polymer	Temperature (˚C)	Pressure (bar)	Compression Time (min)
PPC	130	10	60
Eco-Flex	150	2	20
LDPE	150	2	20
BLFO	150	2	20
PPC-St 50-50	150	7	60
PPC-Cell 75-25	150	7	60

5.5 Mechanical Properties

Tensile Test: Tensile mechanical tests were conducted at room temperature on the dumb-bell shaped samples that were cut from the prepared polymer films. The dimensions of middle rectangular part of the dumb-bells were 8.4 x 17 mm. Universal testing instrument (Instron 5543) equipped with a 100 N load cell was used to perform these tests.

Tear Resistance: Standard trouser-shaped test specimens (25 x 75 mm) were prepared from the hot melt pressed polymer films [243]. The tear resistance of the specimens was determined at room temperature using the tensile mode of the Universal Testing Instrument (Instron 5543) equipped with a 100 N load cell.

5.6 Barrier Properties

Oxygen Transition Rate (OTR): Mocon Ox-Tran 2/21 instrument was used to conduct OTR analysis for thin films of the polymers (~500 μm) according to ASTM D3985-05(2010). The test area for the samples was 5 cm^2 and Mocon self-

adhesive foil masks on both sides were used to seal the test specimens. Pure oxygen was applied in 30˚C and dry condition (<3% relative humidity).

Water Vapour Transition Rate (WVTR): Mocon Permatran W 3/31 was applied to test WVTR of the thin films (~500 μm) of the polymers according to ASTM F1249-06. The test area of the samples was around 5 cm^2. The analysis was conducted at 37.8˚C (estimated temperature uncertainty ±0.5 °C) and 90% Relative Humidity (RH) for a period of 2 days.

5.7 Chemical Resistance in Food Stimulated Media

Polymer film samples with the dimension of 5mm x 5mm were immersed in various food stimulated media such as acidic (pH 4), neutral (pH 7) and basic (pH 10) buffers, 50% ethanol/water solution and edible olive oil (olive oil) for a period of six month at ambient condition. Media was changed on a weekly basis and samples were kept at the sterile condition to avoid the effect of microbial contamination on degradation. The samples were removed from the buffer solutions at different time intervals and washed with milliQ water to remove all media residues and be dried. The weight loss of samples after each time point was recorded. Three samples were collected at each condition to acquire statistically valid data.

5.8 Soil Burial Biodegradation

Soil burial biodegradation test was conducted in the pots contained 10 cm mature compost soil made of food and garden organics (containing active fungi, yeast, actinomycetes and photosynthetic bacteria) sandwiched between 10 cm layers of the wood chips to maintain the moisture content. Polymer films (thickness 800-1000 μm) with the dimension of 4cm x 4cm were buried in the middle part of the mature compost soil. The pots were maintained in a controlled temperature and moisture incubator (T=40˚C, RH=60-70%). The relative humidity of the chamber was controlled by using supersaturated sodium chloride solution and measured in

regular basis [244]. To avoid water loss by evaporation, a known amount of water was added to the soil in every alternative day. The samples were removed from the soil to assess their biodegradation rate in predetermined time intervals up to 6 months. After removal from the soil, samples were washed with milliQ water a couple of times to remove soil residue and dirt and dried in vacuum oven at 40˚C until a consistent weight. The degree of biodegradation of the samples at each stage was assessed by measuring their weight loss, molecular weight (GPC analysis), tensile properties, chemical structure (^{1}HNMR spechtroscopy), and surface morphology.

5.9 Chemical Structure Analysis

Chemical structure of PPC was determined by proton nuclear magnetic response (^{1}HNMR) spectroscopy. 1mg/ml solutions of PPC in chloroform-d_1($CDCL_3$) were analyzed using a Burker NMR spectrometer (Varian 400MR). The characteristic proton peaks were detected for PPC, cyclic propylene carbonate (cPC) and poly(propylene oxide) (PPO). The final molar ratio of carbonate linkages and ether linkages were calculated based on the integration of peaks.

5.10 Molecular Weight Measurement

Gel Permeation Chromatography (GPC) method was applied to determine the number average molecular weight (Mn) and polydispersity index (PDI) of the samples. The test was conducted using SEC on a Shimadzu CBM-20A liquid chromatography system with an Agilent Polargel-M guard column and three Phenomenex Phenogel columns using Dimethylacetamide (containing LiBr 0.03% w/w) as solvent at a flow rate of 1.0 mL min^{-1} at 50 °C. The system was equipped with a Shimadzu RID-10A differential refractive index detector and Wyatt MiniDawn TREOS light scattering. The GPC system was calibrated with narrow polystyrene (PS) standards (PDI < 1.1).

5.11 Scanning Electron Microscopy (SEM)

The surface morphology of the PPC films from biodegradation and chemical resistance tests was observed by the SEM (Zeiss ULTRA Plus SEM). Prior to this analysis PPC samples were mounted on aluminum stubs, using conductive carbon paint, and then gold sputtered using the Emitech K550X sputter coater.

5.12 Synthesis of Metal-Based Catalysts

ZnGA and other metal-based catalysts were synthesized according to a previously established method [245]. Briefly, the synthesis process was conducted by the addition of equimolar ratio of reactants (e.g. ZnO and glutaric acid) into a high pressure stirred vessel. Then the vessel was pressurized with carbon dioxide at 60˚C and 100 bar using a pump (Thar Model 50P) and kept isolated for 4 h. The temperature of the reactor was controlled by using an oil bath and a digital hot plate (KIA HS4 Digital). Prior to pressurizing of the vessel, the air was purged from the system by adding CO_2 to the vessel at 5 bar and then releasing the pressure by opening the exit valve. After a predetermined period of isolation the system was depressurized slightly, high pressure vessel was opened, and the product was collected. To remove reactant residues, the product was washed with water, acetone and ethanol, respectively. The purified catalyst was then dried overnight at 40˚C under vacuum.

5.13 Measuring Catalyst Residue in Polymer

Atomic Absorption Spectroscopy (AAS) was used for measuring zinc residue in PPC. Prior to measuring catalyst residue for each sample nearly 50 mg of PPC was digested at 300˚C in a furnace (VULCAN 3-130). After that, 2.5 ml of HCl (0.6 Molar- pH:1) was added to the digested sample to dissolve catalyst. The resulted suspension was vacuum filtered to remove ash using filter paper (pore size 2 μm). Consequently, 0.5 mg of the filtrate was diluted with HCl (0.6 Molar-pH:1) in a 25ml volumetric flask. The resulted solution was then analyzed using AAS (Shimadzu aa-7000) to measure zinc concentration.

5.14 Thermogravimetric Analysis (TGA)

Thermal behavior of PPC was analyzed using thermogravimetric equipment (SDT Q600). For each analysis, 5 mg sample was added to the TGA pan. Thermal analysis tests were conducted in the range of 25 to 400˚C with a heating rate of 5˚C/min using N_2 at constant flow rate.

5.15 Preparation of Antimicrobial PPC films

Antimicrobial PPC films were fabricated using direct incorporation of thymol into bulk PPC, physical coating, and plasma treatment followed by coating. The final concentrations of thymol on the surface of PPC films were 0.6, 1.25 and 2.5 mg/cm^2 for coating samples and equivalent amounts of the agent were incorporated into the PPC films in the incorporation method. These values are determined according to the preliminary studies that show the minimum surface concentration of thymol for inhibition of bacteria growth is 0.6 mg/cm^2. In both methods, PPC films were prepared by casting technique using acetone as solvent.

Direct Incorporation Method. 20% (wt%) solutions of PPC in acetone were prepared at room temperature, and different amounts of thymol were added to each solution and stirred for 30 min. The solutions were left under stirring in laminar flow hood to be concentrated and then poured into suitable size petri-dishes to evaporate the solvent and form the films. The films were dried at ambient conditions under laminar flow hood until the solvent was completely evaporated and peeled off after 24 h.

Thymol Physical Coating. After the preparation of pure PPC films, a solution of thymol in ethanol was dispersed on the surfaces of casted PPC films to coat the surface. The coated films were then dried at ambient conditions to remove solvent residue. These values are determined according to the preliminary studies that show the minimum surface concentration of thymol for inhibition of bacteria growth is 0.6 mg/cm^2. Accordingly, the entire amount of thymol coated on the is maintained on the surface.

Plasma Treatment Followed by Thymol Coating. Plasma was generated in the chamber of PDC-002 HARRIK PLASMA using room air as plasma gas. After placing the PPC film into the chamber, it was and modified under high vacuum. Then, the plasma power was turned on followed by feeding air into the chamber. Samples were exposed to plasma for 5, 10, or 15 min, and various power levels (low–10, medium–20 and high–30W) were applied for PPC samples to examine the effect of plasma power on the PPC surface activation. Immediately after activation by plasma, PPC films were coated with thymol solution in ethanol and dried at ambient conditions to remove solvent residue. The surface of PPC samples were characterized immediately after plasma treatment and after coating with thymol to examine the effect of plasma power, time of exposure, and presence of the different thymol concentration on the PPC surface properties.

5.16 Attenuated Total Reflectance Fourier Transform Infrared (ATR-FTIR)

The effect of plasma activation and formation of antimicrobial layer on the surface of PPC films was examined with Attenuated Total reflection Fourier Transform Infrared Spectroscopy (ATR-FTIR). The ATR-FTIR spectra of PPC films were collected at a resolution of 1 cm^{-1} from 64 scans with an (FTIR) spectrometer (Thermo Scientific Nicolet 6700) fitted with an attenuated- total-reflection trapezium germanium crystal at an angle of incidence of 45˚ over the range of 600-4000 cm^{-1}. To characterize the effect of surface treatments, subtracted spectra form the samples before and after plasma exposure and thymol coating were analyzed using Grams and Resolution Pro software. Samples were washed with ethanol three times (for 2 min) prior to FTIR analysis to confirm the attachment and stability of thymol on the surface of films. The FTIR chamber was dried using silica- gel for six hours prior to the sample collection to eliminate the effect of humidity on the sample collection. The spectra were normalized against untreated PPC and water vapor spectrum was subtracted.

5.17 Water Contact Angle Measurements

The effect of plasma treatment and thymol coating on the hydrophobicity of PPC surface was measured using water contact angle technique. The drop shape analysis with drop shape tensiometer (KRUSS-DSA25) was used for this study. In each test, 0.8 µl of water was dropped on the film surface, and right and left contact angles were measured.

5.18 Thymol Release Study

Release profile of thymol into aqueous media with 10% and 90% (v%) ethanol was examined in order to assess the stability and attachment of thymol on the surface of PPC films [246]. As ethanol was a strong solvent for thymol, two different concentration of this solvent was used in this part of study. It was anticipated that lower amount of thymol was soluble in other solvents such as oil or an acidic media. Thymol coated PPC films with the surface area of 10 cm^2 were immersed in the 25 ml of the media and stored at ambient condition. Samples were collected from the media as a function of time (up to 8 days) and analyzed using Agilent Cary 60 UV-Vis Spectrophotometer at the wavelength of 274 nm to determine the concentration of released thymol. At the first stage, various concentrations of thymol (5-100 ppm) in the media were analyzed to plot calibration curve (R^2>0.99). Samples were diluted several times depending on their concentration prior to the analysis to have the thymol absorbance within the range of the calibration curve.

5.19 Antimicrobial Activity

Two different methods were used to examine the antimicrobial activity of PPC/Thymol films. In the first method, known as agar disc diffusion, the test culture *E-coli* was grown in a previously prepared media (containing 4g peptone, 2g glycerol, 10g yeast in 200mL of MQ water) at 37˚C overnight [247]. The Colony Formation Unit (CFU) was counted by serial dilutions following by inoculation on agar plates and incubating at 37˚C for 16 hours. Subsequently, four

well-separated colonies were taken from the agar plates and suspended in 3 mL media. The suspension again incubated at 37˚C for another 8 hours. After that, disk-shaped samples with the diameter of 8 mm were placed on agar plates which previously spread with 10 µl of the bacteria culture. The plates then incubated at 37˚C overnight and visually examined for inhibition zones around the films, and the diameter of this zone was measured using calipers. Pure PPC films were applied as a negative control and one drop of Anti-Anti on filter paper with the same size was used as positive control.

In the second method, PPC/thymol samples were soaked in the separated suspensions of the cultured *E-coli* and incubated at 37˚C for different time intervals. At each time point, suspensions were inoculated on agar plates, and their Colony Forming Units were calculated after 16 hours incubation at 37˚C. In either method, a high CFU *E-coli* culture media was used in this study (2.2 log CFU/ml) to demonstrate antimicrobial activity of the films [248].

5.20 Statistical Analysis

Data is reported as mean ± STD for at least three repetitions of the experiments. One way analysis of variance (ANOVA) is performed using Excel for single comparisons. Statistical significance was accepted at $p<0.05$ and indicated in the Figures as * ($p<0.05$), ** ($p<0.01$) and *** ($p<0.001$).

Chapter 6. Assessment of Physico-Mechanical Properties of PPC

6.1 Introduction

Packaging industry consumes 35-40% of the plastic materials that are produced every year. Around 50% of this amount is consumed in food and beverage sectors [33]. The development of new generation of biodegradable packaging products, particularly from renewable materials, is a sustainable solution to prevent the accumulation of non-degradable plastic wastes in landfills. In this context, poly(propylene carbonate) (PPC) is highly advantageous as it is fully biodegradable and partially renewable from carbon dioxide and propylene oxide. Fixing CO_2 into PPC as an applicable polymer may contribute to mitigating global warming effects [56]. Consequently, PPC can be contemplated as a sustainable alternative to conventional polymers for packaging of food products to reduce the issues existing in municipal waste management. To assess the potential of PPC as a promising food packaging material, it was pivotal to characterize it and confirm the minimum requirement for food packaging applications.

The objective of this part of study was to compare for the first time the properties of PPC with other polymers that are commercially used for food packaging and other applications. To this end, in this chapter, the physico-mechanical prosperities of PPC were measured to demonstrate its potential for a broad range of applications, particularly in food packaging. The mechanical strength, barrier properties, chemical resistance and biodegradability of PPC was compared with commonly used polymers, such as LDPE, Eco-Flex and polyethylene/starch blend (with the commercial name of BLFO2). Moreover, the effect of natural polymers such as starch and cellulose on the physico-mechanical properties of PPC was investigated.

6.2 Mechanical Properties

The mechanical properties are critical factors in the selection of material for food packaging application, since any impact during the handling, shipment and storage may affect the safety and the quality of the final food product. Tensile

strength determines the maximum load before the rupture of a material that is an important parameter in food packaging.

The tensile modulus of PPC was three-fold higher than biodegradable Eco-Flex polymer and two-fold higher than BLFO2. It was also within the same range for non-degradable LDPE. Furthermore, the ultimate strength of PPC was significantly higher than LDPF, Eco-Flex and BLFO2 (Figure 6.1.B). These results confirmed that biodegradable PPC films have excellent tensile properties compared to the most commonly used biodegradable and non-degradable polymers for food packaging applications.

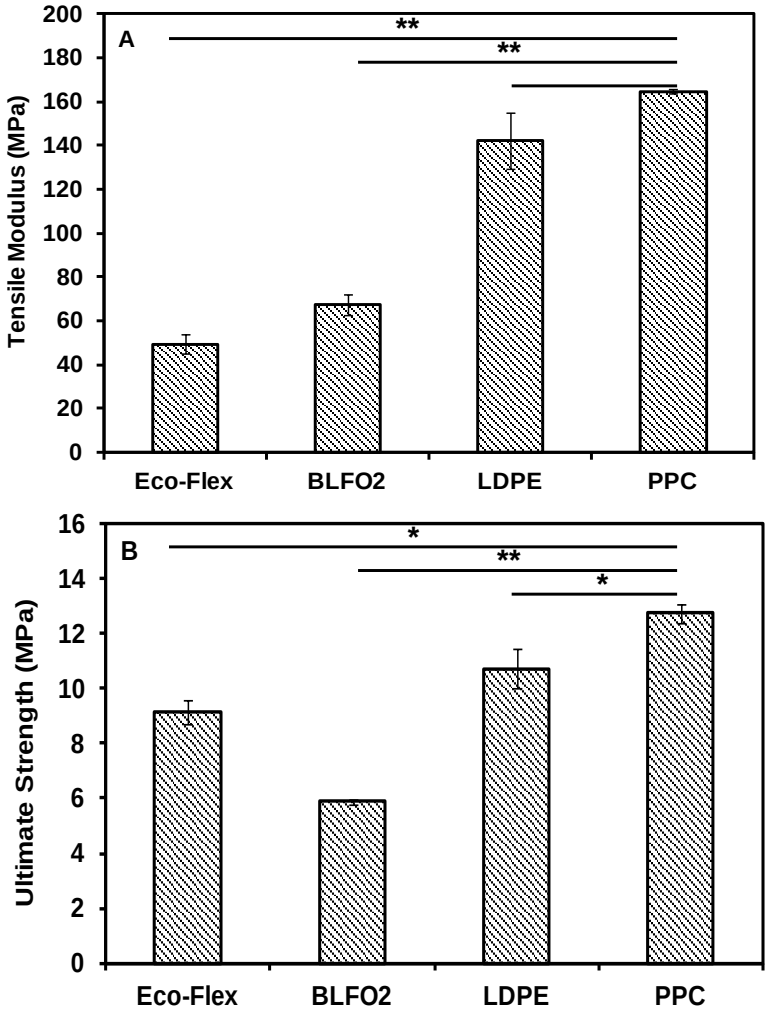


Figure 6.1. A) Tensile modulus and B) ultimate strength of different polymers

Additionally, the durability of the polymers against the tear force and growth of any cut under tension force are of great importance to assure their applicability in food packaging. The results presented in Figure 6.2 show that the tear resistance of PPC is more than three-fold higher than LDPE and significantly higher than BLFO2. **W**hile the data in Figure 6.2show that the tear resistance of PPC is not as high as biodegradable Eco-Flex, it may still suitable for packaging of product that does not need high tear force.

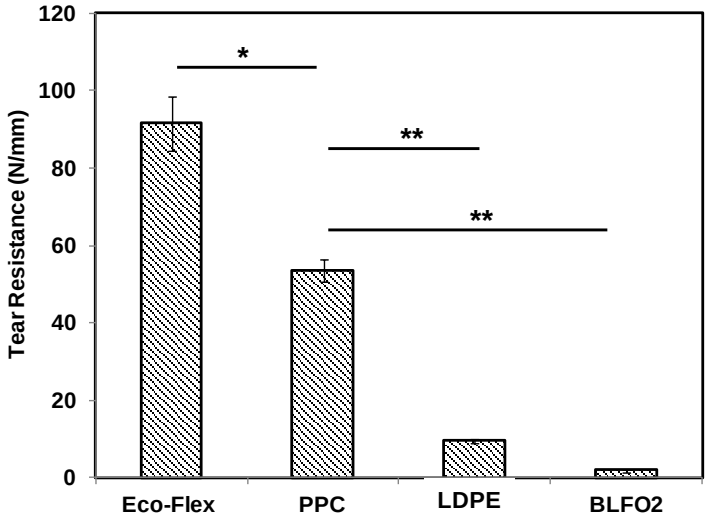


Figure 6.2. Tear resistance of different polymers

6.3 Barrier Properties

The barrier property of a material used in the packaging plays a critical role in the shelf life of a food product. Small molecules, such as oxygen and water vapor may permeate through a polymer and have an adverse impact on the food safety and quality [29]. The results show that PPC has superior barrier properties for food packaging. For example, the results in Figure 6.3 demonstrate that the oxygen transfer rate (OTR) and water vapor transfer rate (WVTR) through PPC are lower than other LDPE and Eco-Flex that are broadly used commercially for food packaging. The results for PPC and LDPE are in the same order of magnitude reported in the literature. The minor differences could be due to the variation in the molecular weights of these polymers and sample preparation

methods. Therefore, application of PPC for food packaging can potentially reduce the risk of food spoilage and thus preserve the food quality by reducing the rate of water loss or absorption.

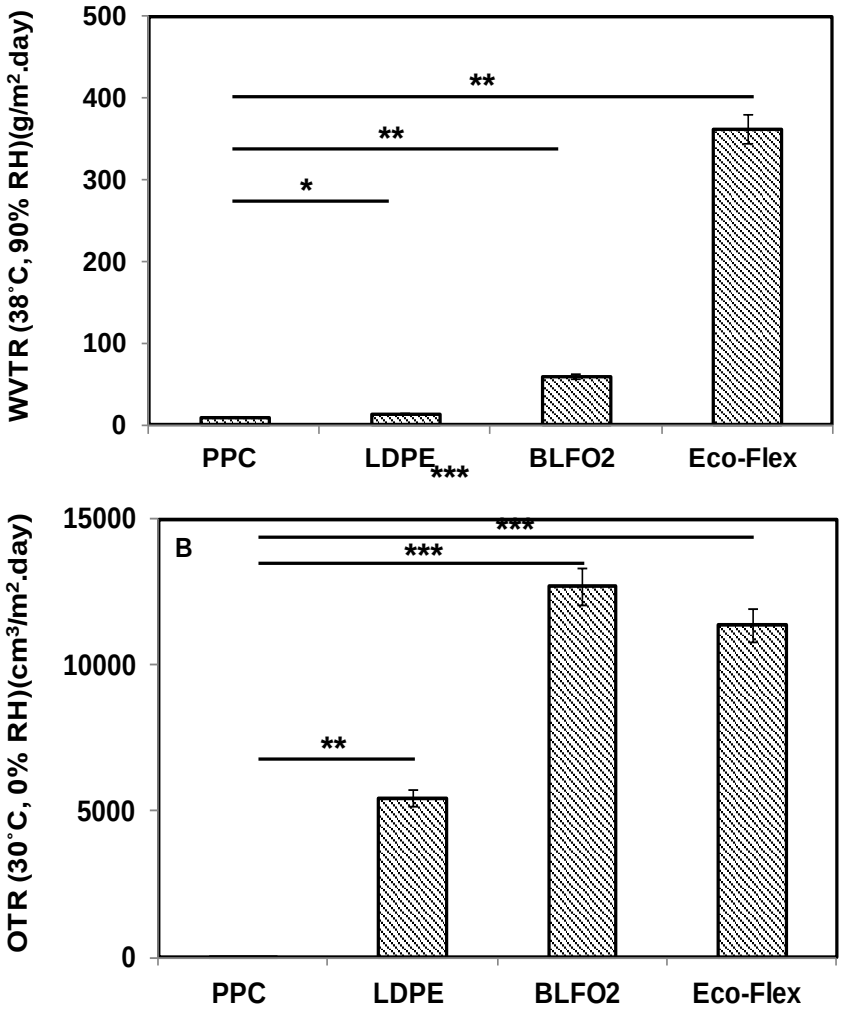


Figure 6.3. Comparison of A) OTR and B) WVTR of PPC with other commercial polymers

6.4 Chemical Resistance in Food Simulated Media

It is pivotal to determine the chemical resistance of a polymer, particularly, a packaging material in different simulated conditions. For instance, the residue of polymer degradation might have a negative impact on food safety and quality [29]. Our previous study demonstrated slow degradation of PPC compared to PLA in buffer solution [76]. Upon the addition of enzymes such as α-amylase and

lipase in the buffer solution the degradation of PPC was only 9% within eight weeks [29]. In this study, food stimulants are used to further examine the degradation of PPC and its chemical resistance [82]. PPC films were placed in several different media at pH 4, 7 and 10, 50% (v%) ethanol and edible oil. The physico-chemical properties of samples were then analyzed by using gravimetric technique, SEM, GPC and NMR analyses.

After six months incubation at ambient conditions, no significant mass loss was observed for PPC, as well as commercial LDPE and Eco-Flex ($p > 0.05$) when exposed to different media. In addition, the results in Figure 6.4 demonstrate negligible effect on surface morphology of PPC after this test. GPC analysis showed that the molecular weight of PPC did not change within this period of incubation in food simulated media ($p > 0.05$). PPC therefore can be used alone or as a coating polymer for packaging a broad range of food products.

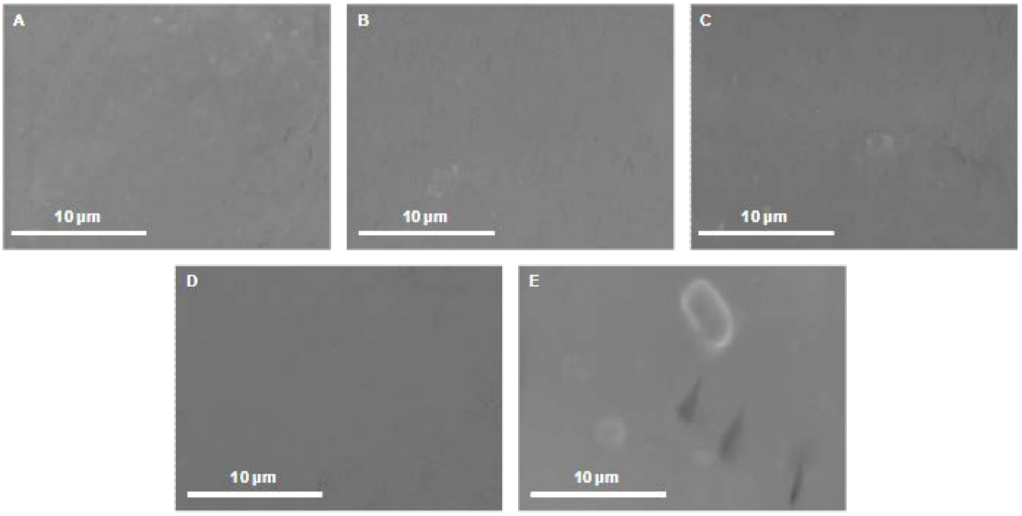


Figure 6.4. SEM images of the PPC films A) before incubation and after 6 months incubation in B) acidic, C) basic and D) 50% ethanol E) fatty food simulated media

The hydrophobic nature of PPC and its chemical resistance make this polymer more suitable for packaging compared to renewable and natural based polymers such as starch. On the other hand, the results in Figure 6.5 show that while mass loss for BLFO2 films was negligible in fatty media, it was nearly 7% within six months period in other media such as acidic, alkaline, and alcoholic. This mass loss is due to the hydrophilic nature of starch in the structure of BLF2.

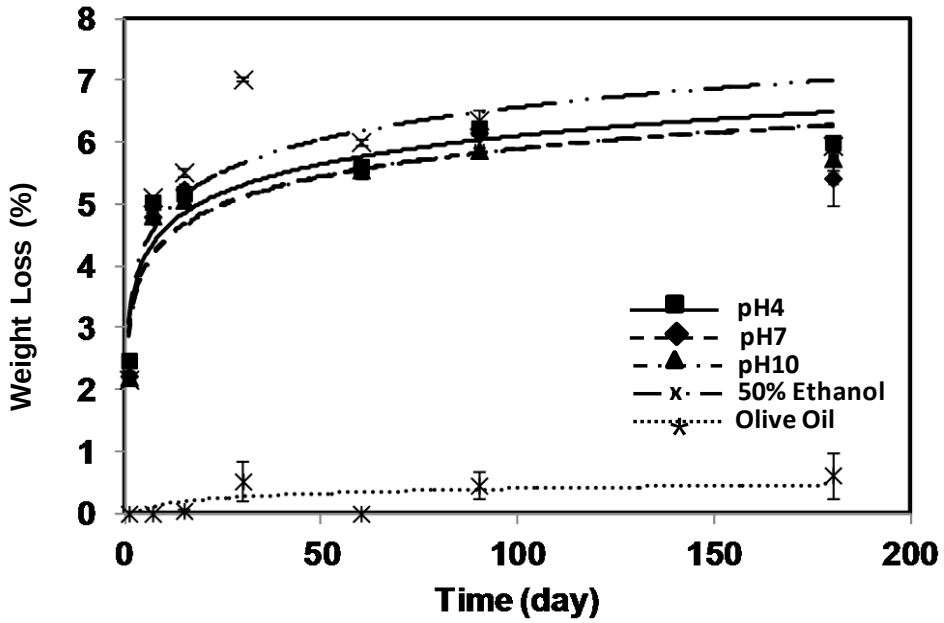


Figure 6.5. Degradation of BLFO2 films in various media in six months period

6.5 Soil Burial Biodegradation

The biodegradation and composting rate of a polymer is governed by several factors such as molecular weight, surface area, concentration and type of additives, bacteria composition and condition of the soil [57]. Previous studies reported 4% mass loss of PPC films (MW=50-65 KDa, thickness ~ 40-50 μm) buried under enriched garden soil for six months [77]. However, the result of another study in the standard composting condition for a 300 μm film of PPC with high molecular weight of 670 KDa demonstrated considerable decomposition of 63% after nearly three months [57]. Such a broad discrepancy in the degradation rate reported for PPC is most likely due to different experimental conditions, i.e. variation in PPC characteristics, types of soil, microorganisms and enzymes presented in different studies. Accordingly, we assessed the biodegradation rate of PPC and other polymers at standard condition to avoid any inconsistency. The degradation behavior of these polymers were compared in two different soil types including sterilized garden soil and compost soil at a controlled temperature and moisture content (40˚C, 50% RH). In the case of sterilized garden soil, less than 10% mass loss was measured for BLFO2 ($p <$

0.01), and no degradation was observed for PPC, LDPE and Eco-Flex after six-month burial at the same temperature and relative humidity condition ($p > 0.05$). The small degradation rate for BLFO2 was solely due to hydrolysis of starch. The degradation of PPC and other polymer samples was significant when they buried under non sterile compost soil. As the results in Figure 6.6 demonstrate, the mass loss of BLFO2 films was nearly 80 wt% after six months due to the presence of starch in their structure that is a hydrophilic and biodegradable polymer. Nonetheless, no significant mass loss was observed for pure LDPE films. In addition, mass loss of PPC films was nearly 8% within six months, which was slightly lower than the biodegradable Eco-Flex. The PPC degradation rate in soil was nearly comparable with the value acquired from buffer solution that contained enzymes (110 U/L from Rhizopus oryzae). It can be concluded that the soil composition and its microbial level have paramount impacts on the PPC biodegradation rate. Therefore, the enzymatic reaction plays a key role in breaking the PPC polymer structure and its degradation.

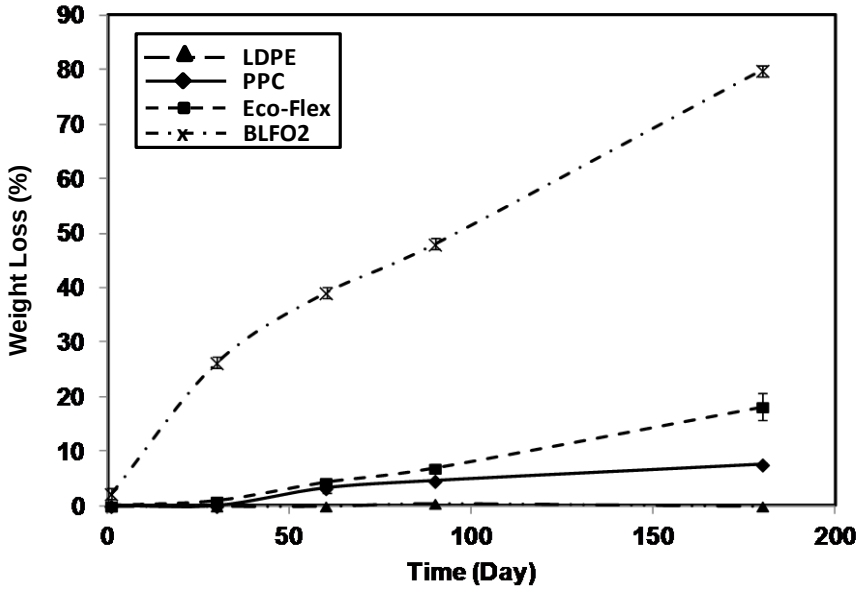


Figure 6.6. The weight loss of polymer films in compost soil as a function of time

The macroscopic images of polymer films at different time points during the biodegradation test are presented in Figure 6.7. As it was anticipated, the degradation of polyethylene films during the six months period was negligible.

However, the surface of BLFO2 films was substantially degraded, and both PPC and Eco-flex films were degraded gradually during this period. Furthermore, the SEM images of PPC films in Figure 6.7. E endorsed the appearance of erosion on the surface of these samples after six months.

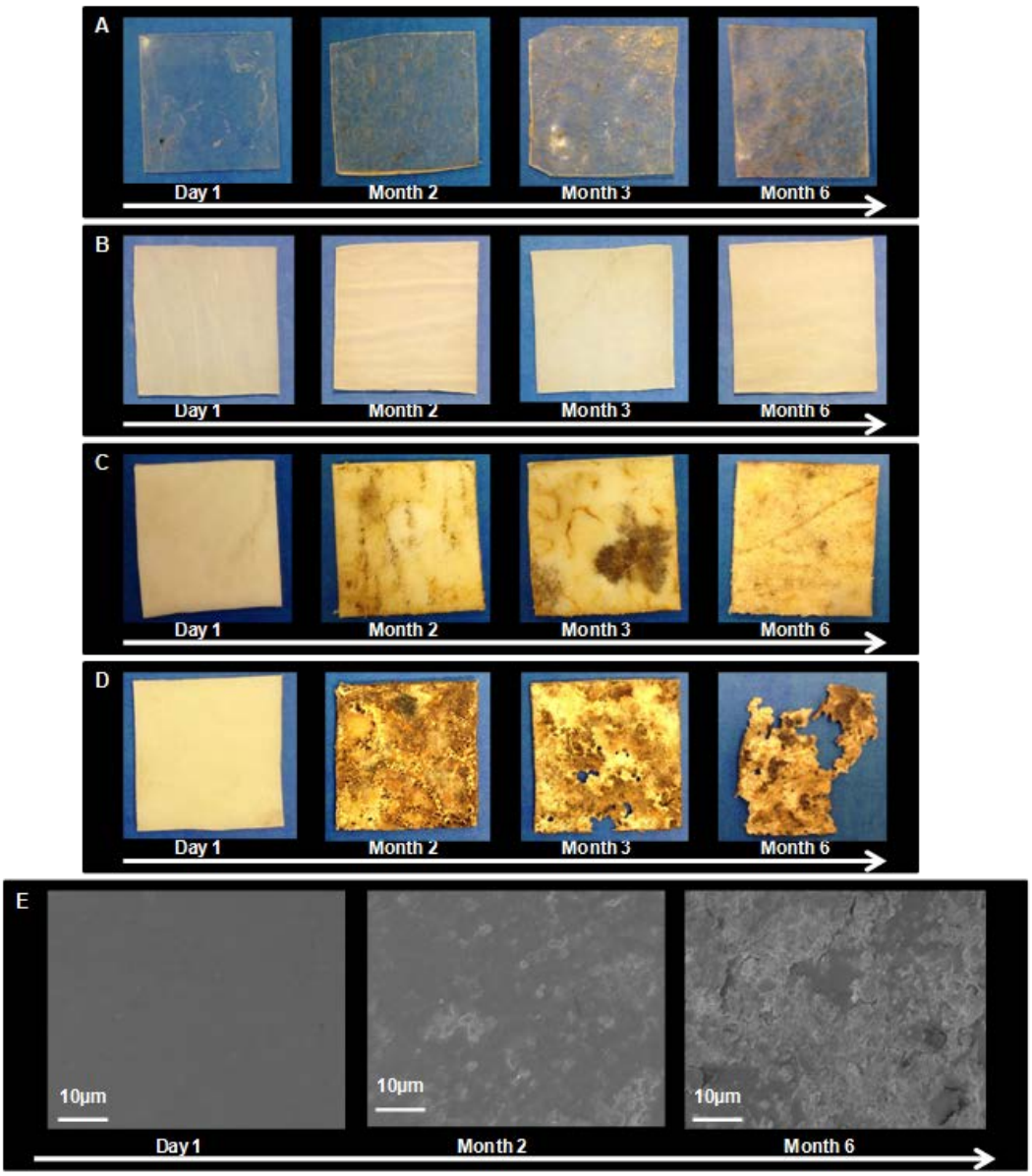


Figure 6.7. The images of A) PPC, B) LDPE, C) Eco-flex, D) BLFO2 and E) SEM images of PPC films at different time points of soil burial

Gel permeation chromatography (GPC) was conducted to investigate the impact of degradation on the average molecular weight and poly-disparity index (PDI) of

PPC films. As shown in Figure 6.8 and Table 6.1, the GPC chromatogram of PPC was gradually broadened by increasing the degradation period, also its average molecular weight was decreased, and the PDI was increased. As an illustration, after six months the PPC molecular weight reduced by 15%. These data confirmed the breakdown of PPC at the molecular level and showed the segmentations of random units from the large polymer chains.

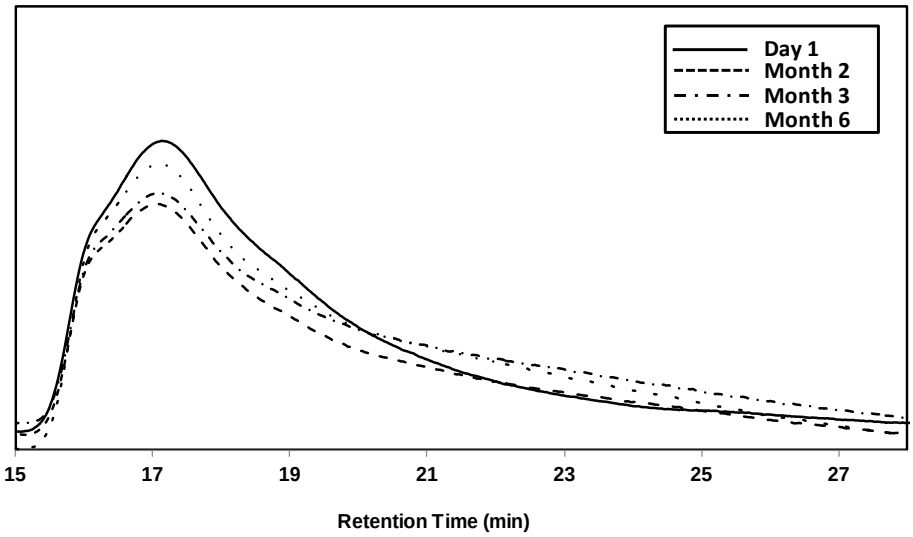


Figure 6.8. GPC chromatogram of PPC samples before and after soil burial biodegradation

Table 6.1. Molecular weight and PDI of the PPC films before and after soil burial biodegradation

PPC Sample	**Mw**	**PDI**
Control (month 0)	463,746	3.26
Second Months	417,026	4.69
Third Months	409,809	5.58
Sixth Month	394,721	6.23

To more comprehensively study this degradation mechanism, ^{1}H-NMR analysis was conducted on PPC films at different time intervals post-soil burial degradation study. The results in Figure 6.9 demonstrate chemical shifts of PPC before and after biodegradation : ^{1}H NMR (δ, $CDCl_3$), 1.31 (3H, CH3), 4.18 (2H,

CH2CH), 4.98 (1H, CH2CH) for carbonate structure (n) [60], and 1.14 (3H, CH3), 3.56 (2H, CH2CH), 3.40 (1H, CH2CH) for ether structure (m) [245]. To assess the effect of biodegradation on PPC films, the ratio of integrations at (4.18, b) and (3.56, d) were compared. The ^{1}H NMR spectra of PPC samples showed that after degradation, the ratio of b/d was significantly decreased due to the degradation. For instance, b/d ratio at day 1 was 14.41 while after first and sixth month burial in soil it was decreased to 13.50 and 12.11, respectively. The reduction in the ratio of b/d integrations endorsed the break-down of carbonate linkages in the polymer backbone during biodegradation. Therefore, the ratio of carbonate linkages to ether linkages was decreased as a function of time.

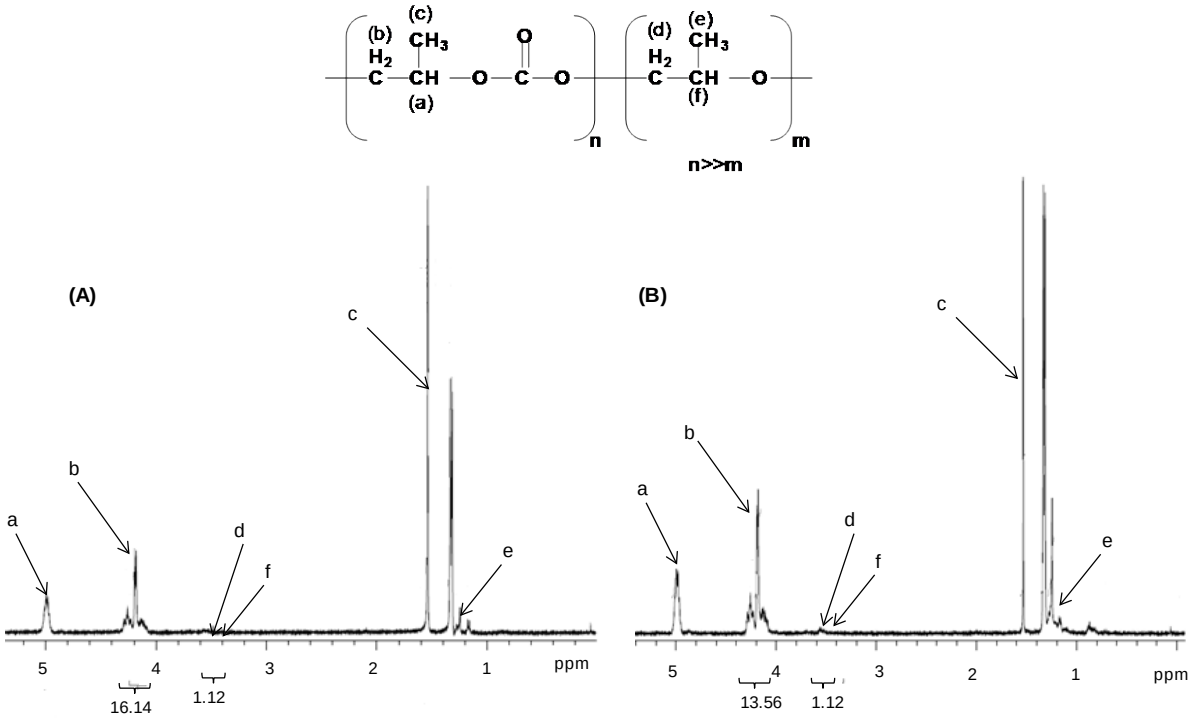


Figure 6.9. ^{1}H NMR spectra of PPC in A) day 1 and B) month 6 of soil burial

The tensile test was conducted to assess the impact of degradation on the mechanical strength of the PPC films. As depicted in Figure 6.10, PPC tensile modulus decreased nearly 45% after six months degradation in soil. In fact, this drop of mechanical strength was attributed to the gradual reduction of molecular weight and the degradation of PPC chemical structure. Conversion of the large

molecular chains with carbonate linkages to the short chains with ether linkages has a direct impact on the mechanical properties of PPC.

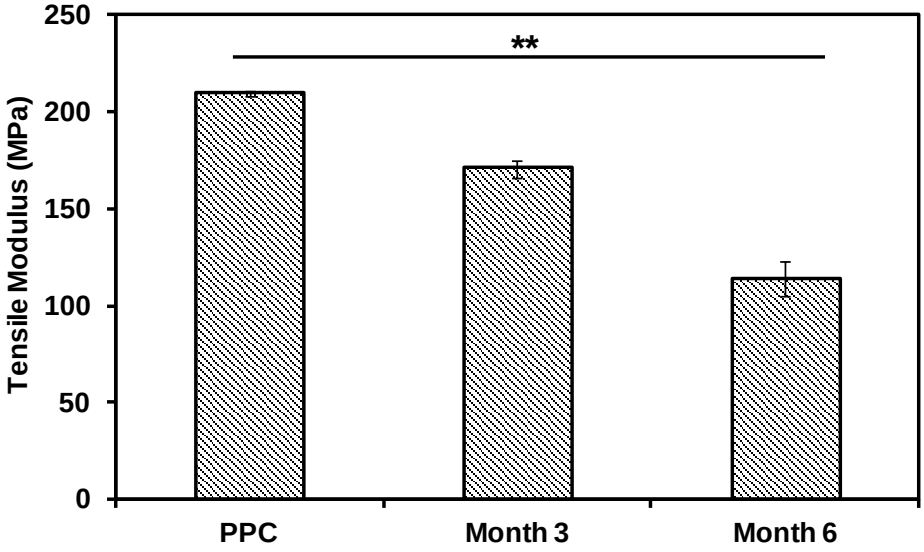


Figure 6.10. Tensile modulus of the PPC films during the biodegradation test

6.6 Effect of Addition of Renewable Natural Polymers on the Properties of PPC

It was attempted to blend PPC with cellulose and starch, two renewable natural polymers, to promote its mechanical properties and, enhance the degradation rate of the material. The preliminary results showed that homogenous blends were achievable when the compositions of starch and cellulose microparticles in PPC were below 50% and 25% (by weight), respectively. These compositions are the maximum amount of starch and cellulose that could be added to PPC to maintain homogeneity, desirable mechanical properties and also higher degradation rate. The addition of both starch and cellulose to PPC enhanced the tensile modulus of PPC remarkably (Figure 6.11). However, the addition of starch polymers had a negligible impact on the ultimate strength of PPC and blending with cellulose only slightly increased its ultimate strength.

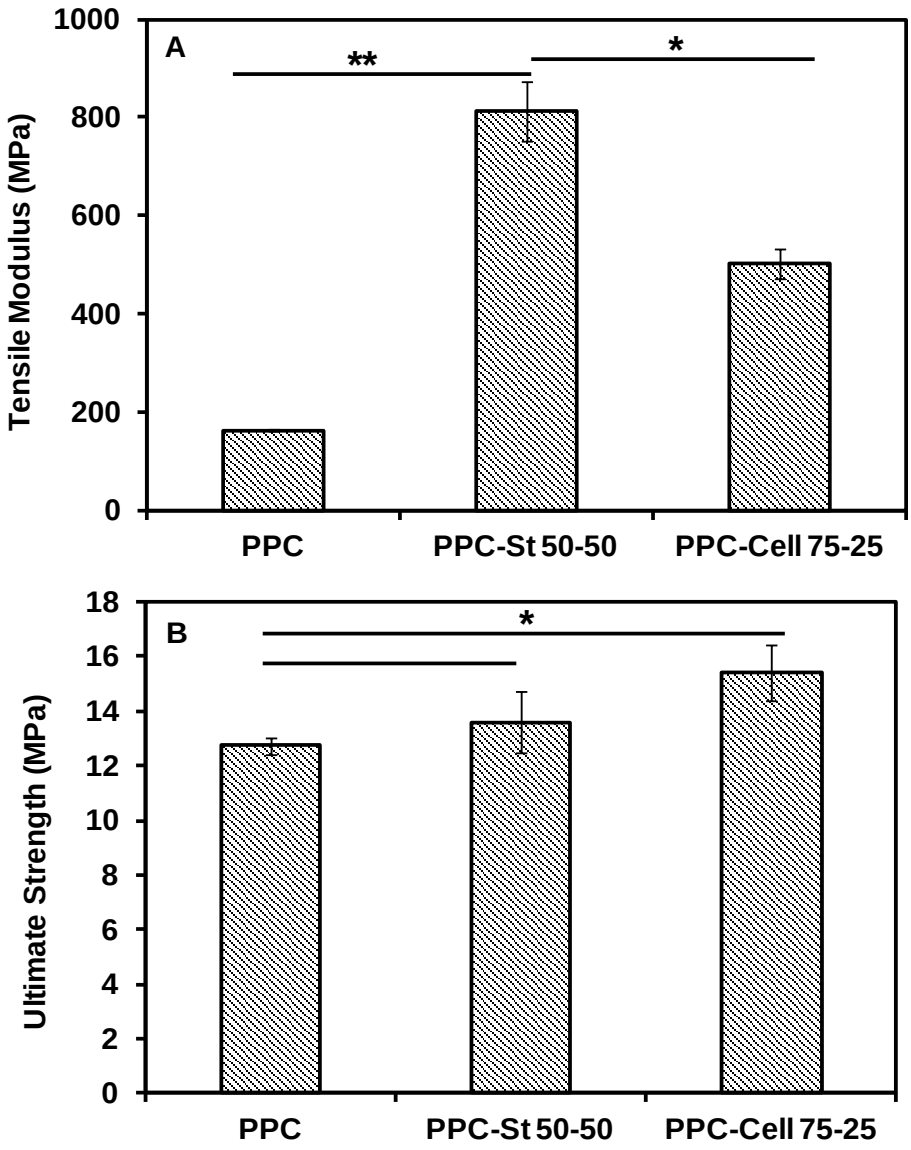


Figure 6.11. A) Tensile Modulus and B) Ultimate Strength of PPC and PPC composites with natural polymers

On the other hand, as shown in Figure 6.12, the presence of starch and cellulose had an adverse effect on the tear resistance of PPC. In fact, the addition of 50% starch significantly decreased the tear resistance of PPC to one forth. Therefore, these blends could not be used for the applications in which the high tear force is critical. However, a lower amount of starch in the composite may have less impact on this property of PPC. For instance, upon addition of 10% starch the tear

resistance was approached to 42.4±0.18 N/mm that was more than four-fold higher than samples that contained 50% starch

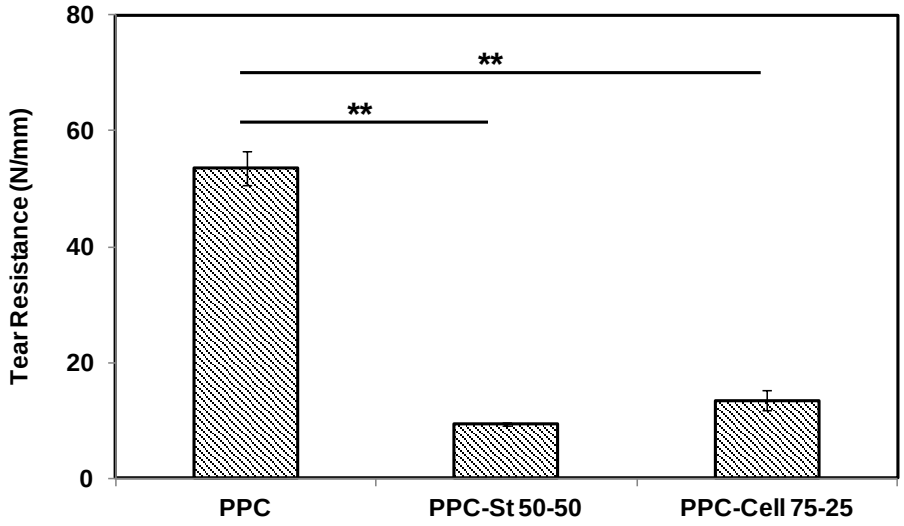


Figure 6.12. Tear Resistance of PPC and PPC composites with natural polymers

We examined the presence of starch and cellulose on the PPC chemical resistance when placed in different food stimulant environment. The results in Figure 6.13 show that degradation of PPC films that contained 50 wt% starch and 25 wt% cellulose were 1% and 3%, respectively during six months in various aqueous media such as acidic, basic, neutral and alcoholic. However, for each sample there is no significant difference in weight loss in various media ($p > 0.05$). The slight weight loss of PPC films blended with starch and cellulose is due to their hydrophilic properties. The micro particles of these natural polymers leached out of from the PPC film. However, the degradation of both blends in fatty food stimulant media was negligible. Nevertheless, pure PPC films were chemically resistant to these environments within six months of soaking. Therefore, for food packaging applications, it should be taken into account that the addition of starch and cellulose to PPC slightly decreased its chemical stability. However, PPC can be used as a thin film coating on the surface of PPC-starch to maintain the chemical stability.

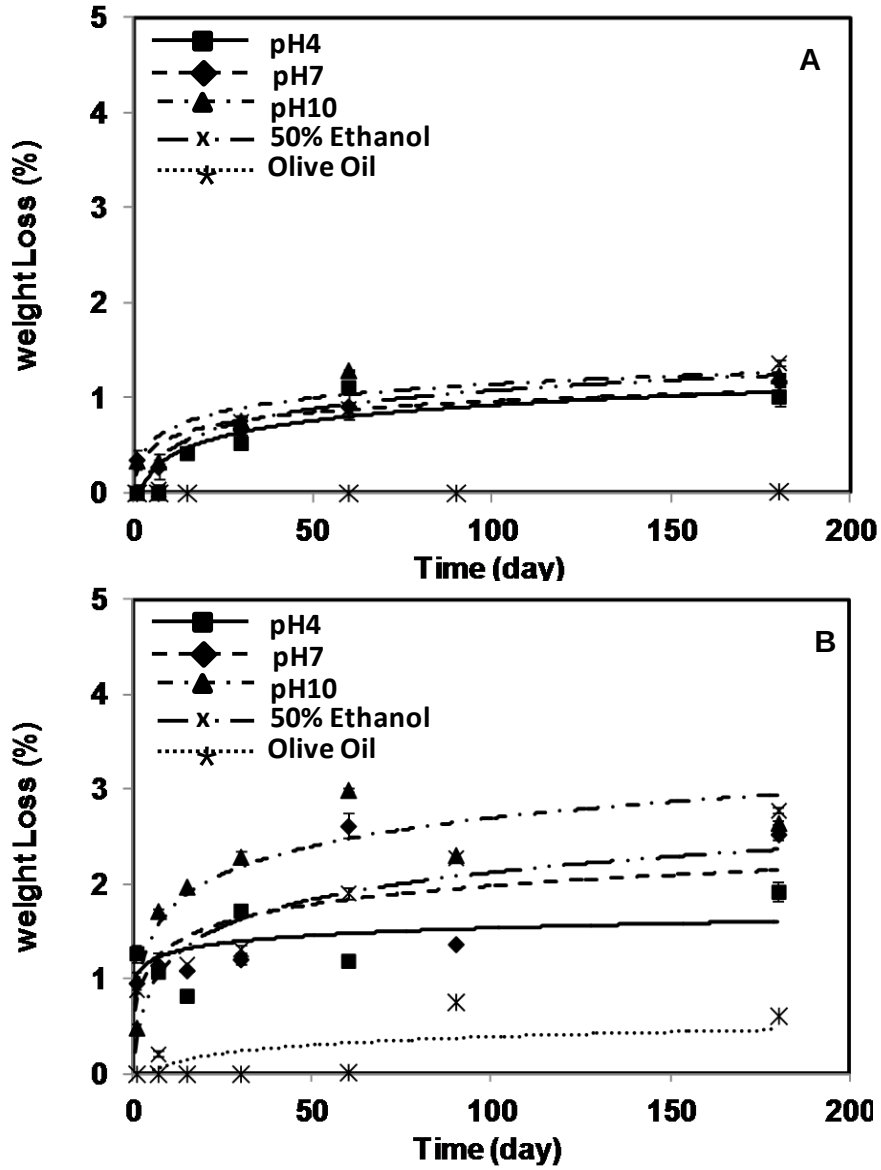


Figure 6.13. Degradation of A) PPC-St 50-50 and B) PPC-Cell 75-25 films in various media in six months period

The addition of starch and cellulose increased the degradation rate of PPC in soil to 50% and 20%, respectively as depicted in Figure 6.14. This enhancement was attributed to the faster degradation of starch and cellulose compared to PPC in soil. However, in the sterilized soil the degradation of PPC films do not exceed 20% and 5% after addition of up to 50% starch and 25% cellulose, respectively.

These results confirmed that microbial level of the soil is a crucial factor governing the degradation of the polymer films.

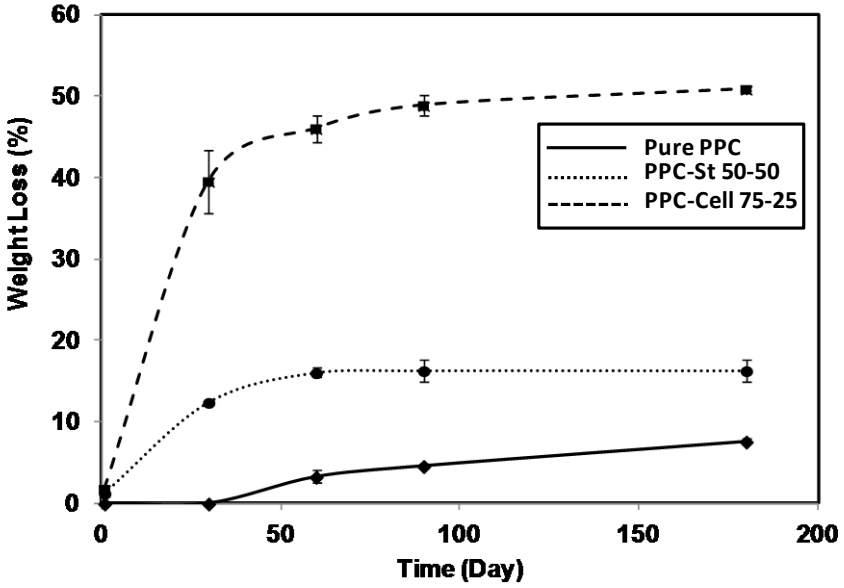


Figure 6.14. Weight loss of the polymer films in compost soil as a function of time

6.7 Summary

In this chapter, it was demonstrated that PPC has superior properties compared with other polymers for packaging of food products and many other applications. The mechanical properties of PPC are higher than biodegradable Eco-Flex and comparable to LDPE. In addition, barrier properties of PPC were significantly higher than other examined polymers. High barrier properties are crucial to prevent food spoilage, maintain the quality of the product and prolong the shelf life. In addition PPC is chemically resistant to aqueous, acidic, organic and fatty foods. Therefore, replacing biodegradable PPC is a remedy for plastic waste management that is one of the major environmental issues. More importantly, PPC degrades in soil, and its degradation rate is comparable with biodegradable Eco-flex in landfill. Finally, it was demonstrated that by the addition of natural polymers such as starch and cellulose to PPC, the mechanical properties and the degradation rate of this polymer can be tuned for desirable applications. However, it may result in loss of chemical stability or tear resistance of the polymer. In

summary, biodegradable PPC can be contemplated as an alternative to LDPE and Eco-Flex for a broad range of packaging applications. Its properties can be also tuned by addition of natural fillers to meet the standards and criteria of different applications.

Chapter 7. Solvent Free Method for the Purification of PPC

7.1 Introduction

PPC is synthesized from the alternative copolymerization of CO_2 and propylene oxide in the presence of zinc glutarate (ZnGA) that is an efficient and low-cost catalyst. However, the presence of the metal-based catalyst residue and other impurities are still the major burden for commercial applications of PPC. This catalyst is soluble in an acidic solution, and either liquid-liquid extraction, or leaching methods can be used to remove it from PPC. It is proposed to utilize CO_2-water at high pressure as a benign system for the purification of PPC and removing zinc glutarate to tackle the issues existing in current methods such as consumption of a huge amount of organic solvents and energy. It was hypothesised that the pH drop of water as a result of CO_2 dissolution can make acidic media that is capable of extracting metallic compounds form the polymer.

In this chapter, firstly, the feasibility of using CO_2 laden water as acidic media to dissolve metal-based catalyst was examined at different operating conditions. After which, the novel method developed for the extraction of metal residues from PPC was described. The operating conditions for increasing the extraction efficiency of the catalyst in this solvent system were determined. The efficiency of conventional solvent extraction methods were also compared with this new technique. Finally, the effect of purification process on the physico-mechanical properties of PPC was examined.

7.2 Development of the Solvent-Free Method for ZnGA Solubility Measurement and Purification of PPC

Custom made high pressure set up was used to measure the solubility of an organometallic catalyst as shown in Figure 7.1 schematically. The set up consists of an ISCO 500D syringe pump, a custom made high pressure extraction vessel, a water bath and a sample collection vial. The temperature was controlled by a Thermoline (TU1 Unistat heater/circulator). A sintered stainless steel container with the porosity of 0.2 μm was made in house to keep the catalyst samples inside the extraction vessel. In each experiment, a known amount of the catalyst was

mixed with glass beads and loaded into the stainless steel container. The container was capped with cotton to avoid blockage of the connection pipelines in the high pressure system and dried under vacuum at 40˚C overnight to remove the moisture. After drying, the container was weighed and placed into the high pressure reactor. Subsequently, the container was immersed in milliQ water (50 ml water/g catalyst). The vessel was then sealed and placed in a water bath at a predetermined temperature for 30 min to reach thermal equilibrium. After that, the system was pressurized to the desired pressure, and then it was isolated for a period. Then, the sample was collected in a cold trap, which was installed at the end of setup. For this step the pump was run at constant pressure mode, then the exit valves were opened slightly to prevent high pressure drop in the system and also to control the CO_2 flow rate within 3 to 5 ml/min. The system was run in two modes: (1) During pressurization step, CO_2 was introduced to the system from the bottom to maintain water in the vessel and (2) for sampling, CO_2 was added from the top of the vessel to purge all water from the system. After sample collection, the extraction vessel was depressurized, and the stainless steel container was dried under vacuum at 40˚C. The gravimetric method was used to measure the solubility of each catalyst in the CO_2 laden water phase.

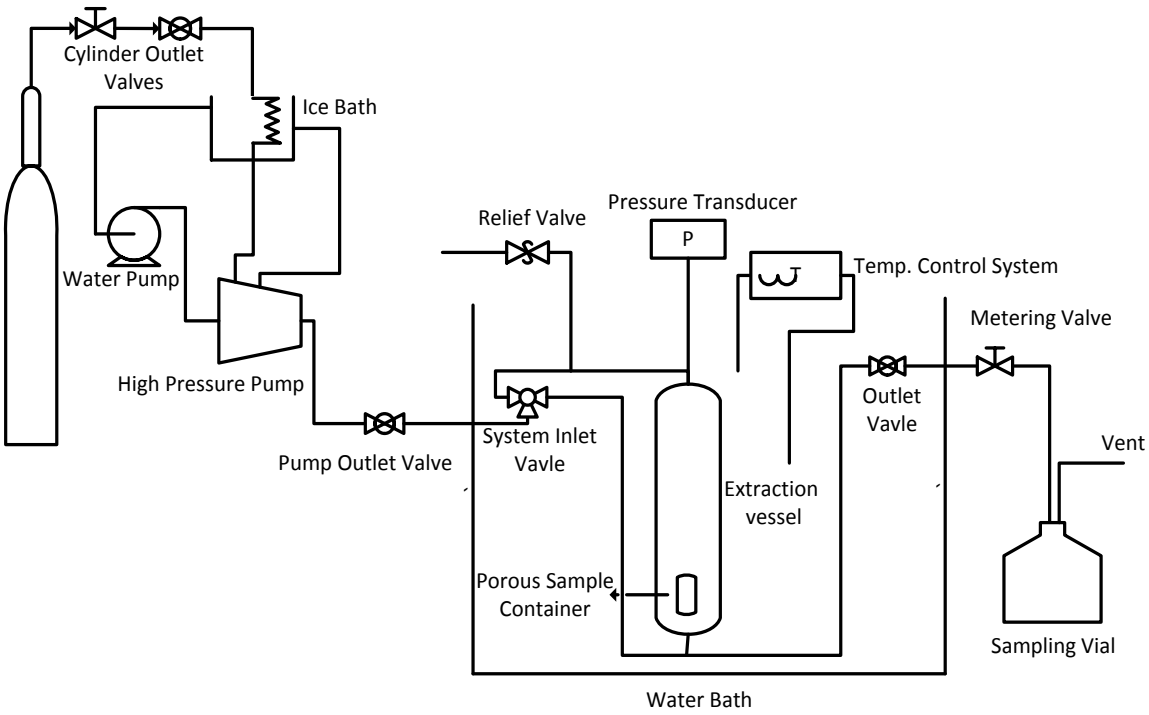


Figure 7.1. Schematic diagram of the apparatus designed for measuring catalyst solubility

7.2.1 PPC Purification

Three different methods were used for the purification of PPC and removing catalyst residues. These included extractions by CO_2 laden water phase, liquid-liquid antisolvent, and solid leaching. These methods are described briefly in this section.

- **CO_2 laden Water system:** The apparatus shown in Figure 7.1 was also used for the purification of PPC. In each run 50 ml water/g PPC was loaded into the high pressure vessel, the system was then pressurized at the desired temperature and isolated for a predetermined period of time. After this static mode, the water was purged from the system at the constant pressure and the system was depressurized. The polymer was then analyzed to determine the residues of impurities.

- **Conventional solvent-antisolvent method** [245]: the polymer was dissolved in DCM (0.1 mg/ml). 1:1 volume ratio of this solution and the aqueous phase that contained 1.5 molar hydrochloric acid (pH:1) were mixed vigorously at ambient temperature for 5 min. Then, two phases were separated to collect the polymer rich phase (DCM). This step was repeated twice, and then the polymer was washed once with distilled water to remove the residue of acid from the polymer. The polymer rich phase was then added to methanol drop by drop to precipitate purified PPC and dried at 40˚C under vacuum to remove methanol.

- **Leaching method** [8]: This method was conducted using maleic acid as a solvent and the extraction was performed at 90°C. PPC was micronized prior to purification to promote mass transfer rate between the polymer (solid phase) and maleic acid (liquid phase) [8]. Micronized PPC was soaked in maleic acid solution (3% w/v water) at 90°C and stirred for 2h. The ratio of maleic acid to PPC was 50 ml maleic acid/ 1g PPC.

7.3 Solubility Measurements of ZnGA in Water Laden CO_2

Prior to use water laden CO_2, it was attempted to examine several media and a broad range of conditions as a solvent for Zinc glutarate. It was found that neither pure high pressure CO_2 nor CO_2 saturated with water at high pressure (50-200 bar) and temperature range of (25°C-55°C) are efficient for extraction of zinc glutarate. Even addition of other co-solvents such as ethanol did not improve the efficiency of the process. Therefore, the process was shifted to use water saturated with CO_2 at high pressure. The solubility of ZnGA in water laden CO_2 phase was measured at a pressure range of 60 bar to 160 bar and temperature from 25 to 45˚C. Prior to running these experiments, the solubility was measured at different time periods (2 to 24 h) at a set pressure and temperature to verify the required time for achieving equilibrium in the system. The results in Figure 7.2 show that the solubility was increased by extending the sampling period and then

approached a plateau after 24 h. Indeed, there is no significant difference in the solubility of the catalyst into CO_2 laden water after 16 hours ($P > 0.05$). The mass transfer driving force in this static system was high at an early stage of the extraction; however, the zinc concentration in the CO_2/water phase gradually increased by prolonging the processing time up to 24 h when the system approached equilibrium. Therefore, for the rest of experiments the solubility at all operating conditions was measured after 24 h to confirm achieving equilibrium in this static system.

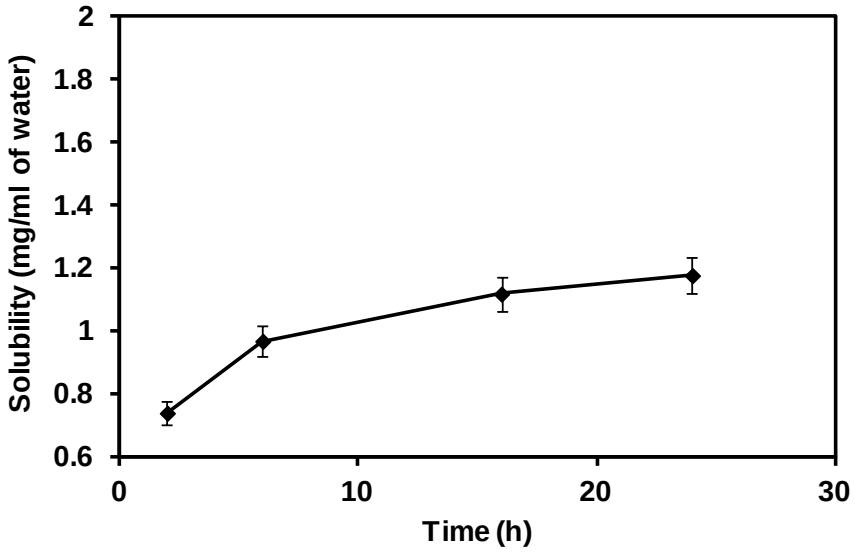


Figure 7.2. The effect of extraction time on the solubility of ZnGA in CO_2 Laden water at 100 bar and 40 ˚C

The solubility of ZnGA was measured at 25˚C and 40˚C and various pressures to examine the effect of pressure on ZnGA solubility. The results in Figure 7.3 show that at each tested temperatures the solubility of ZnGA remarkably increased by elevating the pressure, due to enhancing CO_2 density (concentration of CO_2 in water) and reducing the pH [127, 249]. For instance, the solubility of ZnGA at 40˚C was increased from 0.70 mg/ml at 60 bar to 1.37 mg/ml at 100 bar in which CO_2 solubility in water was enhanced from 22 to 27.81 ml CO_2/ml water while pH only slightly dropped from 2.84 to 2.83, respectively [250].

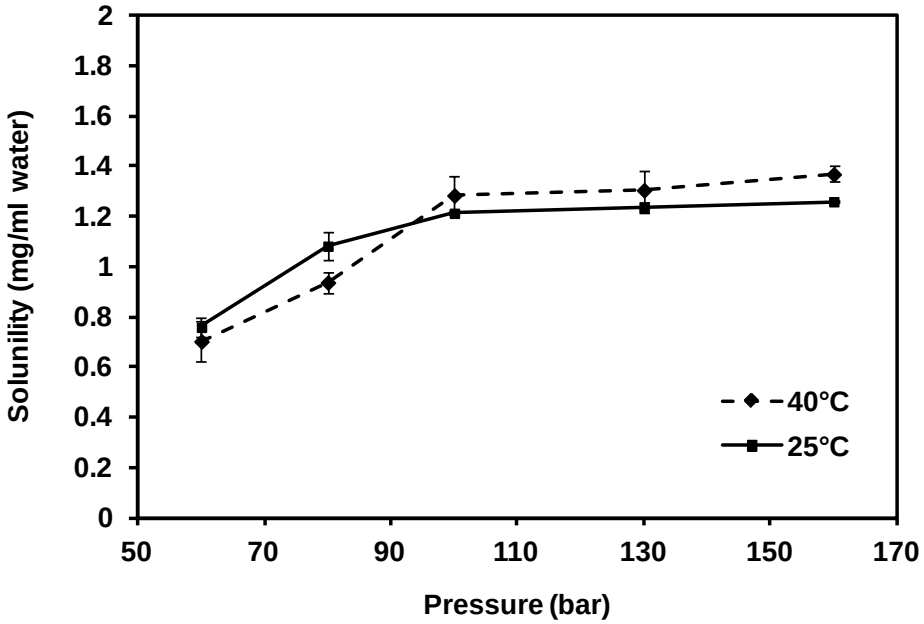


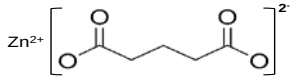
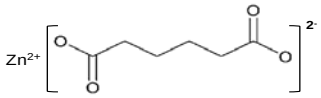
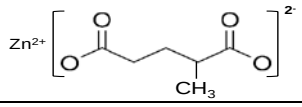
Figure 7.3. The effect of operating pressure and temperature on the solubility of ZnGA in CO_2 laden water

The effect of pressure on CO_2 solubility in water was attributed to the solvent density and the free volume difference between water and CO_2. The definition of the free volume is the total integral of a specific proportion of the potential energy that is caused by the thermal displacements of the centre of gravity of the molecule from its equilibrium [251]. In other words, free volume is the volume available for the molecule after removing the molecule core itself [252]. It is an indication of the compressibility of the molecule. The free volume difference between a solute and solvent affects the interaction level between these molecules in a solution. In a solvent with higher density, the solute is in a closer proximity to interact with the solvent molecules, and it is most likely dissolved [252]. Temperature, however, did not have a significant impact on the solubility of ZnGA at different pressures ($p > 0.05$). This effect was attributed to the fact that at each pressure, the temperature had a negligible effect on pH and partial molar of CO_2 in water [177]. This is due to the fact that the solubility of CO_2 in water is proportional to the partial pressure according to the Henry's law [177].

7.4 Solubility of other Metal-Based Catalysts in CO_2 laden Water

The efficiency of CO_2/water for the extraction of a broad range of zinc based catalysts was demonstrated by measuring the solubility of different catalysts such as zinc methyl glutarate (ZnMGA) and zinc adipate (ZnAA) in this system. Both these catalysts are active for the synthesis of PACs, particularly for PPC [253, 254]. The results in Table 7.1 show that both of these catalysts were soluble in CO_2/water at 100 bar and 40˚C. The higher solubility of ZnMGA and lower solubility of ZnAA compared to ZnGA was attributed to the differences in their polarities. ZnAA has a longer molecular chain; thus, it is less polar than ZnGA and ZnMGA. In contrast, ZnMGA is more polar than the other compounds due to the presence of methyl group on its molecular chain. Therefore, it was demonstrated that carbonic water at high pressure is an efficient solvent for the extraction of metal-based catalysts that are soluble in acidic solvents. It is important to note that the pH of this system was nearly 3, and it was higher than acidic solvents (pH 1) that were reported for dissolving these catalysts in the literature. This facilitates the scaling up and commercialization of this process due to the fact that lower pH causes more corrosion and require stronger and more expensive alloys for the process unit operations.

Table 7.1. Solubility of metal-based catalysts in CO_2 laden water system at 100 bar and 40 ˚C

Compound	Molecular Structure	Solubility (mg/ml water)
ZnGA		1.28 ± 0.08
ZnAA		0.66 ± 0.06
ZnMGA		1.54 ± 0.01

7.5 Purification of PPC Using CO_2 Laden Water

Despite the superior property of PPC, one of the hurdles for its application as a biodegradable material for food packaging is the presence of metal-based catalyst

residues. The current extraction methods such as solvent extraction and leaching are not effective for reducing these catalysts residues below the acceptable level [255]. In addition, these methods involve using toxic chemicals such as acid and large quantities of organic solvents. The solubility tests demonstrated that the catalyst, ZnGA, has a considerable solubility in CO_2 laden water at high pressures. At 70 bar and ambient temperature the solubility of ZnGA in CO_2 laden water was high (1.2 mg/ml). Therefore, this condition was used for the purification of PPC to minimize the processing cost. In addition, the efficiency of this method for removing ZnGA residues from PPC was compared with the optimum operating conditions reported in the literature using liquid-liquid extraction and leaching process. The concentration of zinc residue in the commercial PPC sample was 2450 ppm. It was aimed to reduce this concentration to below 300 ppm. This minimum level was selected as PPC is commonly mixed with another polymer for commercial applications in the 1:1 weight ratio. Therefore, the final composition of metal residue reduces to 150 ppm that is acceptable for composting biodegradable polymers[35]. PPC is an amorphous polymer and is plasticized by CO_2[120]. The preliminary results demonstrated that PPC also is plasticized when exposed to CO_2 laden water system at high pressures. Plasticization promotes the diffusion of carbonic water in PPC matrix. Therefore, the effect of polymer matrix such as its particle size and crystallinity as a function of exposure time to CO_2 on the extraction efficiency was investigated.

7.5.1 Effect of Micronization on the Purification of PPC Using CO_2 Laden Water

It was speculated that size reduction could enhance the surface area of the polymer and solvent system and elevate diffusion of the solvent into PPC. Thus, the effect of PPC particle size on the process efficiency was investigated. PPC granules with the size of (3-5 mm) were ground to 1 mm and 0.2 mm. The results in Figure 7.4 showed that the extraction efficiency was improved to 46% by decreasing the size of PPC particles to less than 1 mm at 70 bar and 25 °C.

Therefore, catalyst residue in the polymer was reduced from 1765 ppm to 1300 ppm within only 2 h extraction process. By increasing the surface area, the mass transfer rate of solvent into the polymer and *vice versa* was increased that enhanced the extraction efficiency. However, it was not possible to extract the total amount of catalyst from PPC structure within two hours even though the total mass of ZnGA in the system was significantly below the saturation concentration in the CO_2-water system.

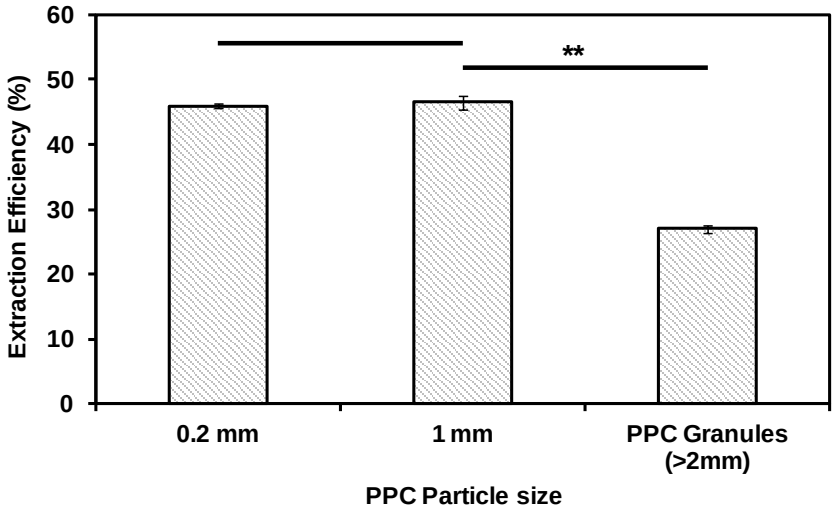


Figure 7.4. The effect of PPC particle size on extraction efficiency (extraction was conducted at 25˚C, 70 bar and 2h) (** $p < 0.01$)

7.5.2 Effect of Extraction Time on the Purification of PPC Using CO_2 Laden Water

CO_2-water phase penetrates into the matrix of amorphous PPC. The thickness of the layer that CO_2 diffuses through is a function of pressure, temperature and processing time. At a longer period, CO_2 diffuses into thicker layers of an amorphous or semi-crystalline polymer and plasticizes larger quantity of this construct [152]. Therefore, it was hypothesized that by increasing the extraction period more catalyst would be dissolved in CO_2-water and removed from the polymer structure.

The results in Figure 7.5 illustrate that by increasing the processing time from 2 h to 24 h the extraction efficiency for removing ZnGA from PPC increased from 44.5% to 64.5% using a static mode. As a result, catalyst residue reduced to below 900 ppm in one step when the extraction was conducted for 24 h. However, increasing the extraction period for longer than 24 h had a negligible effect on the extraction efficiency. It is important to note that the amount of ZnGA extracted within 24 h was still below the saturation concentration in CO_2-water phase. This lower concentration was attributed to the plasticization of PPC and agglomeration of PPC particles in CO_2-water system after a certain period of time. Therefore, the extraction efficiency might be increased further by inhibiting the agglomeration.

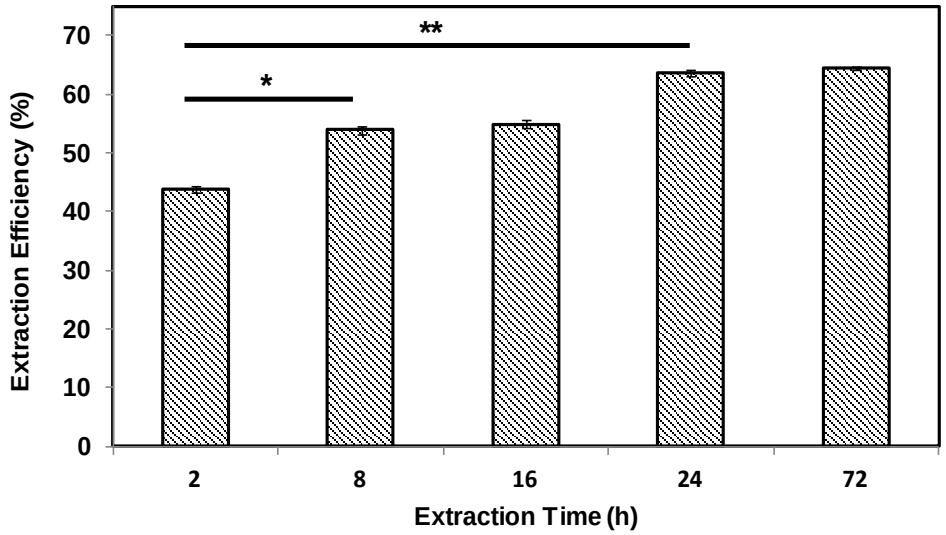


Figure 7.5. Effect of extraction time on PPC purification efficiency (all experiments were performed at 70 bar and 25 ˚C) (** $p < 0.01$, * $p < 0.05$)

7.5.3 Effect of Number of Extraction Stages on the Purification of PPC Using CO_2 Laden Water

It was shown that increasing the extraction time to 24 h reduced zinc residue to 900 ppm in static mode process. PPC is plasticized even at ambient temperature and 60 bar due to the high solubility of CO_2 in this amorphous polymer. Therefore, decreasing the processing temperature and pressure did not improve

the extraction efficiency. It was observed that the degree of agglomeration among micronized PPC particles was enhanced by increasing the processing time. This phenomenon reduced the impact of micronisation; thereby impeding the extraction of catalyst from the core of agglomerated particles. To tackle this issue, it was proposed to run two steps micronisation-purification to further reduce the catalyst residue. The results in Figure 7.6 show that it was feasible to remove more than 80% of the catalyst from PPC when using a two-step process for the period of 8 and 24 h. The extraction efficiency was paramount compared to the results obtained using one step extraction for 72 h. Therefore, it was viable to reduce zinc residue below 300 ppm using CO_2 laden water at a shorter period of time.

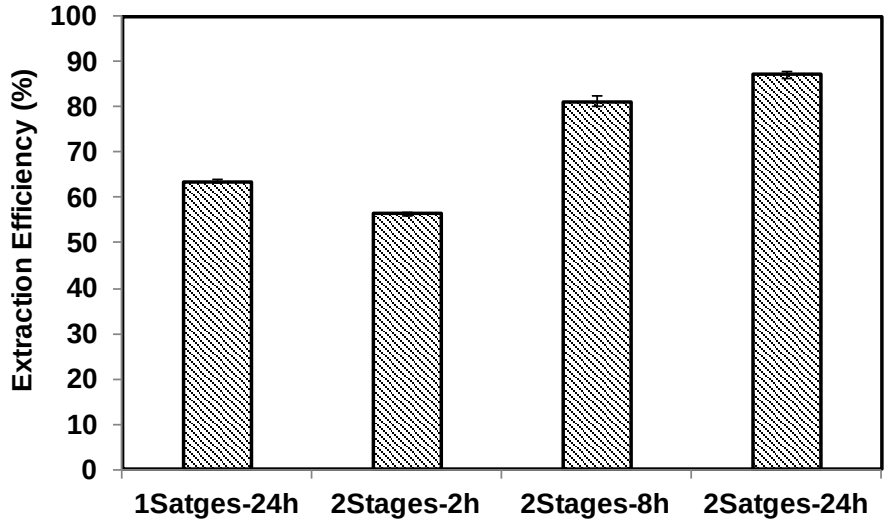


Figure 7.6. The effect of processing time and number of stages on extraction efficiency of CO_2-water for removing ZnGA from PPC (experiments were performed at 70 bar and 25 ˚C)

Finally, the extraction efficiency of CO_2-water system at the optimum condition developed in this study was compared with conventional processes. The results in Table 7.2 show that the extraction efficiency of both liquid-liquid antisolvent and leaching processes were remarkably lower than CO_2 laden water at 25°C and 70 bar. In addition, CO_2 laden water reduced the catalyst residue in PPC to below the required level for compostable polymers and packaging materials [35, 255]. In

addition, it was attempted to use CO_2-water at ambient temperature and lower pressures (e.g. 20 bar). However, the extraction efficiency decreased even at a longer period of extraction due to the lower diffusivity of CO_2-water and higher pH of the solution. The period of time that the polymer is in contact with the aqueous solvent to accomplish the desired level of extraction is varied depending on a number of factors, such as the type of reaction vessel and its operating conditions. For instance, under similar operating conditions, the required period may be reduced by contacting the plastic material with the aqueous solvent in a stirred batch or fluidized bed reactor due to the increase in surface area between the solvent and the solute.

Table 7.2. Extraction efficiency of different methods for removing zinc from PPC

Type of PPC	**Level of Zinc (ppm)**	**Purification Efficiency (%)**
Untreated PPC	2450±49	----
Purified PPC using liquid-liquid extraction method	2002±17	18.2
Purified PPC using leaching method	1429±13	41.5
Purified PPC with CO_2 laden water[1]	312±22	87.25
Target purified PPC [2]	300	88

The advantages of using this process comparing to commercially available techniques for large scale purification of PPC is three folds: (1) elimination of the consumption of several flammable organic solvents for purification of this polymer, (2) removal of the corrosive reagents and made the purification process safer and (3) reduction of the number of stages. In fact, as the polymerisation of PPC in large scale is conducted in high pressure vessel, this stirred reactor can also be used for the purification step. The commercial synthesis of PPC is conducted at elevated pressure and temperature of 50 bar and 60˚C for a period of 40 h. Therefore, the purification by CO_2 laden water is commercially viable as it does not need an extra capital cost for purchasing the equipment. In addition, the

cost of both CO_2 and water are low compared with other solvents used in commercial processes. However, it is pivotal that in the future design of using stirred vessel optimize the processing time to reduce the cost of the process.

7.6 The Effect of Purification Process on Physico-mechanical Properties of PPC

7.6.1 Molecular Structure Analysis

^{1}H NMR analysis was conducted on PPC samples before and after purification to study the effect of purification process on the polymer. The results in Figure 7.7 demonstrate a chemical shifts of PPC and side products of copolymerization of propylene oxide and carbon dioxide at: ^{1}H NMR (δ, $CDCl_3$), 1.31 (3H, CH_3), 4.18 (2H, CH_2CH), 4.98 (1H, CH_2CH) for PPC [60]; 1.14 (3H, CH_3), 3.56 (2H, CH_2CH), 3.40 (1H, CH_2CH) for poly propylene oxide (PPO) [245]; and 1.49 (3H, CH_3), 4.04 (1H, OCH_2), 4.56(1H, OCH_2), 4.85 (1H, CHO) for cPC [256]. To investigate the effect of CO_2 laden water phase purification technique on the chemical composition of the copolymer, the ratio of integrations at (4.18, b) and (3.56, d) were compared. The ^{1}H NMR spectra of PPC samples showed that after purification, the ratio of b/d was significantly increased (from 8.5 to 16.67). The chemical shifts at 3.56 (d) are common between low molecular weight PPO, the byproduct of PPC synthesis, and ether linkages in the PPC backbone. Cleavage of PPC polymer network during the purification process is unlikely. Therefore, the decrease in the b/d ratio after purification underlined that the low molecular weight PPO was partially leached out during the purification. Furthermore, a significant increase in the ratio of integrations at (4.18, b) and (4.85, h) from 2.2 to 3.1 confirmed the removal of cPC from the polymer during the purification process. Decrease in the amount of PPO and cPC in the PPC after purification can play a pivotal role on mechanical properties of this polymer. Furthermore, according to the NMR results, no adverse effect on the Mw and PDI of the polymer was observed after purification process. This effect was due to the fact that PPC is insoluble in both CO_2 and water.

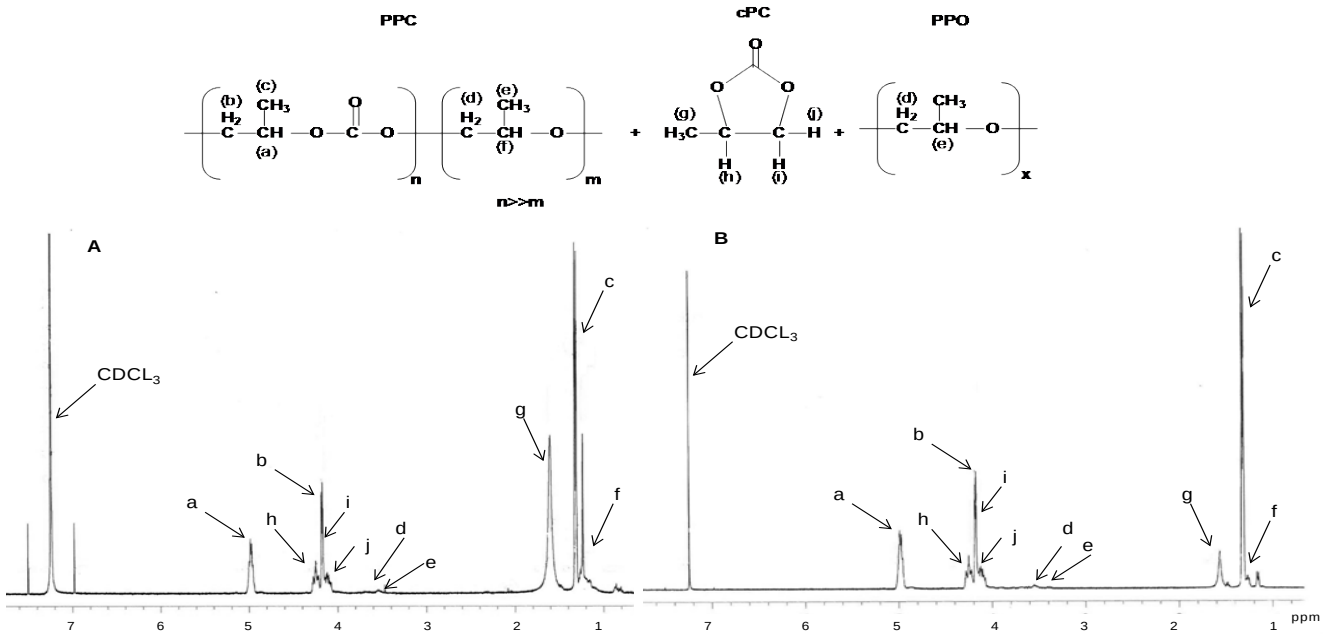


Figure 7.7. ^{1}H NMR spectra of PPC A) before and B) after purification

7.6.2 Thermal Behavior

The thermal stability of PPC purified at different conditions was compared. The results in Figure 7.8 show that the temperature at 5% of weight loss (T 5% (˚C)) increased from 124 to 214˚C for PPC containing 2450 and 250 ppm zinc residue, respectively. A previous study that used conventional leaching method with maleic acid to purify PPC also demonstrated similar improvement in the thermal properties of the polymer due to a decrease in catalyst residue level [8]. This effect was explained by the possibility of metal-ion coordination between zinc compound and the carbonyl group of the polymer that affects the stability of the polymer structure. A similar effect was observed in another study that attempted to remove zinc residue from poly(cyclohexene carbonate) PHCH. Li *et al.* reported that the degradation temperature of PHCH increased by 56˚C by removing zinc residue from 226˚C to 282˚C [125]. Enhancement of PPC thermal decomposition temperature makes the polymer more favorable for blending using high temperature processes such as hot melt extrusion. In addition to catalyst residue, the presence of cyclic propylene carbonate (cPC) which is the side product of PPC synthesis, affects its thermal stability. In the TGA curve of

untreated PPC containing 2450 ppm zinc residue, two distinct variations in the slope are observed. The first slope change, which is due to the presence of cyclic side products was not present in the samples that were purified with high pressure CO_2/water system. Therefore, cPC is also soluble in CO_2 laden water used during the purification process.

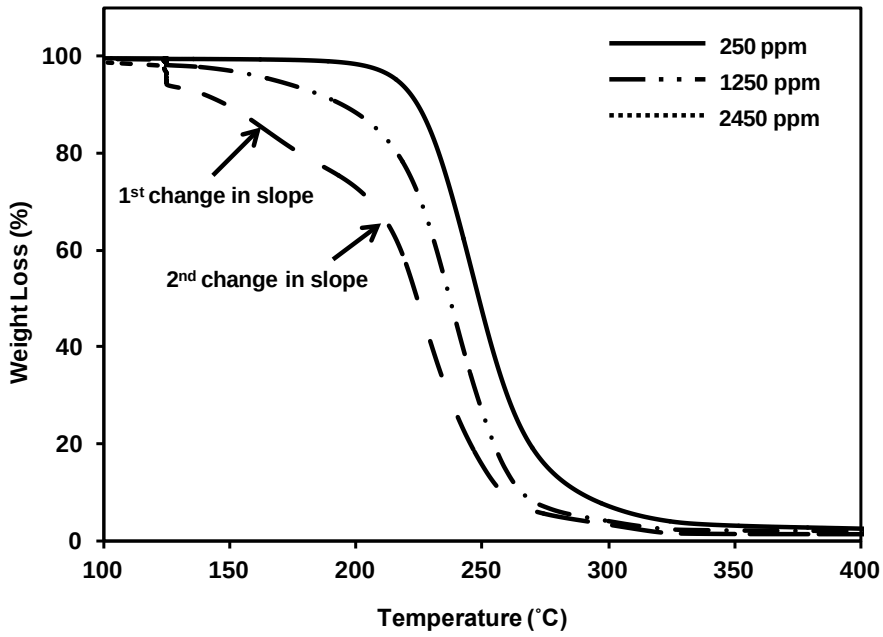


Figure 7.8. Dynamic TGA curves for PPC with various zinc contents (N_2- 5˚C/min) (purifications were performed at 70 bar and 25 ˚C for one stages for 24 h (1250 ppm sample) and two stages for 24 h for (250 ppm sample))

7.6.3 Mechanical Properties

The tensile strength of PPC was compared before and after purification to examine the impact of purification process on the mechanical properties. The results in Figure 7.9 demonstrate that the tensile strength of PPC increased remarkably from 938 to 1386 kPa after purification. This enhancement in mechanical strength was attributed to the absence of cyclic side products and low molecular weight PPO in purified PPC. Removal of side products was confirmed by ^{1}H NMR results in Figure 7.7, which showed an increase in the ratio of integrations b/d from 8.5 to 16.67 and b/h from 2.2 to 3. These side products play

the role of plasticizer for the polymer and have an adverse effect on its mechanical properties [57].

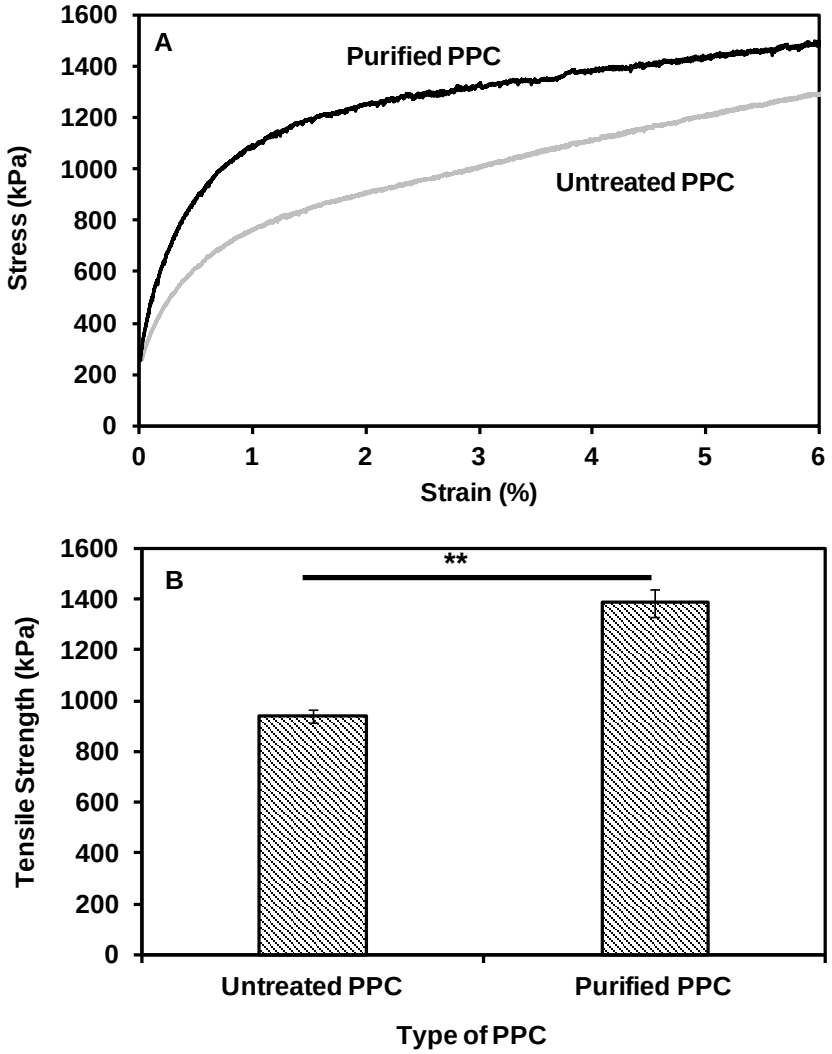


Figure 7.9. A) Stress-strain profile B) tensile strength of untreated and purified PPC by two stages purification (purified sample contained 250 ppm Zn and purification was performed at 70 bar and 25 ˚C for two stages for 24 h for.)

7.6.4 Molecular Weight

Gel permeation chromatography was conducted on the PPC samples containing different levels of ZnGA impurity to calculate the average molecular weight and poly disparity index (PDI). As shown in Figure 7.10 the GPC chromatogram of

the PPC samples was narrower when the concentration of the catalyst impurity was decreased in the sample. Therefore, as presented in Table 7.3, the average molecular weight increased, and the PDI decreased. This effect was due to the removal of the cyclic side products and low molecular weight impurities such as PPO from PPC as a result of purification process which is in line with the other analysis such as thermal degradation and ^{1}H NMR results.

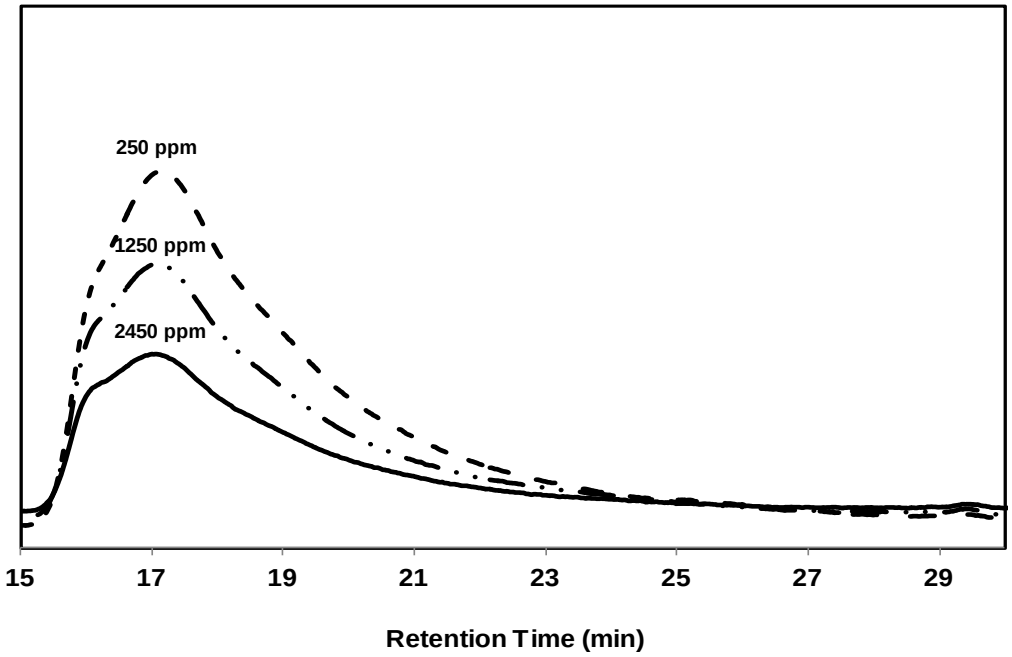


Figure 7.10. GPC chromatogram of PPC samples containing different level of ZnGA impurity (purifications were performed at 70 bar and 25 ˚C for one stages for 24 h (1250 ppm sample) and two stages for 24 h for (250 ppm sample))

Table 7.3. Molecular weight and PDI of the PPC films containing different level of ZnGA

ZnGA Concentration in PPC (ppm)	**Mw**	**PDI**
2450	463,746	3.26
1250	508,373	2.97
250	509,570	2.79

7.7 Summary

In this chapter, a benign method for the extraction of a metal-based catalyst (ZnGA) from PPC was developed. In this method, water saturated with CO_2 was used as a green solvent to dissolve other metal-based catalysts such as ZnMGA and ZnAA. Process conditions such as temperature, pressure and time exhibited a significant effect on the solubility of these metal-based catalysts. This method was then applied to extract ZnGA from PPC. At optimum conditions determined by this study, the residue of zinc in PPC was reduced to 300 ppm and also the cPC and PPO were removed from the PPC structure. It is now feasible to blend PPC with other biodegradable polymers such as starch for a broad range of applications. It was also demonstrated that removing the impurities from PPC significantly promoted its properties such as thermal behavior, molecular weight, and mechanical strength. This method can be used for the purification of other semi-crystalline or amorphous polymers; however, the processing conditions should be optimized due to differences in Mw, and crystallinity. The environmentally friendly method developed in this study has the capacity to dissolve some metal-based catalysts that are soluble in water or acidic water.

Chapter 8. Fabrication of Antimicrobial PPC Films

8.1 Introduction

Conventional food packaging systems act as a barrier between the food and any contamination and preserve it form any mechanical force from the external sources; however, they are not responsible for microbial growth that occurs within the package. Thermal processes, irradiation, and direct addition of chemical preservatives and oxygen scavengers to the food product were applied traditionally to protect the food from the spoilage and microbial growth [10]. However, these methods, either cause loss in quality and texture of the food or have harmful effects such as increasing the chance of cancer or severe allergic reactions on the human health [188]. Alternatively, active, antimicrobial food packaging is an innovative approach to preserve the food and prolong its shelf life [189]. To avoid the side effects associated with chemical based antimicrobial agents and preservatives, extracts from herbs have been broadly used in antimicrobial packaging [12]. For instance, thymol, as one of the major components of oregano essential oil, has received much attention from researchers due to its prominent antibacterial activity [210-212]. This compound can interact with the lipid layer of cytoplasmic membranes due to its hydrophobic nature, and cause the loss of integrity and leakage of the cellular material. From the processing point of view, thymol is stable at elevated temperatures and can be used in melt-blending processes up to 190 ˚C.

This chapter comprised of a feasibility study that was conducted for the fabrication of antimicrobial packaging material from PPC using thymol as an antimicrobial agent. For this purpose, PPC/thymol films were prepared using direct incorporation and physical coating methods. The effect of thymol concentration and fabrication method on the surface properties of the films, their mechanical strength and the growth of *Escherichia coli* (E-*Coli)* as a model gram-negative bacteria was determined. Furthermore, the stability of thymol on the structure of the fabricated films was assessed.

8.2 Effect of Thymol on Hydrophilicity of the PPC Films

Contact angle of the pure PPC and antimicrobial films fabricated with both coating and incorporation methods were measured to investigate the effect of thymol on the affinity of PPC surface to water. As it is shown in Figure 8.1, no significant effect on the water contact angle of the samples prepared with direct incorporation method was detected (p>0.05). This negligible effect of the thymol incorporation on the water contact angle of PPC films is due the absence of thymol on the surface because of the coverage of the thymol molecules by PPC chains. On the other hand, it was found that by elevating the concentration of thymol on the surface of PPC to 2.5 mg/cm^2 water contact angle was significantly increased by 50% suggesting that the presence of thymol on the surface of PPC films enhanced their hydrophobicity. Generally, microorganisms do not have an affinity to form bio-film on hydrophobic surfaces. The reason is that the low energy and slippery nature of the hydrophobic surfaces prevent the adhesion of the microorganism [257].

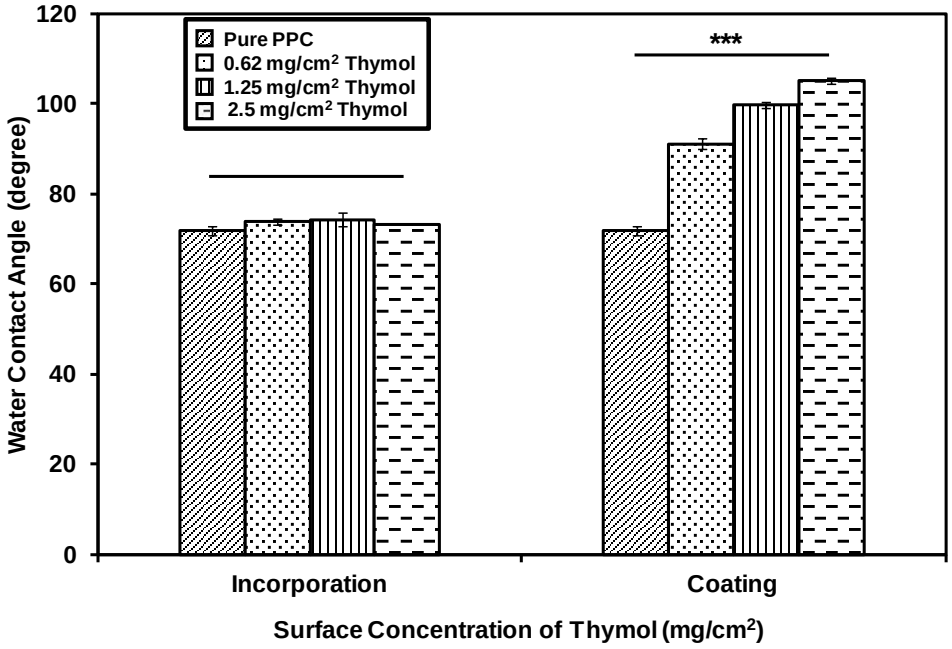


Figure 8.1. Effect of thymol on the water contact angle of the fabricated antimicrobial films (*** $p < 0.005$)

8.3 Effect of Thymol on Mechanical Properties of PPC Films

The tensile test was conducted to assess the effect of thymol on the mechanical strength of the PPC films. According to the results presented in Figure 8.2, coating of the surface of the PPC films with thymol did not have a significant impact on their Young's modulus (p>0.05). However, incorporation of the antimicrobial agent into the bulk of the PPC films reduced their Young's modulus remarkably due to the plasticization by the thymol molecules. Indeed, incorporation of thymol equal to 1.25 and 2.5 mg/cm^2 into the PPC films, decreased its Young's modulus by 35 and 62%, respectively. Therefore, incorporation of thymol into the PPC films is not desirable for the applications that require high mechanical strength.

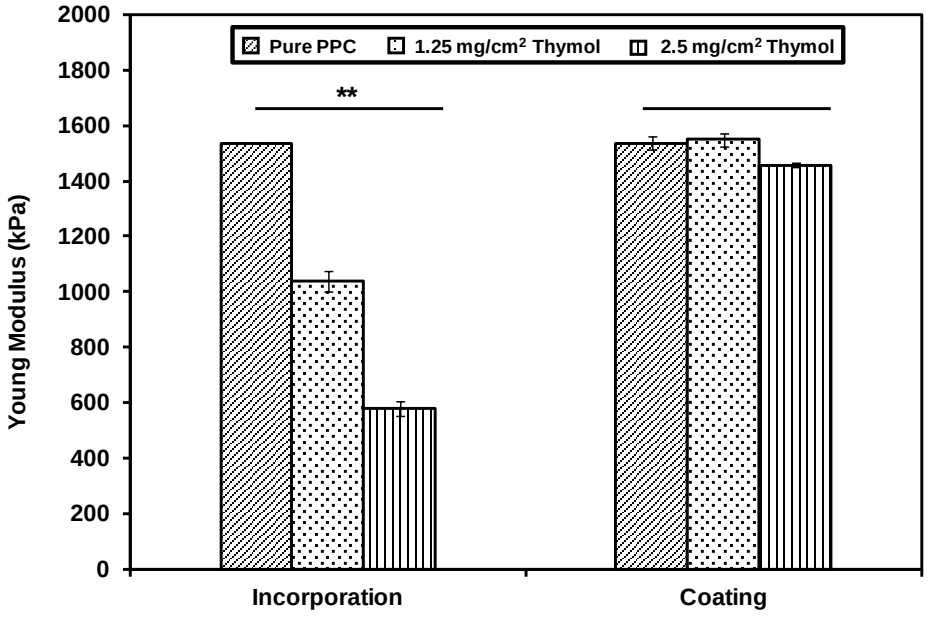


Figure 8.2. Effect of the addition of thymol on the Young's modulus of the fabricated antimicrobial films (**p < 0.01)

8.4 The Effect of Thymol on Antibacterial Properties of PPC Films

Bacteria inhibition zone was measured for the PPC/thymol samples fabricated by direct incorporation and surface coating methods using *E-coli* as model gram-negative bacteria. The results of disk diffusion test in Figure 8.3. B to D exhibited no antimicrobial effect for the incorporated PPC samples with different concentration of thymol. These results are in line with the data obtained from water contact angle measurements indicating that there is no evidence of the presence of thymol on the surface of the samples prepared with incorporation method. However, the results presented in Figure 8.3. E to G illustrated clear bacteria inhibition zone even for the lowest concentration of thymol (0.62 mg/cm^2). Furthermore, by increasing the amount of thymol coated on PPC films to 2.5 mg/cm^2, the size of the inhibition zone formed around the samples was significantly enhanced by five-fold, which confirmed remarkable antimicrobial activity. Therefore, the presence of thymol on the surface of PPC is pivotal for achieving antimicrobial properties.

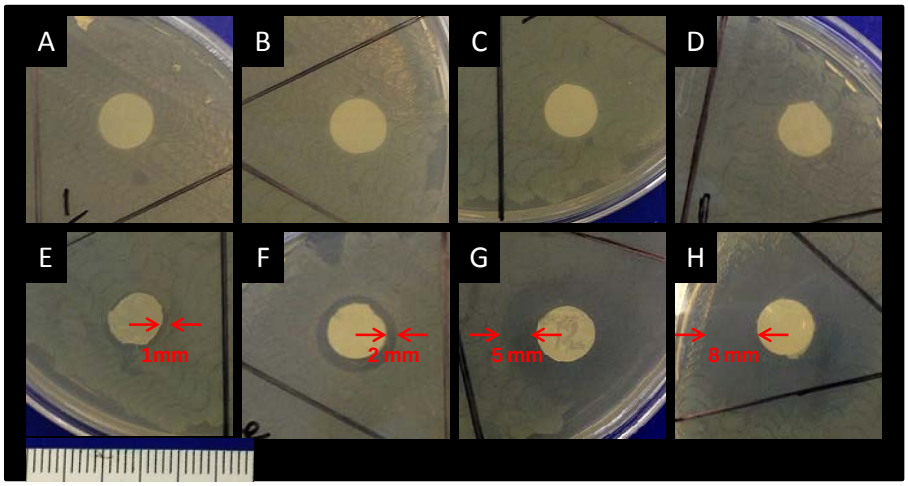


Figure 8.3. Antimicrobial activity of PPC/thymol films against *E-Coli* using disc diffusion method A) pure PPC, PPC/thymol prepared with incorporation method B) 0.62 mg/cm^2, C) 1.25 mg/cm^2, and D) 2.5 mg/cm^2, PPC/thymol prepared with surface coating method E) 0.62 mg/cm^2, F) 1.25 mg/cm^2, and G) 2.5 mg/cm^2, and H) Anti-Anti positive control

Another set of experiments were also carried out to determine the antibacterial properties of PPC surfaces coated with 2.5 mg/cm^2 thymol. In these experiments, the samples were submerged in media that contained a known amount of bacteria. As the data in Figure 8.4.A and B show, after 8 hours the number of bacteria was remarkably lower in the media containing PPC-coated samples compared to neat PPC as a control. Moreover, after 24 hours, no colonies were observed in the media containing thymol coated PPC film, underlining the lethal effect of PPC-thymol (2.5 mg/cm^2) on bacteria left in suspension.

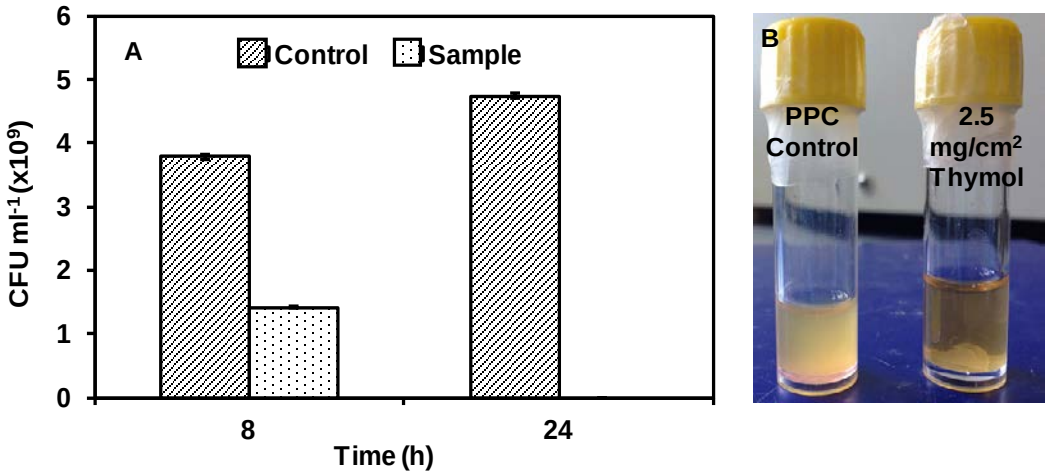


Figure 8.4. A) Concentration of the *E-Coli* in the media at different time intervals, with and without sample (PPC/thymol 2.5 mg/cm^2 – coating method) B) Bacteria growth inhibition in contact with sample (PPC/thymol 2.5 mg/cm^2 – coating method) after 24 hours

8.5 Thymol Release Study

The release of thymol from PPC surface was measured when using media that contained 10% and 90% (v%) ethanol in water to investigate the stability of the antimicrobial agent on the surface of the coated samples. These two media usually are used as the food stimulants [246]. These two concentrations of ethanol have been chosen as ethanol is a strong solvent for thymol; therefore, the release of thymol in these media can be considered as its maximum release. As it is presented in Figure 8.5, it was found that for all samples prepared by coating method; up to 25% of thymol was detached from the polymer surface and released to the media containing 10% ethanol within 48 hours. Furthermore,

nearly all thymol was released and migrated into the media containing 90% ethanol within 96 hours. These data implied that PPC-coated thymol film can only be used for systems with low water content such as solid samples. However, in contact with liquid products they are active only for short periods. Therefore, physical coating method is only suitable for short term applications such as skin patches or some other systems. Stability of the antimicrobial agent on the surface of the packaging material is crucial for design and manufacturing of active packaging products. The reason is that migration of additives from the packaging system into the food product can have a negative impact on the quality and safety of food. Accordingly, physical coating of thymol on the PPC surface may not a promising method for fabrication of some active packaging material that contains high amount of solvent/water or wet.

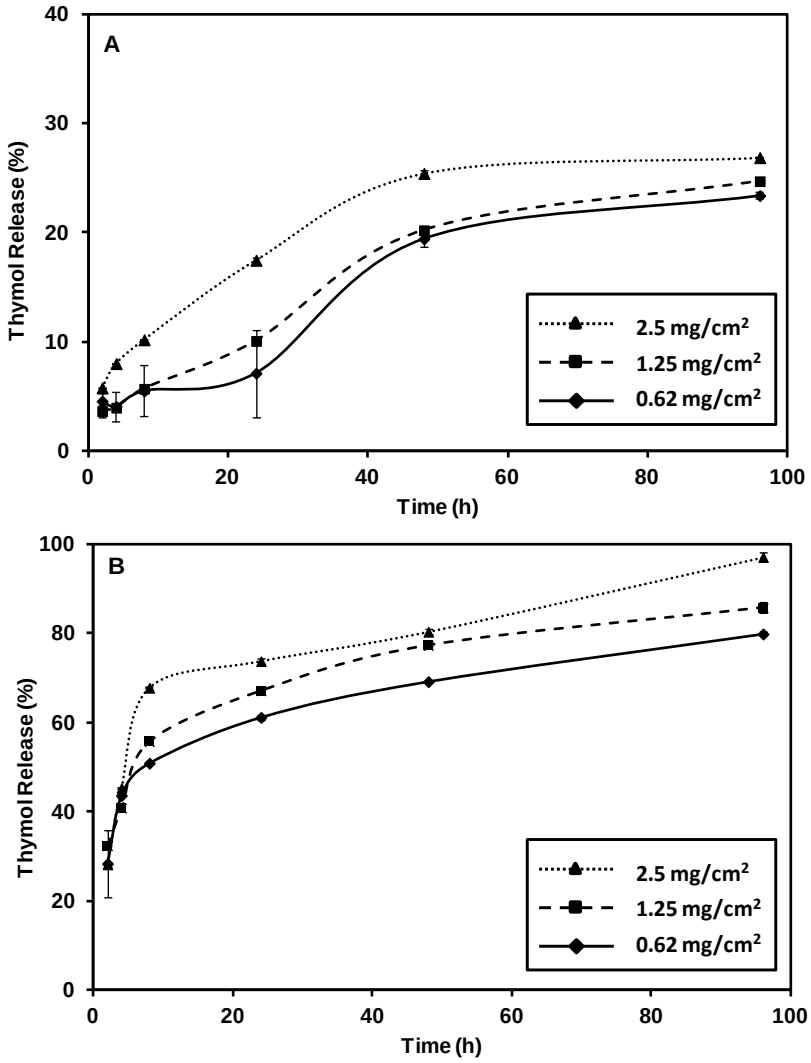


Figure 8.5. Release of thymol from antimicrobial PPC/thymol films with different concentrations, prepared with physical coating method in (A) 10% (v%) and (B) 90% (v%) ethanol in water media

8.6 Summary

Antimicrobial PPC films using a non-hazardous thymol that is stable and robust at high temperature were fabricated via direct incorporation and physical coating methods. The results demonstrated that using incorporation method, the surface of PPC was coated with neat PPC with minimal thymol level that shows no antimicrobial properties. Moreover, the presence of thymol in the bulk of PPC films reduced their mechanical strength significantly. Nonetheless, thymol coating on PPC film significantly increased surface hydrophobicity, which was one of the

factors contributing on the antimicrobial activity, and had minimal effect on their bulk properties such as mechanical strength. While thymol may detach from the PPC surface in exposure to humidity and liquid products, still these samples may be suitable for many other applications that short-term antimicrobial properties and release are desirable.

Chapter 9. Plasma Surface Modification and Immobilization of Thymol on PPC Surface

9.1 Introduction

Among several methods that have been attempted for the addition of antimicrobial reagents on the surface of polymers, chemical immobilization is more preferable than physical as it reduces the release of these active compounds and their impact on food flavor, taste and safety [192]. Activation of the polymer surface and chemical bonding with the reagent is a strategy that could address the shortfall of physical immobilization [14]. Common techniques for the activation of polymer surfaces and chemical immobilization such as wet chemical activation [230], layer by layer assembly [231], and UV irradiation [233] involve using organic solvents, toxic chemicals or may affect the physical properties of the polymer. Plasma treatment is another commercially available technique for the surface activation that tunes the properties of polymer surfaces within a thin layer on the surface (10 nm) [15, 16, 234]. This method is based on gas ionization, electron charge and free radical formations, and has been successfully used for surface modification of materials and chemical bonding with active compounds [235, 236]. This method eliminates the consumption of toxic chemicals, reduces the processing time and exhibits minimal impact on bulk properties of the polymer [228, 229]. Plasma has been used for the fabrication of antimicrobial surfaces for both biomedical and food packaging applications [240]. For instance, nitrogen and argon plasma treatment were used to activate the surface of non-degradable polymers such as polyether ether ketone, and poly(methyl methacrylate) for biomedical applications [238, 241]. Although this method is a promising approach for activation of polymer surfaces and immobilization of different active compounds, it has not yet been used for the chemical bonding of essential oils, particularly thymol, on the PPC surface. The present chapter aimed to fabricate stable antimicrobial PPC films for food packaging using plasma treatment followed by thymol immobilization. To this end, the effect of plasma treatment conditions and thymol coating on the physical and chemical properties of PPC surface was investigated. Moreover, the migration of thymol from the PPC surface into the food stimulated media was assessed. Besides, the effect of

process condition on the growth inhibition of *Escherichia coli* as a model gram-negative bacteria was determined.

9.2 Plasma Treatment and Thymol Immobilization Procedure

Prev iously prepared PPC films via solvent casting method were placed in plasma cleaner and the chamber was evacuated using a vacuum pump for 5 min. Then, the plasma power was turned on followed by feeding air into the chamber by opening the air valve for 1/8 of a turn for a predetermined period of time (5, 10, and 15 min). Various radio frequency level (Low, Medium and High – Maximum power of 30W) was applied for PPC samples to examine the effect of plasma power on the PPC surface activation. Immediately after activation by plasma, PPC films were coated with thymol solution in ethanol and dried at ambient conditions to remove solvent residue. The surface of the PPC samples were characterized immediately after plasma treatment and after coating with thymol.

9.3 The Effect of Plasma Treatment on the Surface Chemistry of PPC Films

The effect of plasma treatment conditions on the surface properties of PPC films was examined using ATR-FTIR spectroscopy. The results in Figure 9.1 confirm the degradation of carboxylic groups and formation of carbonyl and unsaturated C=C groups due to the post oxidation of the polymer surface. The FTIR spectra of treated and untreated samples of PPC were subtracted from each other to illuminate the impact of plasma surface modification. [258]. As depicted in Figure 9.1-A and B, spectral changes associated with the plasma treatment were observed in the finger prints region (750-1500 cm^{-1}). These shift were attributed to the vibrations in the highly carbonized structure of PPC backbone as a result of plasma treatment [259]. Moreover, the bands at 1047, 1195 and 1289 cm^{-1} in this region was associated with C-O group stretching motions. Furthermore, the appearance of new bands in the middle frequency region (1500-1800 cm^{-1}) resulted from the stretch vibration of carbonyl groups and unsaturated C=C bonds [260]. Particularly, the presence of bands within the range of 1720 cm^{-1} to1750 cm^{-1} was from post oxidation of PPC films and formation of new carbonyl bonds

[261]. The two negative bands at 1219 and 1734 cm^{-1} in spectra was due to the degradation of C-O and C=O bonds and structural transformation. The results in Figure 9.1-A and B show that increasing both exposure time and plasma intensity enhanced these effects. According to the fact that the spectra of treated samples have been subtracted from pure PPC, any increase in the intensity of the peaks shows higher amount of free radicals and functional groups on the surface.

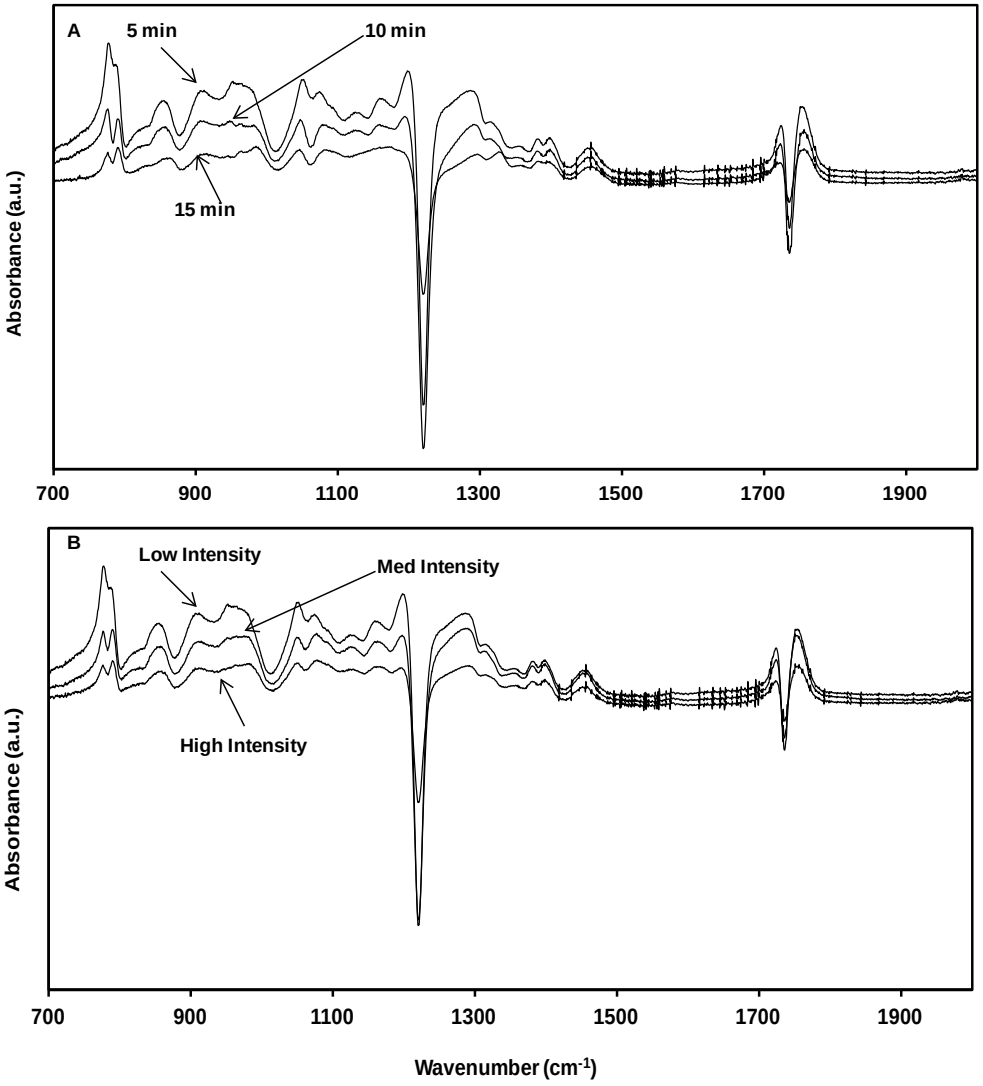


Figure 9.1. ATR-FTIR spectra of PPC films after plasma treatment at A) high intensity and different plasma exposure time B) 15 min exposure to different plasma intensities (All the spectra were subtracted from PPC control film.)

9.4 The Effect of Plasma Treatment on the PPC Surface Properties

The effect of plasma treatment on the wettability and hydrophilicity of PPC film was studied by measuring the water contact angle before and after exposure at different plasma conditions. As shown in Figure 9.2, plasma treatment led to a significant drop of water contact angle, suggesting the enhancement of PPC hydrophilicity due to the creation of active functional groups on the surface [262]. Furthermore, this effect was more pronounced when the plasma exposure time was increased. For instance, the water contact angle of PPC films was decreased from 60.81±0.45˚ to 35.36±2.33˚ when the plasma exposure time was elevated from 5 min to 15 min when using high power. Nevertheless, beyond 15 min was not attempted due to PPC low glass transition temperature (~30-40˚C) and deformation of film. Increasing the plasma power decreased the water contact angle significantly resulting in higher chemical activity of the surface and higher surface free energy that can enable more effective immobilization. As observed in Figure 9.2, at the exposure time of 5 min by elevating the plasma treatment from low to medium and high the water contact angle of PPC films was decreased from 72.67±1.80˚ to 70.11±0.96˚and 60.81±0.45˚, respectively.

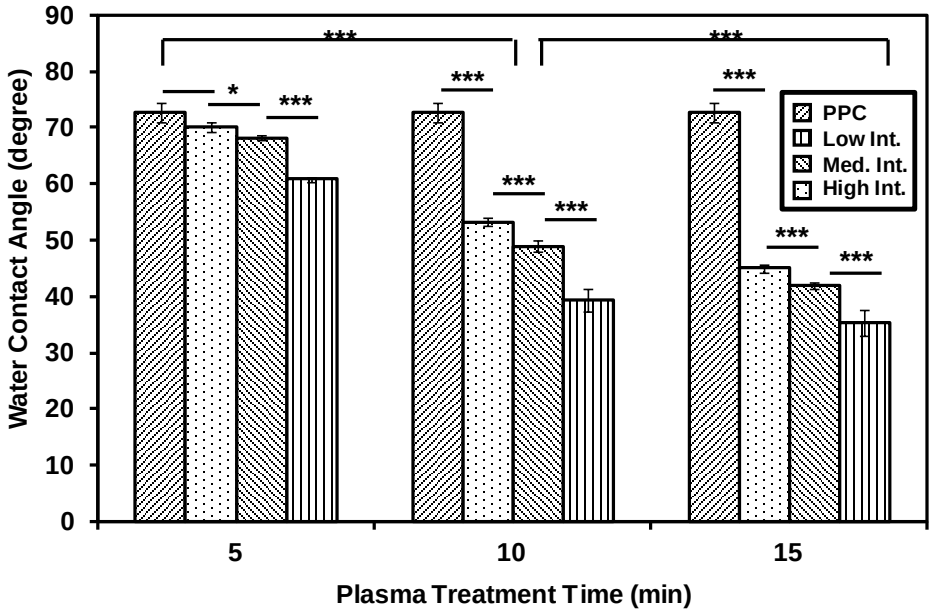


Figure 9.2. Effect of the plasma exposure time on the water contact angle of the plasma treated PPC films at different conditions (*** $p < 0.001$)

9.5 The Effect of Thymol on the Surface Chemistry of PPC

The surface chemistry of plasma treated PPC films after immobilization of 1.25 mg/cm^2 thymol was measured using ATR-FTIR. It was anticipated that thymol chemically bonds on the surface of plasma treated PPC films due to the activation of polymer surface by plasma and post oxidation. The results of ATR-FTIR in Figure 9.3 illuminate the slight shifts of bands at 1235 and 1620 cm^{-1} to the lower values on the spectra of thymol immobilized samples compared to the pure thymol spectra. These shifts are attributed to the chemical interaction of thymol and the surface of plasma treated PPC samples. In addition, the presence of two main bands at 1222 and 1360 cm^{-1}, also another band at 1621 cm^{-1} corresponded to -OH bending and C-O stretching of the phenolic group of thymol [263]. Moreover, the presence of band at 1587 cm^{-1} corresponds to the symmetric stretching of C-C=C bond of benzene ring of thymol. The presence of these bands in the FTIR spectra of all samples in Figure 9.3 compared to pure thymol as a control confirmed the presence of this antimicrobial agent on the surface of PPC even after washing with ethanol. Therefore, it can be concluded that plasma

treatment was an efficient technique for the chemical immobilization of thymol on the surface of PPC at the conditions examined.

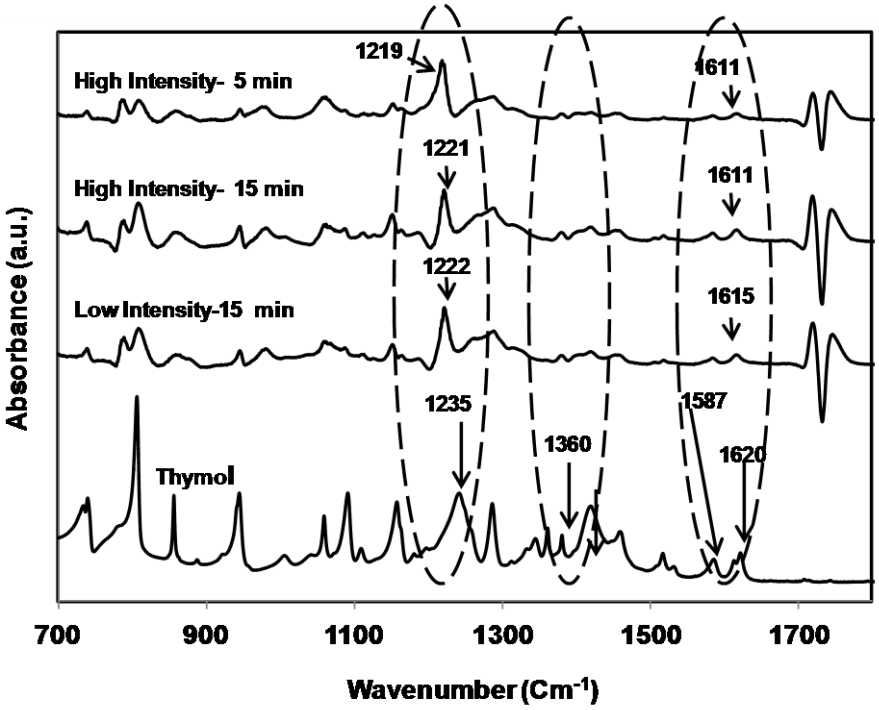


Figure 9.3. ATR-FTIR spectra of plasma treated PPC films after thymol immobilization (1.25 mg/cm^2) at different plasma treatment conditions. (All the spectra were subtracted from PPC films.)

9.6 The Effect of Thymol on the Surface Properties of PPC

The low energy and slippery nature of hydrophobic surfaces prevent the adhesion of microorganisms [257]. It is speculated that the addition of thymol reduces the PPC surface wettability due to its hydrophobic nature. The results of water contact angle measurement for the PPC samples coated with 1.25 and 2.5 mg/cm^2 thymol confirmed this hypothesis. As shown in Figure 9.4, at all conditions examined after immobilization of thymol the surface wettability was reduced significantly. The results in Figure 9.4 also show that increasing the concentration of thymol from 1.25 mg/cm^2 to 2.5 mg/cm^2 had negligible effect on surface hydrophobicity (p>0.05). The noticeable difference was only observed for the PPC sample that was treated at high intensity for 15 min, most likely due to a higher amount of thymol impregnation on the surface.

In addition, the effect of plasma treatment and thymol immobilization on the mechanical strength of PPC films was also investigated. However, no significant change in the young modulus of PPC films was observed after plasma treatment and thymol coating (p>0.05).

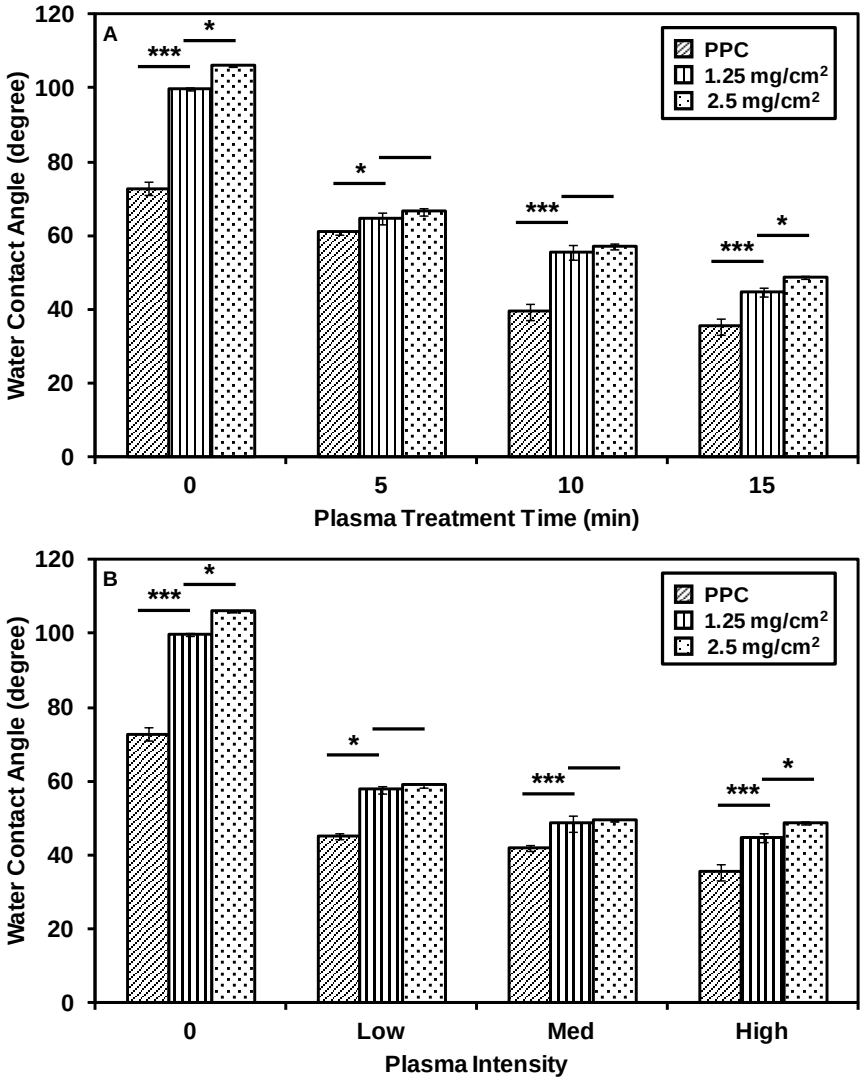


Figure 9.4. Water contact angle of the plasma treated PPC films before and after immobilization with different concentration of thymol at A) constant plasma power (high intensity), B) constant plasma treatment time (15 min) (*** $p < 0.001$).

9.7 Thymol Release

The thymol release from PPC surface was measured for samples soaked in 10% and 90% (v%) ethanol solutions [246]. The effect of media, surface concentration of the antimicrobial reagent and plasma treatment conditions on the stability of thymol on PPC film surfaces were examined. The samples were stored at room temperature for a few weeks prior to the test to make sure that storage has no effect on the attachment of thymol on the surface. The data in Figure 9.5, demonstrate the release of thymol into 10% ethanol media were significantly lower for the samples modified by plasma compared to physically adsorbed coatings (unmodified surface). Up to 25% of the initial thymol was released into the media within eight days (192 hours) from physical immobilization samples at both concentrations (1.25 mg/cm^2 or 2.5 mg/ cm^2), and an upward trend was observed for the release profile of the antimicrobial reagent (Figure 9.5). However, for samples prepared by plasma treatment method, the release of thymol into the media was below 10%. Besides, the released profile of plasma treated samples approached a plateau after the first two days. This trend showed that at the beginning of the test, only free thymol bound to the first directly immobilized monolayer of thymol was released from all samples into the media. We also observed that the release of thymol was lower from the samples that were fabricated at higher plasma power or longer exposure time which is likely due to higher number of free radical in the surfaces that bound covalently thymol and PPC surface [264, 265].

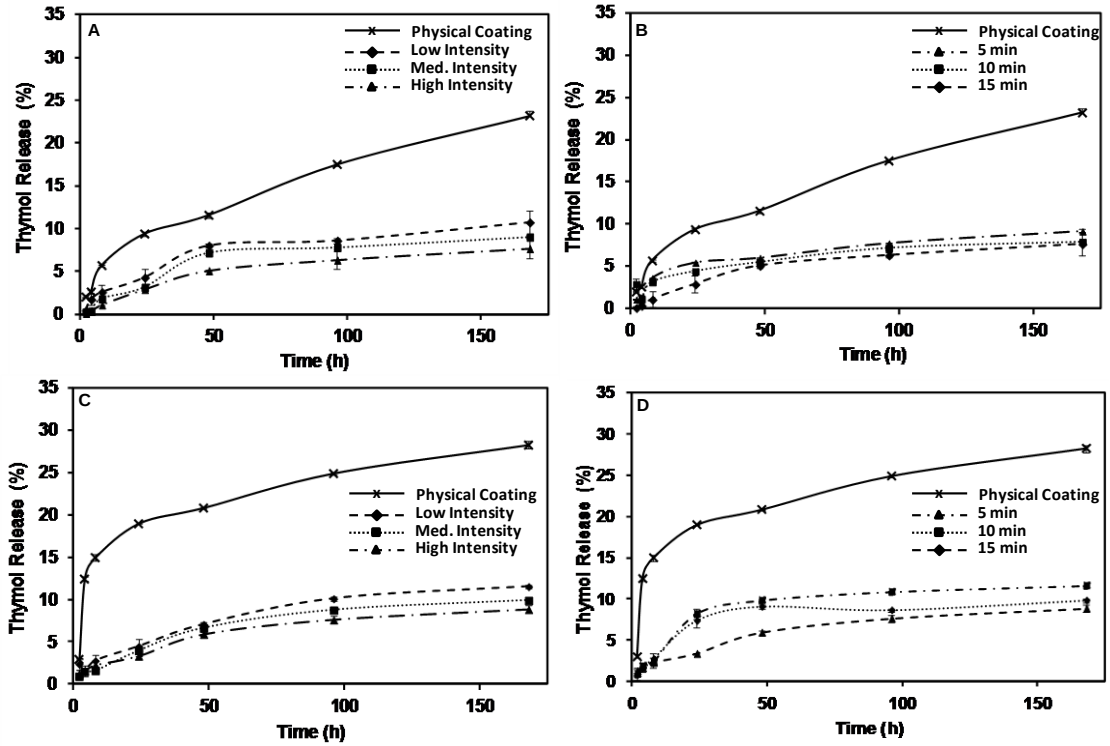


Figure 9.5. Release of thymol from antimicrobial PPC films in 10% (v%) ethanol media A) 1.25 mg/cm^2 thymol coated on plasma treated PPC films at constant exposure time of 15 min, B) 1.25 mg/cm^2 thymol coated on plasma treated PPC films at high plasma intensity, C) 2.5 mg/cm^2 thymol coated on plasma treated PPC films at constant exposure time of 15 min, and D) 2.5 mg/cm^2 thymol coated on plasma treated PPC films at high plasma intensity.

Similar trend of thymol release profile was observed for the PPC samples that were kept in 90% ethanol solution. The burst release of thymol from PPC samples prepared by physical and chemical immobilizations was above 60% and less than 20%, respectively. As the results in Figure 9.6 show, the process parameters for plasma treatment and also the amount of thymol exhibited negligible effect on its release profile from PPC films. Additionally, at all examined conditions, chemical bonding as a result of plasma treatment dramatically reduced the release of thymol from PPC surface. The release of thymol from plasma treated samples in a highly soluble solvent (90% ethanol) was less than 20%. Therefore, the release of thymol from plasma treated PPC would be less than this value in other media with lower solubility level, which further confirmed efficacy of the surface treatment and robustly immobilized antimicrobial compound.

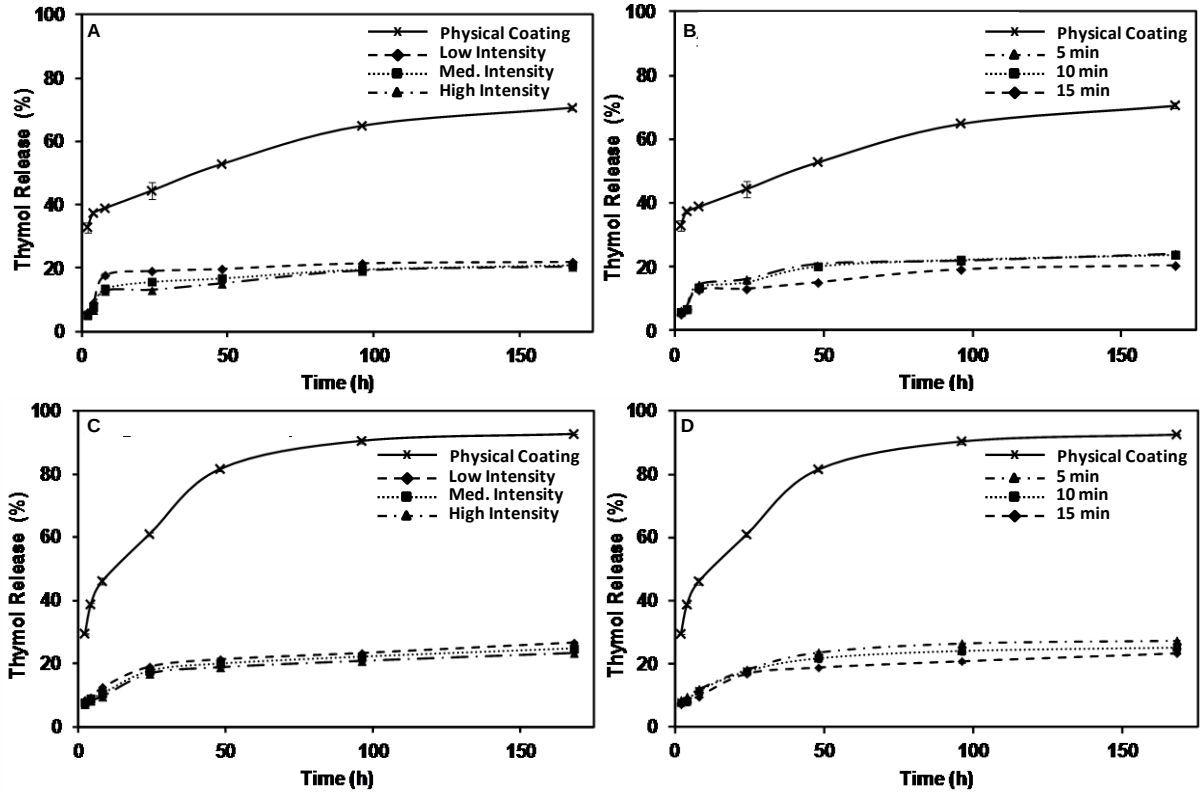


Figure 9.6. Release of thymol from antimicrobial PPC films in 90% (v%) ethanol media A) 1.25 mg/cm^2 thymol coated on plasma treated PPC films at constant exposure time of 15 min, B) 1.25 mg/cm^2 thymol coated on plasma treated PPC films at high plasma intensity, C) 2.5 mg/cm^2 thymol coated on plasma treated PPC films at constant exposure time of 15 min, and D) 2.5 mg/cm^2 thymol coated on plasma treated PPC films at high plasma intensity.

9.8 Antimicrobial Properties

The antimicrobial property of PPC samples were assessed using disk diffusion test technique [247]. To confirm the durability of the biological effect, samples were kept at room condition for more than three months and then were used for antimicrobial assessment. The results in Figure 9.7 demonstrate that clear zone was formed around PPC films prepared both by physical and chemical immobilization techniques. This result endorsed that thymol activity was preserved when used for storage of solid samples. However, the inhibition zone around sample fabricated by physical technique was at least 40% larger than plasma treatment, due to faster release of thymol from the former samples.

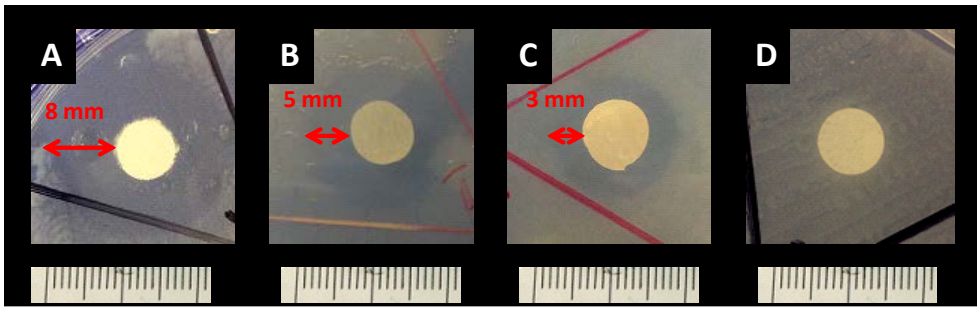


Figure 9.7. Antimicrobial activity of PPC/thymol films against *E-Coli* using disc diffusion method A) Anti-Anti positive control, B) physical coating PPC/thymol (1.25 mg/cm^2), C) plasma treated PPC/thymol (15 min- high intensity- 1.25 mg/cm^2), and D) pure PPC negative control.

PPC samples were placed in a media with a known number of *E-Coli* to determine the antimicrobial activity of films. The results in Figure 9.8 show that the growth of bacteria was lower in the media that contained immobilized samples compared to neat PPC due to the release of thymol within first 8 hours. After one day the differences between samples fabricated by physical and chemical immobilization was negligible and the number of bacteria approached zero in both these media. These results underlined that chemical attachment of thymol on PPC surface did not exhibit any adverse effect on the biological activity of the antimicrobial agent; however, there might be some delay in antimicrobial effect of samples.

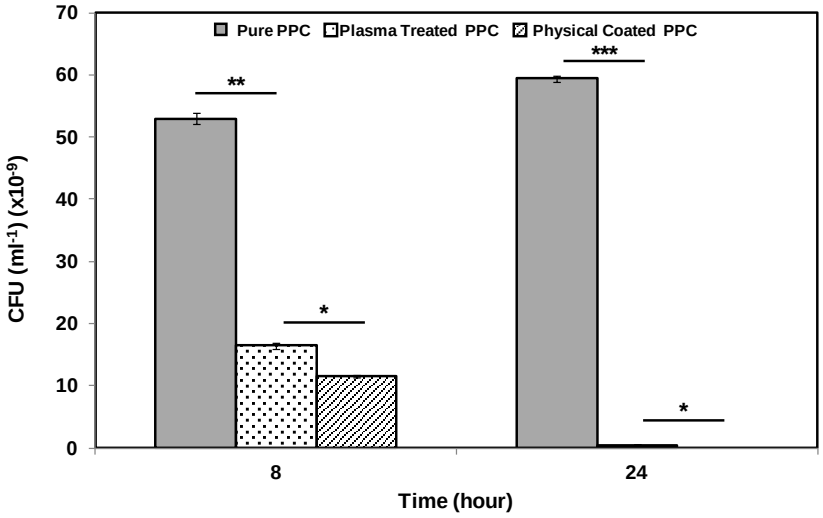


Figure 9.8. Concentration of the *E-Coli* in the media containing pure PPC sample, 1.25 mg/cm^2 thymol coated on PPC using plasma treatment and physical coating method at different time intervals.

The antimicrobial properties of thymol is governed by its impact on ion transport through bacteria cell membrane [13]. Previous studies demonstrated that antimicrobial property of thymol was maintained for long time when it was immobilized on the surface of fabrics by plasma coating [266]. However, within several washing the antimicrobial property was gradually diminished. In this study we examined the activity of thymol coated on the PPC surface by both physical and plasma treatment methods. These samples were incubated in neutral pH condition for up to 14 days. The results in Figure 9.9- A to D demonstrate that thymol was still active on the surface of PPC samples treated by plasma within seven days. However, the PPC films that were physically coated by thymol were not active after three days in contact with aqueous media.

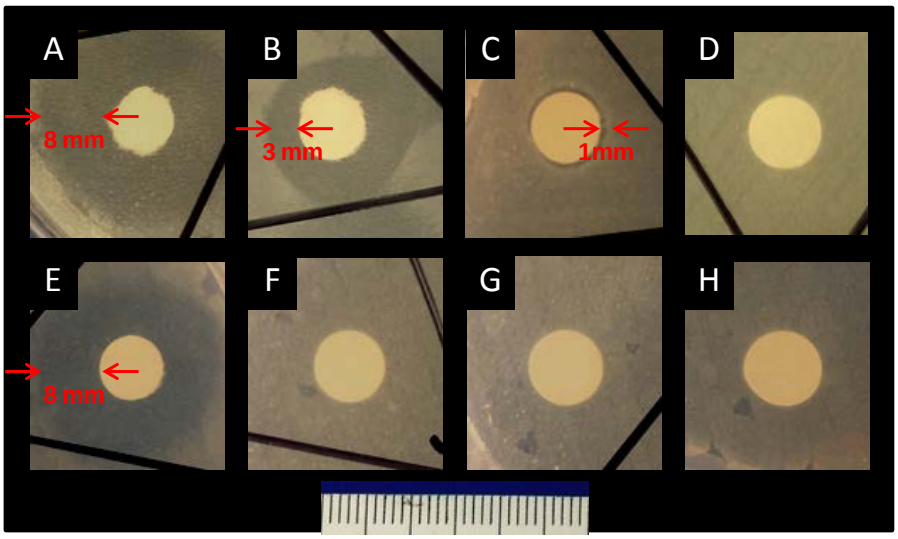


Figure 9.9. Antimicrobial activity of PPC/thymol films against *E-Coli* using disc diffusion method A) Anti-Anti positive control, and thymol coated, plasma treated samples after B) 3, C) 7, and D) 14 days incubation in neutral pH, E) Anti-Anti positive control and physical coated samples after F) 3, G) 7, and H) 14 days incubation in neutral pH.

9.9 Summary

Stable and robust antimicrobial PPC film using thymol as an acceptable ingredient for food packaging was fabricated. The chemical immobilization was successfully conducted by using plasma surface modification for the functionalisation of PPC films followed by bonding with thymol. This method

was more efficient than the physical method for thymol immobilization on the PPC surface. The effect of treatment conditions including plasma power, exposure time and surface concentration of thymol on the release profile of thymol in two simulated media and its antimicrobial properties were determined. Increasing both plasma process parameters significantly enhanced the immobilization efficiency of thymol on the surface of PPC; however, their impact on release profile of thymol was negligible. This modified PPC film has high potential for packaging solid and liquid food and many other commodity products with low alcohol content.

Chapter 10. Conclusions and Recommendations

10.1 Conclusions

In this dissertation, poly (propylene carbonate), a biodegradable and partially renewable polymer, was proposed as a sustainable solution to prevent the accumulation of non-degradable plastics in landfills.

It was demonstrated that biodegradable PPC can be contemplated as an alternative to the commercially used polymers such as LDPE and Eco-Flex for a broad range of packaging applications, particularly for food packaging. PPC possesses physico-mechanical properties that are either superior to or comparable with the examined polymers. The mechanical properties of PPC are higher than Eco-Flex and comparable with LDPE. In addition, PPC has excellent barrier properties that are pivotal to prolong the shelf life of many products. Besides, its soil burial biodegradation rate in simulated landfill condition is comparable with biodegradable Eco-Flex. In addition to its comparable physical properties with other plastics in the market; PPC is chemically resistant to aqueous, acidic, organic and fatty simulated food media. Accordingly, replacing biodegradable PPC is a remedy for plastic waste management that is one of the major environmental issues.

The addition of natural polymers such as starch and cellulose to PPC improved its mechanical properties and enhanced its biodegradation rate. Moreover, the physical properties of the polymer can be tuned for desirable applications by regulating the concentration of these natural renewable additives.

While superior properties of PPC are favorable for many applications, the residue of the metal-based catalyst such as ZnGA is a major burden for its applications. However, the novel benign technique developed in this study tackle this issue. In this method water saturated with CO_2 at moderate conditions was shown to be efficient for reducing zinc residue dramatically. ZnGA is soluble in CO_2/water system as a green solvent. The temperature, pressure and time exhibited a

significant effect on the solubility of metal-based catalysts, but not on the extraction efficiency. At ambient temperature and 70 bar nearly 90% catalyst was removed from PPC and reduced the catalyst level to 300 ppm. The benign technique designed in this study can be used for removing other metal based compounds from polymers.

During the purification process, other low molecular weight impurities such as cPC and PPO were removed from the PPC structure. It was also demonstrated that removing the impurities from PPC significantly promoted its properties such as thermal behavior, molecular weight, and mechanical strength. This method can be used for the purification of other amorphous or semi-crystalline polymers; however, the processing conditions should be optimized due to differences in molecular weight, glass transition temperature and crystallinity.

Antimicrobial PPC films were fabricated using non-hazardous thymol that is stable and robust at high temperature. PPC/thymol films were first prepared using direct incorporation and physical coating methodologies that are the most common methods for fabricating antimicrobial packaging materials. It was found that incorporation and physical mixing of thymol with PPC was not efficient for acquiring antimicrobial surface, due to the absence of thymol on the surface of the PPC films. This method also had an adverse effect on the physical properties of PPC.

Surface modification by physical immobilization was efficient to prepare antimicrobial PPC films. However, thymol could release rapidly into a media in exposure to various media and moisture. While PPC coated with thymol can be used as an antimicrobial packaging for solid products, it may have an impact on the quality of packaging materials that contained high level of water such as acidic, alkaline and fatty foods.

Among the methods examined for the fabrication of antimicrobial PPC, chemical immobilization of thymol was more efficient. In this method, PPC surface was activated by plasma to chemically bond thymol to PPC. This technique enhanced the stability of the antimicrobial PPC/thymol films and remarkably reduced the migration of thymol into the media.

In summary, it was demonstrated that PPC has superior properties compared to the current polymers that are broadly used. The method developed in this study was efficient to reduce the metal residue in PPC and many other polymers that have an issue for composting. The purified and antimicrobial PPC prepared in this study opens an avenue for broad range of applications in different industries, particularly in food packaging.

10.2 Recommendations

This study lays the foundation for further investigation. The followings are a few examples of suggested studies.

Soil burial biodegradation test was conducted at 40˚C and in compost soil. The degradation rate might increase in landfill soil that contains a broader range of microorganism and enzyme. It is suggested to conduct degradation study in landfills to determine the actual degradation rate of PPC to estimate more realistic time for complete degradation of PPC. Other degradation protocols can be used such as measuring the biogas emitted from the landfill soil containing the plastic samples.

PPC can be proposed for many applications such as agricultural mulches, fabrication of biomedical devices, packaging of biomedical products and food packaging. To this end, various blends of PPC and other renewable polymers such as polylactic acid, starch, cellulose and polyhydroxyalcanoates can be examined as an alternative to non-degradable polymers to tackle their shortcomings and acquire properties for desirable for a specific application. The effect of additives

such as non-toxic-low molecular weight plasticizer can be included in blending process to promote the homogenous blending and physical properties of these polymers.

The results reported for the purification of PPC was for a batch and static mode extraction process to demonstrate the feasibility of the proposed solvent system. It is recommended to measure extraction efficiency in other types of reactors such as stirred tank or fluidized bed reactor to increase the mass transfer rate and feasibility of conducting this process in a continuous system.

After the establishment of the methodology in lab-scale, it is recommended to simulate the purification process in large scale using simulating software such as Aspen-HYSYS. This process simulation can help for economical analysis of the process.

The benign process design for purification of PPC has potential for purification of other polymers. It is recommended to assess the potential of using CO_2/water system for removing other metal compounds that have metal atom bonded to an organic complex from other biodegradable and nondegradable polymers.

In this study, the antimicrobial analysis was only performed for *E-coli* as model bacteria. The antimicrobial test can be extended for other microorganisms that are common for each specific application.

Thymol was used as a model essential oil to provide PPC surface with antimicrobial activity. The Feasibility of adding other essential oils using plasma immobilization on the surface of PPC and other polymers can be examined.

Coating of the packaging material with an antimicrobial agent is usually the final stage of its fabrication process. In this context, the feasibility of the plasma treatment and thymol immobilization process for a different range of products after the shaping process should be assessed.

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