Titre: Title:	Development of GRAS Oxygen Scavenging System for Active Film Packaging
Auteur: Author:	Amin Kamyabmehr
Date:	2023
Type:	Mémoire ou thèse / Dissertation or Thesis
Référence: Citation:	Kamyabmehr, A. (2023). Development of GRAS Oxygen Scavenging System for Active Film Packaging [Mémoire de maîtrise, Polytechnique Montréal]. PolyPublie. https://publications.polymtl.ca/10844/

URL de PolyPublie: PolyPublie URL:	https://publications.polymtl.ca/10844/
Directeurs de recherche: Advisors:	Abdellah Ajji, & Amin Saffar
Programme: Program:	Génie chimique

POLYTECHNIQUE MONTRÉAL

affiliée à l'Université de Montréal

Development of GRAS oxygen scavenging system for active film packaging

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Mémoire présenté en vue de l'obtention du diplôme de *Maîtrise ès sciences appliquées*

Génie chimique

Février 2023

POLYTECHNIQUE MONTRÉAL

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Ce mémoire intitulé :

Development of GRAS oxygen scavenging system for active film packaging

présenté par **Amin KAMYABMEHR**

en vue de l'obtention du diplôme de *Maîtrise ès sciences appliquées*

a été dûment accepté par le jury d'examen constitué de :

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DEDICATION

To my beloved family

ACKNOWLEDGEMENTS

I wish to express my genuine thanks to those who have provided invaluable assistance to accomplish this study.

First of all, I would like to express my deepest appreciation to my supervisor, Professor Abdellah Ajji for his patience, kindness, and unconditional support during my research. It was my great honor to be able to conduct my research under his authentic supervision.

I would also like to acknowledge my co-supervisor, Dr. Amir Saffar for his vast knowledge and experience that always cleared the path and put me in the right way throughout this project.

Special thanks to my friends and research group because of their support, guidance, and encouragement during my study.

To my family, for their support and love even though we were far apart.

RÉSUMÉ

L'oxygène contenu dans les emballages alimentaires peut entraîner l'oxydation des vitamines et des lipides et la croissance de micro-organismes qui dégradent les aliments. Pour prolonger la durée de conservation des aliments, garantir la sécurité des emballages alimentaires et répondre aux préoccupations des clients, la protection des aliments sensibles à l'oxygène contre l'oxydation est cruciale dans le secteur de l'emballage alimentaire. Le développement des études sur les antioxydants a proposé des désoxygénants, qui sont fréquemment utilisés dans les emballages alimentaires, comme solution à ce problème.

Le type d'absorbeur d'oxygène le plus courant se présente sous la forme de sachets, cependant, il existe certains inconvénients associés à ce type d'absorbeur d'oxygène tels que la consommation accidentelle par le client, le ralentissement de la vitesse de la ligne, la confusion du consommateur et l'incompatibilité avec les produits semi-solides. et aliments liquides. Récemment, l'incorporation du matériau désoxygénant dans la matrice polymère en tant que film actif a attiré beaucoup d'attention. Les sachets pourraient être remplacés par des matériaux d'emballage actifs ayant des propriétés de désoxygénation ; des solutions sûres et viables sur le plan industriel sont attrayantes pour l'industrie.

La migration et la diffusion des additifs dans les aliments est une question qui devrait être prise en compte. Par conséquent, l'utilisation de matériel généralement reconnu comme sûr (GRAS) qui est évalué et approuvé par la Food and Drug Administration (FDA) avec le processus réglementaire rationalisé compte tenu de sa limite sur l'aide alimentaire pour garantir que les aliments sont sans danger pour les consommateurs.

L'objectif de l'étude était d'évaluer plusieurs substances GRAS possibles aboutissant au gallate de propyle (PG) et au désoxygénant du tocophérol. Le développement de mélanges de films actifs avec une matrice de polyéthylène basse densité (LDPE) par extrusion à l'état fondu, ainsi qu'une évaluation de la capacité de piégeage de l'oxygène des films actifs mélangés, ont tous deux été étudiés.

La mesure de piégeage de l'oxygène a été effectuée sur des films actifs préparés et a démontré l'activité potentielle de piégeage de l'oxygène du film actif dans les différentes conditions du système de piégeage. Ce travail a illustré l'efficacité de nos désoxygénants dans la matrice LDPE.

ABSTRACT

Oxygen in food packaging can cause the oxidation of vitamins and lipids, as well as the growth of microorganisms that degrade food. To extend food shelf-life, keep food packaging safe, and satisfy customer concerns, the food packaging industry must ensure that oxygen-sensitive items are protected against oxidation. The development of antioxidant studies offered oxygen scavengers, which are frequently employed in food packaging, as a solution to this issue.

The most common type of oxygen absorber is in the form of sachets. However, there are some drawbacks associated with this type of oxygen absorber such as accidental consumption by the customer, slowing down the line speed, consumer confusion, and incompatibility with semi-solid and liquid food. Recently, the incorporation of oxygen scavenger material into the polymer matrix as an active film has attracted much attention. Sachets could be replaced by active packaging materials that have oxygen-scavenging properties; safe and industrially viable solutions are attractive to the industry.

The migration and diffusion of additives into foods is one issue that should be considered. Food safety can be guaranteed with the use of generally recognized as safe (GRAS) material that is evaluated and approved by the food and drug administration (FDA), considering the limit on food aid from the regulatory process.

The purpose of the study was to evaluate several potential GRAS substances and it ended up choosing propyl gallate (PG) and tocopherol as oxygen scavengers. The development of active film blends with low-density polyethylene (LDPE) matrix by melt extrusion, as well as an evaluation of the blended active films' oxygen scavenging capacity, were both investigated.

The oxygen scavenging measurement was carried out on prepared active films and demonstrated the potential oxygen scavenging activity of the active film under different scavenging system conditions. This work illustrated the efficiency of our oxygen scavengers in the LDPE matrix.

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LIST OF SYMBOLS AND ABBREVIATIONS

AA	Ascorbic acid
BHT	Butylated hydroxytoluene
DHAA	Dehydroascorbic acid
DPPH	Diphenyl picryl hydrazyl
EVA	Ethylene vinyl acetate
FDA	Food and Drug Administration
GA	Gallic acid
GRAS	Generally Recognized as Safe
HDPE	High density polyethylene
H_2O_2	Hydrogen peroxide
HTPB	Hydroxyl terminated polybutadiene
K_2CO_3	Potassium carbonate
LDPE	Low density polyethylene
LLDPE	Linear low density polyethylene
MAP	Modified atmosphere packaging
Na_2CO_3	Sodium carbonate
NaCl	Sodium chloride
OS	Oxygen scavenging
PA	Polyamide
PBS	Polybutylene succinate
PE	Polyethylene
PET	Polyethylene terephthalate

PHA	Polyhydroxy alkanoates
PLA	Polylactic acid
PVOH	Polyvinyl alcohol
PG	Propyl gallate
RH	Relative humidity
STP	Standard temperature and pressure
TiO_2	Titanium dioxide
TS	Tensile strength
UV	Ultraviolet

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CHAPTER 1 INTRODUCTION

1.1 Content

Although oxygen is essential for life, it can have negative effects on the packaging industry and shelf-life[1]. Oxidation in packages can cause the deterioration of products. This can result in negative changes in the flavor, aroma, or color of foods[2]. Several approaches can be used to exclude oxygen from the package. This protects the quality of the products, inhibits the growth of bacteria, and extends the shelf-life of the package[3].

Vacuum or modified atmospheric packaging (MAP) is an effective method of extending shelf-life and removing oxygen from the package[4, 5]. In this approach, the air inside the package is vacuumed or a specific gas namely nitrogen and carbon dioxide is flushed into the headspace[6]. However, even after MAP, the amount of oxygen in the package often remains considerable ($\geq$2%), and in the MAP method, oxygen can permeate through the package over time and increase the level of oxygen which is enough to reduce shelf-life. Additionally, its benefit is entirely lost due to leakage[7, 8]. It is costly and inefficient to vacuum package and use nitrogen or argon to purge and flush and these methods do not completely ensure that oxygen is completely removed from the package[8].

A more effective method of eliminating oxygen from packages' headspace is to incorporate an oxygen absorber and scavenger. This will reduce the level of oxygen to as low as 0.01%. In this approach, oxygen-scavenging material can be in the form of a sachet, label, or into the packaging film named active packaging[9]. Oxygen scavengers in the form of a sachet are the most common method to eliminate oxygen from the package[10]. The sachets usually are incorporated with metallic compounds like iron powder but also, but they can be based on non-metallic components such as ascorbic acid, ascorbate salts, and catechol[11, 12]. However, there are some disadvantages to sachets. As an oxygen scavenger, sachets present a potential risk of rupture and accidental consumption by customers or contamination of food by leakage of the sachets. In addition, the sachets are unsuitable for scavenging liquid foods[13, 14].

Another method that attracts much attention is the use of active film for scavenging[15]. This approach, with the incorporation of scavengers into the films, eliminates the sachet problem[16].

In the active film, the polymer resin is blended with metallic particles such as iron powder or natural free radicals such as tocopherol[17].

In addition to providing a barrier to external influences, active film packaging is capable of much more. The package can control, and even react to, events that are taking place inside. Food products with longer storage times or needing a longer shelf-life are better suited to oxygen scavenging films.

The higher thickness of the film is necessary for vacuum packaging and gas flushing systems to have a better oxygen barrier. However, in oxygen scavenging films, higher thickness has a negative effect on the scavenging rate because oxygen must be transmitted into the film and react with additives. By finding the optimum film thickness, a combination of the two methods can be used for some medical products[8].

Incorporating oxygen scavenger additives into the active films eliminates the danger of accidental consumption of the sachet contents. In the films, the major issue of oxygen scavengers is the migration and diffusion of inorganic and synthetic additives. Thus, consumers' attention has been shifted to Generally Recognized as Safe (GRAS) materials. Materials in active film packages can diffuse into foods and be consumed by consumers. Therefore, active film materials must be safe and it is necessary to pay attention to the limits of additives in food products[18].

In compliance with Food and Drug Administration (FDA) regulations, conventional foods, food additives, and medical foods must be studied under regulatory concepts. Manufacturers and labelers need to consider these concepts to produce safe food products[19]. The FDA represents GRAS substances that have been evaluated and qualified scientifically. As GRAS materials, they have been shown to be safe by scientific experiments and experts with sufficient training. This has allowed them to generally agree on the safety of the product when used under the intended conditions. If a substance is not FDA-approved or listed as an excluded GRAS food additive, then manufacturers must obtain FDA premarket approval based on safety data. Additionally, any food containing an unapproved food additive will be marked illegal to import and market[20]. The GRAS guidelines help control the diffusion of active film additives into foods[21].

Oxygen scavengers to be used in food packaging should meet some requirements. They need to be safe and harmless to the human body, not alter the color, odor, and taste of the food product, scavenge oxygen at a desirable rate and amount, and be cost-efficient.

1.2 Objective

The main objective of this project is to develop a non-toxic and GRAS based oxygen scavenging active film by melt extrusion for food packaging application

Specific objectives:

1. To investigate and compare the processability of different oxygen scavenging materials to select the most suitable oxygen scavenger

2. To develop oxygen scavenging active film for food application and analyze its antioxidant activity

1.3 Plan of dissertation

This dissertation consists of five chapters. Chapter 1 is an introduction that explains the principal aspects of the project. Chapter 2 presents a brief literature review of oxygen scavenging materials and methods for incorporating oxygen scavengers into a polymer matrix and scavenging system. Chapter 3 will describe the methodology and details of the experimental plan and implementation of the equipment and facilities in this project. Chapter 4 will describe the results obtained in this work. The conclusion and the recommendation for future work will be presented in Chapter 5.

CHAPTER 2 LITERATURE REVIEW

2.1 Introduction

The trillion cells that make up the body are under severe attack from a virus to a shortage of food. Chemicals known as free radicals, which can harm cells, are another ongoing concern. Free radicals are produced by the body as an inevitable by-product of converting food into energy, or they can develop as a result of exposure to cigarette smoke, air pollution, and sunlight. Free radicals in food damage the product and cause food spoilage. In the body, attacking the cells is a cause of neurological diseases such as Parkinson's disease, Alzheimer's disease, and diabetes [7].

Chemicals called antioxidants protect the body's cells by reducing or preventing free radicals. They donate an electron to free radicals to decrease their reactivity. The antioxidants often act as reducing agents, terminating the free radical chain reaction [8]. There are many applications for antioxidants, as they are used as additives in the food processing industry to prevent spoilage of food. Also, several studies have linked neurological diseases to antioxidant decreases [9].

Many foods are extremely sensitive to oxygen. Oxygen by encouraging the growth of microorganisms causes food products to deteriorate either directly or indirectly. Therefore, oxygen is frequently removed to preserve these items. To help remove or lower the amount of oxygen in the container, oxygen scavengers or oxygen absorbers are added to food packages. They are employed to increase shelf-life and ensure product safety [10]. By absorbing oxygen in the headspace, oxygen scavengers increase the shelf-life of the package, but antioxidants, by neutralizing free radicals in foods, prevent damage to the body's cells. However, as most oxygen scavengers have antioxidant properties, it is recommended that antioxidant activity be tested for oxygen scavengers [22].

Generally, any oxidizing substrate, metallic, organic, or inorganic, has the potential to be an oxygen scavenger. The selection of suitable agents for food packaging is constrained by cost, safety, the rate and capacity of reactions with oxygen, and compatibility with food migration regulations.

Earlier in the 20th century, to absorb residual oxygen in the food package, several compounds were added to food products. Plastic packaging began to be widely used in the 1970s. Oxygen

absorbers were created as a result of worries about oxidation caused by residual oxygen and oxygen that passes through packaging materials. The Mitsubishi Gas Company introduced the Ageless® oxygen absorber in 1977; it was made of reduced iron salts that were activated by moisture and placed in gas-barrier food containers, where the iron oxidizes to ferric oxide. These iron sachets were utilized in active packaging oxygen scavenging technology to aid in the preservation of food packages. As a result of the success of this packaging, the Japanese company Toppan Printing Company introduced oxygen scavengers based on ascorbic acid. Due to their commercial success, oxygen scavenger brands were produced more frequently in Japan, the USA, and Taiwan[23].

In recent years, some novel non-metallic substances, such as organic substances, have attracted a lot of interest. Table 2.1 lists and classifies some potential oxygen scavenging agents for use in the food packaging.

Table 2.1 Different classification of oxygen scavenger[24]

Classification	Oxygen scavenger	Oxidation mechanism
Metallic	Iron powder, Platinum, palladium-based system	Oxidation of metal with supply of moisture and action of an optional catalyst
Organic	Ascorbic acid, tocopherol, gallic acid, polyunsaturated fatty acids	Oxidation of organic substrate with metallic catalyst or alkaline substance
Inorganic	Sulfite, thiosulfate, titanium dioxide	Oxidation of inorganic substrate by UV light
Polymer based	Oxidation–reduction resin, polymer metallic complex	Oxidation of polymer components with metallic catalyst

Although iron-based agents are used in the majority of commercial oxygen scavenging films, food safety should be regulated by FDA standards, and the market for oxygen scavenging films has been increasingly interested in the development of novel and safe scavenging agents.

In 1906, Congress passed the Pure Food and Drugs Act to prevent the sale and production of misbranded, tainted, or poisonous foods and drugs. Under the 1958 Food Additives Amendment to the Federal Food and Drug Act, any substance that is purposely added to food is subject to pre-market approval by the FDA unless its safety has been demonstrated by a long history of usage in food, and the use of the substance is generally recognized as safe. These GRAS substances were originally listed by the FDA in the Federal Register on December 9, 1958, as GRAS substances. Currently, the Code of Federal Regulations Parts 182, 184, and 186 contain the GRAS list. Hundreds of different substances are included in it, including those that are used in food packaging[19].

Direct food additives are those that are added directly to foods for specific purposes. They can usually be identified on the ingredient label of foods. The indirect food additives are those found in trace amounts in the food due to its packaging, storage, or other handling. During storage, packaging substances can find their way into foods in minute amounts. For food packaging to be permitted for use, manufacturers must demonstrate to the FDA that all materials that come into contact with food are safe.

The GRAS regulation is divided into 3 groups; Part 182 includes substances that are GRAS in the food, as defined in Part 184, the substances that are added directly to human food have been reviewed and approved as GRAS by the FDA, Part 186 contains the substances that indirectly are added to human food reviewed and affirmed as GRAS. The FDA indicates considerable antioxidant activity for some of Part 182 and 184 GRAS substances, however, for Part 186 GRAS material no antioxidant activity is detected.

Food additives that are direct are usually limited to more than 100 mg/kg of food, however, indirect additives are typically limited to less than 10 mg/kg. As a result, indirect food additives should not be added directly to the food because of the low limitation. If these additives are added to the food,

a migration and diffusion test must be performed[18].Table 2.2 presents the oxygen scavenging of GRAS substances in the various films.

Table 2.2 Oxygen scavenging system conditions

Oxygen scavenger and GRAS type	Form	Reaction catalyst / initiator	Condition	Headspace (cc)	Scavenging result	Reference
Iron nanoparticle (not GRAS)	Polyester / PE sachet	-	75% RH, 25 °C	660	130 cc oxygen after 8 h in atm pressure	[25]
Iron nanoparticle (not GRAS)	Blended in silicone rubber	-	25% RH, 23 °C	117	0.21 oxygen partial pressure to 0.13 in 10 days	[26]
			100% RH, 23 °C		0.21 oxygen partial pressure to 0.13 in 1 day	
iron-based kaolinite (not GRAS)	LLDPE active film	-	100% RH, 24 °C	40	4.2 cc oxygen in 60 days in atm pressure	[27]
	HDPE active film				2.5 cc oxygen in 60 days in atm pressure	

	HDPE active film		50% RH, 24 °C		1 cc oxygen in 60 days in atm pressure	
			100% RH, 5 °C		1 cc oxygen in 60 days in atm pressure	
Sodium ascorbate (GRAS Part 182)	paper/PE sachet	Activated carbon	1 ml water injected to sachet, 25 °C	600	117 cc after 5 days in atm pressure	[11]
Ascorbic acid (GRAS Part 182)	PET / LDPE active film	iron (III) oxide	99% humidity,	20	21% oxygen concentration to 6.07% in 15 days	[28]
Tocopherol (GRAS Part 182)	PLA active film	-	25% RH, 25 °C	117	21% oxygen concentration to 18.9% in 5 days	[29]
Gallic acid (not GRAS)	LDPE active film	Potassium carbonate	95% RH, 50 °C	115	21% oxygen concentration to 11.9% in 7 days	[30]
			95% RH, 23 °C		21% oxygen concentration to 14.7% in 7 days	

			95% RH, 5 °C		21% oxygen concentration to 16.5% in 7 days	
hydroxyl terminated polybutadiene (not GRAS)	PLA active film	TiO_2	25% RH, 25 °C	275	28 cc after 30 days in atm pressure	[31]
	LDPE active film		25% RH, 25 °C		30 cc after 5 days in atm pressure	
Amosorb DFC 4020 a copolyester-based polymer (not GRAS)	PET active film	cobalt salt	25% RH, 23 °C, activated by UV lihgt	9	19% oxygen concentration to 16.5% in 2 days	[32]

2.2 Inorganic oxygen scavengers

2.2.1 Iron powder

Metallic oxygen scavengers are the most common kind of scavenger that is used in the packaging industry. [33]. Palladium-based systems and iron powder are the most remarkable metallic oxygen scavengers [34]. In sachets, as it is reported in Esfandiari et al [24], the oxidation reaction is associated with anode-side and cathode-side reactions on the surface of iron powder nanoparticles. The mechanism of oxygen scavenging of iron powder by ionization in the presence of relative humidity is shown below[25].

$$Fe \rightarrow Fe^{2+} + 2e^{-} \quad (1)$$

$$H_2O + \frac{1}{2} O_2 + 2e^{-} \rightarrow 2OH^{-} \quad (2)$$

$$Fe^{2+} + 2OH^{-} \rightarrow Fe(OH)_2 \quad (3)$$

$$2Fe(OH)_2 + \frac{1}{2} O_2 + H_2O \rightarrow Fe_2O_3.2H_2O \quad (4)$$

In a study by Mu et al [24], the iron nanoparticles were compounded with activated carbon, sodium chloride, and calcium chloride in a weight ratio of 1:1:1:0.2 and were added to polyester/polyethylene sachets. The authors concluded that a high rate of scavenging was observed. It was found that oxygen absorption increased sharply to a maximum of 130 cc under STP conditions, but after 8 hours it remained constant.[25].

The humidity is an essential factor for oxygen absorption of scavengers [35]. In a study by Foltynowicz et al [26], effect effect of humidity on oxygen scavenging was investigated. In this article, silicone was added to iron powder nanoparticles and oxygen absorption was analyzed under STP conditions. The test was based on the partial pressure of oxygen in the container with the use of an oxygen sensor. Approximately 0.8 g of silicone matrix with iron powder was applied to the samples and a humidity of 100% was obtained by adding a petri dish containing water[26].

According to the results, oxygen scavenging is more effective at higher relative humidity levels. As iron powder forms iron hydrates, which are porous, oxygen can readily access the inner parts of the powder, which results in a higher scavenging rate[26].

The iron powder scavengers can also be incorporated into the polymer matrix and blended into films to be used as oxygen scavenging active packaging[36]. However, the quality of the active films could be affected by additives[37].

In a study by Busolo et al [30], the Oxygen scavenging of 10 wt. % iron-based kaolinite additive was studied in polyethylene (PE). Iron kaolinite is added to polyethylene in a twin-screw cast film extruder. Two different polyolefins, high density polyethylene (HDPE) and linear low-density polyethylene (LLDPE), are used to investigate the influence of matrix permeability on efficacy. The result showed that oxygen absorption in the LLDPE is twice HDPE in the same condition.

Since LLDPE has a higher oxygen and water permeability than HDPE, water will have more access to the iron powder and it will have a higher absorption activity[27].

Another factor that influences the compound's ability to scavenge oxygen is temperature[38]. In HDPE, the effect of storage temperature and relative humidity is analyzed, and by increasing them, oxygen absorption is also enhanced. As it is shown, in the same storage time, the additives at 24°C and 50% RH could scavenge approximately 1 cc O_2/g composite. This is almost the same amount as oxygen absorption at 5°C and 100% RH[27].

In conclusion, based on scavenging capacity, the iron powder oxygen scavenger in the form of active film is not as effective as iron sachets, and in any form, it requires high humidity (more than 75% RH) to be effective at scavenging.

2.3 Organic oxygen scavengers

Another type of oxygen absorption is organic oxygen scavengers[39]. In comparison to inorganic oxygen scavengers, organic oxygen scavengers are able to disperse in polymer films, resulting in active films that are more transparent optically[24].

2.3.1 Ascorbic Acid based system

Ascorbic acid (AA) or Vitamin C is a water-soluble vitamin found in fruits and vegetables. It is one of the most remarkable oxygen scavengers. The scavenging reaction starts with the dehydration of ascorbic acid to dehydroascorbic acid (DHAA) as it is described in the reaction below [11].

$$C_6H_8O_6 + \frac{1}{2} O_2 \rightarrow C_6H_6O_6 + H_2O \quad (5)$$

To speed up the scavenging reaction in this material, transition metal catalysts such as iron (III) oxide or copper (II) oxide and light are applied to the oxygen scavenger[11, 24].

In an article by Lee et al [11], ascorbic acid-based system was used as an antioxidant for scavenging. In various concentrations, sodium ascorbate was added to activated carbon to act as a scavenger. To identify the optimum ratio for the formulation of the additives, different ratios of

compounds (1:1, 1:1.2, 1:1.4, 1:1.6, 1:1.8, and 1:2, w/w) were prepared. 0, 0.5, 1, and 1.5 ml of distilled water were injected into the sachets to prepare the humid condition.

A ratio of 1:1.6 is optimum for the additives so that 117 cc of oxygen can be scavenged after five days. A higher injection of water in the sachet results in a reduction in scavenging. Due to the antioxidant's ability to dissolve into the additional injected water, it causes the oxygen scavenger to become inactive. Also, the water in the package may block and inhibit gas diffusion and reduce reaction rates. The optimum water needed for the package was 1 ml in the sachet[11].

In a study by Wolsiak et al [28], ascorbic acid oxygen scavenger film consists of 4 wt% and 6 wt% iron (III) oxide with 1 wt% ascorbic acid, added to polyurethane adhesives to form a core layer, coated on PET film, and then laminated with LDPE film. Two laminated pieces weighing about 4.5 g each were placed in the 20 cc vial for oxygen scavenging. As the iron compound oxygen scavenger needs high relative humidity for activity, 1.5 g agar was added to the container.

It was observed that after 15 days of storage, the oxygen concentration of the film did not change after only one oxygen scavenger was applied. However, when both iron (III) oxide and ascorbic acid are incorporated into the film, there is a sharp reduction in oxygen concentration in the headspace. For the 4 wt% iron (III) oxide and 1 wt% ascorbic acid sample, the oxygen percentage dropped to 6.27 vol% and for 6 wt% iron (III) oxide and 1 wt% ascorbic acid, the oxygen concentration decreased to 6.03vol%. In the reactions below, the iron compound acts as a catalyst for scavenging reactions with dehydrating ascorbic acid[24].

$$C_6H_8O_6 + 2Fe^{3+} \rightarrow C_6H_6O_6 + 2Fe^{2+} + 2H^+ \quad (6)$$

$$2Fe^{2+} + 2O_2 \rightarrow 2Fe^{3+} + 2O_2^- \quad (7)$$

$$2O_2^- + 2H^+ \rightarrow O_2 + H_2O_2 \quad (8)$$

$$H_2O_2 + C_6H_8O_6 \rightarrow C_6H_6O_6 + 2H_2O \quad (9)$$

2.3.2 Tocopherol

The other organic oxygen scavenger substance is -tocopherol, which is a natural free radical with the potential to be incorporated into the polymer matrix to decrease oxidation in food packages[40]. The stabilizing performance of α-tocopherol remains constant under intense extrusion conditions[41].

One article by Maio et al [29], evaluated tocopherol as a viable oxygen scavenging system. PLA was selected as the polymer base for the scavenging system, and 5% α-tocopherol was added to the PLA during the cast extrusion process for producing the active film. The active film ensured the stability and the film quality in terms of mechanical and oxygen permeability test.

The oxygen scavenging rate of the systems was determined using a luminescence lifetime detector as an oxygen measurement system. The system was tested for 5 days and the pure PLA film was found to be inactive in scavenging oxygen. In contrast, PLA active film containing 5% tocopherol instantly reacted with headspace oxygen and after 5 days reached a constant value. The pure α-tocopherol also presented similar scavenging to the active film, demonstrating the same oxygen scavenging kinetics for both systems. In contrast, pure α-tocopherol has a better ability to scavenge. This may be related to the degradation of α-tocopherol in the extrusion process. The oxygen scavenging reaction of tocopherol is summarized below[29].

$$TocH + O_2 \rightarrow dimer\ of\ tocopherol + H_2O\ (10)$$

2.3.3 Gallic Acid

Another organic oxygen scavenger is gallic acid, a polyphenol that can be used for packaging[42]. Gallic acid has the potential to scavenge a large amount of oxygen under alkaline conditions. It needs to mix with a base, and in addition, the presence of high relative humidity is required[43]. In GA oxidation, a color alternation from white (pure GA) to dark green could be observed[44]. As a result, GA can act as an oxygen indicator. In the GA reaction, oxidation is accompanied by the formation of hydrogen peroxide (H_2O_2), quinones, and semi-quinones under alkaline conditions[45].

$$GallicH + O_2 \rightarrow Gallic\ ▪ + HO_2\ ▪ \qquad (11)$$

$$HO_2\ ▪ + GallicH \rightarrow Gallic\ ▪ + H_2O_2 \qquad (12)$$

$$2Gallic\ ▪ \rightarrow Gallic\ acid\ dimer \qquad (13)$$

$$Gallic\ acid\ dimer + O_2 \rightarrow Quinone\ of\ dimer + 2\ H_2O_2 \qquad (14)$$

$$Quinone\ of\ dimer + 2O_2 \rightarrow open\ ring\ product\ of\ dimer \qquad (15)$$

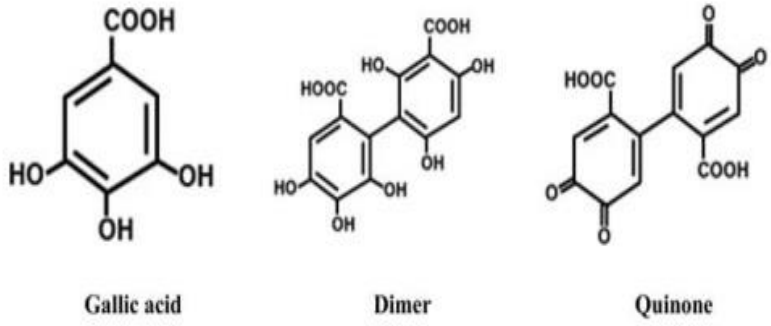

Figure 2.1 Molecular structure of gallic acid, dimer, and quinone of gallic acid in the oxygen scavenging reaction

In one of the articles, potassium carbonate (K_2CO_3) is added to GA to act as a reaction initiator. When dissolved in water, K_2CO_3 forms a powerful alkaline environment that is ideal for scavenging GA oxygen. The reaction is shown below,

$$K_2CO_3 + H_2O \rightarrow 2KOH + CO_2 \qquad (16)$$

Scavenging additives were added in the percentages of 1, 3, 5, 10, and 20 to the LDPE in the laboratory twin screw extruder cast film extrusion system. The ratio between K_2CO_3 and GA was 1:2. 4 grams of the active film were placed in the 115 cc headspace vial. A glass vial containing 0.5 cc of water was also added to the system to provide 95% relative humidity.

The LDPE film showed a constant oxygen percentage during storage. The 1, 3, and 5% oxygen scavenging active film made a small reduction in the oxygen content. Active film systems with 10 and 20% additives indicate a strong oxygen scavenging capacity[30].

2.3.4 Unsaturated hydrocarbon oxygen scavengers

Most metallic and organic oxygen scavengers activate in the presence of water and high relative humidity [35], However, some unsaturated organic oxygen absorbers such as polybutadiene react in the absence of humidity[46]. Polybutadiene scavenger systems use a transition metal catalyst. It is imperative to examine the potential toxicity of the catalyst and its potential to reduce film transparency[47].

In a study by Kordjazi et al [43], Using TiO_2 as a catalyst, hydroxyl terminated polybutadiene (HTPB) was applied as an oxygen scavenger. In this study, LDPE and PLA are used for the polymer matrix and Sasol wax was added to LDPE to address the phase separation problem. In the twin screw cast film extrusion process, additives of different compositions are added to the polymer to prepare active films. 1g of the active film was placed in a 275 cc bottle and stored for 30 days to observe the scavenging activity of the system.

Table 2.2 demonstrates that oxygen scavenging of HTPB with TiO_2 at these concentrations was effective. The highest oxygen scavenging activity was observed for 10% additives in LDPE film nearing 30 cc/g after 30 days. Additionally, for PLA active film, the maximum oxygen scavenging can reach as high as 28 cc/g after 30 days with 13% additives[31].

2.4 Polymer-based scavengers

The use of polymer-based oxygen scavengers is a new trend in oxygen absorption in packages[48]. Research into oxygen scavengers such as polymer-metal compounds and oxidation-reduction resins attracts a lot of attention[49]. Polymer matrixes could contain copolyesters that could be used as oxygen scavengers in package walls[50].

Added as a catalyst to a scavenging active film and polymeric film, nanocrystalline titanium oxide (TiO_2) demonstrated a high scavenging capacity when exposed to UV light. It is because when TiO_2 is exposed to UV light, an electric field with two positive and negative poles will be formed. Electrons on the negative side migrate to oxygen in the headspace, then the radical oxygen reacts with the copolyester, initiating the scavenging process[51].

The metal catalyst can be incorporated into polymers like LDPE or PET and be triggered by UV light to form an oxygen scavenging system. PET was selected as a base polymer, and 5% of

Amosorb DFC 4020, which is an acrylic copolyester-based polymer, was added to the polymer in laboratory cast extrusion. A cobalt salt was used as a metal transition to be activated by UV light and catalyze the unsaturation of hydrocarbon dienes such as polybutadiene.

The scavenging capacity was tested by placing 0.15 g of active film into a 9 cc glass vial. As observed, the control PET film showed inactivity for oxygen scavenging during storage. In contrast, 5% active film in the first two hours showed high oxygen absorption activity. The oxygen concentration in the system reached a constant value after 26 hours of scavenging. The oxygen content dropped by 2.5% in the oxygen scavenging system[32].

2.5 Effect of thermal degradation on material quality

Under certain conditions, polymeric materials can become unstable and degrade. Consequently, the polymer substance may degrade and produce toxic material by-products that are harmful to health and the environment. The degradation of polymer materials could be caused by factors like heat, impurity, humidity, UV light, microorganisms, or a combination of them.

The physical and chemical properties of polymer materials are significantly altered when exposed to heat. During thermal degradation, a chemical process results in chemical degradation of the polymer. A change in these properties affects the molecular weight, molecular weight distribution, crystallinity, chain conformation, and strength of polymer materials. Due to thermal degradation, the alternation may lead to the formation of macro radicals and a change in the physical properties of the polymer. This includes melting, glass transition, and crystallization.

Thermal degradation is accompanied by a change in color, mass, and shape and the development of voids and cracks in the material. Therefore, the aesthetic value of the materials as well as the mechanical and thermal properties of the materials are altered. Depending on the degradation conditions and the material, the changes and their effect on degradation vary widely.

As a result, during melt extrusion processing, the degradation of the polymer material and additives must be considered. The temperature could increase in the extruder due to the shear rate and exceed the decomposition temperature point of the additives. As a result of this thermal degradation of the additives and the formation of radicals, the mechanical properties of the active films alter adversely. The color, crystallinity, strength, and shape of the films could change. So before the

melt extrusion process, a pre-review of the thermal degradation of the oxygen scavenger additives is needed[52].

Although degradation could add some toxic products to the package or food, the by-products of scavenging reactions also should be considered. Regulations by the FDA limit the amount used in food packages and require migration study results to be provided. Testing to determine the risk of migrated components to human health is performed by analyzing quantities of the material added to food or food simulations. Migrated material should always be below the FDA regulation threshold[53].

2.6 Problem identification

This literature review analyzed the most common active oxygen scavenging systems that were used for packaging. Although oxygen scavenging systems showed a strong capability for oxygen absorption, some of them like sachets are unable to address the concerns about oxygen scavenging in semi-solid and liquid food products. Food and Drug Administration (FDA) regulations regarding the limitation of scavenging additives in films and food products should also be examined.

In order to develop an oxygen scavenging system for worldwide packaging requirements, certain characteristics must be taken into consideration. By FDA and European Union (EU) regulations, active film additives should be considered safe. Any substance added to food must pass premarket review, and their migration tests must be approved by the FDA. Materials added to or in contact with foods in the package are subject to a limitation, and the additives should not exceed those limits. Therefore, oxygen scavengers as additives must be qualified and evaluated scientifically. There are also GRAS materials that have been pre-evaluated and can be used as oxygen scavengers if their limitations on foods are taken into account.

Active flexible packaging is a better option for customers to avoid sachet issues. So, the rate of oxygen absorption by these active films should be considered. For polymer selection for the matrix, compostable polymers such as PLA, PHA, and PBS which are made of polyester are not viable options. The reason for this is that GRAS oxygen scavengers generally work in humid conditions, and polyester absorbs humidity and initiates the composting process. Other polymers

such as PVOH, PA, and PET are a high barrier for oxygen transmission that reduces oxygen absorption and are not favorable for oxygen absorption active films. Among PE and PP, two polymers that have high oxygen transmission rates, PP has more moisture barrier properties. PE, the most commonly used polymer in the industry, is the most suitable polymer matrix.

To develop an oxygen scavenging system that is widely applicable it must be effective for all types of foods (solid, semi-liquid, and liquid) and different package conditions. Although the iron sachet is used at high relative humidity to scavenge oxygen from solid foods, GRAS organic oxygen scavenging materials can function at low relative humidity in a variety of food types.

The purpose of this study is to investigate an oxygen-scavenging active film and to develop an effective and nontoxic oxygen-scavenging system.

CHAPTER 3 EXPERIMENTAL METHODOLOGY

3.1 Introduction

The oxygen scavengers were selected from the FDA GRAS material list, and their antioxidant activity was recommended. For the processability of the selected oxygen scavengers, mechanical and thermal property tests were applied to screen the final oxygen scavengers. Then, to analyze the potential oxygen scavenging of materials, an internal mixer was used. Consequently, for the preparation of the oxygen scavenging active film, a cast film study was employed. The DPPH test was used to study the antioxidant activity of active films.

3.2 Materials

Low density polyethylene (LDPE) LM-0724-A resin with melt index of 7.0 g/10 min, was obtained from the Nova Chemicals (Calgary, AB, Canada) as the polymer base. Propyl gallate (PG) (molecular weight Mn=212.2) as one of the oxygen absorbers prepared from the Xi'an Lyphar Biotech (Xi'an City, China). Ascorbic acid (99%), sodium ascorbate (purity≥98%), sodium sulfite (98%), sodium bisulfite, pyrogallol (purity≥98%), butylated hydroxytoluene (BHT) (purity≥99%), isoascorbic acid (98%), Calcium ascorbate (99%), Calcium citrate (99%), tocopherol (purity≥95.5%), ethanol (99.9%), and Diphenyl picryl hydrazyl (DPPH) were purchased from Sigma Aldrich (St. Louis, MO, USA). Sasolwax H1 Fischer-Tropsch hard wax was obtained from Sasol (Johannesburg, South Africa).

3.3 Sample screening

To screen the oxygen scavengers, the drawbacks of the scavengers were studied, and different mechanical and thermal property tests were analyzed to obtain the desired oxygen scavenger. There was a drawback with sodium sulfite and sodium bisulfite. In the presence of high relative humidity, these materials react with water and produce sulfur oxide, a colorless, pungent gas that causes nasal irritation. Therefore, sodium sulfite and sodium bisulfite are not applicable and favorable for all types of scavenging processes, especially in high relative humidity. In the SEM test, the particle size of the additives in the active films was analyzed. In the DSC and TGA tests, the thermal processability and degradation of oxygen scavengers were studied.

3.3.1 Scanning electron microscopy (SEM)

Scanning electron microscopy (SEM) was analyzed using Hitachi TM3030Plus equipment with an electron voltage of 15 kV to study the surface morphology of active films. The films were placed on top of double-sided adhesive carbon tape. SEM test was used to analyze the particle size of additives in films. This was to ensure it was below 75 µm, as that is desired in flexible packaging.

3.3.2 Differential scanning calorimetry (DSC)

Differential scanning calorimetry (DSC) (Q1000, TA Instrument, New Castle, DE, USA) was used to study the thermal behavior of the additives and cast films. The heating cycle is carried out at a rate of 10 °C/min, between 30 and 300 °C under a nitrogen atmosphere.

3.3.3 Thermogravimetric analysis (TGA)

The thermal properties of the oxygen scavenging additives and active films were analyzed by means of a thermo-gravimetric analyzer (Q500, TA Instrument, New Castle, DE, USA). The films were scanned from 20 to 800 °C at a rate of 20 °C/min. Nitrogen gas was used as the balance purge gas at a flow rate of 40 mL/min. Air was used as the sample purge gas at a flow rate of 60 mL/min.

3.3.4 Oxygen scavenging in the sachet

In order to compare the oxygen scavenging activity of the different additives, an oxygen absorber sachet was designed. This is because some oxygen scavengers could not be added to the cast extrusion system because of the low degradation temperature, and they degraded at the processing temperature. As an oxygen scavenger in the sachets, PG, tocopherol, sodium ascorbate, and ascorbic acid were selected. This is because they showed promising scavenging activities in the reviews and have a better processing ability. 1 g of the additives was added to the sachet to study the activity of the different GRAS oxygen scavengers. The sachet was prepared with LDPE in the dimension of 1 × 1 in. Due to LDPE's high water vapor permeability, 0.5 ml water was injected into the sachet before sealing to prepare the desired relative humidity.

3.4 Sample preparation

3.4.1 Internal mixer studies

For analyzing the effectivity and the mixability of compounding materials, a preliminary study of the internal mixer (Brabender) (Leistritz ZSE 18 HP- Nuremberg, Germany) was conducted at a temperature of 170 °C and a speed of 60 rpm with a capacity of 60 cc. A temperature of 170 °C was chosen since it is higher than many oxygen scavengers' degradation temperatures. The temperature is also within the range of industrial PE processing temperatures, between 170 °C and 200 °C. An increase in the melt temperature of material due to high shear rates should be considered. The residence time for melting the polymer was 3 min and for mixing the compound was 7 min. Following the internal mixer's blending of the material, a hot press was used to make the film. The blend was pressed for 10 min at 170 °C under 10000 psi (68.94 Mpa) pressure. Then, it was cooled for 5 min in a 20 °C cold press with 5000 psi (34.47 Mpa) to obtain the film. Tocopherol, propyl gallate, and ascorbic acid, which had better thermal stability, were tested for oxygen scavenging in the internal mixer. For the Brabender, their temperatures were set at 180 °C, 170 °C, and 140 °C, respectively. Iron (III) oxide and sodium carbonate were added to ascorbic acid and PG to act as a catalyst and the reaction initiator.

3.4.2 Melt compounding and cast film extrusion

For compound development and cast film extrusion, a twin screw extruder (Leistritz ZSE 18 HP-Nuremberg, Germany) with a length to diameter (L/D) of 40 and a screw diameter of 18 mm was utilized. A circular die with a 2 mm diameter was attached to the extruder for compound material. After the extruder, a water bath was used to cool the exiting filament. A pelletizer (Model BT 25, Scheer Bay Co.) was added to the system to pelletize the cold filament homogeneously. For cast film extrusion instead of the circular die, a slit die was replaced. Also, an air knife was added to cool the exit material from the die. The films were stretched by cold rolls at room temperature and the film thickness was adjusted by the roll speed to prepare the desirable films.

3.4.3 Propyl gallate/sodium carbonate/low-density polyethylene compounding and cast film extrusion

A mill and 75 µm sieve were used to reduce the particle size of sodium carbonate to 75 µm so that the film thickness can be reduced to under 100 µm. Since sodium carbonate is an absorber of water, it was fed to the extruder to make a masterbatch, and then the masterbatch was added to the feed tank, where nitrogen is being flushed into the feed tank to minimize the material's contact with ambient air. To prepare the masterbatch, PG and Na_2CO_3 were dried in a vacuum oven for two days at 70 °C. Then PG and Na_2CO_3 were separately fed to the extruder by a side feeder to make two different granules. For the first granule, PG was added to the side feeder and LDPE was fed into the hopper and the composition of LDPE/PG masterbatch was 80%/20%. The temperature profile for the system was set at 150/155/160/165/170 °C from the hopper to the die. The same procedure was applied to make the LDPE/Na_2CO_3 masterbatch with a composition of 80%/20%. The PG and Na_2CO_3 masterbatch were mixed in a ratio of 2:1 and then dried for two days at 70°C in the vacuum oven. For film casting extrusion, the temperature profile for the extruder was set at 150/155/160/165/170 °C from the hopper to the die. The speed of the screw was 90 rpm. The dried and mixed granules were added to the feed tank for the 20% additive film. For 5% and 10%, they were diluted with LDPE and then fed to the feeder. LDPE control film, LDPE/PG, and LDPE/Na_2CO_3 films were prepared by adding each of their granules separately to the extruder. The temperature profile and screw speed were the same as for the active films.

3.4.4 Tocopherol/ sasol wax /low-density polyethylene compounding and cast film extrusion

For the tocopherol active films, the same procedure was applied. However, because there was phase separation between tocopherol and LDPE, Sasolwax H1 wax was added to enhance miscibility and fix phase separation. First, the ratio of wax and tocopherol was chosen at 1:2, but the film could not be extruded. The film was then obtained by combining wax and tocopherol in a ratio of 1:1. Also, for tocopherol there was no need to make the masterbatch for cast film extrusion as humidity sensitivity was not observed by the tocopherol additive. Since 20% tocopherol contains a high amount of tocopherol, the active film could not be obtained, so 10% and 5% tocopherol active films were selected for the cast film. The wax granules were mixed with the

LDPE granules and added to the hopper. The tocopherol was added by a side feeder to produce LDPE/Tocopherol/Wax active film compositions of 80%/10%/10% and 90%/5%/5%. The temperature profile for cast extrusion of tocopherol film was 165/170/175/180/185 °C from the hopper to the die, and the screw speed was set at 80 rpm. For the control film, pure LDPE was extruded by cast extrusion.

3.5 Tensile properties

Active films were tested on an Instron universal tensile machine (Model 3365) based on ASTM standard D882-91 for young modulus and elongation at break. The samples were cut into 10 × 2.54 cm rectangular shapes for the test. The extension rate for the samples was 500 mm/min and the final value for young modulus and elongation at break was the average of the 5 tests.

3.6 Oxygen absorption measurement

In the glass bottle container, the active film sample was placed at the desired weight, and the required relative humidity was prepared by placing a vial inside. To simulate the relative humidity for different types of food products, 99%, 75%, and 25% relative humidity were selected. To achieve 99% relative humidity, 5 cc of water was added to a vial and it was placed inside the glass. 2 g sodium chloride (NaCl) salt was added to 5 cc water vial to prepare the 75% relative humidity in the glass container, and the 25% which was the laboratory relative humidity was obtained without adding any vial to the bottle. In addition to 100% relative humidity for beverages, 75% relative humidity was used for food packages containing meat and poultry, and 25% relative humidity for dry food simulations.

Using a MOCON (Minneapolis, MN, USA) OpTech-O2 platinum oxygen analyzer with a sensitivity of 500 ppm (0.05%), the optical sensor was placed inside a glass bottle to measure the concentration of oxygen. The oxygen concentration data was monitored as a function of time by a handheld probe in the acquisition software. Finally, the container was properly sealed to prevent oxygen from penetrating the system. Based on the final and initial oxygen concentration of the container, oxygen scavenging of the system was calculated. For oxygen scavenging result

comparison, all the glass containers were selected in the same volume (275 cc), and the active film samples were cut in 1 g with approximately equal thickness.

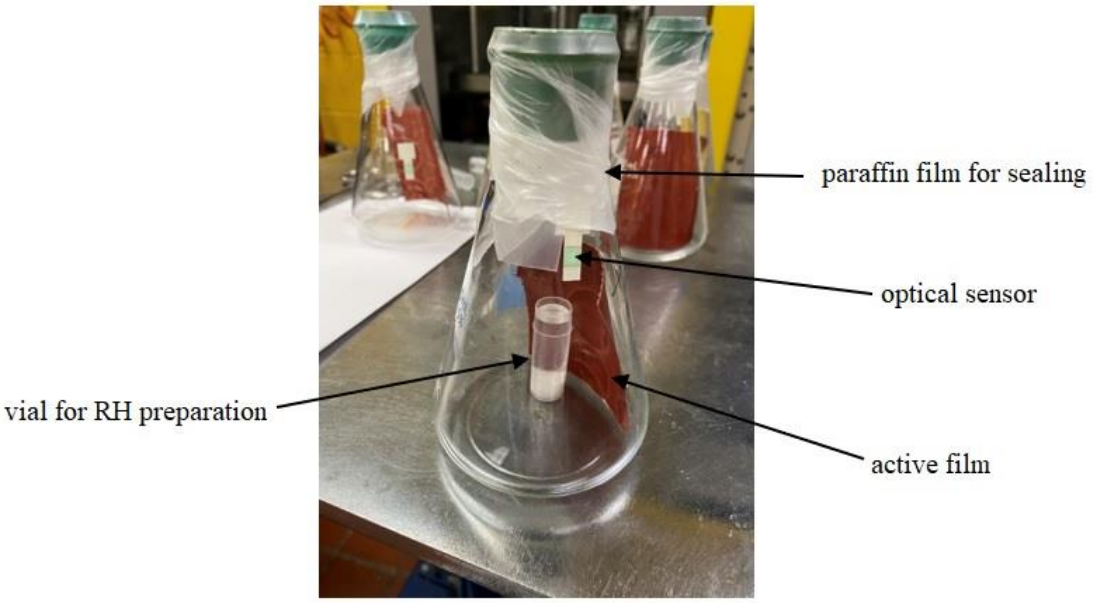

Figure 3.1 Oxygen scavenging system with 1 g active film sample in the 275 cc container in the desired relative humidity

3.7 **DPPH radical scavenging activity**

DPPH radical scavenging activity was measured based on the method of Jongjareonrak[53] with a slight modification. 0.1 g of the 5% active film was cut into small pieces and then added to 2 mL of ethanol. The mixture of ethanol solution and film was vigorously vortexed for 3 minutes. The solution was then allowed to stand at room temperature in the dark for 3 hours. Again for 3 minutes, it was vigorously vortexed. Then, it was centrifuged for 10 min, at the speed of 2300 rpm. 0.1 ml of the aliquot of the mixed solution was added to the 3.9 ml of the 0.06 mM DPPH in ethanol solution. The final mixture was vortexed for 1 min and kept in the dark. The mixture absorbance was studied at 517 nm by means of a spectrometer (Spectronic 200, Thermo Fisher, Montreal, QC, Canada) after 0.5, 1, and 2 hours of residence time. The DPPH ethanol solution was used as a control absorbance. DPPH radical scavenging activity was calculated using the following equation.

$$Radical\ scavenging\ activity\ (\%) = [1- (A_{sample}/A_{control})] \times 100 \qquad (16)$$

Where A_{sample} is the absorbance of the mixed sample and $A_{control}$ is the absorbance of the control[54].

The antioxidant activity value shown was the average of the three tests.

CHAPTER 4 RESULTS AND DISCUSSION

4.1 Oxygen scavenging additives selection

Considering that oxygen scavengers are used in food packaging, the oxygen absorbers in this study were chosen from the FDA's guide list, proving their safety through scientific experimentation. Oxygen scavenging additives were chosen to be studied, and their efficiency was analyzed according to the desired processing conditions. Propyl gallate (PG), ascorbic acid, sodium ascorbate, sodium sulfite, sodium bisulfite, pyrogallol, butylated hydroxytoluene (BHT), isoascorbic acid, calcium ascorbate, calcium citrate, and tocopherol were prepared and their processability and effectivity in the oxygen scavenging additives were analyzed.

The oxygen scavenging system was designed at 170°C because this is the recommended temperature for processing polyethylene (PE), and above this temperature, some additives are degraded. The scavenging additive must be able to process at the desired temperature without any degradation. It is worth mentioning that owing to the high shear rate in the twin screw extruder for the polymer matrix, the temperature of the melted compound in the extruder was increased from the temperature that was selected for extrusion. Thermal degradation and additive particle size in active films were analyzed and reported in Table 4.1.

The particle size of some oxygen scavenger additives was studied using EVA polymer since their degradation points are lower than the processing temperature of LDPE.

Table 4.1 DSC and TGA result of oxygen scavengers

Additive	Thermal degradation point	Additives particle size in film	Film obtainability
BHT	82 °C	Additives melt at 70 °C and particles cannot be visualized	Can not obtain the film by extrusion due to degradation

Pyrogallol	120 °C	Additives degrade in film	Can not obtain the film by extrusion due to degradation
Sodium bisulfite	130 °C	Additives degrade in film	Can not obtain the film by extrusion due to degradation
Calcium ascorbate	150 °C	Additives in LDPE film degrade In EVA film with up to 200 µm particle size	Can obtain the film by extrusion with EVA and polymers that have lower processing temperature than LDPE
Isoascorbic acid	170 °C	Additives degrade in LDPE film In EVA film with up to 200 µm particle size	Can obtain the film by extrusion with EVA and polymers that have lower processing temperature than LDPE
Ascorbic acid	190 °C	Additives with up to 200 µm particle size in LDPE film	Can obtain the film by extrusion with LDPE polymer
Propyl Gallate	192 °C	Additives melt at 150 °C and particles cannot be visualized	Can obtain the film by extrusion with LDPE polymer
Sodium ascorbate	195 °C	Additive with up to 250 µm particle size in LDPE film	Can obtain the film by extrusion with LDPE polymer

Tocopherol	230 °C	Additives melt at 3°C and particles cannot be visualized	Can obtain the film by extrusion with LDPE polymer
Sodium sulfite	310 °C	Additives with up to 250 µm particle size in LDPE film	Can obtain the film by extrusion with LDPE polymer

As it is shown in Table 4.1, for some oxygen scavenging materials, the degradation temperature was above the extrusion temperature process. The degradation of BHT additive began at 82 °C, for pyrogallol it was initiated at 120 °C, and isoascorbic acid was degraded at 170 °C. Due to this, these materials cannot be processed with an oxygen scavenging system whose extrusion processing temperature is over 170 °C. During tests with TGA, it was observed that some of the oxygen scavengers, particularly ascorbic acid that had a large particle size, started decomposing before melting. By using DSC tests for another oxygen-scavenging additive, such as sodium ascorbate and calcium ascorbate, no melting was observed in the desired temperature range. Oxygen additives with larger particle sizes were milled and ground to obtain absorbers of the correct size. However, due to the low density of the material, sieving below 100 µm was not possible.

Thermal behavior for two oxygen scavenging additives was promising, Propyl gallate and tocopherol. PG additive exhibited thermal stability until 192 °C in a TGA test, which made the extrusion process possible. Tocopherol also exhibits stable thermal behavior. The degradation temperature of tocopherol was more than 220 °C. This makes it a thermally suitable material to process with PE-based polymers in extrusion. The DSC test also showed that both additives are melted at the processing temperature, resulting in a uniform distribution in the active film.

Moreover, as the flexible packaging industry is the target of the study, the particle size of the oxygen absorber material is another factor that should be considered. To compare with market package films, it is preferable to keep the extruded film thickness below 100 µm. Therefore, the oxygen absorber additives should be melted at the processing temperature or be smaller than 75

µm. Oxygen additives were mainly powders and crystals, so their particle size had to be analyzed before being blended into the active film.

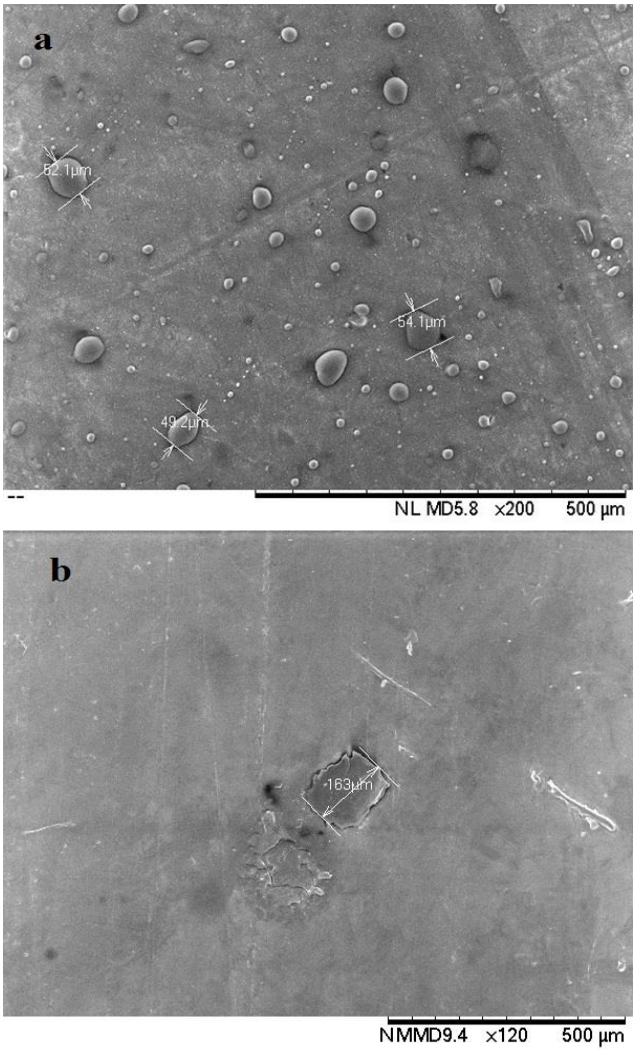

Figure 4.1 SEM images with the electron voltage of 15kv of a) Na_2CO_3 particle in PG active film and b) Ascorbic acid particle

The sodium carbonate and ascorbic acid powders were milled and then the particle size of additives in the 5% active film was analyzed by SEM test. The particle size of the additive is shown in Figure 4.1. For sodium carbonate, the particles were around 50 µm in size, but for ascorbic acid, the particles were 160 µm in size, which is not desirable for flexible packaging.

4.2 Development of GRAS oxygen absorber sachet and the oxygen scavenging result

An oxygen absorber sachet was developed in order to compare the scavenging activity of the various additions. The oxygen scavenging results were taken during 30 days of storage in 275 cc glass bottles. According to the article's scavenging reaction, sodium carbonate was incorporated into the PG and iron (III) oxide was added to the ascorbic acid.

Table 4.2 Abbreviation used in graphs

Material	Abbreviation	Material	Abbreviation
Low density polyethylene	LD	Iron (III) oxide	Fe2O3
Propyl gallate	PG	Tocopherol	Toco
Sodium carbonate	Na	Sodium ascorbate	NaA
Ascorbic acid	AA	Sasol wax H1	Wax

Table 4.3 Nomenclatures in the graphs

Form	Nomenclature
In sachets	Frist material – percentage of first material – second material (if there is) – percentage of second material Example: A sachet with a mixture of 67% propyl gallate and 33% of sodium carbonate → PG 67 Na 33
In films	Base polymer – percentage of polymer – first additive (if there is) – percentage of first additive – second additive (if there is) – percentage of second additive Example: A film with 80% low-density polyethylene as a base polymer and 15% propyl gallate, and 5% sodium carbonate additives → LD 80 PG 15 Na 5

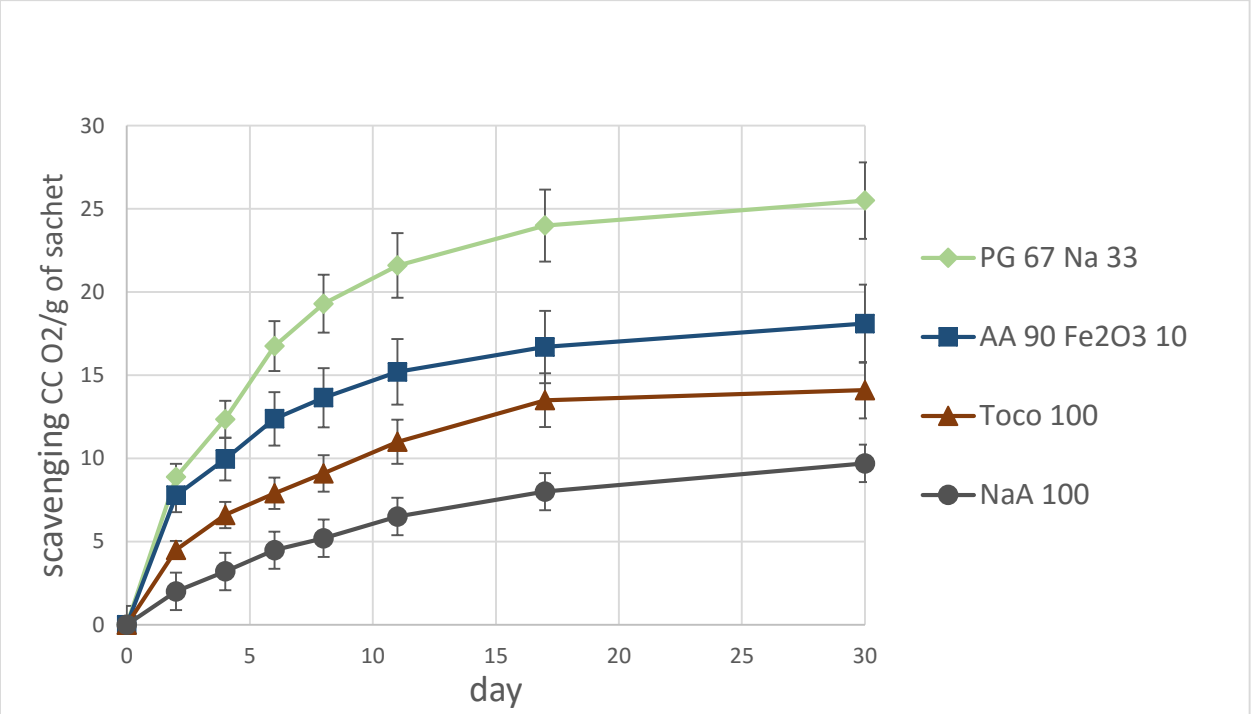

Figure 4.2 Oxygen scavenging result of 1 g antioxidant sachets in 30 days with 0.5 ml water injection

The results presented in Figure 4.2 demonstrated the oxygen scavenging activity of the different oxygen absorbers. It showed that the PG sachet had a higher oxygen scavenging activity compared to the other additives. After PG, ascorbic acid and tocopherol had a higher potential for oxygen scavenging.

4.3 Oxygen scavenging additives limitation on the food

Although the selected oxygen scavengers are GRAS substances, their limitations on food products must be considered. The active film additive can migrate and diffuse into food. Therefore, the limitations of an additive in food need to be studied.

There is a limit of 200 mg/kg of PG in food, 300 mg/kg of tocopherol, and 2000 mg/kg of Na_2CO_3[55]. According to observations of food products packaged in stores, 300 cm^2 is needed to package 1 kg of food. The total amount of additives in the food should not exceed the stated limitation even if all additives migrate into the food. In this case, the percentage of additives in the

film had to be selected. The added amount of Na_2CO_3 does not exceed the limitation, but PG and tocopherol need to be evaluated. The amount of additives in 1 g cast film can be calculated based on the active film percentage. Therefore, the total additives in active films that are needed to package 1 kg of food can be determined. Furthermore, a graph of food limitations can be prepared based on the additive content of the food.

It is necessary to consider the toxicity of scavenging reactions by-products, and based on reactions *(12)* and *(14)*, H_2O_2 is one of the by-products of the PG oxygen scavenging reaction. 20% active film had a higher oxygen absorption capacity, and the amount of oxygen that could be absorbed was 30 cc. According to the reactions *(11)* to *(15)*, 30 cc of oxygen as a reactant could produce nearly 40 mg of H_2O_2. According to literature reviews, H_2O_2 concentrations over 75 ppm are dangerous to health[55]. In the oxygen scavenging reaction, the amount of H_2O_2 produced is below the toxic level.

For tocopherol additives, base on the reaction *(10)*, since the by-product of the tocopherol oxygen scavenging reaction is water, there are no concerns about the toxicity of the by-products in food applications.

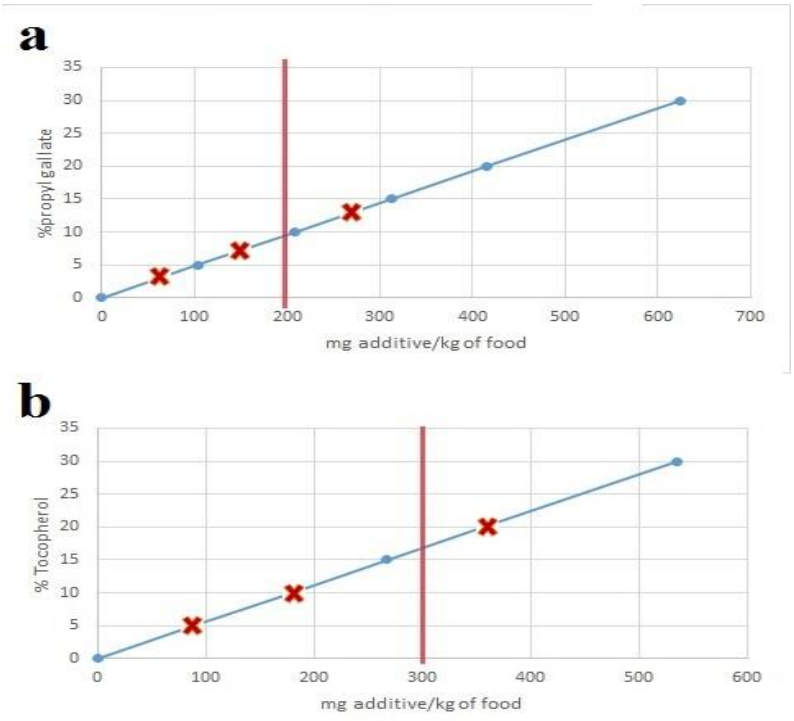

Figure 4.3 Food limitation of a) propyl gallate and b) tocopherol for 1 kg of the food

As shown in Figure 4.3, if all the PG additives migrate into the food, the maximum percentage of PG that can be added to the package is about 10% of the active film. However, in reality, not all of the additives can diffuse into the food, so some of them will remain in the package. So for choosing the percentage of PG films, two percentages were selected below 10% and one of the content was chosen above 10%. Finally, 3,7, and 13% of the PG in Figure 4.5, marked with a red cross, were selected to be analyzed in the next step.

The food limitation of tocopherol is shown in figure 4.6. The percentage limitation for tocopherol is nearly 17% of the active film. The percentages for tocopherol that are shown in Figure 4.6 with red crosses, were selected for 5, 10, and 20% to be analyzed in the next step.

4.4 Development of the oxygen scavenging active film in Brabender internal mixer and oxygen scavenging result

To pre-review the potential scavenging capacity of the additives, an internal mixer was used to make the active films. PE was first added to the internal mixer for melting, and then the additive was mixed in to make the oxygen scavenging compound. In a glass bottle, 1 g of the active film was placed. This was done to determine the oxygen scavenging capacity of the additives as a function of time at 99% relative humidity.

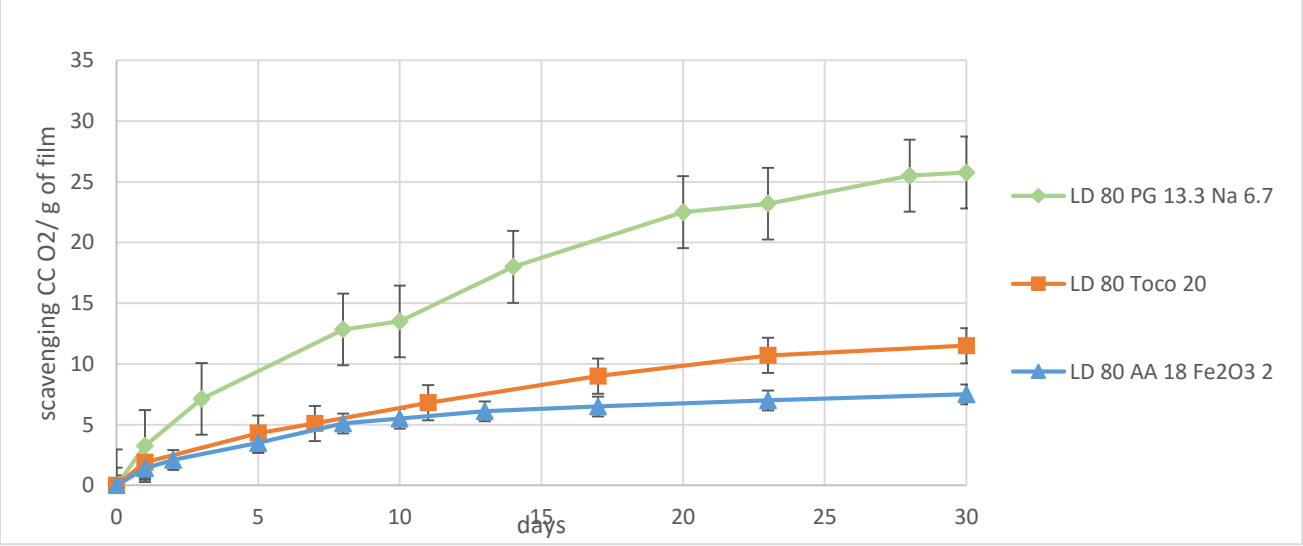

Figure 4.4 Oxygen scavenging result of 1 g of the active film in 30 days at 99% relative humidity for ascorbic acid, tocopherol, and PG

After 30 days in the scavenging system, the propyl gallate active film showed a significant capacity to scavenge oxygen. In conditions with high relative humidity, the film absorbed almost 26 cc/g of oxygen. During the first days of the experiment, oxygen scavenging had a sharp slope that confirmed its high capacity. Gradually, the scavenging slope was diminished in the fourth week of storage. Tocopherol and ascorbic acid have a lower scavenging capacity in comparison with PG. The amount of tocopherol scavenging reached 12 cc/g of the active film, and ascorbic acid had an 8 cc/g scavenging potential.

Scavenging results for internal mixers were another reason for choosing PG and tocopherol in the extrusion study. However, since Na_2CO_3 was introduced as a reaction initiator for the PG scavenging reaction, the optimal ratio of the additives must be determined. To start film preparation, the ratio of 1:2 for Na_2CO_3 and PG was selected according to the trend in the article. To determine the most effective ratio between the additives for an optimized oxygen scavenging capacity in the system, 1:1 and 1:3 ratios were also prepared. All the active films were blended with 20% additives and analyzed at 99% relative humidity for 30 days.

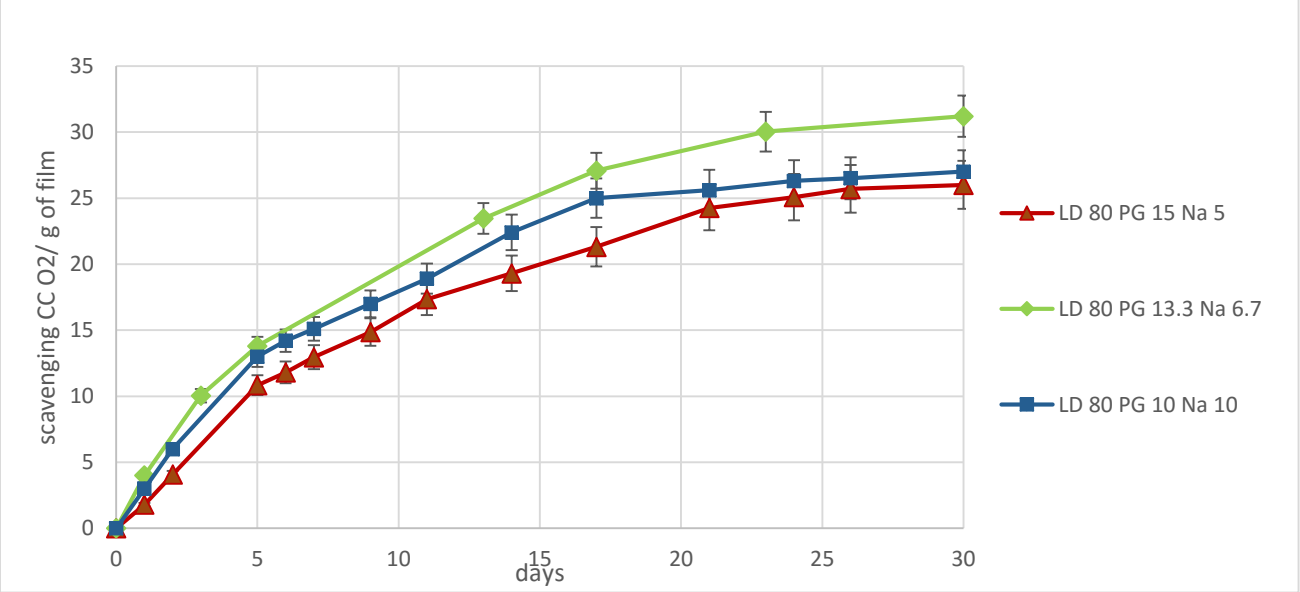

Figure 4.5 Oxygen scavenging result of 1 g of the active film in 30 days at 99% relative humidity for ratio of 1:1 (10% Na_2CO_3 /10% PG), 1:2 (6.7% Na_2CO_3 /13.3% PG), and 1:3 (5% Na_2CO_3 /15% PG)

A 6.7%Na_2CO_3 /13.3% PG active film with a ratio of 1:2 was shown to be the most efficient oxygen scavenging system compared to other ratios. However, total oxygen scavenging was only slightly different. The optimized film absorbed 31 cc/g which was nearly 5 cc/g higher than the other active films. Thus, the ratio of 1:2 for additives was chosen for the extrusion process in the cast film.

4.5 **Development of the oxygen scavenging active film in the cast film extrusion**

PG cast film extrusion cannot provide a viable oxygen scavenging system due to the reduced film quality of active PG films.

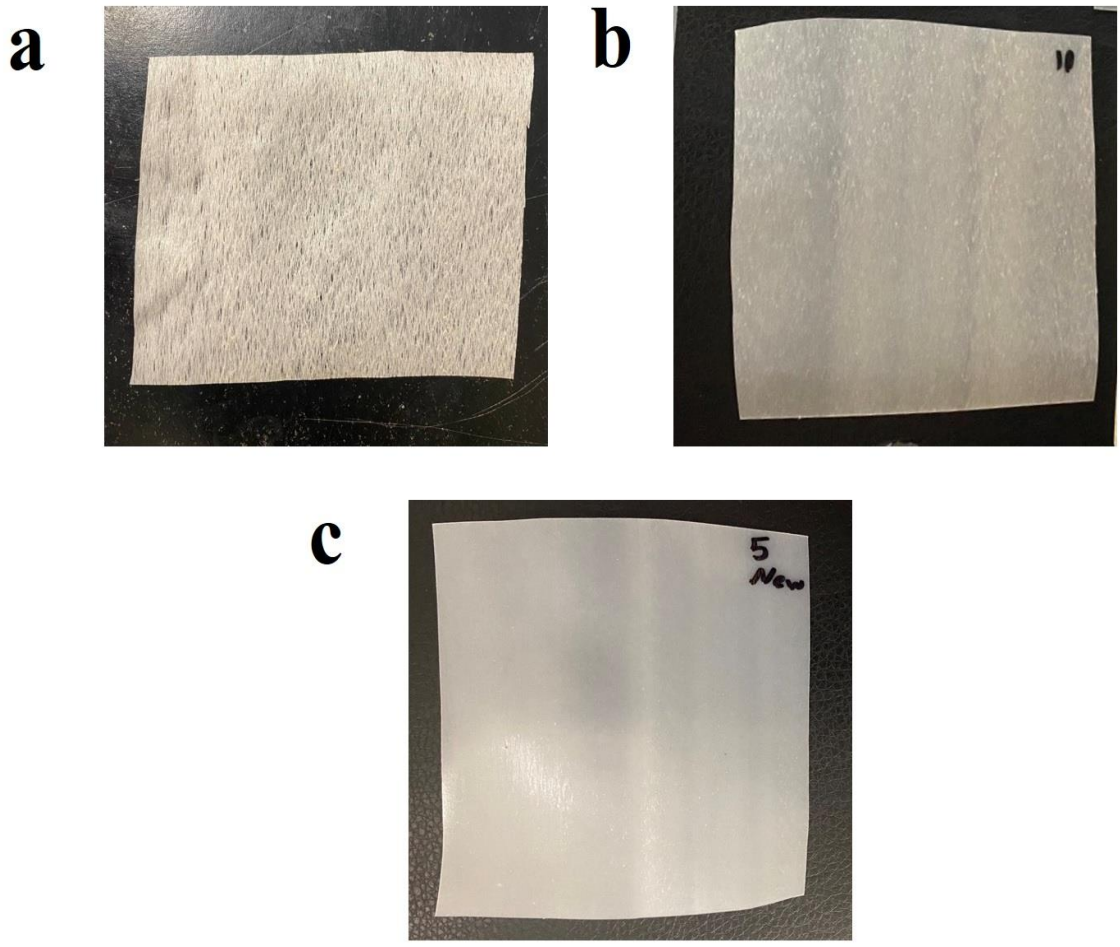

Figure 4.6 Images of PG active films in different concentrations of a) 20%, b) 10%, and c) 5%

For PG three percentages of 20%, 10%, and 5% active film were extruded by the cast film. Figure 4.6 shows that some holes and cracks can be seen in 20% of PG active film, and some bubbles can be seen in 10% of PG active film. This may decrease the quality and mechanical properties of the films. The oxygen absorption of only 10% and 5% PG active films was investigated since a film with holes is not suitable as an oxygen scavenging system.

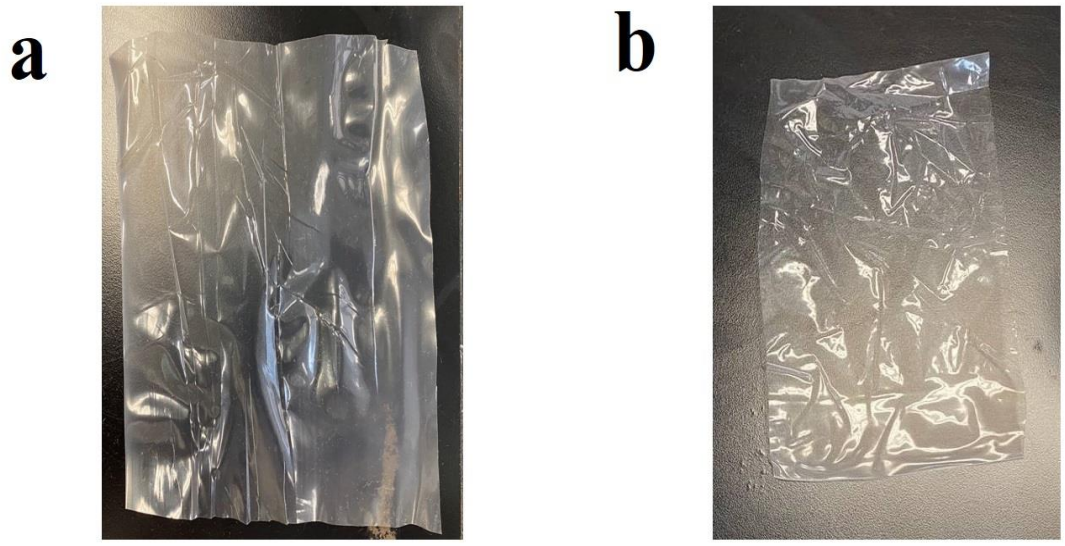

Figure 4.7 Images of tocopherol active films in different concentrations of a) 10% and b) 5% tocopherol

For tocopherol, three percentages of 20%, 10%, and 5% active film were extruded by cast film. Due to the high percentage of tocopherol and phase separation between LDPE and tocopherol, even with Sasol wax, an active film was not possible from 20% tocopherol. Therefore, only 10% and 5% tocopherol active films were tested for oxygen absorption.

The TGA test was used for PG and Na_2CO_3 powders and their mixture to investigate holes and bubbles in PG active film.

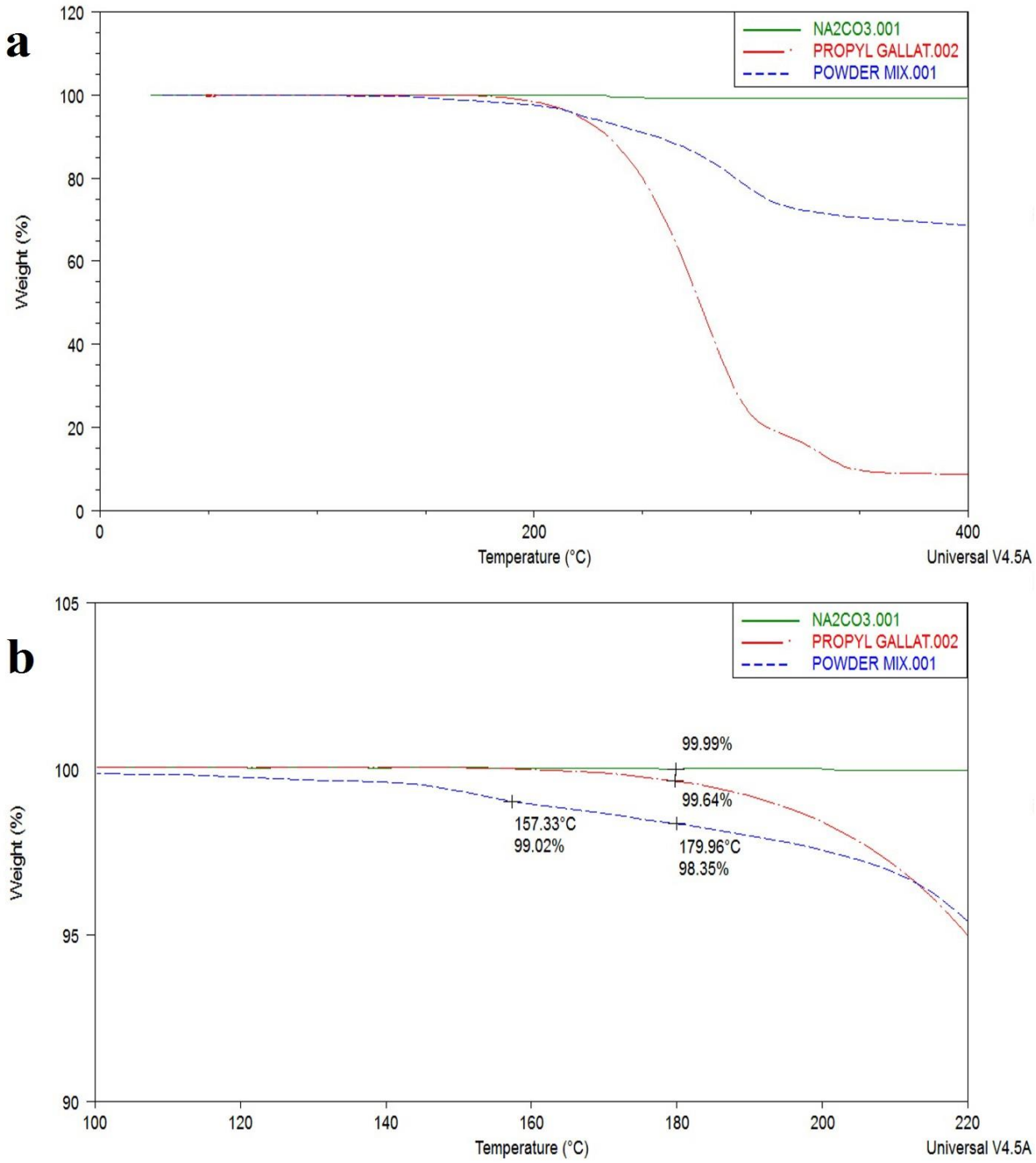

Figure 4.8 TGA test of PG, sodium carbonate, and their mixture at the temperature range of a) 20 to 400 °C b) 100 to 220 °C at the rate of 20 °C/min

Based on the TGA test results in Figure 4.8, in the temperature range of 150 to 190 °C which is the processing temperature for PG blend, in the mixture of PG and Na_2CO_3, there was a reaction

that caused 2% weight loss of the mixture. Using reaction *(16)*, Na_2CO_3 and humidity contribute to the formation of CO2 gas during extrusion, resulting in holes appearing in the cast active film of 20% PG. In active films with lower additive concentrations, bubbles appeared at 10%, while film quality was higher at 5%. Active films containing tocopherol were viable in terms of film quality.

As the film quality for PG 20% was not viable enough for oxygen scavenging systems, for PG active films only 5% and 10% were selected for oxygen scavenging tests.

4.6 Oxygen scavenging result of casting active film

To analyze the oxygen scavenging capacity of the cast film extrusion active film, 1 g of the film was placed in a 275 cc glass container and by using an oxygen concentration analyzer the oxygen percentage reduction was studied during 30 days of storage. A variety of relative humidity conditions were applied to the oxygen scavenging system in order to simulate the scavenging capacity of different types of foods. To represent the liquid phase of food, such as soup and beverages, high relative humidity was studied. In order to achieve 99% relative humidity, a 5 cc water vial was also added to the glass bottle. The final thickness of the active films was 100 to 150 µm. A study by Ahn et al [40], reported that a commercial oxygen-scavenger film should at least absorb 10 cc of oxygen per gram of the film. For more than 20 cc oxygen absorption, the scavenger is considered a viable oxygen scavenger.

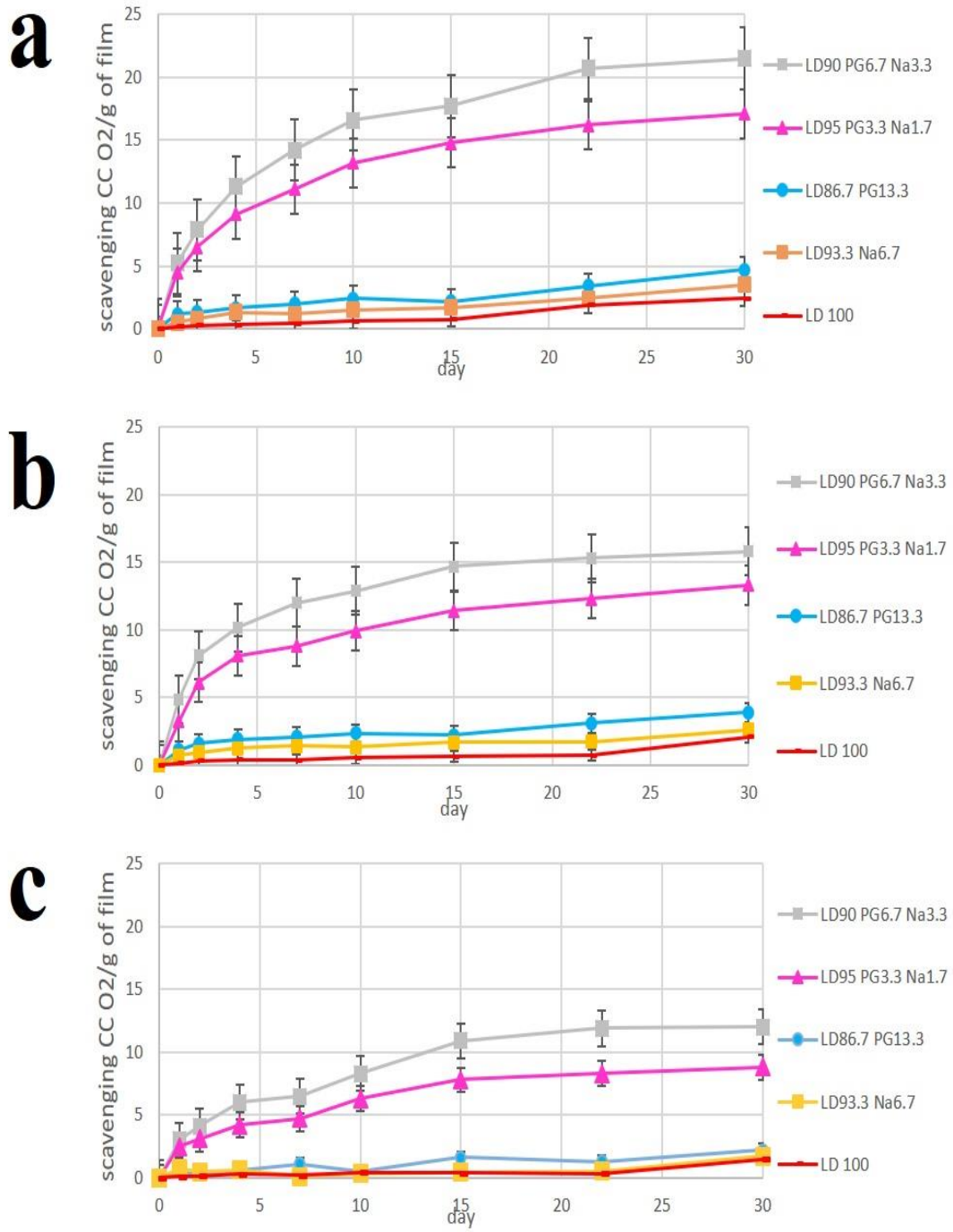

Figure 4.9 Oxygen scavenging result of 1 g of the active film in 30 days at a)99%, b)75%, and c)25% relative humidity for sodium carbonate/PG ratio of 1:2

The oxygen absorption measurement was carried out on the active film. Figure 4.9 shows the amount of oxygen scavenging in the container based on 1 g of the blended film sample as a function of time. The pure LDPE film was also tested as a control film to observe its effects on the scavenging process. LDPE/PG and LDPE/Na_2CO_3 active films were prepared with 86.7/13.3% and 93.3/6.7% concentrations, respectively, to study their effects on oxygen scavenging when blended into LDPE.

The maximum oxygen scavenging result was for 10% PG active film that reached about 22 cc/g of the sample after 30 days. The 5% active film demonstrated a promising oxygen scavenging result of 17 cc/g during storage. Scavenging results for control film, LDPE/PG, and LDPE/Na_2CO_3 were below 5 cc/g, which is negligible based on the literature review [30]. Analyzing the scavenging graph, it was discovered that scavenging activity decreased after 2 weeks to reach a constant value.

In comparison to 99% relative humidity, there was a reduction in oxygen scavenging at 75% relative humidity. Based on the reaction *(16)*, in this system Na_2CO_3 and humidity reacted and made NaOH, which increased the alkalinity of the system. Therefore, a decrease in oxygen absorption was caused by a decrease in the alkalinity of the scavenging system. This decreased the initiation of scavenging reactions, and consequently, oxygen absorption activity was decreased. For 10% additives in the active film, the oxygen scavenging capacity was 16 cc/g, whereas the oxygen absorption capacity was 13 cc/g for 5% additives in the film. Oxygen scavenging for control film, blended LDPE/PG, and blended LDPE/ Na_2CO_3 was also insignificant. This indicates the requirement of both PG and Na_2CO_3 for an adequate oxygen absorption system in the film.

The oxygen scavenging capacity of the active films at 25% relative humidity was demonstrated to be 12 cc/g for the 10% scavenging film. Oxygen scavenging of 5% active film was presented at 9 cc/g. According to the PG additive scavenging results, humidity is crucial for higher oxygen scavenging, however, for low relative humidity, further additive concentration was required for viable oxygen scavenging.

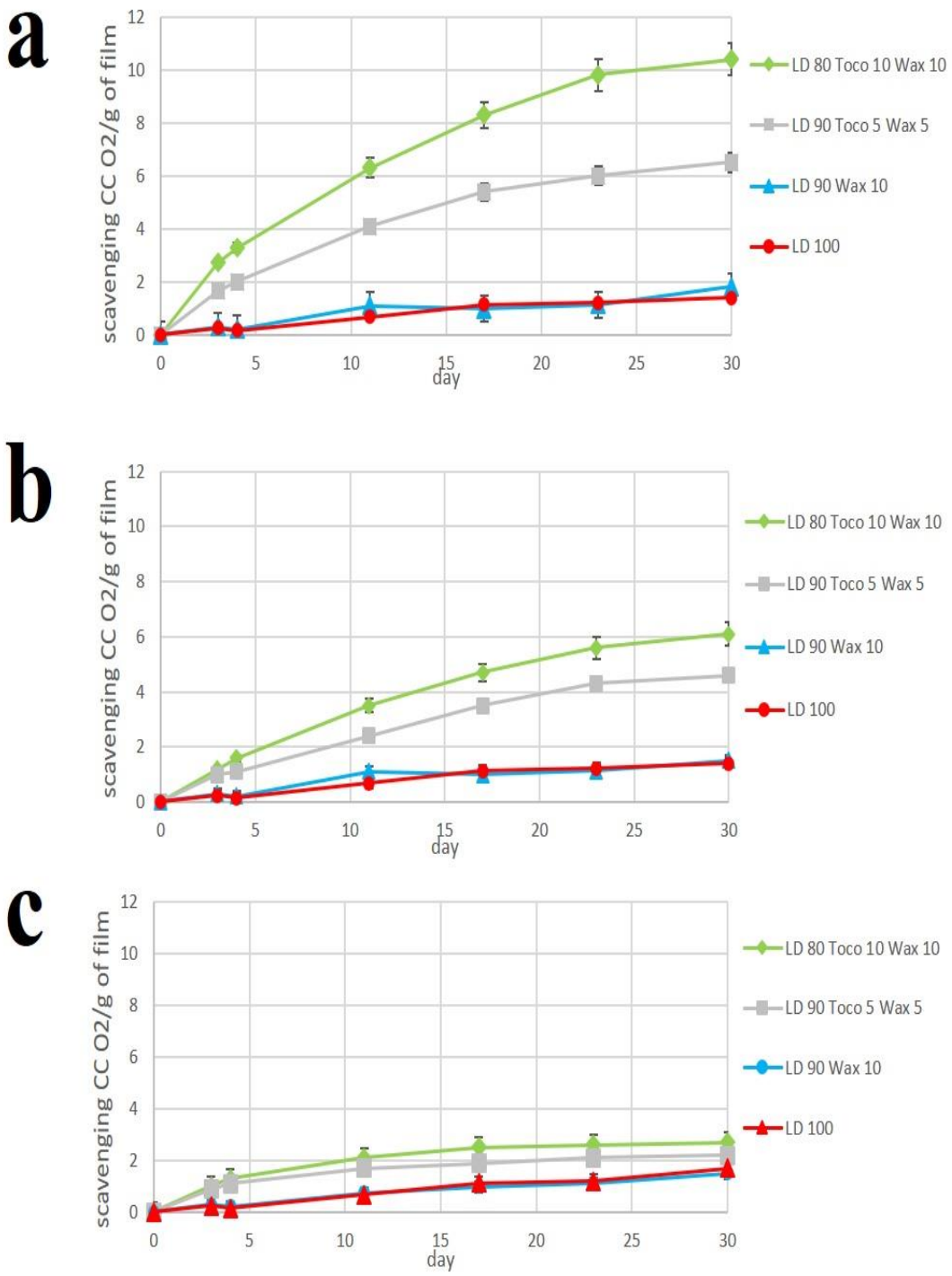

Figure 4.10 Oxygen scavenging result of 1 g of the tocopherol/wax active film in 30 days at a)99%, b)75%, and c)25% relative humidity

As shown in Figure 4.10, the oxygen scavenging capacity of the 5 and 10% tocopherol active film was compared to the control pure LDPE film and the LDPE/wax (90/10%) film. The tocopherol active film had a thickness of 100 µm. At 99% relative humidity and 30 days of storage, 1 g of the 10% active film scavenged 11 cc/g of oxygen, whereas, for the 5% active film, the oxygen scavenging rate was about 7 cc/g. The scavenging activity of the control film and the LDPE/wax film was negligible.

When relative humidity was less than 99%, the tocopherol active film did not perform as a viable oxygen scavenging system and the amount of scavenging was insufficient. At 75% relative humidity, 5% and 10% of the active film absorbed 5 and 6 cc/g, respectively. At 25% relative humidity, oxygen scavenging of active films was near 3 cc/g.

In the scavenging study, the scavenging amount for the cast film extrusion was approximately equal to the internal mixer oxygen scavenging result. This supports the potential oxygen scavenging of additives.

4.7 Thermal behavior of the active films

The polymer's crystallinity increases its strength because more intermolecular bonds are formed when it is in the crystalline phase. Therefore, deformation of the polymer can lead to chains with higher orientations as a result of its increased strength. Therefore, with a decrease in the crystallinity of the polymer its strength also will decrease[51].

The thermal properties of the active oxygen scavengers and the control film were studied by the TGA and DSC analyzer. For active films, the crystalline (X_c) was calculated by using the DSC test for the first heating cycle based on the following equation[56].

$$X_c\% = \frac{\Delta Hm}{\Delta Hf.\ Wpolymer} \times 100 \qquad (17)$$

In the equation, ΔH_m is the melting enthalpy for the first heating cycle of the DSC test of the active film sample, ΔH_f is the heat diffusion of the LDPE film for 100% crystallinity which is 293 J/g, and W is the weight fraction of the LDPE polymer in the matrix[57].

According to the equation, the crystallinity of the active films was calculated. For the pure LDPE film, the crystallinity was 40.31%, whereas, for the PG active film, the crystallinity was reduced.

Crystallinity values for 5, 10, and 20% PG active films were 26.64%, 17.6%, and 16.91%, respectively.

4.8 Active films mechanical properties

Mechanical characteristics of the active and pure LD control films such as Young Modulus and elongation at break were measured by an Instron tensile machine in the MD direction. The thickness of the active films was 3 to 5 mil. The mechanical properties of the films are shown in Table 4.4 and Table 4.5.

Table 4.4 Young modulus and elongation at break of the PG active oxygen scavenging films

	Modulus (Automatic Young's) (MPa)	Tensile strain at Break (Standard) (%)
LD 100	200±42	450±102
LD 95 PG 3.3 Na 1.7	227±43	323±33
LD 90 PG 6.7 Na 3.3	151±34	94±27
LD 80 PG 13.3 Na 6.7	134±29	50±13

Table 4.5 Young modulus and elongation at break of the tocopherol active oxygen scavenging films

	Modulus (Automatic Young's) (MPa)	Tensile strain at break (Standard) (%)
LD 100	203±38	461±68
LD 90 wax 10	202±47	437±47

LD 90 toco 5 wax 5	146±26	70±15
LD 80 toco 10 wax 10	139±22	35±7

The incorporation of oxygen scavengers into the matrix of the active film may result in a change in the modulus and elongation of the film. The PG control film average amount for modulus and elongation was 200 MPa and 450% and for tocopherol/wax film was 202 and 437%, respectively. The addition of additives to the polymer significantly changed the modulus and elongation properties. For 5% PG, the modulus was decreased by 28% compared to the control film. For 10% active film, the modulus decreased by 25% and the tensile strain decreased by 79%. As it is reported in Liu et al [58], the tensile strength of cellulose acetate composite films is reduced by 31.8% because the bubbles inside the films reduce the tensile strength. Also for 20% active film, the modulus decreased by 33% and the tensile strain decreased by 89%. The reduction could result in holes and free spaces in the active film.

A remarkable reduction in modulus and elongation was observed in the mechanical properties of tocopherol active films. The modulus for tocopherol active films fell by 27% for 5% tocopherol active film. The elongation was reduced to 84% of the control LDPE film, which indicates a substantial decline in the mechanical properties of tocopherol active films. Although the active film was formed by adding Sasol H1 wax, the strength of the film was reduced due to phase separation between LDPE and tocopherol.

4.9 **DPPH radical antioxidant activity**

According to the mechanical properties of the active films, a higher percentage of active films reduced film quality. However, 5% PG and tocopherol produced better film quality and mechanical

properties. The DPPH antioxidant activity test was performed on 5% active films and 5% control films.

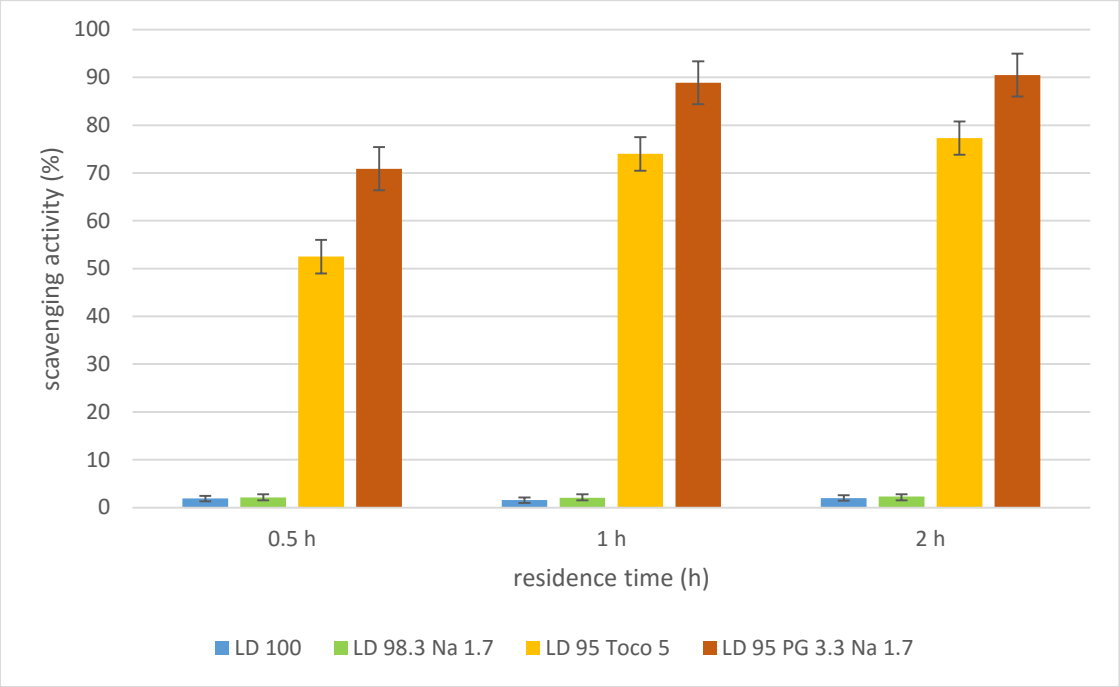

Figure 4.11 DPPH results and antioxidant activity for the control film and active scavenging films after 0.5, one, and two hours residence time

As it is observed in Figure 4.11 the antioxidant activity of the LDPE control film and LD/Na_2CO_3 film was nearly 2% on DPPH. This is negligible compared to the oxygen scavenging active films. The tocopherol 5% active film had an antioxidant activity of 52.5% after 0.5 hours. After one and two hours of residence time, absorbance and antioxidant activity were also tested in order to determine DPPH antioxidant activity. The results for tocopherol active film antioxidant activity were 74% and 77.3% after one hour and two hours, respectively. In the second hour of residence time, there was a slight change in antioxidant activity.

Antioxidant activity was even higher for the PG active film. According to the results of the study, the antioxidant activity on DPPH reached 70.9% after 0.5 hours, which indicates that the material has a high antioxidant potential. PG active film exhibited antioxidant activity of 88.8% after one hour of storage and 90.5% after two hours of residence. The activity values achieved for PG active film in this study had the same order of magnitude as those reported in literature reviews by

Martins et al [51] and Byun et al [55]. in the DPPH test, the film demonstrated above 90% antioxidant activity.

PG and tocopherol active films both exhibited antioxidant activity with DPPH, but PG active films had higher antioxidant activity than tocopherol. Additionally, it was observed that after 1 hour of residence there was a slight change in the antioxidant activity of the active films. Based on the antioxidant activity exhibited in the DPPH test system, the final amount was obtained after 2 hours of residence time.

This study was mainly focused on the oxygen scavenger in some GRAS materials, such as PG and tocopherol. Besides their processability, we wanted to ensure the additives are efficient in the oxygen scavenging system. The mechanical and thermal property tests also showed the compatibility of our oxygen scavenger with flexible packaging and LDPE polymer. The PG and tocopherol studied in this project were evaluated for safety and showed high oxygen scavenging capabilities. As a result, we were able to produce an oxygen scavenging film by using melt extrusion cast film with a high antioxidant activity which was analyzed by DPPH. PG active films can be used for both solid and liquid food applications such as beverages, soups, meat and poultry, and dry foods. However, tocopherol active films can only be applied to liquid food applications like juices and soups.

CHAPTER 5 CONCLUSION AND RECOMMENDATION

In this project, the development of an oxygen scavenging system and the potential scavenging activity were studied and the preparation of active oxygen scavenger films was explained. To be used as an antioxidant additive, this study focused on pre-evaluated, nontoxic GRAS materials.

The processability and efficiency of different oxygen scavenger additives were investigated. By screening oxygen scavengers based on their degradation point and particle size in the film, oxygen scavengers were narrowed down to three additives: PG, tocopherol, and ascorbic acid. In the first scavenging absorption study conducted using an internal mixer, PG and tocopherol were shown to absorb more oxygen. As a result, LDPE/PG active films and LDPE/Tocopherol active films were selected as oxygen scavenging systems for cast film extrusion.

In accordance with FDA limitations, additives were chosen at concentrations of 20%, 10%, and 5% for cast film extrusion. For LDPE/PG active film, different film qualities were provided by different additive concentrations. The film appeared to have some holes in 20% PG active film and bubbles in 10% PG active film. A TGA test indicated that the holes and bubbles in the film were caused by a reaction during the extrusion process that reduced the weight loss of the additives. It was possible to achieve viable film quality with 5% PG and tocopherol active films. The DSC and Instron mechanical tests indicated that the crystallinity of the polymer decreased with an increase in additive concentration in PG active film. This resulted in a reduction in film strength. The phase separation of the additive and the polymer was probably responsible for the reduction in film strength in tocopherol active film. However, the mechanical properties of 5% PG active film were still viable.

The oxygen absorption of the active films was measured at different relative humidity conditions at room temperature. According to the study, oxygen absorption increases with increasing humidity. According to the study, oxygen absorption increases with increasing humidity, as humidity increases the alkalinity that initiates the scavenging reaction for PG active films. While 10% of PG active film scavenged a higher amount of oxygen, the most optimum oxygen scavenger was 5% of PG active film. The 10% active film for tocopherol showed better oxygen scavenging, but the film strength was lower than the 5% active film. The 5% active film of PG provided better results both in terms of oxygen scavenging and mechanical properties when compared to the 5%

active film of tocopherol. As a result of the DPPH test, 5% PG active film demonstrated a higher level of antioxidant activity.

For future studies the following recommendations are suggested:

- Modification of the melt processing conditions and equipment to increase compound uniformity in the melt extrusion
- Investigate the shelf-life of oxygen scavenging additives for food products
- Analyze the oxygen scavenging activity of active films at different storage temperatures
- Study the migration and diffusion of oxygen scavenging additives in foods

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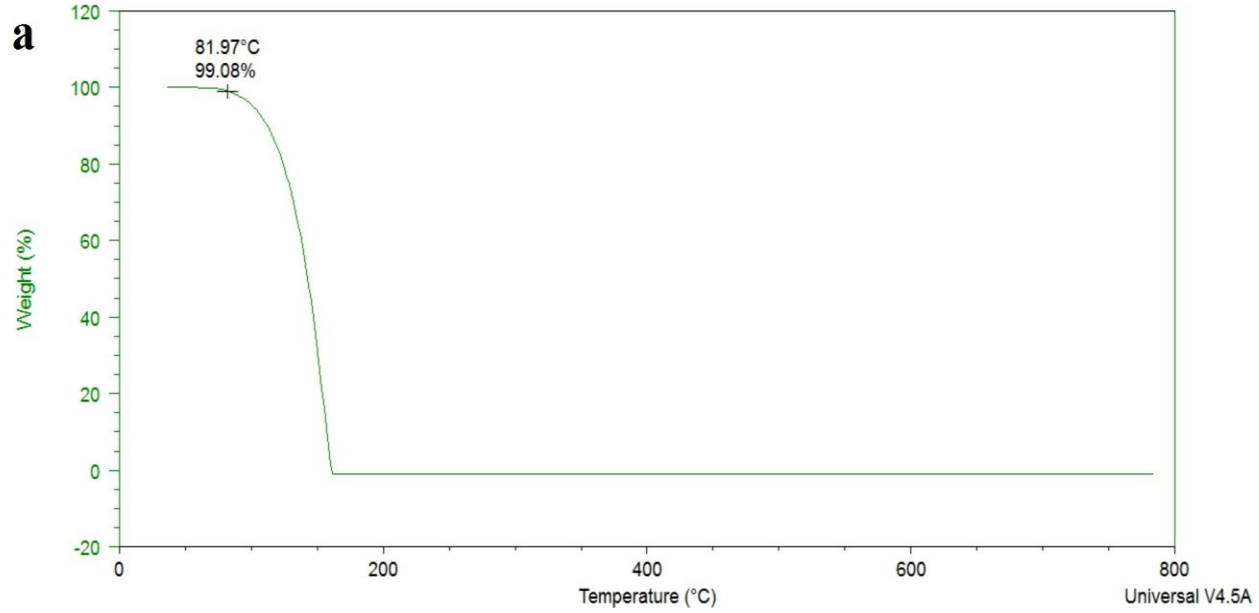
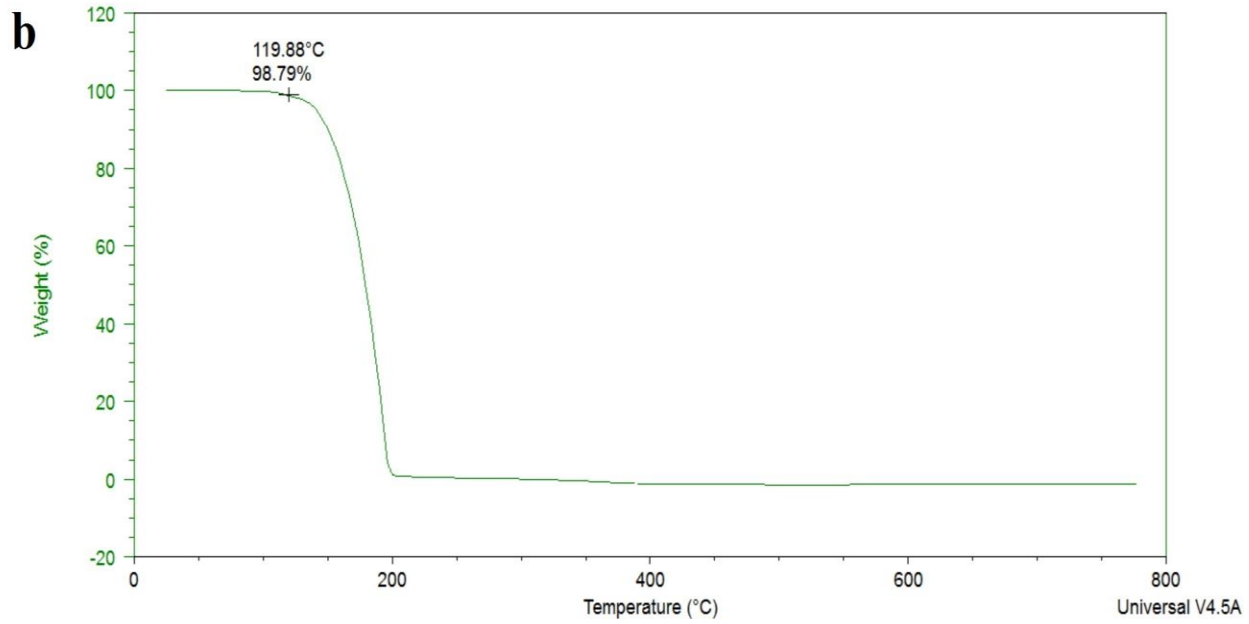
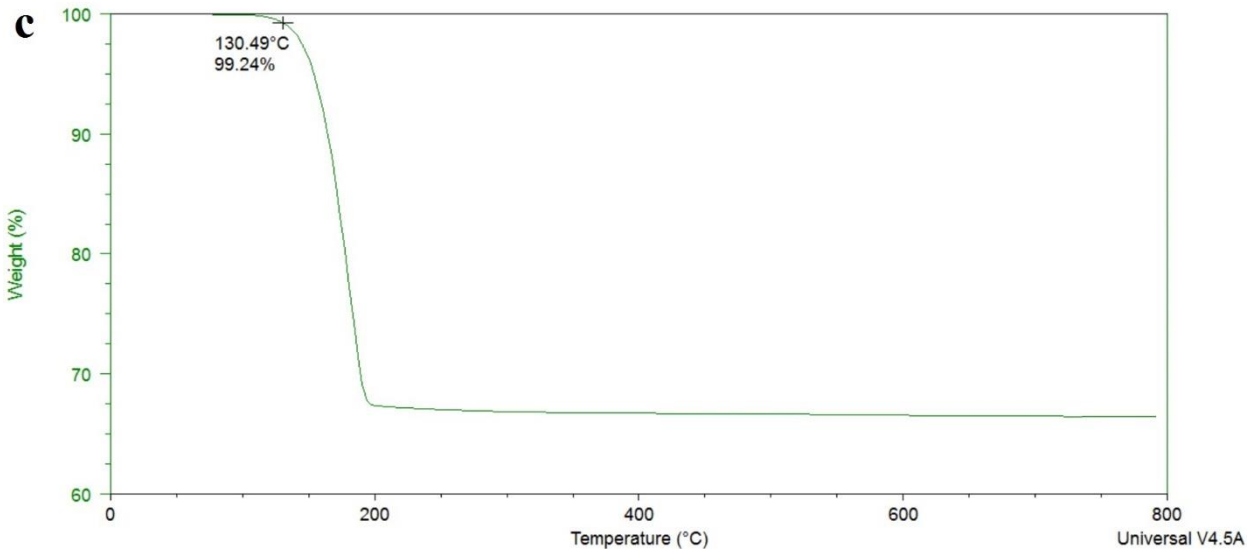
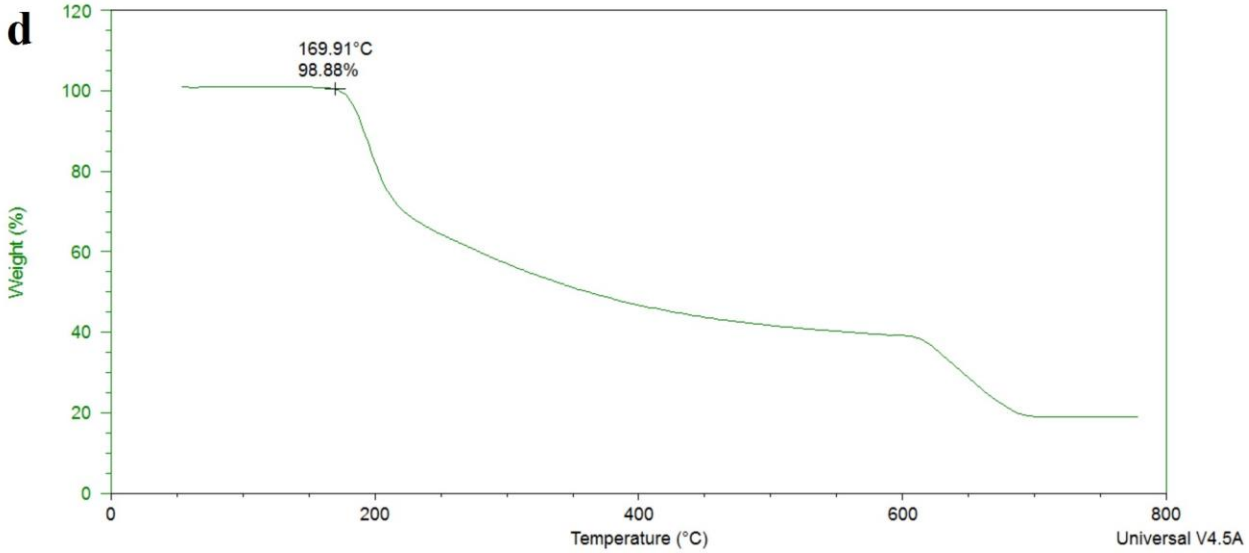
APPENDICES

Appendix A TGA and DSC tests figures






c
130.49°C
99.24%
Weight (%)
Temperature (°C)
Universal V4.5A


d
169.91°C
98.88%
Weight (%)
Temperature (°C)
Universal V4.5A

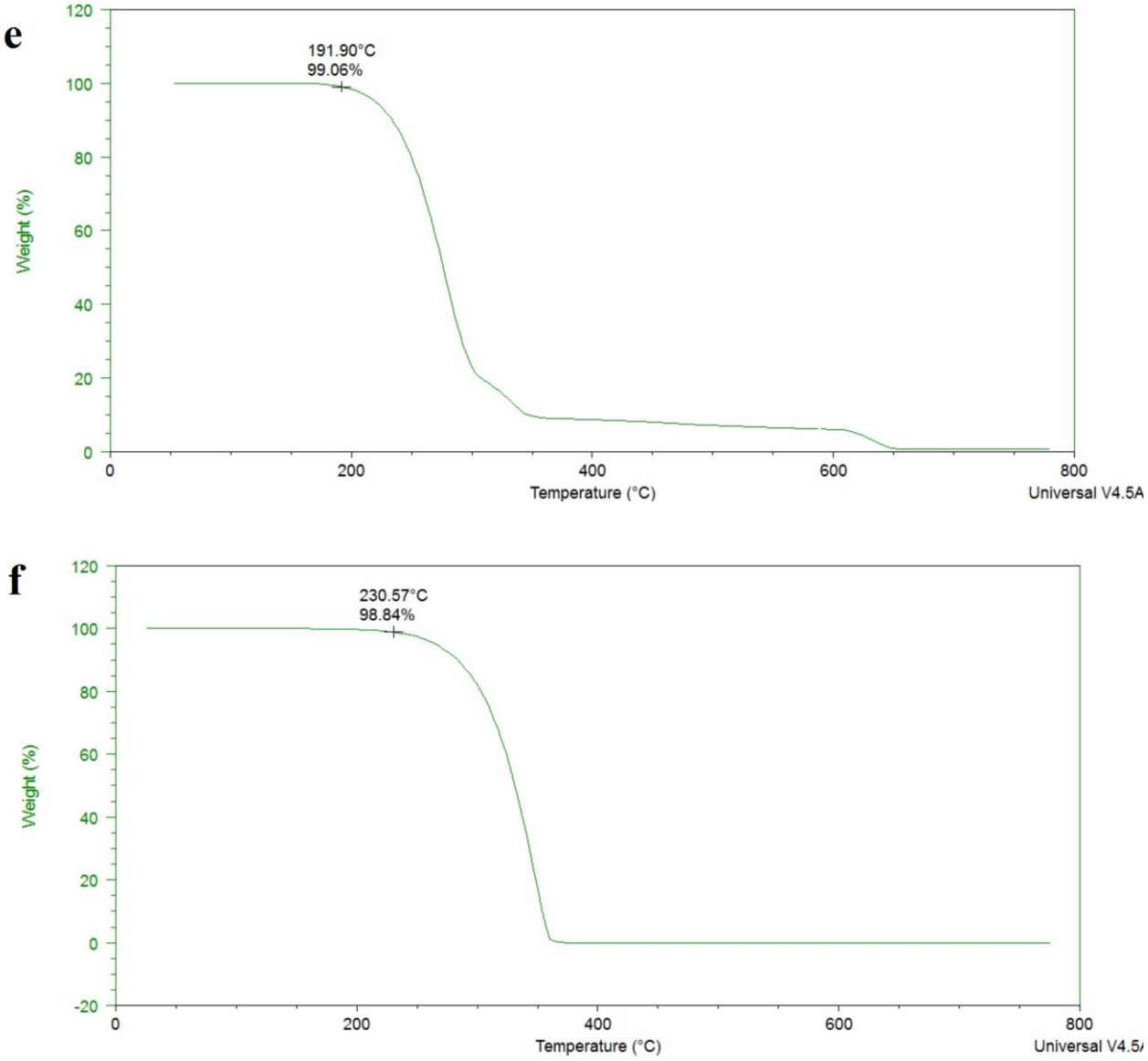
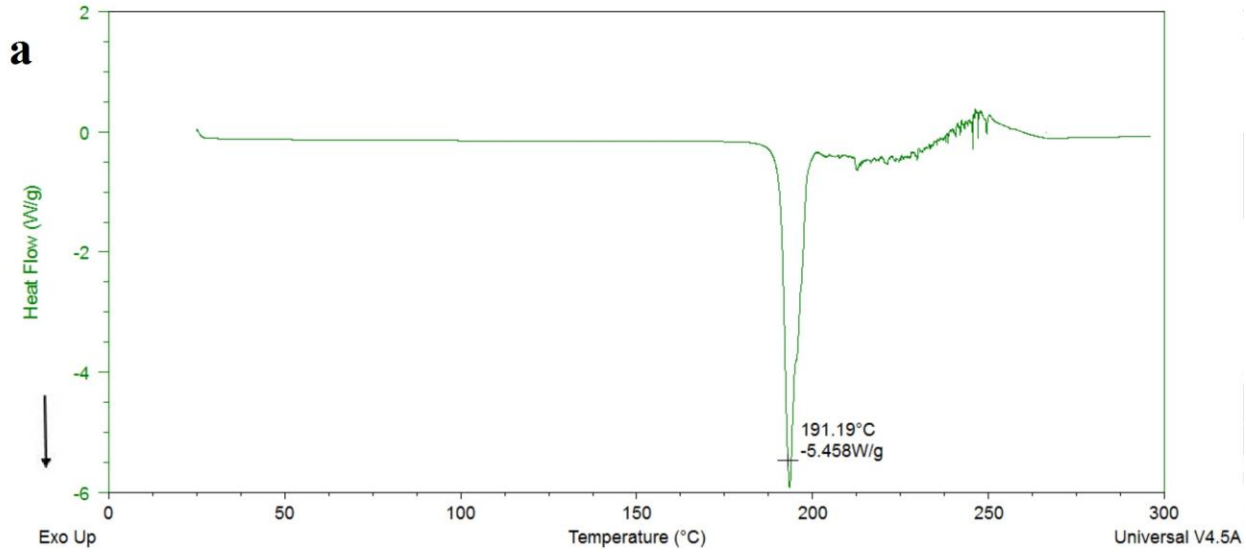
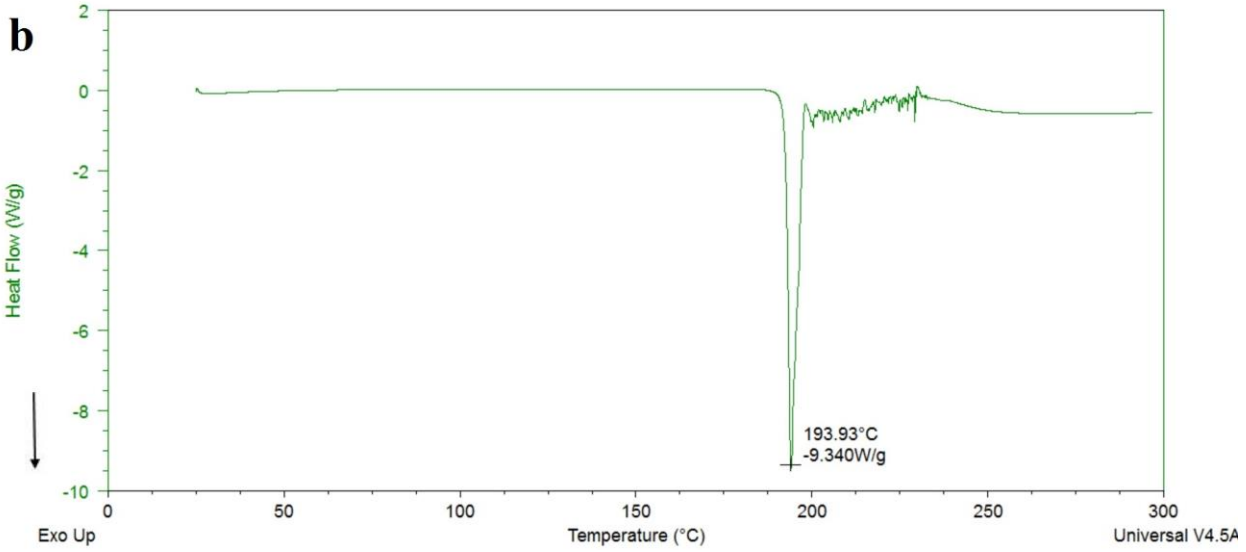


Figure A.1 TGA test of oxygen scavengers a) BHT, b) pyrogallol, c) sodium bisulfite, d) isoascorbic acid, e) propyl gallate, and f) tocopherol between the temperature range of 20 to 800 °C at the rate of 20 °C/min


a
Heat Flow (W/g)
2
0
-2
-4
-6
191.19°C
-5.458W/g
0
50
100
150
200
250
300
Exo Up
Temperature (°C)
Universal V4.5A


b
Heat Flow (W/g)
2
0
-2
-4
-6
-8
-10
193.93°C
-9.340W/g
0
50
100
150
200
250
300
Exo Up
Temperature (°C)
Universal V4.5A

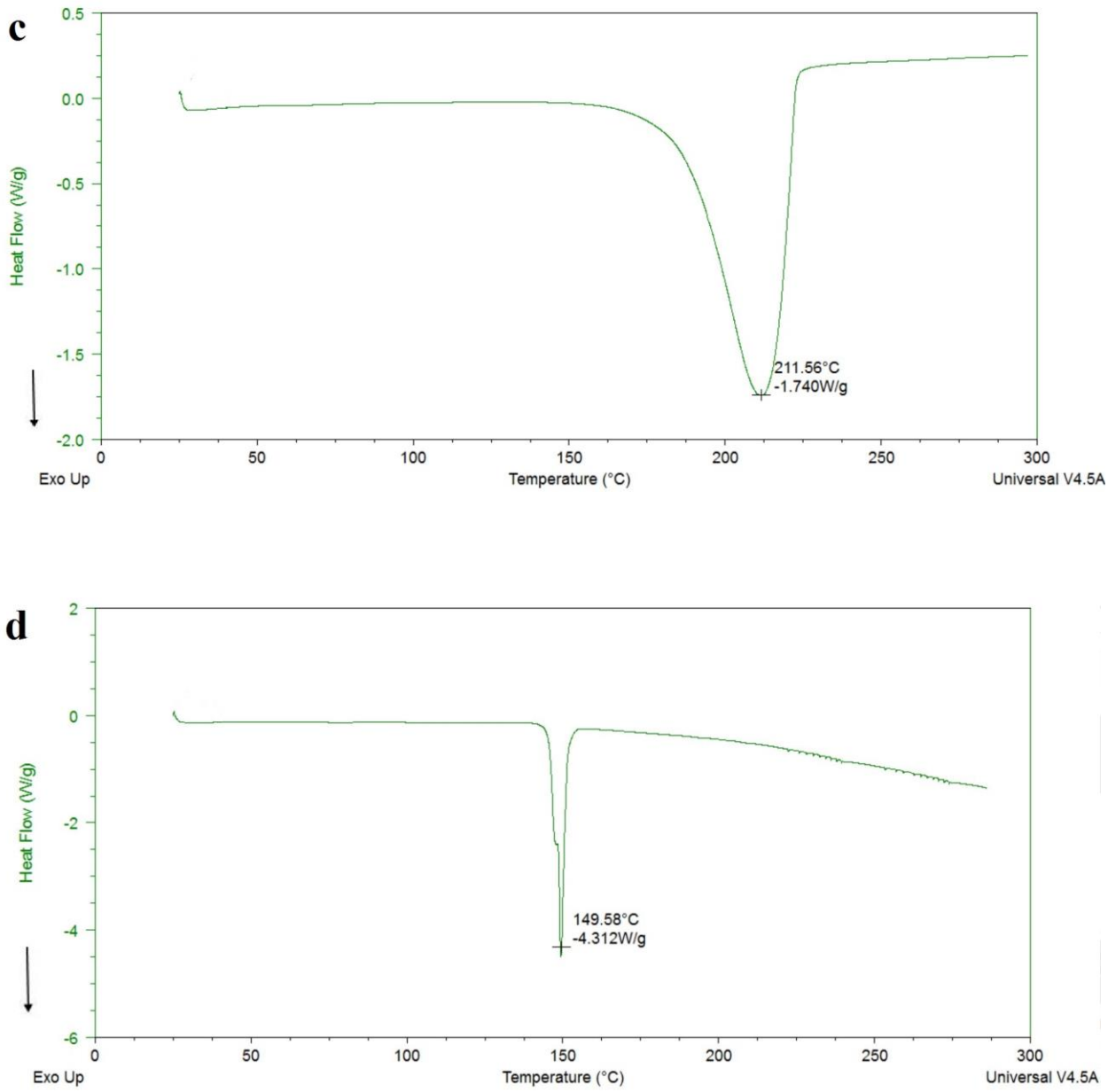
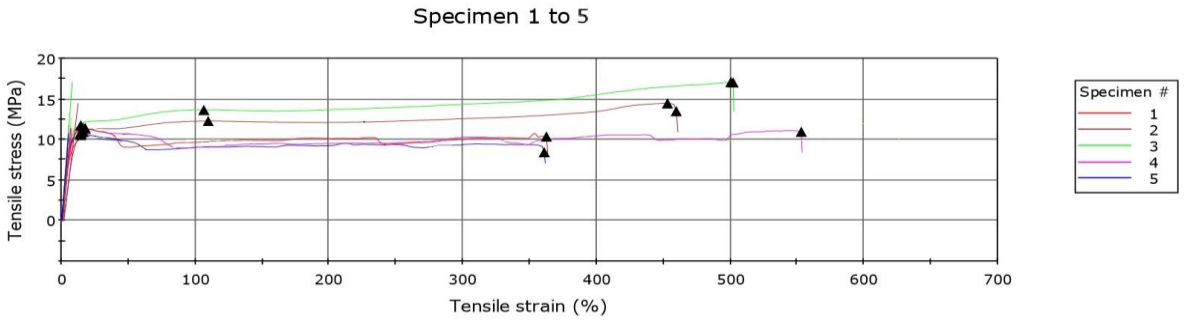


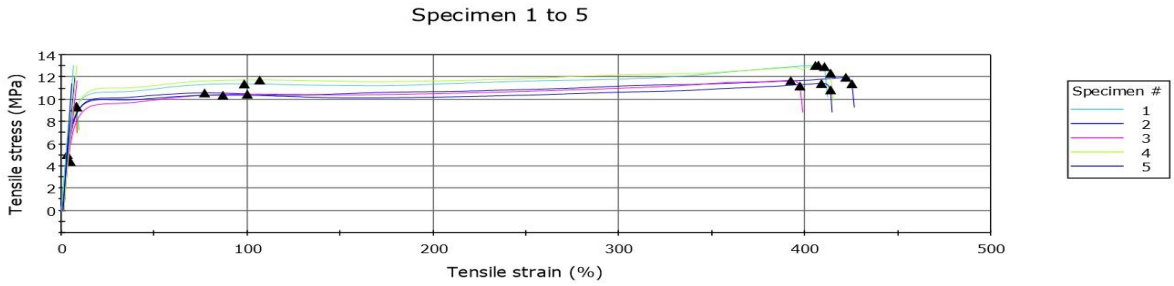
Figure A.2 DSC test of oxygen scavengers a) Ascorbic acid, b) sodium ascorbate, c) calcium ascorbate, d) propyl gallate between the temperature range of 20 to 300 °C at the rate of 10 °C/min

Appendix B Instron test figures

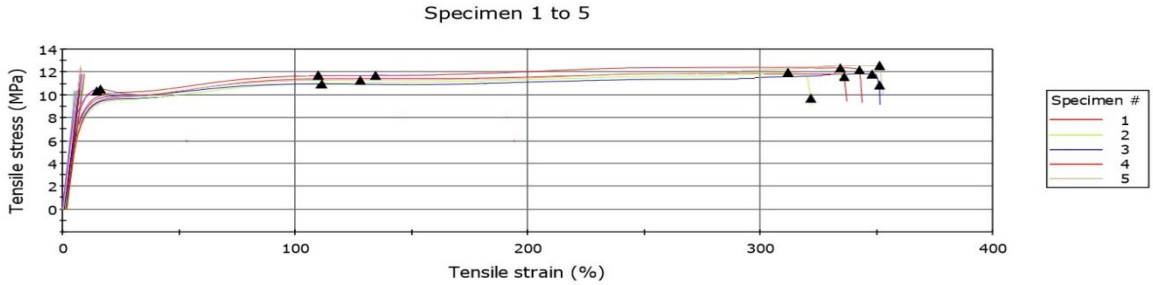
a



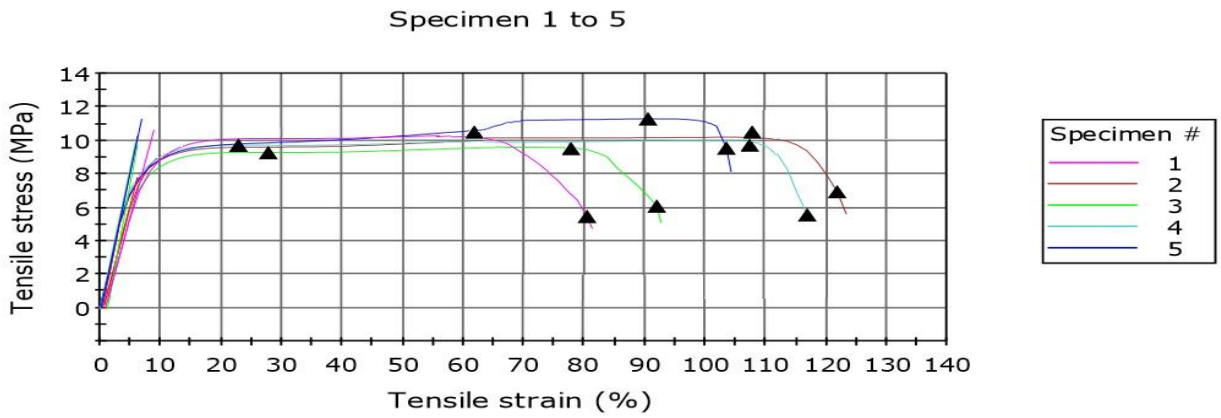
b



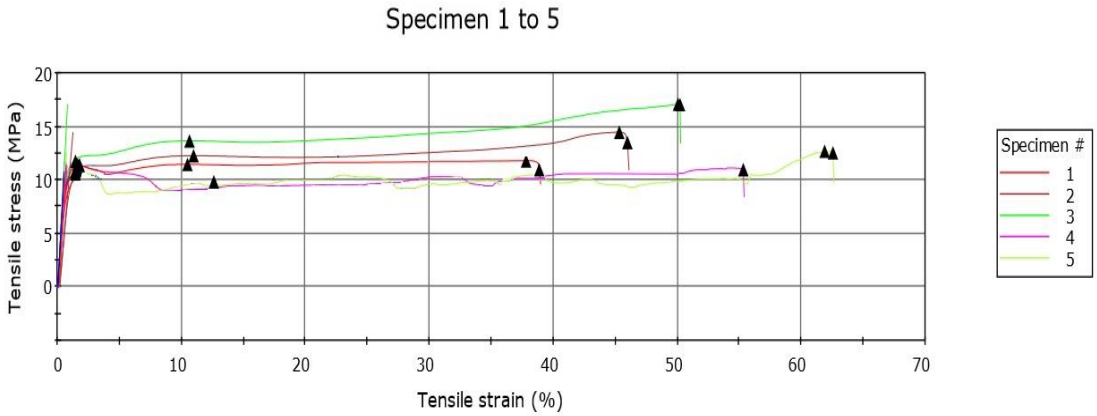
c



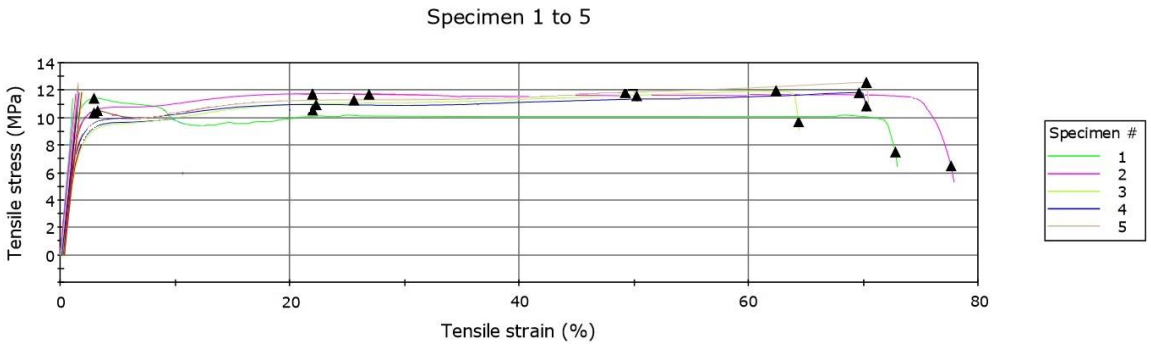
d


Specimen 1 to 5
Tensile stress (MPa)
Tensile strain (%)
Specimen #
1
2
3
4
5

e


Specimen 1 to 5
Tensile stress (MPa)
Tensile strain (%)
Specimen #
1
2
3
4
5

f



g

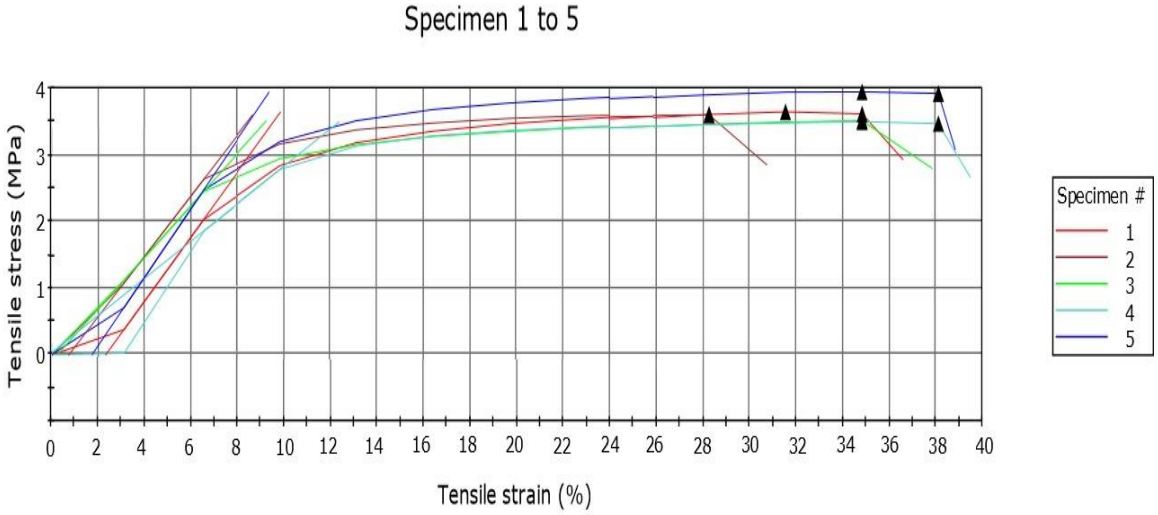


Figure B.1 Instron test of a) LD pure control, b) LD with wax 10%, c) LDLD with 5% PG active film, d) LD with 10% PG active film, e) LD with 20% PG active film, f) LD with 5% toco, g) LD with 10% toco based on the ASTM standard D882-91 for 5 samples