T.R.
GEBZE TECHNICAL UNIVERSITY
GRADUATE SCHOOL OF NATURAL AND APPLIED SCIENCES

DEVELOPMENT OF HIGH BARRIER PET FOILS AND INVESTIGATION OF THERMAL, MECHANICAL AND OXYGEN BARRIER PROPERTIES

MURAT TERGİP
A THESIS SUBMITTED FOR THE DEGREE OF
MASTER OF SCIENCE
DEPARTMENT OF MECHANICAL ENGINEERING

GEBZE
2016

T.R.

GEBZE TECHNICAL UNIVERSITY

GRADUATE SCHOOL OF NATURAL AND APPLIED SCIENCES

DEVELOPMENT OF HIGH BARRIER PET FOILS AND INVESTIGATION OF THERMAL, MECHANICAL AND OXYGEN BARRIER PROPERTIES

MURAT TERGİP

A THESIS SUBMITTED FOR THE DEGREE OF MASTER OF SCIENCE

DEPARTMENT OF MECHANICAL ENGINEERING

THESIS SUPERVISOR

PROF. DR. ALPER ŞEVKİ KONUKMAN

GEBZE

2016

T.C.
GEBZE TEKNİK ÜNİVERSİTESİ
FEN BİLİMLERİ ENSTİTÜSÜ

YÜKSEK BARİYERLİ PET FOLYOLARIN GELİŞTİRİLMESİ VE TERMAL, MEKANİK VE OKSİJEN BARİYER ÖZELLİKLERİNİN İNCELENMESİ

MURAT TERGİP
YÜKSEK LİSANS TEZİ
MAKİNA MÜHENDİSLİĞİ ANABİLİM DALI

DANIŞMANI
PROF. DR. ALPER ŞEVKİ KONUKMAN

GEBZE
2016

GEBZE TEKNİK ÜNİVERSİTESİ	**YÜKSEK LİSANS JÜRİ ONAY FORMU**

GTÜ Fen Bilimleri Enstitüsü Yönetim Kurulu'nun 22/06/2016 tarih ve 2016/41 sayılı kararıyla oluşturulan jüri tarafından 27/06/2016 tarihinde tez savunma sınavı yapılan Murat TERGİP'in tez çalışması Makine Mühendisliği Anabilim Dalında YÜKSEK LİSANS tezi olarak kabul edilmiştir.

JÜRİ

ÜYE
(TEZ DANIŞMANI) : Prof. Dr. Alp Er Şevki KONUKMAN

ÜYE : Prof. Dr. Gürbüz GÜNEŞ

ÜYE : Prof. Dr. Murat ÖZDEMİR

ONAY

Gebze Teknik Üniversitesi Fen Bilimleri Enstitüsü Yönetim Kurulu'nun
...../...../..... tarih ve ...../..... sayılı kararı.

İMZA/MÜHÜR

SUMMARY

To prevent the food contact with the oxygen, packaging materials such as PP (Polypropylene), PET (Polyethylene terephthalate), PVC (Polyvinyl chloride) and PS (Polystyrene) are modified with high barrier polymers which are EVOH (Ethylene vinyl alcohol), PVDC (Polyvinylidene chloride), PA (Polyamide) and COC (Cyclic Olefin Copolymer). In general, oxygen sensitive products are packed in these kind of non-recyclable packaging materials under vacuum or modified atmosphere (MAP).

In this thesis, with the help of coextrusion technology, development of high oxygen barrier active PET sheet, determination of optimum process conditions and investigation of active PET sheet's properties studies were carried out. In the production of multilayer active PET sheet, included A/B/A sandwich and A/B asymmetric structures, oxygen scavenger (OS) was blended into the PET matrix during extrusion process. With the active PET sheet which is consist of just PET and PET based additives, enabling usage of recyclable material; environmentally friendly new product was developed.

After all studies, new generation rigid PET packaging material was obtained which is prolonging shelf life of food and having active and passive barrier properties. Thus, residual oxygen concentration which present in the package under vacuum or modified atmosphere up to 2% can be minimized and oxygen passing through the package coming from outside can be blocked.

Under 23 °C temperature, 0% relative humidity and 1 atmosphere pressure active PET products' OTR (oxygen transfer rate) values were tested and found between 0 and 0.02 cc/(m^2.day.bar). When the results were compared with standard PET and PET//PE/EVOH/PE laminated sheet, active PET sheet have very low oxygen transmission rate. After 6 months aging to the active PET sheet, there were no increment in oxygen transfer rates.

Without sacrificing properties such as optical, mechanical, heat sealability and thermoforming, the developed multilayer active PET sheets have a significant potential in the shelf-life extension of oxygen sensitive food products.

Key Words: Active Packaging, Active PET Sheet, Oxygen Scavenger, Active Barrier PET, PET with High Barrier Properties.

ÖZET

Gıdanın oksijen ile temasını kesmek amacıyla PP (Polipropilen), PET (Polietilen tereftalat), PVC (Polivinil klorür) ve PS (Polistiren) gibi çeşitli polimerlerden mamül ambalajlar oksijen bariyeri yüksek EVOH (Etilen vinil alkol), PVDC (poliviniliden klorür), PA (Poliamid), COC (Sikloolefin kopolimer) gibi polimerler ile modifiye edilirler. Oksijene duyarlı gıdalar genelde pasif bariyer özelliği gösteren ve geri dönüşümü mümkün olmayan bu ambalajlar içerisinde vakum ya da modifiye atmosfer ortamında ambalajlama (MAP) yapılarak saklanır.

Bu çalışmada, koekstrüzyon yöntemi ile çok katmanlı yapıda yüksek oksijen bariyerine sahip aktif PET folyo geliştirilmesi, optimum üretim proses şartlarının belirlenmesi ve özelliklerinin incelenmesi gerçekleştirilmiştir. A/B/A sandviç ve A/B asimetrik yapı olmak üzere geliştirilen çok katklı aktif PET folyo üretiminde oksijen tutucu madde (OS) PET matrisine ekstrüzyon işlemi sırasında entegre edilmiştir. Yalnızca PET ve PET bazlı hammaddelerden oluşan aktif PET folyo ile geri dönüşümlü malzemelerin kullanılmasına imkan verilerek; çevreye duyarlı yeni bir ürün geliştirilmiştir.

Çalışmalar sonrasında gıdanın raf ömrünü uzatan aktif ve pasif bariyer özelliği gösteren yeni nesil rijit PET ambalaj elde edilmiştir. Böylelikle modifiye ortamda ve vakum altında %2'ye kadar bulunan oksijen konsantrasyonunu minimize edilebilmekte ve dışarıdan transfer olabilecek oksijeni engellemektedir.

23°C sıcaklık, %0 bağıl nem ve 1 atmosfer basınç altında aktif PET ürünlerin OTR (oksijen transfer katsayısı) değerlerinin 0 ila 0,02 cc/(m2.gün) arasında olduğu görülmüştür. Sonuçlar standard PET ve PET//PE/EVOH/PE laminasyonlu folyolar ile karşılaştırıldığında aktif PET folyo çok daha düşük oksijen geçirgenlik değerine sahiptir. 6 aylık yaşlandırma sonucunda da aktif PET folyoların oksijen geçirgenlik değerlerinde bir artış gözlemlenmemiştir.

Optik özellikleri, mekanik özellikleri, ısı ile yapışma ve termoform yöntemi ile şekillendirme özelliklerinden ödün vermeden geliştirilen aktif PET folyo, oksijene hassas gıdalarda raf ömrünü uzatabilecek çok ciddi bir potansiyele sahiptir.

Anahtar Kelimeler: Aktif Ambalajlama, Aktif PET Folyo, Oksijen Tutucu, Aktif Bariyerli PET, Yüksek Bariyer Özellikli PET.

ACKNOWLEDGEMENTS

I would never have been able to finish my thesis without the guidance of my committee members, help from friends, and support from my family.

I would like to express my deepest gratitude to my advisor, Prof Dr. Alp Er Konukman, for his excellent guidance, caring, patience, and providing me with an excellent atmosphere for doing research. I would also like to wish my deepest thanks to Prof. Dr. Murat Özdemir, who gave insight in getting me started research and without his technical help and guidance, the thesis wouldn't have been finished.

I would also like to thank Mr. Oktay Aral, who is the packaging R&D director of Yıldız Holding, for guiding my research for the past several years and helping me to gain knowledge and experience in polymers, packaging and laboratory equipment. My special thanks go to Mr. Koray Kırcalı from Farmamak Ambalaj A.Ş., who helped me during analysis, and I would have been lonely in the laboratory without him.

I would like to thank Mr. Kurt Kuruç, who is the general manager of Farmamak Ambalaj A.Ş., for his willingness to help me and permission to pursue a M.S. study. Many thanks to Mrs. Zeynep Demir, Mr. Sezer Tura, Mrs. Ceylan Başardı and other people in the laboratory of quality department for their invaluable help and their friendship.

Tubitak funded the active oxygen scavenging PET sheet production project of Farmamak Ambalaj A.Ş., under 1511 Research Technology Development and Innovation Projects in Priority programme with project number 1120137. Thus, laboratory equipments, which were installed with Tubitak support, were used in M.S. study and provide scientific findings and analysis capability.

I would also like to thank my beloved father İbrahim Tergip, my beloved mother Zeynep Tergip, and my beloved sisters Ms. Gamze Tergip and Ms. Gözde Nur Tergip. They always supported and encouraged me with their best wishes.

Finally, my fiancée Ms. Ceren İçten deserves special thanks here. I want her to know that I have deep and endless love to her, and I would like to thank her for her unconditional love, faith and support. She has been the only source of my inspiration, and this work is especially dedicated to her.

TABLE of CONTENTS

	Page
SUMMARY	v
ÖZET	vi
ACKNOWLEDMENTS	vii
TABLE of CONTENTS	viii
LIST of ABBREVIATIONS and ACRONYMS	x
LIST of FIGURES	xii
LIST of TABLES	xiv
1. INTRODUCTION	1
1.1. Oxygen Scavenging Systems	3
1.2. Applications of PET Based Oxygen Scavenging Systems	8
2. MATERIALS AND METHODS	11
2.1. Materials	11
2.2. Methods	11
2.2.1. Conditioning	12
2.2.2. Multilayer Sheet Production	12
2.2.3. Intrinsic Viscosity	16
2.2.4. Optical Properties	16
2.2.5. Color Measurements	17
2.2.6. Thermal Behavior	17
2.2.7. Tensile Properties	18
2.2.8. Tensile Impact Energy	18
2.2.9. Optical Microscopy Analysis	18
2.2.10. Oxygen Barrier Properties	18
2.2.11. Heat Sealing Properties	19
2.2.12. Acetaldehyde Content	19
2.2.13. Overall Migration Tests	20
3. RESULTS AND DISCUSSION	21
3.1. Intrinsic Viscosity	21
3.2 Optical Properties	23

3.3 Color Measurement 24
3.4. Thermal Behavior 26
3.5. Tensile Properties 28
3.6. Tensile Impact Energy 31
3.7. Optical Microscopy Analysis 32
3.8. Oxygen Barrier Properties 38
3.9. Heat Sealing Properties 44
3.10. Acetaldehyde Content 46
3.11. Overall Migration Tests 47
4. CONCLUSION 50

REFERENCES 53
BIOGRAPHY 55
APPENDICES 56

LIST of ABBREVIATIONS and ACRONYMS

Abbreviations and Acronyms		**Explanations**
η	:	Viscosity
x_c	:	Crystallinity
ΔH_f	:	Heat of melting
ΔH_c	:	Heat of crystallization
ΔH_0	:	Theoretical heat of melting
a	:	Mark–Houwink constant
AA	:	Acetaldehyde
Abbr	:	Abbreviation
COC	:	Cyclic olefin copolymer
DEG	:	Diethylene glycol
DSC	:	Differential scanning calorimeter
EU	:	European Union
EVA	:	Ethylene vinyl acetate
EVOH	:	Ethylene vinyl alcohol
FID	:	Flame ionization detector
GC	:	Gas chromatograph
IPA	:	Isophthalic acid
IV	:	Intrinsic viscosity
K	:	Mark–Houwink constant
MAP	:	Modified atmosphere packaging
MD	:	Machine direction
M_n	:	Numerical molecular weight
M_v	:	Viscosity average molecular weight
Nylon-MXD6	:	Nylon-MXD6 is a generic name given to a wide range of polyamides produced from m-xylene diamine (MXDA) by Mitsubishi Gas Chemical Co., Ind. Nylon-MXD6 is an aliphatic polyamide containing an aromatic ring in its main chain.
OTR	:	Oxygen transfer rate
PA	:	Polyamide

PE	:	Polyethylene
PET	:	Polyethylene terephthalate
PMDA	:	Pyromellitic Dianhydride
PP	:	Polypropylene
PS	:	Polystyrene
PVC	:	Polyvinyl chloride
PVDC	:	Polyvinylidene chloride
RH	:	Relative humidity
T_c	:	Crystallization temperature
TD	:	Transverse direction
T_g	:	Glass transition temperature
T_m	:	Melting temperature

LIST of FIGURES

Figure No:		Page
1.1:	Oxygen Scavenger forms; a) Sachet form b) label form.	2
1.2:	A light-activated oxygen scavenging film.	7
3.1:	Comparison of the DSC thermograms for standard PET sheet and active PET sheets.	27
3.2:	Elastic modulus of active PET sheets and reference samples in machine and transverse directions.	28
3.3:	Tensile strength values of active PET sheets and reference samples in machine and transverse directions.	29
3.4:	Elongation at break values of active PET sheets and reference samples in machine and transverse directions.	30
3.5:	Tensile impact energies of active PET sheets, standard PET sheet and PET//PE/EVOH/PE sheet.	31
3.6:	Optical microscopy image of the active three-layer sheet (Trial 1) from left side (section normal to the extrusion direction, magnification 20X).	33
3.7:	Optical microscopy image of the active three-layer film (Trial 1) from middle (section normal to the extrusion direction, magnification 20X).	33
3.8:	Optical microscopy image of the active three-layer film (Trial 1) from right side (section normal to the extrusion direction, magnification 20X).	33
3.9:	Optical microscopy image of the active three-layer sheet (Trial 2) from left side (section normal to the extrusion direction, magnification 20X).	34
3.10:	Optical microscopy image of the active three-layer sheet (Trial 2) from middle (section normal to the extrusion direction, magnification 20X).	34
3.11:	Optical microscopy image of the active three-layer sheet (Trial 2) from right side (section normal to the extrusion direction, magnification 20X).	35
3.12:	Optical microscopy image of the active two-layer sheet (Trial 3) from Left Side (section normal to the extrusion direction, magnification 20X).	35

3.13: Optical microscopy image of the active two-layer sheet (Trial 3) from middle (section normal to the extrusion direction, magnification 20X). 36

3.14: Optical microscopy image of the active two-layer sheet (Trial 3) from right side (section normal to the extrusion direction, magnification 20X). 36

3.15: Optical microscopy image of the standard PET sheet (section normal to the extrusion direction, magnification 20X). 37

3.16: Optical microscopy image of the PET//PE/EVOH/PE sheet (section normal to the extrusion direction, magnification 20X). 37

3.17: Oxygen transmission rate with respect to time for standard PET. 39

3.18: Oxygen transmission rate with respect to time for PET//PE/EVOH/PE. 39

3.19: Oxygen transmission rate with respect to time for active PET Trial 1 just after production. 40

3.20: Oxygen transmission rate with respect to time for active PET Trial 2 just after production. 40

3.21 Oxygen transmission rate with respect to time for active PET Trial 3 just after production 41

3.22: Oxygen transmission rate with respect to time for active PET Trial 1 after 6 months aging. 42

3.23: Oxygen transmission rate with respect to time for active PET Trial 2 after 6 months aging. 43

3.24: Oxygen transmission rate with respect to time for active PET Trial 3 after 6 months aging. 43

3.25: Heat seal strengths of active PET sheets and standard PET sheet with top film sealed at different pressures and temperatures with the heat sealing machine. 45

LIST of TABLES

Table No:		Page
2.1:	Formulations and structure of active PET sheets.	13
2.2:	Dimensions and L/D ratios of the main and auxiliary screws.	14
2.3:	Measured temperatures in different zones of main and auxiliary screws.	15
3.1:	Intrinsic viscosity of PET raw materials and PET sheets.	21
3.2:	Optical properties of sheet samples.	24
3.3:	Color values of PET sheets.	25
3.4:	Thermal properties of PET sheets.	26
3.5:	Layer thicknesses of active PET sheets.	38
3.6:	Acetaldehyde content of active PET sheets and standard PET sheet.	47
3.7:	Overall migration values for Trial 2 (A/B asymmetric structure with 3% oxygen scavenger in active layer).	48
3.8:	Overall migration values for Trial 3 (A/B/A symmetric structure with 5% oxygen scavenger in active layer).	49

1. INTRODUCTION

Food packaging is designed to contain and protect foods, to provide required information about the food, and to make food handling convenient from distribution to consumer's table. The primary functions of food packaging are to achieve preservation and the safe delivery of food products until consumption. During distribution, the quality of the food product can deteriorate biologically and chemically as well as physically [Marsh and Bugusu, 2007]. Food packaging extends shelf life and maintains the quality and safety of the food products. A food package communicates important information about the product, how to prepare it, and information about the nutritional content. Packaging also allows for consumers to enjoy food the way they want, at their convenience. Food packages can be geared toward a person's own lifestyle through designs like portability and single serving dishes. Although traditional packaging covers the basic needs of food containment, advances in food packaging are both anticipated and expected. Packaging is becoming increasingly complex and innovative packaging is the result of consumers' demand. Active packaging is one of the most important results of innovating thinking in packaging.

Active packaging can be defined as a kind of packaging that can modify the conditions inside the package to extend the shelf life or sensory properties of the food by removing the undesired gases [Vermeiren et al., 1999]. Active packaging can be in the form of scavengers, regulators and emitters according to their functionalities. Their actions can be specific for several substances such as O_2, CO_2, ethylene, moisture and odor [Galdi et al., 2008].

Thermoplastic resins such as polyethylene terephthalate (PET) are generally used to produce plastic packaging materials. PET processed under right conditions have good gas barrier properties, but it has relatively high gas permeability when compared with glass and metal packaging materials [Liu et al., 2011]. Gas barrier properties of PET is improved by laminating PET with a high gas barrier film, or coating with aluminum or polymeric resins [Di Maio et al., 2015]. This is known as passive barrier packaging which prevents gas transmission between the package and the environment. Cyclic olefin copolymer (COC), Polyvinylidene dichloride (PVDC), Ethyl vinyl alcohol (EVOH) and Nylon -MXD6 are the polymers which are commonly

used for modifying and increasing the barrier properties of the PET. However, adding a new layer to a packaging material is not preferred due to the environmental issues and cost. Regarding environmental issues, adding a barrier layer to a polymeric film needs a tie layer or an adhesive, and this disables recycling and scraps, which are being generated during converting the raw material to a packaging material, cannot be reused in the production [Shen et al., 2010].

Recent years, academic and industrial research has been specifically focused on the production and application of oxygen scavengers (OS). Active substances are usually embedded into the package in a sachet or a label form. Oxygen scavengers in the form of a sachet and a label are shown in Figure 1.1. Sachets are sited freely in the package headspace, while labels are attached into the lid of the package. Although these technologies are very interesting because of their functional aspects, they are not widely used, especially in Europe, because of normative problems. Furthermore, sachets cannot be used with liquid products due to their physical structure. They may not be used in a package made of flexible film, as the film will cling to the sachet and prevent it from performing its function. Sachets have the risk of accidental ingestion by consumers [Galdi et al., 2008]. These concerns diverted researchers to seek package-based solutions.

a) b)

Figure 1.1: Oxygen Scavenger forms; a) Sachet form b) label form.

More recent attempts in active scavenging have focused on incorporating the scavenger into the packaging material itself. These methods have potential for use in PET bottles and films, and can be integrated in many plastic containers. Incorporating the scavenger directly into the wall of a food package can be done by placing the scavenger throughout the scavenger wall or placing the scavenger in a unique layer between many layers of the container sidewall. This approach to protect oxygen-sensitive products has many opportunities: i): the active packaging material prevents oxygen from reaching the product from the outside, and ii): it can absorb residual oxygen, which can dissolve from the food and could not be removed from the headspace after the packaging [Gibis and Rieblinger, 2011].

There are many oxygen scavenging systems which are based on metallic or nonmetallic compounds. The mechanism of the important oxygen scavenging systems are given below.

1.1. Oxygen Scavenging Systems

- Iron Powder Oxidation

The commercially iron based oxygen scavengers are available in the form of small sachets. Iron based scavengers are based on the iron oxidation in the presence of water according to the overall theoretical equations given below:

$$4Fe + 3O_2 + 6H_2O \rightarrow 4Fe(OH)_3 \rightarrow 2Fe_2O_3.3H_2O \tag{1.1}$$

$$4Fe(OH)_2 + O_2 + 2H_2O \rightarrow 4Fe(OH)_3 \rightarrow 2Fe_2O_3.3H_2O \tag{1.2}$$

Iron based scavengers mainly consist of two types. A self-reacting type contains moisture in the sachet and as soon as the sachet is exposed to air, the reaction starts. In moisture-dependent types, oxygen scavenging takes place only after moisture has been taken up from the food. These sachets are stable in open air before use because they do not react immediately upon exposure to air; therefore, they are easy to handle if they are kept dry [Miltz and Perry, 2005]. Theoretically, 1 gram of iron reacts with 300 cm^3 of O_2. If the initial concentration of the O_2 and the O_2 permeability of the packaging material are known, appropriate absorber can be chosen. Ageless

(Mitsubishi Gas Chemical Co., Japan) is the most well-known producer of O_2-scavenging systems based on iron oxidation. Other iron based O_2-absorbent sachets are the ATCO O_2-absorber (Standa Industrie, France), the Freshilizer Series (Toppan Printing Co., Japan) and Freshpax (Multisorb Technologies Inc., USA). The sachets can be found in packages of many foods including fresh and pre-cooked pasta, catering, processed meat products (e.g. smoked ham and salami), bakery products (e.g. bread, pizza crust, pastries, cookies and cakes), cheese, coffee, nuts and potato chips [Vermeiren et al., 1999]. Furthermore, a novel oxygen scavenger using iron nanoparticles was produced by liquid phase reduction method in a micro emulsion system and its oxygen absorbing capacity was determined [Anthierens et al., 2011]. The absorption capacity of different kinds of oxygen scavengers was measured as a function of time, and the absorption rate constant was evaluated at 25 °C. The absorption rate constant for nanosized oxygen scavenger is better than those of conventional oxygen scavengers.

- Ascorbic Acid Oxidation

Oxygen scavengers based on ascorbic acid oxidation are another important class of oxygen scavengers. Ascorbic acid, which is vitamin C, is usually used as a food or beverage ingredient, oxygen interceptor or antioxidant as well as a nutrient. Because ascorbic acid is a six carbon compound, the weight required to react with oxygen is quite high. It is readily, but slowly oxidized to dehydroascorbic acid. The conversion to dehydroascorbic acid is catalyzed by the presence of metal ions [Graf and Rapids, 1994]. Ascorbic acid is an expensive chemical to employ as an oxygen scavenger, because it is derived either by extraction from natural plant material of which it is a small constituent, or by other biological means. Ascorbic acid functions only in the presence of water. Therefore, to function as an oxygen scavenger, it must either be accompanied by water or water must be supplied from the environment. Because of its oxygen sensitivity, it is very difficult to incorporate ascorbic acid into a plastic compound.

- Enzymatic Oxidation

Formation of another possible way of oxygen scavenger is incorporation of specific oxygen-reducing enzyme into the packaging material. The most studied oxygen scavenging enzyme system is glucose oxidase combined with catalase.

Hydrogen peroxide is a by-product of the reaction catalyzed by glucose oxidase, and catalase is added to the system to remove the hydrogen peroxide [Johansson et al., 2014]. Glucose oxidase transfers two hydrogens from the -CHOH group of glucose to O_2 with the formation of glucono-delta-lactone and H_2O_2. The lactone then spontaneously reacts with water to form gluconic acid. The reaction is:

$$2G + 2O_2 + 2H_2O \rightarrow 2GO + 2H_2O_2 \tag{1.3}$$

Where, G is the substrate.

Since H_2O_2 is an objectionable end product, catalase is introduced to break down the peroxide

$$2\mathrm{H_2O_2} + \text{catalase} \rightarrow 2\mathrm{H_2O} + \mathrm{O_2} + \text{catalase} \tag{1.4}$$

The sum of these two reactions yields half the oxygen originally present and therefore, ultimately the free oxygen approaches zero [Brody and Bundy, 1995].

- Unsaturated Hydrocarbon Oxidation

Ethylenic unsaturated hydrocarbons, such as squalene, fatty acids and polybutadiene have sufficient oxygen scavenging capacity. These unsaturated hydrocarbons, after functionally modified to make them compatible with the polymer, can be mixed with thermoplastics during the extrusion process.

Polybutadiene-based scavengers seem to be the most promising ones, due to their transparency, mechanical properties and processing characteristics. Transition metal catalyst such as cobalt II neodecanoate or octoate are used to speed up the scavenging rate. Furthermore, photo initiators can also be added to further facilitate and control the initiation of the scavenging process. Adding a photo initiator or a blend of photo initiators to the oxygen scavenging composition is a common practice, especially where antioxidants were added to prevent premature oxidation of the composition during processing and storage. The main problem of this technology is that during the reaction between unsaturated molecules and oxygen, by products such as aldehydes or ketones can be generated and these substances may affect the sensorial quality of the food. First solution is to use functional barriers between food and active layer that limit the migration of undesired products and allow oxygen to migrate.

Another solution comes from the use of adsorber materials like silica gel and zeolites [Galdi et al., 2008].

• Photosensitive Dye Oxidation

Another technique of oxygen absorption is a photosensitive dye applied onto a polymeric film. When the film is irradiated by ultraviolet light, O_2 is activated to its singlet state by the dye, and oxygen-removing reaction become much faster. The singlet excited state of oxygen is highly reactive and so its chemical reaction with scavengers is fast. The technique involves sealing of a small coil of ethyl cellulose film, containing a dissolved photosensitive dye and a singlet oxygen acceptor, in the headspace of a transparent package. When the film is illuminated with visible light, excited dye molecules sensitize oxygen molecules, which have diffused into the polymer, to the singlet state. These oxygen molecules react with acceptor molecules and are become scavenged. While the film is illuminated, the process continues until all the oxygen is reacted [Vermeiren et al., 1999]. Photochemical reaction can be presented as follows:

$$\begin{gathered} photon + dye \rightarrow dye^* \\ dye^* + O_2 \rightarrow dye + O_2^* \\ O_2^* + acceptor \rightarrow acceptor\ oxide \\ O_2^* \rightarrow O_2 \end{gathered} \tag{1.5}$$

A light activated oxygen scavenging film is schematically given in Figure 1.2. This scavenging technique does not require water as an activator so it is effective for wet and dry products. However, scavenging does not occur in the dark.

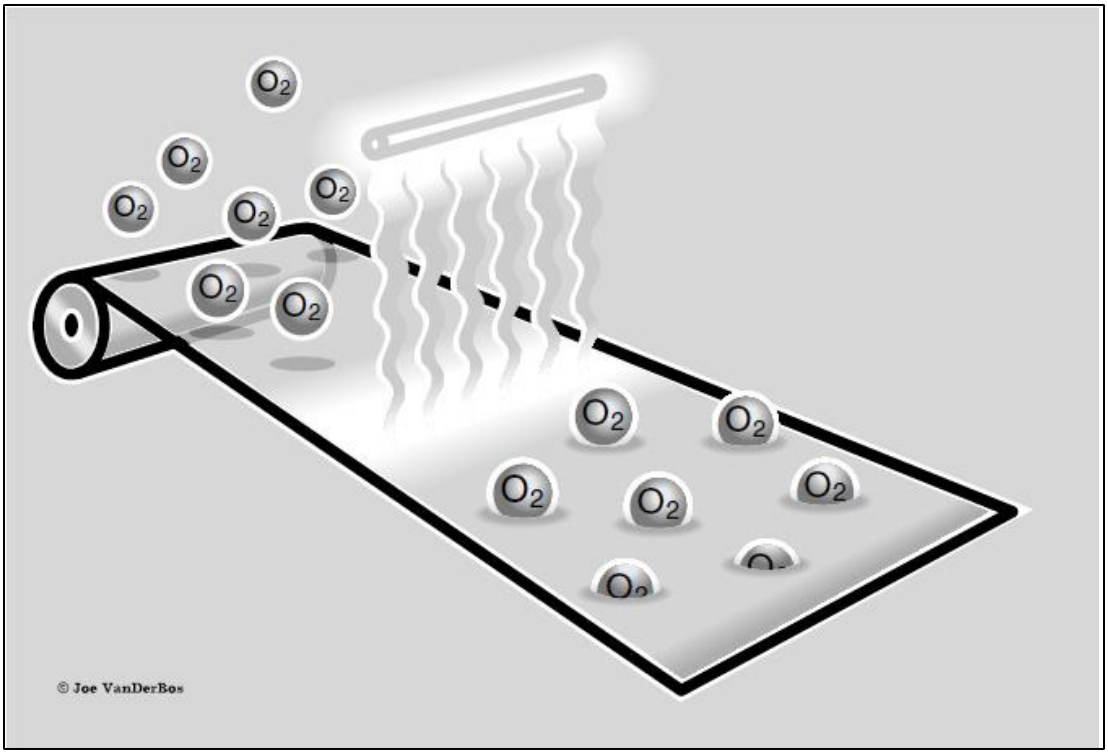

Figure 1.2: A light-activated oxygen scavenging film.

• Copolyamide and Transition Metal Catalyst

The use of low-gas permeable polymers, known as partially aromatic polyamides (nylons) with polyesters increases barrier properties of the packaging materials. Partially aromatic polyamides have passive barrier properties, they restrict carbon dioxide leakage from, and oxygen intrusion into, a container by obstructing the paths of gas molecules. However, partially aromatic polyamides are not miscible, they do not mix well with polyesters like PET, and they also give containers yellow and hazy appearance. It is also known that in multilayer bottle production, thin layer with partially aromatic polyamide such as Nylon-MXD6 increases the barrier properties of the product. But multilayer bottles with Nylon-MXD6 have high haze values either. Oxygen scavenging materials are typically employed with a suitable catalyst, for example an organic or inorganic salt of a transition metal catalyst such as cobalt. The addition of cobalt salt also activates the partially aromatic polyamide to form an active barrier that scavenges oxygen, thereby improving barrier properties. In addition, ionic compatibilizer allows a synergistic reduction in yellowness and haze, and increases barrier properties even further. The system is relatively easy to incorporate into thermoplastics and almost moisture insensitive [Chen and Sun, 2006].

1.2. Applications of PET Based Oxygen Scavenging Systems

In literature, there are several patents and studies conducted regarding the formation of oxygen scavenger systems in which the active agent is incorporated into a bottle or a flexible film. Galdi et al produced 30 μm monolayer active PET films with different concentrations of oxygen scavenger (1%, 3% and 5% by weight) in a laboratory scale extruder and investigated the effect of composition on the structure and the properties of the active films. Oxygen scavenging capability of the films was tested with apples. Fresh untreated apples were peeled, cut into slices and packed into active films. Packages were heat sealed and stored at 8°C for one week. The color changes of the apple slices was used as an index for the effectiveness of the active films. It was observed that apple slices packed in active films preserved their color better than the apple slices packed in a regular PET film. Significant scavenging activity was assessed with active films containing 5% oxygen scavenger known as Amosorb DFC 4020. However, the exhaustion time evaluated by O_2 absorption measurements was limited to 26 h [Galdi et al., 2008]. Therefore, Galdi and Incarnato investigated the performances of the monolayer active PET films with higher concentrations of oxygen scavenger (5%, 10% and 20% by weight). The results showed that the monolayer active film with 10% oxygen scavenger was the best among the compositions analyzed with regard to scavenging capacity and prolonged exhaustion time (170 h). Increasing the oxygen scavenger content up to 20% did not increase the exhaustion time or the oxygen scavenging activity of the film due to poor dispersion and distribution of oxygen scavenger within the film. Banana slices wrapped in the active films at 10% oxygen scavenger showed the lowest color change compared to the samples packaged in regular PET film and active film having 20% oxygen scavenger [Galdi and Incarnato, 2011].

Di Maio et al aimed to further increase the reaction time of active PET-based films, and produced a symmetrical three layer structure (A/B/A) to protect the internal active polyester layer from fast oxidation by sandwiching the active layer between two virgin PET layers. Active PET films were produced in three different individual layer thicknesses (13 μm / 9 μm / 13 μm, 10.75 μm / 13.5 μm / 10.75 μm, 9 μm / 17 μm / 9 μm). Single layer standard PET and single layer active PET films were also produced for comparison. The oxygen scavenger concentration in the active layer was 10%

based on their previous studies. The results showed that three-layer films have an oxygen scavenging rate always lower than the mono active PET films, and oxygen scavenging progressively decreased with the increase of the thickness of the external PET layer. Correspondingly, the exhaustion times for the three layer films are always longer than the mono active PET film (170 h) and progressively increased up to 420 h with increasing the thickness of the external PET layer. Fresh-cut apple slices were packed with the three layer active PET film (9 µm / 17 µm / 9µm), single layer active PET film and single layer standard PET film, then stored at 8°C. Color, acidity and sugar content of the packed apples were measured during 15 days. After 15 days of storage, color change was not noticeable for apples packed in three layer active PET films while there was a perceivable color change in apples packed in single layer active PET film and single layer standard PET film. When the total acidity levels of the samples are compared, only the three layer active film preserved the acidity of the apple slices from a change in which acidity is directly related to the sweetness of the fruit. However, all samples maintained their original sugar content whatever the type of film used for the packaging. The results revealed that the three layer film (9 µm / 17 µm / 9 µm) was found to be the most efficient packaging in preserving the quality of the sliced apple which is very sensitive to oxygen [Di Maio et al., 2015].

Liu et al formed an oxygen scavenging high barrier PET bottle. The bottle is comprised a blend of polyester and a partially aromatic polyamide with an ionic compatibilizer and a cobalt salt. This blend was processed into a bottle that has both active and passive oxygen barrier and carbon dioxide barrier properties with improved color and clarity. It was found that there was a significant reduction in oxygen transmission rate through the bottle sidewalls at 5 wt% MXD6 containing 100 ppm cobalt salt. Oxygen transmission rate of the bottle was found to be less than 0.02 $cm^3/(m^2.day)$ during 300th hours and then it slightly increased [Liu et al., 2011].

In the literature, studies and patents regarding the incorporation of oxygen scavenging agents in PET material were based solely on forming active PET bottles or active flexible PET films. There is no study related to the incorporation of an oxygen scavenging agent into a PET sheet which is thicker than a film, usually thermoformable and used as bottom tray in food packaging. Therefore, the main objective of this work is to produce an oxygen scavenging active PET sheet and characterize its properties. For this purpose, PET sheets with asymmetric and sandwich structures were produced with an active oxygen scavenging layer by the coextrusion technology. An ionic

copolyester containing a metal compound were blended with an oxidizable polymer as the oxygen scavenger to form an oxygen scavenging active PET sheet. The specific objectives of this study are to:

i) verify the activity of the scavenger by measuring the oxygen permeability values of PET sheets
ii) measure tensile and impact properties of PET sheets
iii) determine optical properties (gloss, haze, clarity, total transmittance) of PET sheets
iv) analyze individual layer thicknesses of multilayer PET sheets by optical microscope
v) determine L*a*b* values of PET sheets
vi) measure intrinsic viscosity (IV)
vii) determine the acetaldehyde content of PET sheets
viii) analyze the thermal properties of PET sheets
ix) determine heat sealing properties of active PET sheets as compared with conventional PET based high barrier lidding film
x) conduct overall migration studies whether active PET sheets are in compliant with the current European Union (EU) legislation.

2. MATERIALS AND METHODS

Active PET sheets were produced with an industrial scale extruder by coextrusion, and the raw materials were selected mainly according to their properties, their processing capability in the form of sheet extrusion and compliance with EU food contact legislation.

2.1. Materials

The PET used in the active layer was Polyshield 2300K with an intrinsic viscosity of 0.841 dL/g obtained by Invista Resins & Fibers GmbH, Gersthofen, Germany. The PET used in the passive layer was PET BGC 80 purchased from Koksan PET and Plastik Ambalaj San. ve Tic. A.Ş., Gaziantep, Turkey and it is sheet extrusion grade having an intrinsic viscosity of 0.80 dL/g. Oxyclear 3500 was ionic copolyester containing a metal compound blended with oxidizable polymer, used as the oxygen scavenger supplied by Invista Resins & Fibers GmbH, Gersthofen, Germany. The choice of oxygen scavenger was based on the matrix, physical nature and process ability. Slip/antiblock masterbatch T dc S479 was obtained from Sukano AG, Schindellegi, Switzerland, and used in the passive layer of the sheet to prevent blocking. The carrier material is crystalline PET containing waxes and inorganic additives. All raw materials and additives fully comply with EU food contact legislation. The properties and characteristics of the materials and additives used are given in Appendix.

2.2. Methods

Before extrusion, PET resins and additives were dried and after drying, sheet production were made in a coextrusion PET line.

2.2.1. Conditioning

Prior to extrusion, Polyshield 2300K resin was dried at 180°C for 8 hours in a desiccant type drier until the moisture content is 30 ppm or below. Velocity of the air in the drier was 0.06 kg/min. Koksan BGC 80 PET resin was also dried before processing at the same conditions with Polyshield 2300K in an another desiccant type drier until the moisture content of 30 ppm or below has been reached. Oxyclear 3500 was supplied in pre-dried air tight and sealed aluminized bags, and stored at ambient temperature in a dry place until it was used. Sukano T dc S479 was not dried prior to processing because it was used in very low quantities in the formulations. It was stored in sealed PE bags at ambient temperature in a dry place. The PET sheets prior to analyses were conditioned at 23°C and 50% RH.

2.2.2. Multilayer Sheet Production

Oxygen scavenging PET sheets in asymmetric (A/B) and sandwich (A/B/A) structures were coextruded at PET extrusion facility of Farmamak Ambalaj Mad. ve Amb. Mak. San. ve Tic. A.Ş., Gebze, Kocaeli, Turkey. Oxyclear 3500 was blended at different ratios with Polyshield 2300K PET resin directly via a gravimetric dosing system through the main extruder to form the active layer (B). Koksan BGC 80 PET resin and Sukano T dc S479 slip/antiblock masterbatch were blended with a conventional dosing device through the auxiliary extruder. Two A/B/A active PET sheets having different oxygen scavenger concentrations in the active layers (3 wt% and 5 wt%) and one A/B active PET sheet with 3% oxygen scavenger concentration by weight in active layer were produced with the standard PET sheet as a reference under the same conditions. Formulations of the PET sheets and their structures are given in Table 2.1:

Table 2.1: Formulations and structures of active PET sheets.

Nomenclature	Structure	Layer Gauge %	Layer A Composition by wt%	Layer B Composition by wt%
Standard PET Sheet	Mono A/A/A	10/80/10	1.5% Slip/Antiblock + 98.5% PET	100% PET
Trial 1	Sandwich A/B/A	10/80/10	1.5% Slip/Antiblock + 98.5% PET	3% Oxyclear 3500 + 97% Polyshield 2300K PET
Trial 2	Sandwich A/B/A	10/80/10	1.5% Slip/Antiblock + 98.5% PET	5% Oxyclear 3500 + 95% Polyshield 2300K PET
Trial 3	Asymmetric A/B	20/80	1.5% Slip/Antiblock + 98.5% PET	3% Oxyclear 3500 + 97% Polyshield 2300K PET

Passive layer (A) prevents the active layer from direct contact with the ambient air. Active layer (B) scavenges oxygen molecules passing through the packaging material. Therefore, the sandwich structure was formulated to enhance the oxygen barrier properties of the PET sheets by absorbing oxygen passing through the active middle layer. The asymmetric structure was designed not only to inhibit the ingress of oxygen from the surroundings but also to absorb oxygen in the headspace of the package.

Total thickness of the active PET sheets was 400 µm which is the most preferred thickness for oxygen sensitive foods by the food producing companies such as processed meat and cheese producers. In the A/B/A structure, the thickness of the layers is 40 µm, 320 µm and 40 µm, respectively. In the A/B structure, the thickness of layer A is 80 µm and layer B is 320 µm.

The PET extrusion facility has the capability of producing the PET sheets in the form of 3 layers. It consists of main and auxiliary single screw extruders, conventional

dosing systems, a feed block, a flat die, chill rolls and winding rollers. Dimensions and L/D ratios of main and auxiliary screws are given in Table 2.2.

Table 2.2: Dimensions and L/D ratios of the main and auxiliary screws.

Line	Screw	Diameter (mm)	L/D Ratio	Screw Length (mm)
Coextrusion single screw line	Main screw	150	34	5150
	Auxiliary screw	70	38	2640

The extrusion die was a coat-hanger type manifold die with a lip width of 2000 mm and lip thickness between 0.2 mm and 2 mm. Chill rolls were thermally controlled by circulating water at a temperature of 10°C.

Prior to production, dosing units were calibrated to ensure feeding of the raw materials accurately. Adjustment of the flat die was done with the help of a wrench to obtain films with a thickness of 400 μm and width of 1200 mm. Later, the main screw, auxiliary screw and die were cleaned up with virgin PET resin to minimize the formation of possible quality defects such as fish eye, black points and burned particles.

The main screw speed was set to 50.9 rpm, and the auxiliary screw speed was set to 56.9 rpm. The main and auxiliary screws yielded 727 kg/h and 182 kg/h product, respectively. Measured temperatures in different zones of the main and auxiliary screws are given in Table 2.3. Die temperature was 275°C, and the temperature in the first chill roll was 35°C while the temperature in the second and third chill rolls was 30°C. The pressures in the main screw for melt pump, feed block and die were 75 bar, 36 bar and 60 bar, respectively. The pressures for melt pump, feed block and die in the auxiliary screw were 93 bar, 45 bar and 64 bar, respectively. During winding, the edges of the PET sheets were trimmed with a rotating knife and after trimming final widths of the sheets were 1200 mm. Following winding, PET sheets were wrapped with PE films.

Table 2.3: Measured temperatures in different zones of main and auxiliary screws.

Extruder Main Screw Temperature	Feeding Zone	1. Zone	270°C
		2. Zone	270°C
		3. Zone	270°C
	Screw Zone	1. Zone	270°C
		2. Zone	275°C
		3. Zone	275°C
		4. Zone	275°C
		5. Zone	275°C
		6. Zone	275°C
		7. Zone	275°C
	Filter, Melt Pump and Feed block Zone	1. Zone	275°C
		2. Zone	275°C
		3. Zone	275°C
		4. Zone	275°C
		5. Zone	275°C
		6. Zone	275°C
		7. Zone	275°C
		8. Zone	275°C

Extruder Auxiliary Screw Temperature	Feeding Zone	1. Zone	280°C
		2. Zone	280°C
		3. Zone	280°C
	Screw Zone	1. Zone	285°C
		2. Zone	285°C
		3. Zone	285°C
		4. Zone	285°C
		5. Zone	285°C
		6. Zone	285°C
		7. Zone	285°C
	Filter, Melt Pump and Feed block Zone	1. Zone	285°C
		2. Zone	285°C
		3. Zone	285°C
		4. Zone	285°C
		5. Zone	285°C
		6. Zone	285°C
		7. Zone	285°C
		8. Zone	285°C

2.2.3. Intrinsic Viscosity

Intrinsic viscosity (IV) of the samples were measured using an automatic viscosity system AVS 370 with Ubbelohde viscometer Type 532 20, capillary size II (SI-Analytics, Mainz, Germany). Before measurements, samples were dried in an oven at 70°C for 2 h and then dissolved in dichloroacetic acid at a concentration of 5 g/L (0.026 M). After dissolution, samples were cooled down to room temperature. IV measurements were performed in triplicates at 25 °C according to ISO 1628-5.

For linear monodisperse polymers, intrinsic viscosity is related to the molecular weight according to the Mark–Houwink equation:

$$[\eta] = KM_v^a \tag{2.1}$$

Where [η] is the intrinsic viscosity, K and a are the Mark–Houwink constants which depend on the material, and M_V is the viscosity average molecular weight. Specifically for PET, it is possible to relate number average molecular weight (M_n) with the intrinsic viscosity through the empirical equation of Moore as given below [Galdi and Incarnato, 2007]:

$$[\eta] = 7.50 \times 10^{-4} M_n^{0.682} \tag{2.2}$$

2.2.4. Optical Properties

The optical properties considered in this study were gloss, haze, clarity and total transmittance. Gloss was measured according to ASTM D 2457 using a Gardner Micro Gloss 45 reflectometer (BYK Gardner, Geretsried, Germany) with an incidence angle of 45°. The glossmeter measures the specular reflection at 45°. Haze, clarity and total transmittance were measured in accordance with ASTM D 1003 using a Haze Guard Plus equipment (BYK Gardner, Geretsried, Germany). Haze is defined as the percentage of light which in passing through deviates from the incident beam greater than 2.5° on average. Clarity is defined as the percentage of light that deviates from the incident beam smaller than 0.2° [Poisson et al., 2008]. Total transmittance is the

ratio of transmitted light to the incident light, and influenced by the absorption and reflection properties. Measurements were performed in triplicates.

2.2.5. Color Measurements

A spectrophotometer X-RITE SP62 equipped with a light source of D_{65} (day light) capable of measuring with an angle of 10° (X-Rite, Incorporated, Neu-Isenburg, Germany) was used to determine the color space of the samples in CIE L*a*b* where L* is a measure of brightness, a* is a measure of redness (+) or greenness (−) and b* is a measure of yellowness (+) or blueness (−). L*a*b* color space is based on the theory that a color cannot be both green and red at the same time, nor blue and yellow at the same time. As a result, single values can be used to describe the red/green and the yellow/blue attributes. Measurements were performed in triplicates.

2.2.6. Thermal Behavior

The thermal behaviors of the PET sheets were analyzed using a DSC 400 differential scanning calorimeter (Perkin Elmer, Waltham, USA). Temperature calibration was performed according to the procedures given in the instrument manual. An indium and zinc references were used and heated at a rate of 10°C/min. The heat flow signal was calibrated in accordance with the procedures given in the instrument manual. Then, PET samples (10-12 mg) were weighed in aluminum pans and the lids were closed. The aluminum pan carrying the sample and an empty pan (reference) were placed in the DSC furnace. Samples were tested under a nitrogen gas flow of 20 ml/min in order to minimize thermo-oxidative degradation phenomenon. The samples were heated from 25°C to 300°C at a rate of 10°C/min. Glass transition temperature (T_g), melting temperature (T_m) and crystallization temperature (T_c) were evaluated from the thermograms. The percent crystallinity (x_c) was determined according to the following formula:

$$x_c = \frac{(\Delta H_f - \Delta H_c)100}{\Delta H_0} \tag{2.3}$$

where ΔH_f is the heat of melting expressed in J/g measured during heating, ΔH_c is the measured heat of crystallization expressed in J/g and ΔH_0 is the theoretical heat of melting for PET given as 140 J/g [Ozen et al., 2010].

2.2.7. Tensile Properties

The stress-strain curves of the PET samples were obtained according to ISO 527.1 with a mechanical testing machine Zwick/Roell Z005 (Ulm, Germany) equipped with a 2.5 kN load cell. Samples (25.4 mm × 11 mm) were tested in machine direction (MD) and transverse direction (TD) and average values of the results were taken into consideration. The crosshead speed was fixed at 100 mm/min, gauge length was 50 mm and pre-load was 0.2 N/mm^2 for the determination of tensile stress, modulus of elasticity and elongation at break. Measurements were performed in triplicates.

2.2.8. Tensile Impact Energy

The tensile impact energies of the PET samples (2 mm × 5 mm) were tested with a Zwick 5102.202 pendulum impact tester (Ulm, Germany) according to ASTM D 1822. Measurements were performed in triplicates.

2.2.9. Optical Microscopy Analysis

Optical microscopy analyses were carried out by means of an Olympus BX 51TF-P polarized microscope (Tokyo, Japan) on film sections under 200 times magnification. PET samples (~20 μm thick) were cut by means of a Leica RM 2255 microtome (Wetzlar, Germany) with a 90° angle normally to the machine direction at room temperature. Samples were taken from the left (0 mm), the middle (600 mm) and the right (1200 mm) sides of the rolls with a width of 1200 mm.

2.2.10. Oxygen Barrier Properties

Flux of oxygen through PET sheets was measured with a Mocon Ox-Tran model 2/22H (Mocon, Minneapolis, USA) oxygen permeability testing machine at 25°C, 0%

RH and 1 atm barometric pressure. A mixture of 98% nitrogen with 2% hydrogen was used as the carrier gas, and oxygen with a purity of 99.9% was used as the test gas. Prior to testing, specimens were conditioned with nitrogen inside the unit to remove traces of atmospheric oxygen dissolved in the PET matrix. The conditioning was continued until a steady state was reached where the oxygen flux changed by less than 1% in 30 min cycle. Subsequently, oxygen was introduced into the test cell. In testing of active PET sheets which contain oxygen scavenging agent, the oxygen flux was measured throughout 600 hours (25 days) after the introduction of the oxygen into the cell. In testing of reference PET sheets which do not contain any oxygen scavenging agent, the test ended when the flux reached a steady state where the oxygen flux changed by less than 1% during a 30 minutes test cycle.

2.2.11. Heat Sealing Properties

PET based high barrier lidding film (Lintop PET HB B 35, Pontivy, France) was used in heat sealability tests. Samples were cut in 2.54 cm × 11 cm strips parallel to the machine direction. Active PET sheet samples and lidding films were sealed between a temperature of 140° and 160°C, and pressure of 6 to 8 bars for 1 second by means of a Brugger Munchen HSG-C heat sealing machine (Brugger Feinmechanik, Munich, Germany). Heat seals were made using flat seal bars covered with a layer of Teflon coating. Heat sealing properties were determined according to the sealing temperature range of 140-160°C which is given in the technical data sheet of the lidding film.

Heat seal strengths of specimens (25.4 mm × 11 mm) were tested by means of a mechanical testing machine Zwick/Roell Z005 (Ulm, Germany) equipped with a 2.5 kN load cell. The crosshead speed was fixed at 100 mm/min, gauge length was 300 mm and pre-load was 0.2 N/mm^2. All measurements were performed triplicates.

2.2.12. Acetaldehyde Content

The GC system was calibrated with standard solutions of known acetaldehyde concentrations. All PET samples were stored in a freezer and ground under liquid

nitrogen to prevent volatilization of the acetaldehyde prior to GC analysis. Ground PET samples of 0.1 g were weighed in 20 ml vials.

The vials were placed into HS TurboMatrix 16 headspace auto sampler (Perkin-Elmer, Shelton, USA). Automatic headspace conditions are as follows; temperature of needle was 155°C, temperature of transfer line was 160°C, oven temperature was 150°C, and equilibration time was set to 1 h with pressurization time of 2 min.

Acetaldehyde contents were analyzed with a Perkin-Elmer CLARUS 500 gas chromatograph (GC) (Shelton, USA) equipped with a flame ionization detector (FID). FID temperature was 250°C, hydrogen flow rate was 45 ml/min and dry air flow rate was 450 ml/min. Gas chromatography column was Elite-1 (100% dimethyl polysiloxane) with a length of 30 m, inner diameter of 0.32 mm and film thickness of 5.0 µm. Column temperature was held at 95°C for 8 min, then increased to 200°C at a rate of 10°C/min and held at 200°C for 1 min. Column pressure was 15 psi Nitrogen and split was 50 ml/min. Measurements were carried out in duplicates.

2.2.13. Overall Migration Tests

According to the current European legislation, overall migration studies were performed to assess the safety of active PET sheets. For demonstration of compliance for plastic materials and articles not yet in contact with food, overall migration tests were carried out in accordance with EN 1186-9 with food simulant D_1 (ethanol 50%, v/v), EN 1186-2 with food simulant D_2 (vegetable oil), EN 1186-9 with food simulant A (ethanol 10%, v/v) and EN 1186-3 with food simulant B (acetic acid 3%, w/v). Overall migration tests were performed at 40°C for 10 days.

3. RESULTS AND DISCUSSION

3.1. Intrinsic Viscosity

Intrinsic viscosity measurements were carried out in raw materials and produced PET sheets (Table 3.1) in order to determine degradation of PET that could occur during extrusion due to high temperatures and high shear values in the extruder. There is a significant ($p \leq 0.05$) IV change in extruded PET sheets compared to the IV values of the PET raw materials. This means that there could be a change in molecular weights of the PET raw materials and extruded PET sheets. This could be due to the high extrusion temperature and high shear values in the extruder that caused some degradation in the extruded PET sheets. There was no significant ($p > 0.05$) change among the IV values of active PET sheets. This means that degradation is almost in the same extent in all the active PET sheets. Standard PET sheet has a higher IV value than the active PET sheets. This could probably be due to the partial oxidation of the oxygen scavenger in the active PET sheets. However, when the amount of the oxygen scavenger is increased in the active sheets, there is no change in the IV values indicating that the amount of the oxygen scavenger does not have any effect on the degradation or loss in molecular weight.

Table 3.1: Intrinsic viscosity of PET raw materials and PET sheets.

	IV value (dL/g)*
Polyshield 2300K PET (after drying)	0.814^{a}
Koksan PET BGC 80 (after drying)	0.806^{a}
Standard PET sheet	0.738^{b}
Trial 1	0.702^{c}
Trial 2	0.706^{c}
Trial 3	0.701^{c}
* Average standard deviations are ±0.01.	

Galdi et al produced 30 μm monolayer active PET films with different concentrations of oxygen scavenger (1%, 3% and 5% by weight) in a laboratory scale extruder. They observed that there was no significant ($p > 0.05$) change between the IV values of the extruded PET sheets and PET raw material. The reason of this difference could likely be due to the extruder and extruder conditions. In our study, industrial scale extruder was used having a screw length of 5150 mm and L/D of 34 for the main extruder and a screw length of 2640 mm and L/D of 38 for the auxiliary extruder where Galdi et al used a laboratory scale extruder with a screw length of 288 mm and L/D of 24. The retention time in our extruder is longer than the retention time of the extruder used by Galdi et al. Longer retention times cause more IV drop. PET grade could also affect the IV value. In our study, bottle grade PET resin with higher crystallinity and having an IV value of 0.80 dL/g was used while Galdi et al used an amorphous PET resin having a lower IV (0.58 gL/g). The final IV values for the active PET sheets for this study changed between 0.701-0.706 dL/g while the IV values of the active films produced by Galdi et al were between 0.56-0.58 dL/g. Much higher IV values obtained for the active PET sheets produced in this work showed that active PET sheets have higher molecular weight than the active PET films produced by Galdi et al. Increasing the concentration of oxygen scavenger did not show any significant ($p > 0.05$) difference in the IV values of active PET sheets. This result is in good agreement with the results of Galdi et al who also found that IV change in active PET films was not affected by the amount of oxygen scavenger in the film [Galdi et al., 2008].

Galdi and Incarnato produced active PET films with a thickness of 35 μm and investigated the effect of higher oxygen scavenger concentrations (5%, 10% and 20% by weight) on the IV values of PET films produced with the same raw materials and the same conditions used by Galdi et al. There was no significant ($p > 0.05$) difference among the IV values of PET films containing 5% and 10% oxygen scavenger with the PET raw material. On the other hand, the PET film with 20% oxygen scavenger showed significant ($p \leq 0.05$) reduction in IV value which indicates molecular loss during extrusion. The reason of this drop in IV value was reported to be the presence of water in the oxygen scavenger [Galdi and Incarnato, 2011].

3.2. Optical Properties

The optical properties of the active sheet samples with PET//PE/EVOH/PE and standard PET samples are given in Table 3.2. It is clear that there is no distinct difference in clarity between standard PET and active PET sheets also with PET//PE/EVOH/PE. When the haze values of the samples were compared, it is seen that haze values of active PET sheets are higher than standard PET but it is significantly ($p \leq 0.05$) lower than PET//PE/EVOH/PE laminated sheet. For active PET sheet increment in the haze probably due to the presence of the oxygen scavenger in the matrix which is large enough to be detected by the haze meter. High haze values of PET//PE/EVOH/PE sheet are due to its multilayer structure including EVOH and PE. Galdi et al reported that adding 5% oxygen scavenger Amosorb DFC 4020 (supplied by ColorMatrix Europe Ltd, Knowsley, UK) to the PET matrix (PET Cleartuf P60 amorphous, supplied by MG Polimeri Italia S.p.A, Italy) increased the film haze from 3±0.2% to 5±0.9% where the film thickness was just 30 μm [Galdi et al., 2008]. Tibbit et al also reported that haze increases as the oxygen scavenger concentration in the PET matrix increases for a PET bottle. To produce an active PET bottle, they prepared an oxygen scavenging concentrate by reactive extrusion process. Oxygen scavenging composition was 88 wt% PET (Shell 8416), 10 wt% polybutadiene oligomer, 1 wt% pyromellitic dianhydride (PMDA), 1000 ppm cobalt as transition metal catalyst, and 100 ppm benzophenone. Then, oxygen scavenging concentrate directly blended with PET raw material (Shell 8416) on an injection press with different concentrations (Oxygen scavenging concentrate levels 1, 2, 4, and 6%). Preforms were blow molded on a blow molding machine to produce 20 oz. bottles. In the haze measurement from the side wall of active monolayer PET bottle, they have found haze as 1.4%, 2.9%, 5% and 8.4% for active monolayer PET bottle with oxygen scavenging concentrate levels 1%, 2%, 4% and 6%, respectively. Haze values were increased when the weight percent of the oxygen scavenger concentrate increased in the final packaging article which is in good agreements with our findings [Tibbit et al., 2008].

When the total transmittance values of the active PET trials were compared with PET and PET//PE/EVOH/PE, it is seen that total transmittance of active PET trials are lower than standard PET, nevertheless it is higher than PET//PE/EVOH/PE. The same

situation is valid also for gloss, active PET sheet gloss values are between standard PET and PET//PE/EVOH/PE sheets.

Table 3.2: Optical properties of sheet samples.

Optical Property	Standard	Unit	Standard PET	PET// PE/EVOH/PE	Trial 1	Trial 2	Trial 3
Clarity	ASTM D 1003	%	98.3	96.5	98.5	97.4	98.1
Haze	ASTM D 1003	%	3.75	10.65	5.79	6.37	4.86
Total Transmittance	ASTM D 1003	%	88.9	79.5	85.3	80.3	84.8
Gloss	ASTM D 2457	GU	127.6	98.3	117.7	109.5	117.5
Average standard deviations are ±0.4 for clarity, ±0.1 for haze, ±0.2 for total transmittance and ±3 for gloss.							

3.3. Color Measurement

Color measurement of active PET sheet samples are presented in Table 3.3 according to CIE L*a*b* color scale. It is observed that active PET sheets have the same brightness (L*) with PET//PE/EVOH/PE and have lower brightness than standard PET. This reduction could be promoted by oxygen scavenger. When the L* (Brightness) of the active PET sheets are compared, it is seen that brightness of active sheets decreased when the weight percent of the oxygen scavenger increased. Regarding the b* (yellowness (+) or blueness (−)) values, active sheets are less yellow or more blue than standard PET and PET//PE/EVOH/PE. Among the active PET trials, it is seen that by the increasing amount of oxygen scavenger blueness increased even more. The reason behind the b* variation mainly depends on the raw materials used. As it is given in Appendix, Polyshield 2300K which comprise more than 75% of active sheets have blueness more than Koksan BGC 80 which comprises more than 99% of standard PET sheet. Combination of Oxyclear 3500 and Polyshield 2300K during extrusion caused further rise in b* value. When a* (redness (+) or greenness (−)) values of active PET sheets with PET and PET//PE/EVOH/PE are compared, it is seen that active PET sheets are more red than reference samples and as the weight percentage

of oxygen scavenger increased redness of active PET sheets increased. Besides the color measurement, from a visual observation active PET sheets have a quiet bluish effect. It is thought that this effect comes from Polyshield 2300K PET raw material used in active PET sheets. It might be also due to cobalt catalyst which was used in the scavenger system [Liu et al., 2011].

Liu et al produced high barrier PET bottle with improved clarity. They prepared preforms in an injection molding machine using 24 g of material, and blown into a 0.59 liter contour bottle on a stretch blow molding machine. The bottle sidewall thickness was about 0.25 mm. In order to define the effect of the Co on the yellowness of bottles, series of blends were prepared. 0.84 IV Polyester resin 100% by weight including 0.11 mole% 5-sulfoisophthalic used as control. For first blend 5 wt% MXD6 was added to the polyester resin, for second blend 100 ppm Co was added and for third one 200 ppm Co and 5 wt% MXD6 was added. The b* (yellowness (+) or blueness (−)) value was 4.6 for the control and it was increased with adding MXD6 to 5.2 which means yellowness was increased. Nevertheless, for second and third blend, yellowness apparently decreased with the effect of Co. For second blend b* was 1.1 and for third blend b* was 2 even it includes MXD6 which have a negative effect on yellowness. Effect of Co on blueness or yellowness is in good agreement with our findings [Liu et al., 2011].

Table 3.3: Color values of PET sheets.

Color space in CIE	Abbr	Standard PET	PET// PE/EVOH/PE	Trial 1	Trial 2	Trial 3
Brightness	L*	94.28^{a}	90.13^{b}	90.64^{b}	88.81^{c}	90.85^{b}
Redness (+) / Greenness (-)	a*	-0.52^{a}	-1.29^{b}	$+0.43^{c}$	$+1.45^{d}$	$+0.58^{c}$
Yellowness (+) / Blueness (-)	b*	$+4.92^{a}$	$+4.97^{a}$	$+4.77^{b}$	$+3.23^{c}$	$+4.79^{b}$
Values within the same row $p \leq 0.05$ are significantly different. Average standard deviations are less than ±0.1 for L*, a* and b*.						

3.4. Thermal Behavior

PET is a semi-crystalline polymer and its degree of crystallinity can be modified by changing the processing conditions and the amount of the additives. Especially, the presence of particles can act as nucleating agents and affect the crystalline structure [Galdi et al., 2008]. Thermal properties of the PET sheets are presented in Table 3.4.

Table 3.4: Thermal properties of PET sheets.

Sample	T_g (°C)	T_m (°C)	T_c (°C)	ΔH_c (J/g)	ΔH_f (J/g)	Crystallinity (%)
Standard PET	68.33	246.20	135.12	16.47	28.22	8.39
Trial 1	60.88	247.56	146.24 – 117.61	2.07 – 15.97	33.03	10.70
Trial 2	61.83	246.42	144.56 – 119.42	2.11 – 13.13	26.20	10.68
Trial 3	61.32	246.99	146.24 – 118.28	2.36 – 15.78	33.51	10.98

The calorimetric analysis does not show significant ($p > 0.05$) differences in T_m between reference sheet and active PET sheets. However, Trials with oxygen scavenger showed significantly ($p \leq 0.05$) lower T_g than the standard PET. The reason of the difference is mainly due to the low T_g value of Polyshield 2300K which is only used in active PET trials and it forms more than 77% of the active PET sheets. Galdi et al analyzed T_m and T_g values of monolayer active PET films in which 1wt%, 3 wt% and 5 wt% oxygen scavenger (Amosorb DFC 4020 supplied by ColorMatrix Europe Ltd, Knowsley, UK) was blend with PET raw material PET (Cleartuf P60 amorphous, supplied by MG Polimeri Italia S.p.A. ,Italy). They did not find evident differences in T_g and T_m values between the films containing the scavenger and pure PET film [Galdi et al., 2008]. Their findings regarding the T_m are in accordance with our results however, T_g results differ. The reason behind this dissimilarity is due to the second PET raw material Polyshield 2300K which was used in active PET sheets as mentioned. In the reference study, different from our study only one PET raw material (Cleartuf P60) was used in both pure PET film and active films.

Crystallization temperature (T_c) of standard PET and active PET sheets found different which is evident in the thermograms given in Figure 3.1. Standard PET sheet in which only Koksan BGC 80 PET resin was used have one Tc. However, active PET sheets showed two peaks due to two different resins used. It is clearly seen that the peak for Polyshield 2300K has bigger area rather than PET BGC 80 due to its high weight percentage in active PET sheets. On the other hand, it is seen that T_c value of PET BGC 80 increased apparently with using oxygen scavenger as 3 wt% and 5 wt% which is consistent with study related with oxygen scavenging PET films including the same amount of oxygen scavenger [Galdi et al., 2008]. Between the active PET sheets, Koksan BGC 80 gave similar T_c and also Polyshield 2300K has similar T_c which means that the change in the oxygen scavenger amount did not affect the crystallization temperature significantly ($p > 0.05$).

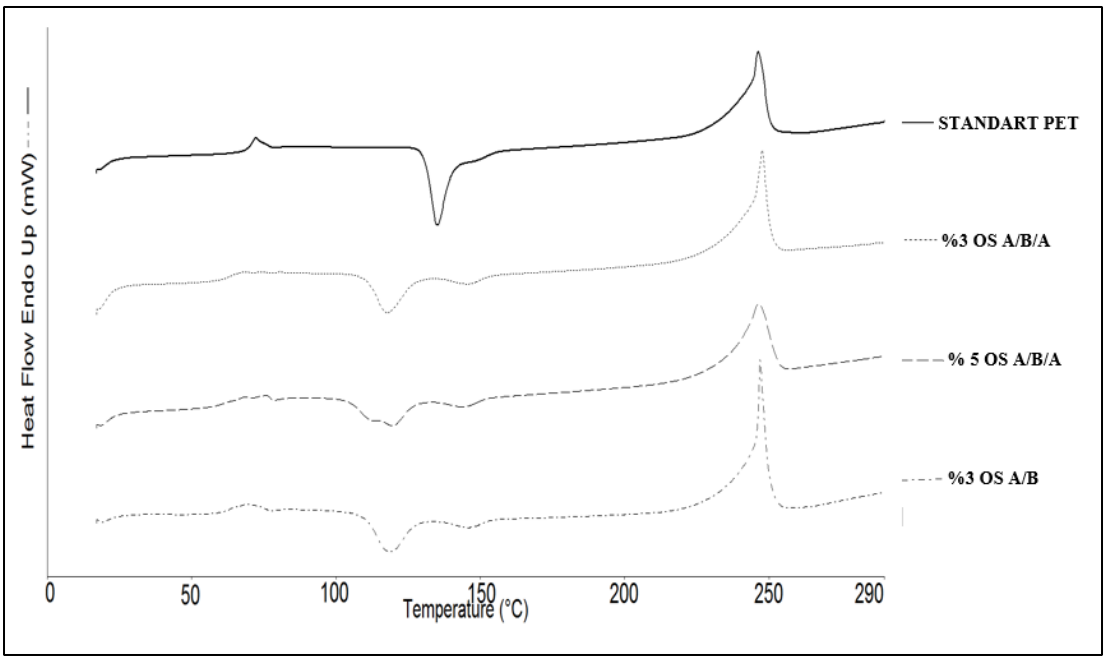

Figure 3.1: Comparison of the DSC thermograms for standard PET sheet and active PET sheets.

The crystallinity of the active PET sheets is higher than standard PET sheet. It increased from 8.4% to 10.7-11% with adding oxygen scavenger to the PET matrix. These results suggest that oxygen scavenger can behave as a nucleating agent in PET crystallization. It is also observed that crystallinity did not change significantly with the amount of oxygen scavenger (3 wt% - 5 wt%). These findings are consistent with active PET film study including 1 wt%, 3 wt% and 5 wt% oxygen scavenger [Galdi et

al., 2008]. It is possible to observe that with the same amount of oxygen scavenger for sandwich and asymmetrical structures crystallinity was found to be almost the same which supports the nucleating effect of the oxygen scavenger.

3.5. Tensile Properties

Elastic modulus, tensile strength and elongation at break of active PET samples were investigated in machine direction and transverse direction in comparison with standard PET and PET//PE/EVOH/PE. Elastic modulus of each samples are given in Figure 3.2.

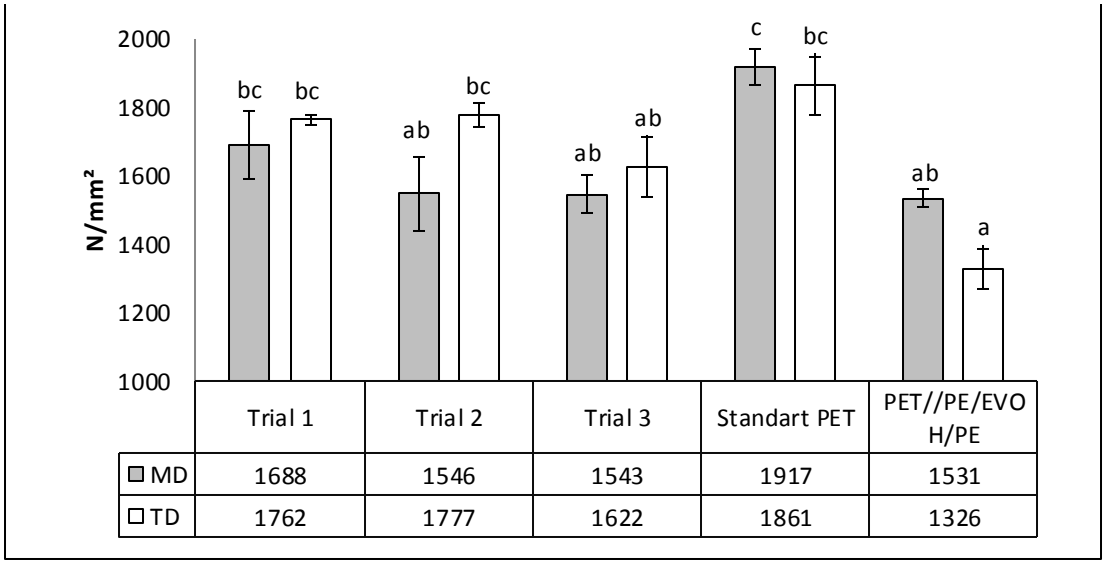

Figure 3.2: Elastic modulus of active PET sheets and reference samples in machine and transverse directions. The vertical bars indicate the average standard error of the mean. Bar plot of means for each level of the independent variable of a one-way analysis of variance (ANOVA). Bars with different letters are significantly different (Tukey's HSD, $p \leq 0.05$).

The elastic modulus values of active PET sheets are remarkably lower than standard PET. This is mainly because of the tensile properties of PET resin Polyshield 2300K used in active layer. Moreover, PET//PE/EVOH/PE laminated sample have the lowest elastic modulus in all samples. It may be attributed to the flexible form of PE/EVOH/PE film laminated on PET sheet. Considering that the amount of oxygen scavenger also influence on the elastic modulus. When Trial 1 and Trial 2 are compared, in machine direction there is significant reduction in Trial 2 but it has no effect in transverse direction. We may expect this result to originate from oxygen

scavenger orientation by considering that the structure has also an influence on mechanical properties. Even, Trial 1 and Trial 3 have the same oxygen scavenger concentration, Trial 3 with its asymmetrical structure have elastic modulus less than Trial 1. This variation may be explained by the fact that the location of Polyshield 2300K PET resin and when it was at the surface in A/B structure it decreased elastic modulus more than in A/B/A structure where it remained in between standard PET resin.

Tensile strength of active PET and reference samples are presented in Figure 3.3.

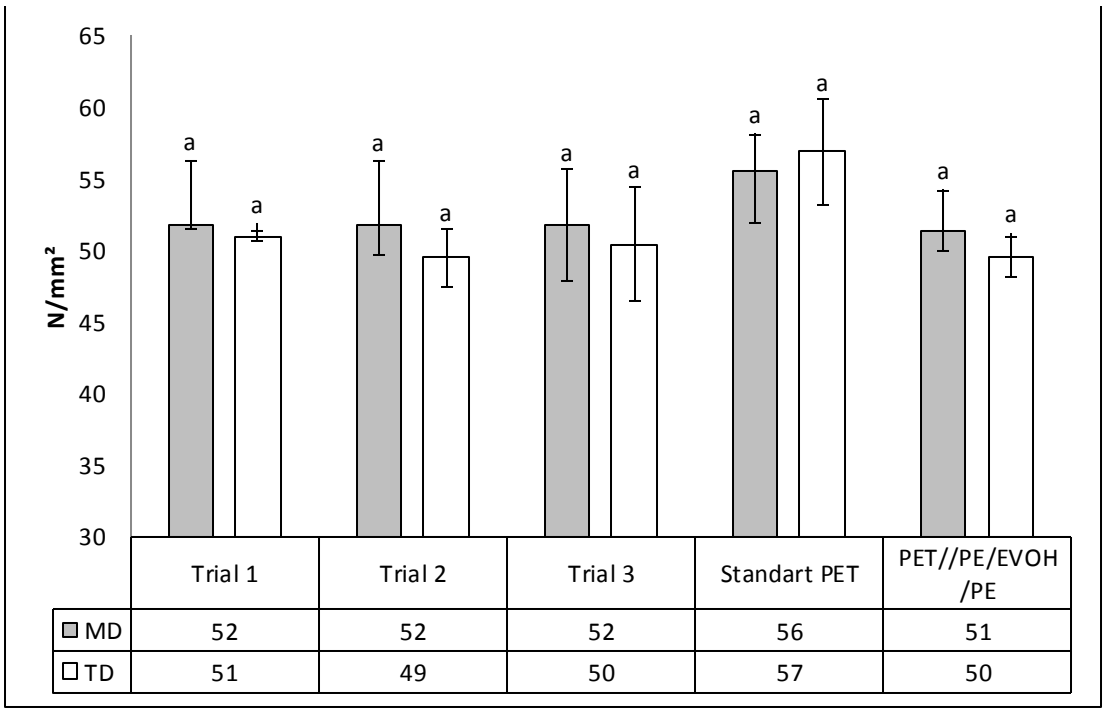

Figure 3.3: Tensile strength values of active PET sheets and reference samples in machine and transverse directions. The vertical bars indicate the average standard error of the mean. Bar plot of means for each level of the independent variable of a one-way analysis of variance (ANOVA). Bars with different letters are significantly different (Tukey's HSD, $p \leq 0.05$).

Tensile strengths of active PET sheets are apparently lower than standard PET both in machine direction and transverse direction like elastic modulus. This difference may be attributed once again to the tensile properties of PET raw material Polyshield 2300K which was used in active sheets only. PET//PE/EVOH/PE laminated sample have even lower tensile strength than active PET samples. This may be explained by the stiffness of PE/EVOH/PE film which comprises important part of PET//PE/EVOH/PE. As the stiffness decreases tensile strength decreases. PE has

lower stiffness than PET; thus, it decreases the tensile strength of the total structure. Besides, concerning the tensile strength of active PET sheets, it is seen that trials are very similar among themselves. It can be said that oxygen scavenger concentration up to 5% and their structure (A/B or A/B/A) do not significantly ($p > 0.05$) affect tensile strength of the active sheets neither in machine direction nor in transverse direction.

The tensile strain of break of active PET and reference samples are shown in Figure 3.4.

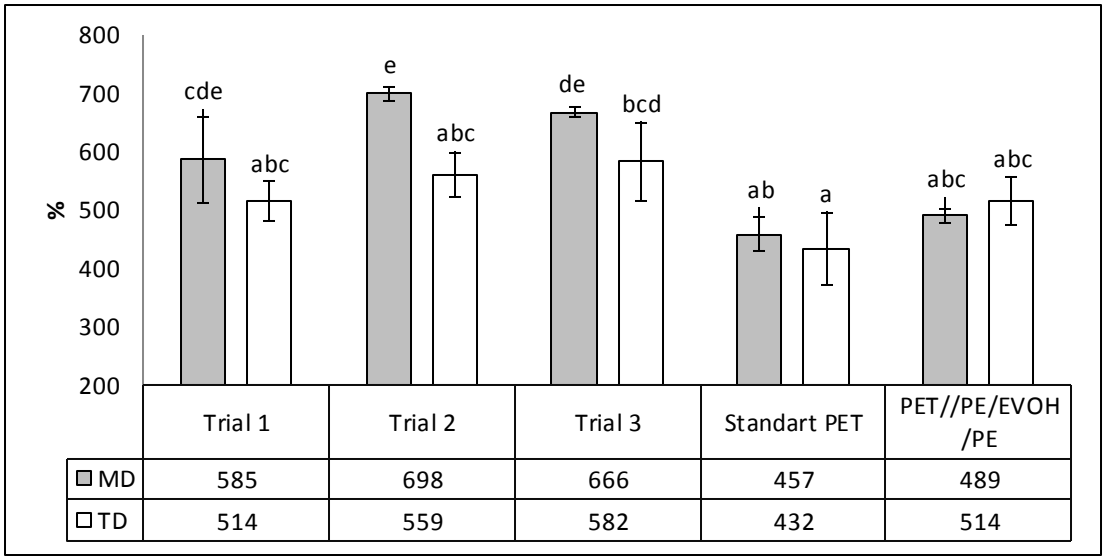

Figure 3.4: Elongation at break values of active PET sheets and reference samples in machine and transverse directions. The vertical bars indicate the average standard error of the mean. Bar plot of means for each level of the independent variable of a one-way analysis of variance (ANOVA). Bars with different letters are significantly different (Tukey's HSD, $p \leq 0.05$).

Concerning elongation at break, it is clearly seen that active PET sheets have significantly ($p \leq 0.05$) higher values than both standard PET and PET//PE/EVOH/PE. These difference may be ascribed again to the mechanical properties of PET resin Polyshield 2300K which was used only in active PET sheets. The increase in the amount of oxygen scavenger in active PET sheets (Trial 1 and Trial 2) resulted in an increase in the elongation at break for both in machine and transverse direction. This result clearly indicates that oxygen scavenger amount between 3-5 wt% is directly proportional with the elongation. This performance may be attributed to particles in the oxygen scavenger additive. The structure has also influence on mechanical properties as mentioned before. Even, Trial 1 and Trial 3 have the same oxygen scavenger concentration, due to its asymmetrical structure where Polyshield 2300K

resin is in the surface layer, Trial 3 elongated more than Trial 1 at break. This may be explained by the fact that Polyshield 2300K resin governs the stiff behavior of standard PET resin Koksan BGC 80. In the literature, there was no data about tensile properties of oxygen scavenging PET based packaging material for comparison.

In conclusion, considering all mechanical properties given, due to its relatively high elongation at break and low tensile strength, it can be said that active PET sheets have high toughness than standard PET and even better than PET//PE/EVOH/PE. This property will give an advantage for active PET packaging material with regard to breakage problem during transportation or storing at lower temperatures on the shelves like + 4°C or - 10°C.

3.6. Tensile Impact Energy

Tensile impact energies of active PET sheets were tested in comparison with standard PET sheet and PET//PE/EVOH/PE. The average tensile impact strengths of sheet samples are given in Figure 3.5.

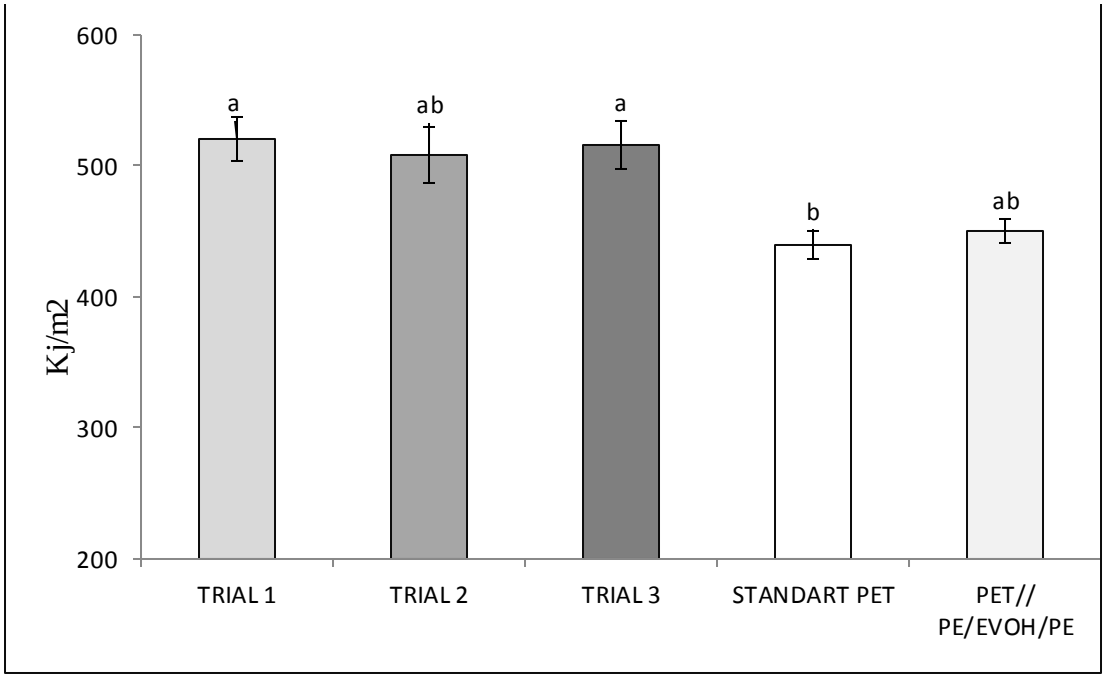

Figure 3.5: Tensile impact energies of active PET sheets, standard PET sheet and PET//PE/EVOH/PE sheet. The vertical bars indicate the average standard error of the mean. Bar plot of means for each level of the independent variable of a one-way analysis of variance (ANOVA). Bars with different letters are significantly different (Tukey's HSD, $p \leq 0.05$).

When the tensile impact energies of sheet samples were analyzed, favorable and significant ($p \leq 0.05$) improvement in the tensile impact strength of active PET sheets is observed. It can be said that the improvement observed in the tensile impact strength of sheet is mainly due to the Polyshield 2300K resin which was used in the active layer as the tensile properties. Increasing the amount of oxygen scavenger from 3 wt% to 5 wt% in active PET sheets (Trial 1 and Trial 2) resulted in a slight decrease in the tensile impact energy. The structure (A/B/A or A/B) did not influence the tensile impact energy. There was no data about tensile impact strength of active oxygen scavenging PET based material in the literature for comparison. But, findings in tensile impact energy are consistent with results of tensile properties.

3.7. Optical Microscopy Analysis

The multilayer coextruded sheets were investigated by optical microscope in order to verify the uniformity of the layer's shape and thickness, which play a key role in the development of the overall sheet properties. The optical microscopy analysis was performed on all the symmetric, asymmetric and reference structures produced according to the formulations specified in the Table 3.1.

The relative layer thicknesses measured by the optical microscope on all produced PET sheets are fairly in accordance with the corresponding structures. Color differences in each trial can be examined from Figures 3.6 to 3.16 by considering different polarization during optical microscope adjustment.

Figures 3.6, 3.7 and 3.8 refer to the image taken on Trial 1 from left edge, middle and right edge. The optical microscopy observations clearly show that Trial 1 has layers with flat interfaces and almost constant thickness along the transversal sheet section.

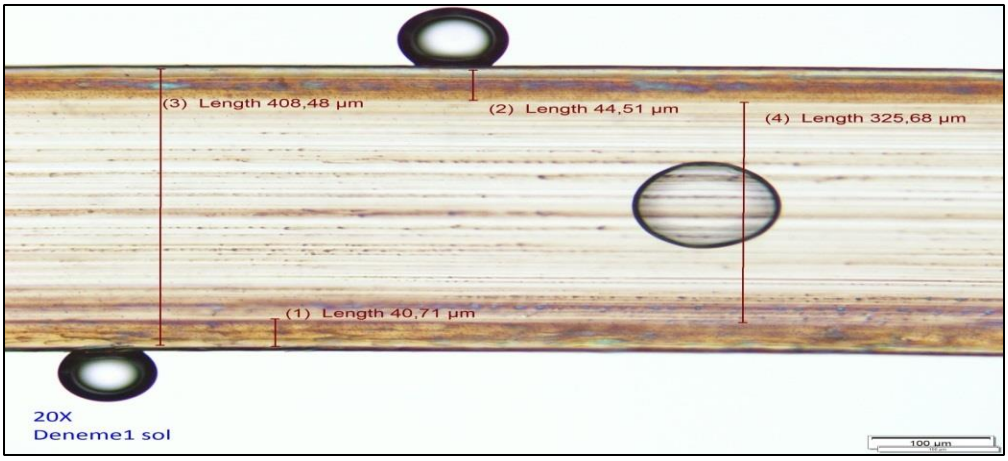

Figure 3.6: Optical microscopy image of the active three-layer film (Trial 1) from left side (section normal to the extrusion direction, magnification 20X).

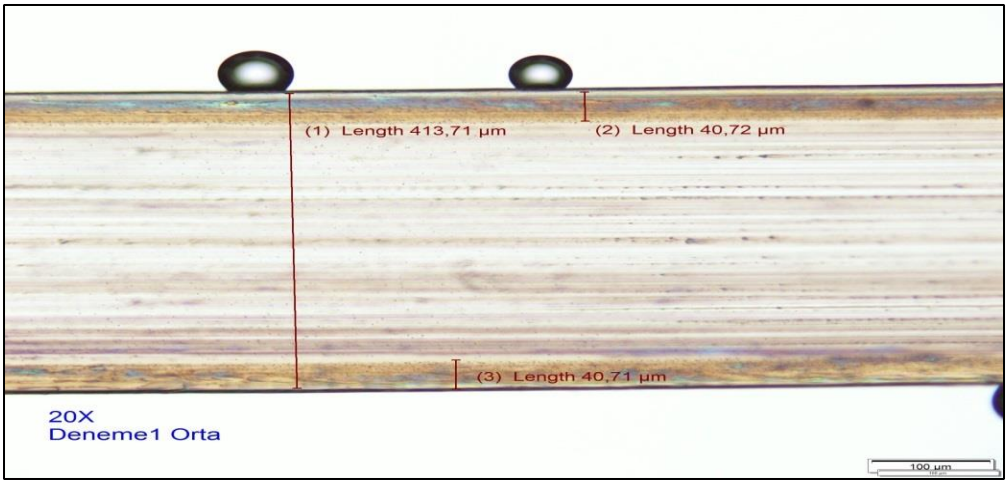

Figure 3.7: Optical microscopy image of the active three-layer film (Trial 1) from middle (section normal to the extrusion direction, magnification 20X).

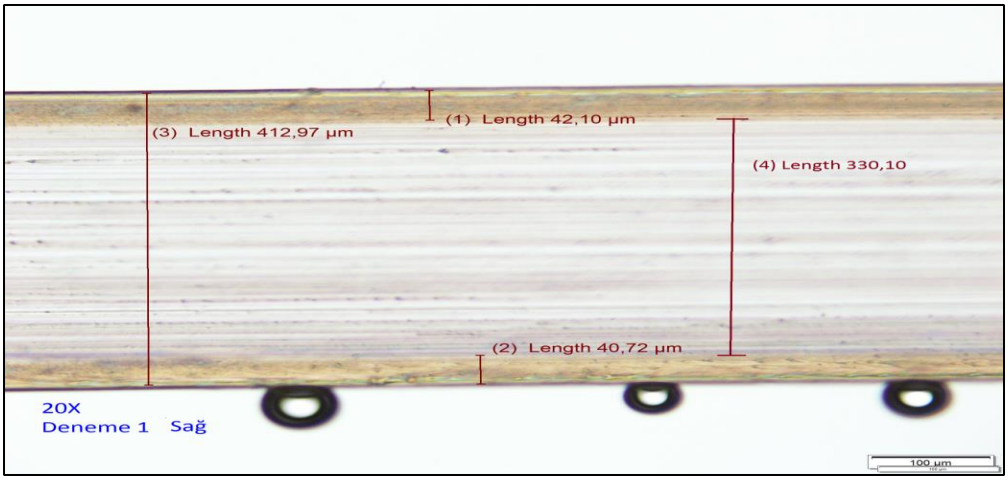

Figure 3.8: Optical microscopy image of the active three-layer film (Trial 1) from right side (section normal to the extrusion direction, magnification 20X).

Figures 3.9, 3.10 and 3.11 show the image taken on Trial 2 from left edge, middle and right edge. The optical microscopy results show that Trial 2 has layers with flat interfaces and almost constant thickness along the transversal sheet section as well.

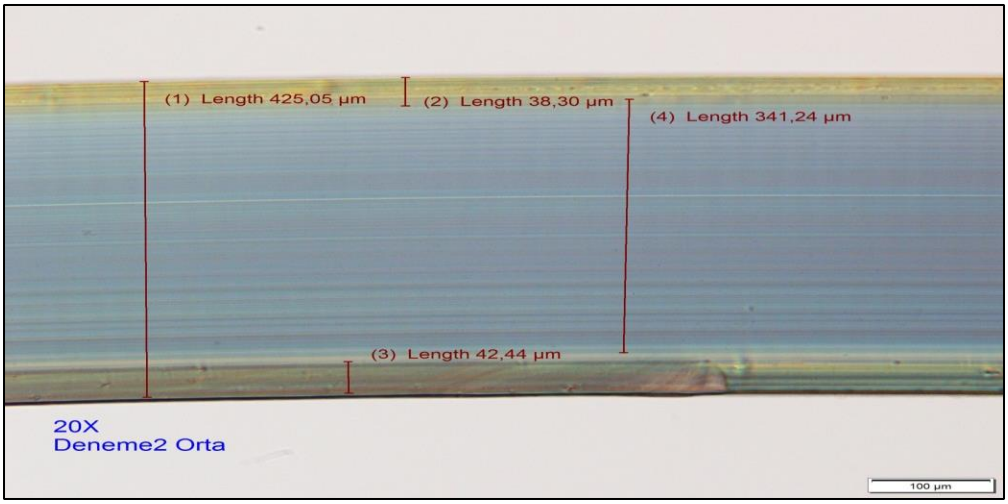

Figure 3.9: Optical microscopy image of the active three-layer sheet (Trial 2) from left side (section normal to the extrusion direction, magnification 20X).

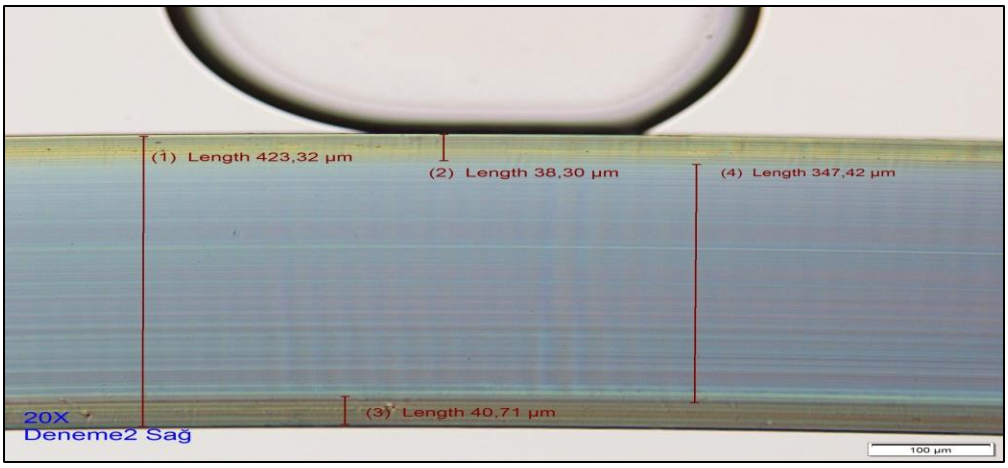

Figure 3.10: Optical microscopy image of the active three-layer sheet (Trial 2) from middle (section normal to the extrusion direction, magnification 20X).

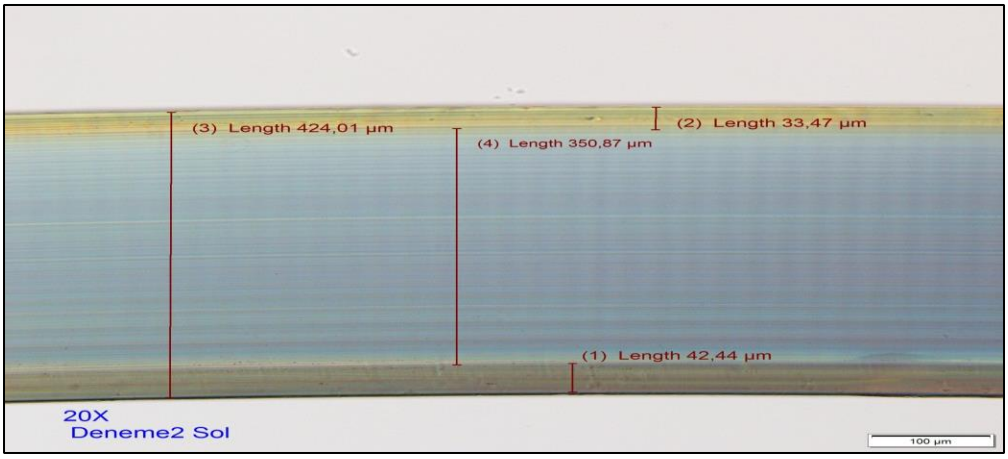

Figure 3.11: Optical microscopy image of the active three-layer sheet (Trial 2) from right side (section normal to the extrusion direction, magnification 20X).

Figures 3.12, 3.13 and 3.14 show the image taken on Trial 3 from left edge, middle and right. The optical microscopy observations shows that Trial 3 has layers are in agreement with the set values with flat interfaces and almost constant thickness along the transversal sheet section.

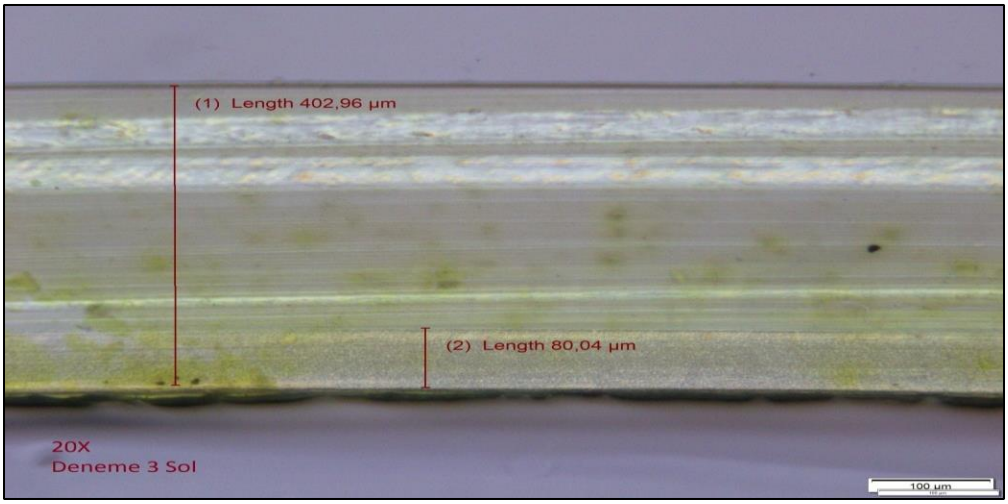

Figure 3.12: Optical microscopy image of the active two-layer sheet (Trial 3) from Left Side (section normal to the extrusion direction, magnification 20X).

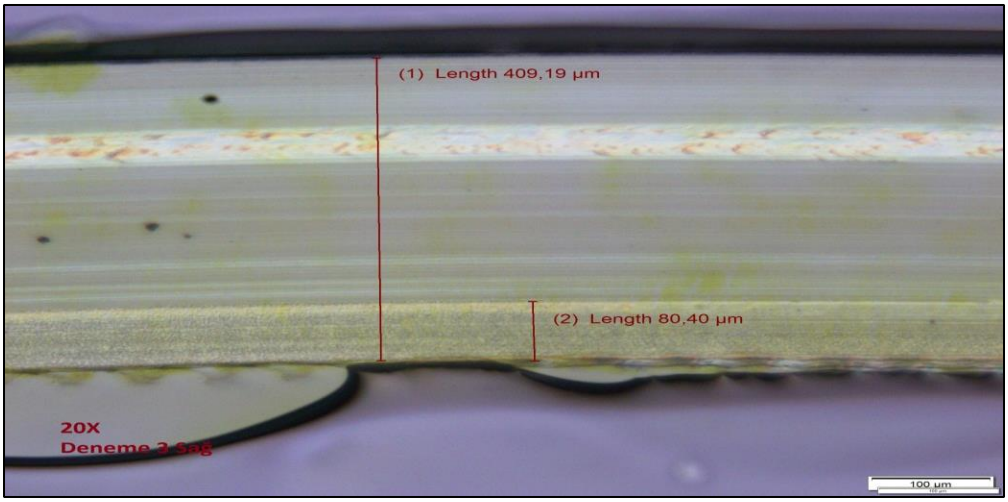

Figure 3.13: Optical microscopy image of the active two-layer sheet (Trial 3) from middle (section normal to the extrusion direction, magnification 20X).

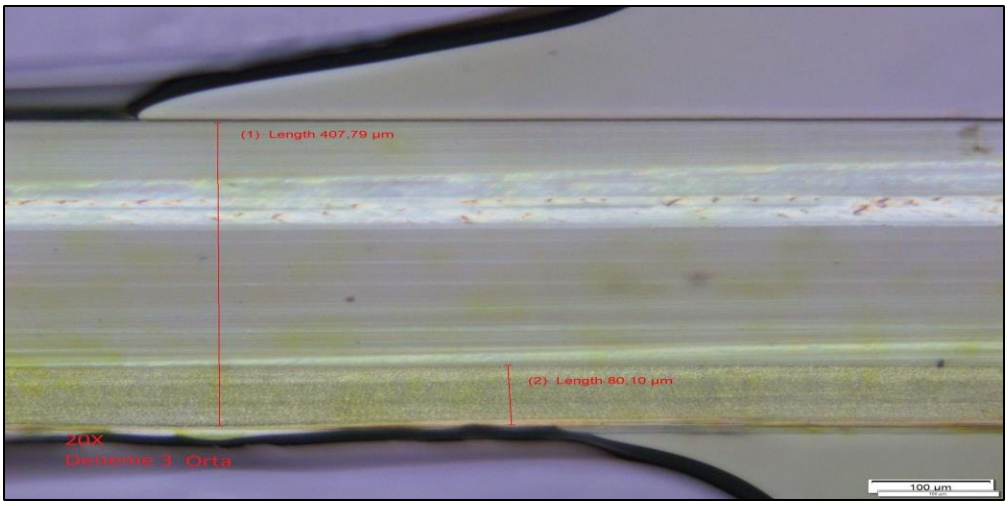

Figure 3.14: Optical microscopy image of the active two-layer sheet (Trial 3) from right side (section normal to the extrusion direction, magnification 20X).

Similar findings were reported by Di Maio et al. They performed a preliminary study on the layer distribution during the coextrusion process before producing three-layer active PET films to calibrate and optimize the relative layer thickness and distribution. At this regard, the external layers of neat PET were colored with 0.1 wt% of red masterbatch (RENOL-ne/C, supplied by Clariant), so that the three layers were well distinguishable in the films. Therefore, their relative thicknesses were measured by optical microscope analyses. The optical microscope observations showed that, co-extruded films have layers almost constant gauge thickness along the transversal film section with small deviations. The small deviations thought to be related with the change in the viscoelastic response of the PET resin because of oxygen scavenger

addition [Di Maio et al., 2015]. It can be said that, our findings are in good agreement with their findings.

Figure 3.15 shows the image from standard PET sample. Although it has A/B/A structure, layers cannot be seen separately. This may be explained by the fact that only one PET resin (Koksan BGC 80) was used in each layer and it was not possible without adding colorant to the surface layers. However, it is seen that total thickness is in accordance with the set thickness.

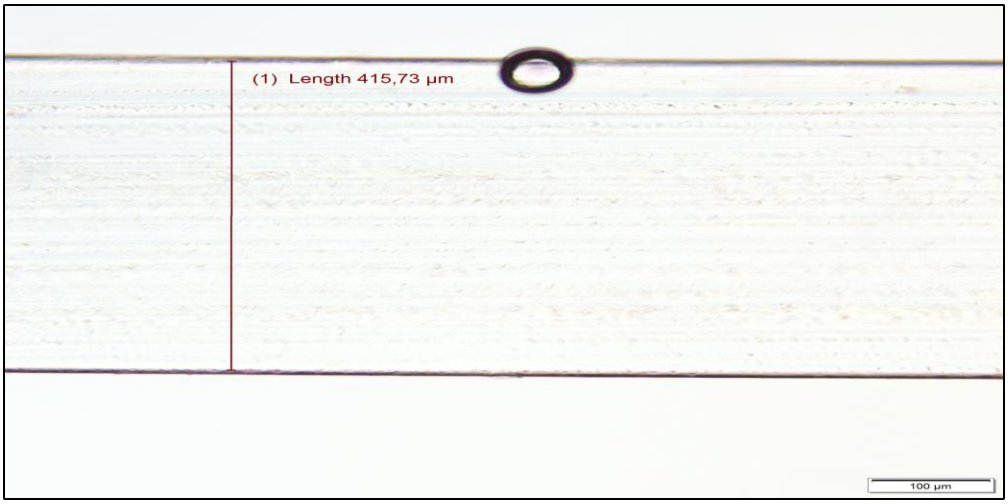

Figure 3.15: Optical microscopy image of the standard PET sheet (section normal to the extrusion direction, magnification 20X).

Optical microscopy image of PET//PE/EVOH/PE film was given in Figure 3.16. It is clear that layer thicknesses are again well matched with set thicknesses.

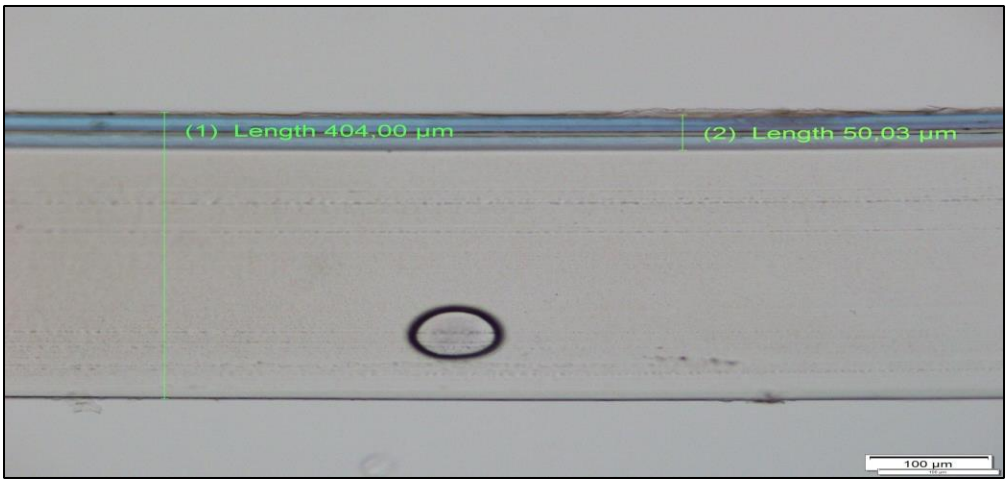

Figure 3.16: Optical microscopy image of the PET//PE/EVOH/PE sheet (section normal to the extrusion direction, magnification 20X).

Di Maio et al stated that activity of monolayer films saturates in few days because of the fast reaction with oxygen of the active phase [Di Maio et al., 2015]. To avoid fast reaction time active PET-based sheets, multilayer active PET sheets were designed and the thickness and thickness deviation of passive layer became very important. Table 3.5 shows the set values of each layer thickness and actual values (average values are calculated from three sample) of active sheets. It is clearly observed that actual values are fairly in line with set values.

Table 3.5: Layer thicknesses of active PET sheets.

Nomenclature	Structure	Set Layer Thickness (µm)	Actual Layer Thickness (µm)
Trial 1	Sandwich A/B/A	40/320/40	42.4/329.4/40.7
Trial 2	Sandwich A/B/A	40/320/40	36.7/346.5/41.9
Trial 3	Asymmetric A/B	80/320	80.2/326.5

3.8. Oxygen Barrier Properties

In order to investigate the oxygen barrier properties, all active PET sheets were submitted to oxygen permeability measurements in comparison with reference sheets (standard PET and PET//PE/EVOH/PE sheets). The oxygen transmission rates with respect to time for standard PET and PET//PE/EVOH/PE samples are shown in Figures 3.17 and 3.18, respectively. As it is seen from the figures, after dissolved oxygen moved away from the surface of the sheets, 400 µm standard PET have an oxygen transmission rate of 5.32 cc/(m^2.day) and 400 µm PET//PE/EVOH/PE having better oxygen barrier properties as it was expected and found as 1.76 cc/ (m^2.day).

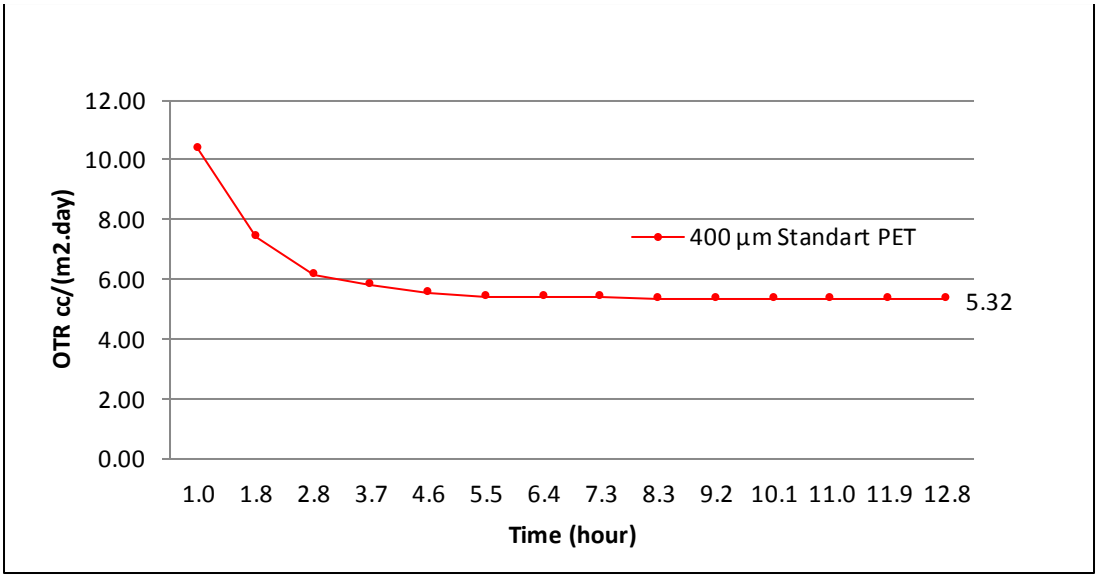

Figure 3.17: Oxygen transmission rate with respect to time for standard PET.

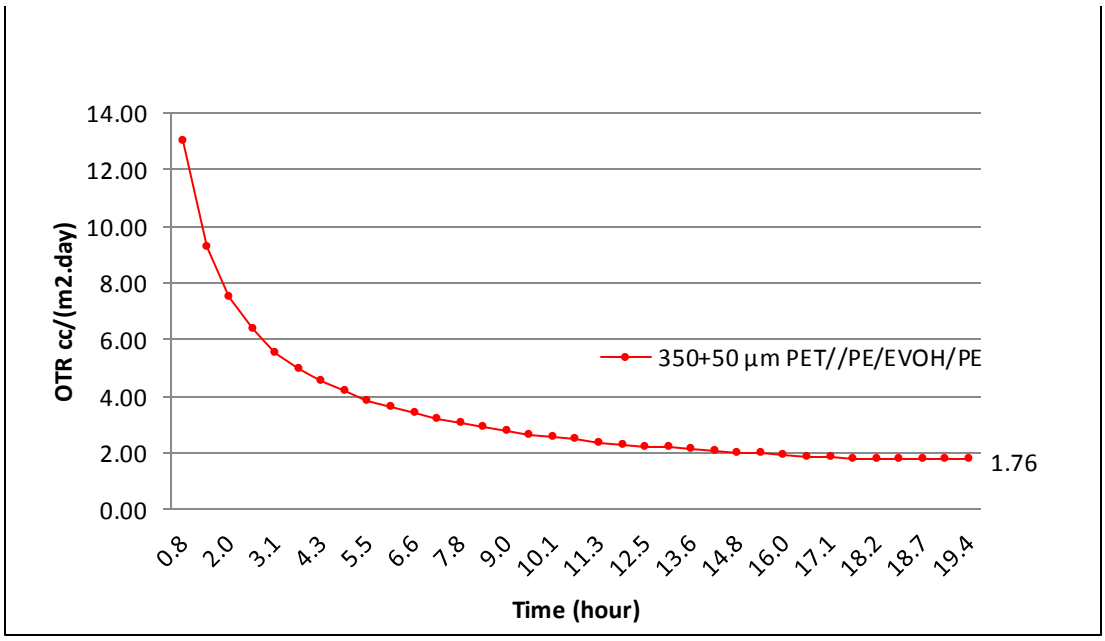

Figure 3.18: Oxygen transmission rate with respect to time for PET//PE/EVOH/PE.

Oxygen transmission rates of the newly produced active PET sheets and PET sheets stored at 6 months were measured at ambient conditions. For fresh samples, scavenger was supposed to be at the highest activity and for 6 months aged samples oxygen scavenger supposed to be partially oxidized. Due to the symmetrical structure of Trial 1 and Trial 2 samples were mounted between the two parts of the test cell regardless of contacting surface with cell parts. On the other hand, Trial 3 which has asymmetrical structure mounted as the passive side is in contact with 99.9% oxygen

test gas. Figure 3.19, 3.20 and 3.21 shows the oxygen transmission rates of fresh samples of Trial 1, Trial 2 and Trial 3, respectively.

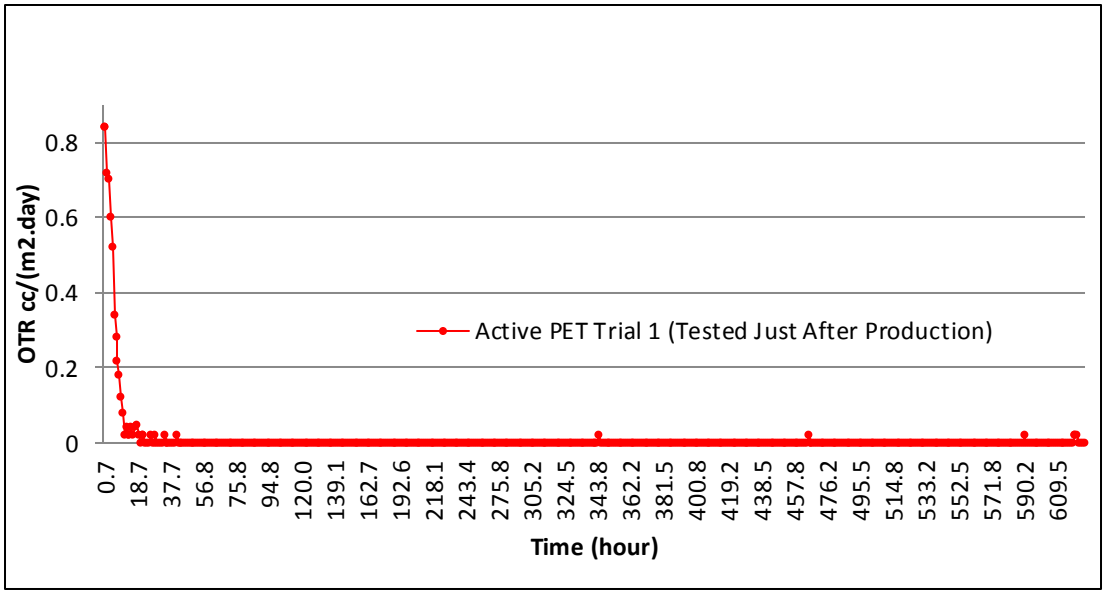

Figure 3.19: Oxygen transmission rate with respect to time for active PET Trial 1 just after production.

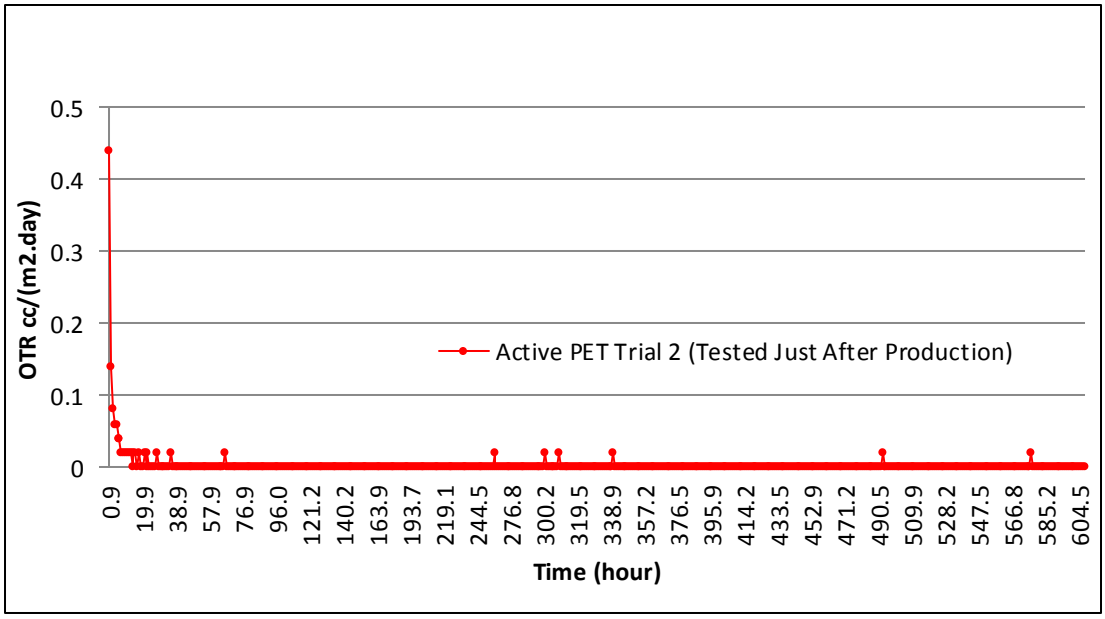

Figure 3.20: Oxygen transmission rate with respect to time for active PET Trial 2 just after production.

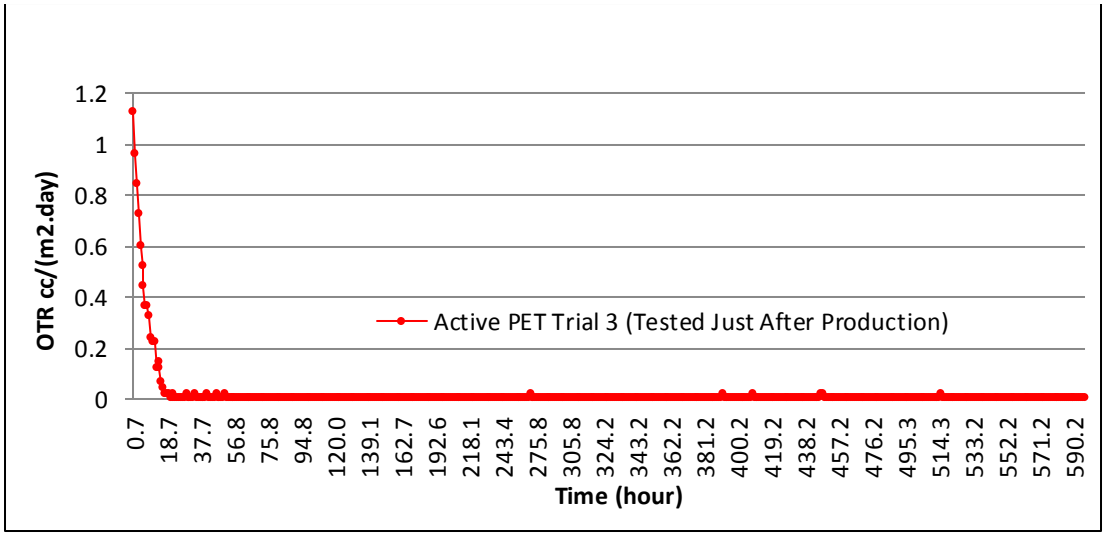

Figure 3.21: Oxygen transmission rate with respect to time for active PET Trial 3 just after production.

Adding 3-5 wt% of oxygen scavenger induced a significant and favorable improvement of the barrier properties of both the sandwich and asymmetrical structure. Oxygen transmission rate of each trials were found as between 0-0.02 cc/(m^2.day) after dissolved oxygen moved away from the cell. And, within 600 hours of measurement period oxygen scavenging activity did not show any decrement. Under atmospheric pressure, %0 RH and at 23 °C all active PET trials' oxygen barrier properties were found as much better than standard PET and PET//PE/EVOH/PE sheets. These results are even much better than our expectations prior to beginning of the study.

Similar to our study Liu et al made an invention about high barrier PET bottles. It comprises a blend of polyester and a partially aromatic polyamide with an ionic compatibilizer and a cobalt salt. This blend was processed into a container that has both active and passive oxygen barrier and carbon dioxide barrier properties at an improved color and clarity. Various polyester (PET) resins reflecting typical commercial recipes were produced. Co-monomers included isophthalic acid and diethylene glycol as crystallization retardants and naphthalene dicarboxylic acid to improve the temperature at which a container can be filled. A masterbatch of the cobalt salt to be used as the transition metal catalyst for active oxygen scavenging was made by addition of 2 wt% cobalt octoate to PET. Partially aromatic nylon used in the blend was Type 6007 from Mitsubishi Gas Chemical, Tokyo Japan. Then, Preforms were prepared on an injection molding machine using 24 g of material, and blown into a

0.59 liter contour bottle on a stretch blow molding machine. The bottle sidewall thickness was about 0.25 mm. In order to define the oxygen transmission rate, series of blends were prepared using selected polyester (having 0.83 dL/g, 2.5 wt% IPA, 1.5 wt% DEG) as the base resin. The concentration of MXD6 used was 1 to 5 wt%, each containing 100 ppm cobalt salt. The oxygen transmission rate through the bottle sidewalls was measured. It was found that there was a surprising reduction in oxygen transmission rate at 5 wt% MXD6. Oxygen transmission rate of the bottle sidewall was found below 0.02 cc/(m^2.day) until 300th hours. However, after 300 hours oxygen scavenging activity decreased and oxygen transmission rate started to increase [Liu et al., 2011].

Furthermore, in order to identify the oxygen barrier properties of active PET sheets after possible partial oxidation, samples were submitted 6 months aging at ambient conditions. After 6 months aging, the oxygen transmission rate of the active PET sheets Trial 1, Trial 2 and Trial 3 were measured and the results plotted in Figure 3.22, 3.23 and 3.24, respectively.

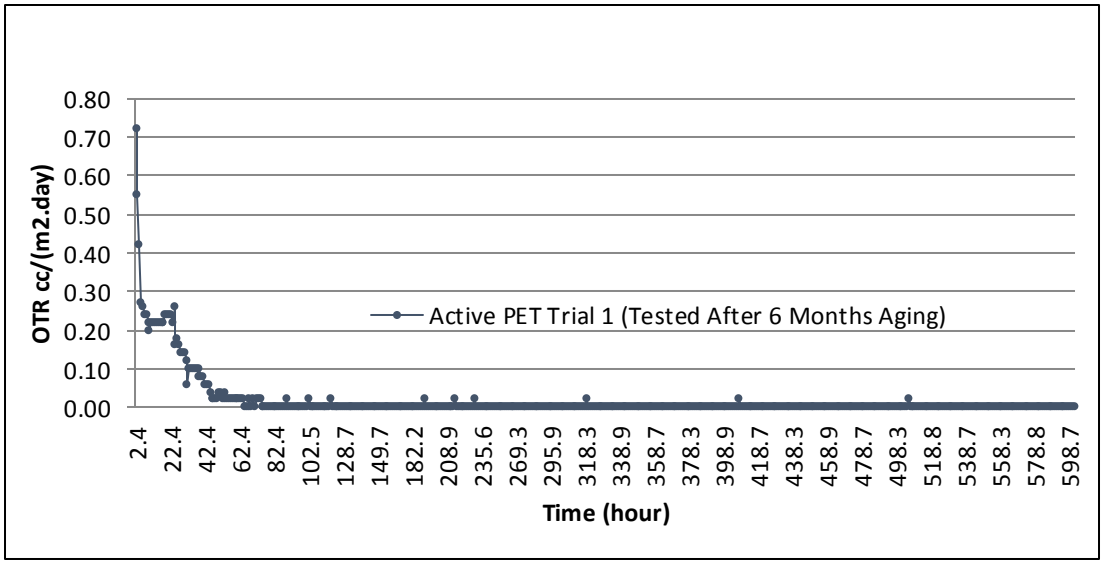

Figure 3.22: Oxygen transmission rate with respect to time for active PET Trial 1 after 6 months aging.

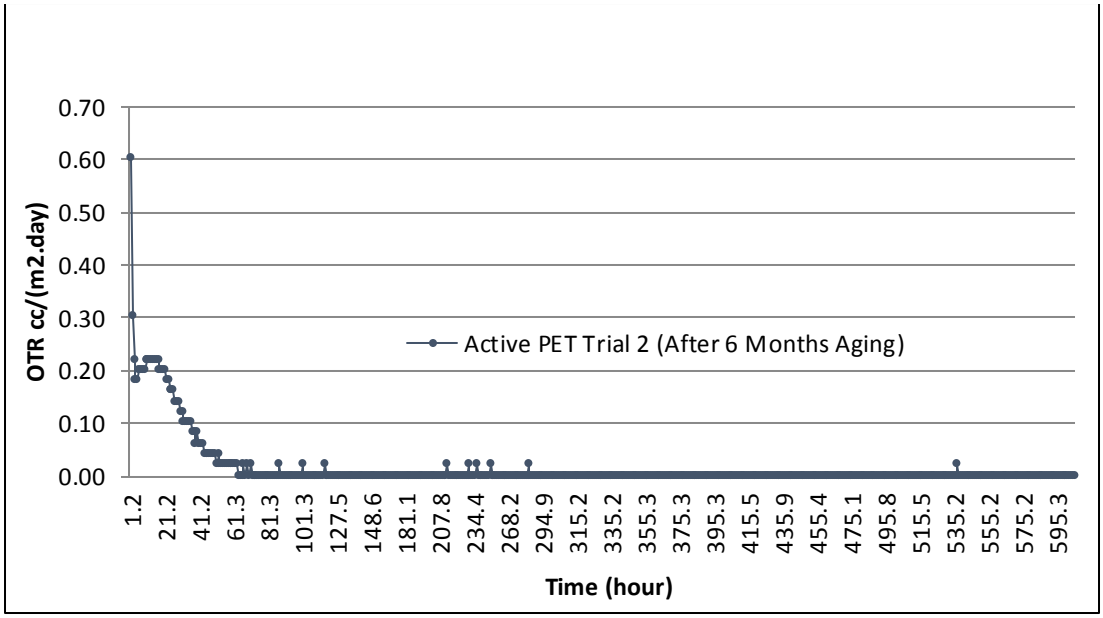

Figure 3.23: Oxygen transmission rate with respect to time for active PET Trial 2 after 6 months aging.

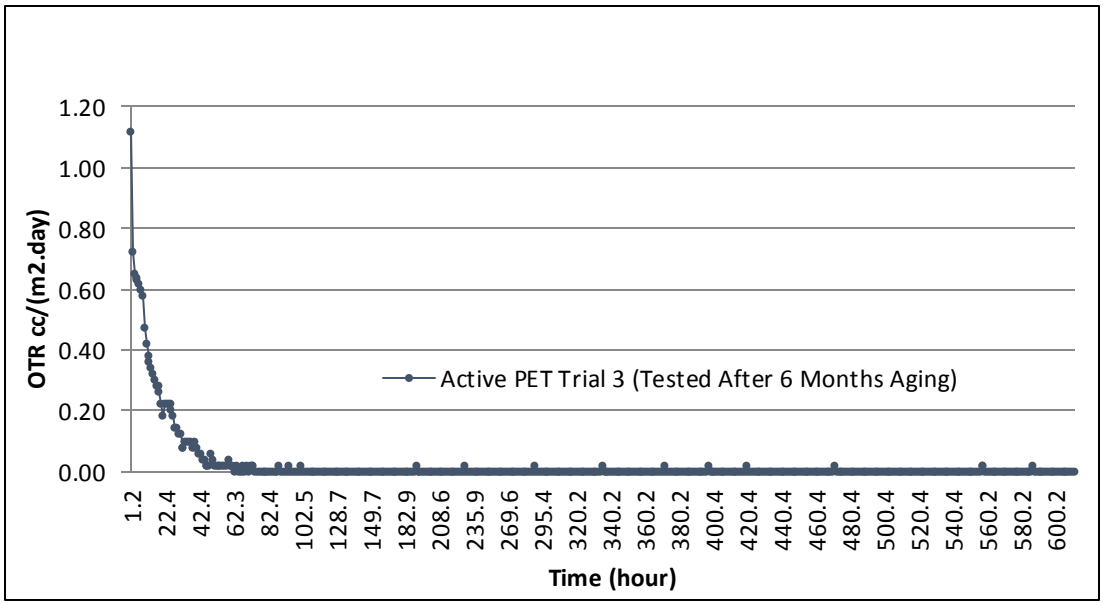

Figure 3.24: Oxygen transmission rate with respect to time for active PET Trial 3 after 6 months aging.

Considering that the aging 6 months did not significantly affect oxygen barrier properties of the active PET samples. After dissolved oxygen moved away from the cell of OTR measuring device, oxygen transmission rate of aged active sheets were found between 0 and 0.02 cc/(m^2.day). The only difference is that, the aged active sheets reached these values relatively longer than fresh active PET sheets. This behavior may be attributed to an increase in the amount of dissolved oxygen due to 6

months exposure time to the air. As a result, under atmospheric pressure, 0% RH and at 23°C all 6 months aged active PET trials have very high oxygen barrier properties as fresh active PET trials. In the beginning of the study, it was assumed to see higher oxygen transfer rates for aged active PET sheets than fresh active PET sheets due to saturation of oxygen scavenger. Surprisingly, there was no increase in the oxygen transmission rate values.

3.9. Heat Sealing Properties

Heat sealing is the process of joining thermoplastic materials and is the most popular method for bonding two polymer films in package closures. It is performed by direct contact of films with heated bars and applying sufficient pressure. Thus, heat sealing properties of packaging material is one of the key properties for many food packaging applications. In order to investigate the heat sealing properties of active PET samples, seal experiments were conducted with commercial lidding film (Lintop PET HB B 35, Pontivy, France) for PET sheets. For Trial 3, active side was used as the sealing layer which would be the inside of the food package. For other trials due to its sandwich structure surface layers are the same and they are the same with standard PET surface layers too. Thus, prior to testing, it was supposed that Trial 1, Trial 2 and standard PET have similar seal strength before testing. Results are presented in Figure 3.25.

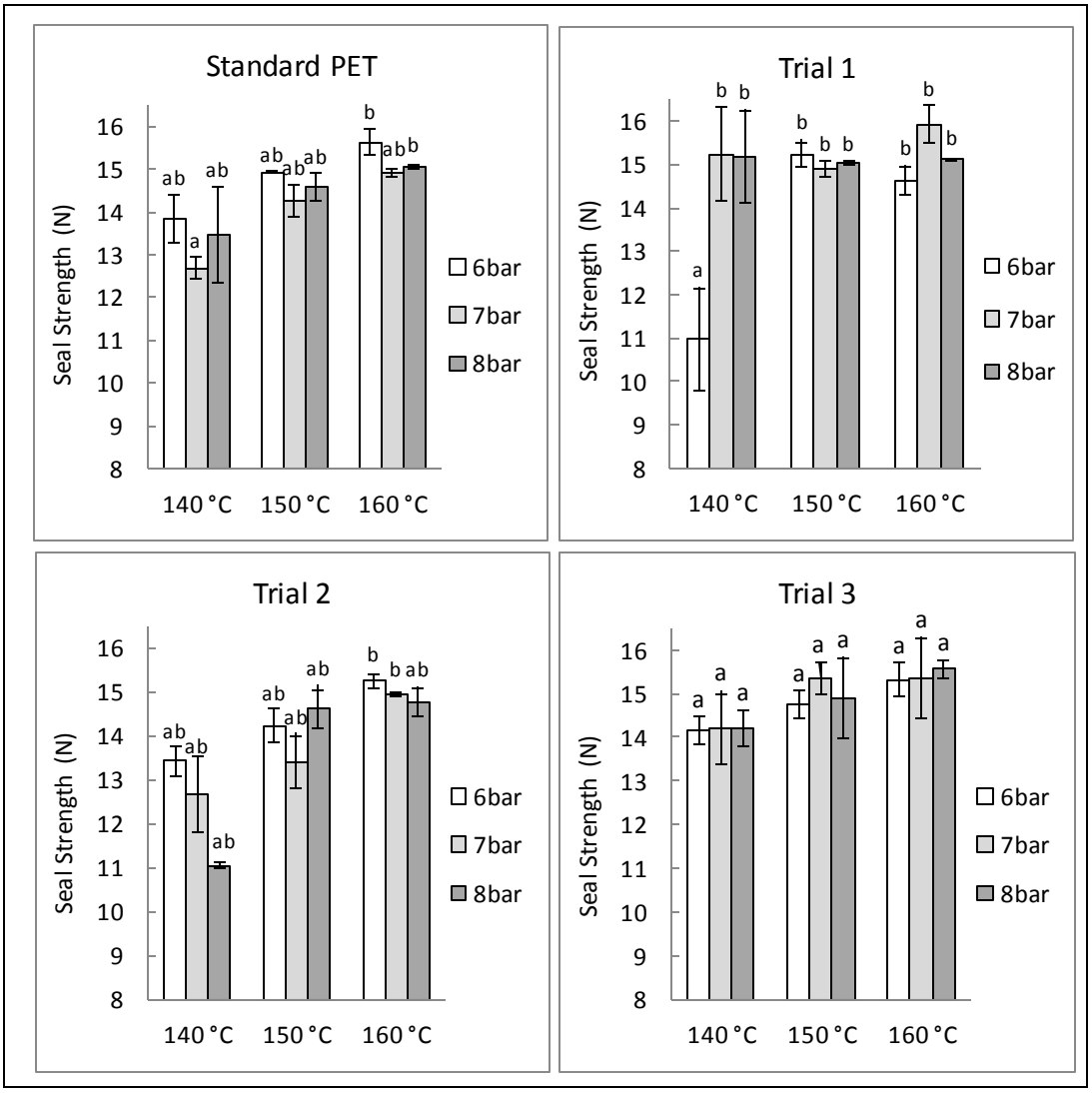

Figure 3.25: Heat seal strengths of active PET sheets and standard PET sheet with top film sealed at different pressures and temperatures with the heat sealing machine. The vertical bars indicate the average standard error of the mean. Bar plot of means for each level of the independent variable of a one-way analysis of variance (ANOVA). Bars with different letters are significantly different (Tukey's HSD, $p \leq 0.05$).

Temperature, dwell time and pressure are known to be the most important variables in heat sealing. The strength of a heat seal is primarily determined by the temperature achieved at the interface during heat sealing. In our study, it is clear that all active PET trials have good seal strength (11-16 N) between 140-160 °C and it slightly increased as the temperature increased. However, at 140 °C Trial 1 at 6 bar and Trial 2 at 6-8 bar have relatively lower seal strength which may be attribute to non-uniform sheet and film thickness. Pressure is required to ensure the film surfaces are in intimate contact for interfacial penetration to occur. For most heat sealed

materials, pressure is less important than either temperature or dwell time (Stehling and Meka; 1994). It was similar in our study that seal strength did not increased significantly as the pressure increased. Small variations observed with the increase in pressure. We may expect this result to originate from excessive pressure or non-uniform sheet and film thickness again. As a result, it may be said that similar results were obtained for seal strength. There is no study in the literature regarding the heat seal properties of oxygen scavenging PET for comparison.

3.10. Acetaldehyde Content

The presence of AA within PET articles is of concern because it has a boiling point at or below room temperature. This low temperature volatility will allow it to diffuse from the PET into either the atmosphere or any product within the container. Diffusion of AA into most products should be minimized, since the inherent taste/odor of AA is known to affect flavors of some packaged beverages and foods [Mrozinski et al., 2012]. So it is important to check the AA value of the PET based new developed products at least for food having high water content.

Adding 3-5 wt% of oxygen scavenger induced a significant generation of acetaldehyde as given in the Table 3.6. Considering that the AA content of Polyshield PET 2300K Koksan PET BGC 80 PET resins have AA below 1 ppm (presented in Appendix) and processing conditions were kept the same for active PET sheets and standard PET, thus we may expect these results to originate from addition of oxygen scavenger. Considering the amount of oxygen scavenger Table 3.6 reveals an increase in the AA content. This result clearly indicates that oxygen scavenger concentration necessarily increase AA content of active PET sheets. In the literature, there is no information regarding the acetaldehyde content of active PET.

Table 3.6: Acetaldehyde content of active PET sheets and standard PET sheet.

Nomenclature	Acetaldehyde Content (ppm)*
Standard PET	4.06[a]
Trial 1	127.49[b]
Trial 2	251.17[c]
Trial 3	190.26[d]
*Average standard deviations are less than ±0.5.	

3.11. Overall Migration Tests

The Oxyclear 3500 / Polyshield Resin 2300K blend is commercial product for active PET bottles set to oxygen-sensitive products and it is accepted by European legislation as direct food contact material. In order to assess the safety in use of the active sheet produced, overall migration tests were carried out on active samples at highest concentration of OS for sandwich (Trial 2) and asymmetric (Trial 3) structure. The values measured were all below the overall migration limit of 10 mg/dm^2 according to Commission Regulation (EU) No 10/2011. Global migration results of Trial 2 and Trial 3 are given in Table 3.7 and Table 3.8 respectively.

Table 3.7: Overall migration values for Trial 2 (A/B asymmetric structure with 3% oxygen scavenger in active layer).

Simulant	Results	Method	Requirement	
Simulant D1, Ethanol (50%, v/v)	<1 mg/dm^2	BS EN 1186-9	<10 mg/dm^2	Pass
Simulant D2, Vegetable oil	3.5 mg/dm^2	BS EN 1186-2	<10 mg/dm^2	Pass
Simulant A, Ethanol (10%, v/v)	<1 mg/dm^2	BS EN 1186-9	<10 mg/dm^2	Pass
Simulant B, Acetic acid (3%, w/v)	6.9 mg/dm^2	BS EN 1186-9	<10 mg/dm^2	Pass

Galdi and Incarnato performed overall migration analyses on the produced films to preliminary assess the safety in use of thin films with high concentration of oxygen scavenger (5%, 10% and 20 % AMS) according to the current European legislation. AMS is a commercial oxygen scavenger for active PET bottles, and as previously reported, it is compliant to be in direct contact with food according to US and European legislation. Overall migration values were below 10 mg/dm^2 which is in good agreement with our findings [Galdi and Incarnato, 2011].

Table 3.8: Overall migration values for Trial 3 (A/B/A symmetric structure with 5% oxygen scavenger in active layer).

Simulant	Results	Method	Requirement	
Simulant D1, Ethanol (50%, v/v)	<1 mg/dm^2	BS EN 1186-9	< 10 mg/dm^2	Pass
Simulant D2, Vegetable oil	6.5 mg/dm^2	BS EN 1186-2	< 10 mg/dm^2	Pass
Simulant A, Ethanol (10%, v/v)	<1 mg/dm^2	BS EN 1186-9	< 10 mg/dm^2	Pass
Simulant B, Acetic acid (3%, w/v)	<1 mg/dm^2	BS EN 1186-3	< 10 mg/dm^2	Pass

4. CONCLUSION

In this thesis, multilayer active PET sheets were obtained by adding oxygen scavenger into the PET matrix during sheet extrusion process. Under optimum processing conditions A/B/A sandwich and A/B asymmetric structures were obtained with the help of industrial scale single screw extruder with coextrusion technology. Solution viscosity measurements have shown that standard PET has higher IV value rather than active PET sheets. IV value which indicates molecular weight shows that active PET sheets were degraded a bit more than standard PET. It is thought that degradation could be promoted by partial oxidation of oxygen scavenger. However, with the increasing amount of oxygen scavenger there was no significant degradation.

Characterization of oxygen barrier properties of active PET demonstrated the effectiveness of oxygen scavenger in reducing oxygen transmission rate of PET. Under 23°C and 0 RH%, 400 μm PET has 5.32 cc/(m^2.day) oxygen transmission rate. However active PET sheets have much smaller oxygen transmission rate (< 0.02 cc/(m^2.day)) which is the minimum limit that the oxygen measurement device Ox-Tran 2/22H can measure. Not only the fresh active PET samples, but also the 6 months aged samples show the same high oxygen barrier properties. Moreover, oxygen transmission rate of active PET sheet is even better than PET//PE/EVOH/PE laminated structure which is being used as high oxygen barrier packaging material in food industry. 400 μm PET//PE/EVOH/PE structure has 1.76 cc/(m^2.day) and that means active PET sheets are promising product as a packaging material. Besides, for high barrier needs, adding more layers with different polymers and using adhesives during lamination process disable recycling and scraps which occurs during production cannot be used in packaging material itself. So on, active PET which consist of just PET and PET based additives, enabling usage of scraps and recycling; it is more environmentally friendly than laminated sheets.

The optimization of a food packaging material requires combination of impermeability to gases with high mechanical and optical performances. Optical and color properties of active PET sheets are quiet similar with standard PET with high clarity, high gloss and low haze and it is better than PET//PE/EVOH/PE sheet. Only observable difference is the bluish effect of active PET sheet and it is thought to be cause of cobalt catalyst used in the scavenger system.

Considering the mechanical properties of active PET sheets, tensile strength of active PET sheets is lower than standard PET and elongation at break of active PET sheets are apparently higher than standard PET. These differences are coming from the PET raw material Polyshield 2300K used in active layer and it can be said that increasing oxygen scavenger or changing structure do not significantly ($p > 0.05$) affect mechanical properties. All in all, it can be concluded as toughness of active PET sheets are higher than standard PET and this gives an advantage to the active PET about brittleness problem which may occur under +0°C conditions. Tensile impact strength test results of active PET sheets also support this investigation. All the active PET sheet samples have higher tensile impact energy than standard PET and even better than PET//PE/EVOH/PE sheet.

Heat sealing properties of packaging material is another important parameter for many food packaging applications. Active PET sheets have similar seal strength with standard PET with conventional high barrier top film as they were supposed.

Acetaldehyde is a thermal degradation product of the PET polymer by the reaction of the vinyl end groups. If acetaldehyde migrates into the food including water, it might influence the organoleptic properties of the food including water. For this reason, acetaldehyde values of the active PET sheets were investigated. It was observed that, with the same processing conditions, active PET sheets have much higher acetaldehyde content than standard PET sheet. Main reason for this side effect is supposed to be due to the oxygen scavenger. As the scavenger content increased the acetaldehyde generation increased, this investigation also support that oxygen scavenger induce acetaldehyde generation.

Overall, with this study very important results for food packaging sector were obtained. The results show that active PET sheets have very big potential for inhibiting food losses for oxygen sensitive foods because they have very high oxygen barrier properties (oxygen transmission rate < 0.02 $cc/m^2.day$). Nevertheless, to being done only in one process and its scraps which can be easily used in itself make active PET cost effective and environmentally friendly product.

A recent strategy for making better barrier films involves the incorporation of active molecules into polymeric matrix. However, there couldn't find any study about oxygen scavenger incorporation to the PET sheet, studies are mostly about bottle production and film production. When the PET sheet consumption raise in recent years and importance for food waste is considered, it would be better to be more studies

about active PET sheet and thermoformed tray production. In this thesis incorporation of oxygen scavenger into PET matrix during PET multilayer sheet extrusion was performed.

In the study, oxygen transfer rates of active PET sheets were tested up to 600 hours. Not only fresh samples but also the 6 months aged samples were analyzed and results were all under 0.02 cc/m^2.day. At the beginning of the study, it was assumed that oxygen scavenger in the active PET sheet samples would reach to the saturation and oxygen transfer rate of active PET sheet samples would increase after a while before 600 hours. However, even 6 months aging none of the active samples lost their oxygen barrier properties. So, for future studies longer aging or longer oxygen transfer rate test time can be evaluated. Also, due to its very high oxygen barrier and long shelf life (at least 6 months), to avoid over engineering, new formulations can be studied with less oxygen scavenger concentration.

One of the important parameter for oxygen barrier properties of material is relative humidity and temperature. In this thesis, oxygen transfer rate values of active PET sheets were tested under 0% RH and at 23°C, but in many food applications, the relative humidity inside a food package would be close to 100% RH at low temperatures. At different relative humidity and different temperatures, oxygen transfer rates can be tested, thus temperature and moisture effect on scavenging property can be analyzed.

For the asymmetrical structure, oxygen scavenging capacity did not tested but as given in the introduction part, in MAP applications residual oxygen in the package may be up to 2% and this concentration may be enough for bacterial growth. So, in asymmetrical structure, active side will be in contact with foodstuff and it may have ability to decrease the oxygen level. In future works, oxygen absorption tests can be performed and it would be a very important study for active PET sheet as a packaging material.

Finally, acetaldehyde values of active PET sheets were too much high and this high value may cause taste problem with food having high water content. This problem must be taken under consideration. In literature, most of the studies did not analyze acetaldehyde content. The root cause of high acetaldehyde content can be found and acetaldehyde content may be decreased with acetaldehyde absorbing additives.

REFERENCES

Anthierens T., Ragaert P., Verbrugghe S., Ouchchen A., De Geest B. G., Noseda B., Mertens J., Beladjal L., De Cuyper D., Dierickx W., Du Prez F., Devlieghere F., (2011), "Use of Endospore-forming Bacteria as an Active Oxygen Scavenger in Plastic Packaging Materials", Innovative Food Science and Emerging Technologies, 12, 594-599.

Brody A. L., Bundy J. A., (1995), "Enzymes as Active Packaging Agents in Active Food Packaging", Blackie Academic & Professional, 174-192.

BS EN 1186–1, Materials and Articles in Contact with Foodstuffs, Plastics. Guide to the Selection of Conditions and Test Methods for Overall Migration, 2002.

Chen Y., Sun Q., (2006), "Oxygen Scavenging Plastic Compositions", E.U. Patent 2,183,318 B1.

Di Maio L., Scarfato P., Galdi M. R., Incarnato L., (2015), "Development and Oxygen Scavenging Performance of Three-Layer Active PET Films for Food Packaging", Journal of Applied Polymer Science, 132, 41465.

Frisk P., (1998), "Oxygen Scavenging Container", U.S. Patent 5,804,236.

Galdi M. R., Incarnato L., (2011), "Influence of Composition on Structure and Barrier Properties of Active PET Films for Food Packaging Applications", Packaging Technology and Science, 24, 89-102.

Galdi M.R., Nicolais V., Di Maio L., Incarnato L., (2008), "Production of Active PET Films: Evaluation of Scavenging Activity", Packaging Technology and Science, 21, 257-268.

Gibis D., Rieblinger K., (2011), "Oxygen Scavenging Films for Food Application", Procedia – Food Science, 1, 229-234.

Graf E., Rapids C., (1994), "Oxygen Removal", U.S. Patent 5,284,871.

Hong K. Z., Kim Y. J., Jornell S. W., (1994), "Barrier Composition and Articles Made Therefrom", U.S. Patent 5,281,360 A.

Johansson K., Kotkamo S., Rotabakk B. T., Johansson C., Kuusipalo J., Jönsson L. J., Järnström L., (2014), "Extruded Polymer Films for Optimal Enzyme-Catalyzed Oxygen Scavenging", Chemical Engineering Science, 108, 1-8.

Kim Y. J., Germonprez R., Kaas R. L., Mehta A., (2001), "Barrier Compositon and Articles Made Therefrom", U. S. Patent 6,288,161 B1.

Liu Z., Mehta Z., Huang X., Schiraldi D. A., (2011), "Method to Make Single-Layer PET Bottles with High Barrier and Improved Clarity", U.S. Patent 7,919,159 B2.

Marsh K., Bugusu B., (2007), "Food Packaging - Roles, Materials, and Environmental Issues", Journal of Food Science, 72(3), R39-R55.

Meka P., Stehling F. C., (1994), "Heat Sealing of Semicrystalline Polymer Films, Calculation and Measurement of Interfacial Temperatures: Effect of Process Variables on Seal Properties", J. Appl. Polym. Sci., 51, 89-103.

Miltz J., Perry M., (2005), "Evaluation of the Performance of Iron-based Oxygen Scavengers, with Comments on their Optimal Applications", Packagıng Technology and Science, 18, 21-27.

Mrozinski B. A., Lofgren E. A., Jabarin S. A., (2012), "Acetaldehyde Scavengers and Their Effects on Thermal Stability and Physical Properties of Poly(ethyleneterephthalate)", Journal of Applied Polymer Science, 125, 2010-2021.

Mu H., Gao H., Chen H., Tao F., Fang X., Ge L., (2013), "A Nanosised Oxygen Scavenger: Preparation and Antioxidant Application to Roasted Sunflower Seeds and Walnuts", Food Chemistry, 136, 245-250.

Ozen I., Bozoklu G., Dalgıçdir C., Yucel O., Unsal E., Cakmak M., Menceloglu Y. Z., (2010), "Improvement in Gas Permeability of Biaxially Stretched PET Films Blended with High Barrier Polymers: The Role of Chemistry and Processing Conditions", European Polymer Journal, 46, 226-237.

Ping X., Wang M., Ge X., (2011), "Radiation Induced Graft Copolymerization of N-Butyl Acrylate onto Poly(ethylene terephthalate) (PET) Films and Thermal Properties of the Obtained Graft Copolymer", Radiation Physics and Chemistry, 80, 632-637.

Poisson C., Guerengomba J., Lacrampe M. F., Krawczak P., Gupta B., Miri V., Lefebvre J. M., (2008), "Mechanical, Optical and Barrier Properties of PA6/Nanoclay Based Single and Multilayer Blown Films', Polymers and Polymer Composites, 16, 349-358.

Shen L., Worrell E., Pate M. K., (2010), "Open-loop Recycling: A LCA Case Study of PET Bottle-to-Fibre Recycling", Resources, Conservation and Recycling, 55, 34-52.

Tibbit J. M., Cahill P. J., Rotter G. E., Sinclair D. P., Brooks G. T., Behrends R. T., (2007), "Oxygen Scavenging Monolayer Bottles", U.S. Patent 7,214,415 B2.

Tugn D., Sisson E. A., Leckonby R. A., (2010), "Oxygen-Scavenging Containers", U.S. Patent 7,740,926 B2.

Vermeiren L., Devlieghere F., Van Beest M., De Kruijf N., Debevere J., (1999), "Developments in the Active Packaging of Foods", Trends in Food Science & Technology, 10, 77-86.

BIOGRAPHY

Murat TERGIP, was born on March 27th, 1984 in Istanbul. He graduated from Anibal Anatolian High School in 2002. In 2007, he graduated from Chemical Engineering Department, Izmir Institute of Technology. He is currently a M.S. student at Gebze Technical University, Departments of Graduate School of Engineering and Sciences, Mechanical Engineering Department. He has been working in Yıldız Holding, as the research and development executive since 2011.

APPENDICES

Appendix A: Properties of raw materials

Table A1.1: Properties of the PET raw material used in active PET sheet.

Property	Unit	Polyshield 2300K PET Resin	Oxyclear 3500 Oxygen Scavenger	Koksan BGC 80 PET Resin	Sukano T dc S479 Slip/Antiblock Masterbatch
Intrinsic Viscosity (IV)	dL/g	0.841	1.14	0.80	0.74
Color L*	-	69.22	51.34	73.68	69.78
Color b*	-	-9.28	11.24	-1.25	9.76
Acetaldehyde	ppm	0.44	-	0.26	6.18
Moisture content	%	0.25	0.10	0.200	0.400
Melting point	°C	250.02	232	248.21	252.53
Degree of crystallinity	%	46.6	19.3	42.5	23.43
Bulk density	g/cm^3	0.89	0.82	0.85	0.80
Chip geometry	-	cylindrical	cylindrical	spherical	cylindrical