

ISTANBUL TECHNICAL UNIVERSITY ★ GRADUATE SCHOOL OF SCIENCE
ENGINEERING AND TECHNOLOGY

**PRODUCTION OF THE FRESH PRODUCE PACKAGING MATERIAL FROM
LOW DENSITY POLYETHYLENE AND POLYMETHYLPENTENE
POLYMERS**

M.Sc. THESIS

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Department of Polymer Science and Technology

Polymer Science and Technology Programme

MAY 2015

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POLİMERLERİNDEN TAZE GIDA AMBALAJ MALZEMESİ ÜRETİMİ**

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To my family,

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ABBREVIATIONS

LDPE	: Low Density Polyethylene
PMP	: Polymethylpentene
ISO	: International Organization for Standardization
ASTM	: American Society for Testing and Materials
L/D	: Length/Diameter
DSC	: Differential Scanning Calorimeter
MFI	: Melt Flow Index
FCF	: Fresh Cut Fruits
MAP	: Modified Atmosphere Packaging
FCM	: Food Contact Material

LIST OF SYMBOLS

T_c	: Crystallization temperature
T_m	: Melting temperature
ΔH_c	: Crystallization enthalpy
ΔH_m	: Enthalpy of fusion
σ_M	: Tensile strength
ε_M	: Strain ratio at failure
l	: Lightness or darkness in color coordinate system
a	: Redness or greenery in color coordinate system
b	: Yellowness or blueness in color coordinate system

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PRODUCTION OF THE FRESH PRODUCE PACKAGING MATERIAL FROM LOW DENSITY POLYETHYLENE/POLYMETHYLPENTENE POLYMERS

SUMMARY

As a result of population growth and global warming, fertile soil lands are decreasing and occurrence rate of natural disasters such as drought and flood are increasing. Because of these reasons millions of people around the world cannot reach the staple food products. Therefore, food supply is one the most urgent problems which is awaiting a solution nowadays. In order to overcome that problem, agricultural harvest is needed to increase or shelf lives of harvested products are needed to extend. Despite the limited arable soil lands, the quantity of product per unit area can be already increased due to increase in fertilisation. In spite of this enormous increase in fertilisation, the food requirements of population growth cannot be met. The main reason of this situation is the loss of post-harvest products which is said approximately 40% by weight. In order to overcome this problem completely, this losses should be eliminated.

In order to eliminate these losses, new searches have been focused on new packaging methods. Active packaging and modified atmosphere packaging are new methods which were recovered from these studies.

Fundamental principle of these methods is obtaining a balanced internal atmosphere between the respiration rate of preserved product and the gas permeabilities of packaging materials in order to extend the shelf lives of post-harvest products. However, the commercial plastics which are used in packaging industry cannot provide these high gas permeability values and because of this reason they cannot offer longer shelf lives.

In accordance with this purpose, in order to obtain high gas permeability values and selectivity properties of packaging material, polymethylpentene (PMP) copolymer was added in different loading levels into low density polyethylene (LDPE) matrix by using a laboratory scale co-rotating twin screw extruder. In this study, LDPE/PMP copolymer blends which were containing 10%, 25%, 50%, 75%, and 90% PMP copolymer ratios were prepared by using extrusion. Also, for blends' structural, morphological, thermal and mechanical evaluations, neat LDPE and PMP copolymer were extruded under the same conditions in order to obtain standard materials which were exposed the same thermal treatment. The package samples were produced by using cast film extrusion method.

Differential scanning calorimetry (DSC), Fourier-transform infrared spectroscopy (FTIR), melt flow index (MFI), X-ray diffraction (XRD), scanning electron

microscopy (SEM), thermometric gravimetric (TGA) analysis, and optical properties were conducted to determine the structural, morphological and thermal properties of the test samples. Tensile tests and gas permeability tests were also carried out to evaluate the mechanical properties of the samples.

Besides, shelf life analysis were done in order to evaluate package samples' efficiency for banana and marrow fruits for 14 days.

DSC analysis were shown that there were two peaks for crystallization and two peaks for melting which belongs to LDPE and PMP copolymer. Crystallinity values of blends were close to each other. XRD analysis was indicated that these crystal structures were in tetragonal symmetry. Increase in PMP copolymer ratio in blends was increased tensile strength and tensile strength at break values. On the other hand it was decreased strain values. Despite of this decrease in strain, usage of the samples as packaging material were not affected negatively.

Appearance of packaging materials is also very important for consumers. In order to evaluate the appearance of package samples, color spectrophotometer was used. Haze, opacity, and color properties of package samples were sufficient for their usage as packaging material.

The most important parameter of this study is O₂ and CO₂ permeability values of the package samples. In order to investigate this property entirely, under 90% relative humidity conditions, O₂ and CO₂ permeability values were determined at 3 different temperatures. Beyond these analysis, according to loading ratio of PMP copolymer into LDPE matrix was increased gas permeability values up to 600%. Increase in gas permeability values can be explained with DSC and XRD analysis. The tetragonal symmetry of PMP copolymer and phase separations between PMP copolymer and LDPE which can be seen in SEM images led to obtain high gas permeability values in our opinion.

The results of shelf life analysis was indicated that the package sample was containing 25% PMP copolymer could extend the shelf lives of banana and marrow fruits 2 times. Thus, the extension of shelf life of preserved products used in this study could be achieved.

DÜŞÜK YOĞUNLUKLU POLİETİLEN VE POLİMETİLPENTEN POLİMERLERİNDEN TAZE GIDA AMBALAJ MALZEMESİ ÜRETİMİ

ÖZET

Artan nüfus paralelinde son yıllarda şiddetini giderek artıran küresel ısınma sorunuyla ilişkili olarak verimli toprak arazilerinin azalması, kuraklık ve sel gibi olumsuzluklar, günümüzde milyonlarca kişinin en temel gıda maddelerine ulaşamadığı büyük bir sorunu ortaya çıkarmıştır. Dolayısı ile insanların yaşamlarını idame ettirebilmesini sağlayacak yeterli oranda gıda maddelerinin temin edilebilmesi, günümüzde en acil çözülmesi gereken sorunlardan bir tanesini teşkil etmektedir. Bu sorunun çözülebilmesi ise ancak tarım rekoltesinde artışı sağlayacak yeni yöntemler ve/veya hasat edilen tarım ürünlerinin daha uzun raf ömrüne sahip olacak şekilde muhafaza edilebilmesine olanak sağlayacak yeni tekniklerin geliştirilebilmesi ile mümkündür.

Aslında geçmişten günümüze kadar uzanan süreçte; makineleşme, gübreleme, ilaçlama, sulama imkanlarının gelişmesi ve ayrıca gen mühendisliği alanında gerçekleştirilen çalışmalar neticesinde kazanılan biyoteknolojik gelişmeler, tarımsal üretimdeki verimliliği inanılmaz ölçülerde arttırılabilmektedir. Yeryüzünde tarıma elverişli topraklar sınırlı olmasına rağmen, verimlilik artışları sayesinde birim araziden elde edilen ürün miktarı büyük oranda arttırılabilmektedir. Fakat bu yöndeki muazzam gelişmelere rağmen, halen artan nüfusun gıda gereksinimleri, tam anlamı ile karşılanamamaktadır. Bunun en önemli nedeni ise hasat sonrası, %40'a yakın olduğu ifade edilen kayıplardır. Bu doğrultuda; ifade edilen sorunun tam anlamı ile ortadan kaldırılabilmesi için hasat sonrası meydana gelen yüksek oranlardaki ürün kayıplarının engellenmesi, en az verimlilik artışı ve hatta verimlilik artışından bile önemli bir husustur.

İfade edilen bu yüksek seviyelerdeki kayıpları engelleyecek, yeni ve etkili muhafaza tekniklerinin geliştirilmesi ile ilişkili güncel araştırmalar incelendiğinde ise son dönemlerdeki çalışmaların ambalajlama teknikleri üzerine yoğunlaşmış olduğu gözlenmektedir. Bu çalışmalar ile günümüzde yoğun bir şekilde kullanılan aktif ambalajlama ve modifiye atmosferde ambalajlama olarak isimlendirilen teknikler geliştirilmiş ve geliştirilmeye devam edilmektedir.

Bu ambalajlama tekniklerinde temel prensip, muhafaza edilen ürünün solunumu ile ambalaj metaryeli arasında bir denge sağlanması sureti ile raf ömrünün uzatılmasıdır. Lakin kullanılan ambalaj metaryellerinin gaz geçirgenlik değerlerinin düşük kalması nedeni ile ifade edilen bu denge konumu elde edilememekte ve raf

ömrü kısa kalmaktadır. Tarafınıza sunulan tez çalışmasının temel dayanak noktası, ifade edilen bu temel sorunun ortadan kaldırılmasıdır.

Bu amaç bağlamında; elde edilmek istenilen yüksek gaz geçirgenlik ve seçicilik özellikleri, alçak yoğunluklu polietilen (LDPE) içerisine, ağırlıkça %10, %25, %50, %75, %90 oranlarında eklenen polimetilpenten kopolimerleri (PMP) ile sağlanmıştır. LDPE içerisine PMP kopolimeri, çift vidalı bir laboratuvar ekstrüderi ile eriyik harmanlama yöntemi kullanılarak eklenmiştir. Ayrıca elde edilen ürünlerin yapısal, morfolojik, termal ve mekanik özelliklerini değerlendirebilmek için aynı proses koşullarında saf LDPE ve PMP kopolimeri ekstrüde edilerek, elde edilen ara karışımlar ile karşılaştırma yapmak adına standart olarak kullanılmıştır. Karışım olarak adlandırabileceğimiz bu iki polimeri içeren ürünler, dökme film (cast film) yöntemi kullanılarak ambalaj haline getirilmiştir.

Üretilen nihai ambalaj numunelerinin fiziksel, morfolojik ve mekanik özelliklerini tayin etmek amacıyla; diferansiyel taramalı kalorimetre (DSC), Fourier transform kızılötesi spektroskopisi (FTIR), taramalı elektron mikroskopisi (SEM), X-ışınım kırınım yöntemi (XRD), termogravimetrik analiz (TGA), eriyik akış indeksi (MFI), optik özellik analizi, çekme-uzama testleri, ve gaz geçirgenliği ölçümleri yapılmıştır. Bunların yanında elde edilen ambalaj numunelerinin etkinliklerini tespit etmek amacı ile örnek ambalajlar içerisinde 14 gün süre ile muz ve kabak ürünleri muhafaza edilerek, raf ömrü analizleri de gerçekleştirilmiştir.

DSC analizleri neticesinde; yapıdaki iki farklı polimere ait erime ve kristalizasyon pikleri net bir şekilde gözlenmiştir. Ayrıca yapılan hesaplarda tüm örneklerin kristalinite değerlerinin, birbirine yakın seviyelerde olduğu tespit edilmiştir. XRD analizleri neticesinde PMP kopolimerinin tetragonal bir simetride kristallendiği gözlenmiştir. Gerçekleştirilen FTIR analizleri, yapıya girilen PMP kopolimerinin yapısal değişiklere neden olmadığını göstermektedir. Mekanik analizler, yapıya girilen PMP oranına bağlı olarak mukavemet değerlerinin yükseldiğini ve kopma uzamalarının düştüğünü göstermektedir. Fakat kullanımı engelleyebilecek bir mekanik düşüş tespit edilememiştir.

Ambalajların görşelliği son kullanıcılar açısından büyük önem arz etmektedir. Ambalajın şeffaf olması, sisli ya da puslu bir yapıda olmaması bu noktada önemli bir parametredir. Bu aşamada tez kapsamında üretilen ambalaj örneklerinin görşel özelliklerini belirlemek amacı ile renk spektrofotometresi kullanılarak ambalajların ışık geçirgenlik, saydamlık ve berraklık gibi özellikleri incelenmiştir. İnceleme neticesinde, tez çalışması kapsamında elde edilen ambalaj örneklerinin, oldukça yüksek ışık geçirgenlik ve dolayısı ile görşelliğe sahip olduğu belirlenmiştir.

Çalışmanın en önemli parametresini oluşturan ambalajların oksijen ve karbondioksit geçirgenlik değerleri ise %90 bağıl nem ve 3 farklı ortam sıcaklık değerlerinde gerçekleştirilen gaz geçirgenlik analizleri neticesinde elde edilmiştir. Bu analizler neticesinde LDPE yapısına eklenen PMP kopolimerinin oranına bağılı olarak O₂ ve CO₂ gazı geçirgenlik değerlerinin %600'e kadar arttırılabildiği tespit edilmiştir. Geçirgenlik değerlerindeki bu artışın; DSC ve XRD spektrumlarında da gösterildiği üzere kristal yapının tetragonal simetriye sahip olması ve SEM analizlerinde gösterildiği üzere meydana gelen faz ayrımlarından kaynaklandığı düşünülmektedir.

Son olarak, muz ve kabak için gerekleřtirilen 14 gnlk raf mr analizleri neticesinde ise %100 LDPE ve %10 PMP ieren LDPE esaslı ambalaj rneklerinde istenilen raf mr artışı elde edilememiş olup, %25 PMP kopolimeri ieren LDPE esaslı ambalajların, muz ve kabağın raf mrlerini en az iki katına kadar uzatabildiğı belirlenmiştir.

1.INTRODUCTION

Around the world, millions of people cannot reach to staple food (fruit and vegetable) because of global warming, economic crisis and rising population. Therefore the shelf-life and preservation of these food products is important. In countries like Turkey more than 25% of fruit and vegetables are discarded without consuming due to lack, poor and insufficient store and package facilities. For preserving foods properly and for increasing their shelf-lives it is important to understand the degradation mechanisms in vegetables, fruit and food and this is a phenomenon called physiological aging. Researches in this field showed that fresh fruit and vegetable can keep their freshness for a while after harvesting. [1]

During this time they consume the stock materials that they stored in their bodies before harvesting. Furthermore, for continuation of respiration this is a part of maturation period. In this process, the sugar existing in the bodies of food products is broken with oxygen in the air to form carbon dioxide, water vapor, aroma materials, and ethylene gas. Although such degradations are observed in fresh fruits and vegetables, the main reason for the degradations in food such as red meat, fish and cheese is the reaction of these materials with oxygen, causing irreversible changes. Although preservation techniques such as “controlled atmosphere storage” and “active packing system” developed on the basis of these degradation mechanisms are effectively used at the present time. Intense research is going on this field because of the current preservation techniques cannot fulfill the effective/economical/ergonomic preservation conditions. [1- 4]

As market demand for fresh and minimally processed fruits increases, quality and shelf life issues increase in importance. A key requirement is to ensure that product is able to reach the consumer with minimal quality deterioration and safety risks. This becomes problematic when we recognize that fresh-cut fruit (FCF) products constitute a delicate, dynamic system that is prone to many forms of deterioration. [5, 6]

In order to investigate how packaging impacts deterioration, we must first understand its causes. The inherent quality deterioration of FCF is largely due to cutting, because it initiates the physiological and biochemical changes at a faster rate than in intact raw fruits. Generally, quality deterioration (color, flavor and texture) is attributed to the combined effect of endogenous enzymes, enhanced respiration, microbial growth, physical abuse and environmental factors. The surrounding environmental factors such as temperature, humidity, atmospheric composition and ethylene concentration directly influence the deterioration process. Mechanical bruises and damage caused by harvesting, handling, storage and transportation are also detrimental to the FCF shelf life. There are no simple answers and no single treatment is known to limit overall quality deterioration. However, there are several strategies that are being implemented in order to reduce the rate of deterioration for FCF. These include, but are not limited to starting with high-quality raw produce, implementing sanitation practices, controlling temperature, lowering respiration rate, lowering ethylene production, and preventing mechanical abuse. Packaging technology is the common denominator that allows us to implement these strategies and, thus, is key to quality preservation. [5, 6]

Packaging is part of a coordinated system that starts from the preparation of goods for shipment and includes distribution, storage and merchandising at the optimum cost compatible with the requirements of the product. It can be considered as a combination of art, science and technology that is used in the transportation and selling of foods. Packaging materials have the four basic functions of providing protection, communication, convenience and containment. The primary role of food packaging is to protect food products from the outside environment and from damage by abrasion, to contain the food, and to provide consumers with information about ingredients and nutrition. The main requirement of food packaging is to maintain the safety, wholesomeness and quality of food. Packaging maintains the benefits of food processing after the process is complete, enabling foods to travel safely for long distances from their point of origin and still be in their natural state at the time of consumption. Traceability, convenience and tamper indication are secondary functions of increasing importance. The objective of food packaging is to contain food in a cost – effective way that satisfies industry requirements, provides

consumer satisfaction, maintains food safety and minimizes environmental impact. [7]

Consumer demand for fresh fruit and vegetables has triggered the need for procedures, including packaging, that maintain the freshness, safety, and quality attributes of these commodities. Research aimed at improving the quality and extending the shelf-life of these commodities has been conducted in the fields of physiology, microbiology, and nutrition. [8]

Developments in food packaging have evolved in response to the need for protection of the food product from both external and internal environments and in response to consumer expectations for convenience and product safety. A recent survey indicated that 72% of consumers in the United States are willing to pay extra for guaranteed product freshness delivered by the type of packaging. Many new packaging developments have focused on extending the shelf life of the product and on delivering a higher quality product to the consumer. These developments would not be possible without significant advances in the materials used in packaging and the incorporation of various types of sensors into food packaging. [9]

Over the past 20 years, there has been an enormous increase in the demand for fresh fruit and vegetable products that has required the industry to develop new and improved methods for maintaining food quality and extending shelf life. Due to the complexities involved with produce, that is, varying respiration rates which are product and temperature dependent, different optimal storage temperatures for each commodity, water absorption, by-products, and so on, many considerations are involved in choosing an acceptable packaging technology. One of the areas of research that has shown promise, and had success, is that of modified atmosphere packaging (MAP). This technique involves either actively or passively controlling or modifying the atmosphere surrounding the product within a package made of various types and/ or combinations of films. In North America, one of the first applications of this technology for fresh-cut produce was introduced by McDonald's (Brody 1995), which used MAP of lettuce in bulk-sized packages to distribute the product to retail outlets.

The major factors responsible for extending the shelf life of fruits and vegetables include: careful harvesting so as not to injure the product, harvesting at optimal horticultural maturity for intended use, and good sanitation. [10]

When these are practiced, the implementation of optimum storage conditions through modified atmospheres can be quite effective at maximizing the shelf life and quality of the product.

Various technologies have been used in the processing of fruit products. Packaging requirements are different among different processes. Packaging technologies have constantly been developed for prolonging the shelf life of fresh fruits as well as processed fruits. For several decades the most common commercially successful technology for various fresh and processed products has been modified atmosphere packaging (MAP). Various active and intelligent technologies have been extensively studied in response to consumers' requirements, which currently focus on high quality and safety for both fresh and processed fruit products. [11]

In this study, LDPE raw material, polymethylpentene copolymer with 10%, 25%, 50%, 75% and 90% ratio were used to prepare blend samples. Also, neat LDPE and PMP copolymer were extruded under the same process and conditions in order to compare with blends. The blends with PMP copolymer were prepared in order to observe the gas permeability properties by using melt mixing method with twin screw extruder, and the film samples were produced by using cast film extrusion method.

2. THEORY

2.1 Degradation Mechanisms of Fresh Cut Produce

Fresh-cut fruits and vegetables are composed of living cells that naturally spoil and deteriorate over time and are affected by all preparation operations and surrounding conditions during pre- and postharvest handling, processing operations, and storage. Respiration and ethylene production rates, color, aroma, and texture change as a response to physical damages produced during cutting operations, as well as to the activity of undesirable microorganisms.

Quality attributes of the fruit and vegetables used as raw materials for processing have a great influence on the final quality and shelf-life of fresh-cut products; hence it is very important to identify and understand relevant changes for specific products and how they are affected by handling, processing and storage.

Fruits and vegetables are composed of living tissues and have to withstand two major hurdles: harvest and processing. When they are harvested, water and nutrient supply from the mother plant ends, and tissues are injured at the incision point. Processing causes further physical damages as the products are cut, and the product skin is removed, causing an increase in respiration and other metabolic activities continue all the way up to the consumer table.

For such a dynamic system, changes are continually occurring, even though they may not be obvious for the first hours or days after harvesting or cutting. Appearance and texture alterations are the first to be noticed, although many more physical, physiological, and biochemical changes are ongoing at the same time at different rates, and are influenced by internal and external factors. [1, 6, 12- 15]

2.1.1 Respiration rate

Respiration rates of fresh-cut produce are generally higher than the intact produce, especially at higher temperature. The changes in respiratory dynamics also differ between fresh-cut and whole produce. Respiration rate is initially stimulated after harvest or fresh-cut processing and then gradually declines, and the stimulation is greater in fresh-cut products than the intact produce, as shown with romaine lettuce in Figure 2.1. [15]

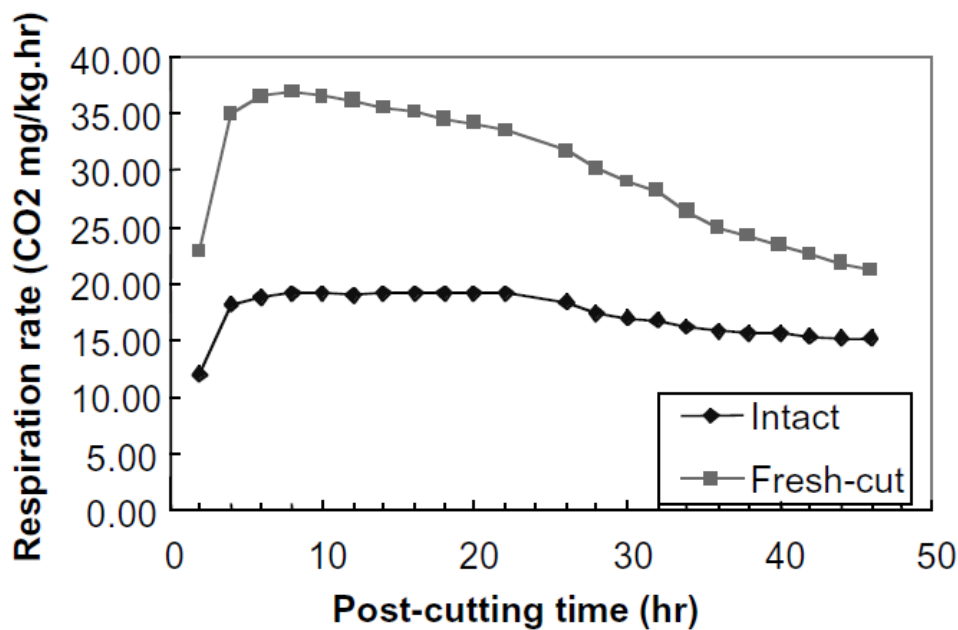


Figure 2.1 : Respiration rate of intact and fresh-cut Romaine lettuce held at 5°C [15]

The rate of respiration is sensible to internal factors, such as product type and maturity stage, and also to external factors like temperature (Figure 2.2), ethylene concentration, stress caused during harvest, postharvest, and processing operations, pathogens and physical injuries. The faster the respiration rate is, the shorter will be the shelf life of the intact and fresh-cut products. Respiration rate is a good indicator of ongoing processes inside a product, products harvested during active growth (vegetables and immature fruits) usually have high respiration rates, while mature fruits have relatively low rates. [12]

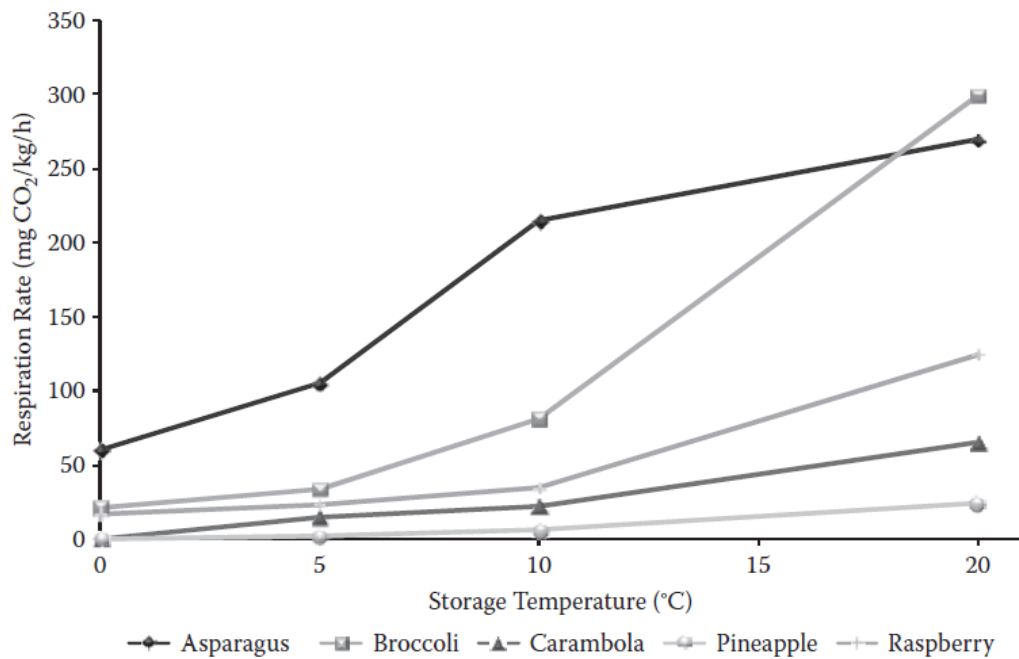


Figure 2.2 : Effect of storage temperature on respiration rate of several intact fruits and vegetables [12]

2.1.2 Ethylene production

Ethylene has an active participation in growth, development, maturation, healing, and senescence of fresh produce. Its production rate varies among products; it increases with temperature, disease incidence, mechanical injuries, water stress, and maturity stage at harvest; and it can be partially controlled by low temperature storage, reduced oxygen composition, or elevated carbon dioxide levels surrounding the commodity. Very small concentrations of ethylene can damage sensible products showed in Table 2.1; hence, they should be handled separately from those that produce it. [12, 16]

Tablo 2.1 : Optimum storage temperature and relative humidity for selected fruits and vegetables [16]

Product	Storage Temperature (°C)	Relative Humidity (%)	Sensitivity to Ethylene
Cydonia	2-4	80–85	Low
Chestnut	2-4	85–90	Low
Cherry	0-1	90–92	Low
Lime	14-16	90–95	Low
Grape	0-2	90–95	Low
Plum	0-3	90–92	Medium
Fig	0-2	90–93	Medium
Pear	1-3	90–93	High
Lemon	10-14	85–90	High
Apricot	0-1	90–92	High
Orange	5-7	85–90	High
Apple	0-4	85–90	High
Gombo	8-12	90–95	Low
Bean	4-8	90–95	Low
Carrot	0-4	90–95	Low
Cucumber	8-12	90–95	Low
Spinach	2-4	90–95	Low
Cabage	0-4	90–95	Low
Garlic	0-4	65–70	Low
Tomato	7-8	90–95	Medium
Onion	0-4	75–80	Medium
Broccoli	2-4	90–95	High
Celery	0-4	90–95	High
Eggplant	8-12	90–95	High

2.1.3 Water loss

Fruit and vegetable water content is very high and can be easily lost through the skin lenticels, stomatas, cuticule, and other structures when the surrounding atmosphere has low relative humidity. The skin of fruits and vegetables act as a natural barrier that helps to partially control water loss, but its effectiveness depends on product morphology, surface characteristics, size, ratio of product surface area to weight and volume, maturity stage, physical injuries, as well as environmental temperature, relative humidity, and air movement around the product. [12]

Water loss in fruits and vegetables is determined by many factors, probably the most important being the resistance of outer periderm or cuticle to transpirational movement of water vapor. However, peeling and cutting result in reduction or elimination of the resistance by these barriers to transpiration. Two issues are important to water loss: reduction of tissue bulk, i.e., increase in surface area to volume ratio, and the removal of protective periderm tissues. Both mechanisms for resultant increases in water loss, are demonstrated by the fact that slicing of kiwifruit results in increased rates of water loss, and subsequent peel removal from the slices results in a further increase in weight loss which can be seen in Figure 2.3. [17]

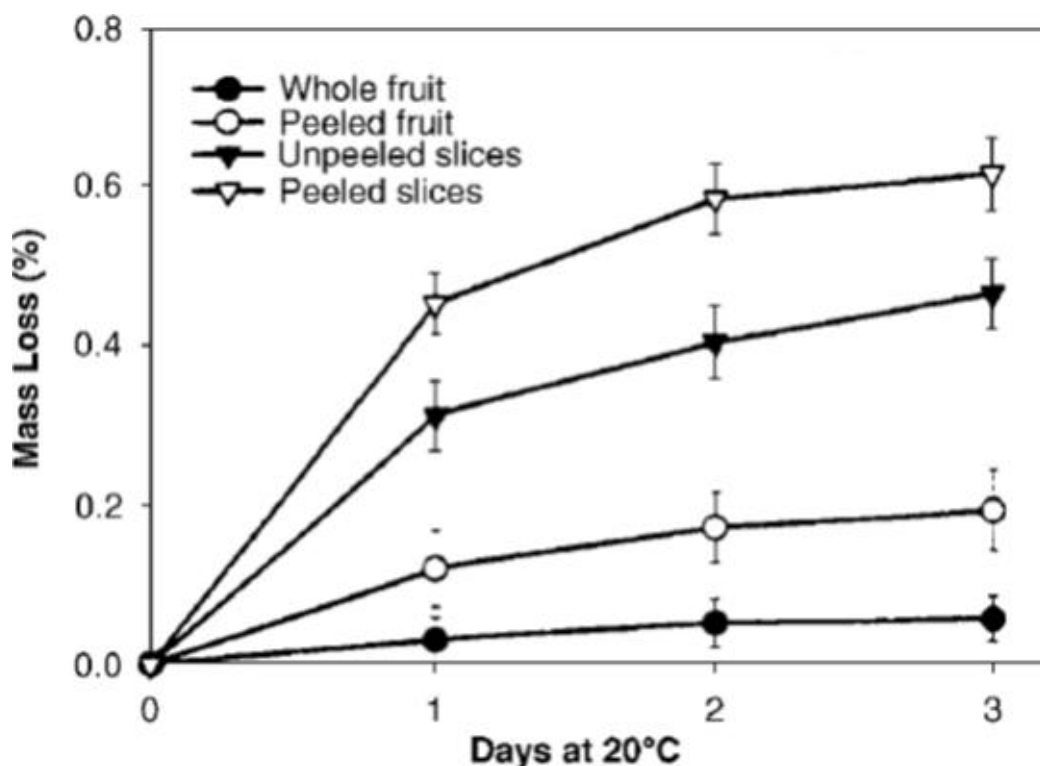


Figure 2.3 : Effect of wounding on mass loss of whole kiwifruit, whole-peeled kiwifruit, peeled slices, and unpeeled slices stored at 20°C for three days [12]

2.1.4 Membrane deterioration

Membrane deterioration results in decompartmentation of cellular structure and organization and loss of normal cellular function. Many secondary events are a consequence of membrane deterioration, the most commonly recognized being tissue browning. Another is the development of off-odors.

Wounding of tissues can result in relatively rapid deterioration in membranes, and this has been associated with oxygen-free radical production in response to wounding. [17]

2.1.5 Microbial spoilage

Fruits and vegetables are good sources of nutrients and water for humans, but also for microorganisms, which can grow easily under ambient conditions. Microorganisms can get into the fruits at different stages of their field production, at the earlier stages of development, or during postharvest handling and processing operations. Some microbes can rapidly deteriorate fruit and vegetables' appearance and other quality attributes, but do not represent a risk for consumers, while others can be harmful for consumer health (food safety related microorganisms). They can be separated into two different groups:

- Fruits and vegetables microorganisms: Include molds, yeast, bacteria and viruses which affect product quality, but do not represent a risk for consumer health.
- Harmful microorganism: They can cause illness and even death to consumers, but in general they affect neither the product appearance nor other quality attributes of the fruit or vegetable. Since no deterioration symptoms are observed in the product, care must be taken to avoid product contamination. Sanitation programs in the fields and processing area and good hygienic practices of the operators are needed to avoid product contamination. [12]

2.2 Importance of Fresh-Cut Produces Packaging

The packaging process is one of the most important among all of the food manufacturing processes, as it maintains the quality of food products for storage, transportation, and end use. Packaging prevents deterioration in the quality of foods and beverages due to environmental influences and contributes to efficient distribution, sales, and consumption. 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. Food packaging extends shelf life and maintains the quality and safety of the food products. An important secondary function of packaging is marketing, in addition to providing traceability, indications of tampering, and portion control. Although food packaging has evolved in its various functions, every package still has to meet the basic requirements. In other words, good packaging systems still must reduce food waste and spoilage during distribution, reduce the costs of preservation, extend the shelf life of foods, provide safe and convenient foods to consumers, maintain the quality of the food product, contribute to sales and marketing efforts, and address environmental issues. The quality of the packaged food is directly related to the attributes of the food and packaging materials. Most food products deteriorate in quality due to mass transfer phenomena, such as moisture absorption, oxygen invasion, flavor loss, undesirable odor absorption, and the migration of packaging components into the food. These phenomena can occur between the food product and the atmosphere, between the food product and the packaging materials, or among the heterogeneous ingredients in the food product itself. It is essential for packaging system designers to understand the effects of mass transfer phenomena on the migration of packaging components and food ingredients; on the absorption and desorption of volatile ingredients, flavors, and moisture; on gas permeation; and on the reaction kinetics of oxidation and ingredient degradation.

The food processing and packaging industries spend an estimated 15% of their total variable costs on packaging materials. The opportunities for food packaging are astronomical. Consumer preferences and innovative technologies have always been the major forces that herd change in the food industry. In the past century particularly, the increases in population, urbanization, education, lifespan and communication drove the food industry to be large - scale and health - conscious, with the safety, attractiveness and convenience of foods being the primary motivation for technological transformations. Along with the concept of eating healthy foods to balance a declining medical system, there emerged a need for convenience foods that nourish, heal and fortify. Shifts in consumer preferences

toward ready - to – cook meals, specialty foods and convenience foods have placed new demands on the food packaging industry.

The use of food packaging is a socioeconomic indicator of increased spending ability of the population, an increase in the gross domestic product or an increase in food availability. Packaging technology must balance food protection with other social and environment issues, including energy and material costs, heightened social and environmental consciousness, and strict regulations on pollutants and disposal of municipal solid waste. One of the main objectives of the packaging of food is to protect it against spoilage or deterioration due to physical damage, chemical changes or microbial growth. Physical protection protects food from mechanical damage during supply and distribution. [18, 19, 20, 21]

2.3 Active Packaging

New food packaging technologies are developing as a response to consumer demands or industrial production trends towards mildly preserved, fresh, tasty, and convenient food products with prolonged shelf-life and controlled quality.

Traditional food packaging is meant for mechanical supporting of otherwise non-solid food, and protecting food from external influences, like microorganisms, oxygen, off-odours, light etc. and, by doing so, guaranteeing convenience in food handling and preserving the food quality for an extended time period. The key safety objective for these traditional materials in contact with foods is to be as inert as possible, there should be a minimum interaction between food and packaging.

The principles behind active packaging are based either on the intrinsic properties of the polymer used as packaging material itself or on the introduction of specific substances inside the polymer.

The intrinsic properties of the polymer can give rise to the active function next to, the intentional grafting of an active group or through the introduction of an active monomer inside the polymer chain. An active agent can be incorporated inside the packaging material or onto its surface, in multilayer structures or in particular elements associated with packaging such as sachets, labels or bottle caps.

The nature of the active agents that can be added is very diverse (organic acids, enzymes, bacteriocins, fungicides, natural extracts, ions, ethanol etc.) nature of the

materials into which they are included such as papers, plastics, metals or combinations of these materials.

The active systems can be placed outside the primary packaging, in between different parts of the primary packaging or inside the primary packaging. In this last case, the systems can be in contact only with the atmosphere surrounding the food, in contact with the food surface or placed inside the food itself (for liquid foods).

Active packaging can be classified into two main types: non-migratory active packaging acting without intentional migration, and active releasing packaging allowing a controlled migration of non-volatile agents or an emission of volatile compounds in the atmosphere surrounding the food (Figure 2.4).

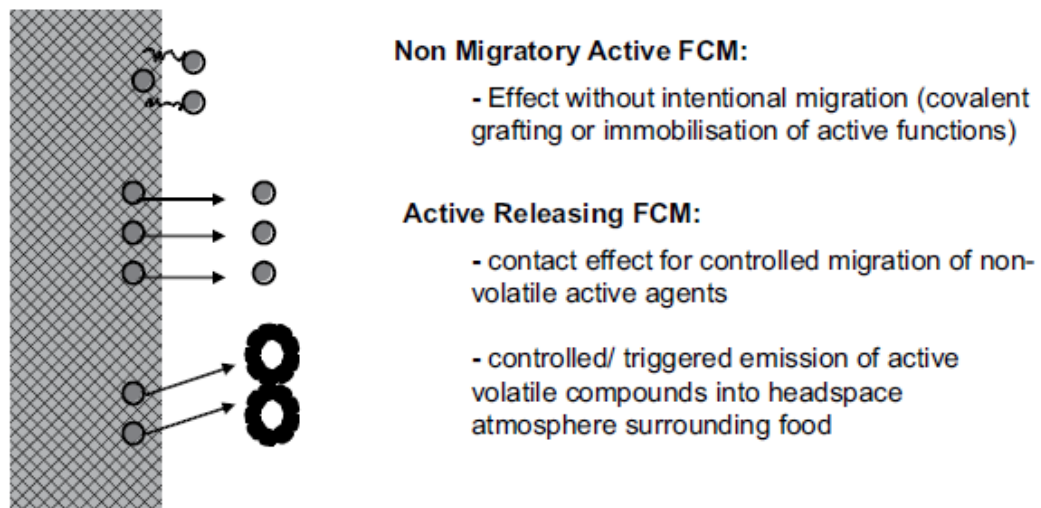


Figure 2.4 : Scheme of the two different types of active food contact materials (FCM) classified as a function of intentional or unintentional migrations [22]

Non-migratory active packaging is a packaging which elicits a desirable response from food systems without the active component migrating from the packaging into the food. [20- 22]

Active packaging can be defined as a packaging technique that actively and constantly either:

- Changes package permeation properties or the concentration of different volatiles and gases in the package head-space during storage; or

- Actively adds antimicrobial, antioxidative or other quality improving agents, flavour enhancing substances, via packaging materials into the packed food in small amounts during storage.

Intelligent, smart or clever packaging is defined as a packaging technique containing an external or internal indicator for the active product history and quality determination. Typical examples of smart packaging methods are as follows:

- Time- temperature indicators intended to be fixed onto a package surface
- O₂ indicators
- CO₂ indicators
- Spoilage or quality indicators, which react with volatile substances from chemical, enzymatic and/or microbial spoilage reactions released from food.

Active packaging is defined as an intelligent or smart system that involves interactions between package or package components and food or internal gas atmosphere and complies with consumer demands for high quality, fresh-like, and safe products.

Active packaging extends the shelf life of foods, while maintaining their nutritional quality, inhibiting the growth of pathogenic and spoilage microorganisms, preventing and/or indicating the migration of contaminants, and displaying any package leaks present, thus ensuring food safety.

Active packaging performs some desired role other than providing an inert(passive) barrier to external conditions. Active packaging concepts thus enhance the performance of the package, by changing the condition of the packaged food to improve quality and shelf life. With consumer interest in ever higher quality and safety in foods, active packaging is a field of high interest and development.

Active packaging includes components of packaging systems that are capable of acting as the following:

- Oxygen scavengers
- Carbon dioxide scavengers/emitters
- Moisture absorbers
- Ethylene and flavor/odor taints

- Releasing carbon dioxide
- Ethanol emitters
- Antioxidants and other preservatives
- Maintaining temperature control compensating for temperature changes
- Microwave [23, 24]

2.3.1 Oxygen scavengers

Oxygen scavenging is today the most important type of active packaging from a commercial point of view. If one looks at the feasible commercial solutions for oxygen scavenging, the following approaches have been used until now:

- The presence of additional sachets containing oxygen-scavenging materials, similar, for example to the familiar sachets of desiccant in packaging containing electronic goods
- The presence of internal labels, or the packaging materials themselves, which contains the O₂ scavengers in very layers

The main cause of most food spoilage is oxygen, since its presence allows a myriad of aerobic food-spoiling microorganisms to grow and thrive. Oxygen also spoils many foods through enzyme-catalyzed reactions, as in the browning of fruit and vegetables, destruction of ascorbic acid, and the oxidation of a wide range of flavors. Japan is the most important market area for O₂ scavengers. Use of O₂ absorber pouches is especially advantageous for O₂ and light-sensitive products, such as bakery products and pizzas, cooked ham, etc., where mould growth or colour changes are a problem.

Active packaging with O₂ scavengers actively decreases the O₂ concentration in the package head-space, even down to 0.01% thus retarding the oxidation processes, colour changes, yeast and mould growth, etc., occurring in foods. Moreover, if the scavenger has sufficient capacity, it will also absorb O₂ that leaks into the head-space through pinholes and prolong the shelf-life of the packed foodstuffs.

Most of the currently used O₂ absorbers are iron based, using treated iron powder. For an O₂ absorber to be effective the packaging material used has to be a relatively

good barrier to O₂ permeation, otherwise the scavenger will rapidly become saturated and lose its ability to trap O₂. [23, 24]

The most significant manufacturers and trade names for O₂ absorbers are listed in Table 2.2.

Table 2.2 : Manufacturers and trade names of oxygen absorber sachets/labels [23]

Manufacturer	Country	Trade name
Mitsubishi Gas Chemical Co., Ltd	Japan	Ageless
Toppan Printing Co., Ltd	Japan	Freshilizer
Toagosei Chemical Industry Co., Ltd	Japan	Vitalon
Nippon Soda Co., Ltd	Japan	Seaqul
Finetec Co., Ltd	Japan	Sanso-Cut
Multisorb Technologies Co., Ltd	USA	FreshMax
		FreshPax
Standa Industrie	France	ATCO
Bioka Ltd	Finland	Bioka

2.3.2 Carbon dioxide scavengers and emitters

While most O₂ scavengers have a single objective, i.e. to remove O₂ from the packaging atmosphere, there are a few examples of absorbents with dual function. One such product is a sachet containing ascorbic acid and iron carbonate, which produces the same volume of CO₂ as that of consumed O₂. This is necessary in order to prevent package collapse and can be taken that any flavour changes that could be caused by the dissolution of CO₂ in the aqueous or fat phase of the product do not take place. Another type of active packaging, which is utilised for ground coffee, scavenges CO₂ as well as O₂. Fresh roasted coffee can release considerable amounts of CO₂. Unless removed, the generated CO₂ can cause the packaging to burst due to the increasing internal pressure. The reactant commonly used to absorb CO₂ is calcium hydroxide which, at a high enough water activity, reacts with CO₂ to form calcium carbonate.

A disadvantage of this CO₂-scavenging substance is that it scavenges carbon dioxide from the package headspace irreversibly and result in depletion of CO₂, which is not always desired. In the case of packaged kimchi, depletion of CO₂ in the kimchi juices causes loss of the product's characteristic fresh carbonic taste. Therefore, reversible

absorption or adsorption by physical sorbents such as zeolites and active carbon may be an alternative.

Since the permeability of CO₂ is three to five times higher than that of O₂ in most plastic films, it must be continuously produced to maintain the desired concentration within the package. High CO₂ levels may, however, cause changes in the taste of products and the development of undesirable anaerobic glycolysis in fruits. Consequently, a CO₂ generator is only useful in certain applications such as fresh meat, poultry, fish, and cheese packaging. [23, 24]

2.3.3 Ethylene scavengers

Ethylene is a plant hormone, which is produced during ripening of fruits and vegetables. Ethylene can have both positive and negative effects on fresh produce. It catalyses the ripening process and exposure to high levels of ethylene can be used to induce rapid ripening of products such as bananas and tomatoes. Ethylene can also be used to de-green fruits of citrus variety. Generally, however, ethylene is seen as an unwanted substance since even in small amounts it can be very detrimental to the quality and longevity of many products. The increased respiration rate, which is an effect of ethylene exposure, leads to softening of fruit tissue and accelerated senescence. Furthermore, ethylene promotes the degradation of chlorophyll and is responsible for a series of post-harvest disorders. Consequently, it is desirable to suppress the effects of ethylene by somehow removing the substance from the horticultural environment.

The most widely used ethylene-scavenging packaging technology today is in the form of a sachet containing potassium permanganate immobilized on an inert porous support, such as alumina and silica, at a level of about 5% w/w. The ethylene is scavenges through an oxidation reaction with the potassium permanganate to form carbon dioxide and water. Although these permanganate-based ethylene-scavenging sachets are effective at removing ethylene, their use is sometimes accompanied by undesirable effects. These include possible migration of the potassium permanganate from the sachet onto the produce, lack of specificity to ethylene resulting in desirable aromas being scalped, and a general lack of user enthusiasm for the use of sachets. Other types of sachet-based ethylene-scavenging technologies utilize activated carbon with a metal catalyst (e.g., palladium).

As ethylene in the atmosphere surrounding the produce increases, the plant's respiration rate increases.

If the ethylene level of the surrounding environment is maintained low, respiration slows. The effect on the respiration rate depends primarily on the relative concentration compared to the ethylene emission of the plant, rather than on the absolute ethylene concentration.

When ethylene is removed from the fresh fruit or vegetable environment, the ripening and deterioration processes of plant products are slowed, and so the storage life is extended.

Ethylene accelerates the respiration rate, resulting in shorter shelf life; therefore, storing fruits and vegetables in refrigeration temperatures is recommended to lower the respiration rate. Ethylene production is also enhanced with increasing amounts of oxygen and it is important to reduce oxygen, but not to levels that inhibit fruit and vegetable respiration or produce anaerobic conditions. Carbon dioxide may inhibit the production of ethylene because it binds ethylene-binding sites of specific enzymes, thus preventing ethylene-induced conformational changes of the tissue. Consequently, reduced oxygen and ethylene concentrations, combined with increased CO levels, may avoid the accumulation of ethylene and in turn prevent accelerated deterioration of the plant tissues. [3, 6, 23, 24]

2.3.4 Moisture/water absorbers

An unwanted accumulation of liquid water can occur in packages due to transpiration of horticultural produce, drip of tissue fluid from meats, or temperature fluctuations in high moisture packages. It is essential to remove excess water since the build-up promotes the growth of moulds and bacteria. Other negative consequences include fogging of films and the appearance of mobile blood and tissue fluid. There is interest not only to absorb the liquid water from the packaging but also to intercept the moisture in the vapour phase in order to lower the water activity at the food surface. As a result unfavourable conditions for mould and bacterial growth are created and an extended shelf-life of the product is obtained.

Drip-absorbent pads can often be found in packaging for cut meat and poultry. They consist of granules of a superabsorbent polymer between two layers of a microporous

or non-woven polymer which is sealed at the edges. The absorbers remove liquid water and prevent discoloration of both the product and the package.

The polymers most frequently used for absorbing water are polyacrylate salts and graft copolymers of starch. These superabsorbent polymers are capable of absorbing between 100 and 500 times their own weight of liquid water. Similar devices, but on a much larger scale, are used in packaging for air transportation of fresh fish and other seafood to absorb melted ice.

By reducing the relative humidity inside a package the water activity at the food surface is lowered. The concomitant result is a positive effect on the longevity of the product. In order to achieve this the water must be absorbed in its vapour phase which is more effectively done using humectants instead of superabsorbing polymers.

During distribution and storage of fresh produce there are great risks for accumulation of water caused by the continuous evaporation from the products and the inevitable temperature fluctuations during handling and transportation. High humidity and condensation of water increase the possibility of microbial growth on the products. This problem can be overcome either by including microporous pads containing water-absorbing inorganic salts or by lining the fibreboard cartons with a protected layer of a solid polymeric humectant.

Anti-fog additives can be blended with the polymer resin before extrusion in order to prevent fogging and forming of droplets on the inside of a package. The amphiphilic additives lower the interfacial tension between the polymer and water condensate. As a consequence, the water droplets coalesce and spread as a thin transparent layer across the polymer film. The customer can see the product clearly, but the water remains in close proximity to the food with the potential of causing spoilage. Therefore this type of treatment can merely be regarded as a cosmetic form of active packaging which does not improve the quality or prolong the shelf life of the packaged product. [23]

2.3.5 Ethanol emitters

Ethanol has been used as a preservative for centuries. At high concentrations ethanol denatures the proteins of moulds and yeasts and, although the action is not as severe,

it exhibits antimicrobial effects even at low levels. Spraying the foodstuff with ethanol prior to packaging can be used to obtain the desired effect, but in some cases a more practical option can be to use sachets generating ethanol vapour.

A product called Ethicap consists of an ethanol/water mixture absorbed onto a silicon dioxide powder, contained in a sachet of a laminate of paper and ethyl vinyl acetate copolymer. The odour of alcohol can be masked by adding traces of flavours, such as vanilla, to the sachet. Ethicap acts by absorbing moisture from the food and releasing ethanol vapour into the packaging head-space. The size of the sachet used depends on the water activity of the food and the desired shelf-life of the product.

The main disadvantage of using ethanol vapour for preservation purposes is its off-odour and off-flavour formation to the foodstuff, and absorption from the head-space by the foodstuff. In some cases the ethanol concentration in the product might reach a couple of percent, which might cause regulatory problems. If the product is heated in an oven prior to consumption the accumulated ethanol will evaporate, leaving only traces in the food. Therefore ethanol vapour generators can safely be used in products intended to be heated before use. They can provide a viable alternative or supplement to gas packaging for prolonging shelf-life of foods with regards to microbial spoilage. [23]

2.3.6 Flavor odors/absorbers

As far as food aromas are concerned, plastics are usually considered to have a negative impact on food quality. Flavor scalping, that is, sorption of food flavors by polymeric packaging materials, may result in loss of flavor and taste intensities and changes in the organoleptic profile of foods. However, flavor sorption could be used in a positive way to selectively absorb unwanted odors and flavors. Odor removers have the potential to scavenge the malodorous constituents of both oxidative and nonoxidative biochemical deterioration. Many foods such as fresh poultry and cereal products develop very slight but nevertheless detectable deterioration odors during product distribution, e.g., such as sulfurous compounds and amines from protein/amino acid breakdown or aldehydes and ketones from lipid oxidation or anaerobic glycolysis. These odors are trapped within gas-barrier packaging so that, when the package is opened, they are released and detected by consumers. Another

reason for incorporating odor removers into packages is to obviate the effect of odors developed in the package materials themselves.

Flavor enhancers are among the most controversial areas of active packaging due to concerns regarding their ability to mask product taint.

In some applications, off-odors are the only by-products of food product spoilage, and their removal does impair the consumers' ability to recognize the point at which a food has become a safety hazard. These devices have been used to mask the impact on food flavor of plastic and other packaging materials by the release of neutralizing substances from the active element. Such devices have been applied to the positive effect of reinforcing and improving the flavors of foods, for example, to the packaging of vitamins with activated carbon used to absorb naturally occurring off-odors. [24]

2.4 Modified Atmosphere Packaging (MAP)

As long ago as the 1930s, controlled atmospheres were used in storage rooms during shipment and transportation to preserve the freshness of fruits. The gas machinery allowed the maintenance of low O_2 and moderate to high CO_2 levels. That is why MAP historically refers to a ratio of O_2 and CO_2 in the headspace of packaging. It can be and is increasingly extended to other gases (e.g., argon and even xenon) or vapors (water vapor, ethylene, aroma compounds, etc.). [25]

The objective of MAP design is to define conditions that will create the atmosphere best suited for the extended storage of a given produce while minimizing the time required to achieve the atmosphere. In other words, the goal of MAP is to achieve the equilibrium concentrations of O_2 and CO_2 within the package within the shortest possible time because of the interaction of the produce, the package and the external atmosphere; and these concentrations lie within the desired level required for maximum possible storage life of the commodity. The equilibrium concentration of O_2 and CO_2 achieved within the package for a packaging system needs to be remained constant throughout the period of storage to continue the respiration rate and the rate of all metabolic processes at a minimum possible rate for maintaining freshness and extending the shelf life of stored commodity. [5]

It is essential to carefully select a film with suitable gas and vapor permeabilities. It should be stressed that most synthetic polymer films exhibit too low permeability to gases and vapors and most often need to be perforated (micro-holes) to allow sufficient gas exchange.

Whatever the packaging material used, the produce can be exposed to unsuitable gas compositions during the transient period, thus preventing the positive effects of the steady state atmosphere. For instance, Barron et al. (2002) showed that, in mushroom packages, the transient CO₂ peak induced browning. [25]

Modified atmosphere packaging describes altering the gases surrounding a commodity producing an atmospheric composition different from that of air. The purpose of modified atmosphere is not necessarily to create a fixed gas composition throughout the shelf life, as in controlled atmosphere storage.

MAP creates a predetermined gas composition, which may change over time. Variables that are related to produce physiology (respiration rate, etc.), physical factors of the environment (temperature, RH, etc.) and barrier properties of the packaging material determine the specific gas composition at equilibrium. [26]

2.4.1 Passive modification

In passive MAP, gas and vapor exchanges occur between the produce and its surroundings as well as through the packaging material, as indicated in Figure 2.5. If there is microbial contamination, respiration pathways of microorganisms (aerobic or anaerobic) are also involved in gas exchanges. Initially the headspace composition is air and then, after a transient period, it reaches a steady state when gas and vapor permeation through the material balances gas and vapor consumption and production from the produce. This steady state atmosphere must be as close as possible to the optimal recommended atmosphere; otherwise it might be detrimental to the quality of the commodity. [25]

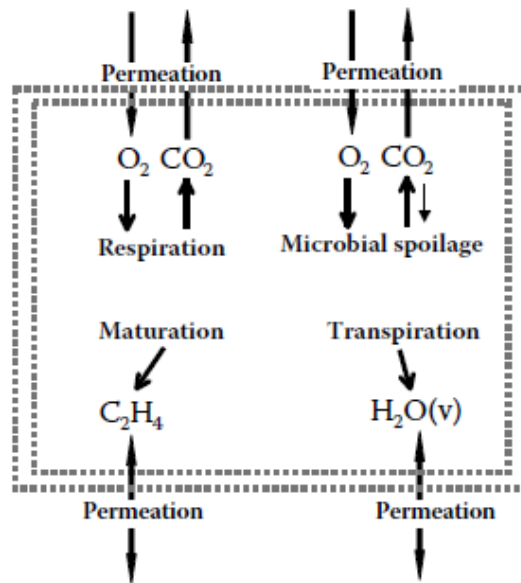


Figure 2.5 : Relations between physiological phenomena and packaging permeation in passive MAP [22]

This technology is targeted at reducing the respiration rate of fresh produce and slowing senescence. The nineteenth century French chemist Berard is reported to be the first to study the effect of modified atmosphere on the shelf life of horticultural products. The result of his work showed that fruits do not ripen in anaerobic conditions. In the 1920s, Kidd and West studied how O_2 and CO_2 affect the shelf life of apples, pears and berries. Their research led to the important finding that low O_2 and moderately high CO_2 storage conditions could extend the shelf life of fruits.

A passive MAP occurs when fresh produce is hermetically sealed in a semipermeable container. The respiration process of the produce and, to a certain extent, the microbial growth, combined with container permeability alters the gas composition. Because of the respiration process, the produce consumes the surrounding O_2 and produces CO_2 , and therefore, the O_2 level is reduced, while the CO_2 level is increased. After a period of adjustment between respiration rate and permeation rate, a steady state is established inside the package equals the O_2 and CO_2 amount permeating through the film. Thus, passive atmosphere modification is a complex process with many interactions among different components and variables. If the container is impermeable to gases, then theoretically, O_2 concentrations may be lowered (from atmospheric 21%) to near %0, while CO_2 (initially %0.03 in the container) concentrations can reach 20% or higher.

On the other hand, an active MAP can be achieved by flushing out the air within the package with a precise mixture of gases to create an initial atmosphere. Usually, nitrogen serves as a filler gas to provide a precise concentration of other gases in the package, as well as to prevent the package from collapsing.

Passive MAP typically applies to fresh or minimally processed produce. It consists of packaging the produce product under ambient conditions (air: $N_2/O_2 = 78/21$) using a permeable film. During the course of storage, the produce product continues to respire by consuming O_2 and producing CO_2 and the atmospheric environment changes accordingly (high in CO_2 and low in O_2). Depending on the film permeability, the atmospheric content in the container will eventually reach a state of equilibrium, extending the keeping quality by a few extra days.

However, it takes time before the atmospheric content in the container reaches the state of equilibrium and it is difficult to obtain optimum results for keeping quality. Also, different produce products have different respiration rates, so it is difficult to optimize the keeping quality by using the film alone. [27]

2.4.2 Active modification

Active MAP has been developed to overcome this drawback and suppress or reduce the transient period. Gas flushing with an inert gas mixture is used to quickly reach a desired ratio of O_2 and CO_2 and suppress the transient period of passive MAP so that the initial head-space composition is different from normal air. As shown in Figure 2.6, active MAP can also be achieved by the release or absorption of gases or vapors from or by active agents in combination with gas/vapor permeation. This opens up new possibilities for packaging such as the controlled release of antimicrobial agents in case of temperature abuse and/or the removal of unsuitable substances such as ethylene when produced. Such systems are commercially available for MAP of fresh produce. [25]

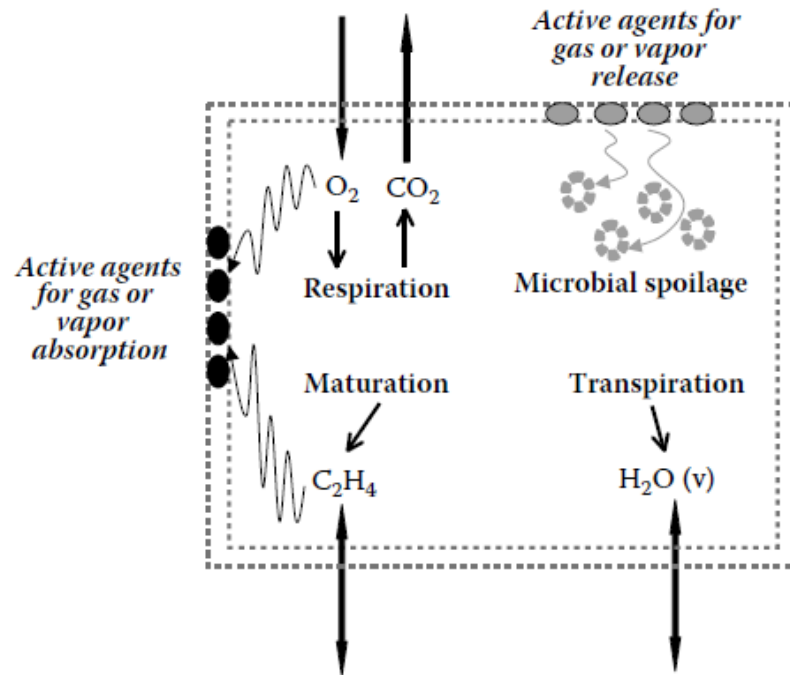


Figure 2.6 : Relations between physiological phenomena and packaging permeation and absorption/releasing properties in active MAP [22]

Active MAP is similar to the passive MAP process except that a special gas mixture is introduced into the container before it is sealed. The gas mixture has three main functions:

- Control the produce product's respiration rate. Instead of relying solely on film permeability, a favorable atmospheric environment is provided to the product at time 0 to regulate the respiration rate and provide more favorable results. Figure 2.7 illustrates the benefit of active MAP; the appropriate combination of a gas mixture ($N_2/CO_2=80\%/20\%$) and a permeable film ($OTR = 1500/m^2$) was applied to the packaged fresh-cut pineapple (approximately 1 x 0.5 in. Size) on day 0. The respiration rate (measured by CO_2 concentration in the headspace) of pineapple was controlled at a constant rate so that the shelf life was noticeably better than the control (the same film was applied, but packaged in air). The film permeability remains a crucial parameter because the atmospheric environment needs to be maintained during storage.

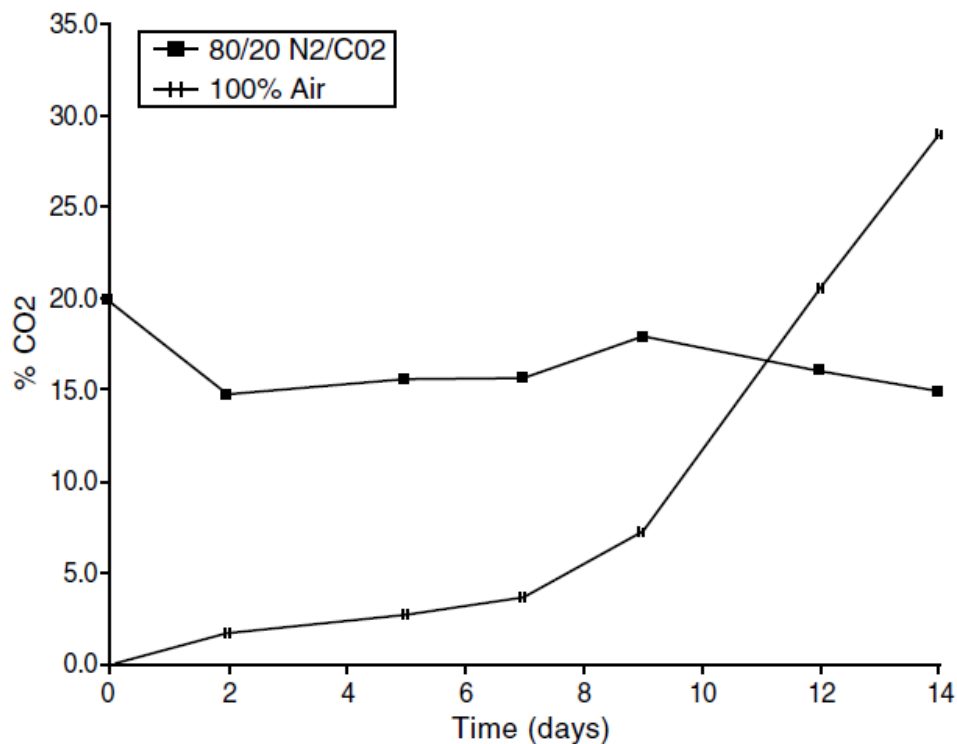


Figure 2.7 : Carbon dioxide production rates of fresh cut pineapples stored under MAP vs. air at refrigerated ($2 \pm 1^\circ\text{C}$) temperature [29]

- Maintain or enhance the product's attributes. For example, O_2 level is essential to make the color of the meat product bloom. On the other hand, any oxygen-sensitive products, e.g., potato chips or deep fried foods, should avoid oxygen in the package.
- Retard the growth rate of spoilage microorganisms. The effectiveness of the gas or gas mixture depends on numerous factors. One factor could trigger the others, and it takes more skill to optimize those factors. Generally speaking, CO_2 at a higher level (more than 20%) can slow down spoilage bacteria and improve keeping quality. Although elevated CO_2 provides a favorable environment for the growth of beneficial lactic acid bacteria in the biopreservation technology, a high concentration of CO_2 (>50%) also has inhibitory effects on them.

2.4.3 MAP design and optimization

To successfully achieve beneficial MAP, the package must be properly designed, taking into consideration the physiology of the product to be packaged. Respiration

of a packaged product will consume O_2 within the package and produce CO_2 (Figure 2.8).

As the product modifies the atmosphere within the package, the concentration gradients of these gases increase, driving a net flux of gases in and out of the package. If the permeability of the package is adequate, the atmosphere composition within the package will reach a steady-state in which the package atmosphere composition remains constant and the rate of O_2 consumption and CO_2 production of the product is equal to the permeation rate of these gases through the package.

Figure 2.8 shows how steady-state atmospheres develop in both solid film and perforated packages of diced red onions after about 7 to 10 days. The time required to reach a steady-state atmosphere is dependent on the headspace volume of the package and the respiration rate of the product. A steady-state will be reached more rapidly with packages having low headspace volumes and products with high respiration rates. For a steady-state atmosphere to be maintained the respiration rate of the product must remain constant. This process of package atmosphere modification is referred to as passive MAP since it is dependent solely on the respiration of the product and the permeation properties of the package.

Several models have been published that describe this relationship of product respiration, package permeability and the environment.

To develop a MAP for fresh-cut produce, a target steady-state package atmosphere must be determined. Target atmosphere compositions must consider both potential benefits of an optimum atmosphere composition and the risks of developing an injurious composition. [27, 28, 29]

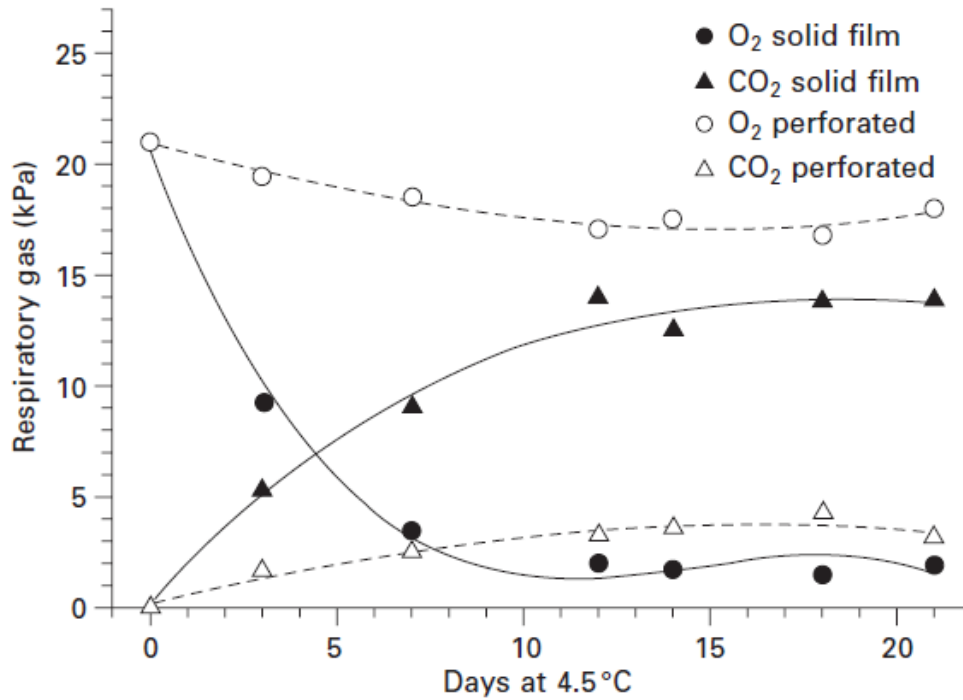


Figure 2.8 : Change in atmosphere composition of passive modified atmosphere packages containing red diced onions during storage at 4.5 °C. Packages consisted of a sealed solid film polyethylene bag and a perforated bag having one 0.7 mm perforation [27]

A fundamental knowledge of gas permeability characteristics of the film as well as of the produce is essential for the development of both types of MAP systems. A successful MAP design requires the determination of respiration rate and respiration quotient (R_{CO_2} / R_{O_2}) of the produce, an appropriate polymeric film with a suitable barrier properties, appropriate film area, appropriate produce weight, and appropriate headspace volume.

MAP technology is an interactive system that permits interplay between the physiological parameters of the commodity and the film characteristics. In such a system, there are four main processes occurring simultaneously: respiration of the produce, transpiration of the produce, permeation of gases through the packaging material and heat transfer. Respiration changes according to the following factors: temperature; produce maturity; and CO_2 , O_2 and ethylene levels within the package. The temperature of the produce is also altered due to the heat generated by the respiration process. Transpiration depends on the produce surface temperature and the temperature and relative humidity (RH) of the surroundings.

Permeability properties of the polymeric film depend on the chemical makeup of the material, ambient temperature, film thickness, permeating gas and the difference in gas concentrations across the film. Understanding the extent of all of these variables is necessary to optimize the effect of MAP on extending the shelf life of a chosen FCF commodity. [26]

The main goal for MAP of minimally processed produce is to extend keeping quality or shelf life. “Keeping quality” is more commonly used than “shelf life” because of consumer demand for product freshness. It is often difficult to label as “fresh” a product that has remained in refrigerated storage for 2 weeks. However, the extension of shelf life remains a key objective for food processors due to economic reasons. Figure 2.9 illustrates the concept of extending keeping quality vs shelf life.

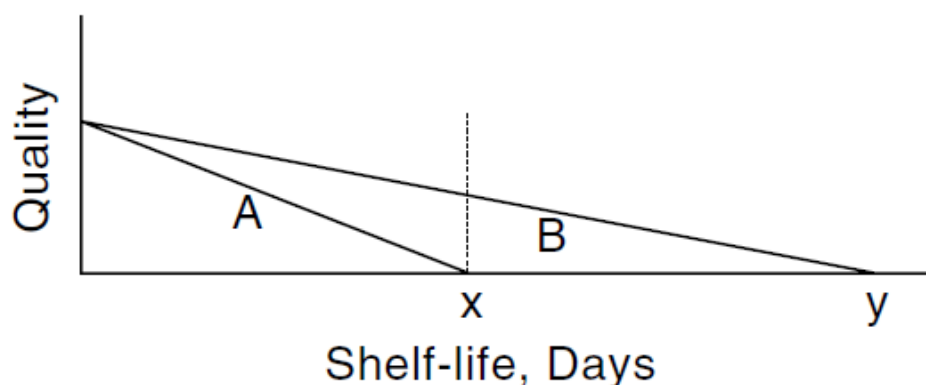


Figure 2.9 : Shelf life vs. quality extension [29]

For any given minimally processed food, line A represents x days of shelf life based on the current packaging format and line B represents extended y days of shelf life by using MAP technology. Properly engineered, MAP can extend the shelf life of a product or better preserve its freshness and quality within the same shelf life. A vertical line drawn on day x clearly shows the quality difference between line A and B. [27,28,29]

2.4.4 Effect of MAP

The effects of MAP are often based on the observed slowing of plant respiration in a low O_2 environment. As the concentration of O_2 inside the package falls below about 10-12%, respiration starts to slow. This suppression of respiration continues until O_2

reaches about 2-5% for most produce. If O₂ gets lower than 2-5% (depending on product and temperature), fermentative metabolism replaces normal aerobic metabolism and off-flavors, off-odors and undesirable volatiles are produced. Similarly, as the concentration of CO₂ increases above the atmospheric level, a suppression of respiration rate, ethylene (C₂H₂) production and sensitivity to ethylene, and suppression of activities of microorganisms and fungal/bacterial growth, result for some commodities. Reduced O₂ and elevated CO₂ concentrations together can reduce the rate of respiration more than by either alone. The diminution of enzymatic activities by providing low temperature and low O₂ and high CO₂ concentrations in general reduces the utilization rate of the substrate (i.e. carbohydrate, organic acid and other reserves) and increase the post-harvest life of the fruits and vegetables beyond its normal span. Others consider that elevated CO₂ might inhibit C₂H₂ production and/or suppress plant tissue sensitivity to the effects of the ripening hormone ethylene rather than having a direct effect on the respiration process. For those products that tolerate a high concentration of CO₂, suppression of the growth of many bacteria and fungi results at greater than 10% CO₂.

Respiration rates vary among and within commodities. Tissues with vegetative or floral meristems such as asparagus and broccoli have very high respiration rates. Vegetables include a great diversity of plant organs (roots, tubers, seeds, fruits, stems and leaves) that have different metabolic activities and consequently different respiration rates. Even different varieties of the same product can exhibit different respiration rates. As plant organs mature, their rate of respiration typically declines. This means that commodities harvested during active growth, such as many vegetables and immature fruits, have high respiration rates. Mature fruits, dormant buds and storage organs have relatively low rates. After harvest, the respiration rate typically declines, slowly in non-climacteric fruits and storage organs, rapidly in vegetative tissues and immature fruits. The rapid decline presumably reflects depletion of respirable substrates that are typically low in such tissues.

An important exception to the general decline in respiration following harvest is the rapid and sometimes dramatic rise in respiration during the ripening of climacteric fruit. This rise, which has been the subject of intense study for many years, normally consists of four distinct phases: pre-climacteric minimum, climacteric rise, climacteric peak, and post-climacteric decline. In general, non-climacteric

commodities have higher respiration rates in the early stages of development that steadily decline during maturation. Respiration rates of climacteric commodities also are higher early in development and decline until a rise occurs that coincides with ripening or senescence. Climacteric products exhibit a peak of respiration and ethylene (C₂H₂) production associated with senescence or ripening.

The division of fruits into climacteric and non-climacteric types has been very useful for post-harvest physiologists. Respiratory rises also occur during stress and other developmental stages, but a true climacteric only occurs coincident with fruit ripening. Table 2.3 shows general classification of fruits according to their respiratory behavior during ripening. [26]

Table 2.3 : Fruits classified according to respiration behavior during ripening [26]

Climacteric fruits		Non-climacteric fruits	
Apple	Papaya	Blackberry	Loquat
Apricot	Passion fruit	Blueberry	Litchi
Avocado	Peas	Cacao	Okra
Banana	Pear	Caju	Olive
Blueberry	Persimmon	Carambola	Orange
Breadfruit	Plantain	Cashew apple	Peas
Biriba	Plum	Cherry	Pepper
Cherimoya	Quince	Cucumber	Pineapple
Fig	Rambutain	Date	Pomegranate
Guava	Sadopilla	Eggplant	Prickly pear
Jackfruit	Sapota	Grape	Raspberry
Kiwifruit	Soursop	Grapefruit	Strawberry
Mango	Tomato	Jujube	Summer squash
Muskmelon	Watermelon	Lemon	Tamarillo
Nectarine		Lime	Tangerine
		Longan	

2.4.5 Polymeric films used for modified atmosphere packaging of fresh-cut produce

Modified atmosphere packaging (MAP) is an essential technology for the success of fresh-cut produce products in the marketplace. Polymeric films are a key element in MAP. Beneficial packaging environmental conditions, such as headspace composition or O₂, CO₂, and relative humidity levels in the fresh-cut produce packages, rely on the balance of produce physiological activities (respirations) and

permeability of polymeric films to water vapor and gases and package integrity (no leakage). Various polymeric films have been tested for packaging fresh-cut fruits and vegetables, including polyethylene, polypropylene, polystyrene, polyvinyl chloride, polyamide, ethylene vinyl acetate (EVA), ionomers, bioplastics, and microperforated films. However, most commonly used packaging polymer films in the current fresh-cut industrial practice are limited to a few polymers: polyolefins (including polyethylene and polypropylene), vinyl compound polymers (polystyrene and polyvinyl chloride), and polyethylene terephthalate (polyester). [30]

2.4.5.1 Polyethylene (PE)

Polyethylene is a thermoplastic polymer consisting of long chains with a repeat unit $-\text{CH}_2-\text{CH}_2-$ which is the largest volume single polymer used in food packaging in both film and blow-molded form. It is one of the most inert polymers and constitutes no hazard in normal handling. Polyethylene is divided based on its density into low-density polyethylene and high-density polyethylene. [30]

2.4.5.1.1 Low-density polyethylene (LDPE)

LDPE is a branched-chain thermoplastic polymer produced by high pressure addition polymerization of the ethylene monomer at 150-350°C using a radical initiator such as oxygen or an unstable peroxide. The vigorous nature of the high pressure process leads to a great deal of chain branching, with both short and long chains being formed. The branch chains prevent close packaging of the main polymer chains (carbon backbone), resulting in a resin having a density ranging from 0,910 to 0,940 g/cm³. The great length of the polymer chains results in a certain amount of entanglement that prevents complete crystallization (having a direct effect on the permeability, transparency, and mechanical properties of polymeric film) on cooling. The crystallinity of LDPE usually varies between 50 and 70%. LDPE can be blow extruded into tubular films or extruded through a slit die and chill-roll cast, with the latter process giving a clearer film. Because LDPE has a good tensile strength, burst strength, can retain strength down to -60°C, and is relatively transparent and flexible, it is predominantly used to manufacture flexible films such as those used for plastic retail bags and grocery bags. It is also used to manufacture some flexible lids and bottles. In Japan, polyethylene was perforated to make a freshness preservative film

(microporous film) by adding inorganic filler materials (particles added to plastics to lower the consumption of more expensive binder material or to improve some properties of the mixed material) to increase the transmission rate of CO₂. In the rigid packaging applications, the surface of polyethylene containers can be treated with fluorine after blow molding to form a very thin, polar, cross-linked surface that decreases the permeability of the polyethylene to nonpolar permeants, O₂ and CO₂. LDPE can also be made shrinkable by blending it with HDPE or by radiation induced cross-linking. LDPE is a good barrier to water vapor but a poor barrier to oxygen and carbon dioxide. [30]

2.4.5.1.2 High-density polyethylene (HDPE)

HDPE is a linear thermoplastic polymer with little branching or few side chains. It has higher crystallinity and density. HDPE film is stiffer and harder than LDPE, and lower transparency and O₂, CO₂ permeability than LDPE. [30]

2.4.5.2 Polypropylene (PP)

Polypropylene is a tough, lightweight and linear polymer. Crystallinity changes due to tacticity of polypropylene. PP has a gas permeability between HDPE and LDPE. [30]

2.4.5.3 Polymethylpentene (PMP)

Polymethylpentene, a 4-methylpentene-1 based polyolefin. This lightweight, functional polymer displays a unique combination of physical properties and characteristics due to its distinctive molecular structure which includes a bulky side chain. PMP characteristics are similar to those of traditional polyolefins and include excellent electrical insulating properties and strong hydrolysis resistance. In addition, PMP features low dielectric, superb clarity, transparency, gas permeability, heat and chemical resistance and release qualities.

This PMP can be used for extruded and film products, injection molded, and blow molded applications. PMP applications include:

- Release film
- Release paper for synthetic leather
- LED molds,

- Mandrels and sheaths for rubber hose production
- Cosmetic caps and tubes
- Heat resistant non-woven
- Chemical tubes
- Animal cages

It is also FDA compliant for use in food processing machinery. PMP is often used in films and coatings for gas permeable packaging. [31]

2.5 Literature Survey

Wanjale and co-workers used PMP polymer with clay. Melt intercalation of PMP is carried out with organoclays of different cation/charge exchange capacities and modifiers to facilitate intercalation of the polymer into the silicate layers. The effect of modifiers on the structure and properties of PMP/clay nanocomposites was explored in this study. XRD patterns confirmed the intercalation of polymer in the layered silicates as evidenced by the increase in the inter-layer spacing which is dependent on the type of modifier used. [32, 33]

Another example for PMP polymer usage in tissue engineering field was studied by Petr Slepíčka and co-workers. The researchers used PMP polymer in order to obtain new biological and biocompatible replacements, which could regenerate or improve the functions of damaged tissues and organs. In this study, the surface properties of PMP polymer such as surface polarity, surface free energy, the surface morphology and roughness were subjected to plasma treatment and thermal annealing. As a result of this alteration it was foreseen that it is possible to obtain a replacement material which provides regeneration of vascular smooth muscle cells. The plasma treatment improves significantly vascular smooth muscle cell adhesion and proliferation on the PMP's surface. [34]

Another tissue engineering application of PMP polymer was studied by Gerson and co-workers. Fixed human erythrocytes were used as model particles for this study of adhesion and phagocytosis by rat peritoneal macrophages. Within this project, adhesion of these cells were provided onto PMP polymer layer. [35]

In addition to PMP usage in tissue engineering applications, another application field of PMP polymer is medical applications as it was mentioned above. Filter parts of

medical devices such as blood filters or respirators are membranes which are based on polymeric materials. For instance, some diseases which show increase recently, make essential the usage of respirators such as lung disease. Hence, necessity of respirator usage is increased. Wu and co-workers aimed to access the biocompatibility of a newly developed long-term wearable artificial pump-lung in a clinically relevant ovine animal model. Inside the oxygen pump of the device, there was a PMP polymer based membrane. This membrane which was produced from PMP polymer separated oxygen without sacrificing oxygen flow. This wearable artificial pump-lung which was included this PMP polymer based membrane was tried for 30 days on 5 ovine animals. Then they were analyzed performance and biocompatibility of this artificial pump-lung. [36]

Searches about PMP membrane usage is not only for medical applications. Zhenjie and co-workers worked about a membrane which was based on PMP polymer in order to separate hydrocarbons from permanent gases which have a considerable importance in the chemical industry. Several types of non-porous, nano-sized, fumed silica fillers were incorporated in PMP to manipulate the molecular polymer chain packaging. The pure and mixed-gas permeation properties of the PMP/silica hybrid membranes were studied within this project. The n-butane/methane selectivity was 13 for pure PMP, but increased to 26 for 45 wt% silica-filled PMP. [37]

The only study which is similar to this thesis was done by Scafati and co-workers. In this study, they were analyzed the effect of PMP copolymer with random polypropylene (PP) on the gas permeability properties by using extrusion process. Different compositions of PP/PMP blends were prepared in a laboratory scale twin screw extruder. The films which were produced from the granules obtained from extrusion process were produced by using laboratory scale cast film extrusion system which has a single screw. They were reported that a commercial grade polypropylene (PP), commonly used for food packaging applications, and a commercial poly(4-methyl-1-pentene) based material (PMP), characterized by very high gas permeability values and excellent optical properties. It was also reported that increasing PMP content was increasing the gas permeability of films. It is also seen that the use of a polyolefin with high bulky branches like PMP nearly doubles the permeability to gases and vapors in blends with PMP content below 20 wt%. [38]

The studies were aimed to obtain higher gas permeability values by blending two or more polymers which was based on basis of this thesis were limited availability and generally about improving gas barrier properties. As an example for this situation was done by Shields and co-workers. In their study, they prepared 30% wt polyethylene terephthalate filled LDPE blends. Oxygen permeability of produced blends were decreased 70% compared to LDPE. [39]

It can be seen that studies about increasing gas permeability of plastic materials were focused on blending LDPE polymer with inorganic fillers like silica, calsite, zeolite etc. Blending LDPE with these inorganic fillers create micro holes in the blend structure. For instance Luo and co-workers evaluated the effects of nano-CaCO₃-based low density polyethylene (nano-CaCO₃-LDPE) packaging on the quality of fresh-cut sugarcane, concentrations of O₂ and CO₂ within the package. They were first prepared a nano-CaCO₃-LDPE masterbatch by using twin screw extruder, and then 3.75 % wt masterbatch added to LDPE. After the compound was blown into film via a plastic extruder. This study showed that adding nano-CaCO₃-LDPE particles also decreased the transmission rate of CO₂ and O₂ lower than that of LDPE, which lead to the more rapid formation of gas environment with low O₂ and CO₂ concentration in the package. [40]

Similarly, Gökkurt and co-workers used 4 wt% clinoptilolite type zeolite in order to obtain compounds with LDPE by using twin screw extrusion method. Then they produced package samples via blown film extrusion method which have 50 micron thickness. Gas permeability measurements showed that O₂ and CO₂ permeability values were increased by 25%. As a result of shelf life analysis which were done with broccolies for 20 days, they evaluated the physical and chemical properties of broccolies in order to assess acceptability of broccolies as food stuff. The package samples which were produced within this project, the shelf life of broccolies was extended up to 4 times without sacrificing broccolies freshness. [41]

Tsujita was studied that CO₂, O₂, N₂, gas permeability coefficients and diffusion coefficients of PMP with various degrees of crystallization were plotted against the degree of crystallization. The plot demonstrated a linear relationship. The gas permeability coefficient and diffusion coefficient of pure amorphous and crystalline PMPs were evaluated by a linear extrapolation to zero and 100% crystallinity. [42]

3. EXPERIMENTAL

3.1 Materials

3.1.1 Low density polyethylene

Low density polyethylene, PETILEN F2-12 (LDPE, $d = 0,918-0,922 \text{ g/cm}^3$, MFI = 2,1-3,0 g/10 min at 190°C/2.16kg) supplied from PETKİM. This LDPE which is suitable for film production was used as matrix. [43]



Figure 3.1 : Low density polyethylene granules

3.1.2 Polymethyl pentene

Polymethylpentene copolymer, MX0020 (PMP, $d = 0,834 \text{ g/cm}^3$, MFI = 21 g/10min at 260°C/5kg) was supplied from MITSUI. PMP is a 4-methylpentene-1 based polyolefin which is made by Ziegler-Natta type catalysis. This lightweight, functional polymer displays a unique combination of physical properties and characteristics due to its distinctive molecular structure, which includes a bulky side chain, as shown in Figure 3.2. Although PMP is a crystalline olefin polymer, but it shows transparency.

Because of its excellent heat-resistance, release property, high permeability, and chemical resistance, it is used for industrial materials, and also for food-related applications such as food wraps, food preservation packs, baking carton and microwave oven tableware. It is also noted that PMP is a halogen-free polymer which denoted as environmentally-friendly material. [31]

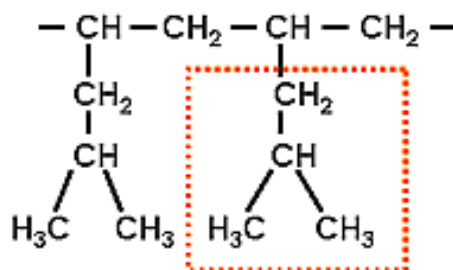


Figure 3.2 : Chemical structure of poly(4-methyl-1-pentene) (PMP) [31]



Figure 3.3 : Polymethylpentene granules

3.2 Equipment

3.2.1 Twin-screw extruder

A intermeshing co-rotating twin-screw extruder was used; Polimer Teknik Poex T-27, with the screw diameter 27 mm and L/D ratio 48:1 to prepare compounds. The scheme of the extruder is given in Figure 3.4.



Figure 3.4 : Poex T-27 twin-screw extruder

This extruder have one volumetric main feeder, two volumetric side feeders, degassing unit, water bath and fixed length pelletizer. Additional temperature and pressure measuring points are located in the closed barrel system. Electrical resistances and water cooling channels controlled by thermoregulator which are connected to each modular barrel zone to ensure play important role to control the set temperature. There are 13 temperature zones have $\pm 1^{\circ}\text{C}$ accuracy. Polymeric materials melt in the barrels by effect of heat and pressure. The gases occurred during compounding are removed and one degassing unit is connected to the vacuum pump by hoses at the 12th barrel zone. Die takes place with a five-strand hole at the forward end of the extruder. Details of Poex T-27 extruder are given in Table 3.1.

Table 3.1 : Poex T-27 twin-screw extruder technical specifications [44]

Specification	Units	Poex T-27
Screw diameter	mm	27
Maximum screw speed	rpm	1200
L/D (shaft length/screw diameter)	-	48:1
Working length	mm	1296
Max. capacity	kg/h	5-100
Motor power	kW	30
Heating power	kW	12
Average water requirement	lt/min	30
Height	mm	1050
Total weight	kg	950
Max. pressure	bar	300
Vacuum pump	kW	0,75
Cooling unit (pump)	kW	0,5
Granulating motor	kW	2,2

The polymer melt can go out of the extruder. It can be cooled down into a water bath and obtained as spaghettis that are cut into small pieces called granules by the fixed length pelletizer or chopper. This system is also known as the classical way of spaghettis pelletizing. Figure 3.5 shows granulating unit. [44]



Figure 3.5 : Granulating unit

3.2.1.1 Screw configuration

The used extruder was design to provide good melting and mixing with high shear and high residence time for compounding process which is shown in Figure 3.6. It has various types of configuration throughout the screw. The screw configuration used in this study contains 9 conveying blocks, 7 kneading blocks and solid conveying zone, plasticizing zone, melt conveying zone, homogenization zone, degassing zone, pressure built up zone. Raw material takes in by first conveying zone; then the material is plasticized, and the molten is obtained throughout following 3 kneading and 4 conveying zones. After that the molten is made homogenized by 3 kneading and 4 conveying blocks. Finally the gases occurred during compounding are removed by degassing zone. [44]



Figure 3.6 : Screw configuration of POEX T-27 [44]

3.2.2 Cast film extrusion line

LDPE based film samples were produced by cast film extrusion which is shown in Figure 3.7. Cast film extrusion machine has two single screw extruders with 25 mm screw diameter. Barrel temperatures were arranged between 280 – 300 °C. Drawing speed was 2.5 m / min and the thickness of films were 40 micron.



Figure 3.7 : Cast film extrusion line

3.2.3 Blown film extrusion line

In order to produce final food package products, GPM-Q20 blown film extrusion which is shown in Figure 3.8 was used. Extruder's barrel temperatures were arranged 280 – 300 °C according to melting temperature of PMP. Screw diameter is 70 mm, and head diameter is 220mm. Thickness of films were arranged to 40 micron.



Figure 3.8 : Blown film extrusion line

3.3 Experimental Procedure

3.3.1 Blend recipes

Sample blends, containing LDPE and PMP polymers were processed using co-rotating twin-screw extruder according to formulation recipes given below in Table 3.2.

Table 3.2 : Formulations of blends (weight per centage)

SAMPLES	LDPE	PMP
LDPE	100	-
LDPE/10% PMP	90	10
LDPE/25% PMP	75	25
LDPE/50% PMP	50	50
LDPE/75% PMP	25	75
LDPE/90% PMP	10	90
PMP	-	100

3.3.2 Blending procedure and process parameters

The extruder has 3 volumetric feeders: 1 main feeder and 2 side feeders which can be seen in Figure 3.4. The raw materials were firstly pre-mixed and mixtures were fed into extruder from inlet zone with using first feeder. The blended materials were taken from the extruder via the holes of the die and cooled down in water bath and the pelletized by pelletizer. The temperature profile which was preferred for PMP in order to obtain good melt properties into the LDPE matrix was 70°C/260°C /265°C /265°C /270°C /275°C /275°C /280°C /280°C /285°C /285°C /290°C /290°C. This temperature profile which was obtained by optimization of the trial production of the blends, provided optimum conditions such as preventing degradations of LDPE and PMP copolymer and shark-skin failure. Since, these temperatures were below degradation temperatures of these two polymers and high enough to prevent shark-skin failure. Screw speed was determined as 500 rpm in order to disperse PMP. All the process parameters were kept constant in order to prevent the occurrence of any differences due to process parameters.

3.4 Characterization

3.4.1 Structural, morphological and thermal properties

3.4.1.1 Differential scanning calorimeter (DSC)

Differential scanning calorimetry (DSC) are the most widely used of all the thermal analysis techniques. The concept underlying the techniques is simple enough: to obtain information on thermal changes in a sample by heating or cooling it alongside an inert reference. Differential scanning calorimetry (DSC) monitors heat effects associated with phase transitions and chemical reactions as a function of temperature. In a DSC measurements the difference in heat flow to the sample and a reference at the same temperature, is recorded as a function of temperature. The reference is an inert material such as alumina, or just an empty aluminum pan. The calorimeter consists of a sample holder and a reference holder as shown in Figure 3.9.

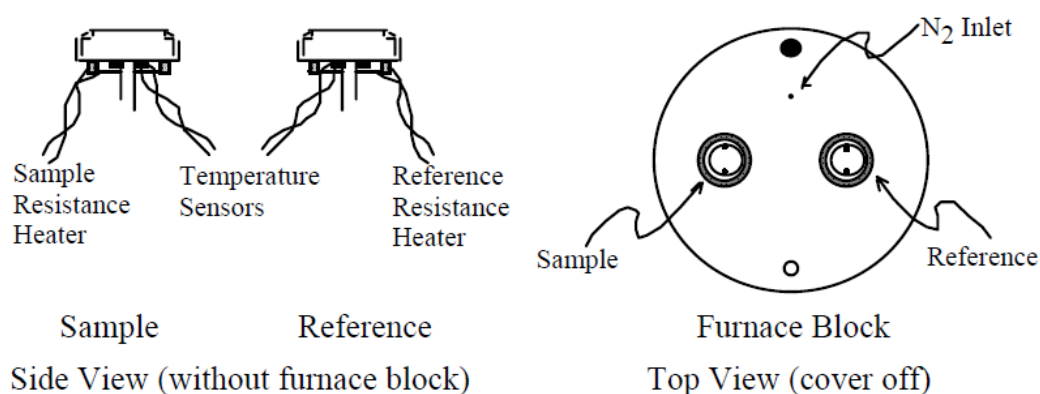


Figure 3.9 : Schematic diagram of differential scanning calorimeter [45]

Both are constructed of platinum to allow high temperature operation. Under each holder is a resistance heater and a temperature sensor. Currents are applied to the two heaters to increase the temperature at the selected rate. The difference in the power to the two holders, necessary to maintain the holders at the same temperature, is used to calculate $\Delta dH/dt$. A flow of nitrogen gas is maintained over the samples to create a reproducible and dry atmosphere.

The nitrogen atmosphere also eliminates air oxidation of the samples at high temperatures.

The heat capacity of the sample is calculated from the shift in the baseline at the starting transient. Glass transitions cause a baseline shift. Crystallization is a typical exothermic process and melting a typical endothermic process, ΔH is calculated from the area under the peaks. Few samples show all the features shown in this thermogram. During the heating of a sample, for example, from room temperature to its decomposition temperature, peaks with positive and negative $\Delta H/dt$ may be recorded; each peak corresponds to a heat effect associated with a specific process, such as crystallization or melting (Figure 3.10).

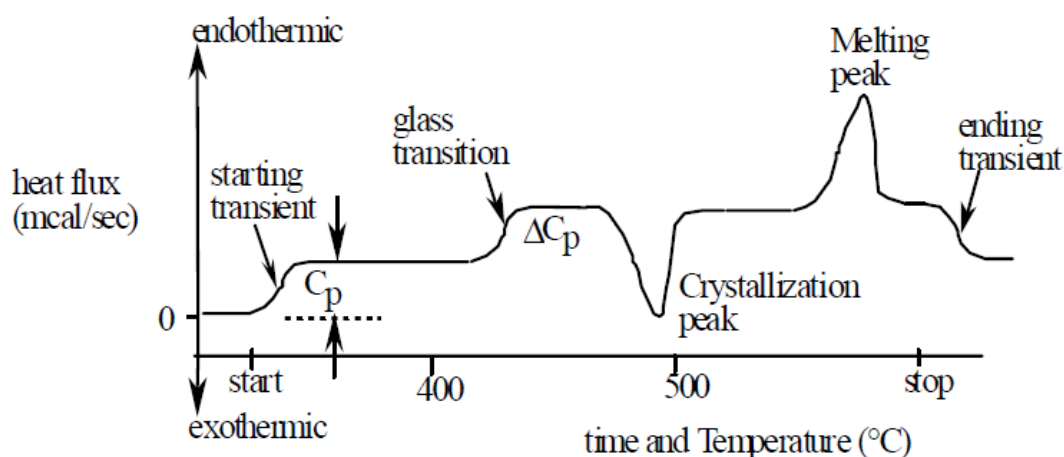


Figure 3.10 : Typical DSC scan [46]

The question arises as to what kind of information is obtainable from a DSC curve. The first and most direct information is the temperature at which a certain process occurs, for example, the melting point of a polymer. The temperature at which a reaction, such as decomposition, may start is another important parameter. The peak temperature is associated with the temperature at which maximum reaction rate occurs. A special case in which the temperature of a phase transformation is of great importance in polymers is the glass transition temperature, T_g . [45, 46]

Thermal analysis of the samples were done with TA Instruments Q20 Differential Scanning Calorimetry machine as shown in Figure 3.11 and technical specifications of the DSC are given in the Table 3.3. [47]

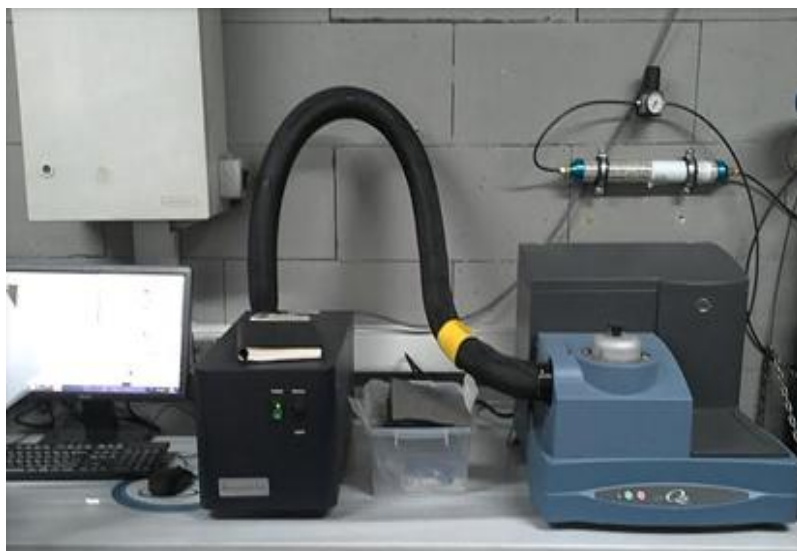


Figure 3.11 : Differential scanning calorimeter

Table 3.3 : TA Q20 DSC technical specifications [47]

Specification	TA Q20
Temperature range	Amb. to 725 °C
With cooling accessories (RCS40)	-40 °C – 725 °C
Temperature accuracy	+/- 0,1 °C
Temperature precision	+/- 0,05 °C
Sensitivity	1,0 µW
Calorimetric precision (indium metal)	+/- 0,1 %
Indium height/width (mW/°C)	8

The analysis were done according to ISO 11957-1 for all blends between 25°C and 300°C at 10°C/min heating rate under nitrogen atmosphere. Melting temperatures (T_m), crystallization temperatures (T_g), the enthalpy of melting (ΔH_m) and the enthalpy of crystallization (ΔH_c) values of the compounds were obtained using a differential scanning calorimeter (DSC).

The mass fraction of crystallinity using DSC was calculated from the following mass fraction relationship (Eqn. 3.1):

$$X_c = \frac{\Delta H_f}{\Delta H_f^0} \quad 3.1$$

where ΔH_f is the measured heat of fusion/gram from the area under the melting endotherm and ΔH_f° is the enthalpy of fusion/gram for a 100 percent crystalline sample. In the case of i- PMP, there have been several reported values for ranging from ΔH_f° 65.4 – 118.9 J/g [34-36]. The value of $\Delta H_f^\circ = 65.4$ J/g was chosen and used throughout this study for no other reason. For LDPE, $\Delta H_f^\circ = 293.0$ J/g was chosen. [48 – 50]

3.4.1.2 Fourier transform infrared spectroscopy (FTIR)

In infrared (IR) spectroscopy, IR radiation is passed through a sample. Some of the infrared radiation is absorbed by the sample and some of it is passed through (transmitted). The resulting spectrum represents the molecular absorption and transmission, creating a molecular fingerprint of the sample.

Like a fingerprint no two unique molecular structures produce the same infrared spectrum. This makes infrared spectroscopy useful for several types of analysis.

FTIR information can provide:

- It can identify unknown materials
- It can determine the quality or consistency of a sample
- It can determine the amount of components in a mixture

FTIR spectrums of films were determined by Bruker Alpha type FTIR-ATR spectrometer which can be seen in Figure 3.12 in order to observe the PMP content effect of the blends. [51]



Figure 3.12 : Fourier transform infrared spectrometer

3.4.1.3 Melt flow index (MFI)

Flowability is an important rheological property of thermoplastic polymers. It is defined as the reciprocal of dynamic viscosity. It is characterized by the melt index. Melt index is marked with MFI (Melt Flow Index, [g/10 min]) or MFR (Melt Flow Rate, [g/10 min]). Melt index is the amount of melt which flows through the capillary of the measuring instrument under a defined time scale at a given temperature and pressure. Figure 3.13 shows the schema of capillary plastometer.

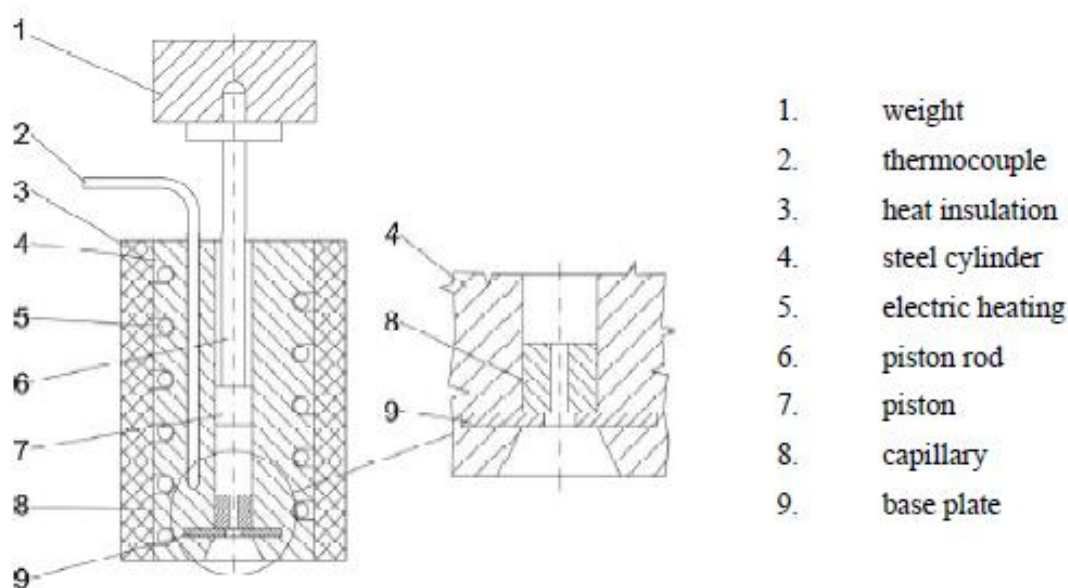


Figure 3.13 : Schema of capillary plastometer [52]

Viscosity is a key determinant of the melting behavior of thermoplastics. A high temperature both increases the mobility of the polymer chains and breaks chemical bonds to create smaller fragments; thus viscosity is a function of both molecular weight and temperature. Polymers having high viscosity value in other words high molecular weight shows low melt flow index. Breaking of polymers chain causes increases on melt flow index.

The flow behavior of molten polymer is defined as an important factor affecting the processability of polymers. Melt flow index (MFI) was measured by using Ceast Modular Base Model testing machine according to ISO 1133 test standard as shown in Figure 3.14. The test temperature and weight were set to 260°C and 5 kg. [52]



Figure 3.14 : MFI measurement instrument

3.4.1.4 Optical properties

Organic or inorganic fillers which are added to the formulation of packages may change the color and transparency of packages affecting more or less the light transmittance. Especially decreasing in transparency could be a big matter for packages.

The optical appearance of the samples which were produced as defined in section 3.3 was determined by Gretagmacbeth Color 17 type colorimetric analyzer seen in Figure 3.15. Before the measurement of color, transparency and light transmittance properties of the samples, the calibration of the device was done with the black and white ceramic calibration apparatus.



Figure 3.15 : Optical properties measurement instrument

3.4.1.5 Scanning electron microscopy (SEM) analysis

The scanning electron microscope (SEM) whose schematic diagram is shown in Figure 3.16 uses a focused beam of high-energy electrons to generate a variety of signals at the surface of solid specimens. The signal that derive from electron-sample interactions reveal information about the sample including external morphology (texture), chemical composition, and crystalline structure and orientation of materials making up the sample. In most applications, data are collected over a selected area of the surface of the sample, and a 2-dimensional image is generated that displays spatial variations in these properties. Areas ranging from approximately 1 cm to 5 microns in width can be imaged in a scanning mode using conventional SEM techniques (magnification ranging from 20X to approximately 30.000X, spatial resolution of 50 to 100 nm). The SEM is also capable of performing analyses of selected point locations on the sample; this approach is especially useful in qualitatively or semi-quantitatively determining chemical compositions, crystalline structure, and crystal orientations.

The SEM provides two outstanding improvements over the optical microscope, it extends the resolution limits and improves the depth-of-focus resolution more dramatically.

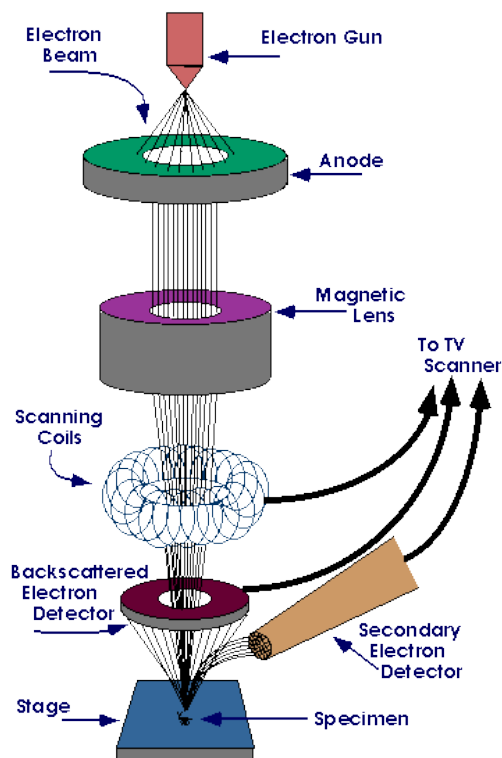


Figure 3.16 : Schematic diagram of scanning electron microscope [53]

The basic philosophy behind specimen preparation is to manipulate the specimen as little as possible insuring that the sample is of appropriate size, stable in the vacuum, electrically conductive, and possessing characteristics resembling the natural state. Most metallic samples meet these conditions with little or no preparation. Many other materials such as ceramics, plastics, and minerals need only to be coated with a conducting metal. For most non-metallic specimens, it is necessary to make them conductive by coating them with metal (Au, Pd, etc). [53, 54]

3.4.1.6 Thermometric gravimetric analysis (TGA)

In thermogravimetric analysis, under controlled heating rate and an atmosphere conditions the mass changes of the sample is measured by a precision scale. 5-20 mg of the sample is put in an aluminium crucible, and according to the sample proper gas is chosen. Generally for polymers is heated to 1000°C with 10°C/min heating rate. At 600°C nitrogen atmosphere is changed to air atmosphere. The amount of change in the sample mass is recorded as a function of time or temperature. Weight loss in the desired temperature range in the illustrated thermograms are calculated as a percentage. Curves 1 and 2 can be derivatized, mathematical operations can be performed between the curves. [55]

With TGA instrument, moisture and volatile material content, and ash content can be determined of polymers. Also thermal behaviors such as melting, thermal decomposition and oxidation can be analyzed in order to evaluate material's type.

In order to determine moisture, volatile and inorganic material amount and thermal degradation temperatures are determined by Perkin Elmer TGA 4000 instrument. Analyzes were done up to 650°C with 10°C/min heating rate under 50ml/min nitrogen atmosphere.

3.4.1.7 X-ray diffraction (XRD) analysis

XRD measurements were carried out for structural analyses of samples. The analyses were performed at a voltage of 45 KV, 40 mA with $\text{CuK}\alpha$ radiation (wavelength = $1.5405 \text{ \AA} = 0.15405 \text{ nm}$) by 2θ at a scan rate of $2^\circ/\text{min}$ in the interval from 2 to 45.

The results of analysis was calculated by using “Bragg’s Law” equation as shown in Figure 3.17. d is the spacing between the planes in the atomic lattice, and θ is the angle between the incident ray and the scattering planes. [56]

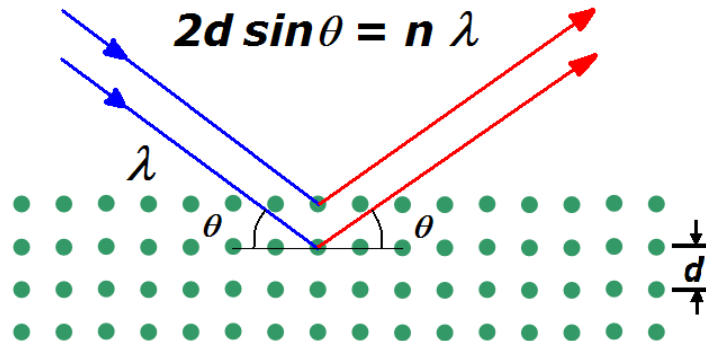


Figure 3.17 : Bragg’s Law [56]

3.4.2 Mechanical properties

3.4.2.1 Determination of tensile properties

Tensile tests are done for to determine the mechanical strengths of plastic materials. Figure 3.18 represents how mechanical tests are done, test specimen is bonded from the bottom and top head, and a constant pulling speed is applied to specimen. [57].

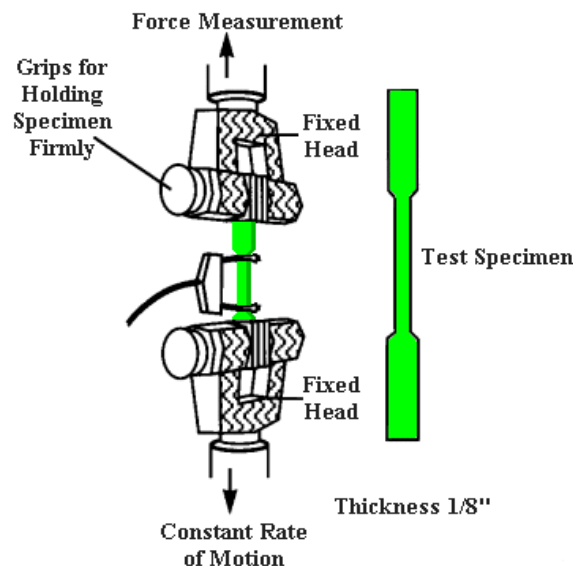


Figure 3.18 : Schematic of mechanical test [57]

Figure 3.19 is illustrated typical stress-strain curve for polymers. Tensile testing determines the amount of stress each material can sustain prior to failure as well as the amount of elongation at the time of failure. The ultimate tensile strength of the

materials was calculated using the maximum force the sample experienced during testing by the cross sectional area of the sample.

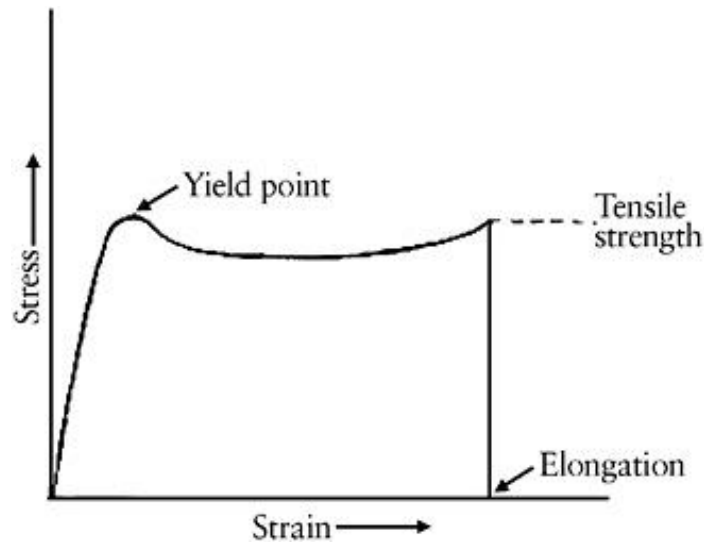


Figure 3.19 : Typical stress-strain curve [58]

Tensile strength is the stress required to break a sample. Polymers expected to be stretched must have good tensile strength. This property is expressed in Pascals or psi. Percent elongation to break represents the strain on a sample at its breaking point, expressed as a percent. Young's modulus is the slope of the linear part of a stress-strain curve. Toughness is the area below the stress-strain curve and represents a measure of the energy a sample can absorb before fracturing. [58, 59]

Mechanical test of the samples were determined according to ASTM D882 standard via Zwick-Roell universal testing instrument which is shown in Figure 3.20.



Figure 3.20 : Zwick-Roell universal testing instrument

3.4.2.2 Gas permeability tests

Permeability is a mass transfer phenomena happens because of the materials which dissolve onto the surface of polymers. Permeability occurs in three ways: [60]

- Absorption and solubility: Molecules are needed to be soluble in order to achieve transferring inside the polymer. Dissolution is a thermodynamic process which is the difference between the total amount of molecules dissolved onto the polymer and the necessary amount for this process. When the molecules reaches a saturated level, diffusion starts into the polymer. [61 – 63]
- Diffusion: Molecules that are absorbed onto the surface of the polymer can transfer into the polymer or outside of the polymer due to the concentration of molecules and partial pressure. Molecules are diffused from high concentration to low concentration. [61, 64].
- Desorption: Desorption is the reverse of absorption, molecules can be evaporate or leave from the polymer. [61, 64].

The most important factor effects the permeability is the structure of the polymer. Chemical composition, polarity, free volume space, crystalline or amorph structure, density, and the fillers of the structure of polymers affect the permeability. Diffusion coefficient can be increased when polar organic molecules are used in polar polymer structures due to similar polarities. Free volume in polymer matrixes represents the voids which eases the permeability of molecules through polymer films. Increase in free volume increases the diffusion and permeability. Crystalline structure of polymers decreases the permability. On the otherhand, usage of fillers increases the permeability.

Except the structural properties of polymers, temperature and relative humidity have an effect the permeability. Especially for small molecules, increasement in temperature increases the movement of molecules. This acceleration of molecules decreases the density. Therefore the polymer becomes more suitable for diffusion. Under constant temperatures, relative humidity balance of foods are increased by the relative humidity of environment. For this reason the relative humidity of environment is an important parameter for water vapor permeability. [63, 65]

O₂, and CO₂ permeabilities of the samples were determined by ExtraSolution O₂/CO₂ Multiperm permeability instrument which is shown in Figure 3.21 according to ASTM F2476 standard for CO₂ permeability and ASTM F2622 standard for O₂ permeability.



Figure 3.21 : Gas permeability measurement instrument

3.4.3 Shelf-life analysis

At this stage, package samples which were produced from the blends that had acceptable efficiency were subjected to the shelf life analysis in order to determine shelf-life extension of chosen fresh cut produces. The package samples have 4 L internal volume, and sizes of these packages are 200*300 mm.

In accordance with this purpose, banana and marrow were packaged under modified atmosphere packaging principles and O₂, CO₂ and ethylene changes inside the packages were recorded. In order to measure ethylene changes inside the package, ICA56 ethylene analyzer which can be seen in Figure 3.22 was used, for measuring O₂ and CO₂ Oxbaby O₂/CO₂ analyzer which can be seen in Figure 3.22 was used.



Figure 3.22 : Ethylene and O₂/CO₂ analyzers

The formulation shown in Equation 3.2 was used in order to obtain reasonable ethylene adsorption capacities and comparison results from the recorded ethylene changes. [66]

$$\text{GEB} = (\text{TSEM}) / (\text{UA} * \text{TDH} * \text{TBS}) \quad 3.2$$

GEB = Accumulation of ethylene gas daily (ppm/g.day)

TSEM = Ethylene gas quantity at the last day of experiment (ppm)

TDH = Internal volume of package (L)

TBS = Duration of test (day)

UA = Product weight (g)

The obtained value from the formulation above shows the ethylene accumulation for one day for one gram produce in a package which has 1 L internal volume.

As a result of these gas permeability values, and atmosphere changes inside the packages were used together in order to analyse the efficient of film samples.

4. RESULTS AND DISCUSSION

In this study, LDPE and PMP blends were prepared as weight percent shown in section 3.3.1 according to procedure given in section 3.3.2. The prepared samples were processed in cast and blown film extrusion line in order to obtain films as described in section 3.2.2 and 3.2.3 respectively. All tests were repeated at least five times and standard deviations of the results were determined.

4.1. Test Results of Structural, Morphological and Thermal Properties

Structural, morphological and thermal properties of LDPE/PMP blends were determined by using DSC, FTIR, MFI, SEM, XRD, TGA and optical properties analyses.

4.1.1 Differential scanning calorimetry analysis

Differential scanning calorimetry test was done according to the procedure explained in section 3.4.1.1. Differential scanning calorimetry test results are given in Table 4.1 ve Tablo 4.2. Besides, graphical displays of test results for samples were also given in Appendix A.1.

Table 4.1 : Melting temperatures, enthalpy values, and crystallization ratios of the samples

Sample	T_m (°C)		ΔH_m (J/g)		Crystallinity (%)	
	$T_{m, PE}$	$T_{m, PMP}$	ΔH_{PE}	ΔH_{PMP}	%X _{PE}	%X _{PMP}
LDPE	111.5	-	124.4	-	42.2	-
LDPE/10% PMP	111.3	223.7	100.1	1.5	34.1	2.4
LDPE/25% PMP	111.3	223.4	90.6	6.2	30.9	9.4
LDPE/50% PMP	110.8	223.4	52.6	10.9	17.9	16.6
LDPE/75% PMP	112.3	224.0	34.7	17.6	11.8	26.9
LDPE/90% PMP	112.3	224.0	33.9	18.6	11.5	28.4
PMP	-	223.0	-	22.6	-	34.5

According to the values were shown in Table 4.1, melting temperatures of neat LDPE and neat PMP copolymer are 111°C and 223 °C, crystallization ratio is 42.4% and 34.5% respectively. These results were a compatibility with the previous studies. For instance, Höhne and co-workers were determined 245°C melting temperature, 40 J/g melting enthalpy, and 34% crystallization ratio for a commercial PMP copolymer under atmospheric pressure. In this regard, it can be said that DSC analysis results of package samples were shown conformality with literature sources. [67]

These DSC results presented that LDPE and PMP copolymer have similar crystallinity ratios and partial crystalline structures. This situation is a remarkable detail because it is known that the structure of polymeric material affects the gas permeability.

According to these studies, chemical composition, polarity, amount of free volume, and crystalline or amorphous structure of polymeric material have an effect on gas permeability. Thereby, it is conceivable that polymers have high gas permeability and light transmittance values such as PMP copolymer have amorphous structure. Because increase in crystalline structure decreases gas permeability values. As it was shown in Table 4.1 the crystallization ratio of PMP copolymer is 34%. In other words PMP copolymer has partially crystalline structure as LDPE. The explanation

of this contradiction is the difference in crystal lattice structure rather than their crystallinity ratios. The previous studies were shown that PMP copolymer crystallize in a tetragonal symmetry. This tetragonal crystal lattice structure leads to lower packaging fraction, higher free volume and higher diffusion ratio. Due to increased free volume and diffusion ratio, higher gas permeability values can be obtained. [67, 68]

Evaluation of LDPE/PMP copolymer blends were shown that the melting temperatures did not show major alterations. Despite of increase in PMP copolymer ratio, all interblends were shown averagely 111°C and 223°C melting temperature peaks for LDPE and PMP copolymer respectively. The deviations on the melting temperature of the blends can be ignored. Another remarkable detail in these DSC analysis was crystallinity ratios did not change in direct proportion to addition ratio. For instance, it was determined from DSC analysis that the crystallinity ratios were 17.9% and 16.6% for LDPE and PMP copolymer, respectively of package sample which were containing 50% PMP copolymer. Theoretically these crystallinity ratios should have been 21.2% and 17.2% for LDPE and PMP copolymer, respectively. The reason of this difference between theoretical and practical crystallinity ratios is LDPE and PMP copolymer are incompatible and have different crystallinity kinetics in our opinion. In addition, crystallinity of LDPE was decreased with decreasing LDPE ratio, and crystallinity of PMP copolymer was increased with increasing PMP copolymer ratio in blends' structure.

Table 4.2 was shown crystallization temperatures and crystallization enthalpies of the package samples. These results were shown coherence with literature studies. It was not observed that any nucleating affect in package samples' structure.

Table 4.2 : Crystallization temperature and enthalpy of the samples

Sample	T _c (°C)		ΔH_c (J/g)	
	T _{c, PE}	T _{c, PMP}	ΔH_{PE}	ΔH_{PMP}
LDPE	100.1	-	86.2	-
LDPE/10% PMP	100.1	205.4	66.8	2.9
LDPE/25% PMP	100.2	206.6	56.9	1.5
LDPE/50% PMP	100.0	205.8	31.4	11.1
LDPE/75% PMP	100.6	206.2	24.9	12.3
LDPE/90% PMP	100.5	206.1	23.8	13.4
PMP	-	205.3	-	17.6

4.1.2 Fourier-transform infrared spectroscopy analysis

FTIR analysis were done as described in section 3.4.1.2 which were given in Appendix A.2. Comparative spectrums of samples were shown in Figures 4.1 and 4.2. Spectrums of neat LDPE and PMP copolymer were used as standard spectrums for comparing blends' spectrums. Peaks which were belong to PMP copolymer were become apparent due to increase in PMP copolymer ratio. On the other hand, peaks that belong to LDPE were got smaller due to decrease in LDPE ratio in the blends' structure.

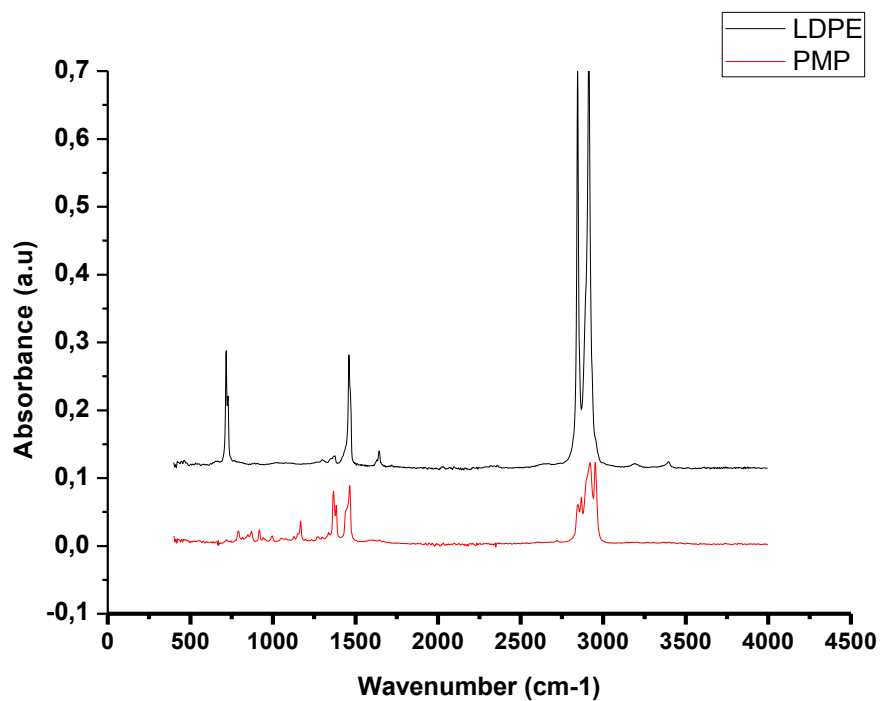


Figure 4.1 : FTIR spectrums of LDPE and PMP copolymer

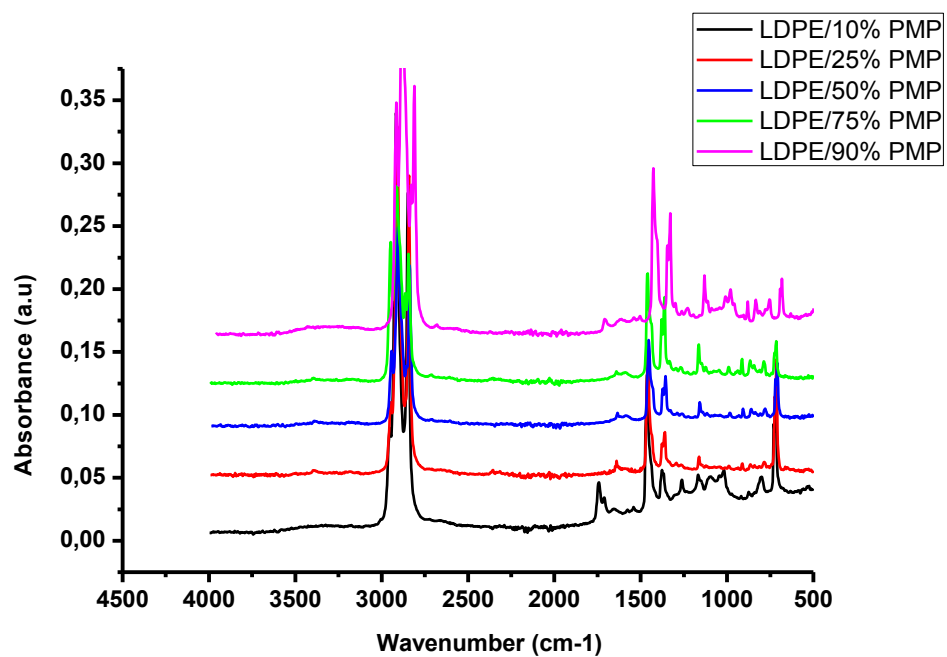


Figure 4.2 : FTIR spectrums of different PMP copolymer loaded samples

4.1.3 Determination of melt flow index

Melt flow index (MFI) test was done as described in section 3.4.1.3. The densities of samples were used for measurement. Test results are given in Table 4.3. Furthermore, graphical displays of test results for samples were given Figure 4.3.

MFI test results indicated a decrease with increasing loading level of PMP. LDPE has MFI value of 30 g/10 min. The loading of 25% PMP decreased MFI to 27.8 g/min, and the loading of 50% EPDM decreased MFI to 25.3 g/10min as shown in Figure 4.4.

Table 4.3 : Test results of MFI measurements of the samples

SAMPLES	MFI (g/10 min)
LDPE	30.0±0.3
LDPE/10% PMP	28.9±0.2
LDPE/25% PMP	27.8±0.6
LDPE/50% PMP	25.3±0.3
LDPE/75% PMP	23.1±0.4
LDPE/90% PMP	22.4±0.9
PMP	21.0±0.8

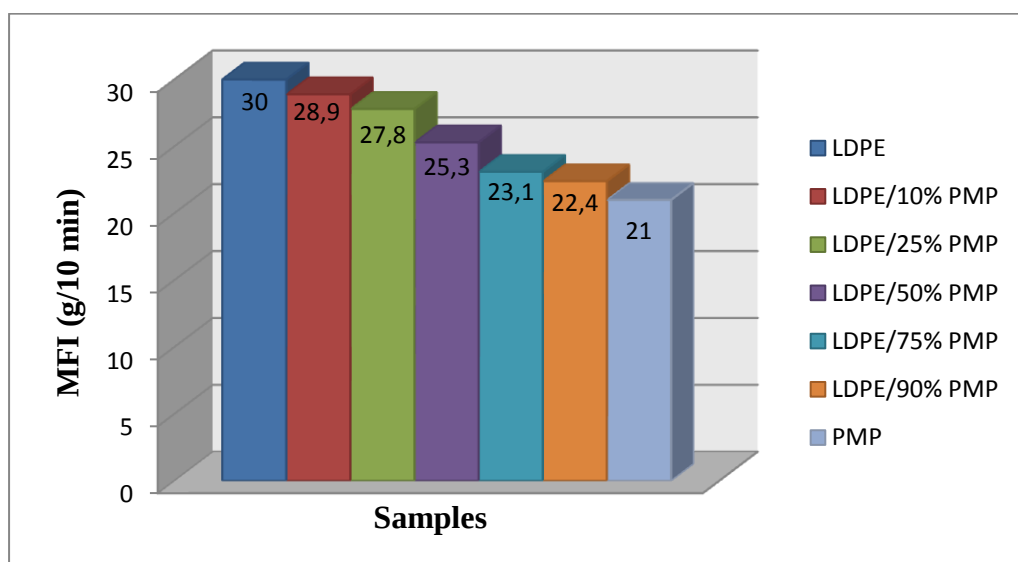


Figure 4.3 : MFI values of the samples

4.1.4 Analysis of optical properties

Optical properties of the samples were determined as described in section 3.4.1.4, and the results of optical tests are given in Table 4.4.

Table 4.4 : Test results of optical properties of the samples

SAMPLES	l	a	b	Haze	Light Transmittance
LDPE	95.82±0.2	0.10±0.01	0.70±0.02	9.48±0.07	89.44±0.5
LDPE/10% PMP	95.83±0.3	0.11±0.04	0.71±0.01	9.40±0.02	89.50±0.1
LDPE/25% PMP	95.85±0.7	0.11±0.01	0.72±0.04	9.32±0.05	89.57±0.3
LDPE/50% PMP	95.88±0.1	0.13±0.03	0.79±0.01	9.25±0.03	90.02±0.2
LDPE/75% PMP	95.89±0.9	0.14±0.02	0.84±0.02	9.15±0.01	90.35±0.6
LDPE/90% PMP	95.91±0.5	0.16±0.01	0.87±0.03	9.10±0.04	90.43±0.1
PMP	95.93±0.8	0.17±0.02	0.90±0.01	9.00±0.02	90.52±0.4

L, a, and b values were given in Table 4.4 represents the colors of the film samples according to color coordinate system. As it can be seen in Figure 4.4, according to color coordinate system l value refers the lightness/darkness index, a value refers to redness/greenness index, b value refers to yellowness/blueness index. Haze and light transmittance are the numerical values of these properties.

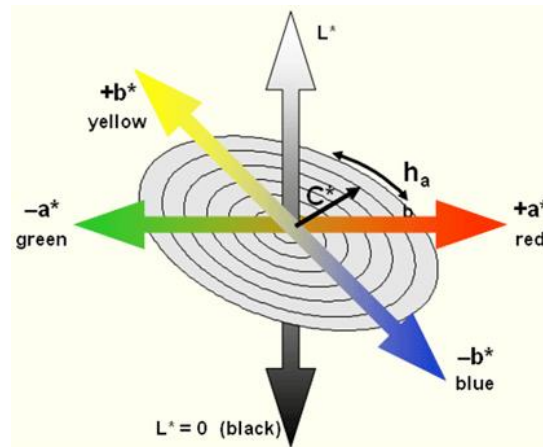


Figure 4.4 : Color coordinate system [69]

According to the values in the Table 4.4, PMP copolymer has more white, red and yellow colors than LDPE. Also PMP copolymer has higher light transmittance and

less haze values than LDPE which probably because of PMP's lower crystallinity or smaller crystalline structure.

Beside this film samples were obtained by blending different ratios of LDPE and PMP copolymer have optical values between LDPE and PMP copolymer's optical values. These values were interpreted that these film samples have any internal structure or defects which would prevent the light transmittance.

Eventually, because of LDPE and PMP's close color coordinate system values, the film samples were obtained from LDPE and PMP copolymer have close color coordinate system values. The film samples were given in Figure 4.5.



Figure 4.5 : Film samples

4.1.5 SEM analysis

SEM analysis was done as described in section 3.4.1.5. Nonhomogeneous mixing and agglomeration of the components in the polymer matrix affect the mechanical and gas permeability properties of final product. These agglomerations and nonhomogeneity can lead to failure of films, and decrease in plasticity. [66] Beside all of these, interaction between inorganic additives and polymeric material is also very important. As it is shown in Figure 4.6 tears that called internal defects can be formed in micron size on the film surface of the inorganic material loaded polymeric films. These tears have a big influence on the final properties.

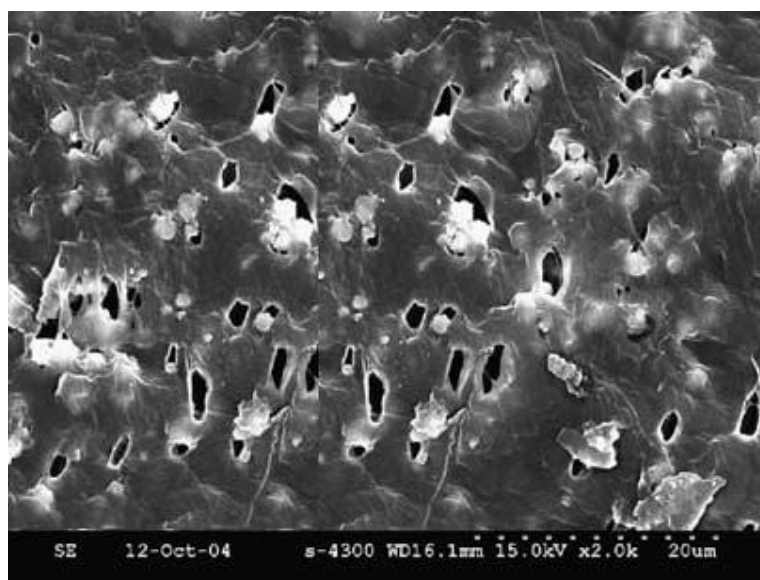


Figure 4.6 : SEM image of LDPE/Zeolite composite film [70]

In Figure 4.7, 1 mm scale and 100x magnification SEM image which was taken from film's cross-section was shown. According to this image, increasing in PMP ratio reduced fracture pattern to brittle structure. These results were adjusted to mechanical analysis of the samples. Any inhomogeneities or agglomerations was seen in these SEM image.

In Figure 4.8, 20 μm scale and 6000x magnification SEM images which were taken from their cross-section were shown. As it is seen in images, according to increased PMP ratios, the existence of an oriented in the slow direction laminated structure was observed. This layered structure is thought to occur as a result of phase separation of these two incompatible polymers with each other. The main reason of this

incompatibility is the different surface energies of LDPE (31 mN/m) and PMP (24 mN/m) copolymer. [70, 71]

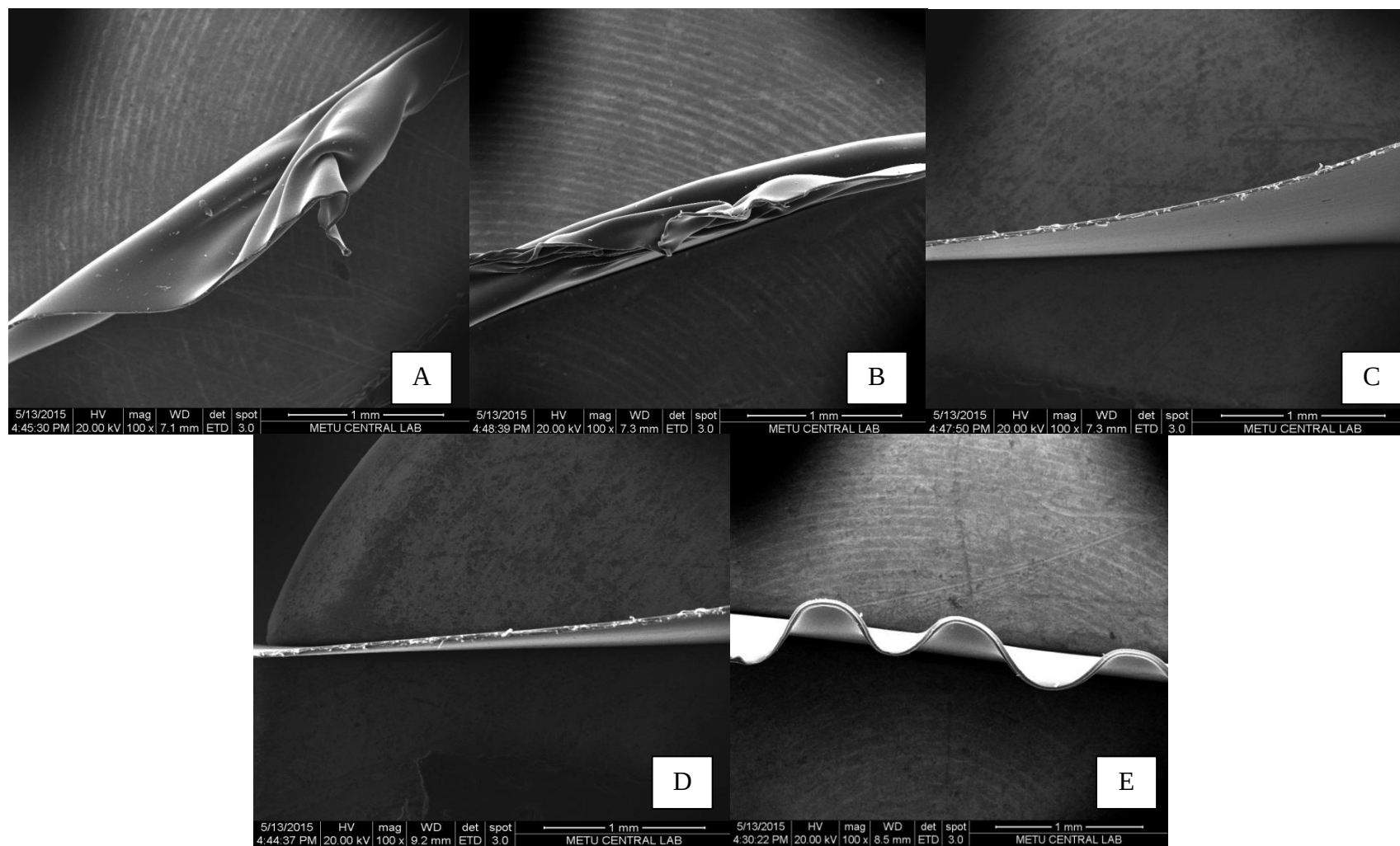


Figure 4.7 : SEM images of film samples magnified 100x (A: LDPE, B: LDPE/25% PMP, C: LDPE/50% PMP, D: LDPE/75% PMP, E: PMP)

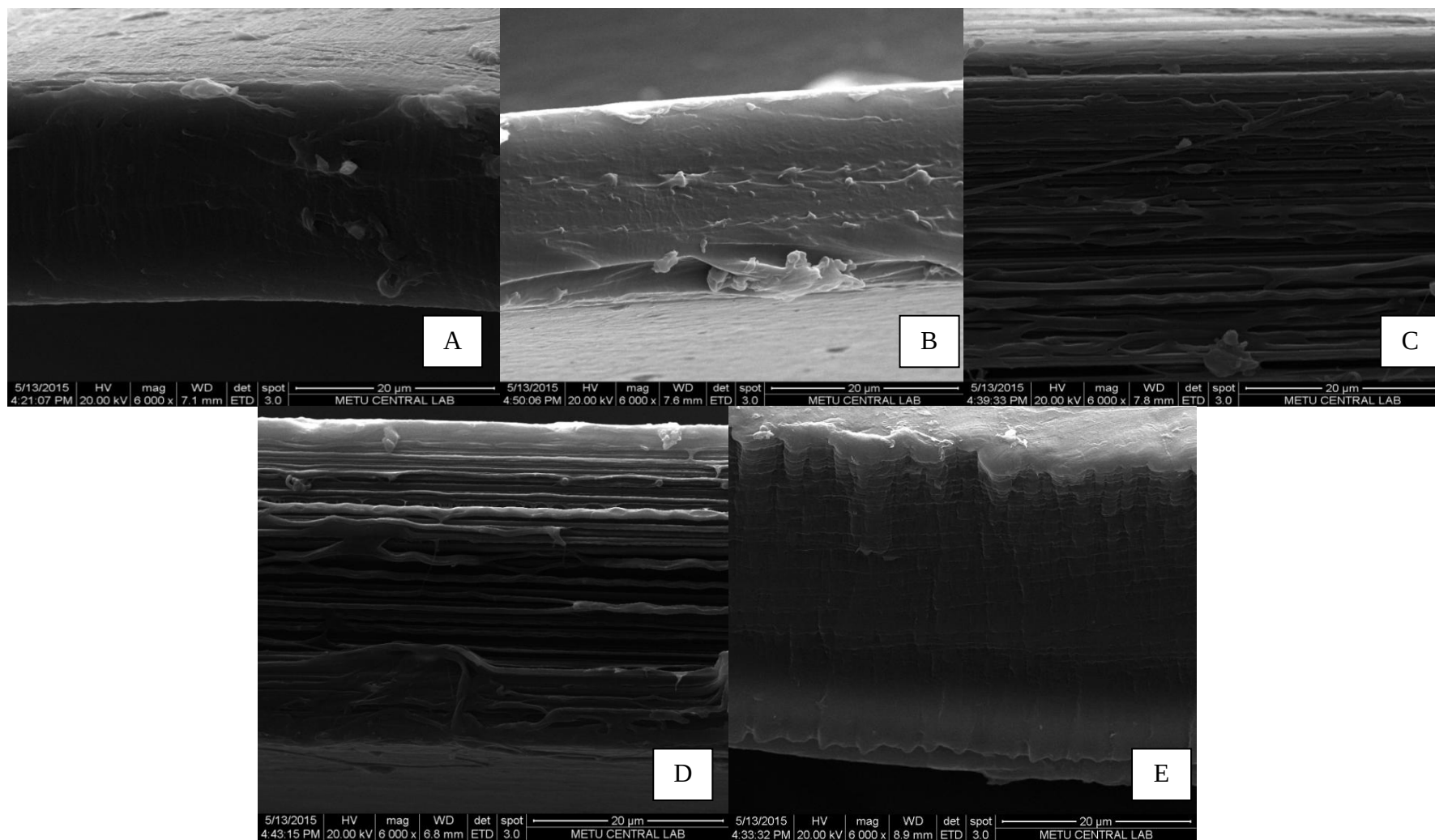


Figure 4.8 : SEM images of film sample magnified 6000x (A: LDPE, B: LDPE/25% PMP, C: LDPE/50% PMP, D: LDPE/75% PMP, E: PMP)

4.1.6 TGA analysis

TGA analysis were done as described in section 3.4.1.6. Test result of TGA analysis is given Table 4.5 and graphical displays is given Figure 4.9. Besides, thermograms of samples were given in Appendix A.3.

Table 4.5 : Results of TGA analysis

SAMPLES	(T _{deg}) _{Start} (°C)	(T _{deg}) _{Finish} (°C)	%Ash (900°C)
LDPE	417.9	506.9	0.52
LDPE/10% PMP	396.1	498.5	0.15
LDPE/25% PMP	358.8	482.5	0.59
LDPE/50% PMP	365.1	493.4	0.39
LDPE/75% PMP	406.2	495.5	0.49
LDPE/90% PMP	372.2	480.8	0.30
PMP	351.7	471.6	0.25

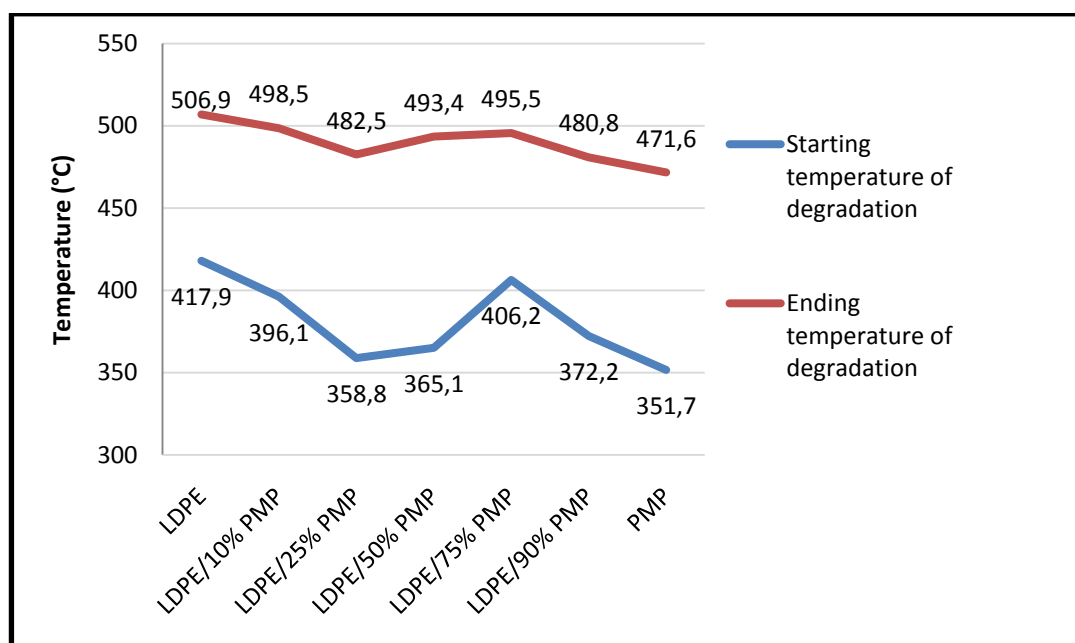


Figure 4.9 : TGA result of samples

Table 4.5 is shown that decomposition of LDPE started at 417.9°C and finished at 506.9°C. Decomposition of PMP copolymer started at 351.7°C and finished at 471.6 °C. Starting and finishing temperatures of interblends were between these two

temperatures. Also, ash content of all samples were determined between 0.15-0.52%. Ash content of all samples were calculated 0.15-0.52%. It is thought that existence of ash content was proceed from the stabilizers inside the structure of raw materials.

4.1.7 XRD analysis

XRD spectrums of the samples were given in Figure 4.10 and characteristic peaks were listed in Table 4.6 Besides, graphical displays of test results for samples were given in Appendix A.4.

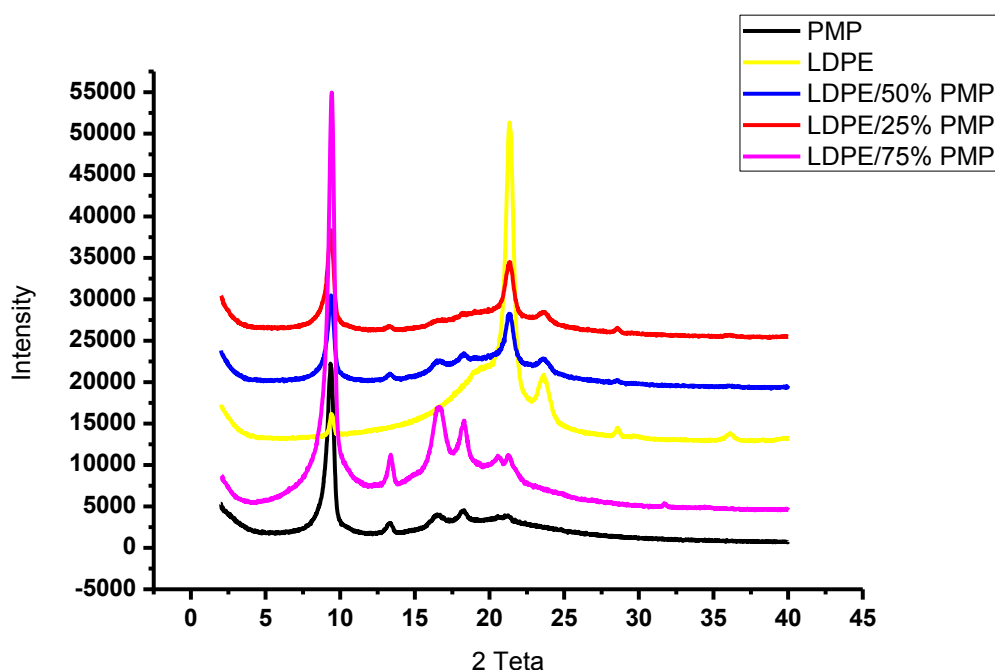


Figure 4.10 : XRD spectrums of the samples

Table 4.6 : Characteristic peaks of samples

Samples	Characteristic Peaks						
	2θ	2θ	2θ	2θ	2θ	2θ	2θ
LDPE	9.41	19.79	21.33	23.59	28.53	29.69	36.10
LDPE/25% PMP	9.37	21.31	23.81	28.52	-	-	-
LDPE/50% PMP	9.40	13.41	16.44	20.04	21.39	23.68	28.6
LDPE/75% PMP	9.41	13.35	16.55	18.22	19.11	21.26	34.56
PMP	9.39	13.32	16.56	18.22	20.08	-	-

According to Table 4.6, characteristic peaks for LDPE are 19.79, 21.33, 23.59, 28.53, 29.69 ve 36.10, while for PMP copolymer characteristic peaks are 13.32, 16.56, 18.22 ve 20.08. Interblends from LDPE and PMP copolymer were shown the peaks mentioned above.

Literature studies has shown that poly(4-methylpentene-1) can crystallize in various crystal lattices. The modification of PMP are denoted as I, II, III, IV, and V. The various forms differ from the conformation of the polymer chains and for the mode on packing of chains having the same conformation. The crystallographic data of PMP are reported in Table 4.7. [67]

Table 4.7 : Crystallographic data of PMP [68]

Form	Crystal system	Lattice constants (Å)	Molecular conformation	Crystal density (g/cm ³)
I	Tetragonal	a = 18.66, c= 13.80	Helix (7/2)	0.812
II	Tetragonal	a = 19.16, c= 7.12	Helix (4/1)	-
III	Tetragonal	a = 19.38, c= 6.98	Helix (4/1)	-
IV	Hexagonal	a = 22.17, c= 6.50	Helix (3/1)	-
V	Hexagonal	a = 22.17, c= 6.69	-	-

Modification I is characterized by chains in the 7/2 helical conformation packed in a tetragonal unit cell with axes a=b=18.66 Å and c=13.80 Å. For modification proposed a tetragonal unit cell with axes 19.16 Å and e=7.12 Å with the chain in the 4/1 helical conformation. Modification III is characterized according to Charlet et al. By a tetragonal unit cell with parameters a=19.38 and c=6.98 Å and a chain in the 4/1 helical conformation. For modification IV a hexagonal unit cell with axes a=22.17 and c=6.96 Å. a hexagonal unit cell has also been proposed for modification V. For this modification the cell parameters are a=22.17 and c=6.69 Å. The different modifications can be obtained by changing the crystallization conditions, nature of solvent, solution concentration, thermal history of the solution, and cooling rate. Crystallization from the melt only generates modification I. Crystallization from solution, however, promotes the formation of various crystalline modifications.

Solid-solid transitions from a modification to others have been observed. In fact, PMP is found to exhibit changes in crystal modification on uni-axial draw. In particular He and Porter report that the crystal structure at lower planar zigzag (2/1)

draw ratio is a common tetragonal form and that at higher draw it is orthorhombic. The effect of pressure and temperature on the phase diagram of PMP was studied. The polymer crystalline under ambient conditions becomes amorphous reversibly on increasing pressure in two widely separated temperature regimes (200°C and 2000°C). The transformation occurs via a liquid crystalline state. The lower temperature amorphous phase becomes crystalline on heating and reverts to the glass disordered phase on cooling. [68, 72]

In light of these informations, it was clearly observed that under atmospheric pressure conditions PMP copolymer crystallize in a tetragonal symmetry. XRD results were verified the results in section 4.1.1 that PMP copolymer has a partially crystalline structure and its lattice structure is tetragonal.

4.2 Test Results of Mechanical Properties

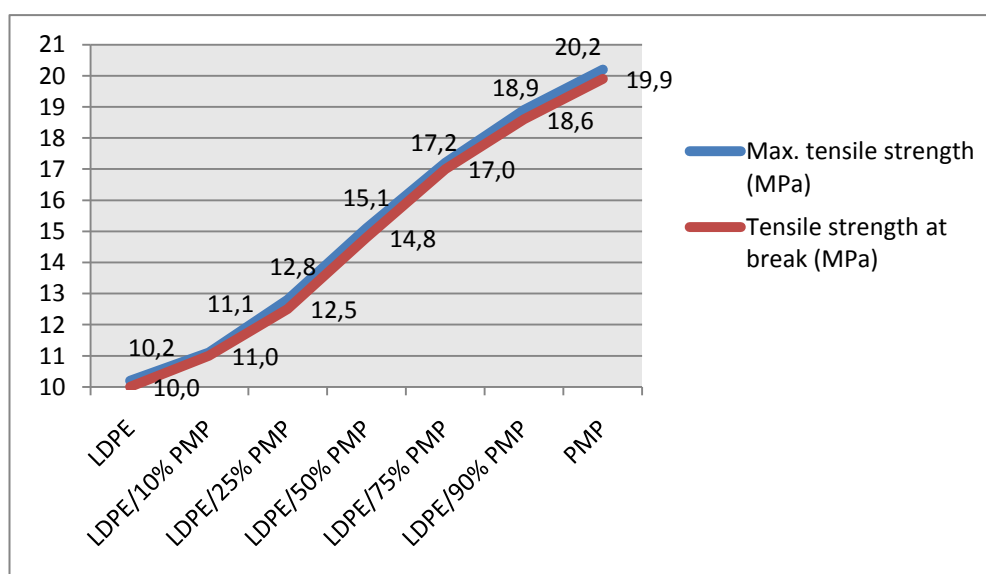
Mechanical properties of LDPE/PMP blend samples were determined by using mechanical testing methods such as universal testing, and gas permeability tests.

4.2.1 Determination of mechanical properties

Tensile test was done according to the procedure explained in section 3.4.2.1. The effects of PMP copolymer on maximum tensile strength (MPa), tensile strength at break (MPa), elongation at break (%) and modulus of elasticity (MPa) of the prepared and neat samples were evaluated and test results of all samples are shown in Table 4.8. Graphical displays of mechanical properties were given in Figures 4.11, 4.12, 4.13. All tests were repeated at least five times and standard deviations were calculated.

Table 4.8 : Tensile test determination of the samples

SAMPLES	Maximum Tensile Strength (MPa)	Tensile Strength at Break (MPa)	Elongation at Break (%)	Modulus of Elasticity (MPa)
LDPE	10.2±0.4	10.0±0.3	290±15	165±10
LDPE/10% PMP	11.1±0.7	11.0±0.5	275±20	171±15
LDPE/25% PMP	12.8±0.2	12.5±0.9	250±22	182±20
LDPE/50% PMP	15.1±0.1	14.8±0.4	201±20	195±15
LDPE/75% PMP	17.2±0.8	17.0±0.1	181±25	206±20
LDPE/90% PMP	18.9±0.6	18.6±0.6	169±20	205±10
PMP	20.2±0.1	19.9±0.5	155±10	220±20

**Figure 4.11 :** Maximum tensile strength and tensile strength at break values of the samples

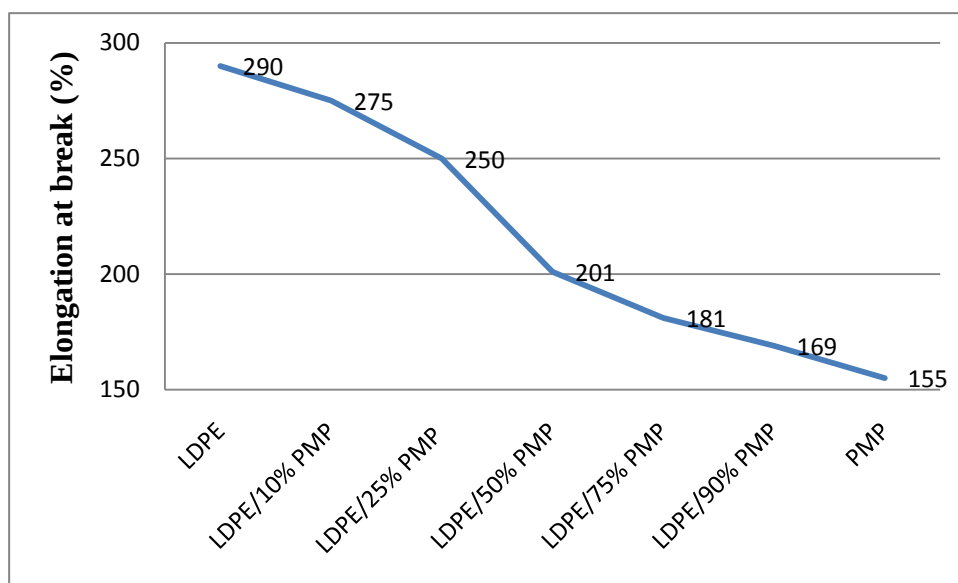


Figure 4.12 : Elongation at break values of the samples

These results showed that maximum tensile strength and tensile strength at break was increased with the increase of PMP content of the samples. The tensile strength of LDPE was around 10 MPa and PMP gradually increased tensile strength up to nearly 20 MPa. On the other hand, elongation at break value was decreased compared to neat LDPE as shown in Figure 4.12. Elongation at break values of the samples was decreased while tensile strength was increased. Decrease in elongation at break values were indicated that PMP copolymer addition is made the film samples more brittle. Nevertheless, all determined mechanical properties of film samples in acceptable limits for packaging applications.

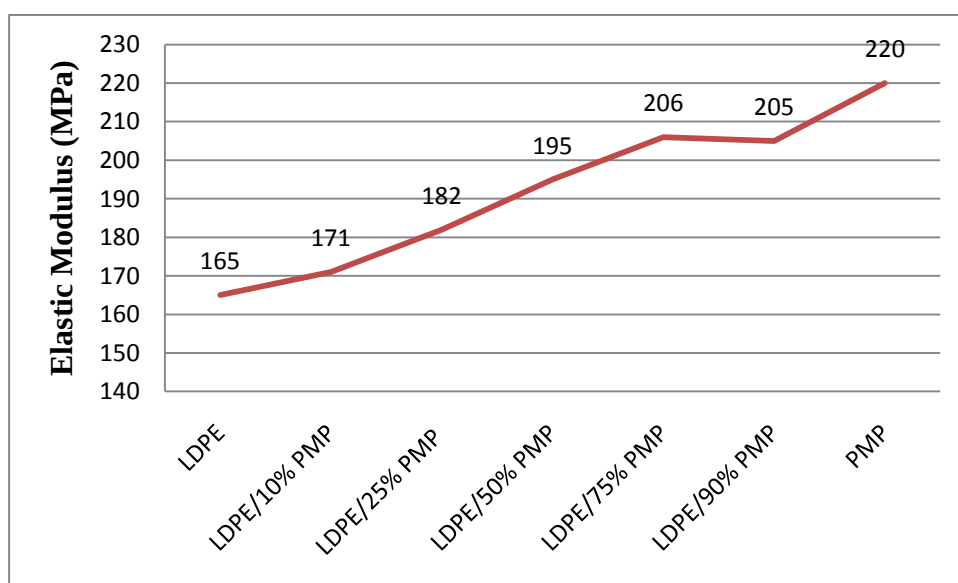


Figure 4.13 : Elastic modulus values of the samples

PMP copolymer is stiffer and has higher strength values than LDPE, therefore adding PMP copolymer into LDPE matrix was increased strength values and elastic modulus values. The decrease in elongation at break was shown that LDPE and PMP copolymer are incompatible. The main reason of this incompatibility is the surface energy difference of these two polymers. Surface energy of LDPE is 31 mN/m while surface energy of PMP is 24 mN/m. [70, 71] Besides, this incompatibility can be seen clearly in SEM images as phase separations.

4.2.2 Gas permeability determination

O₂, and CO₂ permeability values of the film samples were determined as described in section 3.4.2.2. In terms of modified atmosphere packaging principles, generally ambient temperature changes according to the product which will be preserved inside the package. In order to prevent water loss of product, the relative humidity inside the package is kept at high levels such as 90% RH. For instance, marrows which were analyzed in shelf life analysis section are needed to keep under 8-12 °C and 90% RH conditions, but bananas are needed to keep under 15 °C and 90% RH conditions. [14, 30] Therefore, the gas permeability values of the film samples which were given in Tables 4.9, 4.10, and 4.11 were determined under constant relative humidity (90% RH) and at 3 different temperatures. All tests were repeated five times and standard deviations of the results were determined.

Table 4.9 : Results of gas permeability determination under 25 °C and 90% RH conditions

SAMPLE	OTR (cc/m ² .day.atm)	Change (%)	COTR (cc/m ² .day.atm)	Change (%)
LDPE	3.432±1.4	-	15.053±1.5	-
LDPE/10% PMP	3.970±1.3	16	18.133±1.4	20
LDPE/25% PMP	5.229±1.5	52	24.317±1.5	62
LDPE/50% PMP	6.529±1.2	90	32.572±1.3	116
LDPE/75% PMP	12.901±1.7	276	62.184±1.6	313
LDPE/90% PMP	15.818±1.2	361	78.874±1.1	424
PMP	18.982±1.1	453	109.242±1.2	626

Table 4.10 : Results of gas permeability determination under 15 °C and 90% RH conditions

SAMPLE	OTR (cc/m ² .day.atm)	Change (%)	COTR (cc/m ² .day.atm)	Change (%)
LDPE	1.787±1.2	-	8.960±1.1	-
LDPE/10% PMP	2.089±1.1	17	10.990±1.0	23
LDPE/25% PMP	2.889±1.3	62	15.198±1.1	70
LDPE/50% PMP	3.796±1.0	112	21.571±1.2	141
LDPE/75% PMP	8.013±1.1	348	43.485±1.0	385
LDPE/90% PMP	10.272±0.9	475	57.155±0.8	538
PMP	12.655±0.8	608	80.920±0.9	803

Table 4.11 : Results of gas permeability determination under 5 °C and 90% RH conditions

SAMPLE	OTR (cc/m ² .day. atm)	Change (%)	COTR (cc/m ² .day. atm)	Change (%)
LDPE	889±0.9	-	4.507±0.7	-
LDPE/10% PMP	1.050±0.8	18	5.462±0.6	21
LDPE/25% PMP	1.453±0.6	63	7.647±0.7	70
LDPE/50% PMP	1.920±0.9	116	10.857±0.8	141
LDPE/75% PMP	4.031±0.7	353	22.051±0.6	389
LDPE/90% PMP	5.169±0.8	481	28.998±0.7	543
PMP	6.370±0.4	616	41.068±0.3	811

According to these values, it can be easily seen that O₂ and CO₂ permeabilities of the film samples were increased due to increase in PMP copolymer ratio. The reason of this increase is the structure of PMP copolymer which is very convenient to gas permeability. It is known that the structure of the polymer is the most important parameter for gas permeability. The composition, polarity, amount of free volume, crystalline or amorphous structure, physical aging, drawing of the polymer and filler affect the permeability. [73, 74] In polar matrixes, because of the increase in

solubility of polar organic molecules results in increment in diffusion coefficient. Free volume describes the pores of the matrix. These pores creates pathways for materials which desire to pass through from these polymers. Increase in free volume will lead the increase in diffusion and permeability. Polymers consist of crystalline and amorphous structures. Increase in crystalline structure decreases the permeability. Physical aging, drawing, and high density causes a decrease in free volume which decrease the permeability. On the other hand, using fillers increase the permeability. Accordingly, it can be observed that high free volume and diffusion coefficient of PMP copolymer due to its low density and crystallinity cause these increases in gas permeabilities.

However, it can be seen that this increase in gas permeability values were not in direct proportion to increasing PMP copolymer ratio. It is foreseen that the reason of this situation is the phase separations due to the incompatible structures of these two polymers or micro holes between these two phases. In the literature, there are studies which are about inorganic materials filled polymer composite packages can confirm our prediction. [66, 75 - 78] In addition to these informations, SEM images were confirmed our prediction clearly.

Besides as it is seen in Tables 4.9, 4.10., 4.11, depending on the increase in PMP copolymer ratio in LDPE matrix, percental change in CO₂ permeabilities of the film samples are 15% - 20% higher than O₂ permeabilities. Also, graphical displays of O₂ and CO₂ permeability values of the film samples were given in Figures 4.14, 4.15, 4.16.

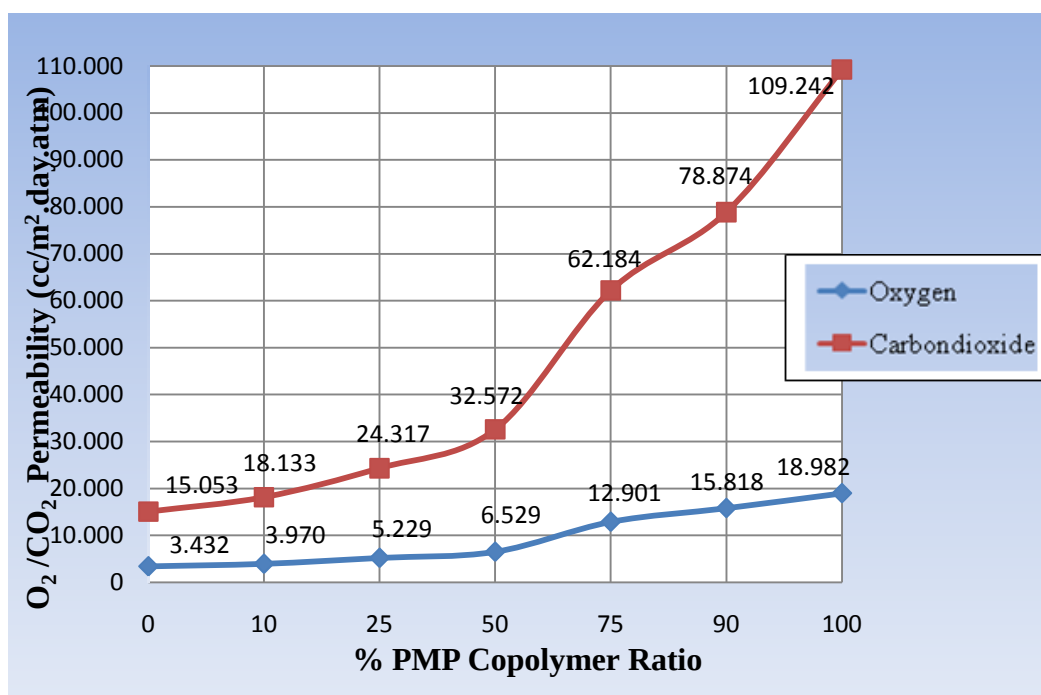


Figure 4.14 : Increase in gas permeabilities due to increasing PMP copolymer ratios at 25°C

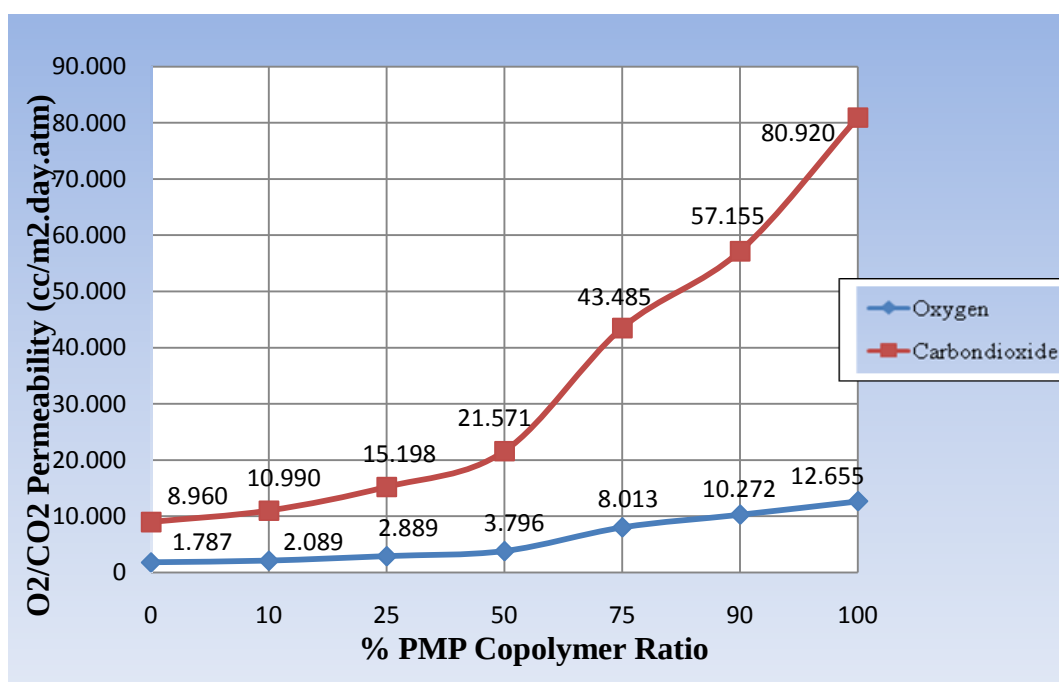


Figure 4.15 : Increase in gas permeabilities due to increasing PMP copolymer ratios at 15°C

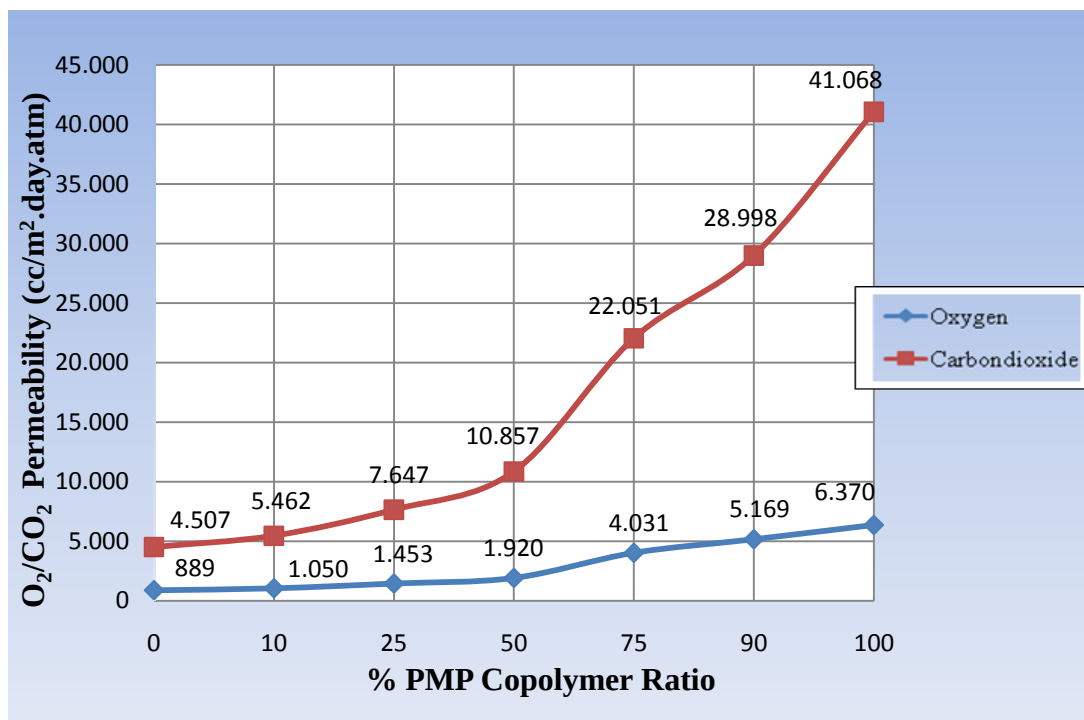


Figure 4.16 : Increase in gas permeabilities due to increasing PMP copolymer ratios at 5°C

As it is stated in several literature sources, CO₂ has higher diffusion rate than O₂ or CO₂ has higher adsorption, diffusion, and sorption capacity and rates in PMP copolymer existence compared to LDPE. [30, 74, 79 - 81]

As a result of all of these gas permeability analysis, another remarkable point is PMP copolymer is less sensitive to temperature changes. Increase in gas permeability ratios depending on the temperature changes can be clearly seen in Figures 4.11 and 4.12. As it can be seen in Figures 4.17 and 4.18, every 10 °C increase in temperature was increased O₂ permeability 1.92 times of LDPE, and CO₂ permeability 1.68 times. On the other hand, every 10 °C increase in temperature was increased O₂ permeability 1.50 times of PMP copolymer, and CO₂ permeability 1.35 times. These ratios we calculated coincided with Mangaraj and co-workers studies. [82]. Hence, gas permeabilities of PMP copolymer and blends which were contained PMP copolymer were less sensitive to temperature changes.

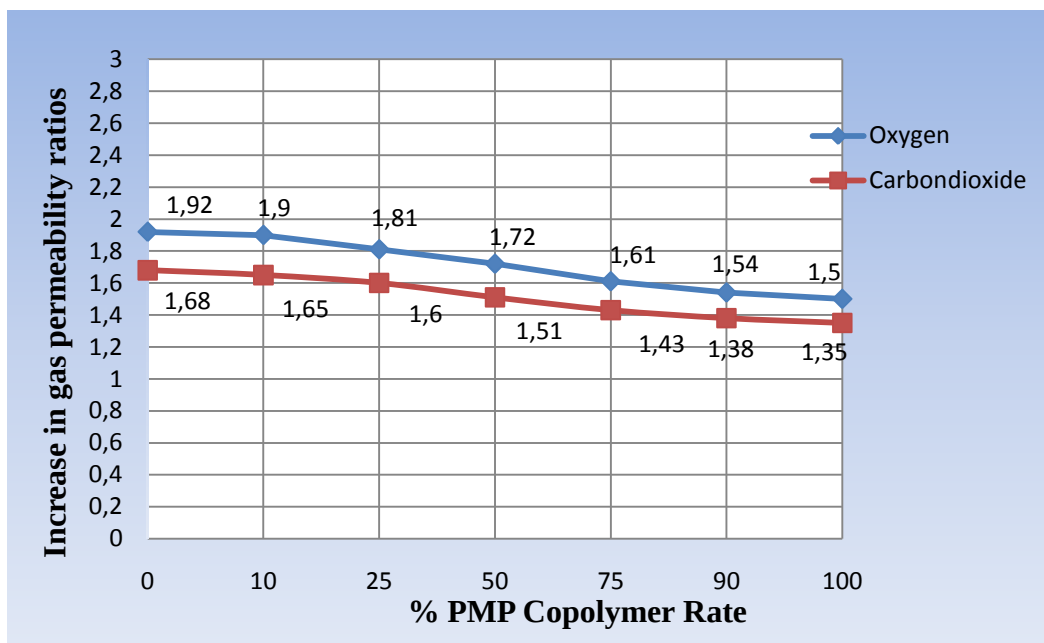


Figure 4.17 : Increase in gas permeability ratio between 15 °C – 25 °C

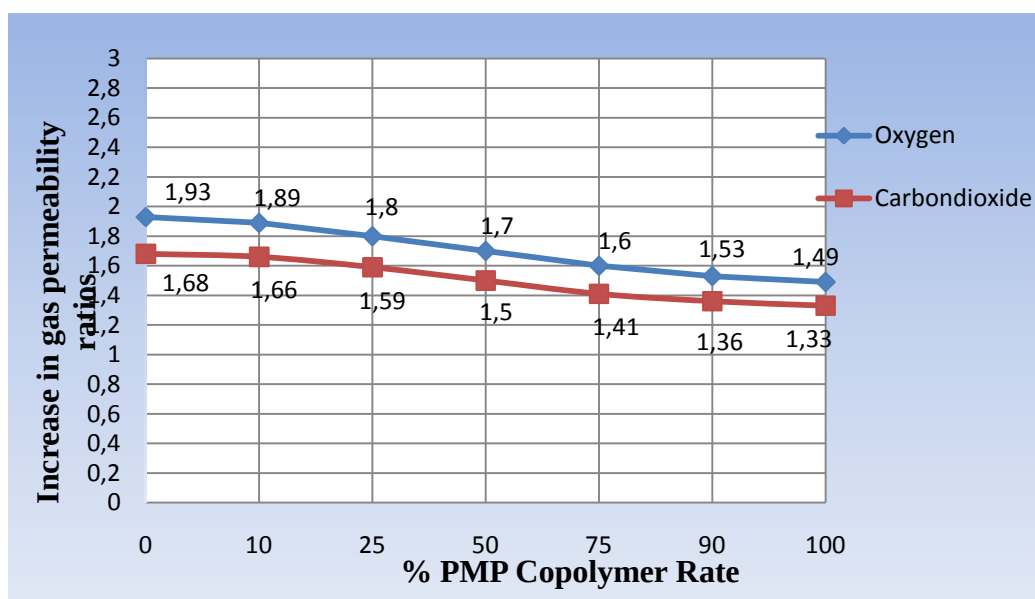


Figure 4.18 : Increase in gas permeability ratio between 5 °C – 15 °C

4.3 Results of shelf-life analysis

Shelf-life analysis were determined as described in section 3.4.3.

4.3.1 Shelf-life analysis of banana fruit

The average weight of 500g bananas were packaged under modified atmosphere packaging principles and kept at constant temperature (15 °C) for 14 days. The main reason of using bananas for shelf-life analysis is high respiration rate, high ethylene gas production rate and high sensitivity to ethylene gas of bananas. The O₂/CO₂ and C₂H₂ gas changes inside the packaging atmosphere were recorded during storage time. Test datas about these records were given in detail in Appendix A.5. The remarkable results of this shelf-life analysis were given in sections 4.3.1.1 and 4.3.1.2.

4.3.1.1 O₂/CO₂ changes inside the package samples

Recorded O₂/CO₂ changes inside the packages were given in Figures 4.19 and 4.20. According to these values, O₂ level inside the neat LDPE based package dropped down below 1% within first day of analysis and remained constant during storage time, while CO₂ level rose to 18% but then dropped down to 16% and remained constant on that level. In the same way, O₂ level of the blend which was containing 10% by weight PMP copolymer was dropped down instantly. However O₂ and CO₂ values inside the package were at higher levels such as 16% for O₂ and 23% for CO₂. Because of this reason O₂ level inside the package was dropped down below at the end of the second day while CO₂ level remained constant at 14%.

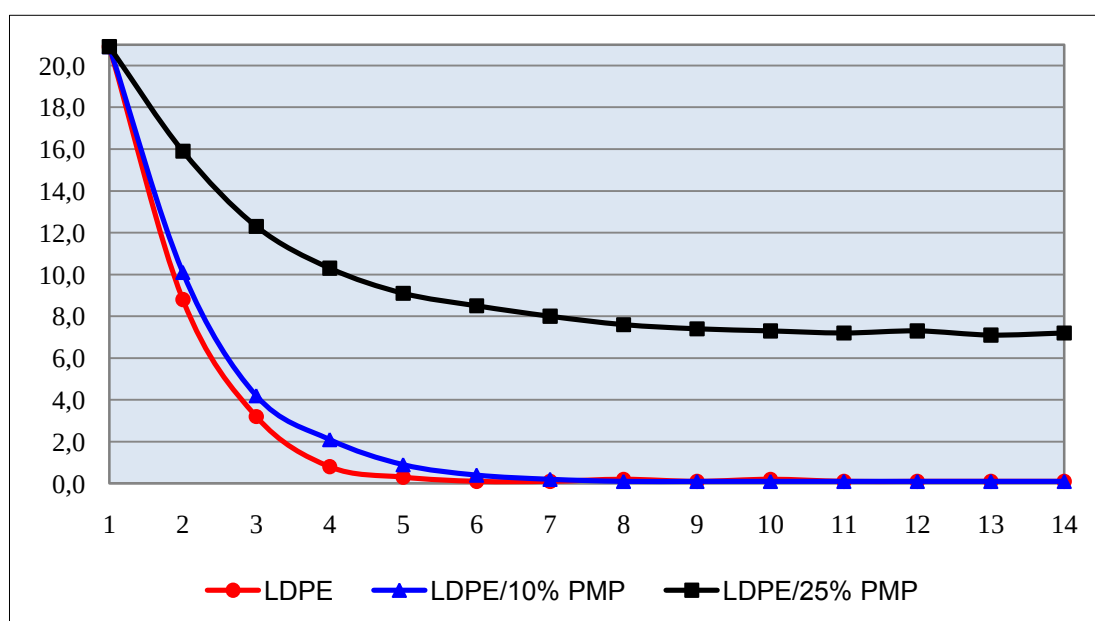


Figure 4.19 : Percentage O₂ changes inside the packages

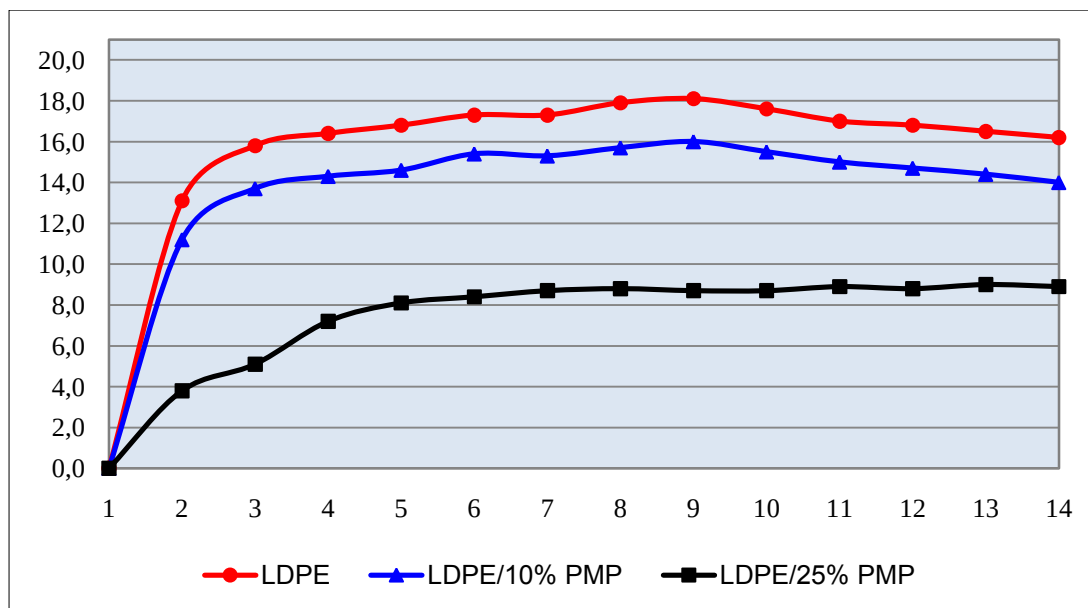


Figure 4.20 : Percentage CO₂ changes inside the packages

Existing studies about preservation of fresh cut fruits and vegetables inside the plastic packages have been suggesting that when O₂ level inside the package is dropped down below 5%, the preserved produce is quit aerobic respiration and started to make anaerobic respiration. [21, 83 - 88] Aerobic respiration occurs in the presence of oxygen, the stock materials that fruits and vegetables stored in their bodies are broken down with oxygen in order to obtain energy. On the other hand, in anaerobic respiration energy is obtained by the oxidation of stock materials. [83] As a result of anaerobic respiration which is occurred under insufficient O₂ levels, aroma and taste of the product are affected unfavorably. The reason of this situation is underwhelmed cytochrome oxidase enzyme inside the plant cell. Also, increase in CO₂ levels prevents the krebs and glycolysis ways which make accumulate some metabolites such as succinic acid [21, 83-88] In line with this information, it can be clearly seen that the products inside the neat LDPE and LDPE/10% PMP package samples started to make anaeronic respiration at the end of the second day. Thereby, aroma and taste of the products were affected unfavorably.

On the other hand, O₂ level of dropped down below 7% at the end of the seventh day and CO₂ level reached to 8% levels of package sample which was containing 25% PMP copolymer. These O₂ and CO₂ levels had been stable for 14 days.

Thereby, reverse of 100% LDPE and LDPE/10% PMP package samples, this one clearly did not cause anaerobic respiration due to high oxygen and low carbondioxide levels. [83 - 88] Bananas which were preserved inside this package

sample were kept fresh during 14 days. Also it is foreseen that aroma and taste of these bananas were not affected unfavorably.

4.3.1.2 Ethylene gas changes inside the package samples

Recorded ethylene gas changes inside the packages were given in Figure 4.21, and daily average ethylene gas accumulation is given in Table 4.12 which were calculated from the equation mentioned in section 3.4.3.

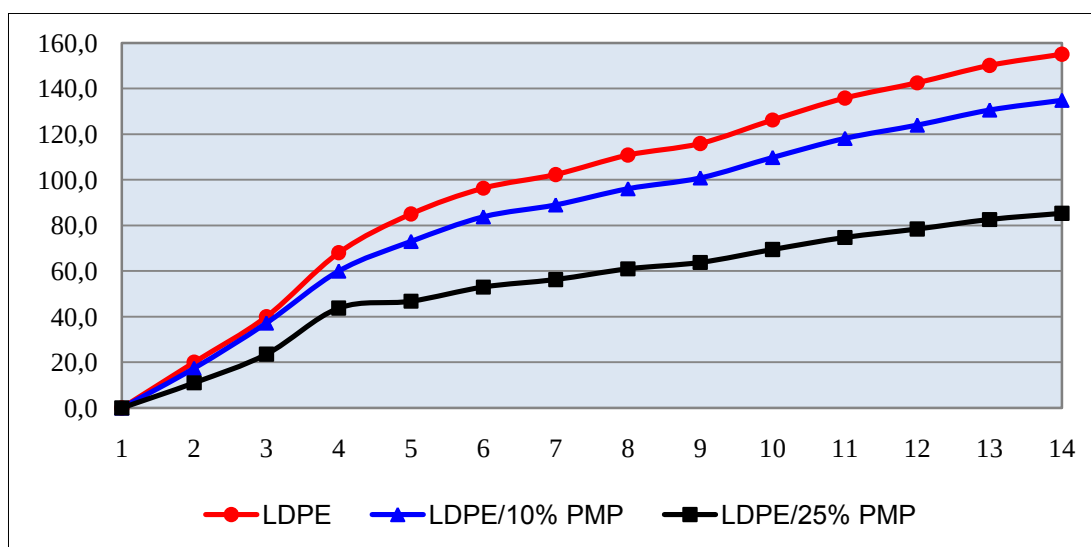


Figure 4.21 : Percentage C₂H₂ changes inside the packages

Table 4.12 : Daily average C₂H₂ accumulation of banana fruits

Package Sample	Daily Average C ₂ H ₂ accumulaton (ppm/g.day)	Decrease In Daily Average C ₂ H ₂ Accumulation (%)	Amount Of C ₂ H ₂ At The End Of The 14 th Day (ppm)
LDPE	5.54×10^{-3}	-	155.0
LDPE/10% PMP	4.72×10^{-3}	% 14.8	134.9
LDPE//25% PMP	2.18×10^{-3}	%60.6	85.3

According to these values, C₂H₂ gas concentration inside the 100% LDPE package sample was shown linear increase and reached 155.0 ppm at the end of the 14th day. Daily ethylene gas accumulation was determined 5.54×10^{-3} ppm/g.day. On the other hand, ethylene gas levels inside the package samples were containing 10% and 25% PMP copolymer were shown linear increase. Daily ethylene gas accumulations of these package samples were determined respectively 4.72×10^{-3} ve 2.18×10^{-3} ppm/g.day which are less than 100% LDPE package sample.

In this respect, daily ethylene gas accumulation inside the package sample atmospheres decreased to 14.8% and 60.6% respectively due to increase in PMP copolymer ratio. These proportional decrease in ethylene gas accumulation were close to increasing ratios of O₂ permeabilities of the package samples. In addition to increase in O₂ and CO₂ permeability values, C₂H₂ permeability of package samples were increased due to PMP copolymer addition into LDPE matrix.

Ethylene gas is needed to be in small amounts or not at all inside the packages which are used for preserving fresh cut fruits and vegetables for shelf life of the foods. The studies about preserving fresh cut fruits and vegetables inside the plastic packages were clearly highlighted that existence of ethylene gas inside the packaging atmosphere is increased the respiration rate and consequently ripening and softening of the most fruits and vegetables are accelerated. Besides that softening due to ethylene gas existence makes the fresh cut products more sensitive to microorganisms. These effects of ethylene gas cause spoilage very shortly and shorten the shelf lives of these products. [2-4, 13, 16, 88]

According to the values which were shown in Table 4.12 and Figure 4.21 were supposed that the bananas inside the last package sample which was containing 25% PMP copolymer have much better sensorial properties when compared to previous package samples at the end of the 14th day.

4.3.1.3 Evaluation of shelf life analysis of bananas

Today's most widely used plastic materials for packaging of fresh cut fruits and vegetables are low density polyethylene (LDPE) and derivatives. The reason of this widely used of LDPE has higher gas permeability values than other commercial plastics and relatively lower costs.

As it was shown in our study, O₂ and CO₂ permeabilities of 40 micron package sample which was produced from LDPE were respectively 3000 and 15000 cc/m².day.atm that are assumed as high permeability values. In spite of these high gas permeability values, atmospheric conditions inside the package cannot be met the requirements for the products have high respiration rates such as banana. It can be clearly seen in shelf life analysis that O₂ level inside this package sample consumed within a few days, so anaerobic respiration was started and the product lost its

commercial value. Figure 4.22 is presented the periodically recorded images of 100% LDPE package samples.



Figure 4.22 : Recorded banana fruits inside 100% LDPE package sample

On the other hand, with the addition of PMP copolymer into LDPE polymer matrix gas permeability values can be increased and extension of shelf life for preserved fresh cut fruits and vegetables can be obtained. For instance, due to the addition of 10% PMP copolymer into LDPE matrix was increased O_2 and CO_2 permeability values approximately 20%, and transition time to anaerobic respiration of bananas inside this package sample delayed 1 day, thus the shelf life was extended 1 day. Figure 4.23 is presented the periodically recorded images of LDPE/10% PMP package samples.



Figure 4.23 : Recorded banana fruits inside LDPE/10% PMP package sample

With the addition of 25% PMP copolymer into LDPE matrix, gas permeability values can be approximately 60% increased, O_2 level inside this package did not drop below 5%, and it remained constant during 14 days. This balanced atmospheric conditions which was highlighted many times in previous sections can be obtained in last package sample that was containing 25% PMP copolymer. Also, O_2 level inside that package sample could be kept at 5% which prevents anaerobic respiration of banana fruits. Therefore, other package samples which were containing more PMP copolymer ratios than 25% were not subjected to shelf life analysis for banana fruit. Figure 4.24 was shown periodically recorded images of LDPE/25% PMP package sample.



Figure 4.24 : Recorded LDPE/25% PMP package sample images

Consequently, consisting of 25% PMP copolymer LDPE based package sample was increased gas permeability values nearly 60%, and the images were clearly shown that this package sample can be preserved products have high respiration rates such as banana and provided longer-term shelf life.

4.3.2 Shelf-life analysis of marrow

The average weight of 600g green marrows were packaged under modified atmosphere packaging principles and kept at constant temperature (4°C) for 14 days. Theoretically, marrows are needed to be preserved under 8°C-12°C temperature conditions. On the other hand, practically they are preserved in refrigerator temperature. For this reason, the shelf life analysis of marrows were done under 4°C temperature condition. The main reason of using marrows that its respiration rate

which is lower than banana and its spoilage which is higher than banana. Due to these properties of marrows, evaluation of gas permeability effects on produce which were given have more sensitive and certain results. The O_2/CO_2 and C_2H_2 gas changes inside the packaging atmosphere were recorded during storage time. Test data about these records were given in detail in Appendix A.6. The remarkable results of this shelf-life analysis were given in sections 4.3.2.1 and 4.3.2.2.

4.3.2.1 O_2/CO_2 changes inside the package samples

Recorded O_2/CO_2 changes inside the packages were given in Figures 4.25 and 4.26. According to these values, O_2 level inside the 100% LDPE based package dropped down below 5% and 1% respectively at the end of the 6th and 9th days and remained constant during storage time, while CO_2 level rose to 12%. Existing studies about preservation of fresh cut fruits and vegetables inside the plastic packages have been suggesting that when O_2 level inside the package is dropped down below 5%, the preserved produce is quit aerobic respiration and started to make anaerobic respiration. [81, 83-88] Another remarkable detail in this study is when CO_2 level rises above O_2 level, the product lose its commercial value even if O_2 level does not drop down below that critical level. In this regard, it can be said that the shelf life of marrows inside the 100% LDPE package sample is 5 or 6 days.

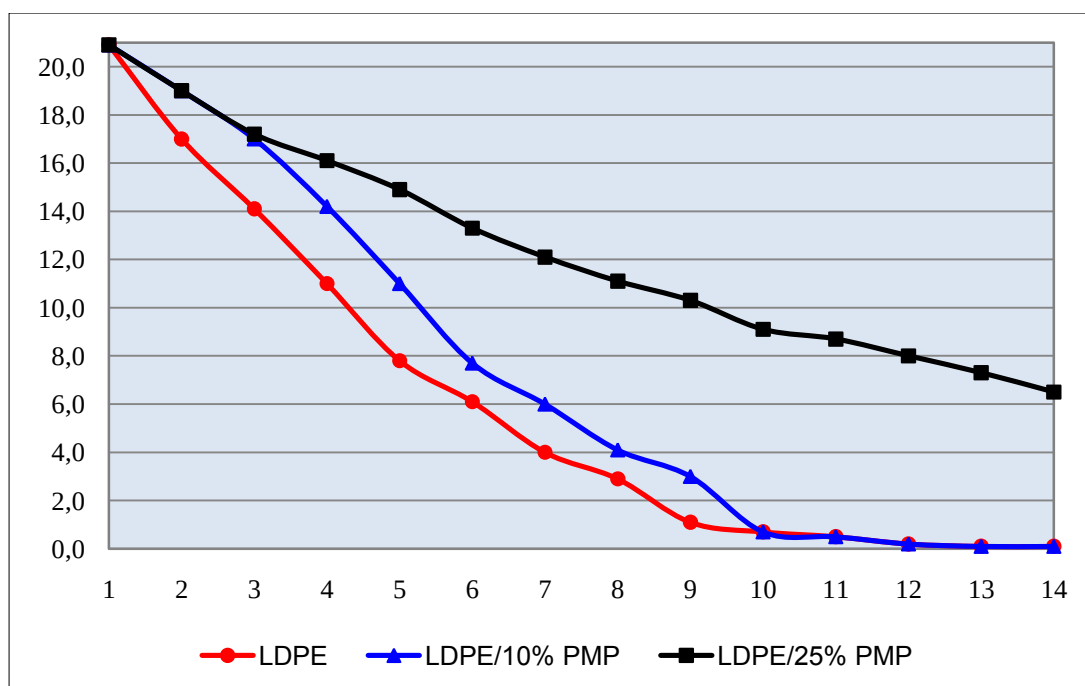


Figure 4.25 : Percentage O_2 changes inside the packages

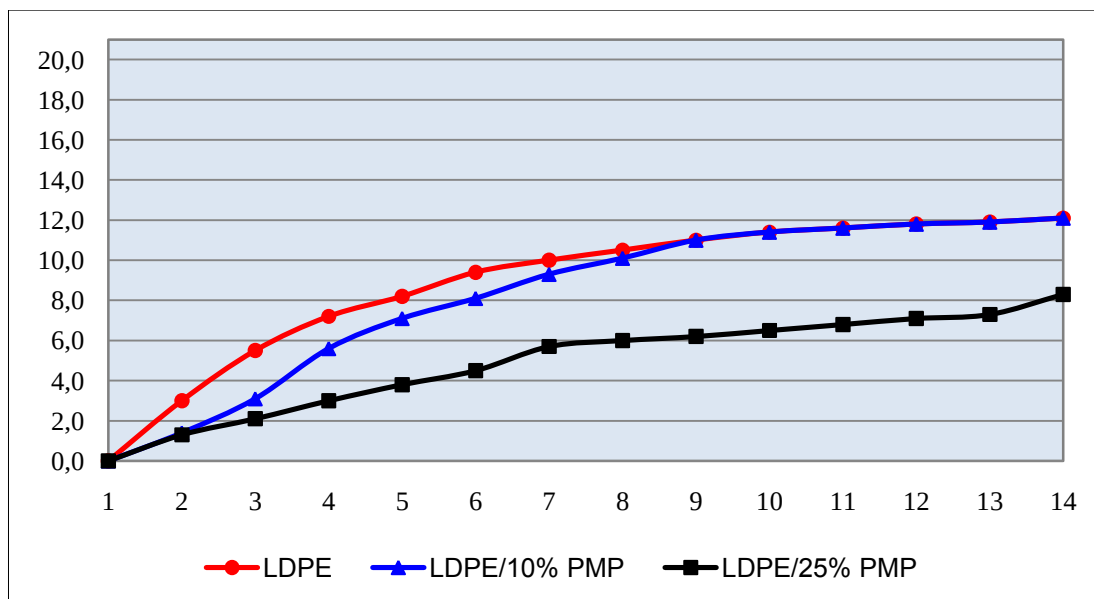


Figure 4.26 : Percentage CO₂ changes inside the packages

Inside the package sample which was containing 10% PMP copolymer, O₂ level dropped down below 5% at the end of the 7th day, and 1% at the end of 9th day. After that it remained constant at the end of the 14th day while CO₂ level rose to 12%. At the end of the 6th day, CO₂ level rose above O₂ level, thus the shelf life of marrows inside this package sample is 6 or 7 days.

On the other hand, inside the third package sample which was containing 25% PMP copolymer, O₂ level did not drop down below 5% for 14 days and CO₂ level reached 8% levels. These levels remained constant till the end of the 14th day. At the end of the 13th day, CO₂ level rose above O₂ level. Thus, similar to other package samples it was clear that the levels of O₂ and CO₂ did not allow anaerobic respiration. [81, 83-87] Hence, marrows inside this package sample can be preserved for 13 or 14 days without lack of taste and aroma properties.

4.3.2.2 Ethylene gas changes inside the package samples

Recorded ethylene gas changes inside the packages were given in Figure 4.27, and daily average ethylene gas accumulation is given in Table 4.13 which were calculated from the equation was given in section 3.4.3.

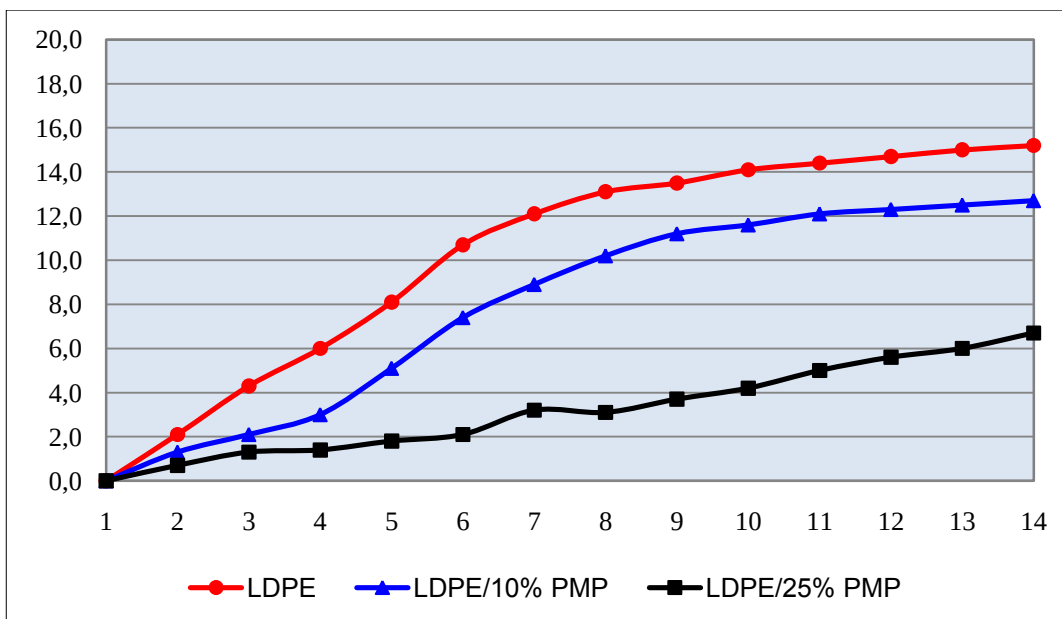


Figure 4.27 : Percentage C₂H₂ changes inside the packages

Table 4.13 : Daily average C₂H₂ accumulation of marrow fruits

Package Sample	Daily Average C ₂ H ₂ accumulation (ppm/g.day)	Decrease In Daily Average C ₂ H ₂ Accumulation (%)	Amount Of C ₂ H ₂ At The End Of The 14 th Day (ppm)
LDPE	0.45x10 ⁻³	-	15.2
LDPE/10% PMP	0.37x10 ⁻³	% 17.7	12.7
LDPE/25% PMP	0.15x10 ⁻³	%66.6	6.7

According to these values, C₂H₂ gas concentration inside the 100% LDPE package sample was shown linear increase and reached 15.2 ppm at the end of the 14th day. Daily ethylene gas accumulation was determined 0.45x10⁻³ ppm/g.day. On the other hand, ethylene gas levels inside the package samples were containing 10% and 25% PMP copolymer were shown linear increase. Also daily ethylene gas accumulations of these package samples were determined respectively 0.37x10⁻³ ve 0.15x10⁻³ ppm/g.day which are less than 100% LDPE package sample.

In this respect, daily ethylene gas accumulation inside the package sample atmospheres decreased to 17.7% and 66.6% respectively due to increase in PMP copolymer ratio. These proportional decrease in ethylene gas accumulation were close to increasing ratios of O₂ permeabilities of the package samples. In addition to

increase in O₂ and CO₂ permeability values, C₂H₂ permeability of package samples were increased due to PMP copolymer addition into LDPE matrix.

Ethylene gas is needed to be in small amounts or not at all inside the packages which are used for preserving fresh cut fruits and vegetables for shelf life of the foods. The studies about preserving fresh cut fruits and vegetables inside the plastic packages were clearly highlighted that existence of ethylene gas inside the packaging atmosphere is increased the respiration rate and consequently ripening and softening of the most fruits and vegetables are accelerated. Besides that softening due to ethylene gas existence makes the fresh cut products more sensitive to microorganisms. These effects of ethylene gas cause spoilage very shortly and shorten the shelf lives of these products. [2-4, 13, 16, 88]

According to the values which are shown in Table 4.13 and Figure 4.26 were supposed that the marrows inside the last package sample which was containing 25% PMP copolymer have much better sensorial properties when compared to previous package samples at the end of the 14th day.

4.3.2.3 Evaluation of shelf life analysis of marrows

As it is mentioned above today's most widely used plastic materials for packaging of fresh cut fruits and vegetables are low density polyethylene (LDPE) and derivatives. The reason of this widely used of LDPE is higher gas permeability values than other commercial plastics and relatively lower costs. Despite of these high gas permeability values with 100% LDPE package sample the desired atmospheric conditions cannot be obtained as can be seen in section 4.3.1.3. Similar problems were encountered during marrows' shelf life analysis. Marrows' respiration rate is lower than banana fruit, but again 100% LDPE package sample could not meet the requirements for such low respiration rates. The main reason of using marrows that its respiration rate which is lower than banana and its spoilage which is higher than banana. Thus, evaluation of gas permeability effects could analyze more sensitively due to these properties of marrows. Lower respiration of the product can only delay the beginning of anaerobic respiration. It can be clearly seen that preserving products have lower respiration rate, at the end of the 5th day O₂ level inside the package dropped down below the critical O₂ level, and the products lost its commercial value.

Figure 4.28 was presented the periodically recorded images of 100% LDPE package samples.



Figure 4.28 : Recorded marrow fruits inside 100% LDPE package sample

On the other hand, with the addition of PMP copolymer into LDPE polymer matrix gas permeability values can be increased and extension of shelf life for preserved fresh cut fruits and vegetables can be obtained. For instance, due to the addition of 10% PMP copolymer into LDPE matrix was increased O_2 and CO_2 permeability values approximately 20%, and transition time to anaerobic respiration of marrows inside this package sample delayed 1 day, thus the shelf life was extended 1 day. Figure 4.29 was presented the periodically recorded images of LDPE/10% PMP package samples.



Figure 4.29 : Recorded marrow fruits inside LDPE/10% PMP package sample

With the addition of 25% PMP copolymer into LDPE matrix, gas permeability values can be approximately 60% increased, O_2 level inside this package did not drop below 6%, and it remained constant during 14 days. This balanced atmospheric conditions which was highlighted many times in previous sections can be obtained in last package sample that was containing 25% PMP copolymer. Similar to banana fruits analysis, O_2 level inside that package sample could be kept at 6% which prevents anaerobic respiration. Therefore, other package samples which were containing more PMP copolymer ratio than 25% were not subjected to shelf life analysis for marrow fruits. Figure 4.30 was shown periodically recorded images of LDPE/25% PMP package sample.



Figure 4.30 : Recorded marrow fruits inside LDPE/25% PMP package sample

Consequently, consisting of 25% PMP copolymer LDPE based package sample was increased gas permeability values nearly 60%, and the images were clearly shown that this package sample can be preserved products have lower respiration rates such as marrow and provided longer-term shelf life.

5. CONCLUSION

In this study, low density polyethylene (LDPE) and polymethylpentene (PMP) blends were produced in order to observe the alterations in the gas permeability properties of LDPE-based plastic films by using a twin screw extrusion method for blend production and cast film extrusion method for film production. The raw materials were firstly pre-mixed and then blended in the intermeshing co-rotating twin screw extruder. Screw speed was determined as 500 rpm in order to obtain good dispersion between LDPE and PMP. Temperature profile of the extruder was arranged for to get well melted PMP copolymer, because the melting temperature of PMP is higher than LDPE. For the preparation of the samples, all the process parameters were kept constant in order to prevent the additional effects.

Rheological properties were affected by the addition of PMP into matrix at different loading levels. The results indicated that the melt flow index (MFI) values decreased gradually with increasing loading level of PMP. LDPE has a MFI value of 30 g/10 min. The highest loading of 90 wt% PMP decreased MFI to 22.4 g/10 min. By the inclusion of PMP to the matrix the melt flow index values decreased due to decreasing of chain movements of LDPE.

FTIR analysis showed that PMP has a broad peak between $2800\text{--}3000\text{ cm}^{-1}$ and $1500\text{--}1300\text{ cm}^{-1}$. FTIR spectrums of blends showed that the peaks which were mentioned above broadened with the addition of PMP copolymer into LDPE matrix,

The mechanical tests results showed that tensile strength and tensile strength at break were increased with the increase in PMP copolymer ratio of the samples. The tensile strength of LDPE was around 10 MPa and PMP gradually increased tensile strength up to nearly 20 MPa. However elongation at break decreased compared to LDPE. Strain values of the samples were decreased while tensile strength was increased. Increase in PMP copolymer ratio makes the films more brittle. However, all mechanical property values of the film samples were in acceptable limits for packaging applications.

DSC diagrams showed that crystallization point of LDPE decreased with PMP copolymer addition. Melting point of LDPE decreased with PMP addition. And also DSC results presented that LDPE and PMP copolymer have similar crystallinity ratios and partial crystalline structures. Evaluation of LDPE/PMP copolymer blends were shown that the melting temperatures did not show major alterations. Despite of increase in PMP copolymer ratio, all interblends were shown averagely 110°C and 223°C melting temperature peaks for LDPE and PMP copolymer respectively. Another remarkable detail in DSC analysis was crystallinity ratios did not change in direct proportion to addition ratio of PMP copolymer. The previous studies were shown that PMP copolymer crystallize in tetragonal symmetry. This tetragonal crystal lattice structure leads to lower packaging fraction, higher free volume and higher diffusion ratio. Due to increased free volume and diffusion ratio, higher gas permeability values can be obtained.

Increasing PMP copolymer ratios in the blend structure, it can be easily seen that O₂ and CO₂ permeabilities of the film samples were increased. The reason of this increase is the structure of PMP copolymer which is very convenient to gas permeability. Accordingly, it can be observed that high free volume and diffusion coefficient of PMP copolymer due to its low density and crystallinity cause these increases in gas permeabilities.

However, it can be seen that this increase in gas permeability values were not in direct proportion to increase in PMP copolymer ratio. It is foreseen that the reason of this situation is the phase separations because of these two polymers' incompatible structures or micro holes between these two phases. As a result of all of these gas permeability analysis, another remarkable point is PMP copolymer is less sensitive to temperature changes. As it can be seen in Figures 4.17 and 4.18, every 10 °C increase in temperature was increased O₂ permeability 1.92 times of LDPE, and CO₂ permeability 1.68 times. On the other hand, every 10 °C increase in temperature was increased O₂ permeability 1.50 times of PMP copolymer, and CO₂ permeability 1.35 times.

As it was shown in our study, O₂ and CO₂ permeabilities of 40 micron package sample which was produced from LDPE were respectively 3000 and 15000 cc/m².day.atm that are assumed as high permeability values. In spite of these high gas permeability values, atmospheric conditions inside the package cannot be met the

requirements for the products have high respiration rates such as banana. It can be clearly seen in shelf life analysis that O_2 level inside this package sample consumed within a few days, so anaerobic respiration was started and the product lost its commercial value. On the other hand, with the addition of PMP copolymer into LDPE polymer matrix gas permeability values can be increased and extension of shelf life for preserved fresh cut fruits and vegetables can be obtained. For instance, due to the addition of 10% PMP copolymer into LDPE matrix was increased O_2 and CO_2 permeability values approximately 20%, and transition time to anaerobic respiration of bananas inside this package sample delayed 1 day, thus the shelf life was extended 1 day.

With the addition of 25% PMP copolymer into LDPE matrix, gas permeability values can be approximately 60% increased, O_2 level inside this package did not drop below 5%, and it remained constant during 14 days because this oxygen level prevents the anaerobic respiration. This balanced atmospheric conditions which was highlighted many times in previous sections can be obtained in last package sample that was containing 25% PMP copolymer.

Consequently, consisting of 25% PMP copolymer LDPE based package sample was increased gas permeability values nearly 60%, and the images were clearly shown that this package sample can be preserved products have high respiration rates such as banana and provided longer-term shelf life.

Similar problems were encountered during marrows' shelf life analysis. Marrows' respiration rate is lower than banana fruit, but again pure LDPE package sample could not meet the requirements for such low respiration rates. The main reason of using marrows that its respiration rate which is lower than banana and its spoilage which is higher than banana. Lower respiration of the product can only delay the beginning of anaerobic respiration. It can be clearly seen in shelf life analysis that, at the end of the 5th day O_2 level inside the package dropped down below the critical O_2 level, and the products lost its commercial value. On the other hand, with the addition of PMP copolymer into LDPE polymer matrix gas permeability values can be increased and extension of shelf life for preserved fresh cut fruits and vegetables can be obtained. For instance, due to the addition of 10% PMP copolymer into LDPE matrix was increased O_2 and CO_2 permeability values approximately 20%, and

transition time to anaerobic respiration of marrows inside this package sample delayed 1 day, thus the shelf life was extended 1 day.

With the addition of 25% PMP copolymer into LDPE matrix, gas permeability values can be approximately 60% increased, O₂ level inside this package did not drop below 6%, and it remained constant during 14 days because this oxygen level prevents the anaerobic respiration. This balanced atmospheric conditions which was highlighted many times in previous sections can be obtained in last package sample that was containing 25% PMP copolymer.

Consequently, consisting of 25% PMP copolymer LDPE based package sample was increased gas permeability values nearly 60%, and the images were clearly shown that this package sample can be preserved products have lower respiration rates such as marrow and provided longer-term shelf life. According to shelf life analysis, the last package sample which was containing 25% PMP copolymer was increased the gas permeability values up to desired levels for banana and marrow fruits. Other package samples were containing higher PMP copolymer ratios would clearly provide higher gas permeability values due to shelf life analysis results. Therefore, other package samples were not subjected to shelf life analysis.

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APPENDICES

APPENDIX A.1 : Diagrams of Differential Scanning Calorimetry (DSC) Analysis

APPENDIX A.2 : Diagrams of Fourier Transform Infrared (FTIR) Analysis

APPENDIX A.3 : Diagrams of Thermogravimetric Analysis (TGA)

APPENDIX A.4 : Diagrams of X-Ray Diffraction (XRD) Analysis

APPENDIX A.5 : Shelf Life Analysis Of Banana Fruits

APPENDIX A.6 : Shelf Life Analysis Of Marrows

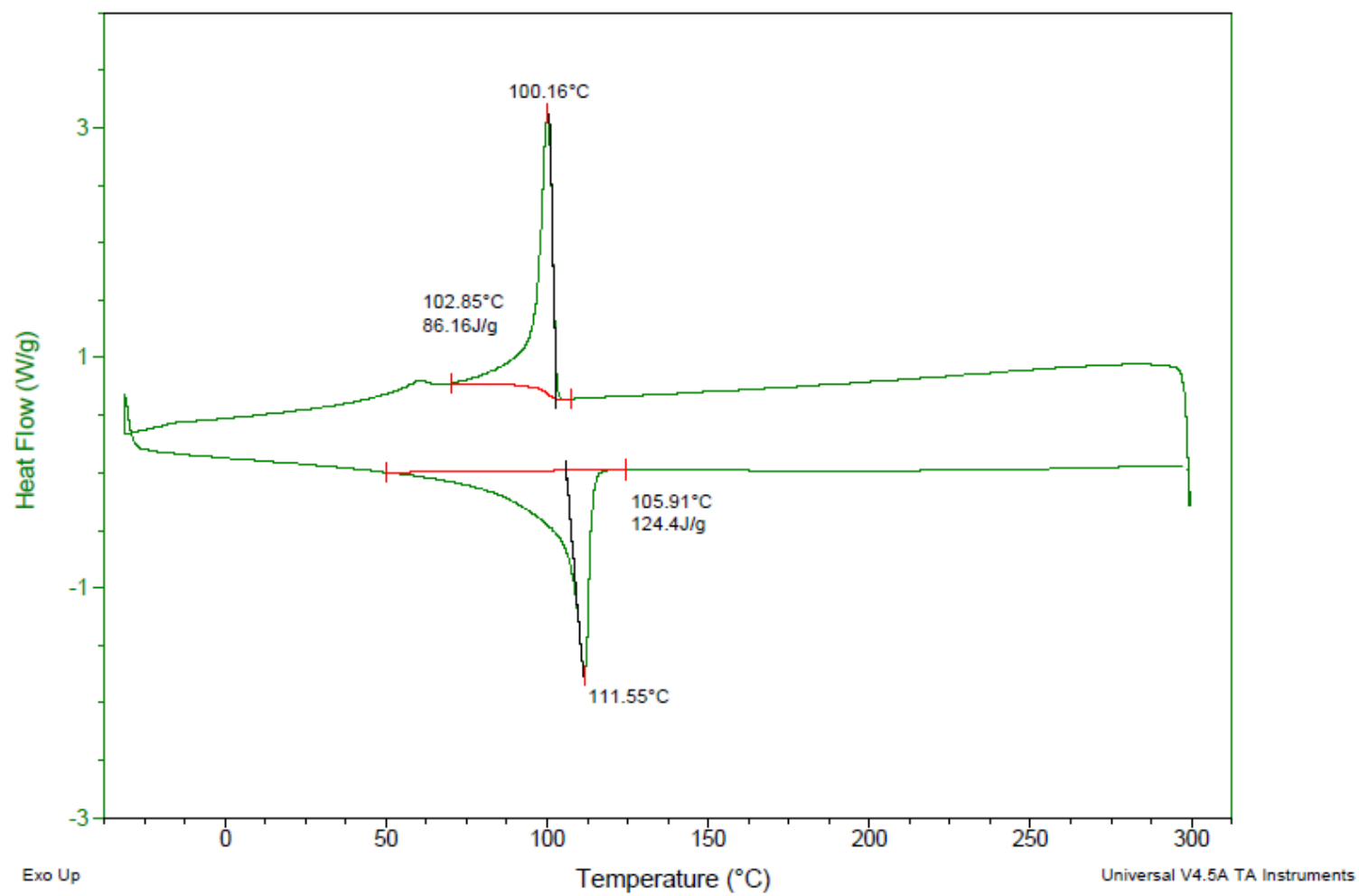


Figure A.1.1 : DSC diagram of LDPE

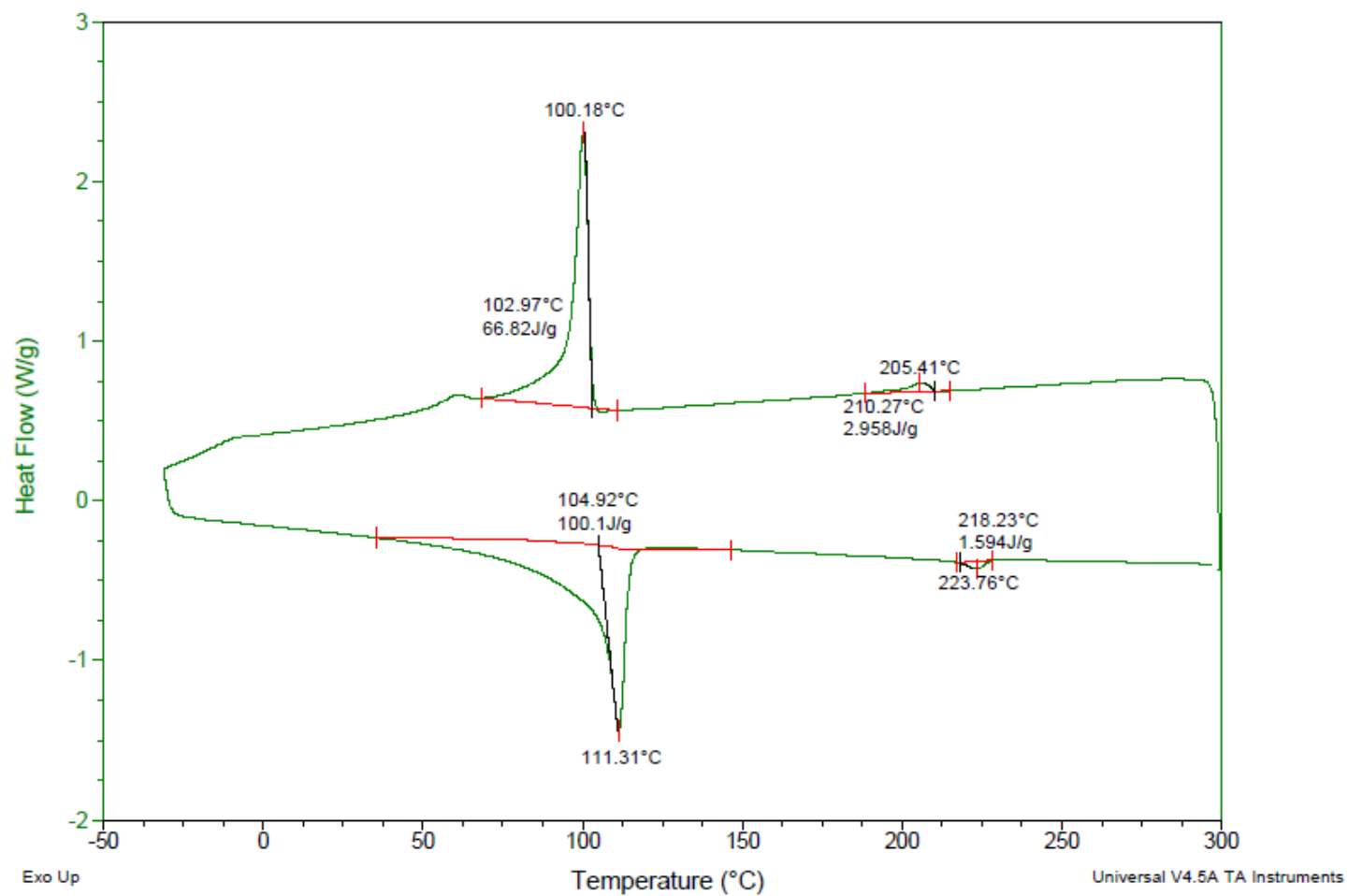


Figure A.1.2 : DSC diagram of LDPE/10% PMP

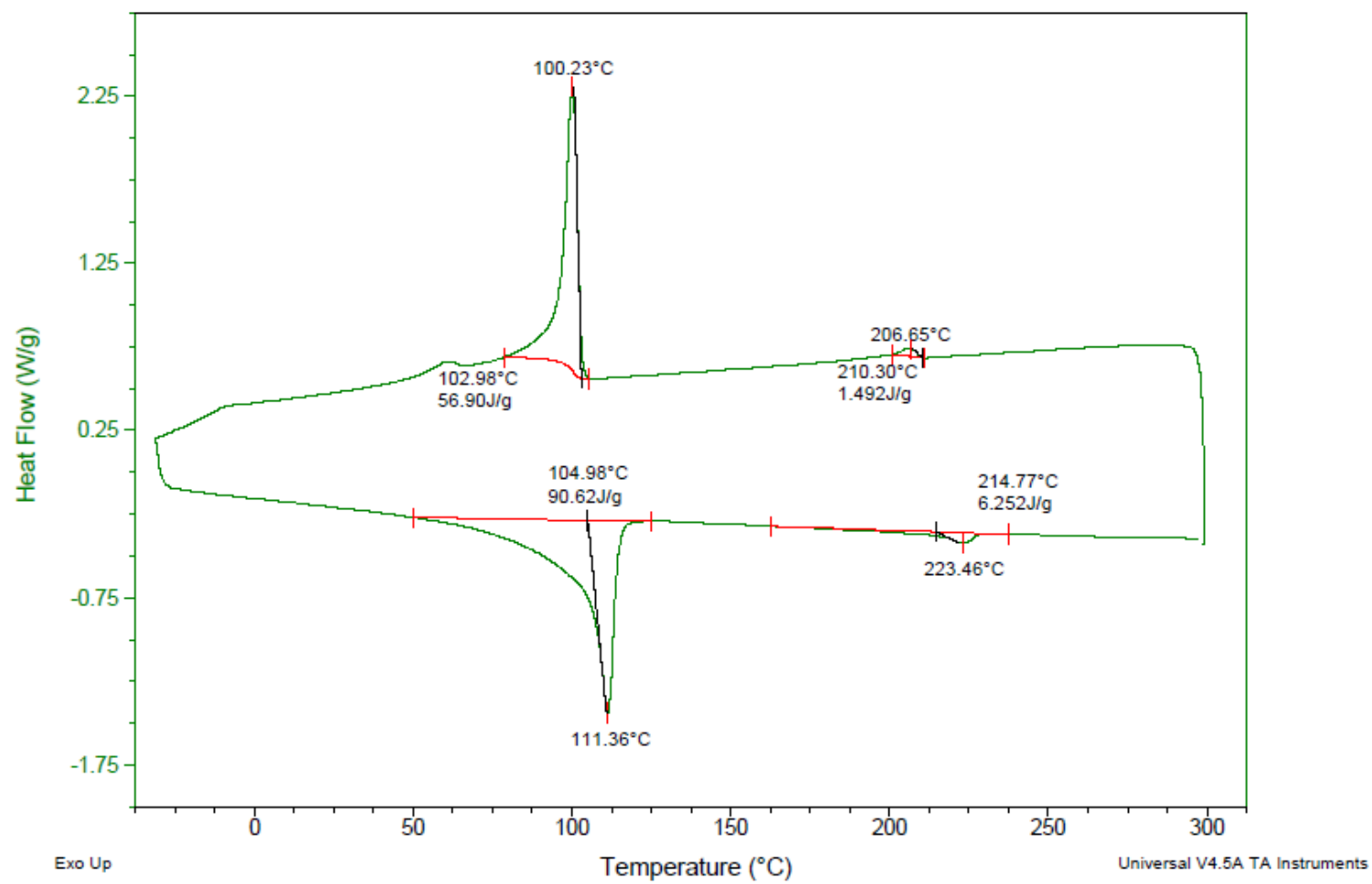


Figure A.1.3 : DSC diagram of LDPE/25% PMP

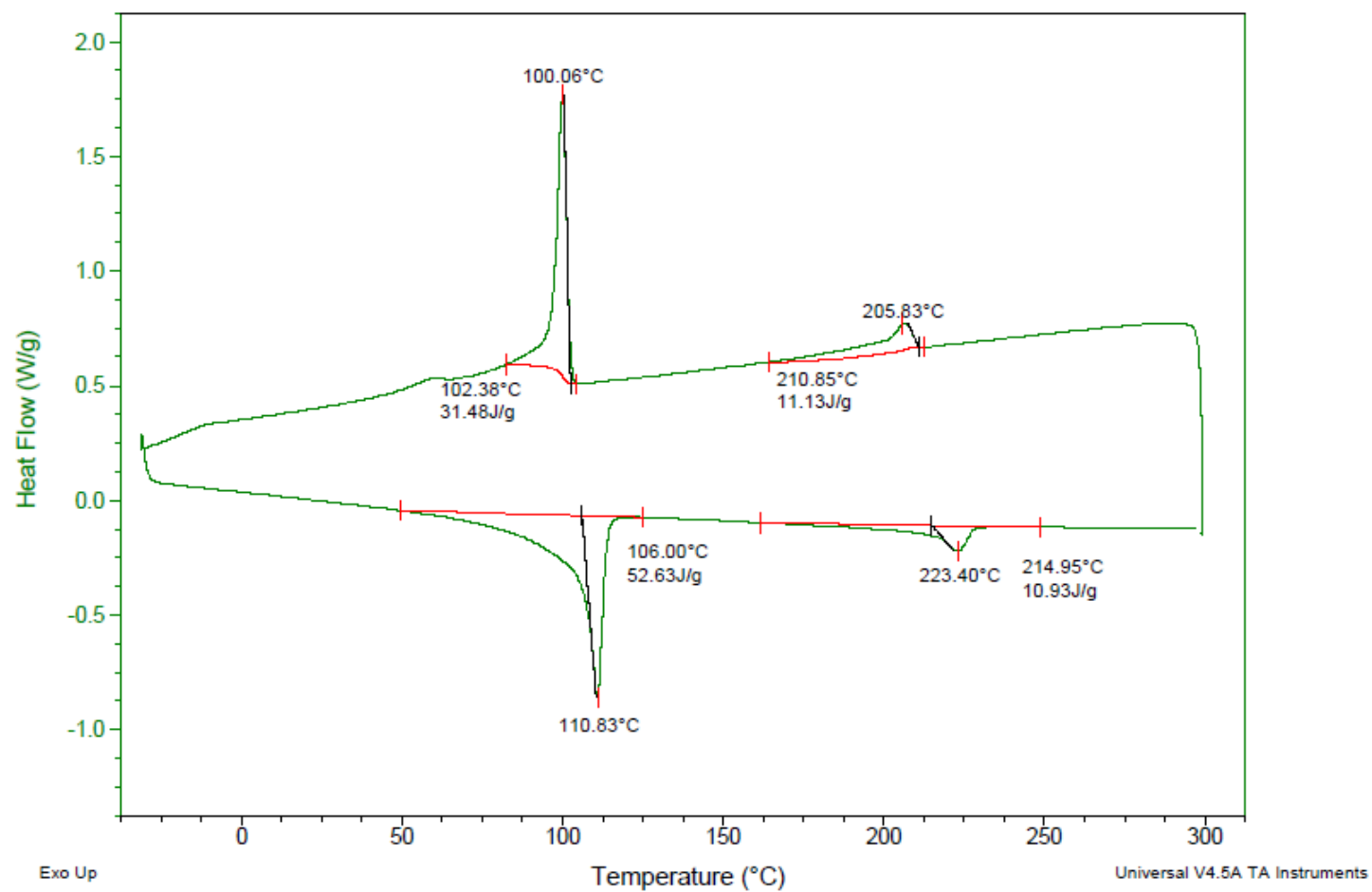


Figure A.1.4 : DSC diagram of LDPE/50% PMP

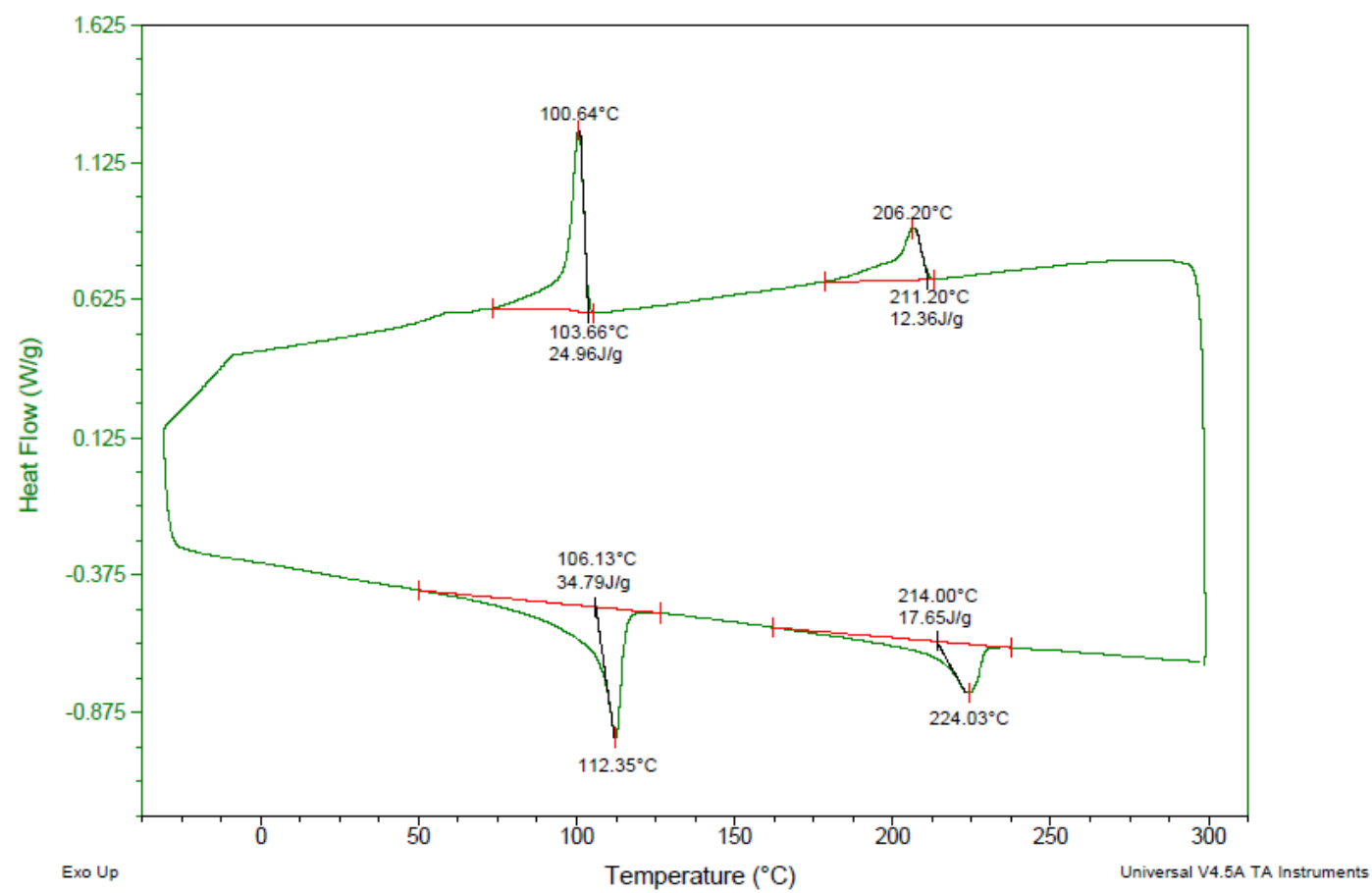


Figure A.1.5 : DSC diagram of LDPE/75% PMP

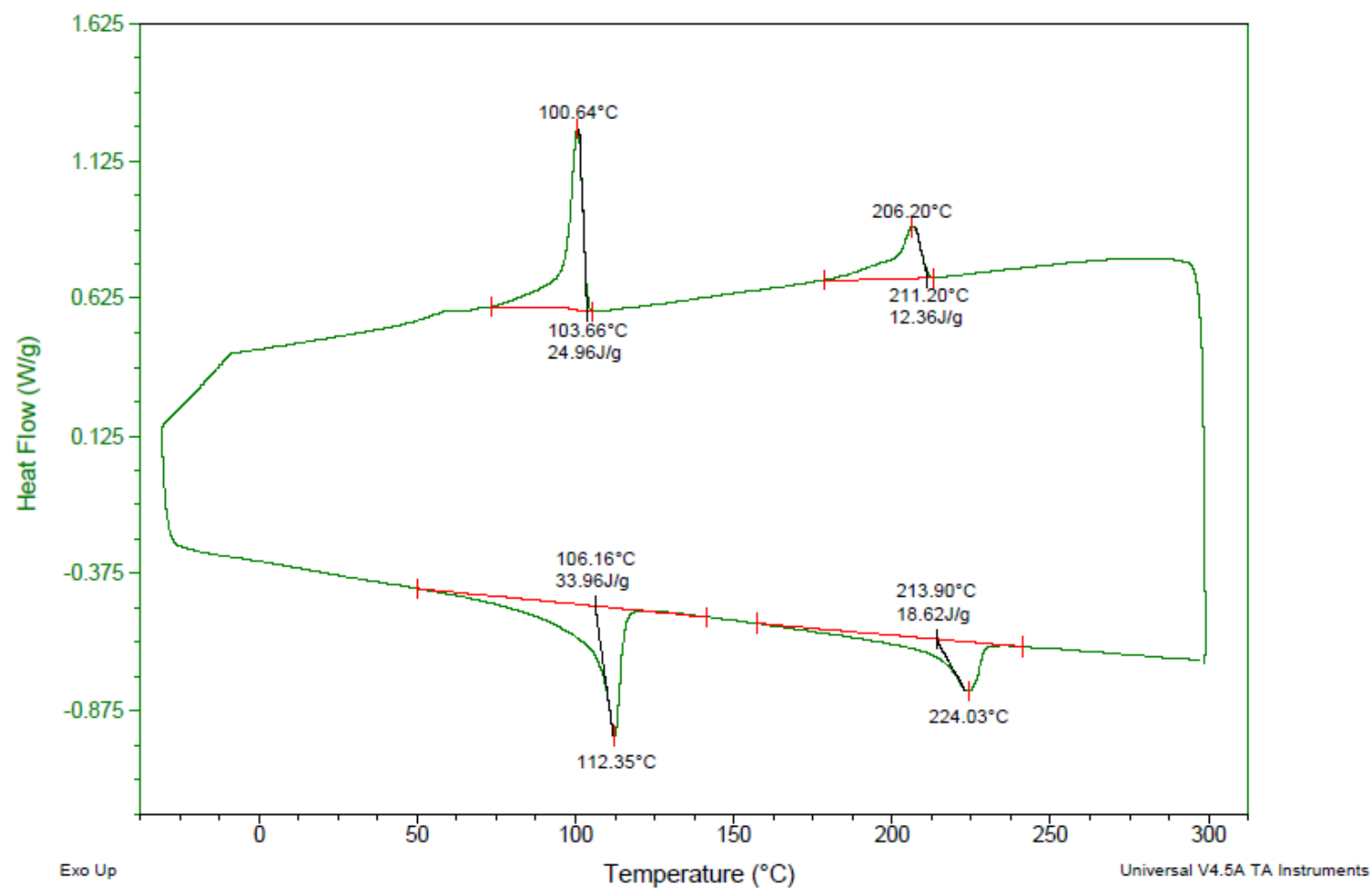


Figure A.1.6 : DSC diagram of LDPE/90% PMP

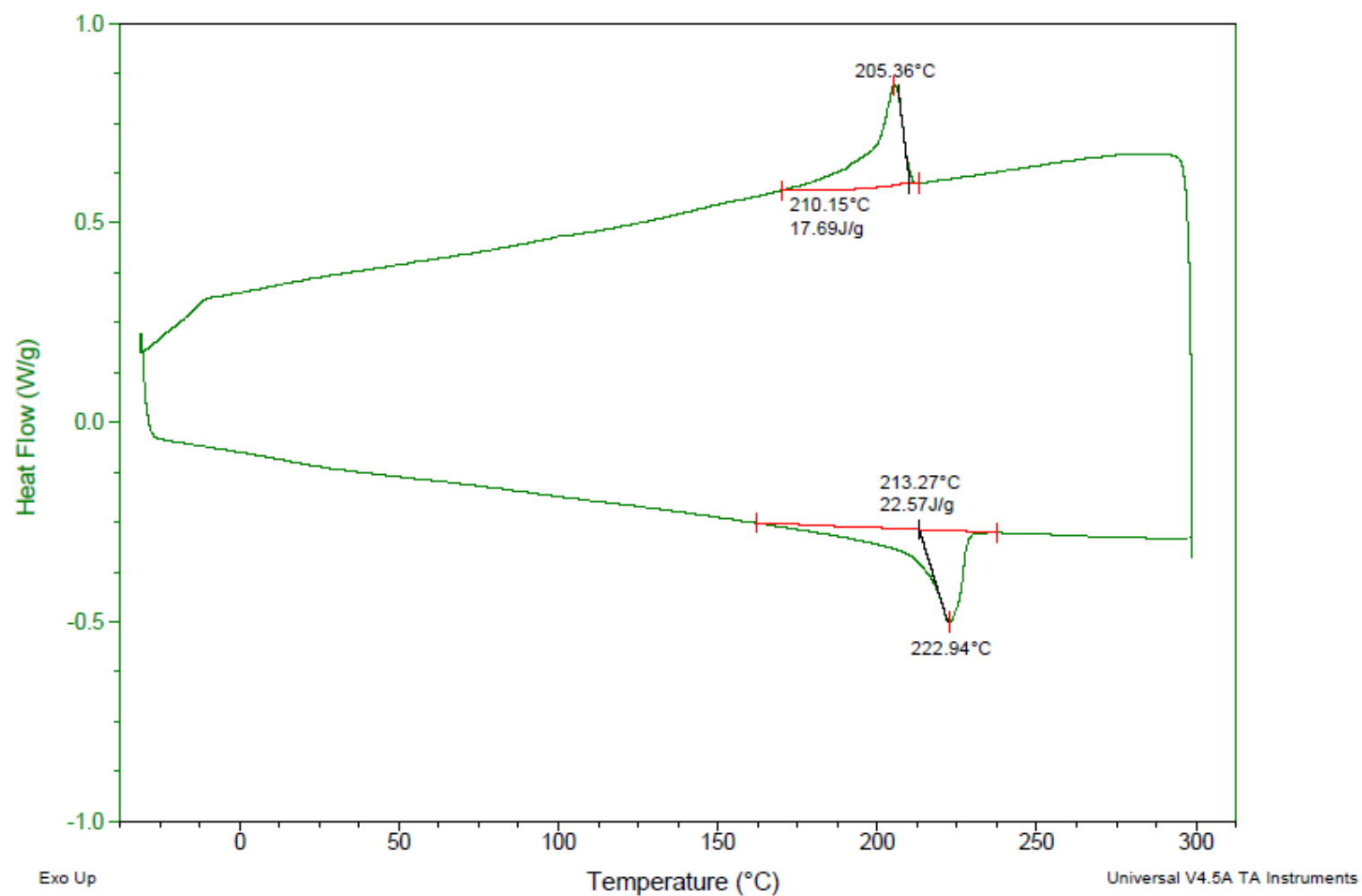


Figure A.1.7 : DSC diagram of PMP

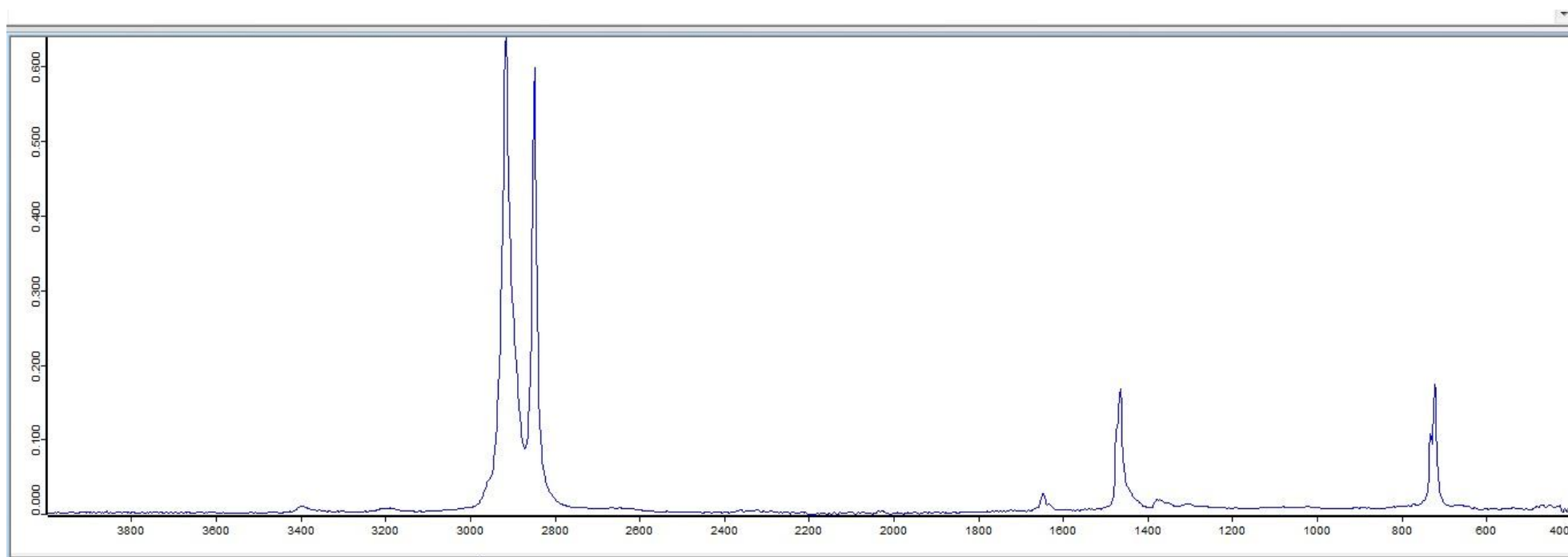


Figure A.2.1 : FTIR diagram of LDPE

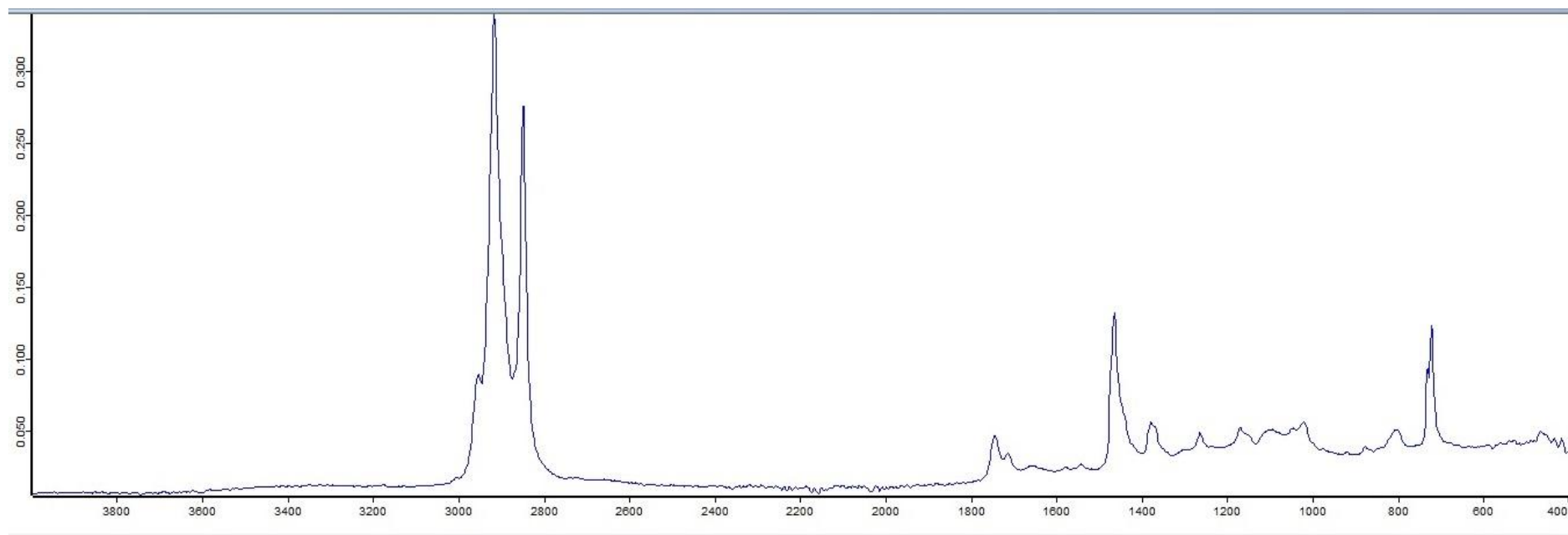


Figure A.2.2 : FTIR diagram of LDPE/10% PMP

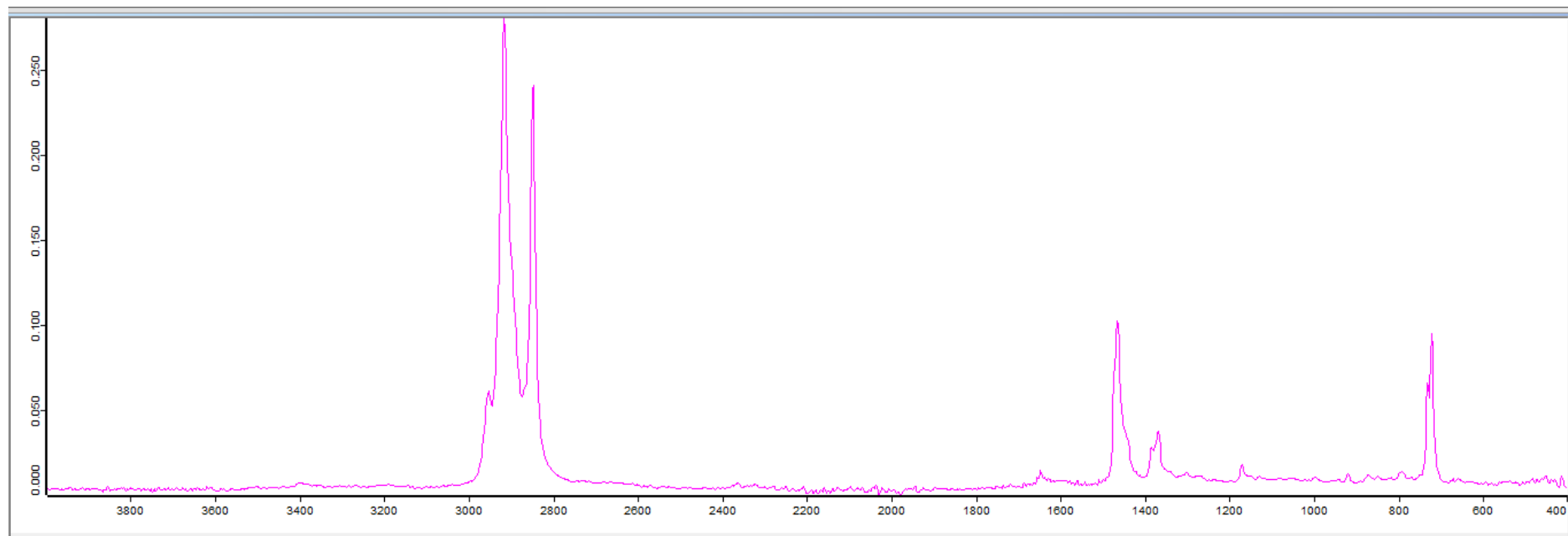


Figure A.2.3 : FTIR diagram of LDPE/25% PMP

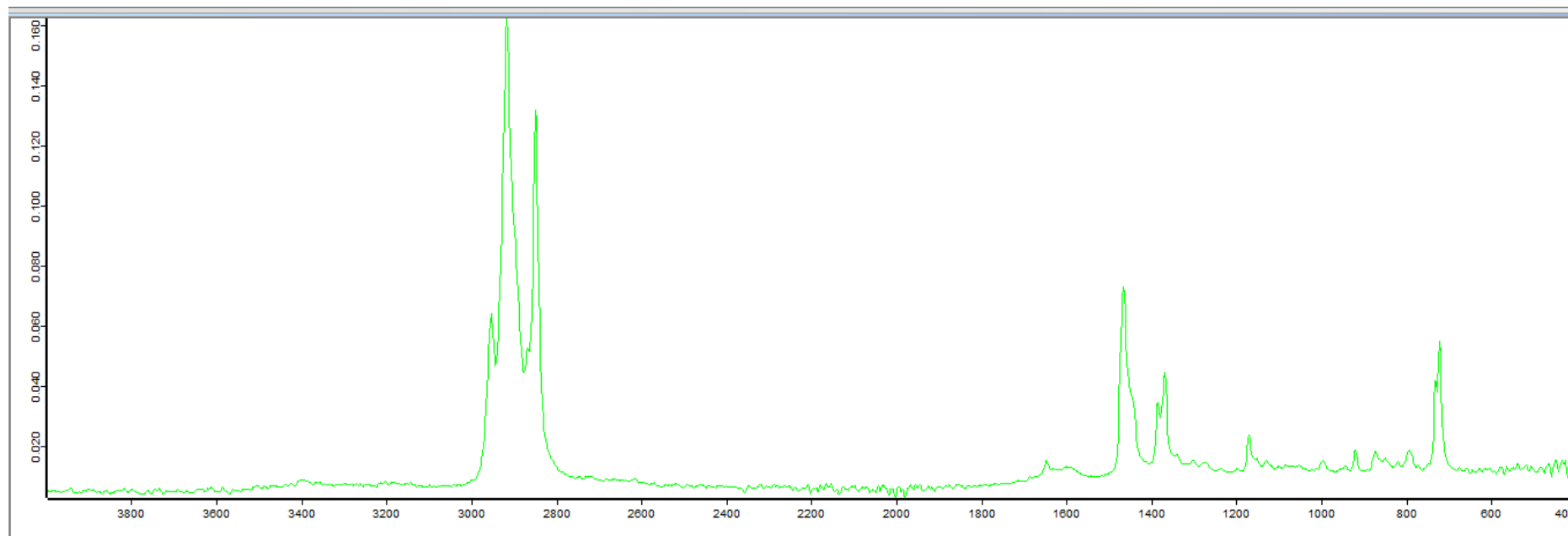


Figure A.2.4 : FTIR diagram of LDPE/50% PMP

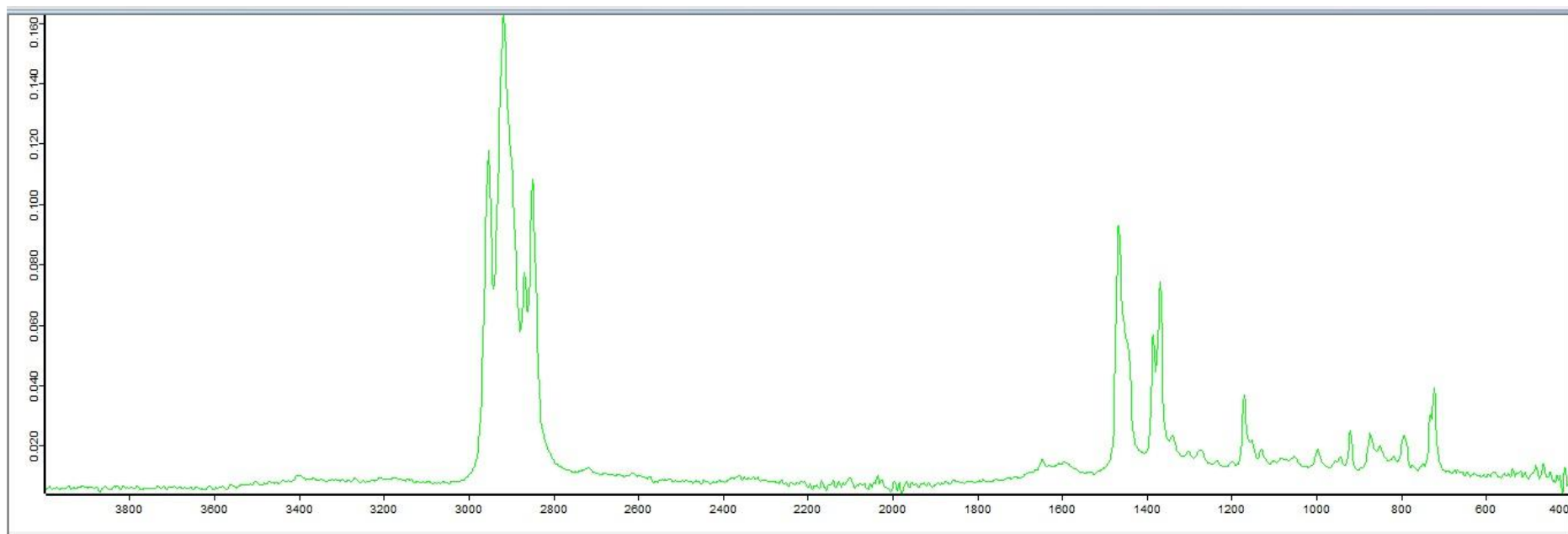


Figure A.2.5 : FTIR diagram of LDPE/75% PMP

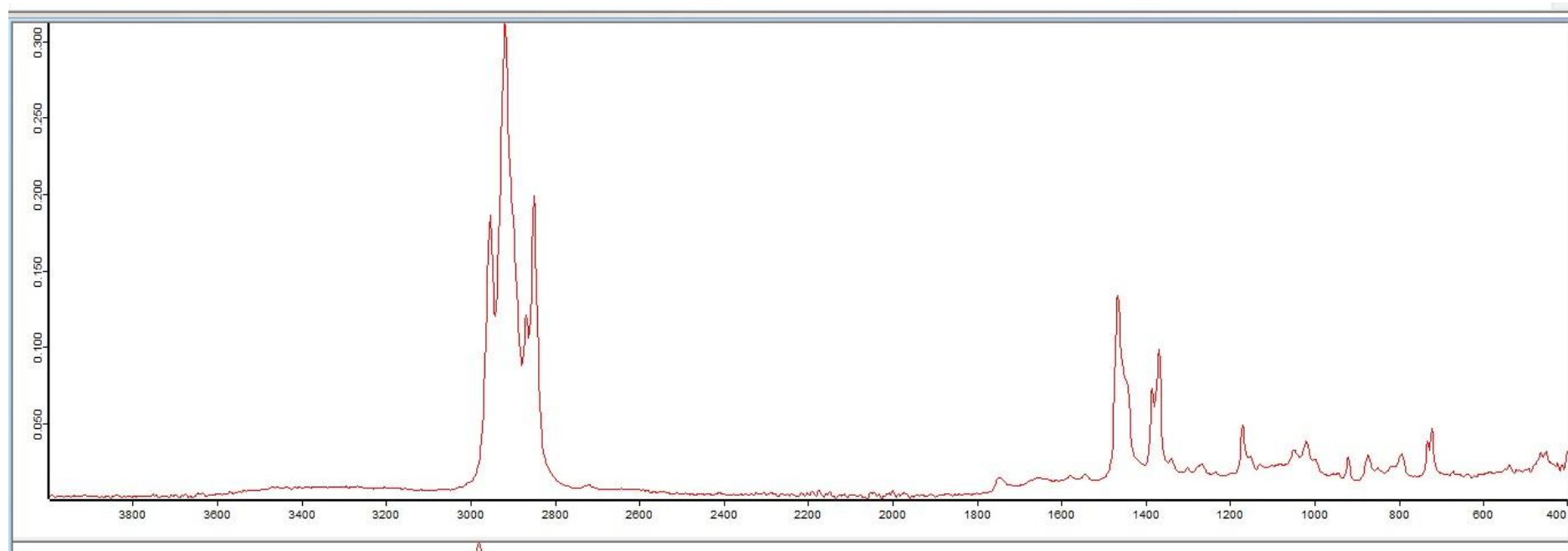


Figure A.2.6 : FTIR diagram of LDPE/90% PMP

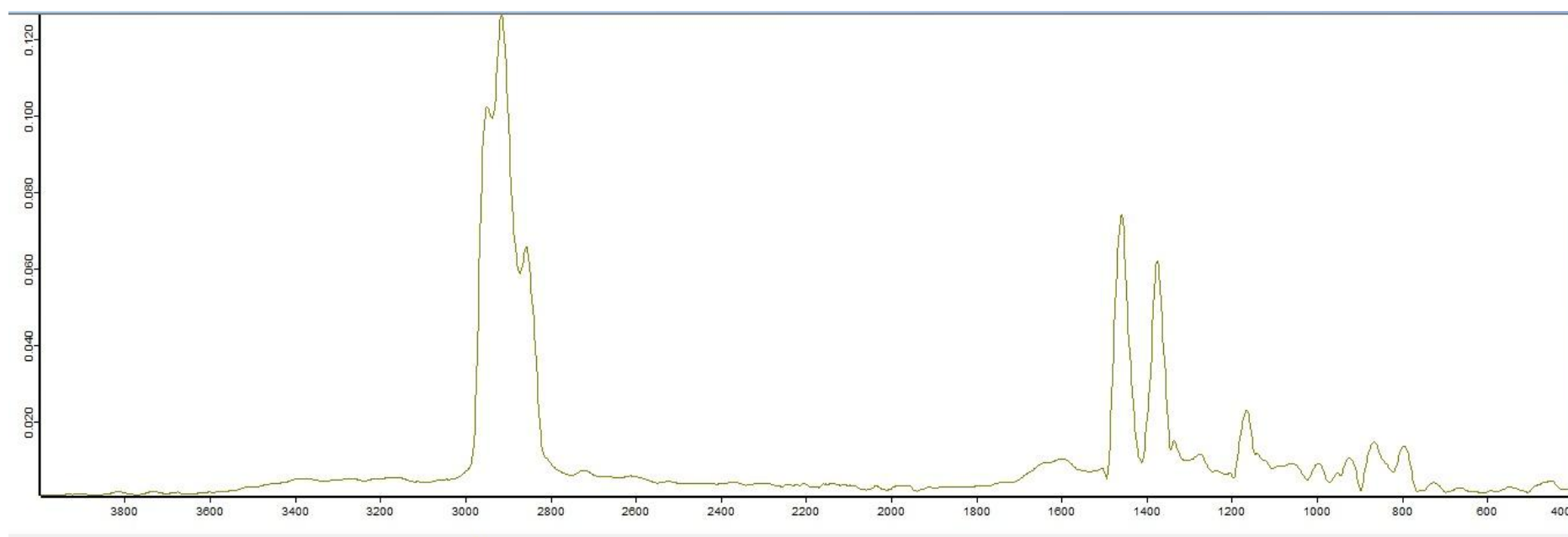
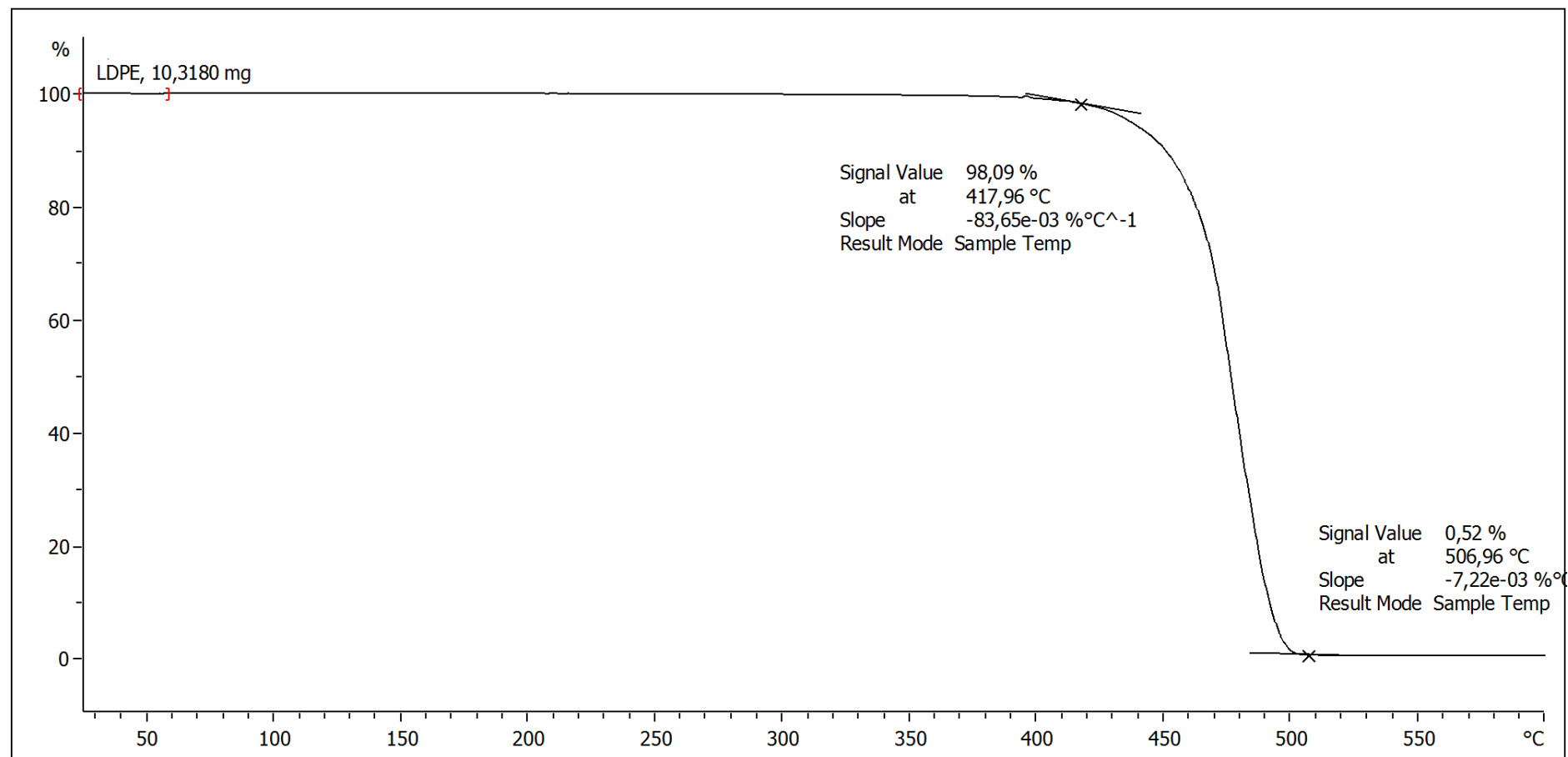


Figure A.2.7 : FTIR diagram of PMP



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Figure A.3.1 : TGA thermogram of LDPE

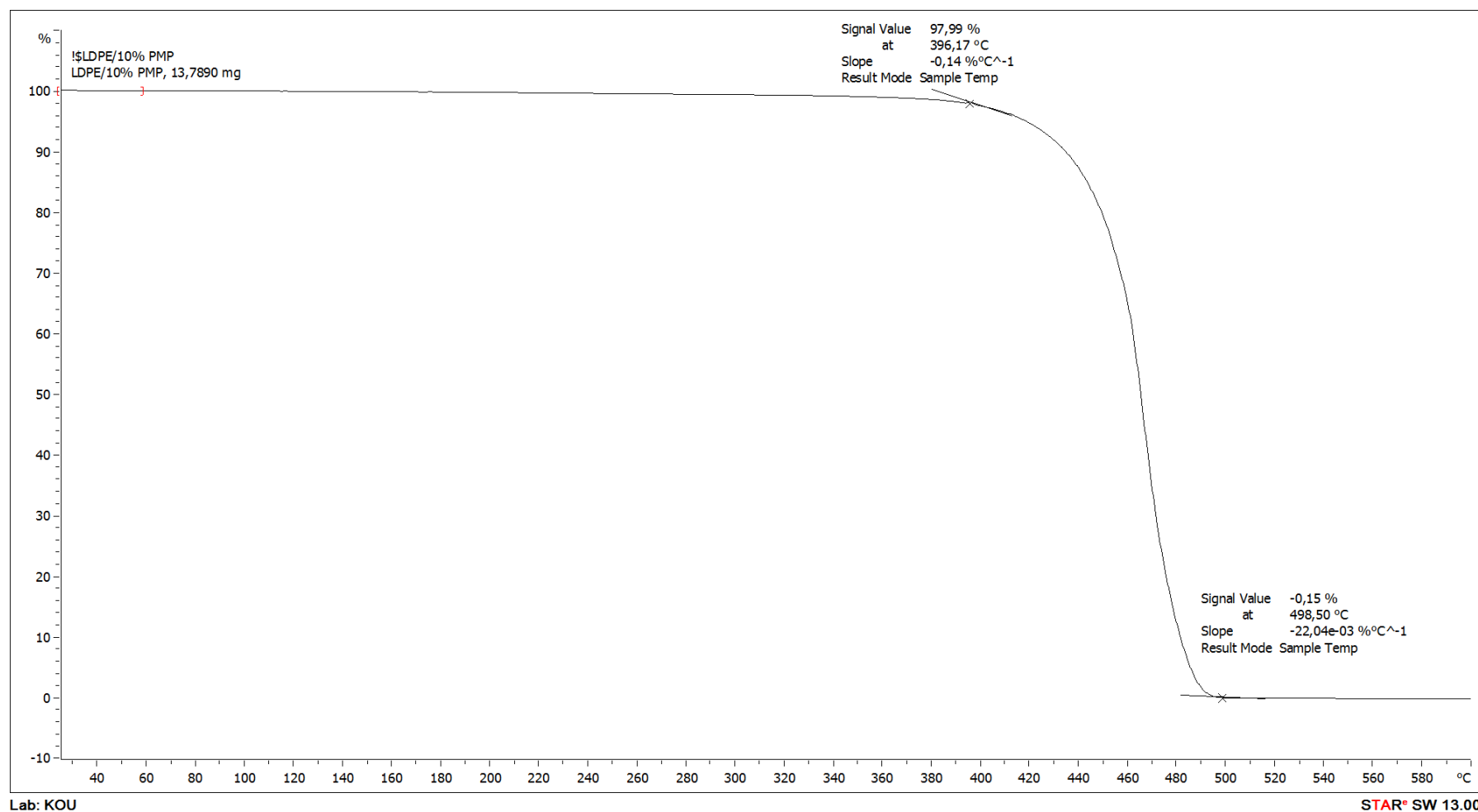


Figure A.3.2 : TGA thermogram of LDPE/10% PMP

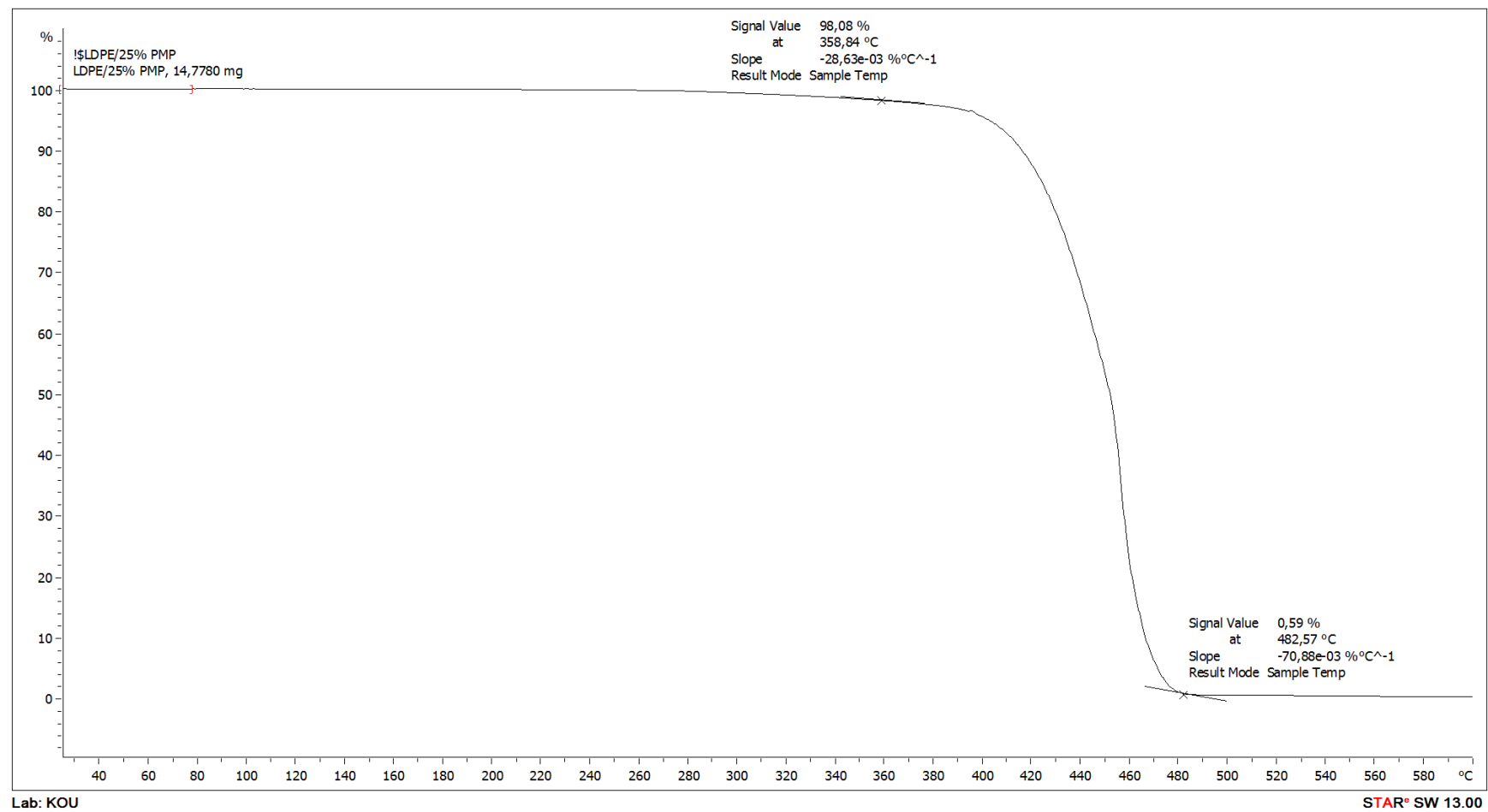


Figure A.3.3 : TGA thermogram of LDPE/25% PMP

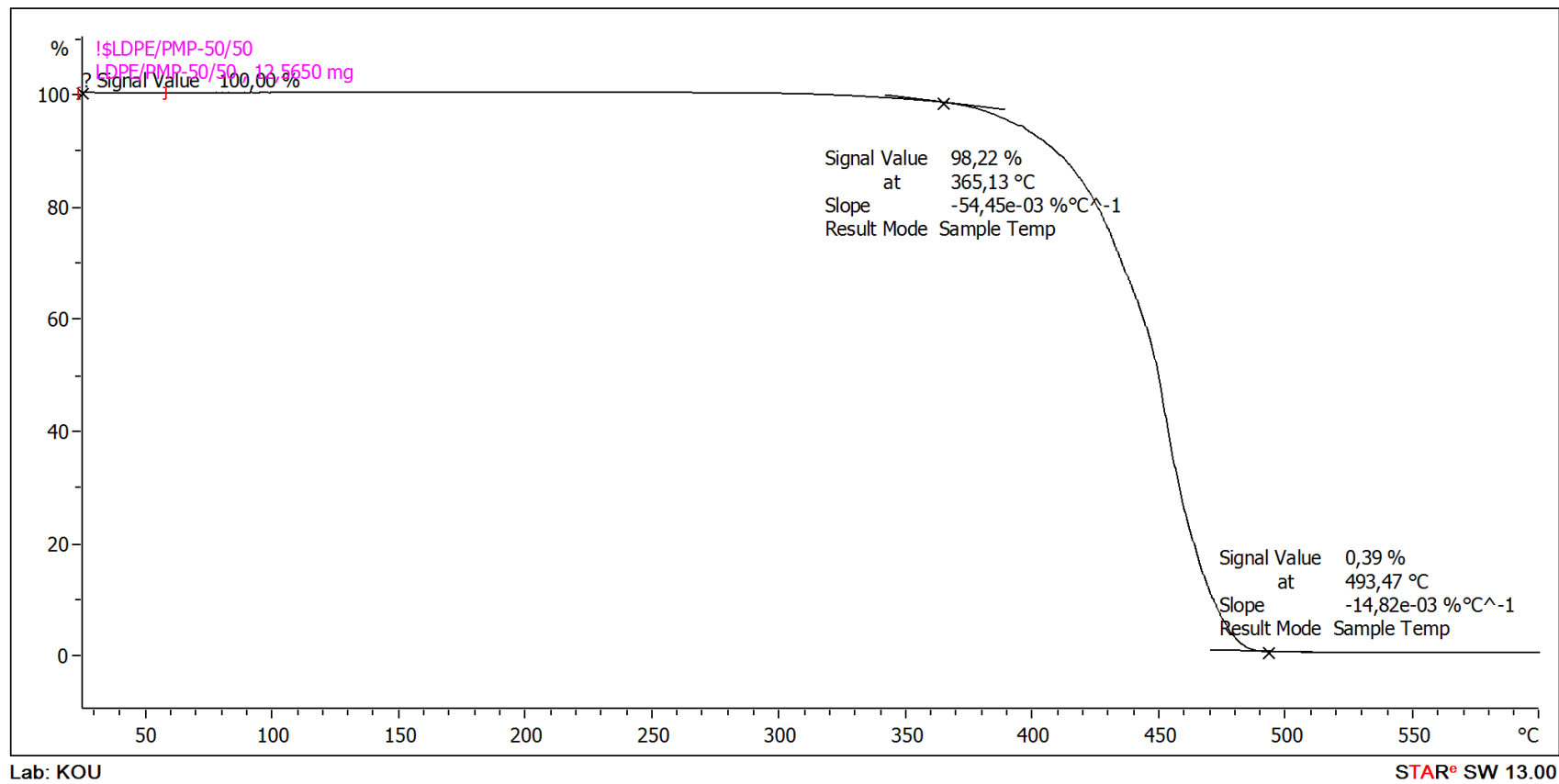


Figure A.3.4 : TGA thermogram of LDPE/50% PMP

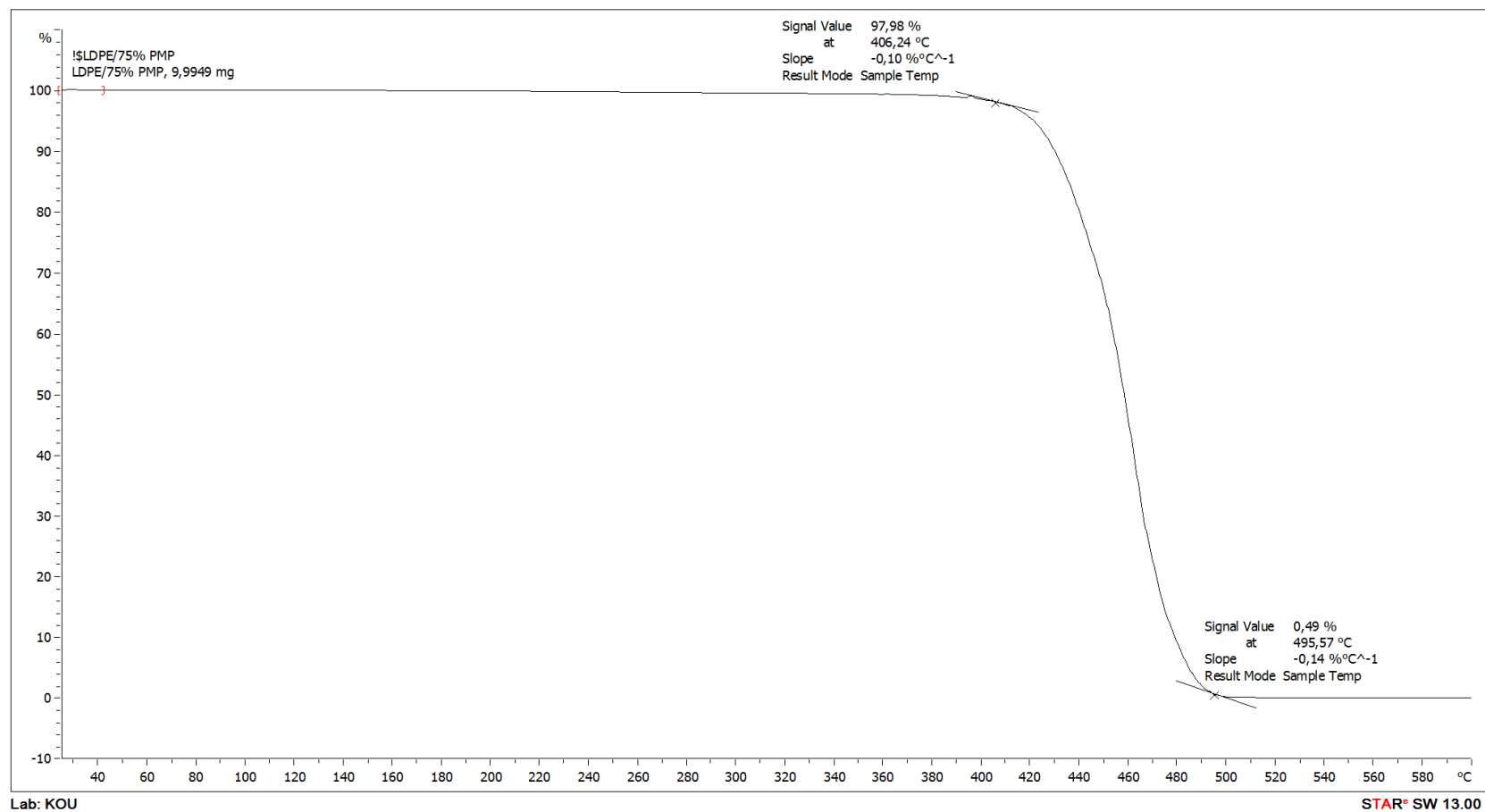


Figure A.3.5 : TGA thermogram of LDPE/75% PMP

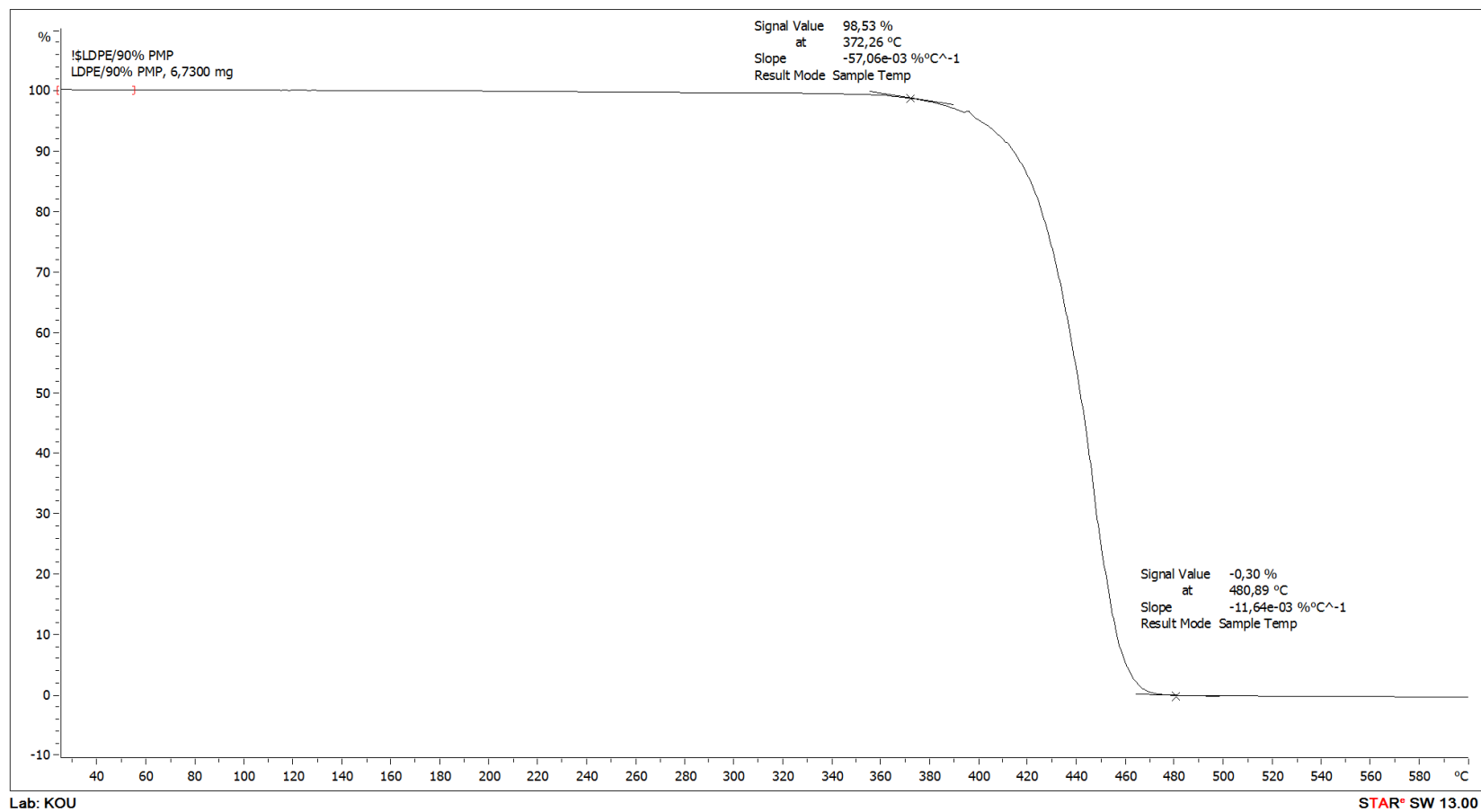


Figure A.3.6 : TGA thermogram of LDPE/90% PMP

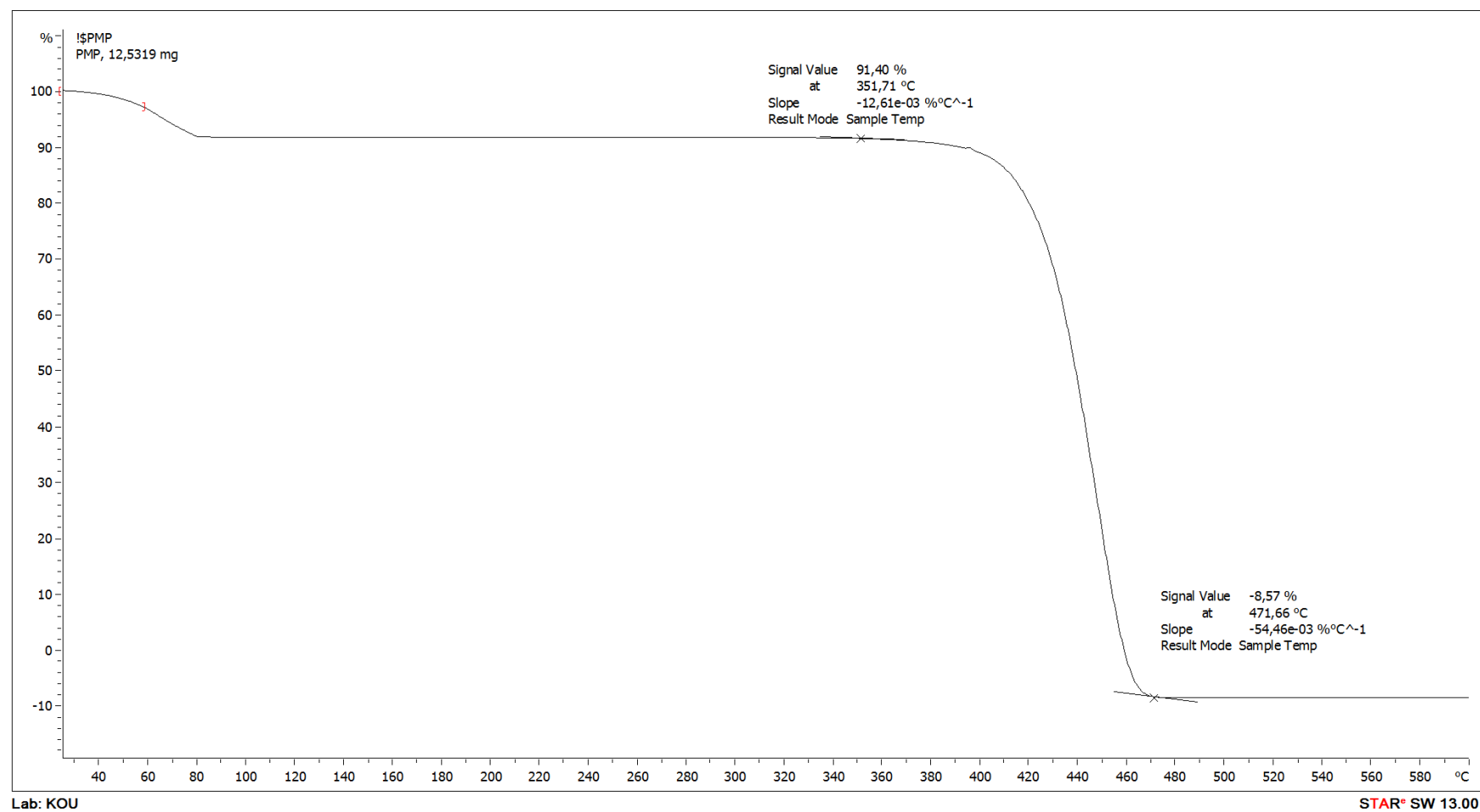


Figure A.3.7 : TGA thermogram PMP

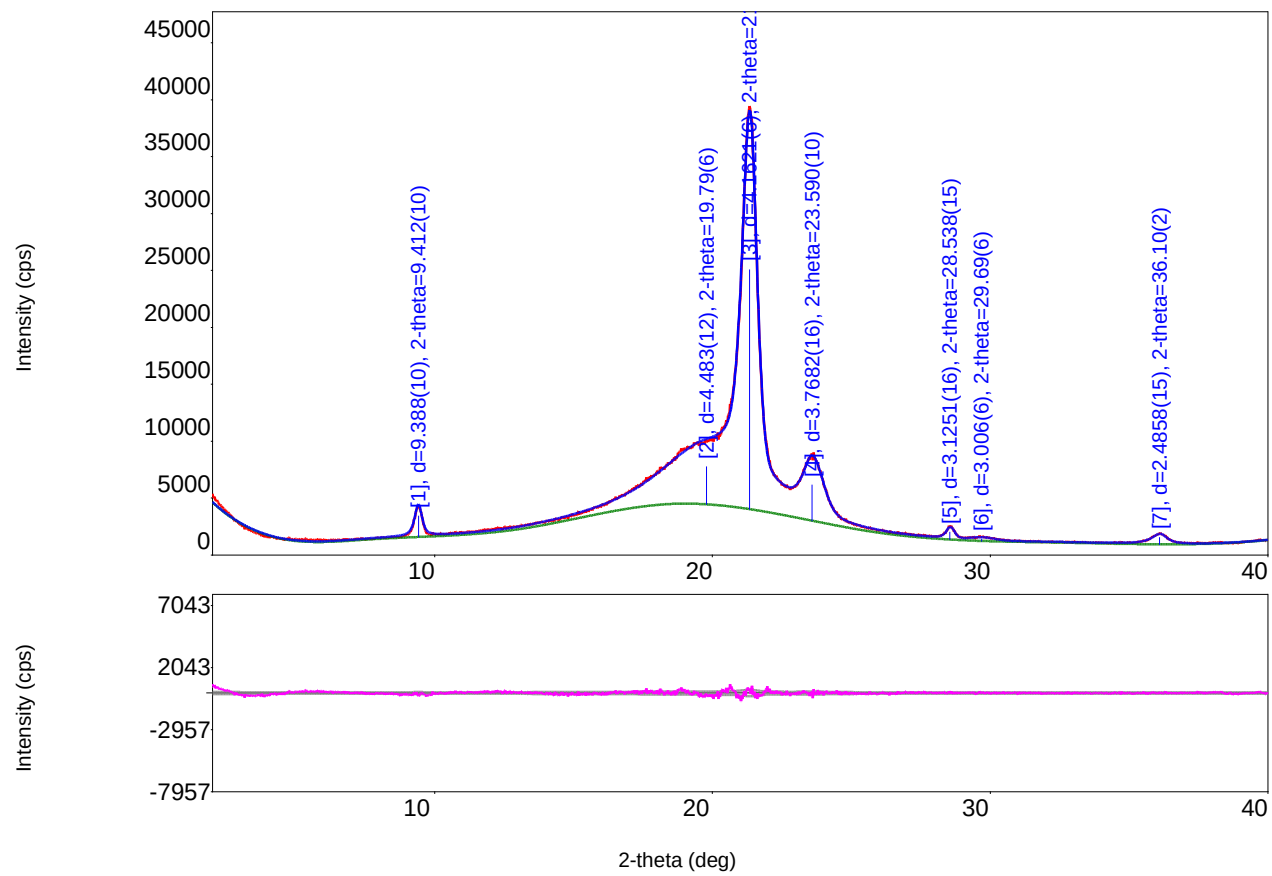


Figure A.4.1 : XRD diagrams of LDPE

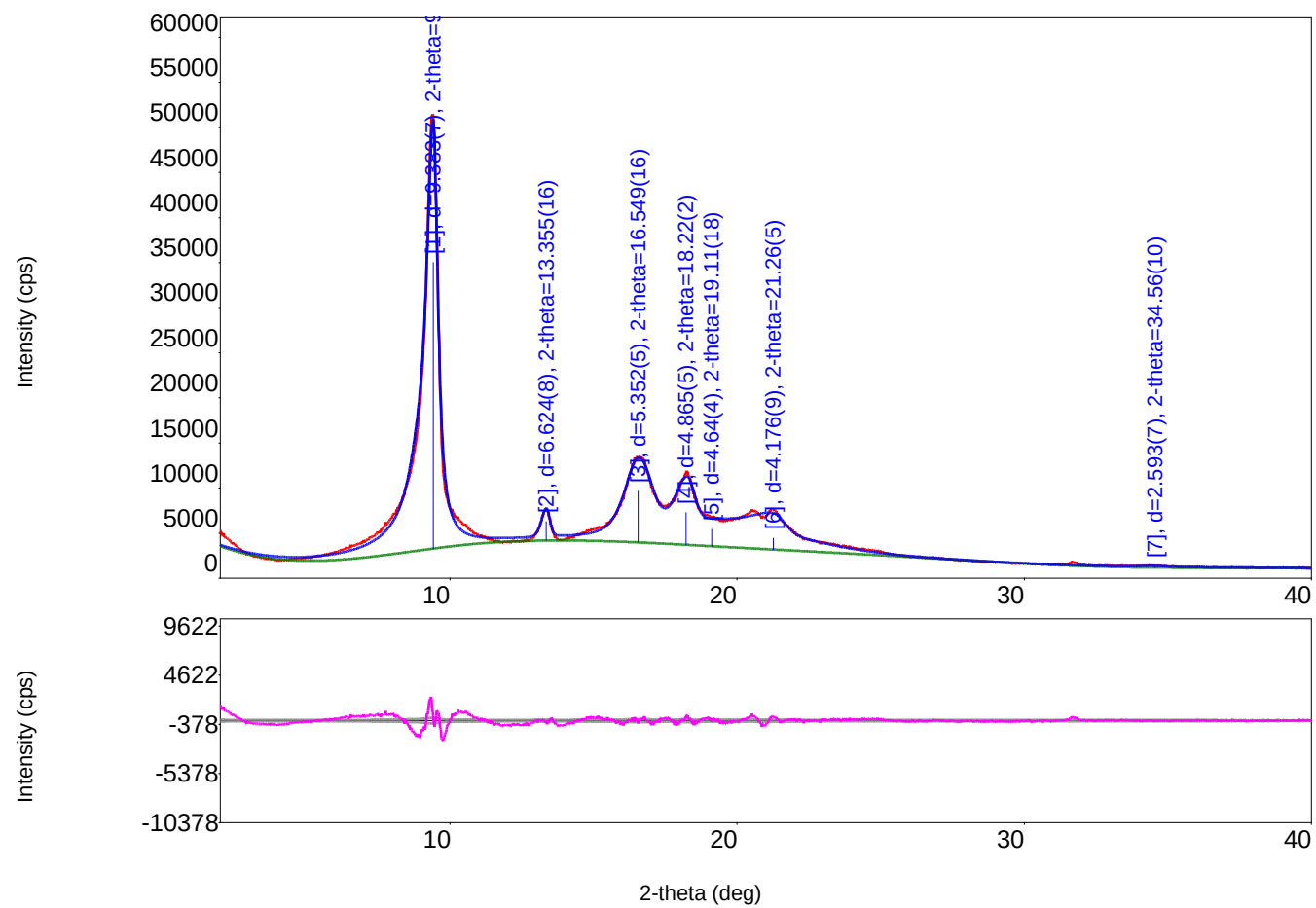


Figure A.4.2 : XRD diagrams of LDPE/25% PMP

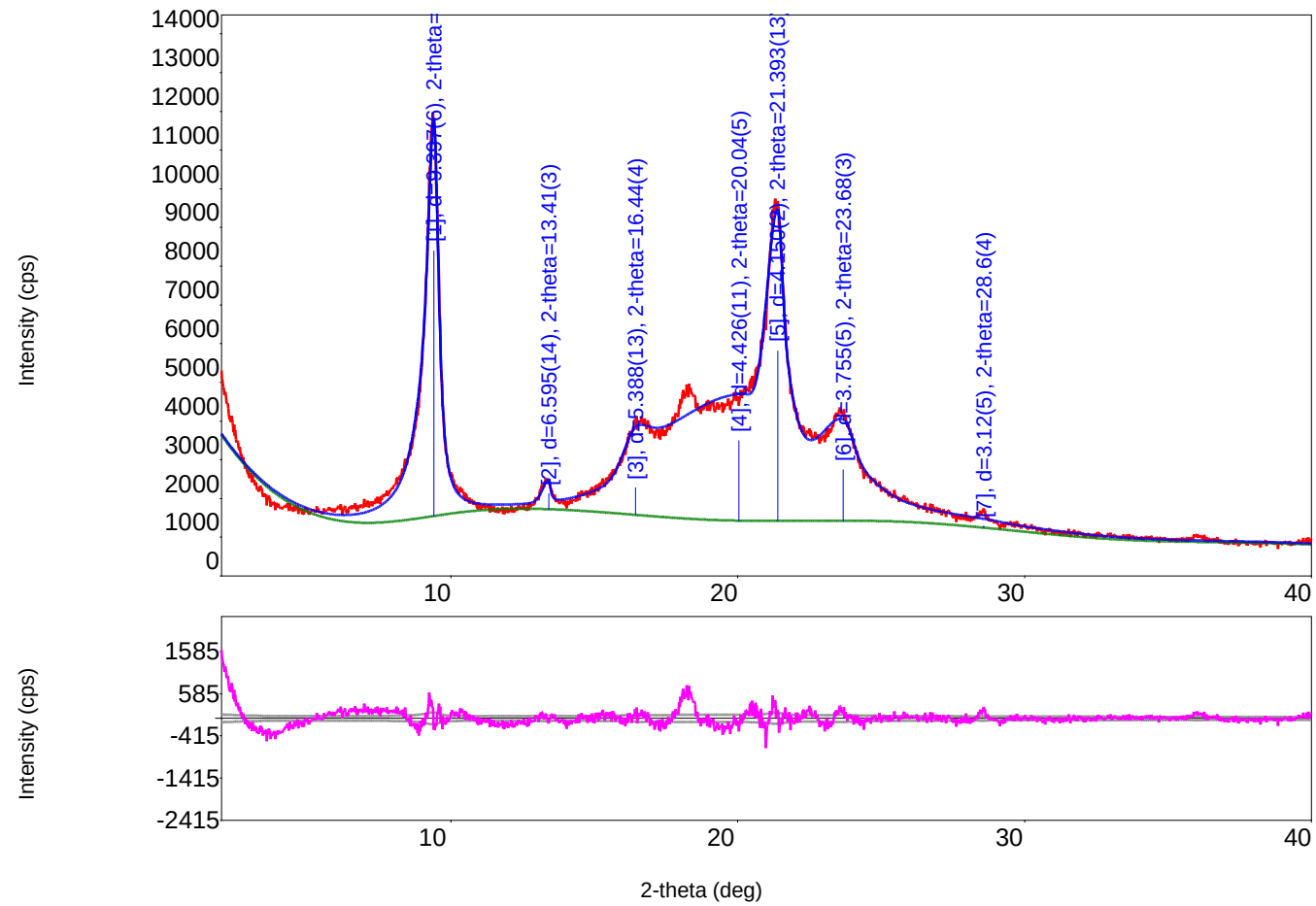


Figure A.4.3 : XRD diagrams of LDPE/50% PPMP

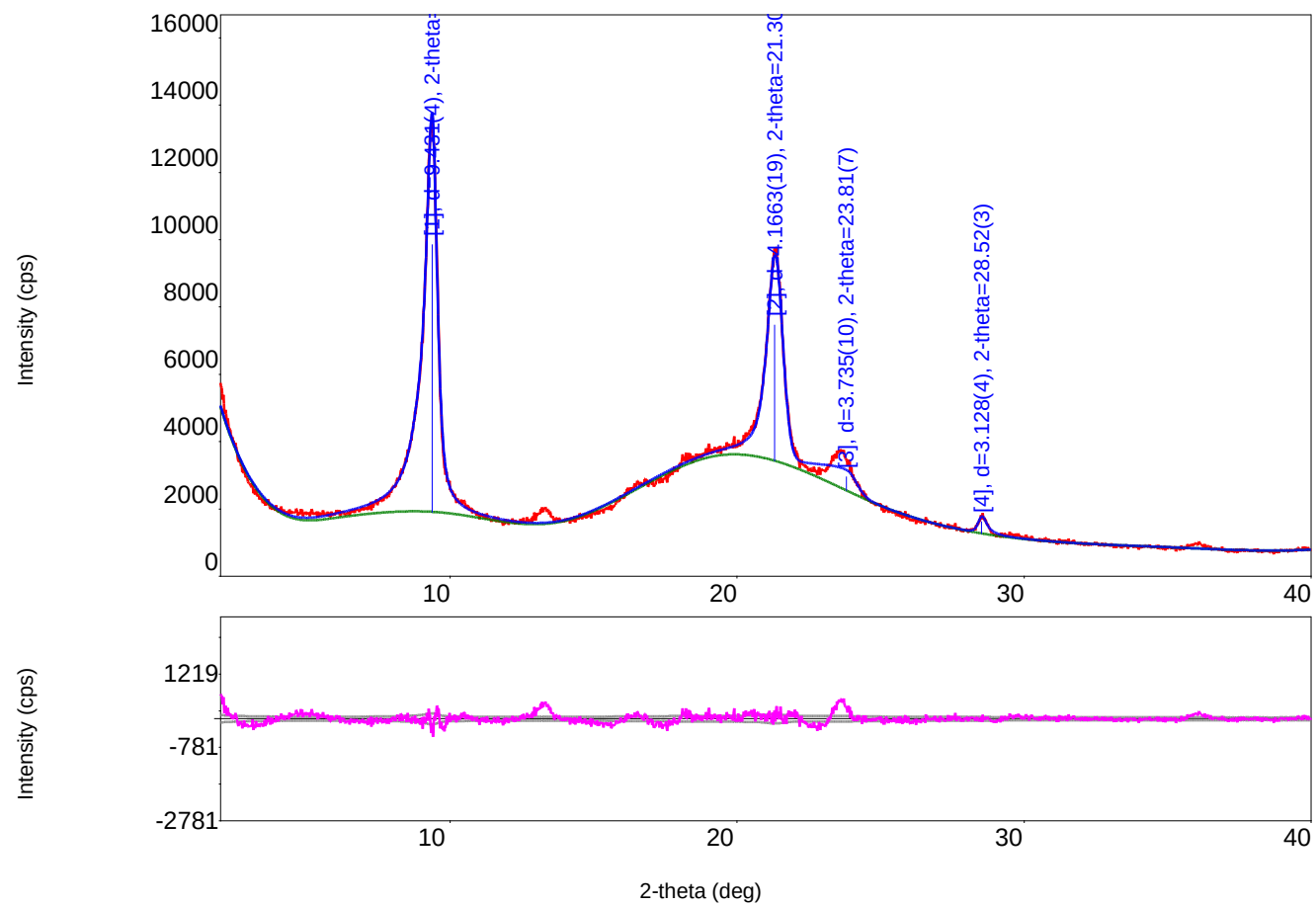


Figure A.4.4 : XRD diagrams of LDPE/75% PMP

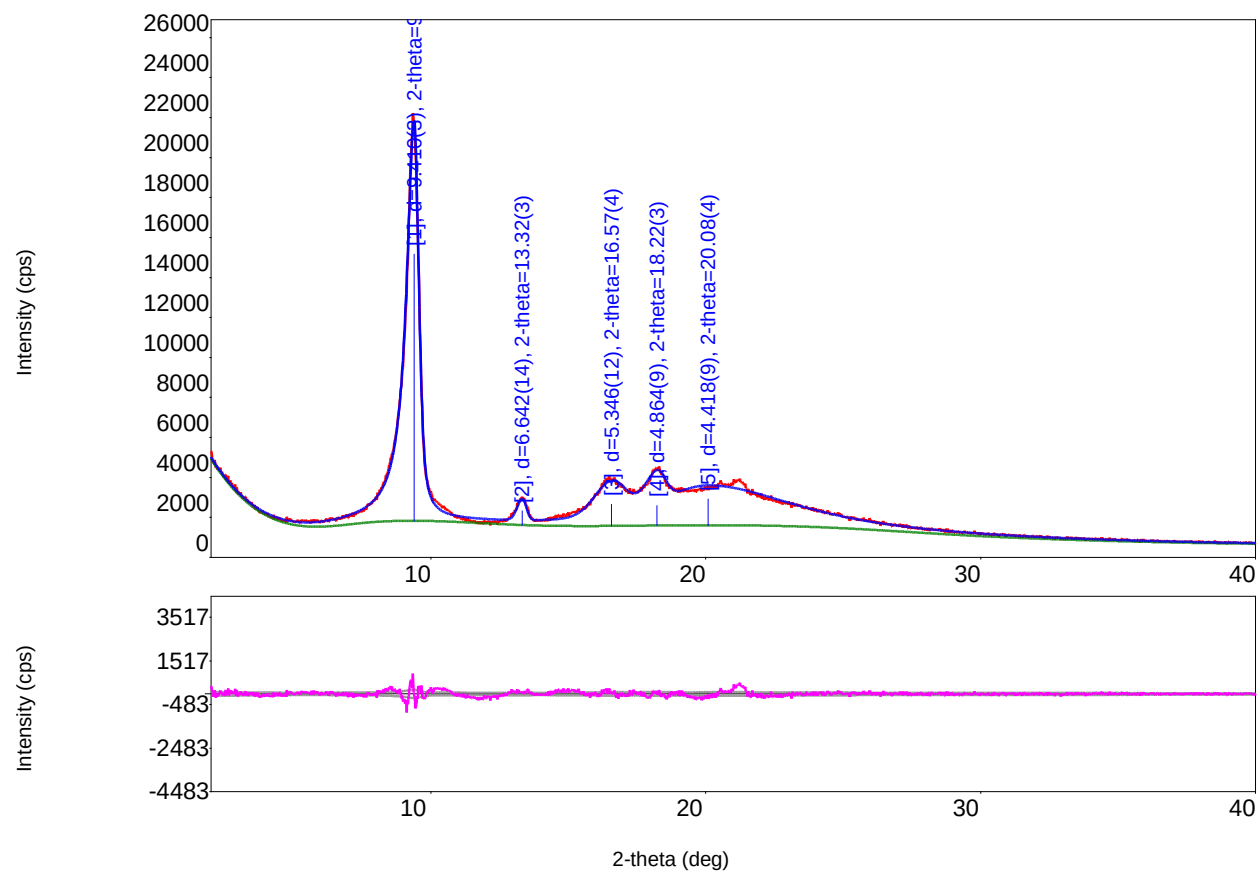


Figure A.4.5 : XRD diagrams of PMP



Figure A.5.1 : Shelf life analysis of bananas inside the 100% LDPE package sample

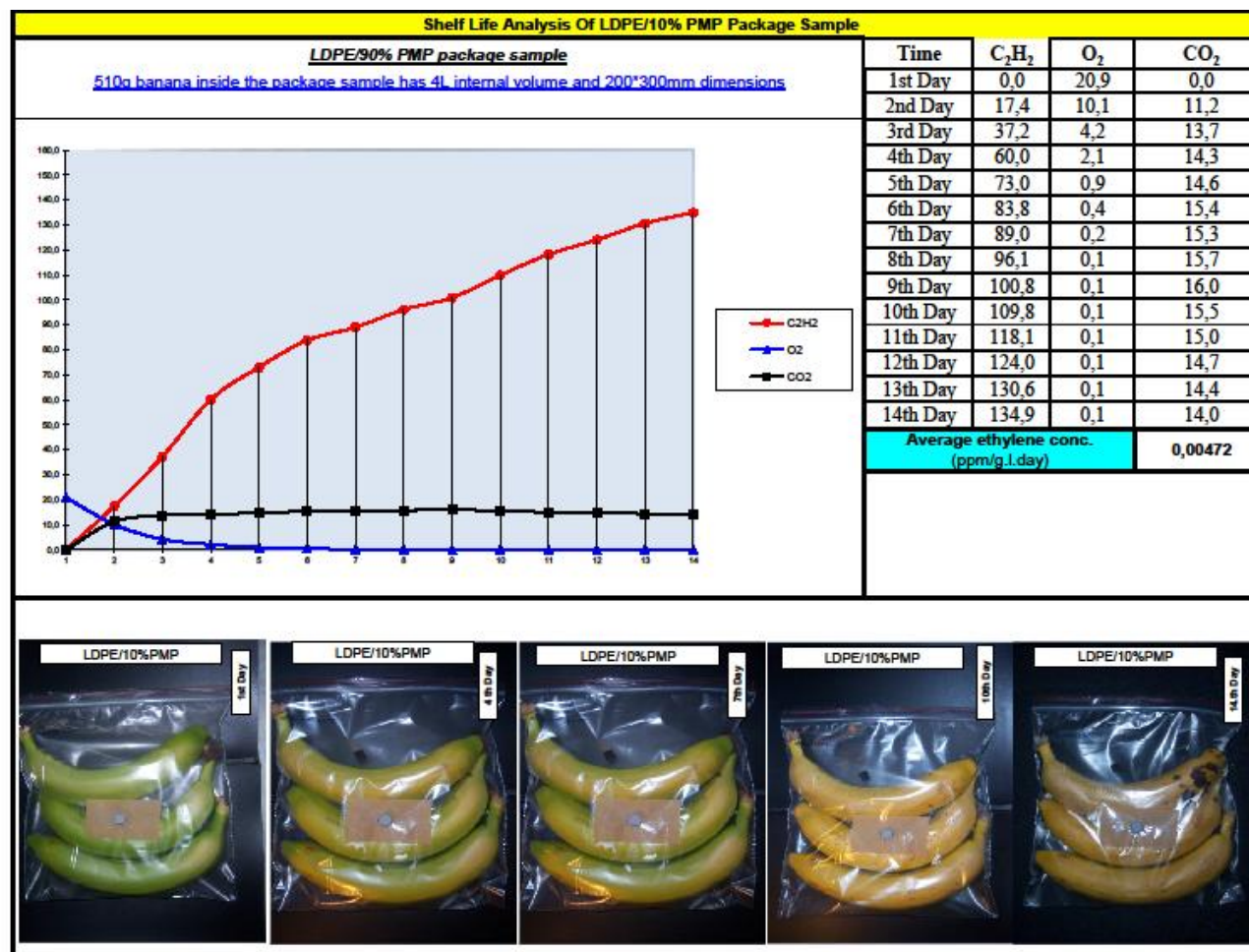


Figure A.5.2 : Shelf life analysis of bananas inside the LDPE/10% PMP package sample

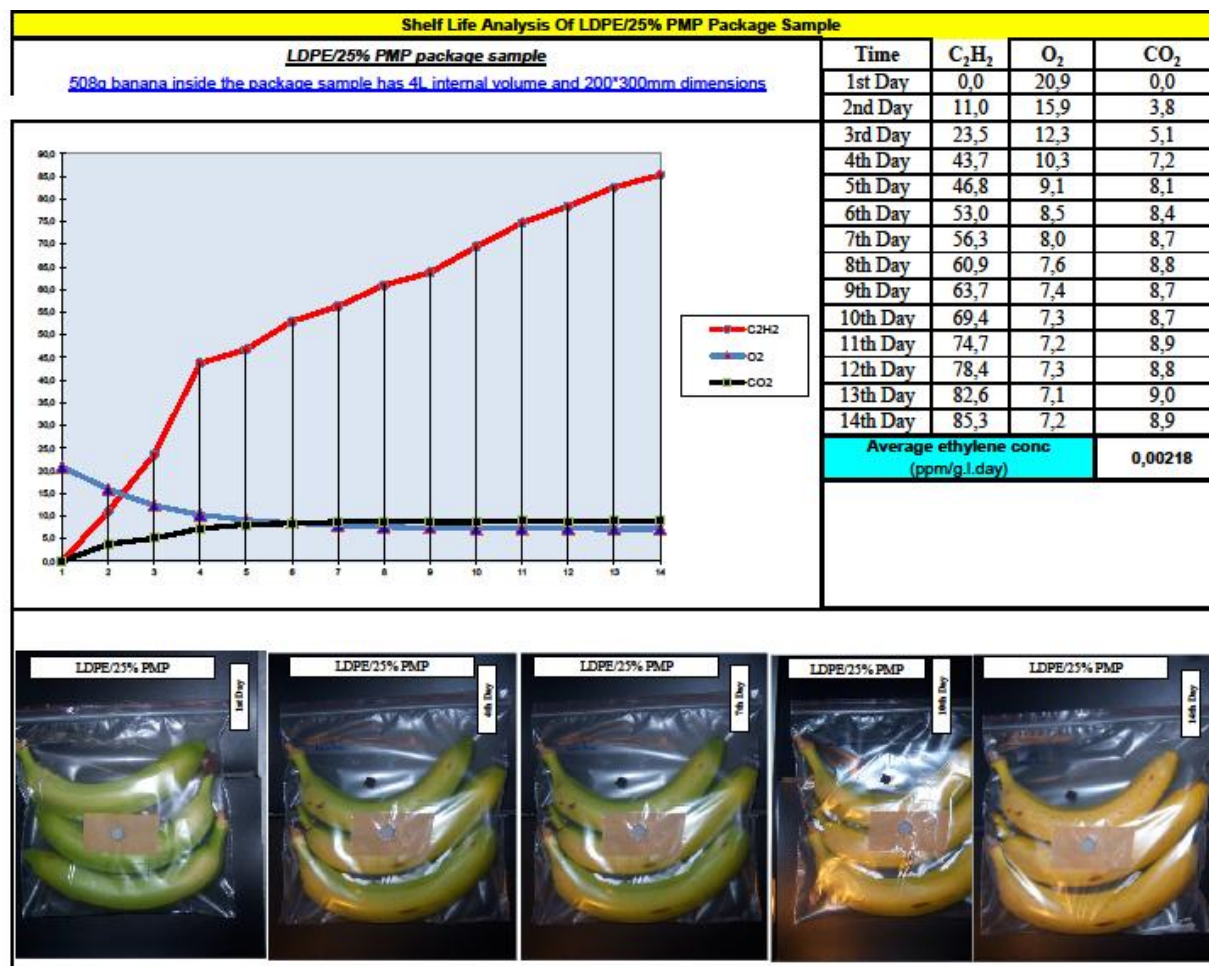


Figure A.5.3 : Shelf life analysis of bananas inside the LDPE/25% PMP package sample

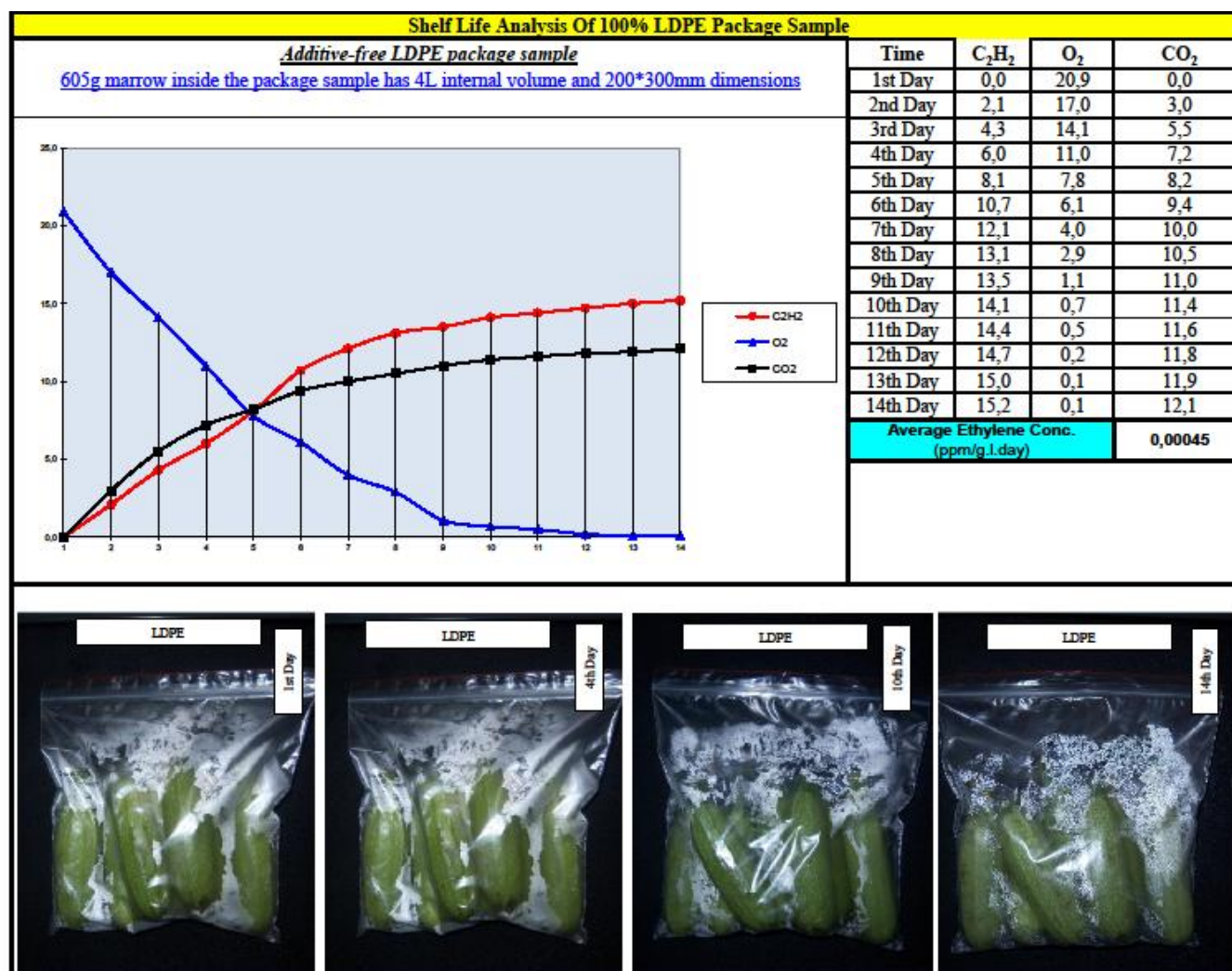


Figure A.6.1 : Shelf life analysis of marrows inside the 100% LDPE package sample

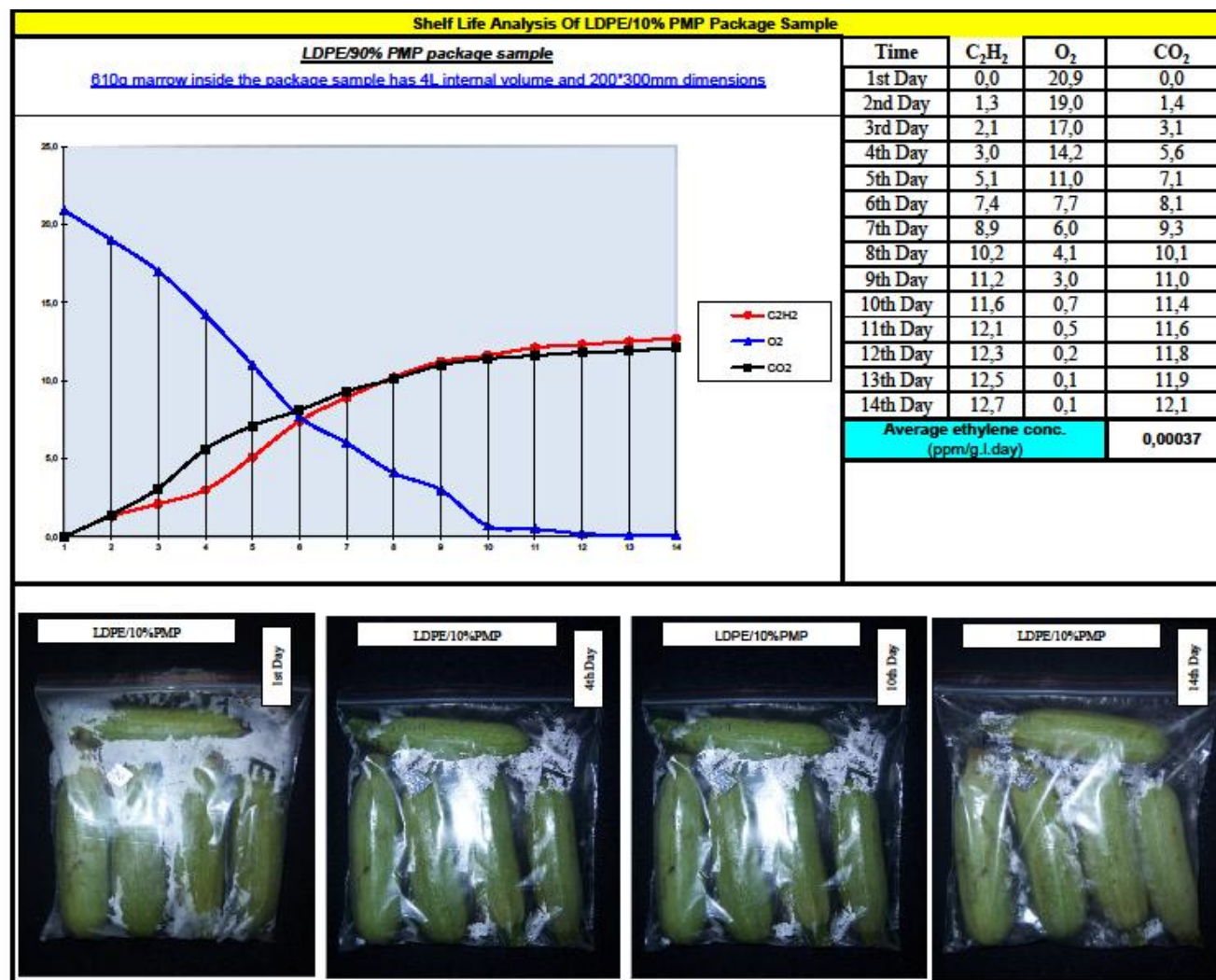


Figure A.6.2 : Shelf life analysis of marrows inside the LDPE/10% PMP package sample



Figure A.6.3 : Shelf life analysis of marrows inside the LDPE/25% PMP package sample

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