ISTANBUL TECHNICAL UNIVERSITY ★ GRADUATE SCHOOL OF SCIENCE ENGINEERING AND TECHNOLOGY

PRODUCTION OF MICROPOROUS POLYPROPYLENE BREATHABLE FILMS

M.Sc. THESIS

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Polymer Science and Technology Programme

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To my precious family,

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ABBREVIATIONS

PE : Polyethylene
PP : Polypropylene
MFR : Melt Flow Rate
TPU : Thermoplastic Polyurethane
PTFE : Polytetrafluoroethylene
LDPE : Low Density Polyethylene
LLDPE : Lineer Low Density Polyethylene
MDO : Machine Direction Orientation
PH1 : Pre Heating 1 (MDO Unit)
PH2 : Pre Heating 2 (MDO Unit)
SD1 : Slow Dimension 1 (MDO Unit)
FD1 : Fast Dimension 1 (MDO Unit)
A1 : Annealing 1 (MDO Unit)
A2 : Annealing 2 (MDO Unit)
C1 : Cooling 1 (MDO Unit)
C2 : Cooling 2 (MDO Unit)
WVTR : Water Vapor Transmission Rate
DSC : Differential Scanning Calorimetry
FTIR : Fourier Transform Infrared Spectroscopy
SEM : Scanning Electron Microscopy
GSM : Grams per Square Meter
C1 : Compound 1
C2 : Compound 2
BF1 : Breathable Film 1
BF2 : Breathable Film 2
BF3 : Breathable Film 3
BF4 : Breathable Film 4
MD : Machine Direction
CD : Cross Direction

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PRODUCTION OF MICROPOROUS POLYPROPYLENE BREATHABLE FILMS

SUMMARY

Polymeric structures that pass water vapor and air, but exhibit barrier properties against liquids are called breathable films. Breathable films, that find new uses in the direction of evolving and changing living standards, can be grouped under two main types; monolithic and microporous. In addition to monolithic structures that inherently breathe, microporous structures are obtained by the addition of inorganic fillers to the polyolefin matrix. Stretching this filler loaded polyolefin matrix creates the micro pores and achives the breathability. Microporous breathable films potentially capable of creating new markets because of their low cost and usefulness. They are widely used in many industries, especially hygienic products (baby diapers, single wraps, patient gowns), construction materials (roof insulation, wall insulation) and personal protective clothing.

A standard microporous polyolefin, - generally polyethylene-, mineral filler breathable film contains billions of micropores. The mineral fillers are active ingredients which give the film unique features enabling it to breathe through the network of micropores. The hydrophobic nature of the filler is a desirable feature as it will reduce water retention during production processes. Examples of the inorganic filler include calcium carbonate, talc, clay, kaolin, silica, magnesium carbonate, magnesium sulfate, calcium sulfate, aluminum hydroxide, zinc oxide, zeolite. The filling rate to the polyolefin matrix usually varies between 10-70%.

Breathable films are used in backsheets, for example as a backsheet component laminated to a nonwoven and/or other layers. They are used in many of today's personal care absorbent articles. Filled and stretched polyolefin films are making the diapers more comfortable to the wearer since they provide good water vapor transmission. With the using laminates of breathable films and nonwoven webs, the relative humidity and temperature within the personal care products can be reduced. The breathable films themselves provide vapor breathability and liquid barrier, but are typically not strong enough to be used alone. The nonwoven webs provide strength as well as fabric-like properties to the laminates.

To making a polymeric film vapor permeable, includes mixing a matrix polymer with the inorganic filler via double-screw compound extrusion process. The resulting mixture is using to produce monolayer or multilayer film via cast or blown extrusion process. Then, the film is heated and stretched, causing voids to form in the areas surrounding the filler particles via stretching unit.

The aim of this thesis is to use polypropylene matrix instead of the classicized polyethylene matrix used in the production of microporous breathable films. As the inorganic filler, surface-modified calcium carbonate is preferred. The use of polypropylene matrix in microporous film will ensure a more consistent structure since used laminates are generally made from polypropylene. This compliant construction is expected to reduce the use of glue and improve process difficulty such as reduce the differences of melting point of films and laminates in the lamination process. Moreover, it is one of today's needs to obtain films with high strength that will not be laminated and used as a single layer.

In the first step of the thesis study, polypropylene based two different compounds that contained 50% (C1) and 60% (C2) of surface modified calcium carbonate were prepared in a twin screw extruder. The motor speed was 600 rpm during the compounding process and the reverse temperature profile was prefered. In the second stage, the experimental design was planned for the samples obtained by the blown film extrusion method and the variable parameters were determined. In terms of experimental design, weight, width, and stretching ratio were accepted as constant parameters. The ratio of linear low density polyethylene to be used during the blown film extrusion process and the two prepared compounds (C1 and C2) were determined as variable parameters. In this direction, it was planned to obtain four film samples (BF1, BF2, BF3 and BF4) with 0% and 15% of linear low density polyethylene added to C1 and C2 compounds. At the last stage, the micropores were obtained by using the stretching unit to achive breathability. MDO (Machine Direction Orientation) unit was used as the stretching unit with the 1:4 stretching ratio. Temperatures of the preheating, stretching, annealing and cooling rollers in the MDO unit were determined in terms of material structure and kept constant throughout production.

In the study, a commercial polypropylene and polyethylene based compounds were characterized and compared with the prepared compounds, C1 and C2. The DSC, FTIR and ash analysis were investigated according to the material structure of the compounds. Increasing the amount of calcium carbonate in the compound has been found to increase the melt flow rate and density. Linear low density polyethylene can be added to improve the processability of the polypropylene based compounds.

The obtained film samples were analyzed with the DSC, FTIR, ash tester, melt flow rate tester and density tester. The thermal characteristics and the IR absorption peaks of the film samples were determined. As a result of the ash analysis, the ratio of inorganic filler in the film matrix, namely calcium carbonate, was determined. The effect of the ratio of calcium carbonate contained in the film samples on the melt flow rate and density values was observed by analysis.

A polyethylene based commercial microporous film was analyzed comparatively with BF1, BF2 and BF4 film samples for mechanical properties such as tensile strength at break, tensile strength, elastic modulus and tear strength. As the polypropylene is more rigid, it has been found that the tensile strengths and elastic modulus of the film samples are higher than commercial microporous polyethylene breathable film sample. Tensile elongation at break of the film samples are lower than commercial microporous polyethylene breathable film sample. It has been found that the tear strength values are rather low compared to the commercial microporous polyethylene breathable film sample. When the obtained film samples are compared within themselves, it is seen that the strength values change with the calcium carbonate ratio in the film matrix. Increase in the amount of calcium carbonate results in a decrease in strength values.

The breathability (water vapor permeability), one of the most important parameters, was evaluated comparatively by using the MOCON analysis method. The water vapor permeability can be basically related to the material structure, the amount of calcium

carbonate and the rate of stretching in the stretching unit. When the obtained film samples are compared within itself, it was found that water vapor permeability was proportional to the calcium carbonate ratio in the film matrix. BF1 and BF4 film specimens are particularly acceptable when compared with the commercial microporous polyethylene breathable film sample in terms of water vapor permeability.

Within the scope of the thesis study, it is aimed to obtain micropores. For this reason, by using SEM analysis, surface morphology of the obtained film samples was examined and random micropores were observed at different sizes. It has been determined that the size of the micro pores in the vertical level is higher than the horizontal level. This is due to the fact that the vertical level exposed to more stress. It was seen that the stretching direction is vertical.

The resulting microporous polypropylene breathable films can be used in the hygiene sector in terms of water vapor permeability values. More rigid materials were obtained compared to polyethylene based microporous film. It is known that the nature of the polypropylene structure is coming from the propylene monomers is more rigid than the polyethylene.

MİKRO GÖZENEKLİ POLİPROPİLEN NEFES ALABİLEN FİLM ÜRETİMİ

ÖZET

Su buharı ve havayı geçiren ancak sıvılara karşı bariyer özellik gösteren polimerik yapılar nefes alabilen filmler olarak adlandırılır. Nefes alabilen filmler günümüzde oldukça geniş kullanım alanına sahiptir. Gelişen ve değişen yaşam standartları doğrultusunda yeni kullanım alanları bulan nefes alan filmler, monolitik ve mikro gözenekli olmak üzere temel olarak iki tür altında toplanabilir. Doğası gereği kendiliğinden nefes alan monolitik yapıların yanında poliolefin matrisine inorganik dolguların eklenmesi ve filmin gerdirilmesi ile elde edilen mikro gözenekli yapılar, ucuz ve kullanışlı olması nedeniyle kendisine yeni pazarlar oluşturabilecek potansiyeldedir. Nefes alabilen filmler başta hijyenik ürünler (bebek bezleri, kadın bağları, hasta bezleri), inşaat malzemeleri (çatı izolasyonu, duvar izolasyonu) ve kişisel koruyucu kıyafetler olmak üzere birçok endüstri dalında yaygın bir şekilde kullanılmaktadır.

Mikro gözenekli nefes alan filmler genellikle poliolefin matrisine inorganik dolguların eklenmesi ve elde edilen filmin gerdirilmesi ile yapıya mikro gözeneklerin kazandırılması sonucu elde edilir. Poliolefin matrisine dolgu yüklemesi oranı genellikle %10-70 aralığında değişir. Mikro gözenekli nefes alan film üretiminde yaygın olarak polietilen matrisi kullanılmaktadır. Dolgu olarak ise düşük elastikliğe ve poliolefinler ile düşük afiniteye sahip inorganikler kullanılabilir. Söz konusu dolguların hidrofobik olması, üretim prosesleri sırasında su tutmasını azaltacağı için istenilen bir özelliktir. İnorganik dolgu olarak kalsiyum karbonat, talk, kil, kaolin, silika, magnezyum karbonat, magnezyum sülfat, kalsiyum sülfat, alüminyum hidroksit, çinko oksit, zeolit, mika vb. yapılar kullanılabilir.

Kişisel bakım ürünleri içerisinde kendisine kullanım yeri bulan mikro gözenekli nefes alan filmler kumaş ve/veya başka katmanlarla lamine edilerek alt tabaka olarak kullanılmaktadır. Bebek bezi bu duruma örnek verilebilir. Dolgu yüklenmiş ve gerdirilmiş film su buharı geçirgenliği sayesinde bez kullanıcılarına konfor sağlar ve lamine edilmiş hali ile birlikte bebek bezi içerisinde bağıl nem ve sıcaklık dengesi kurmaya yardımcı olur.

Nefes alabilen film tek başına kullanıldığında sıvılara karşı bariyer özellik gösterirken su buharı geçirgenliği sağlayabilecek özelliğe sahiptir fakat tek başına kullanılacak kadar sağlam değildir. Bu nedenle kumaş ve/veya başka katmanlarla lamine edilerek hem kumaş benzeri özellikler hem de sağlamlık elde edilir. Lamine katman olarak polipropilen bazlı kumaşların kullanımı yaygındır. Polietilen matrisli mikro gözenekli nefes alabilen filmlerin ısı ile laminasyon prosesine tabi tutularak polipropilen bazlı kumaşlarla birleştirilmesi esnasında klasik yapıştırıcı, tutkal teknikleri kullanılır.

Mikro gözenekli nefes alan filmlerin üretimi bir dizi prosesten oluşmaktadır. Öncelikle poliolefin matrisine dolgu yüklemesi, çift vidalı ekstrüderde karışım haline getirilerek

(compounding) yapılır. Elde edilen karışım, dökme (cast) ekstrüzyon veya şişirme (blown) ekstrüzyon yöntemi kullanılarak film haline getirilir. Son olarak filme mikro gözeneklerin kazandırılması için gerdirme tekniği uygulanır.

Tez çalışması kapsamında mikro gözenekli nefes alan filmlerin üretiminde kullanılan klasikleşmiş polietilen matrisi yerine polipropilen kullanımı amaçlanmıştır. İnorganik dolgu olarak ise yüzeyi modifiye edilmiş kalsiyum karbonat tercih edilmiştir. Polipropilen kumaş ile yapılan laminasyon prosesinde, polietilen yerine polipropilen matrisli mikro gözenekli film kullanımı daha uyumlu bir yapı elde edilmesini sağlayacaktır. Bu uyumlu yapının, laminasyon prosesindeki tutkal kullanımını azaltması ve proses zorluğunu iyileştirmesi beklenir. Ayrıca lamine olmayacak ve tek kat olarak kullanılacak yapılar için de mukavemeti yüksek filmlerin elde edilmesi günümüz ihtiyaçlarından biridir.

Tez çalışmasının birinci aşamasında %50 (C1) ve %60 (C2) oranlarında yüzeyi modifiye edilmiş kalsiyum karbonat içeren polipropilen matrisli iki farklı bileşik çift vidalı ekstrüderde hazırlanmıştır. Ters sıcaklık profili ile 600 rpm hızında çalışılmış ve 3 mm boyutunda granüller elde edilmiştir. İkinci aşamada ise şişirme film ekstrüzyonu yöntemi ile elde edilecek örnekler için deneysel tasarım kurgulanmış ve değişken parametreler belirlenmiştir. Deneysel tasarım doğrultusunda gramaj, çekim eni ve gerdirme oranı sabit parametreler olarak kabul edilmiştir. Hazırlanan iki farklı bileşik (C1 ve C2) ve şişirme film ekstrüzyon prosesi sırasında kullanılacak olan lineer alçak yoğunluklu polietilen oranı değişken parametreler olarak belirlenmiştir. Bu doğrultuda, C1 ve C2 bileşiklerine %0 ve %15 oranında lineer alçak yoğunluklu polietilen katılması ile BF1, BF2, BF3 ve BF4 kodlu dört adet film örneği elde edilmesi planlanmıştır. Son aşamada ise nefes alabilirlik özelliği kazandırabilmek için gerdirme ünitesi kullanılarak mikro gözenekler elde edilmiştir. Gerdirme ünitesi olarak MDO (Machine Direction Orientation) ünitesi kullanılmış ve 1:4 oranında gerdirme yapılmıştır. MDO ünitesinde yer alan ön ısıtma, gerdirme, tavlama ve soğutma merdanelerinin sıcaklıkları malzeme yapısı doğrultusunda belirlenmiş ve üretim boyunca sabit tutulmuştur. Üretilmesi hedeflenen dört adet film örneğinin üçü malzeme yapısı doğrultusunda belirlenen kafa-vida sıcaklık profili ile 16 GSM olarak elde edilmiştir.

Çalışma kapsamında polipropilen ve polietilen matrisli bileşikler temin edilmiş ve C1 ve C2 bileşikleri ile karşılaştırmalı olarak karakterize edilmiştir. DSC, FTIR ve kül testi uygulanan bileşiklerin malzeme yapısı analizlerle desteklenerek açıklanmıştır. Bileşik içerisindeki kalsiyum karbonat miktarının artması ile erime akış hızının ve yoğunluğun arttığı tespit edilmiştir. Polipropilen matrisli bileşiklerin içerisine işlenebilirliği arttırmak ve son ürün olarak elde edilecek mikro gözenekli filmin nefes alabilirliğini dengelemek için lineer alçak yoğunluklu polietilen eklenebileceği görülmüştür.

Elde edilen film örnekleri DSC, FTIR, kül testi, erime akış hızı ve yoğunluk gibi yapı analizlerine tabi tutulmuştur. Film örneklerinin termal karakteristikleri ve içerdikleri yapıların absorpsiyon pikleri tespit edilmiştir. Kül testi sonucunda ise film matrisinde yer alan inorganik dolgu, yani kalsiyum karbonat oranı tespit edilmiştir. Film örneklerinin içerdikleri kalsiyum karbonat oranının erime akış hızı ve yoğunluk değerleri üzerine olan etkisi analizlerle gözlenmiştir.

Polietilen matrisli bir mikro gözenekli film ise BF1, BF2 ve BF4 film örnekleri ile kopma uzaması, kopma kuvveti, elastik modülüs ve yırtılma direnci gibi mekanik özellikler açısından karşılaştırmalı olarak analiz edilmiştir. Polipropilenin daha rijit olmasından dolayı, tez çalışması kapsamında elde edilen film örneklerinin kopma kuvvetlerinin ve elastik modülüslerinin polietilen matrisli film örneğine göre daha yüksek olduğu kopma uzamalarının ise daha düşük olduğu görülmüştür. Yırtılma direnci değerlerinin ise polietilen matrisli film örneğine göre oldukça düşük seyrettiği tespit edilmiştir. Elde edilen film örnekleri kendi içerisinde kıyaslandığında ise mukavemet değerlerinin film matrisi içerisindeki kalsiyum karbonat oranı ile değiştiği görülmektedir. Kalsiyum karbonat miktarının artması ile mukavemet değerlerinde düşüş görülmektedir.

En önemli parametrelerden biri olan nefes alabilirlik (su buharı geçirgenliği) ise MOCON analiz yöntemi kullanılarak karşılaştırmalı olarak değerlendirilmiştir. Su buharı geçirgenliği temel olarak malzeme yapısı, kalsiyum karbonat miktarı ve gerdirme ünitesindeki gerdirme oranı ile ilişkilendirilebilir. Elde edilen film örnekleri kendi içerisinde kıyaslandığında su buharı geçirgenliğinin film matrisindeki kalsiyum karbonat oranı ile orantılı olduğu görülmüştür. Polietilen matrisli film örneği ile su buharı geçirgenliği açısından kıyaslandığında özellikle BF1 ve BF4 film örneklerinin kabul edilebilir olduğu görülmektedir.

Tez çalışması kapsamında mikro gözeneklerin elde edilmesi amaçlanmıştır. Bu nedenle taramalı elektron mikroskobu kullanılarak, elde edilen film örneklerinin yüzey morfolojisi incelenmiş ve farklı çaplarda rastgele mikro gözeneklerin oluştuğu görülmüştür. Dikey düzlemde meydana gelen mikro gözeneklerin çaplarının yatay düzleme göre daha yüksek olduğu belirlenmiştir. Bu durum, gerdirme yönünün ve daha fazla strese maruz kalan düzlemin dikey yön olduğunu göstermektedir.

Hijyen sektöründe kullanımı hedeflenen polipropilen matrisli mikro gözenekli nefes alan filmlerin su buharı geçirgenliği değerleri açısından pazara hitap edebileceği görülmüştür. Polietilen matrisli mikro gözenekli nefes alan filmlere göre daha mukavim malzemeler elde edilmiştir.

1. INTRODUCTION

All living organisms including plants and animals require a mechanism to breathe gases such as oxygen or carbon dioxide, in the fundamental habitat. Inhaling and exhaling create the roots for life. Basing on the fact that all the respiratory mechanisms achieve breathability, they may differ from organism to organism [1].

Breathability has various descriptions, but the core principle remains the same: the material must be permeable enough to permit air particles and moisture vapor through. Breathability in polymer films is generally evaluated by moisture vapor transmission rate (MVTR) of the material, in other words, water vapor transmission rate (WVTR), and often linked directly with the ability of the film to enable the passage of moisture vapor. Using industrial equipment, it is possible to plan and produce breathable films at high speed for many industrial applications where air and moisture breathability is demanded such as disposable hygiene items, protective apparels in health care or building construction sectors [2, 3].

Several applications of breathable films are expected to produce a film appearance to provide visual evidence for the manufacturer and consumers that the products are made of breathable films compared to those made from non-breathable films [4].

A standard microporous polyolefin, generally polyethylene,-mineral filler breathable film contains billions of micropores which of many are linked. In this particular case, the mineral fillers, especially calcium carbonate, are active ingredients which give the film unique features enabling it to breathe through the network of micropores [3,5].

Besides the cost-effectiveness of the formulations and methods of producing these polyolefin-mineral filler compositions, monolithic nonporous films are also present which have molecular passages with cross-sectional sizes obtained by a polymerization procedure. The raw materials of these quintessentially breathable films are remarkably overpriced contrary to renowned and broadly applied polyolefins namely polyethylene, polypropylene and their copolymers [3, 6].

In general, the ratio of mineral filler in the polyolefin-mineral filler compound is approximately 10— 70% according to the film weight. After the compound is extruded as a “precursory” non-porous film, the precursor film is stretched whether in-line or in an auxiliary procedure, in order to produce a microporous film enabling breathability for air and moisture vapor. It can be produced with blown or cast extrusion [7, 8].

As the plastic resin is melted at the beginning of the extrusion process, tiny particles of mineral filler are blended in with the melted resin to form a filled film. The last step to create breathability in a film is creating thousands of microscopic pores connecting to each other to create a tortuous passage within the material. Permitting moisture vapor to pass, this tortuous passage is so small that a water molecule can not fit through. Hence, the breathability features can be formed in a variety of techniques such as machine direction orientation (MDO), tentering, or incremental stretching [2].

Since the polyolefin-mineral filler breathable films have enhanced features along with their lesser cost, Japan has been already using to manufacture hygienic products, and latterly Europe countries have also begun to use it as well as the US. Microporous and films with various utilizations can be observed in our everyday environments. The methods and products are now industrially verified and they are surely more cost-effective against other competitors [5].

Microporous breathable structures are so comparably low-priced to manufacture, yet yield so superior performance that they have become very successful. For producing more cost-effective products that are customizable by means of high-speed manufacturing processes and unique material compositions to match specific applications, microporous film technology will proceed to develop in the coming years [2].

Microporous films available in the industry are generally made of polyethylene. The film market requires polypropylene resins which can provide a specific combination of film properties: a soft feel polypropylene microporous breathable film with high tear and impact strengths.

The aim of this study is to produce cost-effective microporous breathable films by using polypropylene-mineral filler blend. Calcium carbonate will be employed as a mineral filler since it is cheap and has a wide range of use. In the context of this thesis, polypropylene and calcium carbonate will be blended and then will be fed to the extruder to get a precursor film. Afterwards, in order to obtain breathability, stretching technique will be applied to film.

To be more precise, this thesis is focused on filled polypropylene microporous breathable films with an increased WVTR and mechanical properties in order to be used in hygiene industry.

2. THEORETICAL PART

2.1 Breathable Films

The historical perspective shows that microporous film, as it is today, was formulated for the hygiene industry and especially for back sheet diaper films, in Japan in 1983. Against the perforated or standard back sheet films, the Japanese market was eager to purchase films of higher quality despite the higher expense. Then, years later, the microporous films which had been first formulated in the United States also produced in Europe.

In healthcare both for infants and adults, the microporous films quickly adapted to be utilized in a vast majority of the product lines. And furthermore, a large number of customers began to prefer the high-quality hygienic protection products offered on the market, those which are based on microporous films and proved to be quiet comfortable.

Using the mineral fillers in the manufacturing duration of breathable films has enabled a significant advancement of these type of films, particularly hygienic films. The mineral fillers and especially calcium carbonate are, in this unique case, active ingredients, providing the film special features which enable it to breathe by virtue of the micropore network [5].

In microporous breathable film structures, there are numerous microvoids allowing the vapors pass through the film whilst stopping liquids. These structures are formed as a result of stretching a blend of two nonadaptive substances, such as a polymer mixed with inorganic particles. The microcavities around the filler particles are caused by this stretching [9, 10, 11].

On the other hand, there are monolithic films with homogenate structure absorbing the water vapor. The monolithic film permits the passage of vapors via a process named activated diffusion. As the vapor reaches the opposite surface, the permeant material desorbs and it becomes a part of the surrounding airspace as gas or vapor.

Although at first designed solely for the hygiene and healthcare markets, microporous and monolithic breathable films are now also used in the building and construction markets [5, 11].

Breathable film technology is focused on preparing a variety of breathable films with varied characteristics in order to meet the demands of diverse applications. Thus, in modern day science and technology, the breathable film is a fascinating topic for researchers.

2.2 Breathability and Moisture Vapor Transmission Rate

Breathability refers to the easy transfer of moist air through micropores of the film without losing its liquid blocking capability. The breathability of the film provides comfort for the skin through eliminating undesirable moisture caused by the vapor [13].

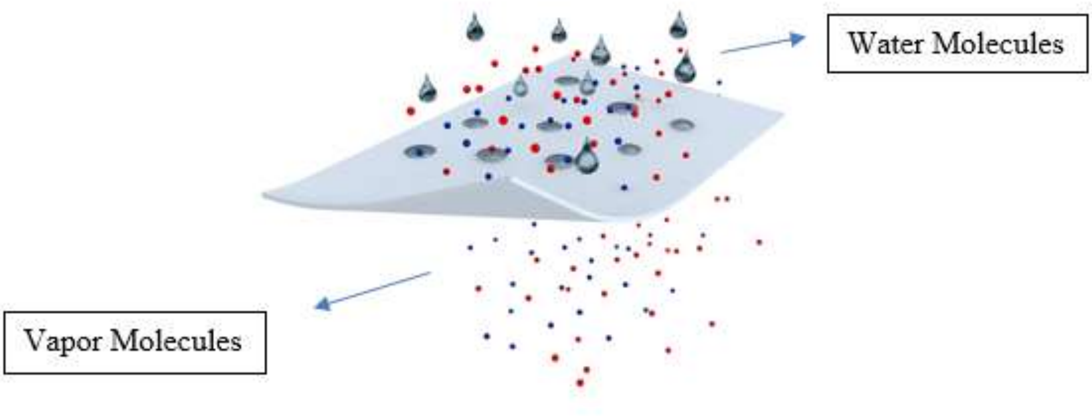

Figure 2.1 : The mechanism of breathability [12].

Comfort in personal care products very much depends on the breathability provided by the microporous film and it can not be expressed adequately since there are a lot of probabilities for the end-use. While the body is resting, normal skin excretes moisture at an average rate which is 60 g per 100 square inches per 24hr. Hence, when the perspiration is added, the minimum moisture vapor transmission rate (MVTR) needed for the feeling of comfort would be approximately 100 g per 100 square inches per 24 hr.

The breathability of a film is ordinarily stated by means of moisture vapor transmission rate or MVTR which is also typically known as the microporosity of the film. It is basically the time rate of water vapor transmission through unit area of flat material of unit thickness induced by unit vapor pressure difference between two particular surfaces, under determined conditions of temperature and humidity [14, 15].

Water Vapor Transmission: $\mathrm{WVT} = \frac{\mathrm{G/t}}{\mathrm{A}}$

In metric units:

G = weight change (from the straight line), g,

t = time, h,

G/t = slope of the straight line, g/h,

A = test area (cup mouth area), m^2, and

WVT = rate of water vapor transmission, $g/h \cdot m^2$ [16].

2.2.1 Monolithic breathable films

One of the way to create the breathability is monolithic structures. Monolithic membranes or films are described as nonporous, solid polymer membranes made of polymer resins enabling the transmission of water vapor due to the hydrophilic character of the resin itself. Both are waterproof and windproof [2, 3].

Monolithic films are known as “breathable” blocks because the film forms a barrier against liquids and particles of matter, however, permits the passage of water vapor and air. Monolithic films are offered by controlling the regional breathability with high WVTR regions and low WVTR regions [6].

Monolithic films carrying an inherent breathability because of the hydrophilic blocks in a copolymer, and perforated (or apertured) films are the current competitors to the microporous technology based on calcium carbonate. Types of breathable structures are shown in Table 2.1. in line with their performance [8].

Polymers including polyether block ester elastomers, polyether block amide elastomer and thermoplastic polyurethanes are resins which can be easily manufactured into monolithic films. Gore-Tex® film is which is an expanded microporous polytetrafluoroethylene (PTFE) is a costly polymeric material. In fact, all of these raw materials are too expensive in comparison to polyolefins such as polyethylene and polypropylene and their copolymers, which are prevalently used [3].

Table 2.1 : Breathable performance by type.

Types of Breathable	Air Flow	Liquid Flow	Cost
Perforated	Easy	Easy	Low
Microporous	Moderate	None to difficult	Low to moderate
Monolithic	Difficult	None	High

[2].

The very first and most likely the best known microporous membrane was developed by Gore in 1976 which is a thin film of PTFE polymer with 1.4 billion microscopic holes per cm2. The nature of these holes is that they are smaller than the rain droplets (2-3 μm compared with 100 μm), and larger than the water vapor molecules (0.0004 μm) [17].

Moreover, it is viable to produce a garment that is more comfortable to wear by obtaining and preserving high breathability because the passing of water vapor throughout the fabric serves to decrease and/or limit discomfort caused by the excess moist trapped in. Hence, it can certainly help to improve the overall skin wellness.

2.2.2 Microporous breathable films

Cost-efficient microporous films and composites can be produced with polyolefinic material and inorganic fillers which are thin, polymeric materials with holes made in the resin sheet through debonding of the polymer from a solid, dispersed material embedded in the matrix. The mineral fillers are, in this sense, dispersed materials. The dispersed polymer phase may include rigid inorganic fillers such as calcium carbonate, clay, or titanium dioxide as well. The adhesion between the matrix polymer and the dispersed phase is believed to be inadequate, and as the composite film is stretched, microvoids will develop around the dispersed phase inclusions [3,8].

The use of mineral fillers in the fabrication process of breathable films has allowed a considerable development of these type of films, particularly hygienic films. The mineral fillers, and particularly calcium carbonate, are in this special case active ingredients, giving the film special characteristics, which allow it to breathe thanks to the network of micropores [5].

Containing billions of micropores, many of them being connected to each other, is a common feature of a water blocking microporous breathable film (see Figure 2.2. showing a typical microporous polymer-calcium carbonate [$CaCO_3$]. structure). If produced with a proper formulation, these materials can be stretched to create a porous structure permitting for the diffusion of water vapor yet at the same time being a liquid water barrier, under appropriate conditions. Water drops such as rain can not penetrate since the pore sizes are much smaller than the droplets, provided that too much pressure is not applied on. Yet, the pores are much bigger than the water vapor molecules, so steam and perspiration can easily pass through the film and get from one side of the film to the other [3,18].

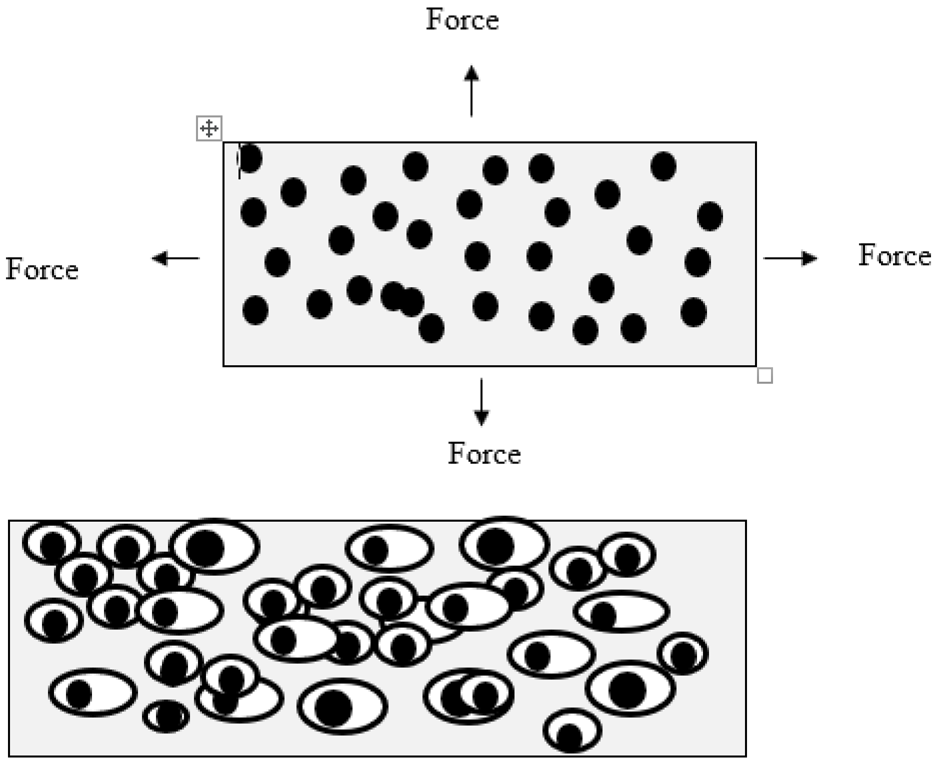

Figure 2.2 : Formation of micropore via stretching [19].

If the stress level becomes high enough and simultaneously the rate of deformation becomes fast enough, most unfilled plastic films should go through stress cracking and micropores should be formed. However, under normal settings of our daily environment, many of the unfilled plastic materials will not undergo stress cracking and won’t form micropores. Even if some stress cracking occurs, the number of pores will not be high sufficient for enabling connections amongst pores in order to shape the tortuous routes essential for air and moisture to pass through without any barriers [3].

2.2.1.1 Polyethylene microporous breathable films

The monomer ethylene (ethene) is the key chemical substance used to produce the scope of polyethylene polymers. The co-monomers joined to change the properties of polymers' are the a-olefins: 1-butene, 1-hexene, and 1-octene.

Ethylene and 1-butene are gases at ambient temperature and pressure. The two other monomers are colorless liquids.

ethylene $CH_2=CH_2$ b.pt –104°C

1-butene $CH_2=CHCH_2CH_3$ b.pt –6°C

1-hexene $CH_2=CH(CH_2)_3CH_3$ b.pt 63°C

1-octene $CH_2=CH(CH_2)_5CH_3$ b.pt 121°C

Figure 2.3 : The polyethylene polymer types.

Varied polyethylene polymer types are produced by polymerizing ethylene either alone or with the above-mentioned a-olefin monomers. Polymerizing ethylene produces the homopolymer and a-olefin monomers produce the olefin co-polymers.

Using high pressures ranging from 100 to 135 MPa, low-density polyethylene (LDPE) is produced from ethylene monomer at temperatures in the range of 150 °C to 300 °C, with a small amount of oxygen or an organic peroxide. Both stirred autoclave and tubular reactor methods can be applied. The density/crystallinity of the resulting polymer is dependent on the reaction temperature applied. If the reaction temperature decreases, the density increases the pressure used in the process and the concentration of chain transfer agents determines the other critical polymer characteristics, such as molecular weight and molecular weight distribution. Molecular weights are usually in the range 10,000 to 50,000 Daltons.

Linear low-density polyethylene (LLDPE) is often produced by co-polymerizing ethylene with one or more of the a-olefin monomers under low pressure such as from 2 to 7.5 MPa, and the temperature should be up to 250 °C with a catalyst, for instance the Ziegler type. It is fabricated in either gas phase or slurry reactor processes.

The density mainly depends on the amount of comonomer used.Typical usage is 2.5 to 3.5 mole %. The higher amounts produce lower densities. The other characteristics of the polymer manufactured are also affected by the type of co-monomer which are1-butene, 1-hexene, or 1-octene. Molecular weights vary between 50,000 and 200,000 Daltons.

High-density polyethylene (HDPE) is produced as the homopolymer using reaction processes, catalyst systems, and pressure and temperature conditions similar to those used for linear low-density polyethylene. Small amounts of co-monomer can be employed to manufacture polymers at the lower end of the density scope. The molecular weight distribution depends on the type of catalyst used , although it is regulated by the proportion of hydrogen added.

Molecular weights are at high levels such as 250.000 Daltons (Brown, 1992). LLDPE and HDPE polymers can be fabricated with the metallocene catalysts. It makes polymers with identical structures both in molecular weight distribution and in co-monomer incorporation. LLDPE films produced from these polymers own numerous improved features, such as enhanced toughness, puncture resistance, and clarity [20].

Calcium-carbonate-filled polyethylene films have a significant role in the hygienic market since these materials enable breathability as being a barrier for liquids [18].

Favored polyethylene polymers are linear low-density polyethylene and its blends selected from among LDPE, HDPE, LLDPE and metallocene PE. The linear low-density polyethylene resin, which is produced by copolymerizing ethylene with a C4 to C10 alpha-olefin, is a copolymer of ethylene and an a-olefin. It is not similar to a conventional low-density polyethylene resin which is manufactured by a high-pressure process. It is. Examples of the comonomer component for linear low-density polyethylene are usually 1-butene, 4-methyl-1- pentene, 1-hexene, 1-octene, 1-decene, etc. Among them, 4-methyl-1-pentene and 1-octene are favored in regards to extrudability and material features of the products. A linear low-density polyethylene resin is produced by low-pressure [3, 14, 21].

The low-density polyethylene resin manufactured by a high-pressure process is not similar to the low-density polyethylene resin produced by a low-pressure process. The low-density polyethylene resin is a long chain branched structure and the low-density polyethylene resin is a straight chain structure [14].

Blending polyethylene (PE) with small amounts of $CaCO_3$ has been proven to have enhanced impact features, attributed to a rise in PE shear yielding caused by debonding at the PE/ $CaCO_3$ interface which can be used for applications where the breathability is crucial; such as the personal care market [4].

PE is compounded with large amounts (10-70 wt%) of a suitable mineral and cast or blown into film. Then this film is stretched at temperatures below the softening point of the PE matrix to form a connecting network of microvoids created by debonding at the PE/ mineral interface. The type of PE, the type and loading of $CaCO_3$ and the extrusion, stretching, and post-stretching processing conditions shape the features of such materials [19].

Figure 2.4 presents the influence of the calcium carbonate loading on the WVTR of a PE film and Figure 2.5 presents the core production steps.

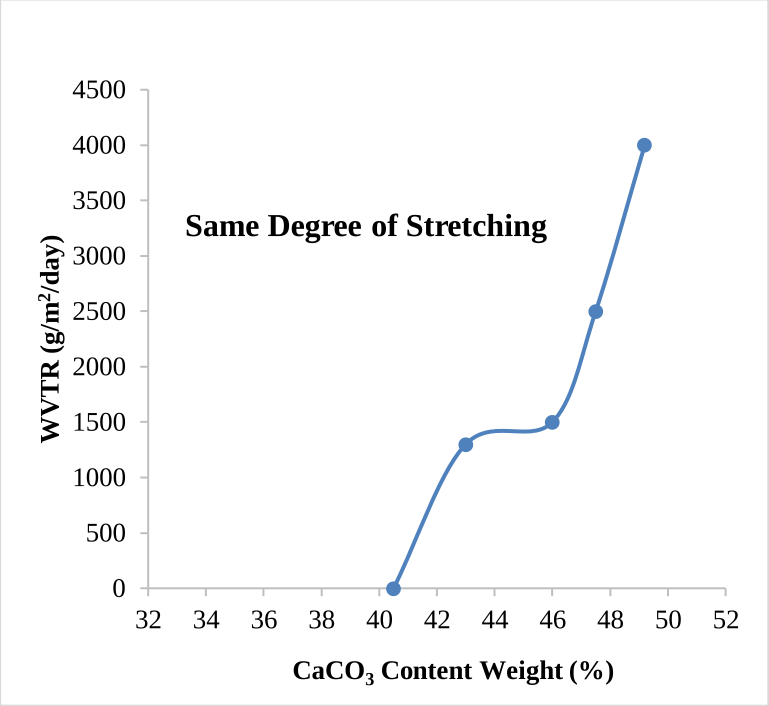

Figure 2.4 : Influence of the calcium carbonate loading on the WVTR of a PE film [3].

As mentioned in the literature, the particle sizes of calcium carbonates that are to be utilized in breathable films should be between 1 µm (mean particle size, d50) and 8 µm (the biggest particle size, d97) [22].

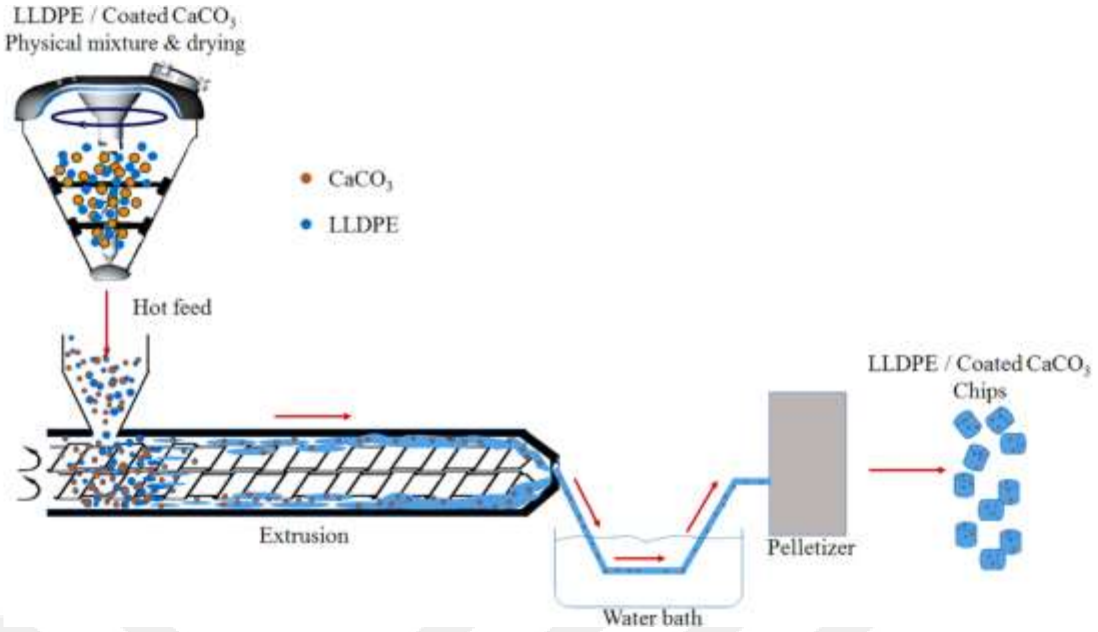

Figure 2.5 : Production steps of the LLDPE/CaCO$_3$ compounds.

2.2.1.2 Polypropylene microporous breathable films

Conventionally, polypropylene (PP) is prepared from propylene monomer by a method similar to that conducted for HDPE. PP gains the ability to crystallize for this method yields a very ordinary pattern along the chain. Since propylene monomer is a little larger than ethylene monomer, PP crystal structure differs from PE crystal structure in a way and displays a higher melting point. Besides, PP usually has more strength and stiffness than PE. Thus, it can be employed in applications demanding a higher use of temperature and more strength such as medical bags and hot liquid drum liners, as well as release films for construction materials.

Since a lot of new polypropylene grades have been prepared recently by using metallocene technology (like the one used for ethylene) the number of properties offered in means of stiffness, impact strength, melting point, and clarity have been increased. Other property combinations are accessible by PE/PP copolymers and materials prepared with both ethylene and propylene monomers. There are many applications for them in food packaging due to better clarity which is an effect of low crystallinity.

Synthesizing PP is as easy as synthesizing PE, except for the potentially higher temperature profile (melt temperature = 330 °F, 165 °C). Both PP and PE have advantageous properties such as being thermally stable, not requiring drying, and decrease in viscosity readily at higher screw speeds which is also known as shear thinning when compared with other polymers [23].

It is possible to employ Polypropylene (PP) resins in a large spectrum of applications and technologies, especially in the industry of plastics since they have diverse properties [24].

Characteristically high clarity, high gloss polypropylene films can be manufactured by cast, double bubble (tubular), and water quenched blown film processes. These polypropylene resins that can produce various property combinations are specially required by the film market [25].

Due to its high resistance to most of the traditional chemicals, proper mechanical features, and steady temperature, Polypropylene is one of the ideal membrane polymers which is also a low-cost option for large-scale manufacturing. It is believed that polypropylene microporous films could be very beneficial in various substantial applications [26].

Modifying PP with nanometer inorganic rigid particles have been tried by many researchers and they attempted to understand the dispersion mechanisms. Thus, it has been stated that adding nanoparticles of $CaCO_3$ which is one of the most frequently used inorganic fillers could improve the thermal and mechanical aspects of polypropylene (PP). Besides, the surface of nanoparticles is commonly changed in an effort to hinder the agglomeration of the particles [27].

There is a series of papers about $CaCO_3$-filled polypropylene (PP) microporous films in which the effects of filler size and biaxial stretch ratio on pore structure were studied. The $CaCO_3$ loading was fixed at 60 wt % because the literature states that minimum of 30 vol % is demanded to form an interconnecting series of pores that enables vapor diffusion. For the PP/ $CaCO_3$ combination, it was revealed that a higher average $CaCO_3$ particle size and/or higher stretch ratios bring the forming of higher degrees of porosity; but, larger stretch ratios were revealed to form an imbalance in particular mechanical properties without introducing the increased WVTR benefit. The number of pores was revealed to expand with the stretch ratio, though the pore Radius stayed rather stable [18].

PP interacts inadequately with common polar fillers such as $CaCO_3$ by reason of its non-polar chemical structure, and maximum dispersion is hard to obtain in general.

Compatibilizers are frequently used to advance the interfacial adhesion between $CaCO_3$ and PP, to get the planned improvement in mechanical features [28].

Studies show that filled polypropylene films create smaller micropores than the filled polyethylene films when processed at the same filler loading and level of stretching. This is because of partly the morphological variances, like crystalline forms, between the two polymers, and in addition, because of the adhesion which is different between the matrix polymer and the rigid calcium carbonate filler. According to researches, polypropylene possesses an enhanced adhesion to the filler than polyethylene [3].

Polypropylene can be utilized along with one or more polyethylenes, or by itself as the polyolefin component of the precursor film. By adding an ethylene copolymer, like an ethylene propylene copolymer helps to control the film bubble, because ethylene homopolymers and copolymers work properly on this kind of equipment [29, 30].

2.3 Production Techniques of Breathable Films

The same procedure applies to all microporous breathable films in the beginning. It is first made using either a cast film or blown film process to produce a microporous breathable film. After the plastic resin is melted to start the extrusion process, fillers are blended in with the melted resin to form a filled film. After that, the breathability properties can be formed in numerous stretching ways such as machine direction orientation (MDO), tentering, or incremental stretching [2, 8].

2.3.1 Blown film extrusion

At first sight producing film by extruding molten resin into a continuous tube seems rather easy. Heat and friction convert the pellets to a melt which is pushed through an annular or ring-shaped die to obtain a tube.

The tube is inflated to enhance its diameter and lower the film gauge. Concurrently, the tube is drawn away from the die, also to lower its gauge. The tube, which is also known as a “bubble,” is cooled by blowing air. Air is applied to the outside of the bubble to cool the film; to raise production rates, internal bubble cooling may also be utilized. Bubble stability is crucial for gauge control and uniformity. Then, it is flattened by collapsing frames and drawn through nip rolls and over idler rolls to a winder which makes the finished rolls of film. The biaxial orientation of the film is obtained by stretching the film in the longitudinal and circumferential directions during production. The degree of orientation depends on the amount and relative degree of stretching.

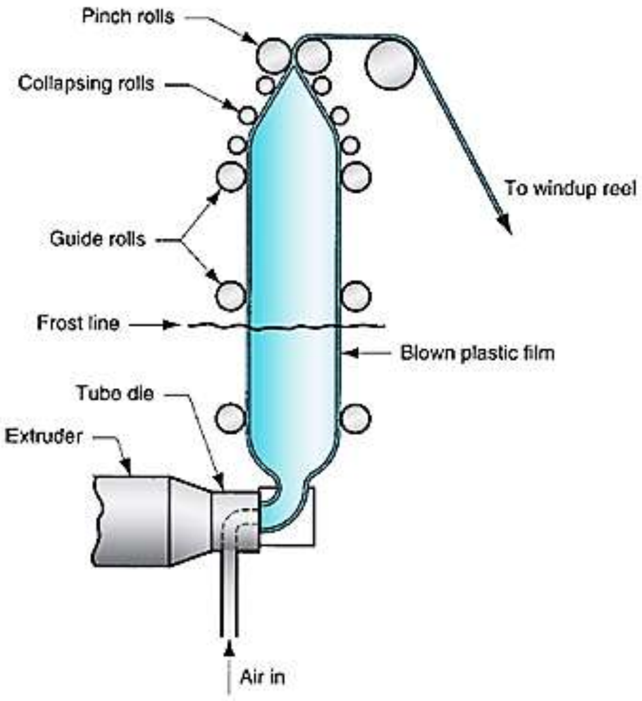

Figure 2.6 : Scheme of blown film extrusion process [33].

Nonetheless, this clarified explanation is not even half the process. Indeed, one of the most complicated and sensitive of all plastics processing technologies is the blown film extrusion system. The tubular blown film process which is beneficial and cost-effective can manufacture a magnificent range of products. From a light gauge, clear converter film to a heavy gauge construction film that may measure 40 feet or more in width when opened [31, 32, 34, 35].

Consequently, the physical demands of the end application determine the finance of producing a cellular tubular blown film.

2.3.2 Cast film extrusion

Cast films are manufactured by placing molten polymer directly from the die on a highly polished, high-speed chilled roll. There the film is cast and stretched consecutively or at once in both directions: the machine direction (MD) and transverse direction (TD). In less than one turn, the chill roll solidifies the product while it brings it down to the right thickness. After the molten polymer is laid down across the roll surface by the film die, it is rapidly quenched because of the roll temperature and the film thickness which restrains the crystallization of semicrystalline resins. The process explained above enables the optical clarity needed in packaging film manufactured through cast film technology with increased gloss, increased production rates, and fine gauge control.

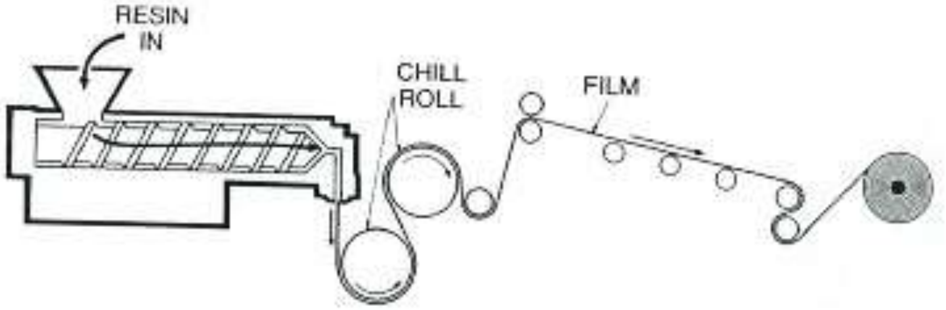

Figure 2.7 : Scheme of cast film extrusion process [36].

In cast film process, the extrudate touches the first chill roll tangentially, and follows an S-pattern around two or more chill rolls. The first chill roll generally runs at a temperature of at least 40 °C (104 °F), with subsequent rolls running at gradually decreased temperatures to cool the film sufficiently and so that it can be trimmed and wound. An air knife is commonly utilized to pin the plastic on the first chill roll. The film dimensions are due to the die dimensions, extrusion rate, and take-off speed [14, 34, 37].

2.3.3 Stretching methods

In the course of stretching, the filler particles detach from the polymer and form cavity. Since no solvents are needed, the stretching method is deemed to be cost-effective and technologically suitable. Usually, three common techniques are used for stretching microporous film precursor in order to render the film microporous.

The machine direction orientation (MDO) which is a frequently used process, includes passing the film between minimum two pairs of rollers. The second pair of rollers (T2) is operating faster (V2) than the first. The of stretching is determined by the ratio of V2/V1.

The cross-machine direction tentering involves grabbing the side edges of t and stretching the web sideways. This was traditionally the only way to stretch the film in the cross-machine direction. It is a slow process and due to the forces concentrated on the edges of the film, it usually does not stretch the film equally.

The third technique is known as incremental stretching, intermeshing or interdigitating stretching. The grooves or teeth intermesh without contacting each other as the rollers are put together. While the film passes between the two rollers, it is stretched as zigzags between the intermeshing teeth. Stretching by intermeshing bears the benefit of inducing the film to stretch in many small increments that are equally spaced over the entire film both in the machine (MD) and the cross (CD) directions, or at oblique angles to the MD, or in any combination [3, 26, 38].

Criteria of Stretching:

- To make a thin film (25 µ or below) at an increased speed rate.
- To stretch a film in 1 or 2 directions to form evenly spaced micro-holes on the surface
- To form a fine pore size structure and distribution [5].

2.3.3.1 Machine direction orientation (MDO)

Although the Machine Direction Orientation (MDO) has been applied successfully for decades, the advancements in film clarity, stiffness, barrier, and tensile strength which are all considered as significant achievements, has been seen since the 1950s. Recently, the companies have started to industrialize this technology more and more. The advancement in mechanical operation through MDO processes is advantageous for cost saving.

The orientation of MDO films is generally quite high when compared to non stretched cast and blown films. Here, the tube or flat film is directed over a number of heated rollers to increase its temperature. In order to stretch the temperature should range from 60 to 150 °C concerning the film material type. The heated film is drawn between slow and fast rolls in the machine direction. After that, the film is annealed to decrease stress and then finally cooled. This stretching process lowers the film thickness and selectively modifies the morphology of the film material.

The MDO unit can be run in-line or off-line with extrusion and it is controlled through parameters including draw ratio (DR), drawing speed, drawing temperature, and heat-setting conditions. The drawing process often enhances the strength, barrier, and clarity, in relation to the high orientation with the machine direction (MD), however, lowers the tear resistance along MD as well as elongation at break along the transverse direction (TD).

Below, the four primary phases of an MDO are explained.

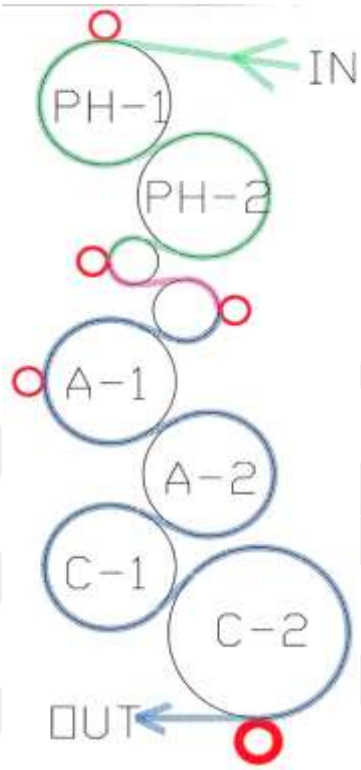

Figure 2.8 : The parts of machine direction orientation [39].

Preheat:

In the figure, the rolls are labeled as PH-1 and PH-2. Their function is to increase the temperature of the film up to orientation temperature, and while doing this, not causing hard wrinkles into the film.

Besides, the first Preheat roll (P1) functions as a nip for tension control of the web coming into the MDO.

Drawing:

These are the rolls seen between PH-2 and A-1. When the film is heated to the requested orienting temperature, it is stretched across a pair of draw rolls. Having a smaller in diameter than the preheat rolls, the distance between the tangent points is lower. The gap between these rolls is generally alterable.

The film is stretched as much as 10:1 or more in this phase.

Annealing:

The third phase of an MDO is the Annealing Rolls. The film is heated and the property changes are prevented. How much the film will shrink back when later exposed to heat depends on this. It is applied on rolls A1 and A2 in the figure.

Cooling:

The last phase is the cooling (rolls C-1 and C-2). Here, the film is cooled back to normal setting [35, 39, 40, 41].

2.4 Basic Requirements of Breathable Films

The end application demands specific properties for breathable films. The most known property of this film is bearing very high levels of vapor transmission, yet still repelling liquid water.

The consumer drives influence the category or the brand. For example, the hygiene market has very specific demands that can only be reached by breathable products. So, in order to achieve the demanded specifications, it is important to choose the right resin and the right filler.

Some important requirements can be seen below.

- Excellent wettability for compounding in breathable films
- Superior output rates
- Superior stiffness for down gauging and repeat print
- Cloth-like softness and aesthetics
- Body conformance
- Skin health maintenance
- Odor prevention and control
- Liquid management [42, 43].

In this section, we will investigate including WVTR, mechanical properties, UV and chemical resistance, water pressure and properties of filler which are the basic requirements of breathable films.

2.4.1 Water vapor transmission rate (WVTR)

WVTR, which is defined as the steady-state time rate of water vapor flow through the unit area of a specimen, should have a norm under specific conditions of temperature and humidity at each surface according to different markets.

For the hygiene market, the WVTR varies between 3000 – 15000 g/m^2/day according to the standards when measured at the temperature of the skin (38 °C/ 100% humidity).

This WVTR could be modified by managing:

- The structure of the polymers of the matrix
- The stretching ratio applied on the film
- The filler content of $CaCO_3$
- The choice of $CaCO_3$

While manufacturing clothing for adults, the WVTR value could be lower with an average value between 5000-6000 (g/m^2/day) due to the larger surface area. For the construction sector, the measuring temperature must be 23 °C and the humidity must be 85 % in accordance with the standards.

Furthermore, the WVTR may differ due to the final application (such as wall covering or roofing films) [5, 44].

This thesis deals with the hygiene market. So, the aforementioned standards will be utilized throughout the analysis.

2.4.2 Mechanical properties

The tensile strength elongation and tear strength values are predefined for the nonlaminated films depending upon the end application. For a stable thickness, the choices of the resin and the filler are vital in determining the final values.

In this sense, the variation of the thickness of the final result is the most reliable parameter to determine. Hence, for the baby diapers they use films of 12 to 25 μ while for the adult incontinence products the films which are 2 times thicker are preferred. For the construction industry the thickness is expected to be approximately 50 μ.

The terms ‘‘stretching degree,’’ ‘‘stretching ratio,’’ and ‘‘extension ratio’’ can be used in place of each other and described as “the changed length on stretching divided by the original length before stretching”. They are all pertinent to the degree of elongation, and they have an impact on both the microporosity and the mechanical properties of the films [5, 14].

2.4.3 UV and chemical resistance

The construction industry generally demands film properties such as good acid, alkali and UV resistance. Choosing the proper polyolefin and the suitable filler secures these properties. Additionally, there is frequently a demand for a flame retardant film [5, 45, 46].

2.4.4 Water pressure

Without considering the surface tension, the physical and chemical behavior of liquids cannot be comprehended. The attraction between the molecules of the liquid by various intermolecular forces causes the surface tension.

In addition to the film blocking the liquids, the resistance to water pressure is a factor that has to be taken into account. For the hygiene market, the films require a resistance value of approx. 1,2 kg/cm^2, however, the building industry needs 1.6 kg/cm^2.

The water pressure (P) of a microporous breathable film is directly linked to the pore radius and the contact angle as stated by Laplace:

$$P = - \frac{2 * \gamma \, H_20 * \cos. (\gamma \, H_20 \, , \gamma \, v)}{r}$$

where γ H20 is the surface tension of the water, r is the radius of the pore and (γ H20, γ v) is the angle of contact between the surface and the water droplet. This angle will expand by progressing the surface coating of the filler and hence, the value of P is raised [5, 47].

2.4.5 Properties of filler

It is generally known that functional additives are materials providing a specific functionality to a formulation, but the fillers simply put instead of a bulk material to lower costs. Profitable microporous films and composites can also be obtained by combining polyolefinic material and inorganic fillers. The incorporation of filler particles can create large voids as the film is stretched because of the cavitation of the polymer at the filler particle surface [3, 48, 49].

Fillers may be any organic or inorganic materials that have less affinity and a significantly reduced elasticity than the polyolefin component. Also, the filler particles can be separated from the thermoplastic polymers in the course of a stretching process to create interconnecting micropores. Ideally, the filler should be a rigid material with a non-smooth hydrophobic surface or a material that is treated to render its surface hydrophobic. Maximum dispersion of the filler, easier processing of highly filled compounds, and higher impact strengths than in polyolefins filled with untreated filler are enabled by the surface-treating filler particles. The favored mean average particle size of the filler is between 3 to 5 microns for films those having a thickness between 4-6 mil before stretching. Some of the examples of the inorganic fillers are calcium carbonate, talc, clay, kaolin, silica, diatomaceous earth, magnesium carbonate, barium carbonate, magnesium sulfate, barium sulfate, calcium sulfate, aluminum hydroxide, zinc oxide, magnesium hydroxide, calcium oxide, magnesium oxide, titanium oxide, alumina, mica, glass powder, zeolite, silica clay, etc. Calcium carbonate is specially selected for reduced cost, whiteness, inertness, and availability. The inorganic fillers such as calcium carbonate are preferably surface treated to be hydrophobic in order to make the filler repel water to reduce agglomeration of the filler. In addition, the surface coating should advance binding of the filler to the polymer while permitting the filler to be pulled away from the polyolefin under stress. An ideal coating is calcium stearate which is FDA approved and readily accessible [21, 50, 51].

In order to create the precursor film, fillers may be integrated at comparatively high levels, restricted only by the ability of the combination (polyolefin/filler) to be turned into a film. The demanded properties of the film including tear strength, WVTR, and stretchability determines the amount of filler added to the polyolefin [29].

In this thesis, due to cost advantage and accessibility, calcium carbonate will be blended with polyolefin as an inorganic filler.

2.4.5.1 Hydrophobicity

Being hydrophilic and lipophilic calcium carbonate needs to be applied with suitable chemicals to make compatible with polymers which have a hydrophobic character. Accordingly, calcium carbonate is coated to be used in plastic industry. To get this result, the calcium carbonate is made hydrophobic through the application of a surface coating. Most often this is achieved by carefully controlled treatment conducted with stearic acid [8, 9, 52].

Hydrophobicity is useful to prevent moisture and moisture pick up in the course of the compounding, storage, transport and extrusion processes [5].

2.4.5.2 Particle size

The microporosity is greatly effected by the particle size of the filler. If the average particle size is high, the stretchability of the film is inferior and stretching breakage occurs before uniform stretching. Hence, the production stability is minor to make uniform pore formation impossible. Reasoning from this fact, if the average particle size is so low, the mineral fine powder cannot be highly filled to be unable to make the film porous [14].

For the PP/$CaCO_3$ system, it was revealed that a higher average $CaCO_3$ particle size and/or higher stretch ratios bring in the formation of higher degrees of porosity; but, larger stretch ratios were revealed to cause an imbalance in certain mechanical properties without the advantage of increased WVTR [18].

Considering such information, as the mean particle size of the filler is reduced, the effective porosity is increased. The ideal mean average particle size of the filler is between 3 to 5 microns for films having a thickness between 4-6 mil before stretching [21, 22, 53].

2.4.5.3 Thermal stability

Thermal stability is one of the most crucial property for fillers. The first stage of making the microporous breathable films is compounding. Filler has to show perfect thermal stability, such as durable at the 280 -300 °C temperature range. After the first stage, it has to demonstrate fine thermal behavior in the course of the second extrusion process.

2.4.5.4 Whiteness and hiding power

The favored property is having an opaque and stable surface without adding the TiO_2.

2.5 Usage Areas of Breathable Films

Microporous film, in its current form, was developed in Japan in 1983 for the hygiene market and especially for back sheet diaper films. In contrast to the perforated or standard back sheet films, the Japanese market was eager to accept films of higher quality despite the additional costs.

The breathable films possess a wide variety of applications in the hygiene field including a large majority of the product lines in infant and adult health care. End product for several key applications are;

- Baby diapers and training pants
- Feminine hygiene
- Adult incontinence

Existing trends in the diaper market demand water vapor permeable breathable backsheets. Also, they are expected to have a fine potential of applications in the fields such as medical and surgical supplies, apparel and household furnishings, tape and packaging, and filtration membranes. Breathable films can also be utilized to replace porous films in applications including burn dressings, sterile packaging, rain coats, shoe linings, nonfogging packaging film, bacteria filters, water purification filters, and wind insulation of houses and buildings.

One of the growing sectors regarding the breathable films is building. There is a demand for roof components. These type of films and laminates are utilized in pitched and flat roofs in order to save the substructure from moisture and to provide wind resistance. After the films are applied to the internal side of the thermal insulation, they are sealed with tapes to block moisture from penetrating the insulation.

The hygiene and building sectors have a very noteworthy position amongst the markets with the highest shares. If we take a look at the two film markets, the hygienic sector should represent in 2005 approx. 450.000 tons and the building industry approx. 150.000 tons.

Since the industrialization degree and the coverage of the market differ, dealing with microporous film progress is very disparate from one region to another.

The interesting properties of these films, connected with an advancement of the high speed production lines, will let the product be more attractive, allowing the market to consider some application diversification.

The packaging sector should definitely benefit the possibility of the transfer of proper water or gas vapor for fresh food packaging. A food which needs to respire can be packed in a unit and the freshness will be kept by virtue of this film.

Another usage of these films could be seen in the agriculture sector. For example in greenhouses films have to prevent the phenomena of condensation which causes drop falls damaging plants.

In the medical field operating garments are already produced with these kinds of films but their use could be intensified as the perspiration can be evacuated bringing a supplementary comfort.

Some other similar applications include bed sheets or drapes. Mostly, the substitution of textile composites in the garment industry, which provides more or less the same type of benefit (breathable water barrier), could be the most major source of advancement in the near future [5, 43, 54].

2.6 Literature Review

There is a research about PP and $CaCO_3$ interactions conducted by Karim Shelesh-Nezhad, Hamed Orang, and Mahdi Motallebi. They saw that as a consequence of their chemical structure, an optimum dispersion was difficult. Having a non-polar chemical structure PP interacts inadequately with the polar fillers. For obtaining a good dispersion, compatibilisers are generally employed to advance the interfacial adhesion between $CaCO_3$ and PP. In this work, maleic-anhydride grafted PP (PP-g- MAH) was utilized as a compatibilizer and the dispersion was assessed. The results showed that the compatibilizer enhanced the interfacial adhesion between nano-$CaCO_3$ and PP and to extend dispersion of nanoparticles in the polymer matrix [28].

As stated by A. Buasri et al., it has been found that the addition of a few percent by weight of these nanoparticles can bring valuable advancement in relation to physical and chemical features. However, these advantages can be utilized provided that the filler nanoparticles are distributed homogeneously not forming aggregates in the polymer matrix. Frequently seen in particulate filled polymers, article aggregation can cause many problems such as deteriorated mechanical properties or poor aesthetics. According to them, coating the surface of the filler with a surfactant is one of the most functional ways to prevent aggregate formation. Surface treatment results in the decrease of both particle/particle and matrix/filler interaction. PP/$CaCO_3$ nanocomposites which are formulated with different filler contents have been created. The surface treatment effects on the mechanical and thermal features of composites have been examined. By the treatment of filler with sodium stearate, the interfacial bonding strength increased and the wettability of the filler by PP matrix gave rise to the improvement of the composites in terms of mechanical properties. The outcome of TGA and DSC experiments showed that adding filler improved the thermal stability of the composites [27].

The mechanical and hardening properties of ternary nano-composites (polypropylene/polyolefin elastomer/calcium carbonate) were studied by A. Elloumi et al. They revealed that to blend PP with a high content of elastomer like ethylene-based copolymer is an effective way for increasing its toughness at the cost of its mechanical strength and stiffness. In the light of the results, it was found that the formation of a filler-network structure was essential for the toughness improvement [55].

According to the research conducted by P. P. Kundu and friend which was about the transportation of moist air through microporous polyolefin films, industrially, such microporous films are heat-set under controlled conditions and let to shrink slightly to decrease residual stresses existing in the final stretched films. It is believed to be crucial during both the process of manufacturing the hygienic products that contain such porous film and the consumer use. Annealing is used following the extrusion in polymer processing and the process is to allow crystallization of a remelted polymeric film at a predetermined temperature which is preferred to be 5–30 °C below the melting temperature [14].

Calcium-carbonate-filled LLDPE films were readied by W.R. Hale et al. They were effectively stretched by the interdigitation method to form a porous material that enables the diffusion of water. Higher degrees of stretch caused increased WVTRs and reduced E modulus due to the forming of more pores. These films were heat-set to remove residual stresses and to obtain a smooth, more clothlike that is appealing aesthetically while retaining required WVTRs [18].

The invention of Exxon Chemical put forth that especially in the lamination process, there is a crucial limitation about delivering breathable films. Producing a cost effective lamination between polypropylene nonwoven materials and polyethylene breathable films is tough. Traditional glue, hotmelt, or meltblown adhesive techniques might be applied, however, the additional cost and process complexity of the glueing system and the adhesive would be faced. The heat lamination which is preferred technique was usually not reliable due to the difference in melting points of the polypropylene nonwoven (~161 °C) and the polyethylene film (~125 °C). The efforts to attain a satisfactory lamination bond strength between the two materials resulted in pin holes or damage to the breathable film at the film/nonwoven bond site. Besides, an industrial demand for a polypropylene microporous breathable film with high tear and impact strengths well as a soft feel is also present. The prepared formulation of this invention is shown in Table 2.2 [29].

Table 2.2 : Formulation 1 of PP breathable compound.

Material	WVTR MOCON
57% $CaCO_3$ 33% Impact Copolymer PP 2% LDPE 8% Plastomer	3000 g/m^2.day

In accordance with Kimberly Clark’s invention, a breathable film providing an excellent barrier to penetration by liquids with high strength and integrity can be produced by using an impact polypropylene copolymer contributing some or all of the polymer matrix. Various filled polymer formulations were compounded, made into a film on a blown film line, stretched uniaxially by a machine direction orienter. The provided films were checked for WVTR and are shown in Table 2.3 and Table 2.4 [7].

Table 2.3 : Formulation 2 of PP breathable compound.

Material	WVTR MOCON
64% $CaCO_3$ 23,4% Impact Copolymer PP 12,6% Random Copolymer PP	4700 g/m^2.day

Table 2.4 : Formulation 3 of PP breathable compound.

Material	WVTR MOCON
64% $CaCO_3$ 23,4% Impact Copolymer PP 12,6% Metallocene LLDPE	3800 g/m^2.day

Pursuant to the invention of Tredegar Film Products Corporation, it has been found that providing a precursor film with a polypropylene and a filler (especially Calcium Carbonate), after that gradually aligning the precursor film in the machine direction, or the transverse direction, or both, will produce a film rather soft to the feel having a good dart impact and a good tear strength. Moreover, it has been realized that the extrusion workability can be improved remarkably if a minority amount of a low density polyethylene to the polypropylene and filled blend is added. It has been also observed that the addition of a minimum amount of an elastomer or a plastomer further enhanced dart impact strength and tear strength, as well as contributing to an even softer film feel to the human touch. In this study WVTR values and some mechanical features has been revealed. Based on the outcomes of some physical features, enhancements have been obtained by applying diverse formulations. The diverse formulation matrix is shown in Table 2.5 and Table 2.6 [56].

Table 2.5 : Formulation 4 of PP breathable compound.

Material	WVTR MOCON (g/m^2.day)	MD Elongation (%)	MD Elmendorf Tear Strength (gr)	Dart Impact Strength (gr)
52% $CaCO_3$ 48% Impact Copolymer PP	1457	423	79	210

Table 2.6 : Formulation 5 of PP breathable compound.

Material	WVTR MOCON (g/m^2.day)	MD Elongation (%)	MD Elmendorf Tear Strength (gr)	Dart Impact Strength (gr)
52% $CaCO_3$ 40% Impact Copolymer PP 2% LDPE 6% Plastomer	1462	482	195	315

3. EXPERIMENTAL PART

3.1 Materials

3.1.1 Calcium Carbonate- $CaCO_3$

$CaCO_3$ is supplied from Omya International AG. It is a white, marble based, fine ground calcium carbonate of the highest purity. Its particle size distribution (PSD), combined with its uniquely formulated surface treatment, make it especially suitable for breathable films within the hygiene and industrial markets. The main datas of material can be seen in Table 3.1.

Table 3.1 : Specific product data of $CaCO_3$.

Property	Value	Test Method
Median particle size, d50%	1.9 µm	Sedigraph 5120 (measured on untreated material)
Brightness, Ry, C/2°	94 %	DIN 53163
Moisture content (ex works)	0.1 %	ISO 787/2
Apparent density, tamped	1.1 g/ml	ISO 787/11

3.1.2 Polypropylene

Information will be given about two different types of polypropylene used in thesis experimental part.

PP-1 is a very soft random heterophasic copolymer which is suitable for hygienic applications. The molecular structure can be seen in Figure 3.1. It is supplied from Borealis Group. The main datas of material can be seen in Table 3.2.

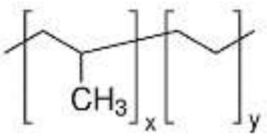

Figure 3.1 : Molecular structure of PP-1.

PP-2 is a heterophasic copolymer and it is supplied from Borealis Group. The main datas of material can be seen in Table 3.3.

Table 3.2 : Specific product data of PP-1.

Property	Value	Test Method
Melt Flow Rate (230 °C/2.16 kg)	0.8 g/10min	ISO 1133
Flexural Modulus	500 MPa	ISO 178
Melting temperature (DSC)	140 °C	ISO 11357-3
Tensile Strain at Break MD	700 %	ISO 527-3
Tensile Strain at Break TD	800 %	ISO 527-3
Tensile Strength MD	60 MPa	ISO 527-3
Tensile Strength TD	50 MPa	ISO 527-3

Table 3.3 : Specific product data of PP-2.

Property	Value	Test Method
Melt Flow Rate (230 °C/2.16 kg)	1.2 g/10min	ISO 1133
Flexural Modulus	1100 MPa	ISO 178
Melting temperature (DSC)	166 °C	ISO 11357-3
Tensile Strain at Break MD	700 %	ISO 527-3
Tensile Strain at Break TD	776 %	ISO 527-3
Tensile Strength MD	65 MPa	ISO 527-3
Tensile Strength TD	35 MPa	ISO 527-3

3.1.3 Polyethylene

LLDPE (linear low density polyethylene) is ethylene-octene copolymer and designed for high quality blown film applications. To increase the processability and homogeneity, it is used in formulation.

The molecular structure can be seen in Figure 3.2. It is supplied from Dow Chemical Company. The main datas of material can be seen in Table 3.4.

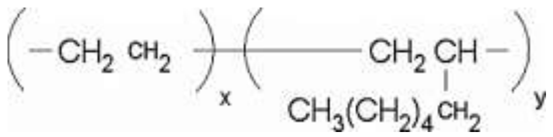

Figure 3.2 : Molecular structure of LLDPE.

Table 3.4 : Specific product data of LLDPE.

Property	Value	Test Method
Melt Flow Rate (190 °C/2.16 kg)	1.1 g/10min	ISO 1133
Density	0.919 g/cm^3	ASTM D792
Melting temperature (DSC)	120 °C	ASTM D1525
Tensile Elongation MD	810 %	ISO 527-3
Tensile Elongation TD	920 %	ISO 527-3
Tensile Stress at Break MD	38 MPa	ISO 527-3
Tensile Stress at Break TD	37 MPa	ISO 527-3

3.1.4 Plastomer

Plastomer is primarly composed of isotactic propylene repeat units with random ethylene distribution. It is produced using metallocene catalyst technologhy and supplied from Exxon Chemical and main properties can bee seen in Table 3.5.

Table 3.5 : Specific product data of plastomer.

Property	Value	Test Method
Melt Flow Rate (190 °C/2.16 kg)	3,7 g/10min	ASTM D1238
Density	0.878 g/cm^3	ASTM D1505
Ethylene content	9 %	
Elongation at yield	30 %	ASTM D638
Elongation at break	920 %	ASTM D638

3.1.5 Slip&Antiblock

Slip&Antiblock is general purpose erucamide slip and antiblock concentrate based in LDPE. This masterbatch providing balanced surface properties. The amide slip agents are extremely pure and are combined with finely dispersed silica for their optimum optical properties. It is supplied from A. Schulman. The main datas of material can bee seen in Table 3.6.

Table 3.6 : Specific product data of slip&antiblock.

Property	Value	Test Method
Additive Content	5 %	
Loss of Ignition	10 %	ASTM D2584
Bulk Density	600 g/L	
Melt Flow Rate	13 g/10min	ASTM D1238
Spesific Gravity	0.98 g/cm^3	ASTM D792

3.1.6 Zinc Stearate

Zinc stearate is natural zinc soap and most powerful mould release agent. It has hydrophobic effect and as an adhesion protector in rubber. It used as an external lubricant. It is very compatible with all rubber and plastic material. It is supplied from Zirve Polimer. The main datas of material can be seen in Table 3.7.

3.1.7 Phosphite processing stabilizer

Phosphite processing stabilizer is a hydrolytically stable. As a secondary antioxidant, it reacts during processing with hydroperoxides formed by autoxidation of polymers preventing process induced degradation and extending the performance of primary antioxidants.

It is an organophosphite of low volatility and is particularly resistant to hydrolysis. It protects polymers which are prone to oxidation, during the processing steps (compounding/pelletizing, fabrication and recycling) from molecular weight change (by chain scission or crosslinking) and prevents discoloration. It is supplied from BASF Company. The main datas of material can be seen in Table 3.8.

Table 3.7 : Specific product data of zinc stearate.

Property	Value
Chemical Characteristic	Neutral zinc soap
Appearance Fine	White powder
Melting Point, ºC	120 ± 2
Zinc Content	%11±0,5
Free fatty Acid	Below 0.5
Ash Content	%13.5 ± 0.5
Solubility	Soluble in hot toluene and xylene

Table 3.8 : Specific product data of phosphite processing stabilizer.

Property	Value
Chemical Name	Tris(2,4-di-tert.-butylphenyl) phosphite
Appearance Fine	White, free-flowing powder
Melting Point, °C	183 – 186 °C
Specific Gravity (20 °C)	1.03/ml

3.1.8 Commercial PP based breathable compound

A commercial PP based breathable compound has been analyzed as a control sample. The analyzes are very important in terms of the experimental work done.

3.1.9 Commercial PE based breathable compound

A commercial PE based breathable compound has been analyzed as a control sample. The analyzes are very important in terms of the experimental work done.

3.1.10 Commercial microporous PE based breathable film

A commercial PE based breathable film has been supplied from a commercial firm and analyzed. The analyzes are very important in terms of comparison of produced film samples within the scope of the thesis experimental study, as an alternative for microporous PE breathable film.

3.2 Equipments

3.2.1 Production equipments

3.2.1.1 Compound extrusion

In compound extrusion process, the inorganic filler and polypropylene are blended with the essential additives. To obtain required blending of different form materials, it is important to achieve effective mixing during compounding. Generally double screw extruders are preferred in compounding because of such reasons. Compounding lines with connected with water bath and pelletizing unit. The material processed in the extruder and is removed from the die as filament shape and enters the water bath. The material should have optimum temperature and stability to gain effective pelletizing process. It is also very important to purify the material from moisture.

The schematic view of compound extrusion screw profile can be seen below in Figure 3.3.

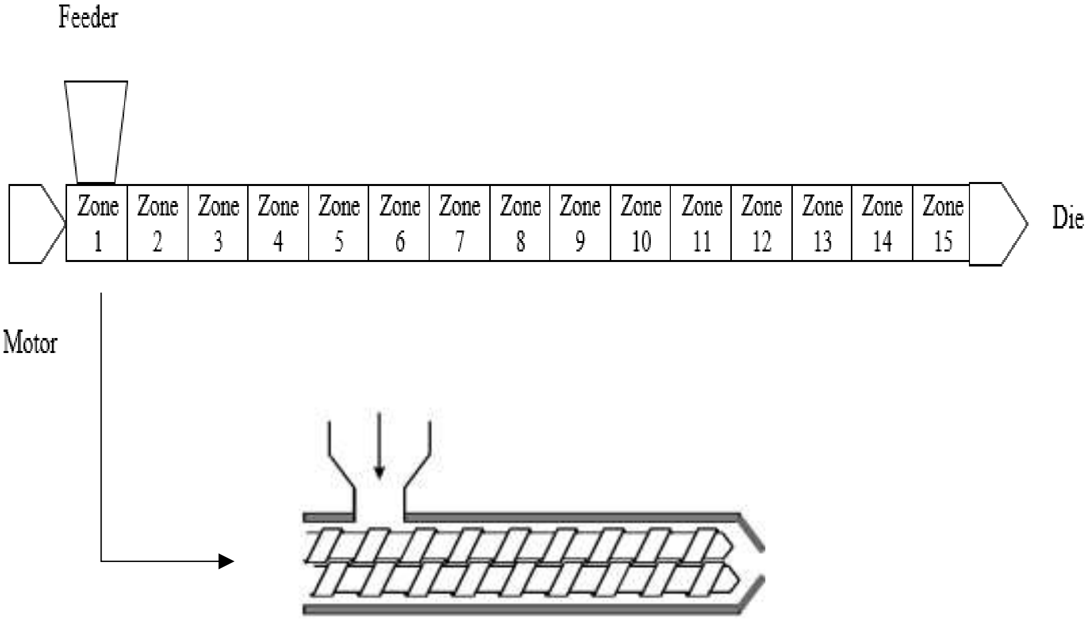

Figure 3.3 : Compound extrusion line [34].

3.2.1.2 Blown film extrusion

In blown film extrusion process, prepared compounds are used for making the breathable films. The blown film extrusion line is a coex production line which can produce 5 layer with maximum 750 kg/h output. The die width is 55 cm and L/D rate is 30. It has the MDO unit with water heating system which is required for microporous film production. There are 4 different areas called preheating, stretching, annealing and cooling in MDO unit. The basic scheme of blown film extrusion line with MDO unit can bee seen in Figure 3.4.

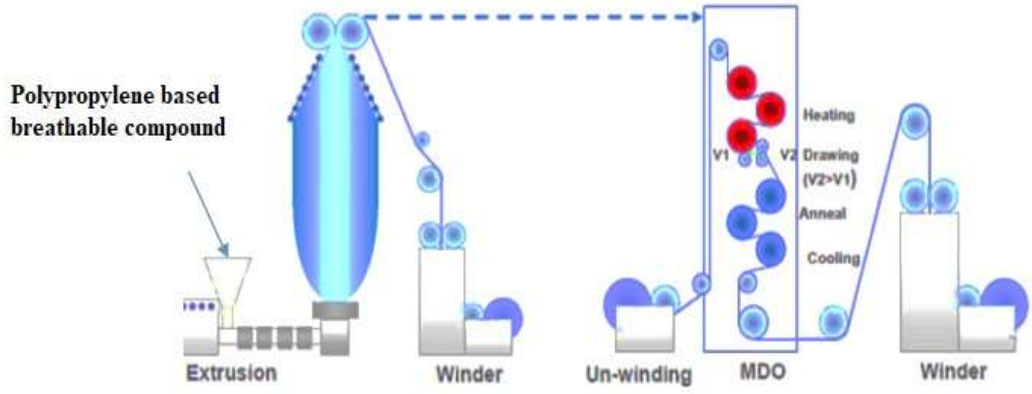

Figure 3.4 : Blown film extrusion line [35].

3.2.2 Testing equipments

3.2.2.1 DSC (Differential scanning calorimetry)

Differential Scanning Calorimetry, or DSC, is a thermal analysis technique that looks at how a material’s heat capacity (Cp) is changed by temperature. A sample of known mass is heated or cooled and the changes in its heat capacity are tracked as changes in the heat flow. This allows the detection of transitions such as melts, glass transitions, phase changes, and curing. Perkin Elmer DSC 4000 system (see in Figure 3.5) is used to characterize the thermal behaviour of samples according to ASTM E974 standard.

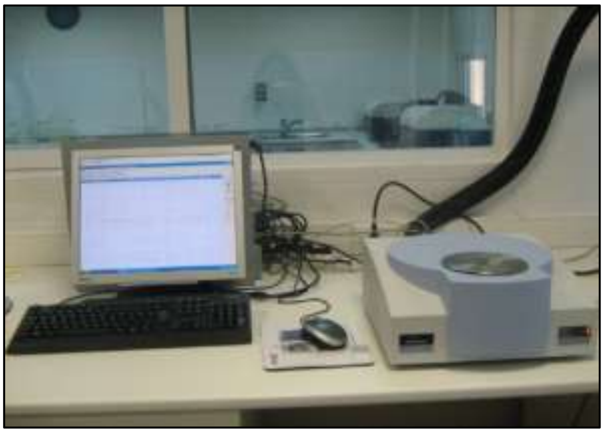

Figure 3.5 : DSC device.

3.2.2.2 FTIR (Fourier transform infrared spectroscopy)

FTIR stands for Fourier Transform Infrared, the preferred method of infrared spectroscopy. In infrared 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. Perkin Elmer FT-IR system (see in Figure 3.6) is used to achive FTIR spectrum according to ASTM 5477 standard.

Figure 3.6 : FTIR device.

3.2.2.3 Density analyzer

The gas pycnometer consists of two chambers of known volume connected by a valve. One of the chambers, the calibrated sample chamber, is accessible for insertion of the test specimen and is connected to a source of high purity (at least 99.99 %) helium gas. The ratio of the pressure change is directly related to the volume of the sample chamber displaced by the specimen. Pycnometer determines density and volume by measuring the pressure change of helium in a calibrated volume. The density analysis were made according to ASTM D6226 standard.

3.2.2.4 Melt flow rate analyzer

The melt flow rate (MFR) is a measure of the mass of polymer that is extruded through a capillary die at a certain temperature and force. The sample can be in the form of virgin resin pellets or ground material from a finished product. A sample is loaded into the preheated barrel of the instrument, together with a piston and weight is placed on the piston to apply force. The melt flow rate analysis were made with Zwick roell MFR instrument.

3.2.2.5 Ash content analyzer

This test method was developed to determine the inorganic content of plastics by destructive ashing procedures according to ASTM D5630. An ash test involves taking a known amount of sample, placing the weighed sample into a dried / pre-weighed porcelain crucible, burning away the polymer in an air atmosphere at temperatures above 500 °C, and weighing the crucible after it has been cooled to room temperature in a desiccator.

3.2.2.6 Zwick roell- mechanical testing device

The measurement of mechanical properties is concerned with load-deformation or stress-strain relationships. In this study, for evaluation of mechanical properties, tensile test method was used. Tensile test is a measure of the withstanding ability of material to the force of pulling and shows the stretching amount of material until breaking. Mechanical tests were made by using Zwick/Roell X Force-P testing machine (see in Figure 3.7) according to ASTM D882 standard.

Figure 3.7 : Zwick roell resting device.

3.2.2.7 Elmendorf tear strength analyzer

Elmendorf tear testing determines the force required to continue the tearing of an initial cut in sheet materials such as paper, plastic film, textile and non-woven.

A pendulum impact tester (see in Figure 3.8) is used to measure the force required to propagate an existing slit a fixed distance to the edge of the test sample according to ASTM D1922 standard. Measurement ranges include 200, 400, 800, 1600, 3200 and 6400 gf.

Figure 3.8 : Elmendorf tear testing device.

3.2.2.8 WVTR MOCON analyzer

The water vapor transmission rate is a measure of the rate at which water vapor flows through breathable materials. WVTR is measured according to WSP 70.4, which is the standard test method for water vapor transmission rates of 500 to 100.000 g/m^2/day.atm PERMATRAN-W Model 101K (see in Figure 3.9) has six test cells and is used to analyze the permeability properties of samples with the 20-50 °C temperature range.

Figure 3.9 : WVTR MOCON device.

3.2.2.9 SEM (Scanning electron microscopy)

A Scanning Electron Microscope (SEM) is a mightily magnification tool that employs focused beams of electrons to obtain data. It provides particulars surface data by following a sample in a raster pattern with an electron beam. The operation starts with an electron gun generating a beam of energetic electrons down the column and onto a series of electromagnetic lenses. The lenses are tubes, wrapped in spiral and referred to as solenoids. The spirals are modulated to focus the incident electron beam onto the sample; these modulates cause fluctuations in the voltage, increasing/decreasing the speed in which the electrons come in contact with the specimen surface. SEM analysis is performed according to ASTM E986 standard and conducted at 15 kV.

3.3 Experimental Procedure

3.3.1 Production of samples

In experimental procedure part, in order to produce the samples, compound extrusion and blown film extrusion processes are used.

3.3.1.1 Production of compound samples

The first step for obtaining samples is compounding process. In this step, the raw materials are fed to compound extruder line according to below ratios (see in Table 3.9 and Table 3.10). There are two compound formulation which contain 50% (C1) and 60% (C2) calcium carbonate. The second formulation contains the plastomer to make more calcium carbonate loading. Plastomer is expected to both ease the process and provide dispersibility. The effect of both will be observed.

Table 3.9 : Formulation of C1.

Material	Ratio
$CaCO_3$	50 %
PP-1	23 %
PP-2	13 %
LLDPE	12 %
Slip&Antiblock	1 %
Zinc Stearate	0.7 %
Phosphite Processing Stabilizer	0.3 %

Table 3.10 : Formulation of C2.

Material	Ratio
$CaCO_3$	60 %
PP-1	18 %
PP-2	9 %
LLDPE	8 %
Plastomer	4 %
Zinc Stearate	0.7 %
Phosphite Processing Stabilizer	0.3 %

As can be seen from formulations, prepared compounds contain 50% and 60% filler respectively and they are based on polypropylene. Two heterophasic polypropylenes, with different thermal and density properties, are used to provide a smooth transition in the formulations. The ethylene comonomers embedded in the polypropylene homopolymer structure and the impact copolymers or heterophasic copolymers are obtained. Good impact properties and good aesthetic properties are obtained by using heterophasic copolymers. When the improved mechanical properties are desired in polypropylene based microporous breathable structures, good aesthetics and flexibility are demanded at the same time. Heterophasic structures are intended to provide these properties. For this reason, heterophasic copolymers are preferred in the scope of the study. In order to improve processability, there is an octene-based linear low density polyethylene in the formulations. Slip&Antiblock and plastomer are added to improve dispersibility and calcium carbonate loading. Zinc stearate and secondary antioxidant are fed as process additives.

Due to formulations matrix, reverse temperature profile is used in screw and it can be seen in Figure 3.10. The motor speed is 600 rpm and the pressure is 38 bar at the die of extruder.

	260° C	255° C	255° C	260° C	255° C	240° C	240° C	240° C	240° C	235° C	225° C	240° C	245° C	245° C

Figure 3.10 : Temperature profile of screw zone.

The material processed in the extruder and is removed from the die as filament shape and enters the water bath. The water bath temperature has to be at optimum temperature in order to achieve effective pelletizing process. Because of that the temperature range is 50-60 °C. Filaments enter the pelletizing unit after the water bath and break into desired pieces. The size of obtained granules is 3 mm and pelletizer speed is 35 rpm.

3.3.1.2 Production of film samples

Experimental design and film production

In the experimental design part, selected parameters, and levels for blown film extrusion were determined. For the improved processability, breathability and mechanical properties, especially tear and impact resistance, which are the main aim of the thesis, 2 parameters are designed with 2 levels. The variable and constant paramerers for blown film extrusion process are included in Table 3.11 and Table 3.12.

Table 3.11 : Variable parameters and levels for blown film extrusion.

Parameter	Level 1	Level 2
Compound	C1	C2
LLDPE (%)	0	15

Table 3.12 : Constant parameters for blown film extrusion.

Parameter	Value
GSM (g/m^2)	16
Width (mm)	2020
Stretching ratio	1:4

According to the factorial experimental design, for each of parameter in total 2 levels can be found by simple combination calculation ($2^2=4$). The number of experiments and level changes can be seen in Table 3.13.

Breathable film 1, 2, 3 and 4 coded films are planned to be produced according to below design.

Table 3.13 : Factorial experimental desing for blown film extrusion.

Experiment	Compound	LLDPE (%)
BF1	C1	0 %
BF2	C1	15 %
BF3	C2	0 %
BF4	C2	15 %

The content information of each experiment is included in Table 3.14, Table 3.15, Table 3.16 and Table 3.17.

Table 3.14 : Content of BF1.

Code	Recipe
BF1	Compound: C1 LLDPE: 0 %

Table 3.15 : Content of BF2.

Code	Recipe
BF2	Compound: C1 LLDPE: 15 %

Table 3.16 : Content of BF3.

Code	Recipe
BF3	Compound: C2 LLDPE: 0 %

Table 3.17 : Content of BF4.

Code	Recipe
BF4	Compound: C2 LLDPE: 15 %

The second step is blown film extrusion process. In this step, the prepared compounds are firstly dried at 80 °C for 3 hour to prevent moisture problems. Such moisture problems can cause pitting and spotting on the film surface. The contents stated in the above tables are the same for each layer of the extruder. The production was carried out with the target of 16 g/m^2 and stretching ratio was 1:4. Although the risk of tearing due to the rigidity of the polypropylene raw material, the stretching ratio is planned as maximum 1:4.

The temperature profile of screws and MDO unit can be seen in Table 3.18 and Table 3.19. The temperature of the die was kept at 220 °C. Production yields were observed in the range of 500-550 kg/h.

Table 3.18 : Temperature profile of screws.

Extruder A (°C)	Extruder B (°C)	Extruder C (°C)	Extruder D (°C)	Extruder E (°C)
220	220	220	220	220

Table 3.19 : Temperature profile of MDO unit.

PH1 (°C)	PH2 (°C)	SD1 (°C)	FD1 (°C)	A1 (°C)	A2 (°C)	C1 (°C)	C2 (°C)
80	90	95	95	120	110	30	25

During the blown film extrusion, different LLDPE ratios and different PP breathable compounds were used to overcome the processing hardship (to control the bubble), low breathability and high stiffness, which are the potential difficulties in microporous PP breathable film production. The effects of these parameters will be shown by analysis.

It is targeted to produce 4 production under the stated conditions. BF3 coded production could not be produced in the blown film process. The rigidity of the film is thought to cause the balloon to break. Due to this probable cause, it was aimed to improve the processability with adding LLDPE in the experimental design.

The analysis results of the BF1, BF2 and BF4 will be shared.

3.3.2 Analysis of samples

Analysis will be made of the produced samples with the tests which are useful to characterize.

3.3.2.1 Analysis of breathable compound samples

DSC analysis

The samples were heated at 10 °C/min and were cooled at 10 °C/min in the range of 30-300 °C under 50 ml/min pure nitrogen gas.

FTIR analysis

All spectra were recorded at 4-cm^{-1} resolution.

Density analysis

The density analysis were made with 5 gr sample. It was determined with high purity helium gas.

Melt flow rate analysis

The melt flow rate analysis are taken under 190 °C, 2.16 kg conditions.

Ash content analysis

In this analysis, the amount of ash content was determined.

A: Weight of empty porcelain crucible

B: Weight after 2 gr sample

C: Weight after heating in the ash oven at 600 and 900 °C

The equation of ash content as follows.

[(C-A) / B]. * 100

3.3.2.2 Analysis of film samples

DSC analysis

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C: Weight after heating in the ash oven at 600 and 900 °C

The equation of ash content as follows.

$[(C-A) / B]. * 100$

Mechanical properties analysis

The mechanical properties analysis of samples were made under the following conditions:

Sample width is 2.5 cm.

Jaw distance 5 cm.

Section speed is 500 mm/min.

Elmendorf tear strength analysis

Ten samples each are cut from the plastic film in the machine direction and in the cross direction. A sample is positioned in the device and clamped in place. A cutting knife in the device is used to create a slit in the sample which ends 43mm from the far edge of the sample. The pendulum is released to propagate the slit through the remaining 43 mm. The energy loss by the pendulum is used to calculate an average tearing force.

WVTR MOCON analysis

The tests were made under the specidied conditions. Temperature of the test apparatus is set at 38 °C and relative humidity is 100%. Test cell area is 10 cm^2.

Grammage analysis

From each sample, 5 circular sections of 10 cm^2 were taken and their weights were measured and the averages of the obtained values were taken. The weight values are given in g/m^2.

SEM analysis

SEM analysis was carried out in 2000-fold magnification by thin-layer coating with gold-palladium at variable pressure mode and 15 KV acceleration voltage.

4. RESULTS AND DISCUSSIONS

4.1 Evaluation of Results

4.1.1 Results of breathable compound samples analysis

Within the scope of the study, PE and PP based commercial breathable compounds were investigated. The properties of commercial breathable compounds were compared with the prepared breathable compounds. DSC, FTIR, density, MFR and ash content analyzes were performed to characterize the structures of PE and PP based commercial breathable compounds. During the production of C1 and C2, the data obtained from these analyzes and literature researches were taken over.

In accordance with literature researches and analyzes, the breathable compounds with the following structure (see in Table 4.1) were prepared. Two compounds with different contents of calcium carbonate were prepared via double screw extruder. The formation of micropores is required for breathable films and it can be correlated with the content of calcium carbonate. The filler loading capability of polypropylene is lower than polyethylene, since polymer chains of polypropylene are close to each other and have less free volume due to it's nature. For this reason, rates of 50% and 60% were chosen. When 60% load was applied, the processability was tried to be improved by plastomer reinforcement. Production was carried out successfully and granules with a size of 3 mm were obtained. They were subjected to some tests for characterization.

Table 4.1 : Formulation of C1 and C2.

C1	C2
50% $CaCO_3$	60% $CaCO_3$
23% PP-1	18% PP-1
13% PP-2	9% PP-2
%12 LLDPE	8% LLDPE
1% Slip&Antiblock	4% Plastomer
0.7% Zinc Stearate	0.7% Zinc Stearate
0.3% Phosphite Processing Stabilizer	0.3% Phosphite Processing Stabilizer

In this section, the analysis of the commercial breathable compounds (PE and PP based) and prepared breathable compounds, C1 and C2, will be given.

4.1.1.1 Results of commercial breathable compounds

Some analyzes have been made to understand the polymeric structures, melt rheology and the ratio of calcium carbonate contained in commercial PE and PP based compounds.

While comparing commercial compounds made of two different polymers, it is necessary to review their properties. Although polypropylene and polyethylene are similar thermoplastics, there are some obvious differences. Polypropylene has higher melting temperature and rigidity than polyethylene. The structures seen in the analyzes are co-polypropylene, homo-polypropylene and linear low-density polyethylene. A general comparison has been made for PP and PE used in the experimental study (see in Table 4.2). This data will be used in comparison with the prepared breathable compounds.

Table 4.2 : Comparison of PP and PE.

Material	Density (g/cm^3)	Melt flow rate (g/10min)
PP	0.89	0.8-1.2
PE	0.92	1.1

DSC results

In order to determine the crystallization behaviors of the commercial breathable compounds, DSC analysis are done. During preparation of sample, it may have some thermal history. By having first heating, we are removing all thermal history. In next heating, our samples show real thermal response and they are free from any thermal history. For this reason, we will evaluate the DSC analysis based on the second heating line.

The melting temperature peaks of PP based commercial breathable compound were observed and determined. The DSC analysis graph can be seen in Figure 4.1. As can be seen from the analysis graph, melting peaks at 145° C and 159° C were observed. It is known that these peaks belong to co-PP and homo-PP structures according to investigations. Another melting point is at 116° C and it belongs the LLDPE structure. It shows us that LLDPE structures have been added to polypropylene-based compounds for processability and breathability. This situation is supported by literature researches.

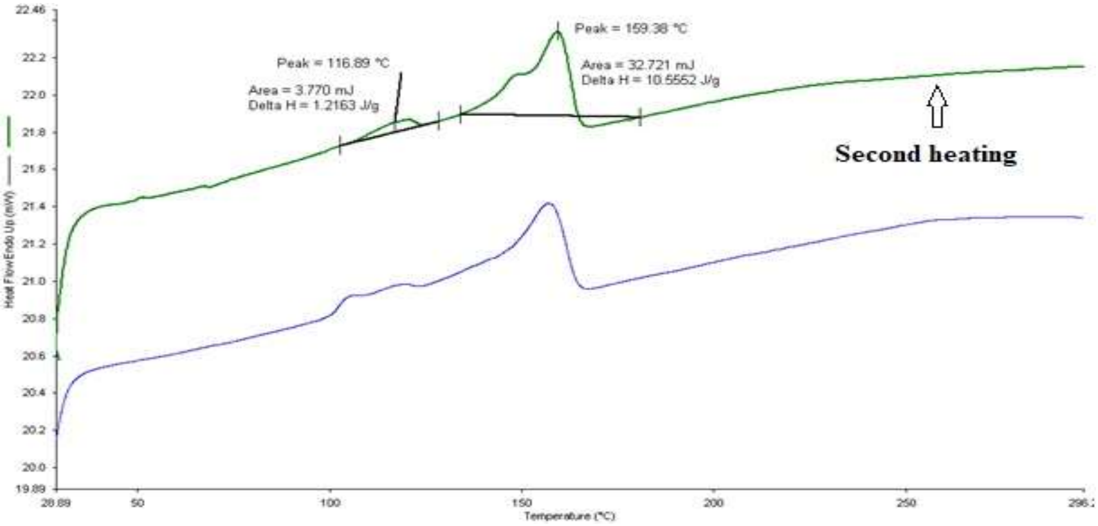

Figure 4.1 : DSC analysis of PP based commercial breathable compound.

The melting temperature peaks of PE based commercial breathable compound can be seen in Figure 4.2. As can be seen from the analysis graph, melting peaks at 109° C and 120° C were observed. It is seen that there is no structure other than PE in PE based commercial breathable compound.

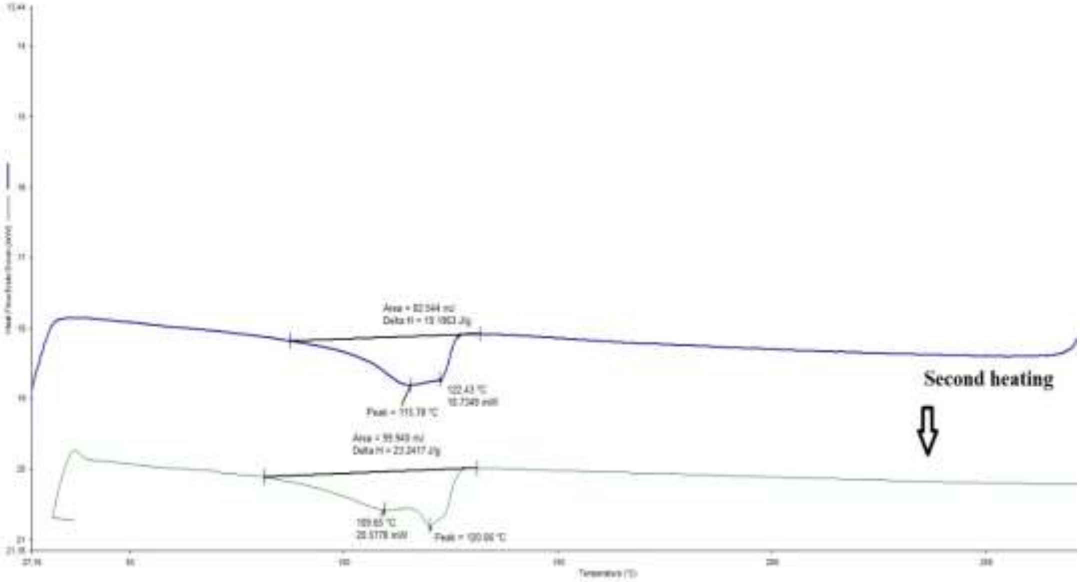

Figure 4.2 : DSC analysis of PE based commercial breathable compound.

FTIR results

According to FTIR analysis of PP based commercial breathable compound (see in Figure 4.3), the stretching vibration of CH_3 is 2950.20 cm^{-1} (PP) and the stretching vibration of CH_2 is 2917.57 cm^{-1} (PE). 2838.73 cm^{-1} refers to as CH_2 functional groups and 1375.10 cm^{-1} refers to as CH_3 functional groups. They belong to PE and PP respectively. The other characteristic peak 1796.30 cm^{-1} is belong to $CaCO_3$ and it is combination functional group (vibration of 1080 and 713). CO_3^{-2} stretching asymmetric peak, which are characteristic peak of $CaCO_3$, can be seen in 1440-1375 cm^{-1}. Peaks at 1165.92 cm^{-1}, 997.38 cm^{-1} and 972.74 cm^{-1} are correspond to isotactic band of PP. CO_3^{-2} deformation, asymmetric and symetric, can be seen in 872.85 cm^{-1} and 712.35 cm^{-1} peaks. It shows us that compound contains the polypropylene, polyethylene and calcium carbonate structures. This situation is supported by literature researches.

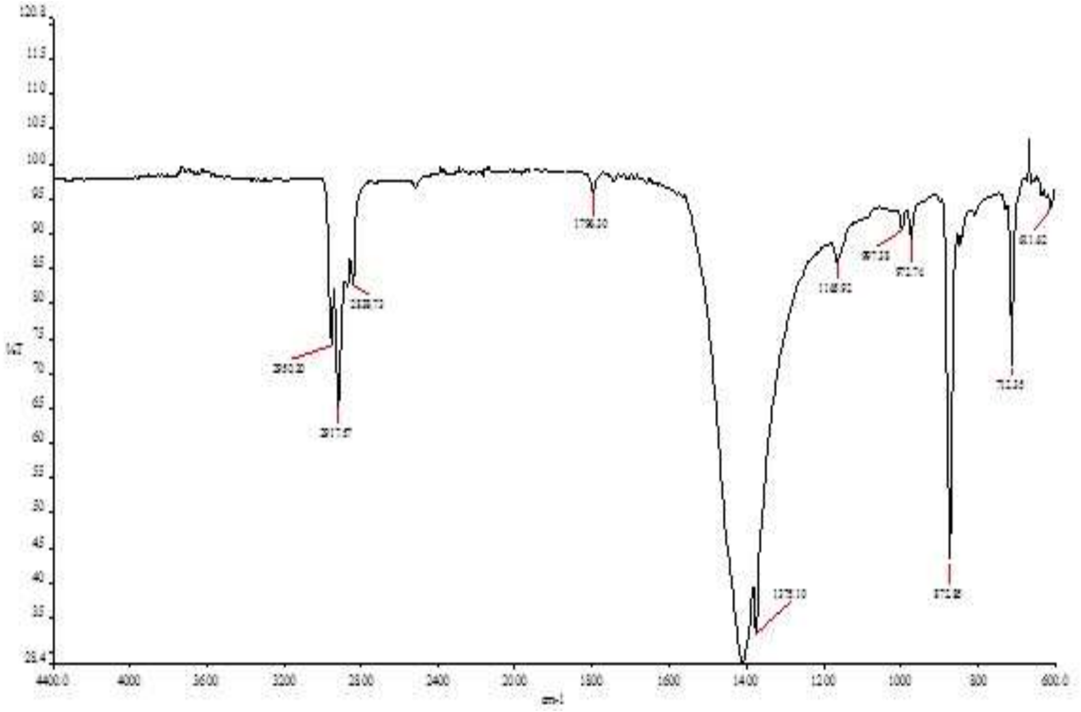

Figure 4.3 : FTIR analysis of PP based commercial breathable compound.

According to FTIR analysis of PE based commercial breathable compound (see in Figure 4.4), the stretching vibration of CH_2 is 2915.79 cm^{-1} (PE). 2838.73 cm^{-1} refers to as CH_2 functional groups and it belongs to PE. The other characteristic peak 1794.37 cm^{-1} is belong to $CaCO_3$ and it is combination functional group (vibration of 1080 and 713). CO_3^{-2} stretching asymmetric peak, which are characteristic peak of $CaCO_3$, can be seen in 1440-1375 cm^{-1}. CO_3^{-2} deformation asymmetric and symetric peaks can be seen in 872.85 cm^{-1} and 712.35 cm^{-1}. It shows us that compound contains the polyethylene and calcium carbonate structures. This situation is supported by literature researches.

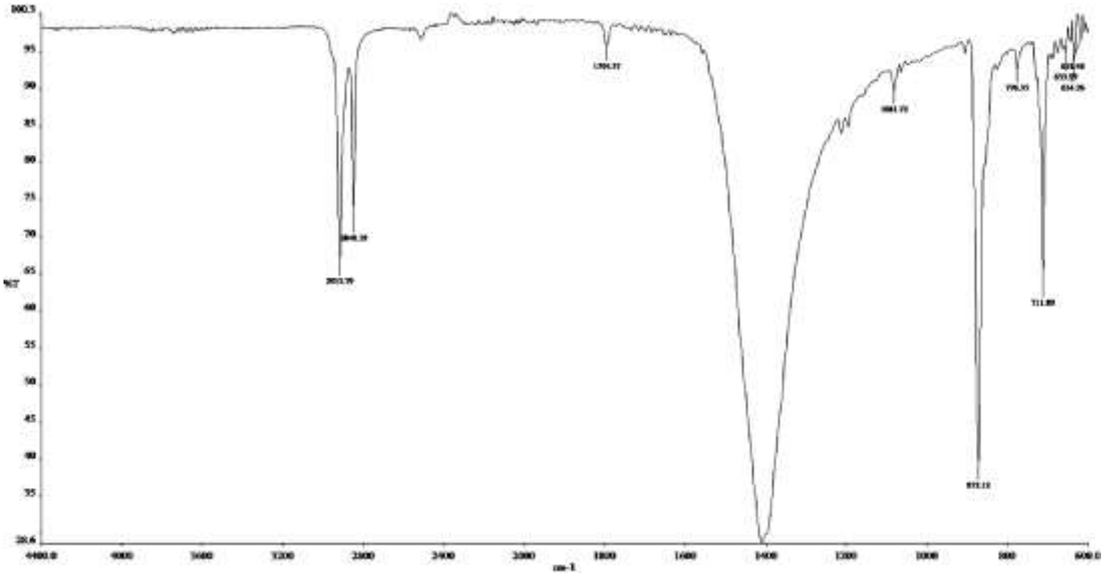

Figure 4.4 : FTIR analysis of PE based commercial breathable compound.

Density results

The measured density of PP and PE based commercial breathable compounds can be seen in Table 4.3.

Table 4.3 : Density results of PP and PE based commercial breathable compounds.

Sample	Density (g/cm^3)
PP based commercial breathable compound	1.49
PE based commercial breathable compound	1.71

The density of the PE based commercial breathable compound is higher than the PP based commercial breathable compound. This is related to the amount of calcium carbonate. Traditionally, structure of PE is suitable to load more filler.

Melt flow rate results

The measured melt flow rate values of PP and PE based commercial breathable compounds under 190 ºC, 2.16 kg condition are shown in Table 4.4.

Table 4.4 : MFR results of PP and PE based commercial breathable compounds.

Sample	MFR (g/10min)
PP based commercial breathable compounds	1.5
PE based commercial breathable compounds	0.6

The MFR of PE based commercial breathable compound is lower than PP based commercial breathable compound. It is related to difference of PP and PE structure. On the other hand, when compared to PP based commercial breathable compound, the filler content in PE based commercial breathable compound is high and it might hinder the plastic flow.

Ash content results

The amount of ash was analyzed to find out how much calcium carbonate contained in the compounds. The PP and PE based commercial breathable compounds were weighed out after the ash oven and the weight loss was determined. Since PP and PE is decomposed at high temperatures, the weight of the calcium carbonate is coming out of the furnace.

The PP based commercial breathable compound has burned away in an air atmosphere at temperatures above 600 °C to find the ash content. Calculations show that the amount of ash is around 59%. It was also supported by the FTIR analysis (see in Figure 4.5) taken after the compound was burned. The absence of the characteristic peaks of calcium carbonate at 900 °C indicates that the burning process is nearly realized.

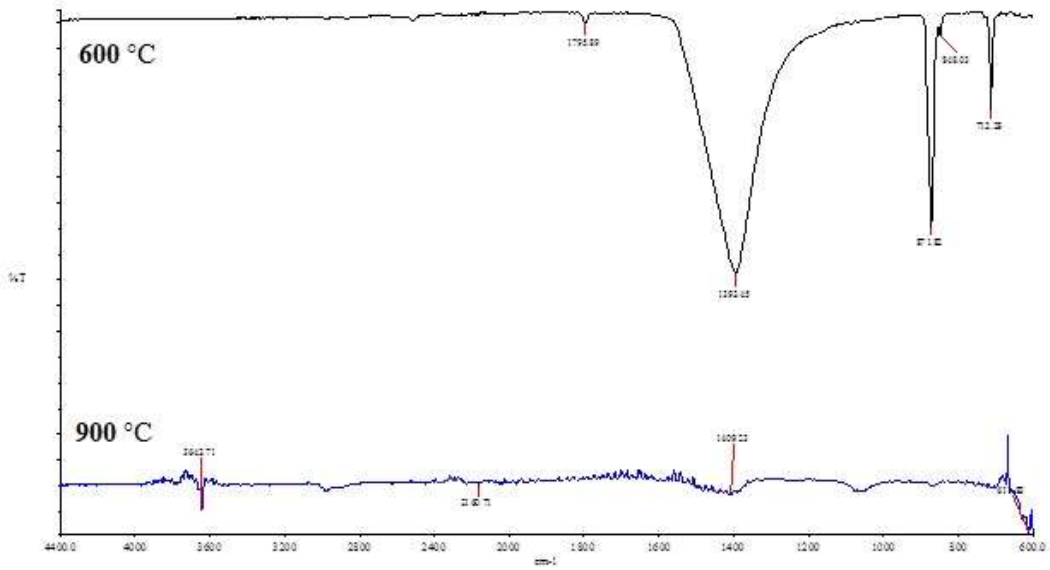

Figure 4.5 : Ash content- FTIR analysis of PP based commercial breathable compound.

The PE based commercial breathable compound has burned away in an air atmosphere at temperatures above 600 °C to find the ash content. Calculations show that the amount of ash is around 70.4%. It was also supported by the FTIR analysis (see in Figure 4.6) taken after the compound was burned. The absence of the characteristic peaks of calcium carbonate at 900 °C indicates that the burning process is nearly realized.

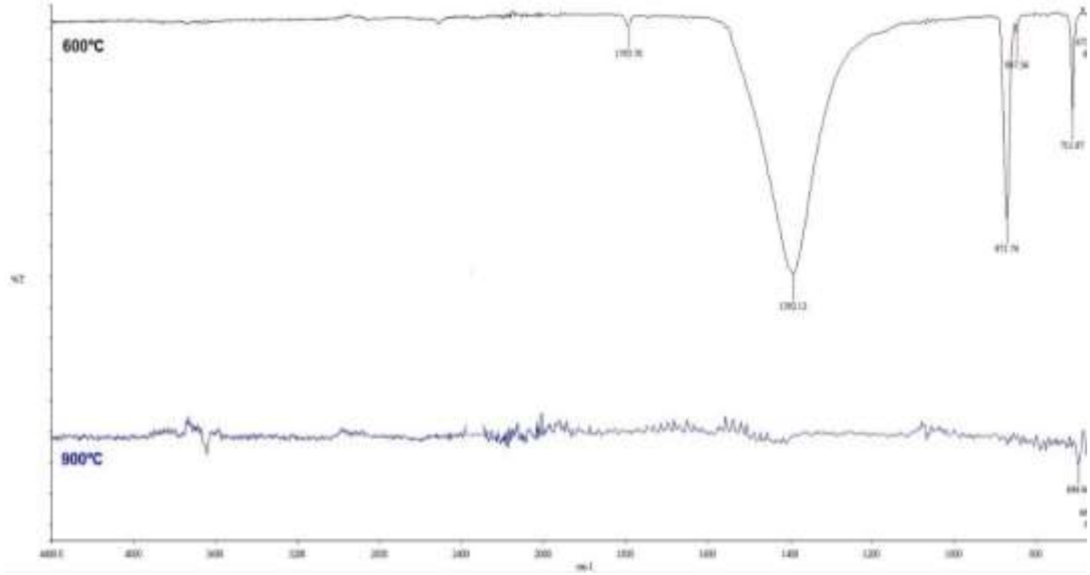

Figure 4.6 : Ash content- FTIR analysis of PE based commercial breathable compound.

The ash content of commercial breathable compounds can be seen in Table 4.5.

Table 4.5 : Ash content results of commercial breathable compounds.

Sample	Ash content (%)
PP based commercial breathable compound	59
PE based commercial breathable compound	70.4

The filler rate is higher in PE based commercial breathable compound.

4.1.1.2 Results of prepared breathable compounds

DSC results

In order to determine the crystallization behaviors of the prepared breathable compounds, DSC analysis are done. We will evaluate the DSC analysis based on the second heating line.

DSC thermogram of C1 is shown in Figure 4.7, which exhibit the peaks at 162.05 ºC and 120.90 ºC. Melting peaks of the materials in the compound 1 were observed. 120.90 ºC belongs to the LLDPE structure and 162.05 ºC belongs to the polypropylenes structures.

DSC thermogram of C2 is shown in Figure 4.8 which exhibit the peaks at 163.51 ºC 112.29 ºC and 120.90 ºC. 112.29 ºC and 120.90 ºC belong to the LLDPE structure and 163.51 ºC belongs to the polypropylenes structures.

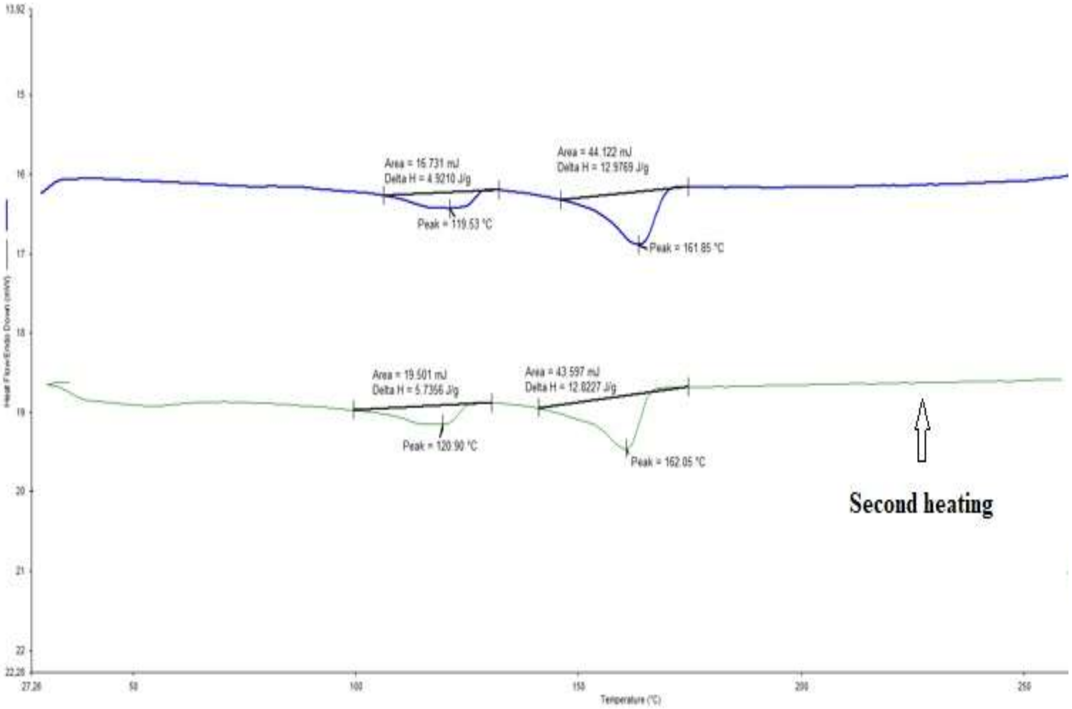

Figure 4.7 : DSC analysis of C1.

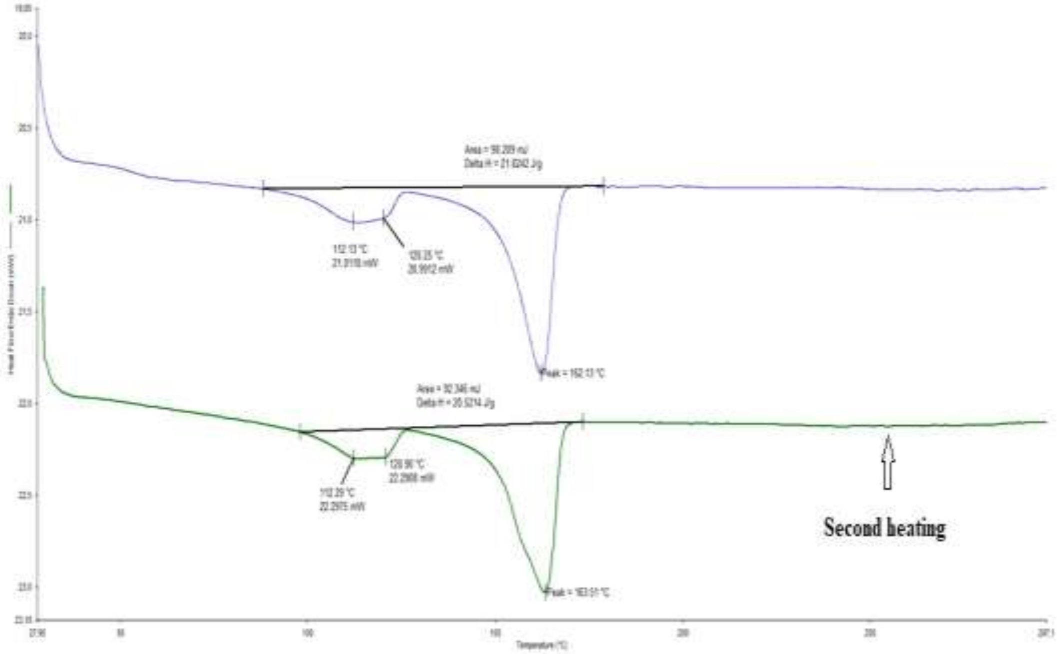

Figure 4.8 : DSC analysis of C2.

FTIR results

According to FTIR analysis of compound 1 (see in Figure 4.9), the stretching vibration peak of CH_3 cm^{-1} is 2948.88 cm^{-1} and belongs to PP structure. The stretching vibration of CH_2 is 2916.01 cm^{-1} and belongs to PE structure. 2848.08 cm^{-1} refers to CH_2 functional groups of PE and 1374.95 cm^{-1} refers to CH_3 functional groups of PP. The other characteristic peak 1794.57 cm^{-1} and belongs to $CaCO_3$. It is combination of functional group (vibration of 1080 and 713). CO_3^{-2} stretching asymmetric peak, which is characteristic peaks of $CaCO_3$, can be seen in 1440-1375 cm^{-1}. Peaks at 1166.21 cm^{-1}, 996.58 cm^{-1} and 972.30 cm^{-1} are correspond to isotactic band of PP. CO_3^{-2} deformation asymmetric and symetric can be seen in 873.48 cm^{-1} and 712.01 cm^{-1} peaks. It shows us that compound contains the polypropylene, polyethylene and calcium carbonate structures. This situation is supported by literature researches.

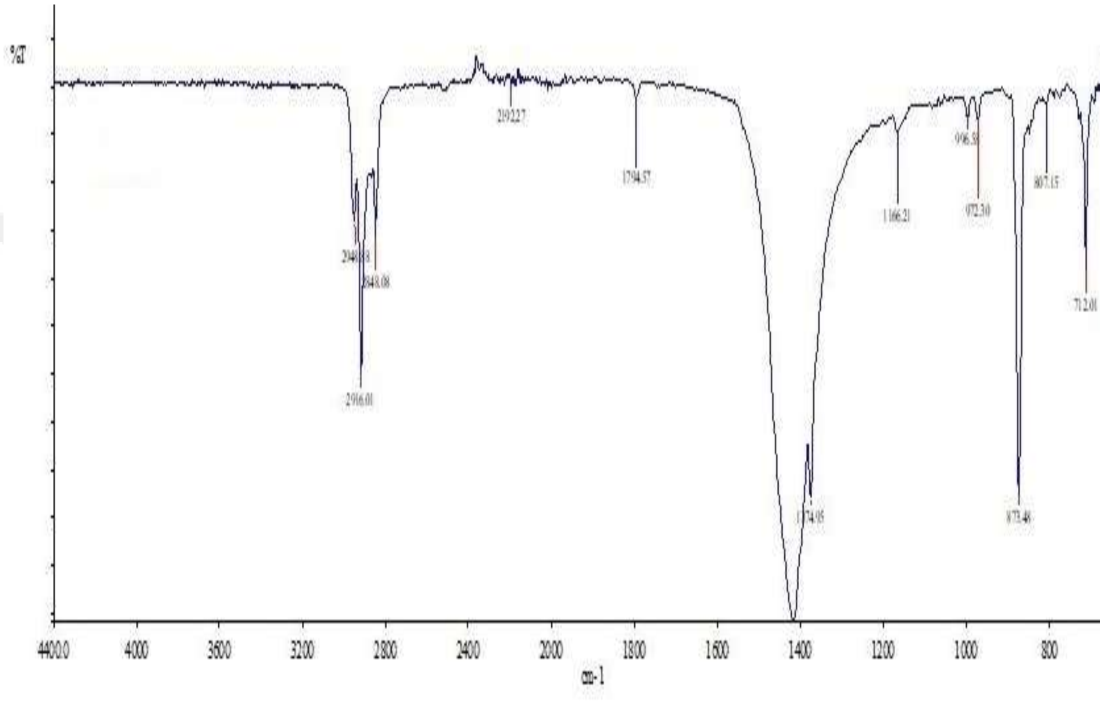

Figure 4.9 : FTIR analysis of C1.

According to FTIR analysis of compound 2 (see in Figure 4.10), the stretching vibration peak of CH_3 cm^{-1} is 2948.87 cm^{-1} and belongs to PP structure. The stretching vibration of CH_2 is 2916.34 cm^{-1} and belongs to PE structure. 2848.05 cm^{-1} refers to CH_2 functional groups of PE and 1374.54 cm^{-1} refers to CH_3 functional groups of PP. The other characteristic peak 1794.03 cm^{-1} and belongs to $CaCO_3$. It is combination of functional group (vibration of 1080 and 713). CO_3^{-2} stretching asymmetric peak, which is characteristic peak of $CaCO_3$, can be seen in 1440-1375 cm^{-1}. Peaks at 1164.48 cm^{-1}, 993.58 cm^{-1} and 972.18 cm^{-1} are corresponds to isotactic band of PP. CO_3^{-2} deformation asymmetric and symetric can be seen in 872.74 cm^{-1} and 711.89 cm^{-1} peaks. It shows us that compound contains the polypropylene, polyethylene and calcium carbonate structures. This situation is supported by literature researches.

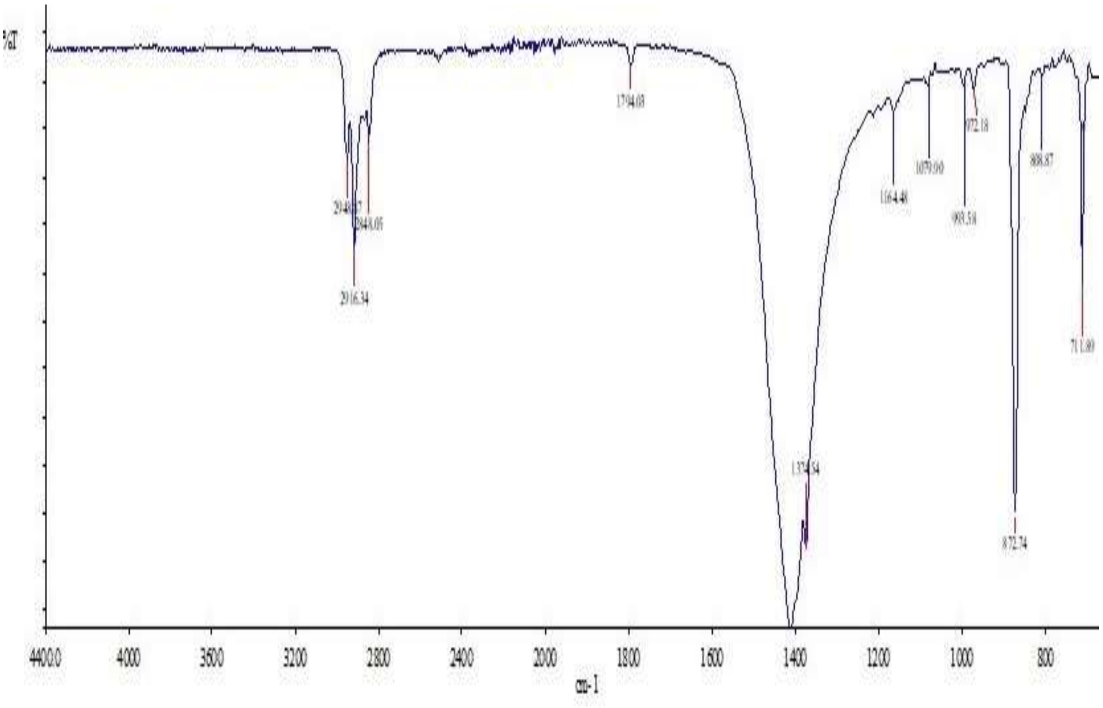

Figure 4.10 : FTIR analysis of C2.

Density results

The measured density values of C1 and C2 can be seen in Table 4.6.

Table 4.6 : Density results of C1 and C2.

Sample	Density (g/cm^3)
C1	1.36
C2	1.50

The calcium carbonate, which is forming the majority of the matrix, is particularly important in determining these density values. It can be seen that from Figure 4.11 that the density is increased by increasing the amount of calcium carbonate.

As is known from literature studies, the addition of filler to virgin polymers increases the density. This is confirmed when the prepared compounds, C1 and C2, are compared with virgin PP and PE. Since the ratio of calcium carbonate contained in C2 and PP based commercial breathable compound is close, the densities are similar. The analysis of PE based commercial breathable compound showed that the ratio of calcium carbonate was higher than that of all samples. For this reason, the density of this sample is high.

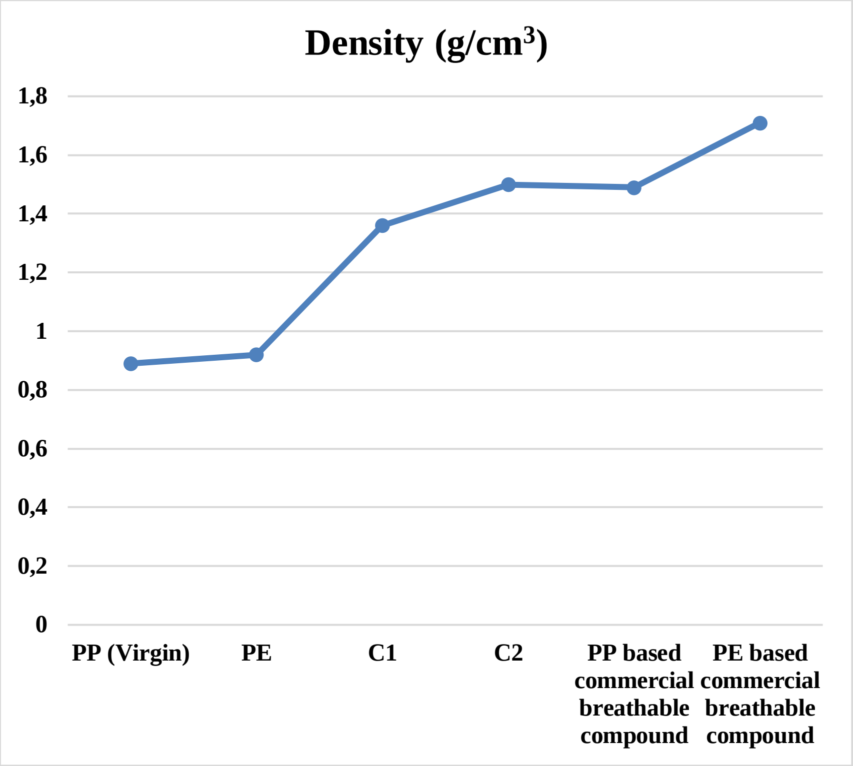

Figure 4.11 : Comparison of density results with virgin polymers and commercial breathable compounds.

Melt flow rate results

The measured melt flow rate values of C1 and C2 under 190 ºC, 2.16 kg condition are shown in Table 4.7. The melt flow rate value is important to determine the extruder conditions during the production phase and to understand the flow of the material through the screw. The prepared compounds have the values that can be fed to the blown film extruder.

Table 4.7 : MFR results of C1 and C2.

Sample	MFR (g/10min)
C1	1.42
C2	1.90

The calcium carbonate is particularly important in determining MFR values. It can be seen that from Figure 4.12 that the MFR is increased by increasing the amount of calcium carbonate. It is known that the melt rheological properties of compounds are directly related to the degree of dispersion of the polymer matrix and the level of interfacial interactions between the filler and polymer. Because the incorporation of fillers hinders plastic flow and increases the viscosity of a polymer melt, a reduction of MFR with the filler loading is expected. We can see this when we compare the PE-based commercial breathable compound with virgin PE.

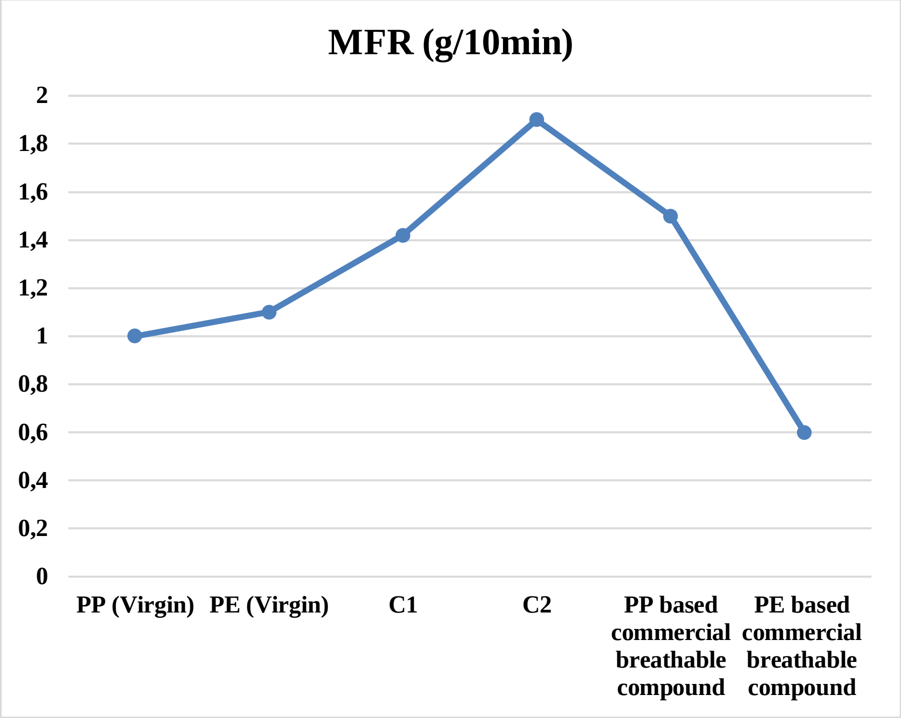

Figure 4.12 : Comparison of MFR results with virgin polymers and commercial breathable compounds.

On the other hand, the overall MFR values of $CaCO_3$-filled PP based breathable compounds are higher than virgin PP. This may signify that $CaCO_3$ has the ability to increase the plasticity and processability of the PP matrix. Also, it can be expected that filler treatmant improves the particle distribution and increases the MFR because it inhibits agglomeration. The surface of the calcium carbonate particles used in the thesis study is coated and it has the lower particle size that can be well dispersed.

According to the literature researches, it is known that PP and calcium carbonate have better interaction than PE.

Ash content results

According to the weight loss analysis and FTIR graph (see in Figure 4.13), it was determined that, C1 contained amounts of calcium carbonate between 49-50%. According to this, we did authenticate the rate of calcium carbonate loading with analysis. This shows us that there is a homogeneous distribution in the polymer matrix. Otherwise we could see the difference between the calculated and applied amount of calcium carbonate because of the clustering/aggregation problem.

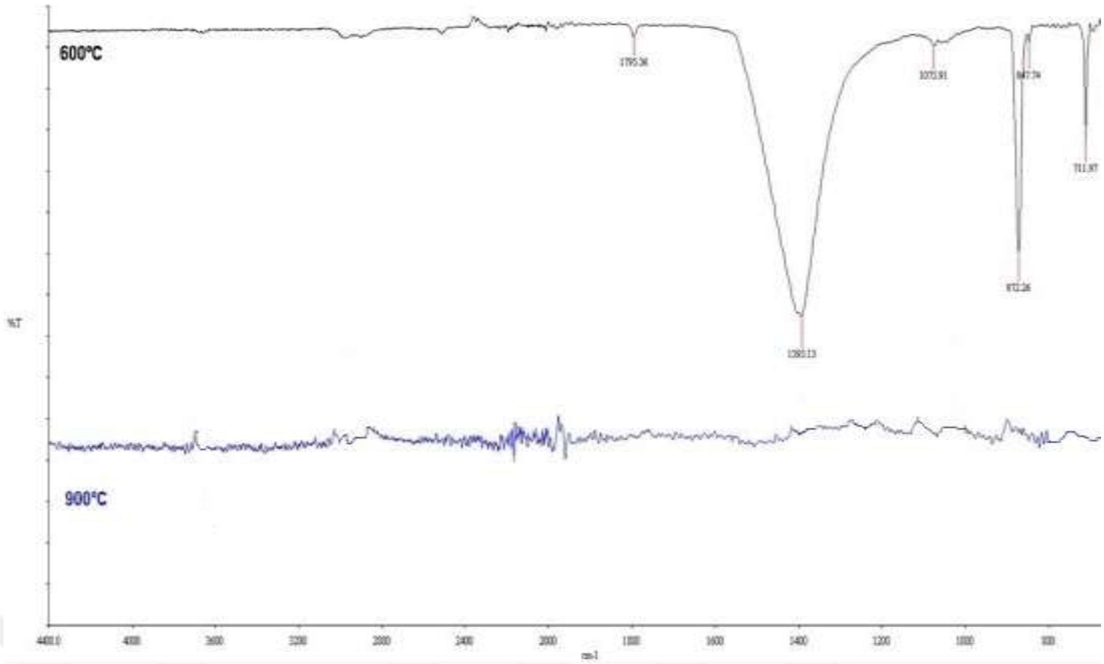

Figure 4.13 : Ash content- FTIR analysis of C1.

According to the weight loss analysis and FTIR graph (see in Figure 4.14), it was determined that, C2 contained amounts of calcium carbonate between 59-60%. According to this, we did authenticate the rate of calcium carbonate loading with analysis. This shows us that there is a homogeneous distribution in the polymer matrix. Otherwise we could see the difference between the calculated and applied amount of calcium carbonate because of the clustering/aggregation problem.

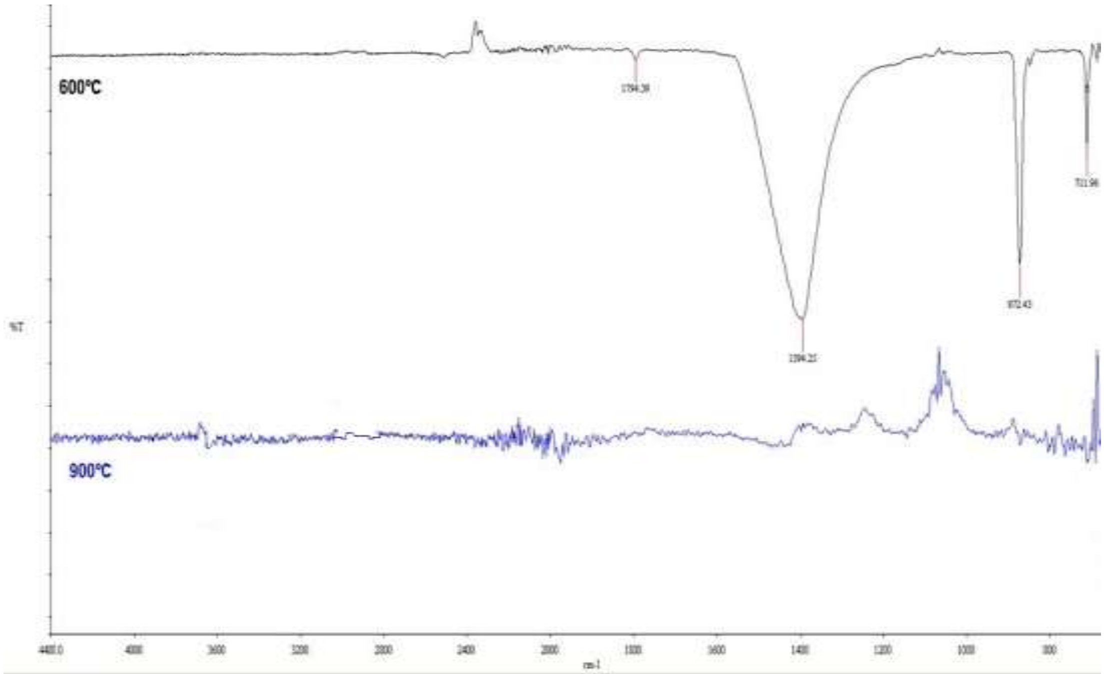

Figure 4.14 : Ash content- FTIR analysis of C2.

The ash content of C1 and C2 can be seen in Table 4.8.

Table 4.8 : Ash content results of C1 and C2.

Sample	Ash content (%)
C1	50
C2	60

As can be seen from Figure 4.15, filler rate of PE based commercial breathable compound is higher than other samples. It has been observed that filler loading is made at higher ratios in the compounds prepared with polyethylene.

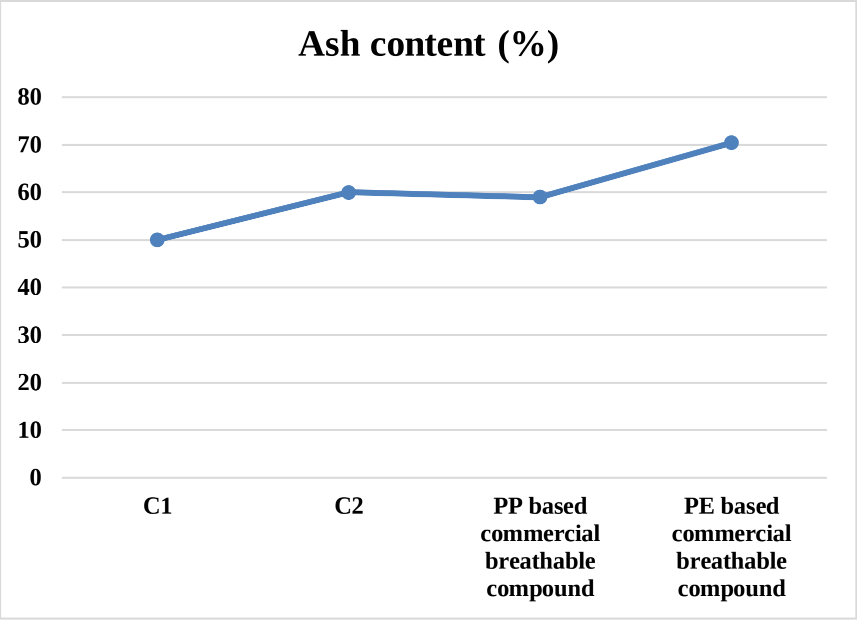

Figure 4.15 : Comparison of ash content results with commercial breathable compounds.

4.1.2 Results of breathable film samples analysis

Within the scope of the thesis, films were produced by blown film extruder with using C1 and C2 compounds. Experimental design was planned based on different LLDPE and different compound levels according to Table 4.9.

4 films were planned to be produced, but 3 films were produced during production.

Table 4.9 : Experimental desing of blown film extrusion.

Material	BF1	BF2	BF3	BF4
Compound	C1	C1	C2	C2
LLDPE (%)	0	15	0	15

The properties of the produced films will be compared to a commercial microporous PE based breathable film.

4.1.2.1 Results of commercial breathable film sample analysis

The commercial microporous PE based breathable film was analyzed as control sample and the results were compared with the prepared microporous PP breathable film samples. The commercial microporous PE based breathable film is considered as a control film especially in terms of mechanical properties and WVTR MOCON analysis.

Some analyzes have been made to understand the structure and processing characteristics of commercial microporous PE based breathable film sample.

DSC result

Thermal analysis was done by DSC. During preparation of sample, it may have some thermal history. By having first heating, we are removing all thermal history. In next heating our sample shows real thermal response and it is free from any thermal history. For this reason, the second heating line will be considered.

The melting temperature peak of commercial microporous PE based breathable film was determined. The melting peak at 121° C was observed according to the Figure 4.16, which refers to PE structure. This shows us that the matrix mostly involves linear low density polyethylene. There is no other melting peak except for the PE structure.

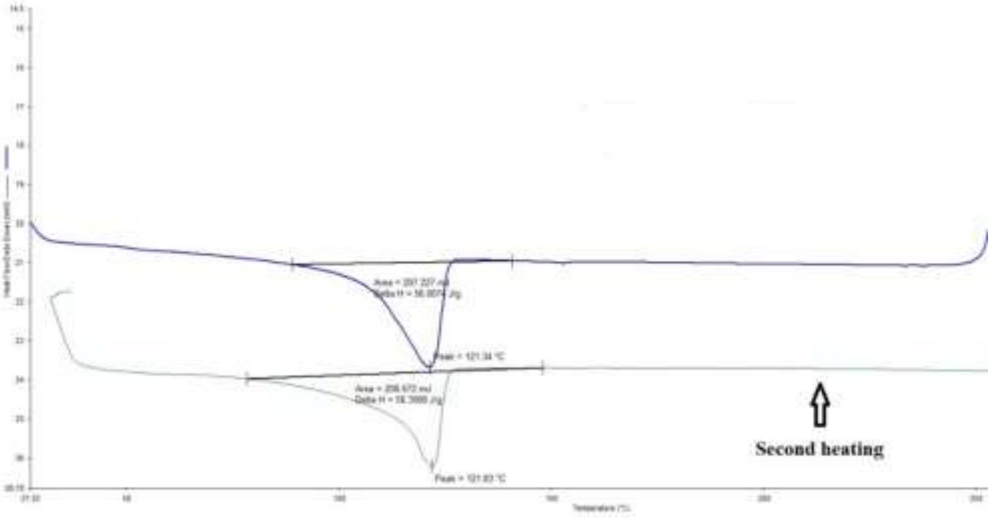

Figure 4.16 : DSC analysis of commercial microporous PE based breathable film.

FTIR result

Surface 1 and Surface 2 of film have similar absorption peaks. For this reason, the comments have made based on surface 1.

According to FTIR analysis of commercial microporous PE based breathable film (see in Figure 4.17), the stretching vibration of CH_2 is 2916.07 cm^{-1} (PE). 2848.69 cm^{-1} refers to as CH_2 functional group and it belongs to PE. The other characteristic peak 1795.35 cm^{-1} is belong to $CaCO_3$ and it is combination functional group (vibration of 1080 and 713). CO_3^{-2} stretching asymmetric peak, which is characteristic peak of $CaCO_{3,}$ can be seen in 1440-1375 cm^{-1}. CO_3^{-2} deformation asymmetric and symetric peaks can be seen in 874.02 cm^{-1} and 712.41 cm^{-1}. It shows us that the film contains polyethylene and calcium carbonate structures. This situation is supported by literature researches.

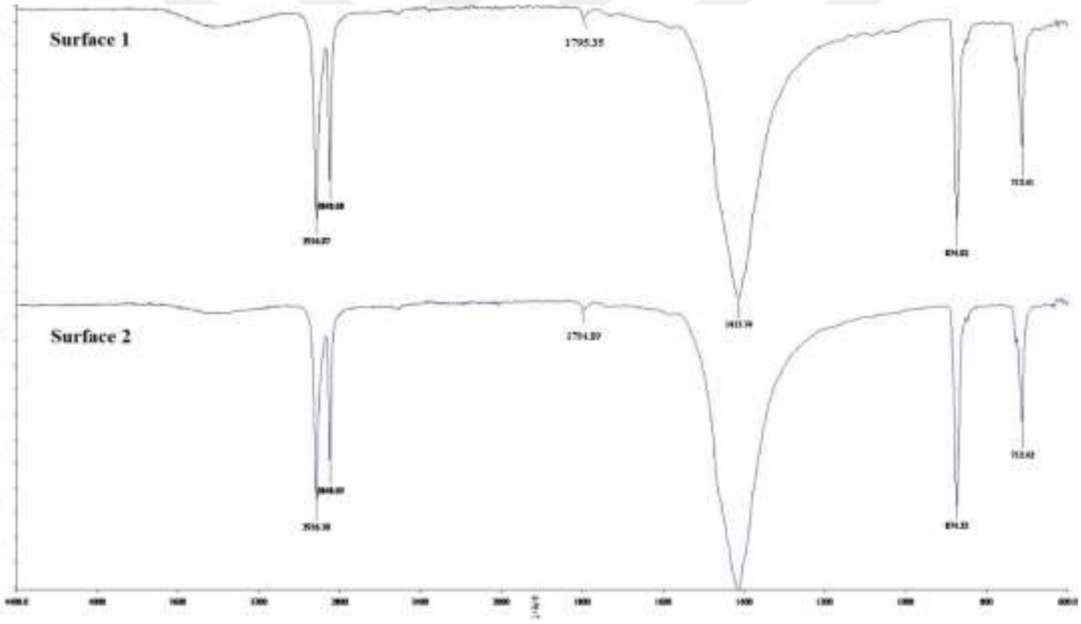

Figure 4.17 : FTIR analysis of commercial microporous PE based breathable film.

Density result

The measured density value of commercial microporous PE based breathable film is 1,41 g/cm^3. As is known, the most important parameter affecting the density value in such structures is the amount of calcium carbonate. The amount of calcium carbonate increases the density values.

Melt flow rate result

The measured melt flow rate value of commercial microporous PE based breathable film is 0.83 g/10 min. The result was taken under 190 ºC, 2.16 kg condition. It can be considered that the viscosity increases and the MFR decreases, since the filler ratio is high.

Ash content result

The amount of ash was analyzed to find out how much calcium carbonate contained in the commercial microporous PE based breathable film. Since PE is decomposed at high temperatures, the weight of the calcium carbonate is coming out of the furnace.

The commercial microporous PE based breathable film has burned away in an air atmosphere at temperatures above 600 °C to find the ash content. Calculation shows that the amount of ash is around 51.2%. It was also supported by the FTIR analysis (see in Figure 4.18) taken after the film was burned. The absence of the characteristic peaks of calcium carbonate at 900 °C indicates that the burning process is nearly realized.

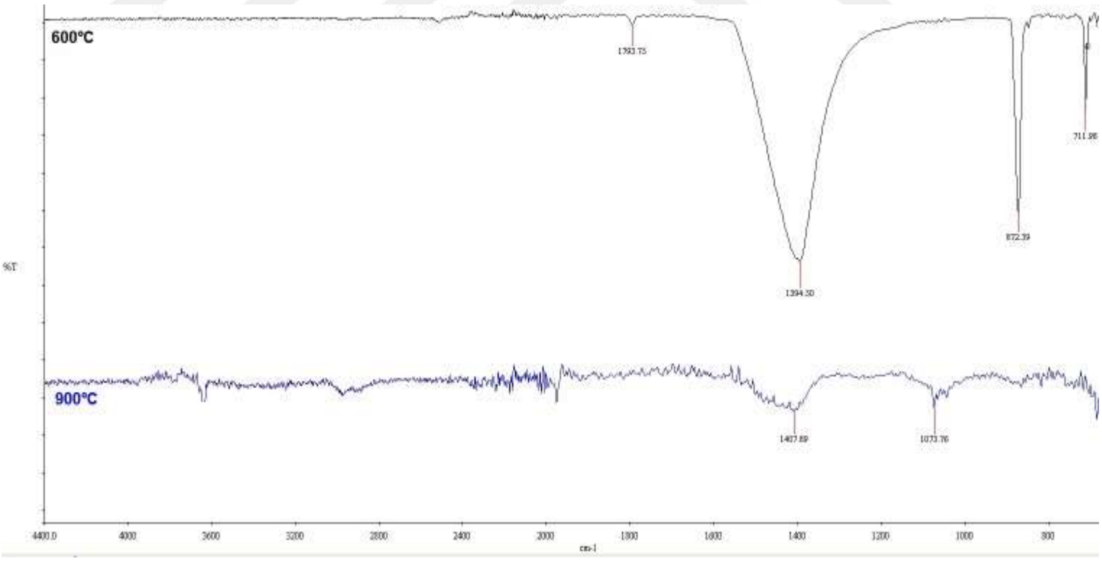

Figure 4.18 : Ash content- FTIR analysis of commercial microporous PE based breathable film.

Mechanical properties result

The mechanical properties result of commercial microporous PE based breathable film is given in Table 4.10.

Table 4.10 : Mechanical properties result of commercial microporous PE based breathable film.

Sample	Tensile Elongation at Break (%)		Tensile Strength (N/mm^2)		Elastic Modulus (N/mm^2)	
	MD	CD	MD	CD	MD	CD
Commercial Microporous PE Breathable Film	65	513	68	5.5	232	102

The difference in MD and CD may be indicative of blown film production and MD direction stretching.

Elmendorf tear strength result

The tear strength result of commercial microporous PE based breathable film is given in Table 4.11.

Table 4.11 : Elmendorf tear strength result of commercial microporous PE based breathable film.

Sample	Tear Strength (N/mm)	
	MD	CD
Commercial Microporous PE Breathable Film	554	3483

The result can be associated with the material structure. The difference in MD and CD may be indicative of blown film production and MD direction stretching.

WVTR MOCON result

WVTR is a measure of the passage of water vapor through a film under specified conditions. The ambit conditions are 38 °C and 100% relative humidity. The WVTR MOCON result of commercial microporous PE based breathable film sample is given in Table 4.12.

Table 4.12 : WVTR MOCON result of commercial microporous PE based breathable film.

Sample	WVTR MOCON (g/m^2.day.atm)
Commercial Microporous PE Breathable Film	3500

There are many parameters that affect permeability. Vapor permeability can be explained by the material structure and the calcium carbonate ratio in general, if we consider the conditions of the stretching constantly. The number and size of the micropores formed by the stretching depends on the material structure and the amount of calcium carbonate.

Grammage result

The grammage result of commercial microporous PE based breathable film is given in Table 4.13. Especially 16 g/m^2 was selected for comparison with the prepared breathable film samples.

Table 4.13 : Grammage result of commercial microporous PE based breathable film.

Sample	Grammage (g/m^2)
Commercial Microporous PE Breathable Film	16

SEM result

The dispersion of $CaCO_3$ in the matrix and micro pores between the matrix and filler upon stretching are investigated using a Scanning Electron Microscopy (SEM) photographs. The micropores obtained in breathable films are unseeable with eyes. For this reason, SEM analysis is an important method for interpreting surface morphology. It is expected that polyolefin and inorganic fillers will physically separate from each other and form micropores.

The SEM image of commercial microporous PE breathable film can be seen in Figure 4.19.

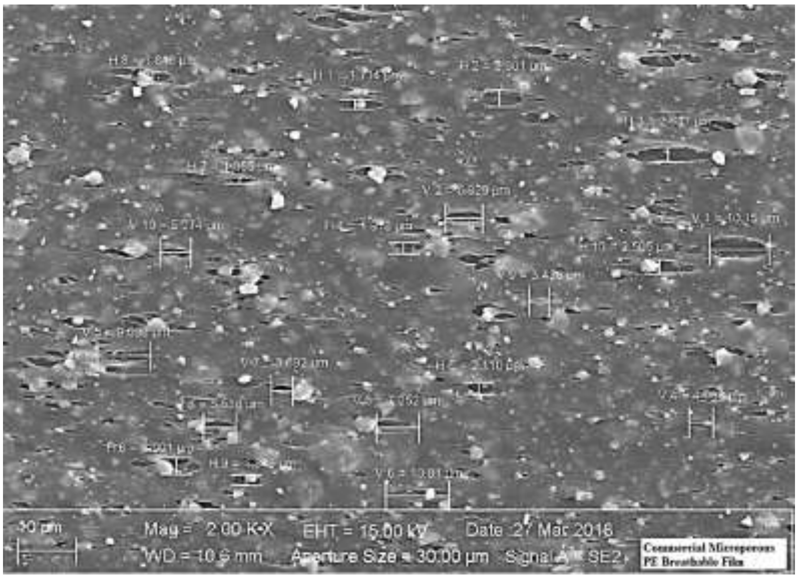

Figure 4.19 : SEM micrograph of commercial microporous PE breathable film.

As can be seen from the figure, the pores are dark, the polyolefin, which is PE in this sample, is mid-gray, and the $CaCO_3$ particles are white. This useful contrast is ideal for the image processing and analysis to follow. SEM images of the film exhibit a porous structure at the surface skin layers, in the range of µm.

The micropores are present on the surface of the commercial product, as can be seen in the 2000-fold magnified view. The size and alignment of the micro pores are random. The dispersion of $CaCO_3$ in the matrix gives a good image. This can be explained as a reduction of the surface energy between the filler and the matrix by coating of the filler.

Table 4.14 : Por sizes of commercial microporous PE breathable film.

Sample	Por Sizes (µm)	
	Horizontal	Vertical
Commercial Microporous PE Breathable Film	1.714	10.15
	2.901	6.329
	2.637	7.252
	1.978	4.088
	2.110	9.098
	2.901	10.81
	1.055	3.692
	1.846	5.538
	1.846	3.428
	2.505	5.274

It is seen that the sizes of micro pores are changed at vertical and horizontal level. The Table 4.14 shows that the por size is larger at the vertical level. This indicates that the vertical level is the direction of stretching.

4.1.2.2 Results of prepared breathable film samples analysis

In this section, the specified analyzes were made for all film samples that produced according to experimental design.

BF1, BF2, BF4 coded samples and PE film samples can be seen in Figure 4.20.

DSC results

Thermal analysis of the blend films shows their melting temperatures and crystallization behaviours. It is an important tool to perform retrospective characterization of prepared samples. In this regard, we will be able to compare the theoretical expectation with reality. We will evaluate the DSC analysis based on the second heating line.

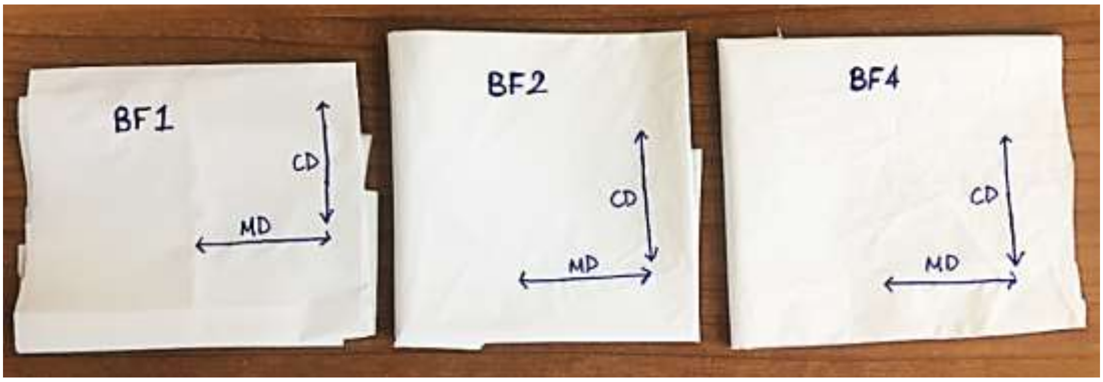

Figure 4.20 : Samples of experiments.

DSC thermogram of BF1 is shown in Figure 4.21. Regarding to the second heating of the thermogram, melting peaks can be seen at 161.15 ºC, 115.82 ºC and 120.88 ºC. 115.82 ºC and 120.88 ºC belong to the LLDPE structure and 161.15 ºC belongs to the polypropylenes structures.

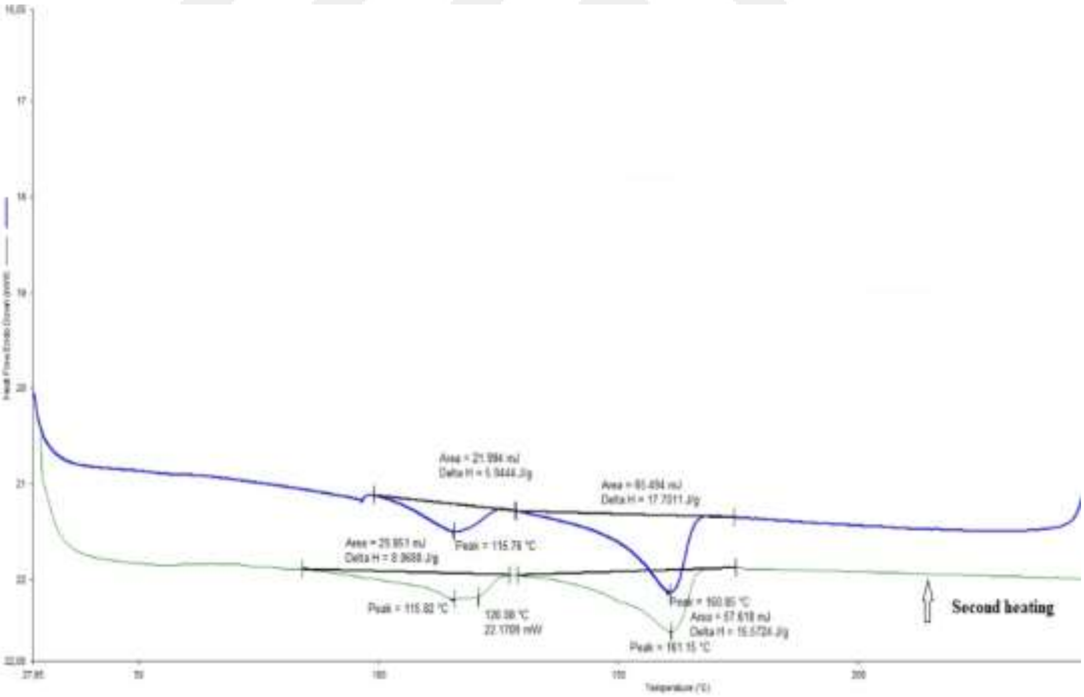

Figure 4.21 : DSC analysis of BF1.

DSC thermogram of BF2 is shown in Figure 4.22. Regarding to the second heating of the thermogram, melting peaks can be seen at 159.51 ºC, 117.34 ºC and 121.02 ºC. 117.34 ºC and 121.02 ºC belong to the LLDPE structure and 159.51 ºC belongs to the polypropylenes structures.

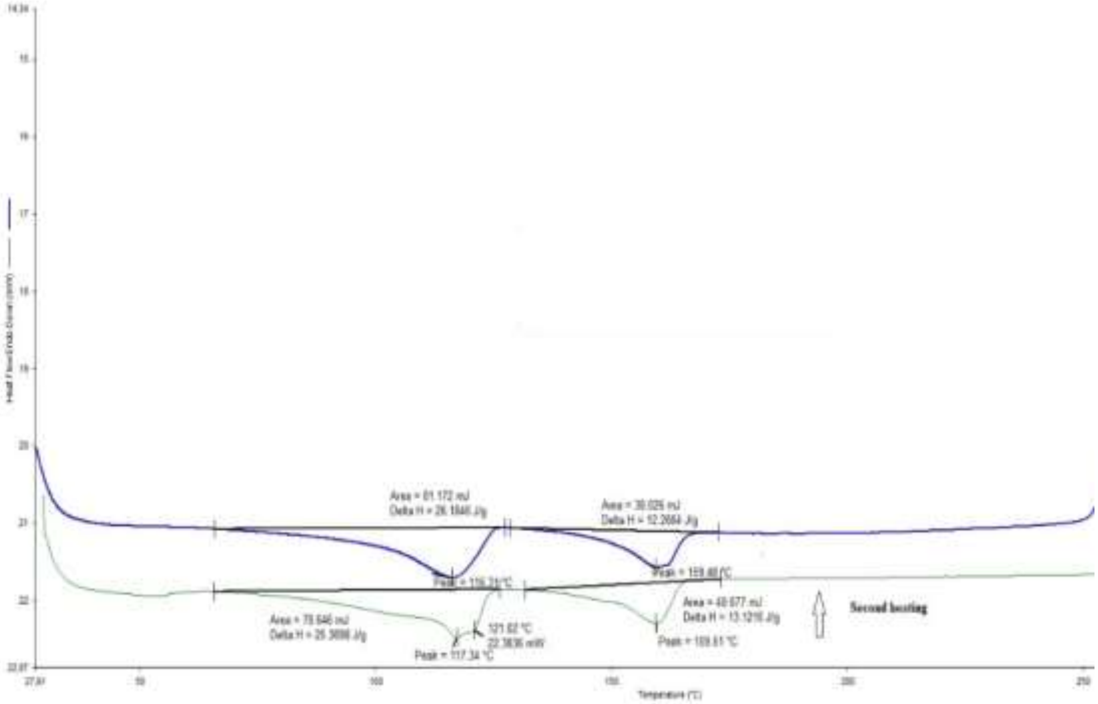

Figure 4.22 : DSC analysis of BF2.

DSC thermogram of BF4 is shown in Figure 4.23. Regarding to the second heating of the thermogram, melting peaks can be seen at 161.83 ºC, 117.00 ºC and 121.04 ºC. 117.00 ºC and 121.04 ºC belong to the LLDPE structure and 161.83 ºC belongs to the polypropylenes structures.

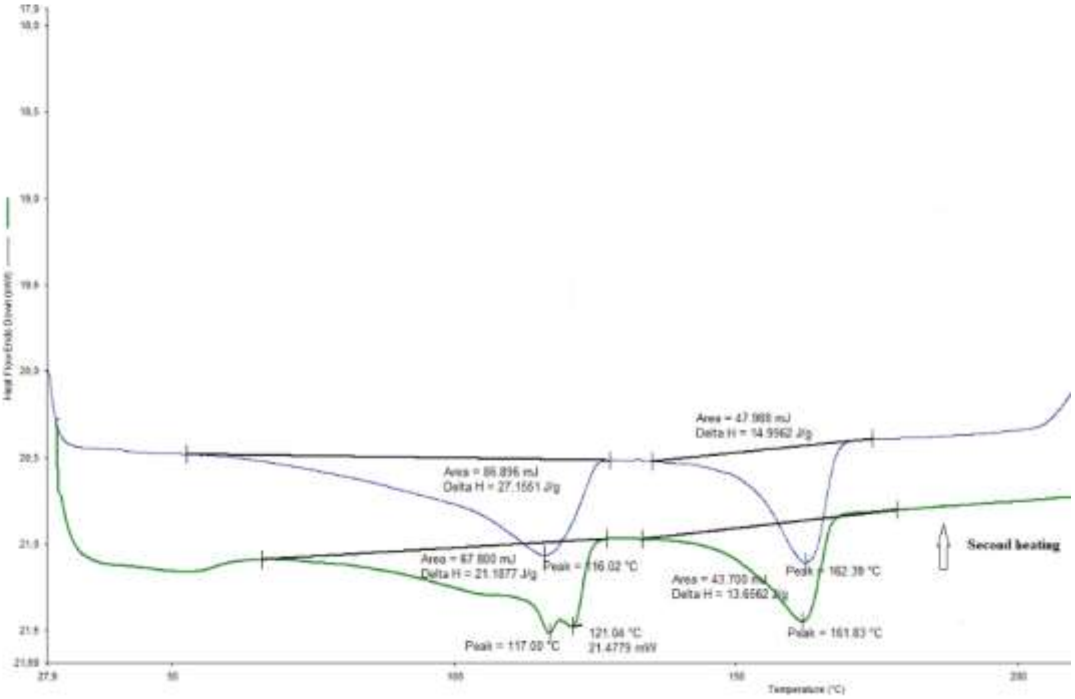

Figure 4.23 : DSC analysis of BF4.

FTIR results

FTIR analysis was taken for both surfaces of films since the produced films are coex structure. As each layer of the coex structure contains the same formula, the FTIR graph on both surfaces should show frequency at similar wavelengths. Comments were made based on wavelengths of surface 1 of each experiment.

According to FTIR analysis of BF1 (see in Figure 4.24), the stretching vibration peak of CH_3 cm^{-1} is 2949.53 cm^{-1} and belongs to PP structure. The stretching vibration of CH_2 is 2916.39 cm^{-1} and belongs to PE structure. 2848.50 cm^{-1} refers to CH_2 functional groups of PE and 1375.27 cm^{-1} refers to CH_3 functional groups of PP. The other characteristic peak 1795.57 cm^{-1} and belongs to $CaCO_3$. It is combination of functional group (vibration of 1080 and 713). CO_3^{-2} stretching asymmetric peak, which is characteristic peak of $CaCO_3$, can be seen in 1440-1375 cm^{-1}. Peaks at 1166.07 cm^{-1}, 997.05 cm^{-1} and 972.25 cm^{-1} are correspond to isotactic band of PP. CO_3^{-2} deformation asymmetric and symetric peaks can be seen in 873.75 cm^{-1} and 712.08 cm^{-1}. It shows us that BF1 contains the polypropylene, polyethylene and calcium carbonate structures. This situation is supported by literature researches.

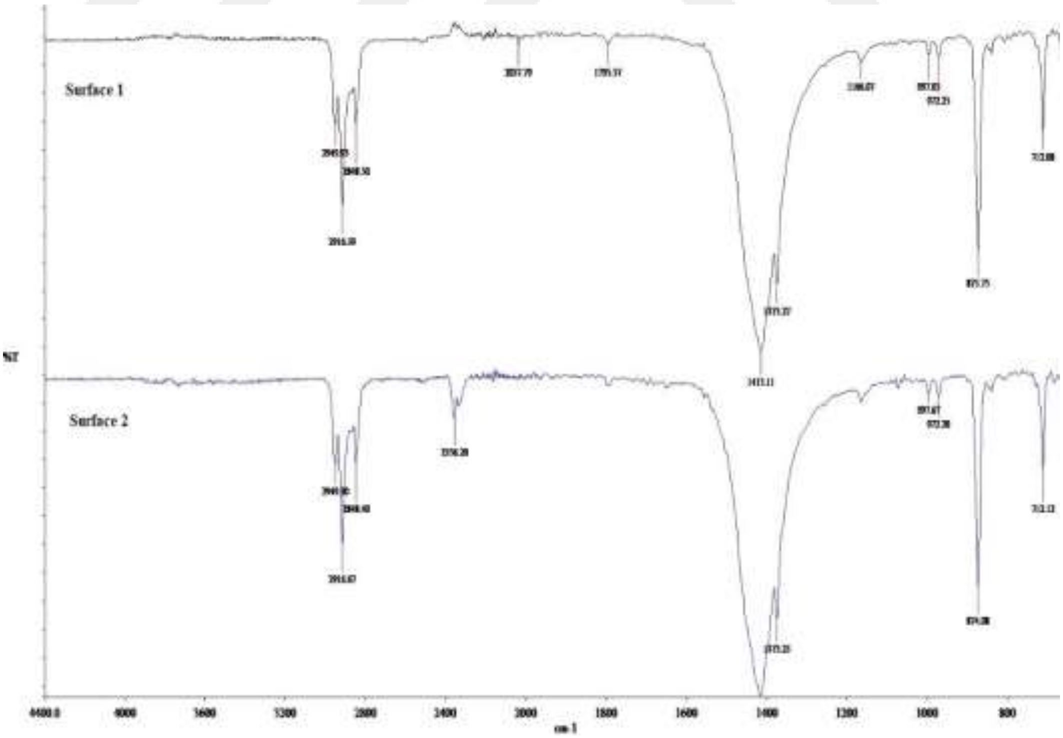

Figure 4.24 : FTIR analysis of BF1.

According to FTIR analysis of BF2 (see in Figure 4.25), the stretching vibration peak of CH_3 cm^{-1} is 2949.37 cm^{-1} and belongs to PP structure. The stretching vibration of

CH_2 is 2915.97 cm^{-1} and belongs to PE structure. 2848.15 cm^{-1} refers to CH_2 functional groups of PE and 1375.35 cm^{-1} refers to CH_3 functional groups of PP. The other characteristic peak 1795.01 cm^{-1} and belongs to $CaCO_3$. It is combination of functional group (vibration of 1080 and 713). CO_3^{-2} stretching asymmetric peak, which is characteristic peak of $CaCO_3$, can be seen in 1440-1375 cm^{-1}. Peaks at 1166.42 cm^{-1}, 998.01 cm^{-1} and 972.36 cm^{-1} are correspond to isotactic band of PP. CO_3^{-2} deformation asymmetric and symetric peaks can be seen in 874.08 cm^{-1} and 712.17 cm^{-1}. It shows us that BF2 contains the polypropylene, polyethylene and calcium carbonate structures. This situation is supported by literature researches.

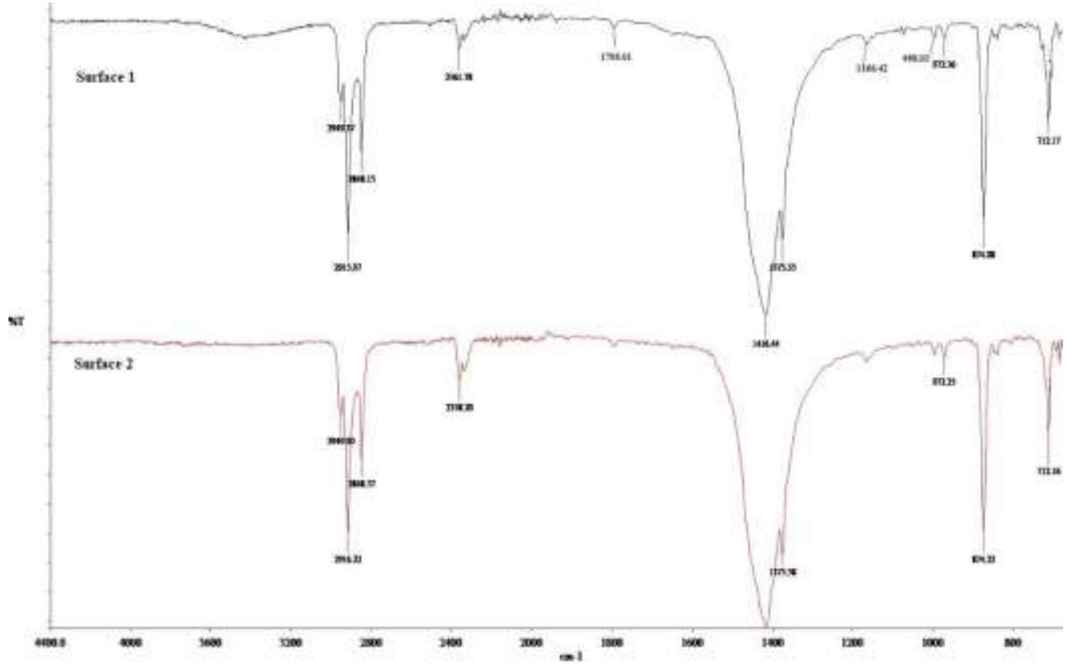

Figure 4.25 : FTIR analysis of BF2.

According to FTIR analysis of BF4 (see in Figure 4.26), the stretching vibration peak of CH_3 cm^{-1} is 2949.95 cm^{-1} and belongs to PP structure. The stretching vibration of CH_2 is 2916.17 cm^{-1} and belongs to PE structure. 2848.26 cm^{-1} refers to CH_2 functional groups of PE and 1375.49 cm^{-1} refers to CH_3 functional groups of PP. The other characteristic peak 1795.04 cm^{-1} and belongs to $CaCO_3$. It is combination of functional group (vibration of 1080 and 713). CO_3^{-2} stretching asymmetric peak, which is characteristic peak of $CaCO_3$, can be seen in 1440-1375 cm^{-1}. Peaks at 1167.03 cm^{-1}, 997.36 cm^{-1} and 972.10 cm^{-1} are correspond to isotactic band of PP. CO_3^{-2} deformation asymmetric and symetric peaks can be seen in 873.88 cm^{-1} and 712.09 cm^{-1}. It shows us that BF4 contains the polypropylene, polyethylene and calcium carbonate structures. This situation is supported by literature researches.

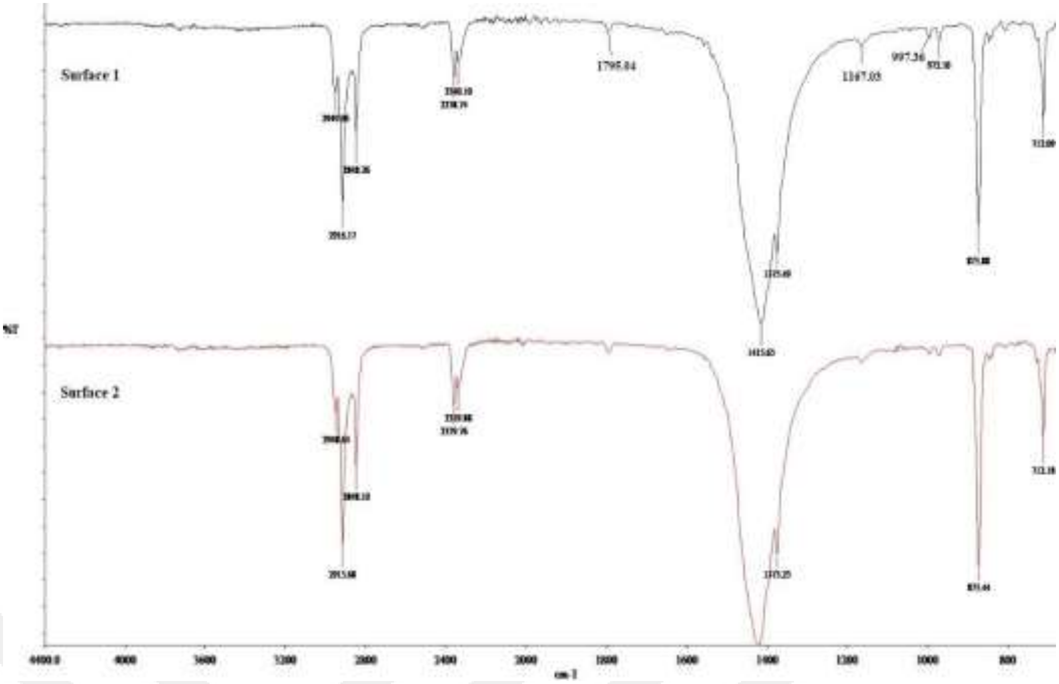

Figure 4.26 : FTIR analysis of BF4.

Density results

The measured density values of BF1, BF2 and BF4 are shown in Table 4.15. The calcium carbonate, which is forming the majority of the matrix, is particularly important in determining these density values. The ratio of calcium carbonate in the film content is analyzed with ash content analysis. This analysis is directly influential in the interpretation of the density.

Table 4.15 : Density results of film samples.

Sample	Density (g/cm^3)
BF1	1.36
BF2	1.28
BF4	1.37

The ratio of calcium carbonate in the film content is analyzed with ash content analysis. This analysis is directly influential in the interpretation of the density. As can be seen from the Figure 4.27, the density is directly proportional to the ratio of calcium carbonate.

Melt flow rate results

The measured melt flow rate values of BF1, BF2 and BF4 are shown in Table 4.16. The results were taken under 190 °C, 2.16 kg condition.

Table 4.16 : MFR results of film samples.

Sample	MFR (g/10min)
BF1	1.77
BF2	1.43
BF4	2.81

According to the examination of experimental film samples based on PP, it is seen that the melt flow rate increases with increasing amount of calcium carbonate in film matrix (see in Figure 4.28). As previously described, the flow of polymer may increase when the coated and well dispersed filler is load. It can increase the interaction between filler and polymer.

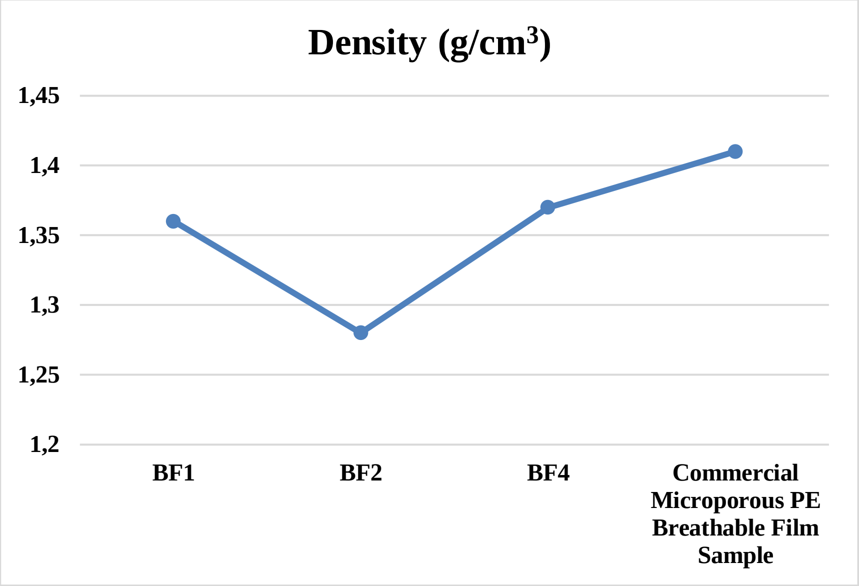

Figure 4.27 : Density results comparison of film samples.

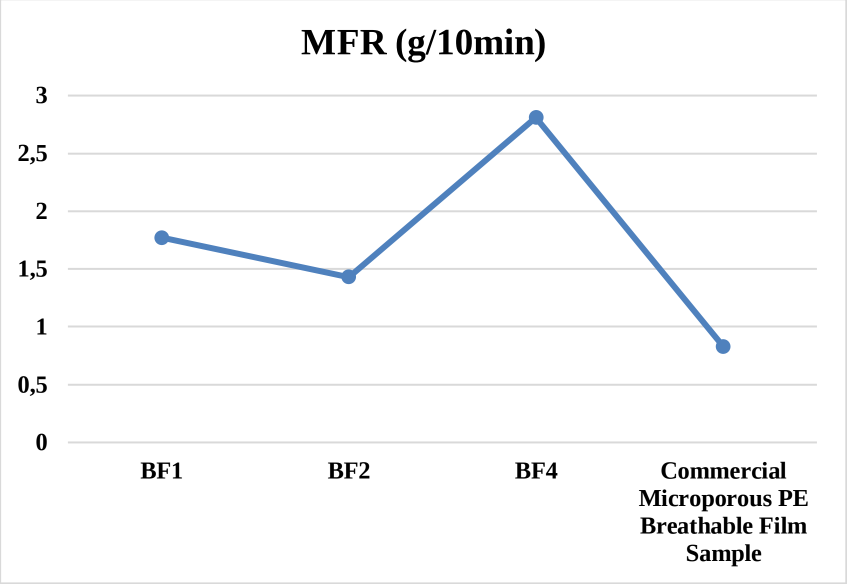

Figure 4.28 : MFR comparison of film samples.

The interaction between PP and calcium carbonate is better than PE. The lower flow of polymer in the case of PE can be explained in this way.

Ash content results

The amount of ash was analyzed to find out how much calcium carbonate contained in the films. The PP based breathable films were weighed out after the ash oven and the weight loss was determined. Since PP and PE is decomposed at high temperatures, the weight of the calcium carbonate is coming out of the furnace.

BF1 film has burned away in an air atmosphere at temperatures above 600 °C to find the ash content. Calculation shows that the amount of ash is around 50.4%. It was also supported by the FTIR analysis (see in Figure 4.29) taken after the film was burned. The absence of the characteristic peaks of calcium carbonate at 900 °C indicates that the burning process is nearly realized.

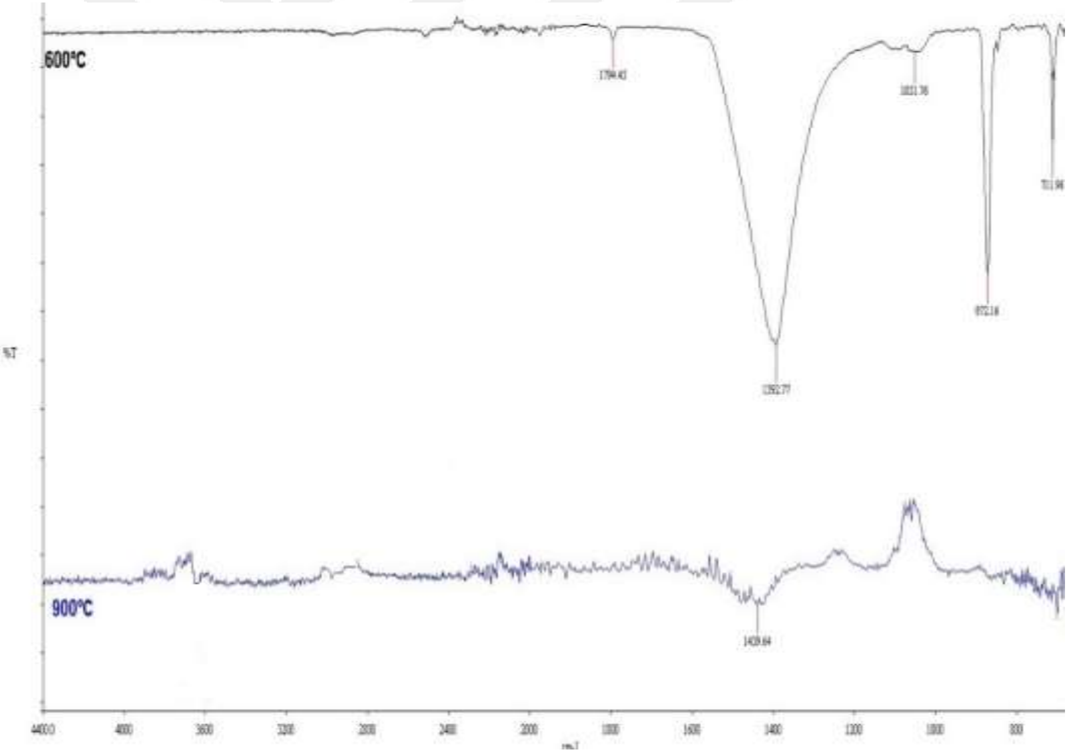

Figure 4.29 : Ash content- FTIR analysis of BF1.

BF2 film has burned away in an air atmosphere at temperatures above 600 °C to find the ash content. Calculation shows that the amount of ash is around 43.1%. It was also supported by the FTIR analysis (see in Figure 4.30) taken after the film was burned. The absence of the characteristic peaks of calcium carbonate at 900 °C indicates that the burning process is nearly realized.

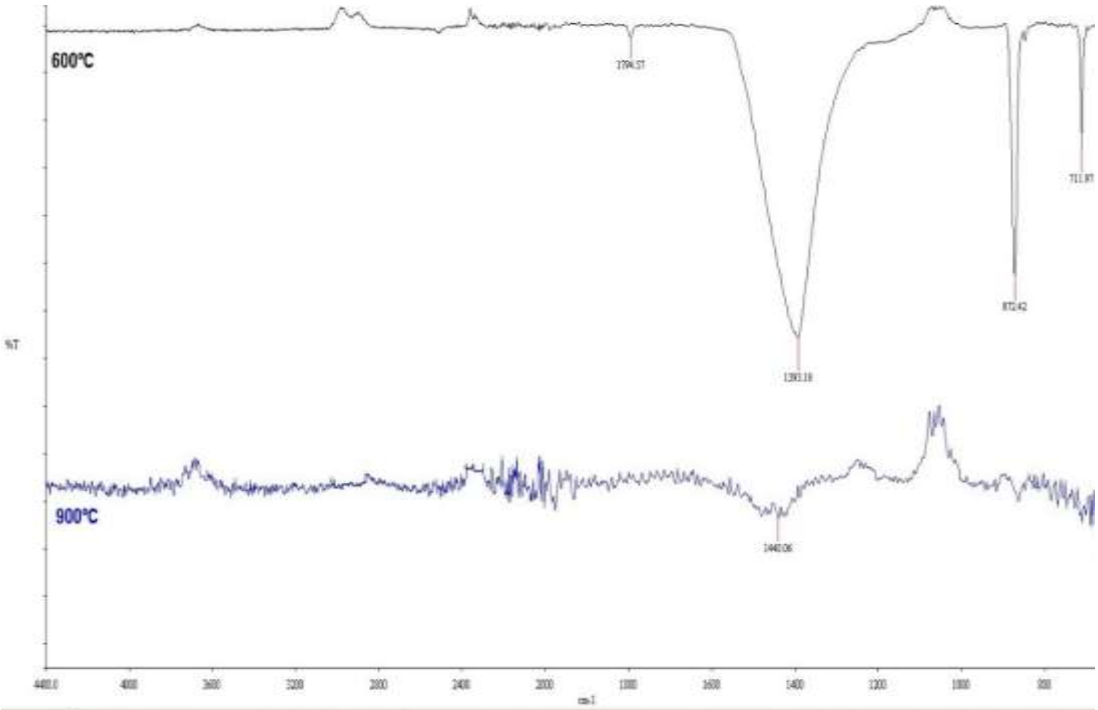

Figure 4.30 : Ash content- FTIR analysis of BF2.

BF4 film has burned away in an air atmosphere at temperatures above 600 °C to find the ash content. Calculation shows that the amount of ash is around 50.7%. It was also supported by the FTIR analysis (see in Figure 4.31) taken after the film was burned. The absence of the characteristic peaks of calcium carbonate at 900 °C indicates that the burning process is nearly realized.

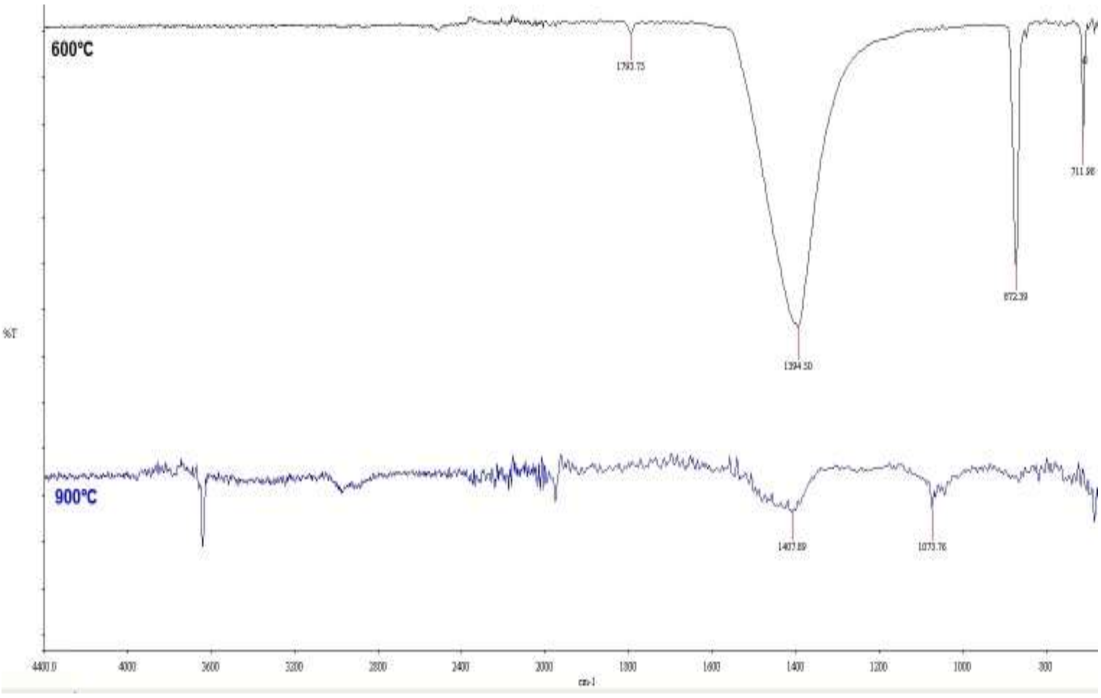

Figure 4.31 : Ash content- FTIR analysis of BF4.

Mechanical properties results

The mechanical properties result of experiments are given in Table 4.17. The same analyzes were also taken for the commercial microporous PE based breathable film sample for comparison.

Table 4.17 : Mechanical properties results of film samples.

Sample	Tensile Elongation at Break (%)		Tensile Strength (N/mm^2)		Elastic Modulus (N/mm^2)	
	MD	CD	MD	CD	MD	CD
BF1	42	390	70	7.5	450	131
BF2	55	446	69	7.6	503	195
BF4	50	350	65	6.8	441	123

Blown film extrusion is take place under the influence of blowing air and material is oriented towards machine direction which are affect the crystallization behaviour. In the scope of this study, extra stretching is applied to the material with MDO unit at the same time. This causes a difference in the mechanical properties in the MD and CD direction.

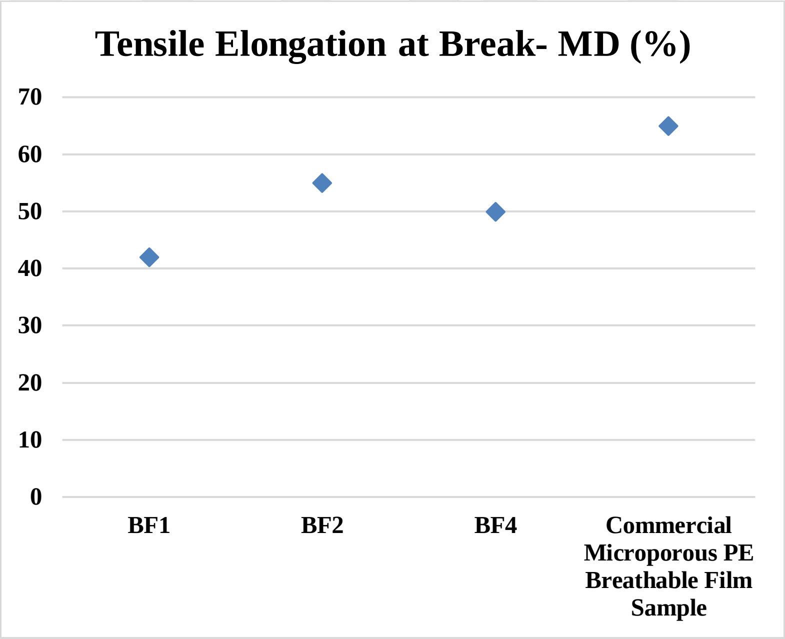

Figure 4.32 : Tensile elongation at break (MD) analysis results.

Both the elongation at break (MD) and the elongation at break (CD) of the commercial microporous PE based breathable film sample are higher than of the samples of experiments as can be seen from Figure 4.32 and Figure 4.33. This is because the polyethylene structure is more flexible and less rigid. Being flexible means absorbing more energy and making more prolongation until the material breaks.

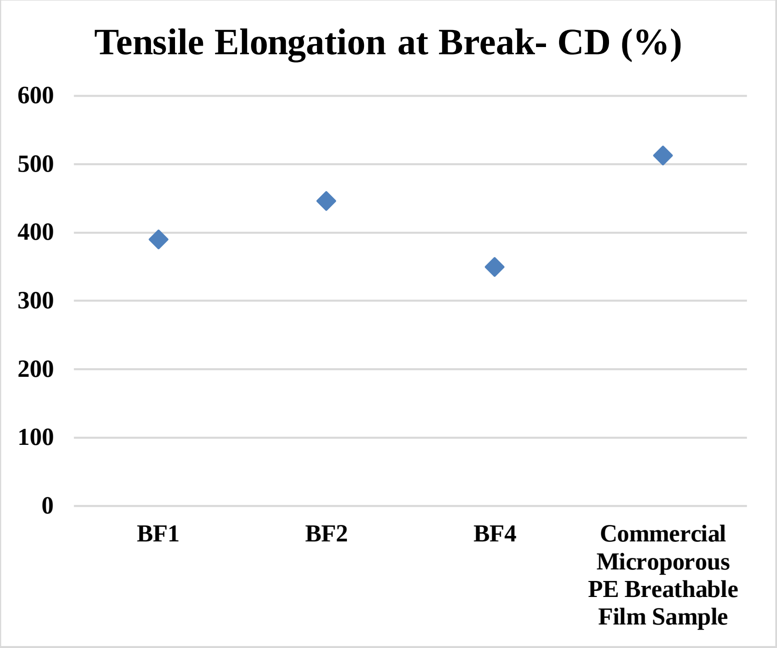

Figure 4.33 : Tensile elongation at break (MD) analysis results.

The amount of polyethylene in BF1 experiment, caused it to remain more rigid and less elongated than the other examples. In the case of BF2, the amount of polyethylene is increased. In the case of BF4, the amount of calcite is increased. Therefore, the elongation at break of BF4 is lower than that of BF2.

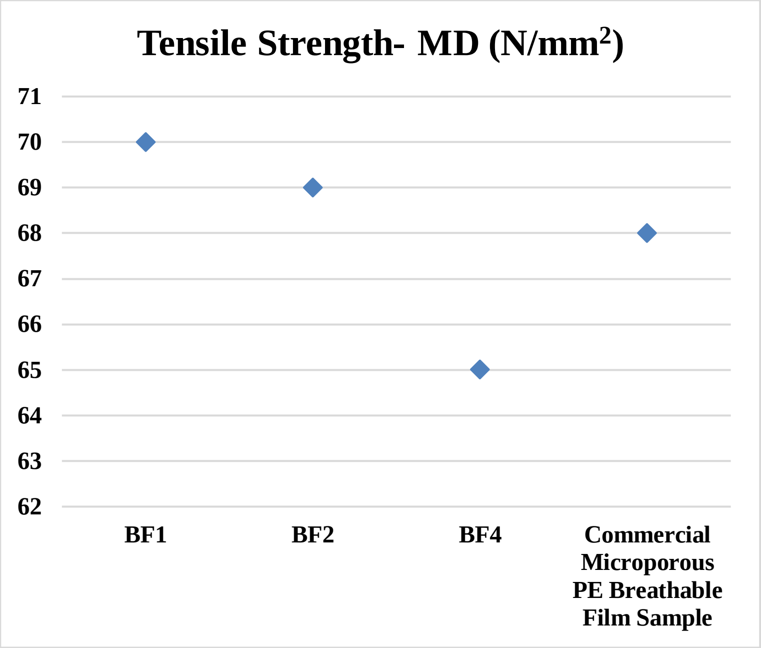

Figure 4.34 : Tensile strength (MD) analysis results.

The tensile strength of a material is the maximum amount of tensile stress that it can take before failure, such as breaking or permanent deformation. Orientation in the machine direction, extra stretching with MDO unit and material structure are effective to gain these values.

In comparison, the amount of polypropylene in the matrix directly affected the tensile strength (MD). As Figure 4.34 shows, the tensile strength (MD) of BF1 is higher than other samples of experiments and than commercial microporous PE based breathable film sample. In the case of BF4 sample, it is observed that tensile strength (MD) decreases with increasing calcium carbonate content.

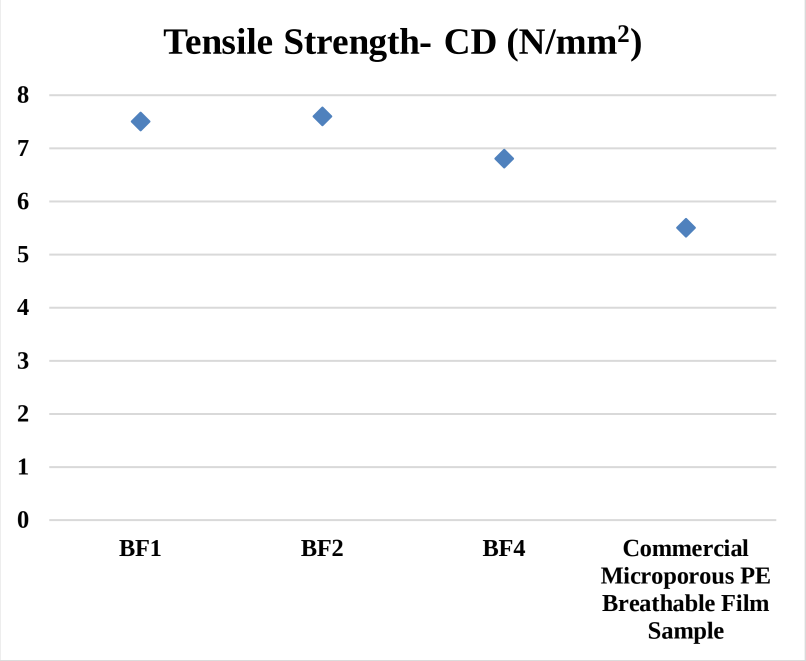

Figure 4.35 : Tensile strength (CD) analysis results.

The cross-direction values are obtained in the opposite direction of the machine which cause less orientation. For this reason, the cross-direction strength values are lower than the values obtained in the machine direction. As Figure 4.35 shows, the tensile strength (CD) values of BF1, BF2 and BF4 are show similarity. They have higher tensile strength (CD) values when compared to commercial microporous PE based breathable film sample since nature of polypropylene is more rigid than polyethylene.

The elastic modulus is the ratio of stress to elastic strain in tension. A high elastic modulus means that the material is rigid - more stress is required to produce a given amount of strain. Higher values are seen in the machine direction due to the orientation with the blowing air and stretching with the MDO unit.

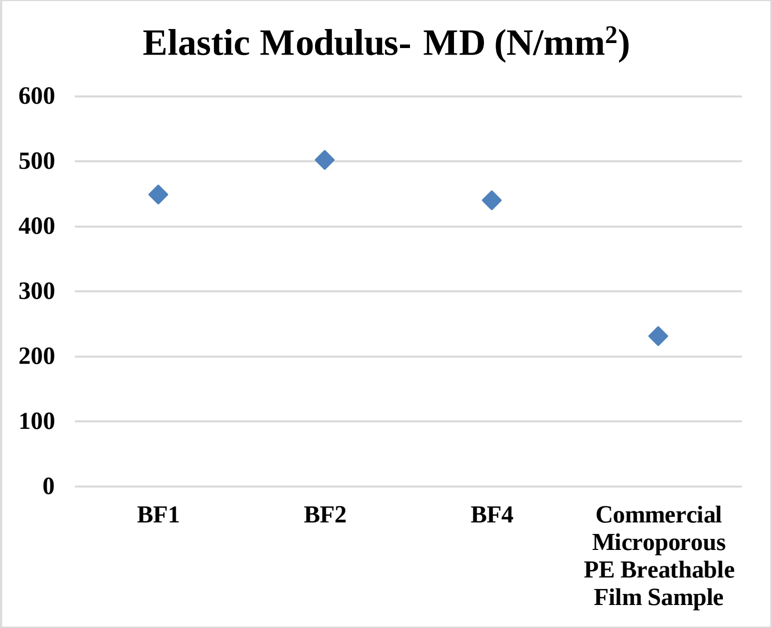

Figure 4.36 : Elastic modulus (MD) analysis results.

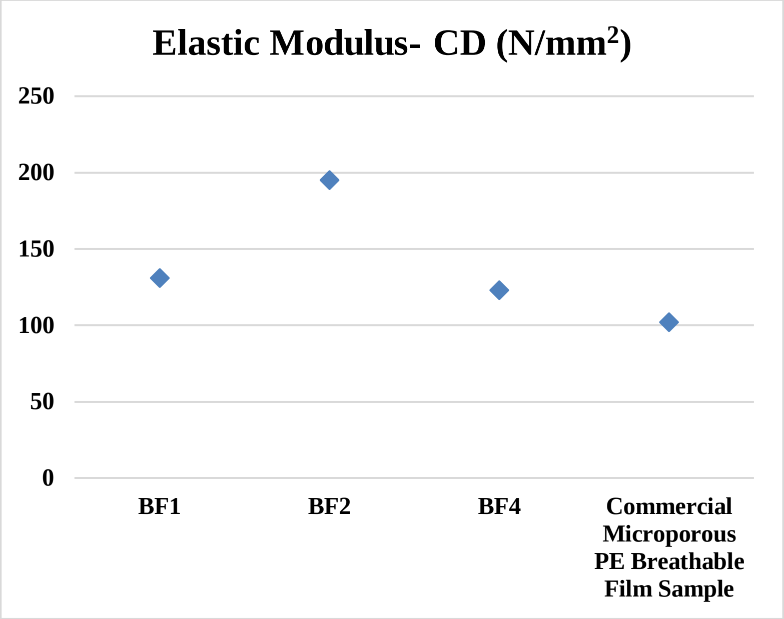

Figure 4.37 : Elastic modulus (CD) analysis results.

According to Figure 4.36 and 4.37, BF1, BF2 and BF4 have higher elastic modulus both in MD and CD compared to commercial microporous PE based breathable film sample. It can be explained by the fact that polypropylene is more rigid. When the samples of experiments are examined among themselves, it is seen that the amount of plastic is higher in the BF2-coded experiment. For this reason, it is possible to say that the elastic modulus values decrease with the increase of the amount of calcium carbonate.

Elmendorf tear strength results

The tear strength results of experiments are given in Table 4.18.

Table 4.18 : Elmendorf tear strength results.

Sample	Tear Strength (N/mm)	
	MD	CD
BF1	24	1471
BF2	25	2212
BF4	27	2060

Tear strength correlated with orientation in both the crystalline and amorphous phases of material and is related with its flexibility and elasticity. In this study, stretching ratio and material structure are parameters that directly affect the tear strength. Since the stretching ratio is constant, it will be correct to associate it with the material structure.

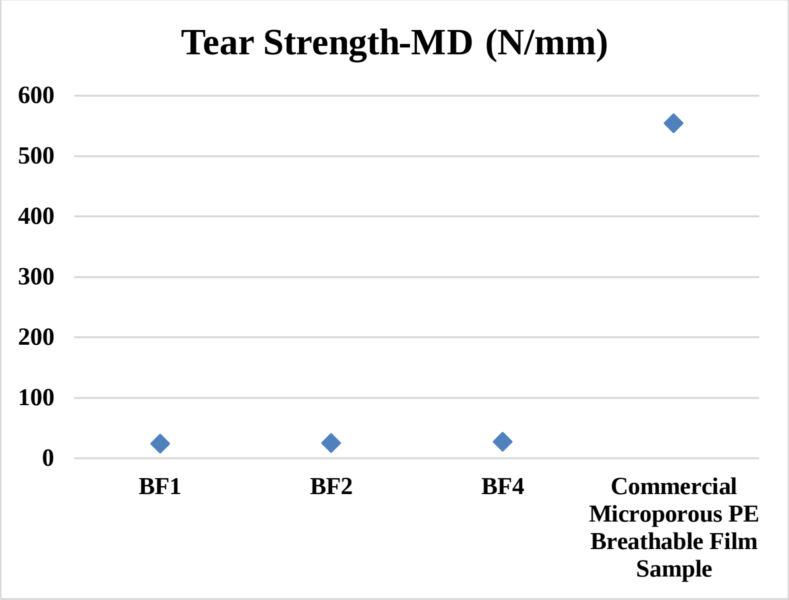

Figure 4.38 : Tear strength (MD) analysis results.

When tear strength (MD) of materials are examined, it is seen that the results of experiments are show similarity (see in Figure 4.38). The tear strength (MD) of commercial microporous PE based breathable film sample is higher than the samples of experiments. Polypropylene is made up of propylene monomer units, which are three carbon alkane units. Due to its nature, it is known that polyopropylene is more rigid than polyethylene.

The amount of calcite and polyethylene contained in the BF1, BF2 and BF4 appears to have little effect on the tear strength (MD). It is therefore possible to say that the tear strength (MD) of the experiments are directly related to the polypropylene matrix.

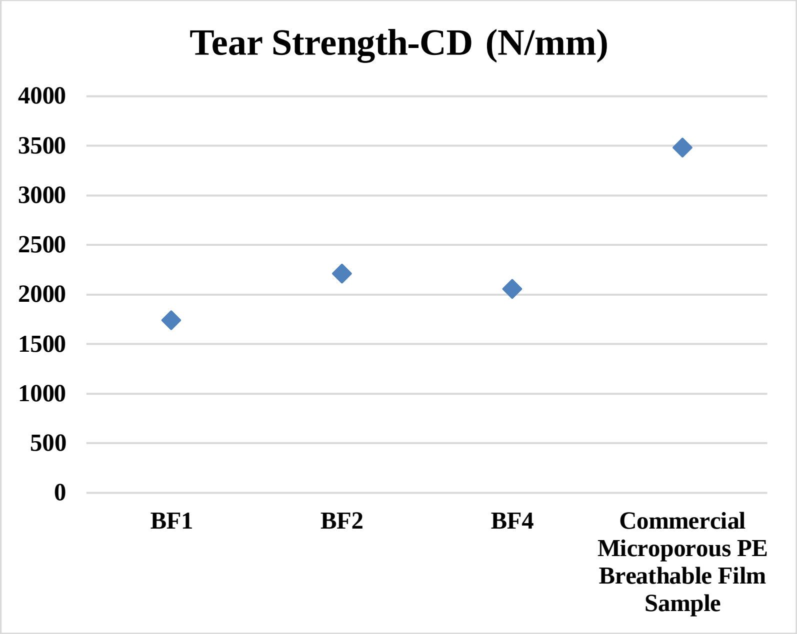

Figure 4.39 : Tear strength (CD) analysis results.

The tear strength (CD) of commercial microporous PE based breathable film sample is also higher than the samples of experiments since polyethylene much more flexible due to its nature. It is seen that from Figure 4.39, tear strength (CD) of BF1 is lower than BF2 and BF4. During the production of BF2 and BF4, the ratio of polyethylene in the matrix was increased by adding LLDPE to C1 and C2 compound, and it may have caused the tear strength (CD) to increase.

WVTR MOCON results

WVTR is the steady state rate at which water vapor permeates through a film at specified conditions of temperature and relative humidity. Within the scope of this study, the analyzes were based on 38 °C and 100% relative humidity. The WVTR MOCON results of experiments are given in Table 4.19.

Table 4.19 : WVTR MOCON results.

Sample	WVTR MOCON (g/m^2.day.atm)
BF1	3000
BF2	570
BF4	4000

The formation of micropores in the material directly affects the permeability values. The amount of calcium carbonate in the material and the structure of the material affects this situation. The number and size of the micropores formed by the stretching depends on the material structure and the amount of calcium carbonate.

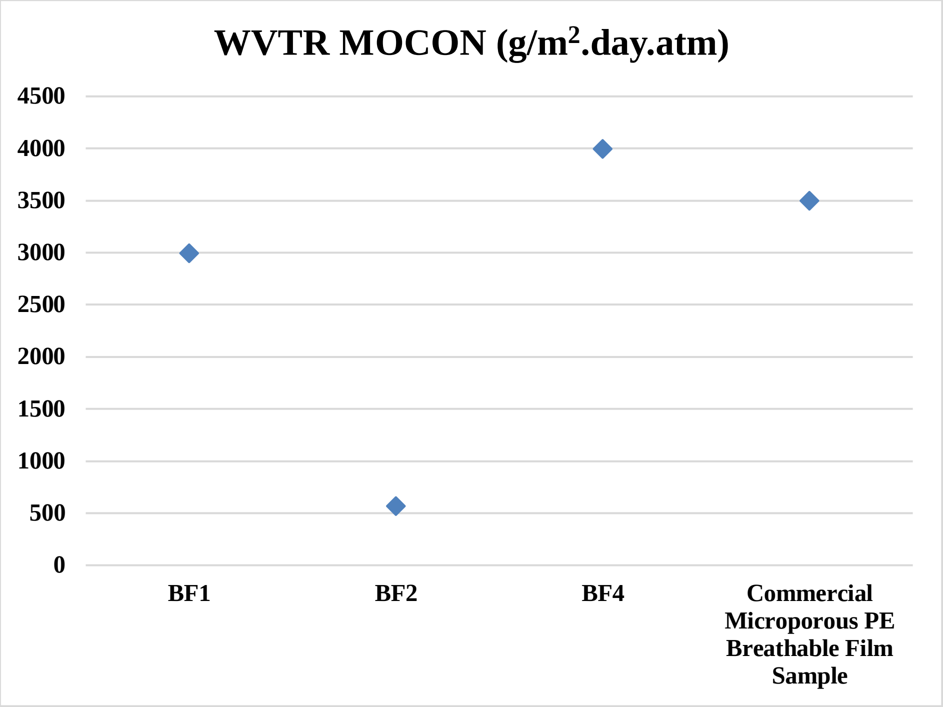

Figure 4.40 : WVTR MOCON results.

The water vapor permeability of the microporous PP breathable film examples as a function of calcium carbonate content. Increasing the calcium carbonate content increases the amount of larger micropores originating from the interfacial debonding between the calcium carbonate particles and PP matrix, and this helps to improve permeability. According to Figure 4.40, if the samples of experiments are compared between themselves, the difference between them will be the amount of calcium carbonate or plastics since the rate of stretching and the materials used are similar. When assessed for use in the hygiene sector, the water vapor permeability values of the BF1 and BF4 specimens are acceptable. It can be assumed that they are within the limit values. In the case of commercial microporous PE breathable film sample, the amount of calcium carbonate is close to the BF4.

Grammage results

The grammage results of experiments are given in Table 4.20.

Table 4.20 : Grammage results of film samples.

Sample	Grammage (g/m^2)
BF1	16
BF2	16
BF4	16

Production has been carried out with the target of 16 GSM. For structures with high levels of inorganic particles and subjected to stretching, it is difficult to produce at low weights. The fact that the problem is not encountered during the production and the analysis results show that, it is possible to produce polypropylene based breathable films at lower weight with the prepared compounds.

SEM results

SEM analysis was performed to observe the $CaCO_3$ dispersion in the matrix and micropores formation in the prepared films. The formation of micropores is directly related to breathability. A sample SEM image of pure PP is shown below (see in Figure 4.41) to better understand the formation of the micro pores on the surface of prepared breathable films.

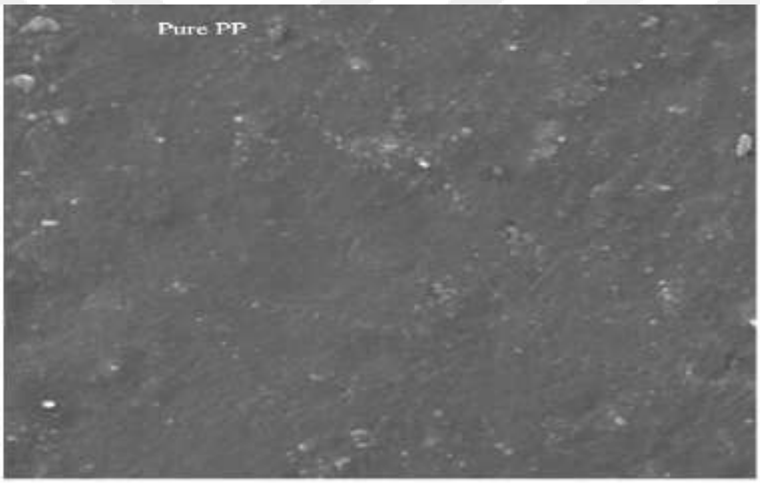

Figure 4.41 : SEM Micrograph of pure PP [57].

For the BF1, BF2 and BF4 samples, a 2000-fold magnified SEM images were taken. The pores are dark, the polyolefins, which are PP and PE in these samples, are mid-gray, and the $CaCO_3$ particles are white.

According to the Figure 4.42, the micropores were formed randomly and at different sizes. When the surface morphology of BF1 examined, agglomeration was not appeared on a scale that can be taken into account. This can be explained by the coating of the $CaCO_3$. The coating reduces the surface energy between the $CaCO_3$ and the matrix and ensures a good dispersion.

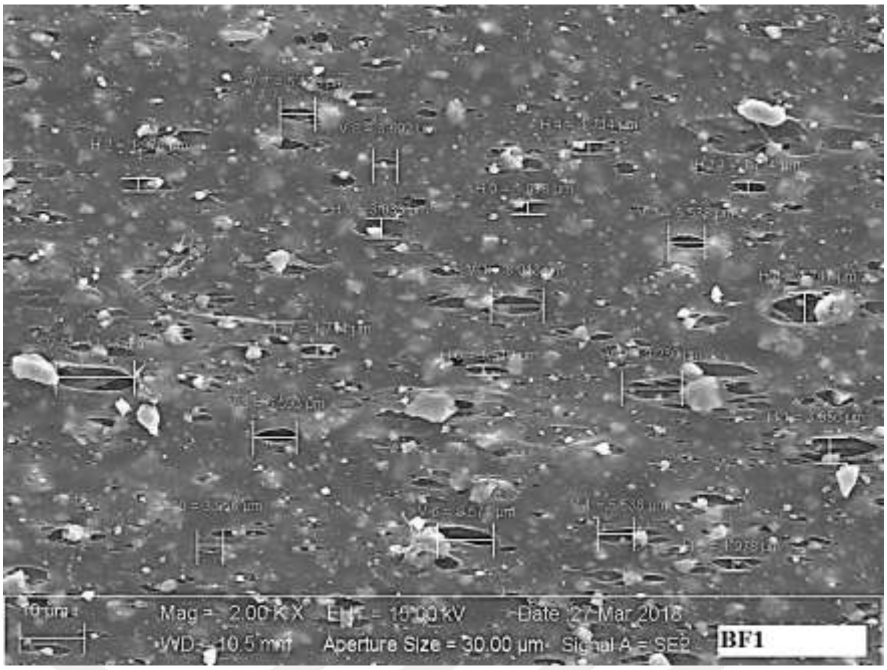

Figure 4.42 : SEM micrograph of BF1.

Table 4.21 : Por sizes of BF1.

Sample	Por Sizes (µm)	
	Horizontal	Vertical
BF1	3.956	8.043
	1.978	5.538
	3.033	6.593
	1.714	5.538
	1.978	12.13
	1.319	8.571
	1.714	5.406
	4.747	3.692
	1.928	9.230
	1.714	3.956

The samples were stretched to the machine direction. According to the Table 4.21, observation of larger pore sizes at the vertical level is indicates that the vertical level is the stretching direction.

As in the case of BF1, agglomeration was not appeared in surface image of BF2. This indicates that the dispersion is at a good level. The micropores were arranged randomly and at different sizes (see in Figure 4.43).

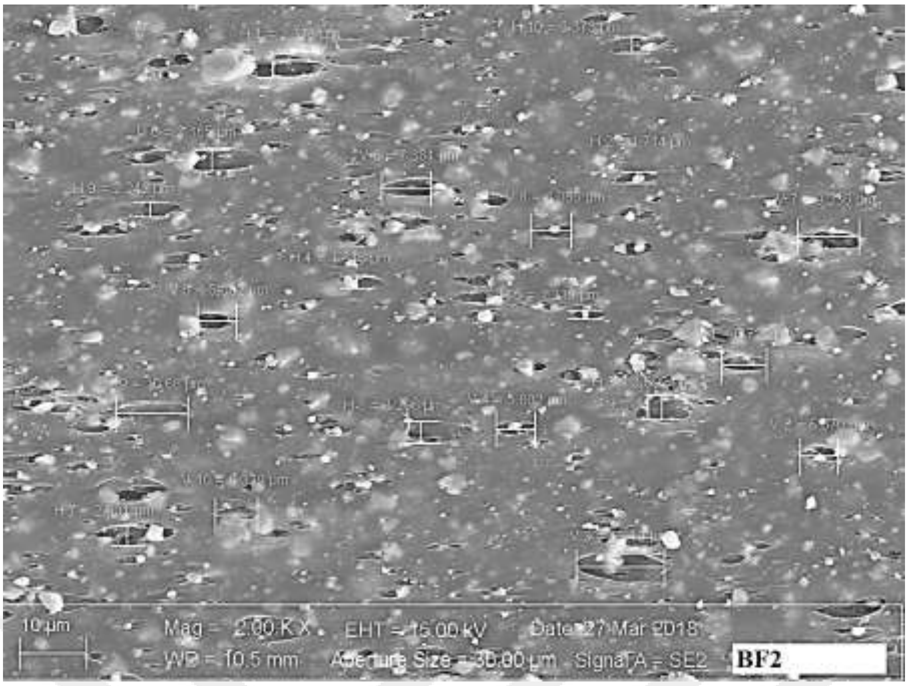

Figure 4.43 : SEM micrograph of BF2.

According to the Table 4.22, the formation of larger sizes pores at the vertical level means that it is stretched in this direction.

Table 4.22 : Por sizes of BF2.

Sample	Por Sizes (µm)	
	Horizontal	Vertical
BF2	2.373	6.725
	1.714	5.670
	3.692	13.19
	1.846	5.802
	1.319	5.802
	3.165	7.384
	2.901	9.230
	3.296	6.065
	2.242	10.68
	2.373	6.329

According to the Figure 4.44, agglomeration was not appeared in surface image of BF4. This indicates that the dispersion is at a good level. As in the other prepared samples, the micropores were arranged randomly and at different sizes.

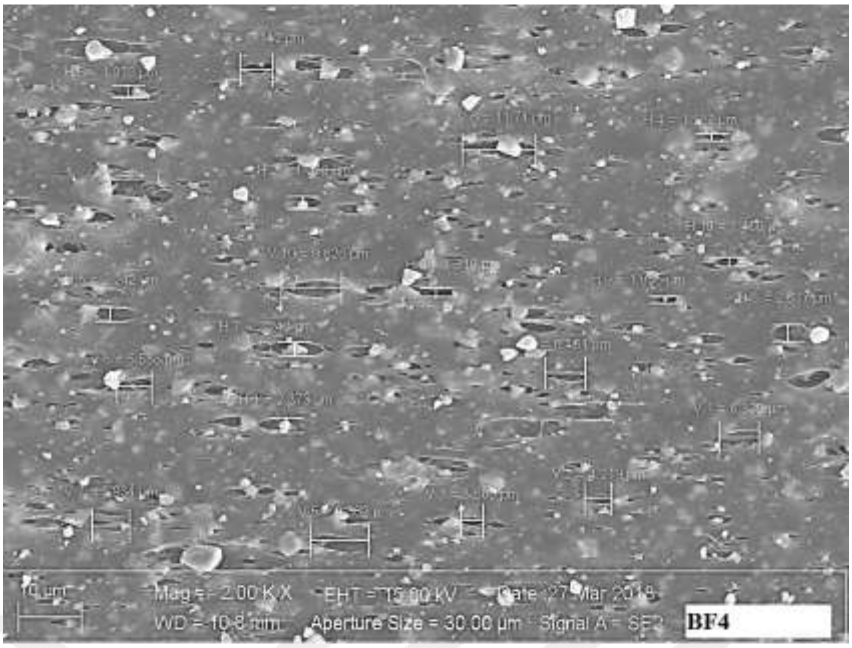

Figure 4.44 : SEM micrograph of BF4.

Table 4.23 : Por sizes of BF4.

Sample	Por Sizes (µm)	
	Horizontal	Vertical
BF4	2.373	6.329
	1.978	4.219
	2.637	3.560
	1.187	6.461
	2.242	9.362
	1.978	11.74
	2.242	5.934
	1.319	5.538
	1.055	5.142
	1.450	9.626

According to the Table 4.23, the sizes of pores are larger at the vertical level. It is expected that larger diameter pores will be seen as a result of stretching at the vertical level.

5. CONCLUSIONS

In this study, microporous polypropylene breathable films were prepared via blown film extrusion with two different prepared polypropylene-based compounds. Compounds having different formulations were obtained in pellet form via twin-screw compounding extruder. The prepared compounds, C1 and C2, were used to obtain film samples in blown extruder under specified conditions. The prepared compounds and produced film samples were examined using various analysis methods. At the same time, PP and PE based commercial breathable compounds and PE based commercial microporous breathable film were analyzed to make a comparison.

Primarily, commercial PP and PE based breathable compounds were analyzed to guide the experimental works. According to the DSC analysis, PP and PE structures were observed in the PP based commercial breathable compound and only PE structure was observed in PE based commercial breathable compound. It was verified by FTIR analysis. In the density analysis, it was found that the density is higher in PE based commercial breathable compound than the PP based. A higher $CaCO_3$ content was observed in the PE based commercial breathable compound according to the ash analysis. This situtation was verified the density results. MFR analysis showed that the melt flow rate of the PE based commercial breathable compound was lower than the PP based commercial breathable compound. It is known that a high $CaCO_3$ content may hindered the plastic flow and reduced the MFR.

The prepared compounds, C1 and C2, were investigated by determined analyzes. The melting peaks of the prepared compounds were observed according to the DSC analysis. Two compounds have the similar melting peaks and and show the presence of polyethylene (LLDPE) and polypropylene structures. Depending on the matrix ratios of the C1 and C2, it is seen that the polypropylene melting peak of C2 is more dominant. In order to improve the processability and the properties, the incorporation of polyethylene structures in PP based breathable compounds is important. In the direction of FTIR analysis of the prepared compound samples, polyethylene, polypropylene, and calcium carbonate absorption peaks were observed and the presence of the materials was confirmed. Density and melt flow rates values of the compound samples were investigated and it was found that these values were significantly changed with the amount of calcium carbonate. The calcium carbonate amount increases the density and melt flow rate values. It is known that incorporation of fillers hinders plastic flow and increases the viscosity of a polymer melt, a reduction of MFR with the filler loading is expected. However, in the prepared compounds, MFR values increased relative to the original raw material. This is explained by the coating of the surface of $CaCO_3$. It increases the plasticity and prevents the agglomeration. As the result of ash analysis, calcium carbonate amounts of C1 and C2 are 50% and 60% respectively. The calcium carbonate loading in the compounding process via twin-screw extruder is successful since the amounts of calcium carbonate loaded and analyzed are consistent.

In order to compare breathable films produced using C1 and C2, a commercial microporous PE breathable film was investigated. In the direction of DSC and FTIR analysis, it is seen that the commercial microporous PE breathable film contains only the PE structure. It has been determined that the MFR and density values are directly influenced by the $CaCO_3$ content. The mechanical properties indicate that the film is stretched in MD direction. The micropores were observed on the surface of the commercial product according to the SEM analysis. The size and alignment of the micro pores are random.

At the last stage, the properties of produced microporous PP breathable films, BF1, BF2, BF4, were examined. The change in the volume of the melting peaks between BF1, BF2 and BF4 varies according to the ratios of the materials in the matrix. Basically, melting peaks of LLDPE and PP structures were observed. FTIR analysis was taken for both surfaces of film samples since the produced films are coex structure. As each layer of the coex structure contains the same formula, the FTIR graph on both surfaces shows frequency at similar wavelengths which are belong to polyethylene, polypropylene, and calcium carbonate structures. Density and melt flow rates values of the film samples significantly changed with the amount of calcium carbonate. The density values of BF1 and BF4 are close to each other since the amount of calcium carbonate contained is almost the same. As a result of the ash analysis, BF2 has the lowest content of calcium carbonate. BF1 and BF2 have similar proportions. C1 compound was used in the BF2 sample and it was produced by LLDPE reinforcement in the blown film extrusion process. In the case of BF2, the proportion of plastic is higher than that of calcium carbonate.

When the results of mechanical analysis are taken into consideration, it is seen that the values obtained mostly vary depending on the raw material and calcium carbonate ratio used in the film matrix. Compared to microporous PE breathable film, it is seen that microporous PP breathable films have higher modulus values and tensile strengths, while elongation values are lower. This is because polypropylene is more rigid than polyethylene. When the prepared microporous PP breathable film samples are compared with each other, it is seen that the elongation values are increased by increasing the ratio of LLDPE. With increasing polypropylene content, modulus values increase, and elongation values decrease.

Tear strength is an important issue for polypropylene films. When the tear strength values are examined, a partial improvement is observed with the addition of LLDPE. However, when compared with microporous PE breathable films, there appears to be a serious difference. It is expected that the tearing resistance will be low due to the fact that polypropylene is more rigid and subjected to stretching. It has been seen that the adding plastomer to compound C2 during the compounding process, and adding LLDPE during the blown film extrusion do not have a serious effect.

Since the raw materials used and the rate of stretching are constant, the permeability values are directly dependent on the amount of calcium carbonate. For this reason, the permeability values of the BF1 and BF4 film samples are close to each other. As the amount of calcium carbonate increases, the permeability values increase.

According to the SEM analysis, a 2000-fold magnified images of BF1, BF2 and BF4 were taken. The micropores were formed randomly and at different sizes. When the surface morphology of film samples are examined, agglomeration was not appeared on a scale that can be considered. This can be explained by the coating of the $CaCO_3$. The coating reduces the surface energy between the $CaCO_3$ and the matrix and ensures a good dispersion. In BF1, BF2 and BF4, the larger micro por sizes were seen at the vertical level. The film samples were stretched at a vertical level and more stress was exposed at this level.

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