

ISTANBUL TECHNICAL UNIVERSITY ★ GRADUATE SCHOOL OF SCIENCE
ENGINEERING AND TECHNOLOGY

**ENHANCING MECHANICAL PERFORMANCE AND FLAME RETARDANCY
OF POLYETHYLENE FIBERS**



M.Sc. THESIS

Beyza Nur GUNAYDIN

Department of Nano Science and Nano Engineering

Nano Science and Nano Engineering Programme

JULY 2020

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Beyza Nur GUNAYDIN
(513171003)

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Thesis Advisor: Assoc. Prof. Dr. Ali KILIC
Thesis Co-advisor: Assoc. Prof. Dr. Huseyin AVCI

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**POLİETİLEN LİFLERİN MEKANİK VE ALEV GECİKTİRİCİLİK
ÖZELLİKLERİNİN GELİŞTİRİLMESİ**

YÜKSEK LİSANS TEZİ

**Beyza Nur GÜNAYDIN
(513171003)**

Nano Bilim ve Nano Mühendislik Anabilim Dalı

Nano Bilim ve Nano Mühendislik Programı

**Tez Danışmanı: Doç. Dr. Ali KILIÇ
Tez Eş Danışmanı: Doç. Dr. Hüseyin AVCI**

TEMMUZ 2020

Beyza Nur Gunaydin, a M.Sc. student of ITU Graduate School of Science Engineering and Technology student ID 513171003, successfully defended the thesis/dissertation entitled “ENHANCING MECHANICAL PERFORMANCE AND FLAME RETARDANCY OF POLYETHYLENE FIBERS”, which she prepared after fulfilling the requirements specified in the associated legislations, before the jury whose signatures are below.

Thesis Advisor : **Assoc. Prof. Dr. Ali KILIC**
Istanbul Technical University

Co-advisor : **Assoc. Prof. Dr. Huseyin AVCI**
Eskisehir Osmangazi University

Jury Members : **Prof. Dr. Ali DEMIR**
Istanbul Technical University

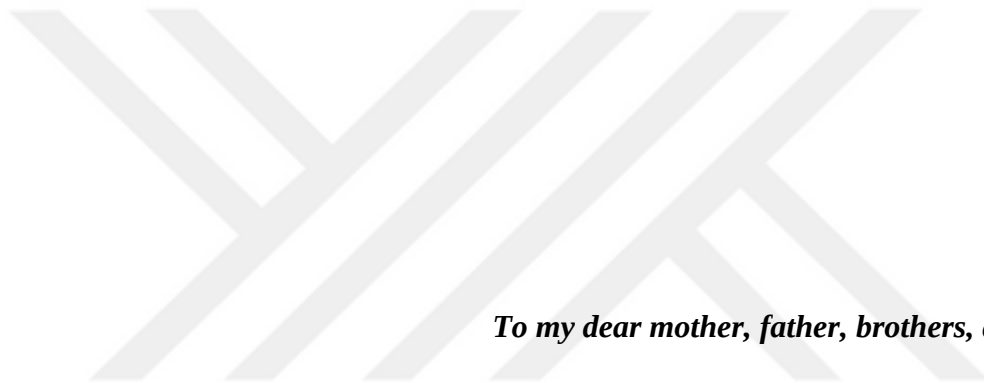
Prof. Dr. Mustafa Erdem UREYEN
Eskisehir Technical University

Asst. Prof. Dr. Sule SELCUK
Istanbul Technical University

Date of Submission : 15 June 2020

Date of Defense : 7 July 2020





To my dear mother, father, brothers, and spouse,



FOREWORD

First of all, this thesis was financially supported by The Scientific and Technological Research Council of Turkey, TUBITAK 117Z673 project and I would like to gratefully thank TUBITAK for all supports. I also acknowledge Dow Chemical Company for providing ASPUN™ 6000 and Kordsa Global for their polarized light microscopy contribution.

Secondly, I express my gratitude to my thesis advisors Assoc. Prof. Dr. Ali KILIC and my thesis co-advisor Assoc. Prof. Dr. Huseyin AVCI for their support, guidance and all the opportunities they have provided to me. I would like to special thank my dear partner Aybeniz SEYHAN for all support throughout this thesis and her endless friendship. I also would like to thank members of TEMAG Lab. for their guidance and valuable. In addition, I would like to thank Prof. Dr. Mustafa Ureyen and his laboratory at Eskişehir Technical University for providing all the facilities in flame retardant tests.

Finally, I would like to express the greatest gratitude to my husband and parents for their encouragements, supports and guidance even in the most difficult times.

July 2020

Beyza Nur GUNAYDIN
(Nano Science and Nano
Engineering)



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ABBREVIATIONS

DSC	: Differential scanning calorimeter
FR	: Flame retardant
LLDPE	: Linear low density polyethylene
LOI	: Limiting oxygen index
MCC	: Micro combustion calorimeter
PE	: Polyethylene
PP	: Polypropylene
pHRR	: Peak heat release rate
SEM-EDAX	: Scanning electron microscopy energy dispersive X-Ray analysis
TG/DTG	: Thermogravimetric analysis/ Derivative thermogravimetry
XRD	: X-Ray diffraction



SYMBOLS

f_a	: Amorphous orientation
f_c	: Crystalline orientation
L_{110}	: Crystal size
Δn	: Chain orientation
$x\%$	: Crystallinity percentage





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ENHANCING MECHANICAL PERFORMANCE AND FLAME RETARDANCY OF POLYETHYLENE FIBERS

SUMMARY

Production of high performance functional fibers is widely investigated in the literature. Although traditional melt spinning is commonly used in the production of regular fibers using thermoplastic polymers, gel spinning, or other solvent-assisted systems are preferred with high molecular weight polymers for high performance fibers. These types of fibers have various uses in industrial applications, thanks to their performance to be utilized well in demanding areas such as ballistic (bulletproof vests), automotive, aerospace, energy, and electronics. In addition, these fibers have the potential to be used as reinforcements in fiber and fabric form in the composite applications. The fibers used in composite materials generally require high mechanical performance, however, in the aviation and defense industry, in addition to mechanical performance, the properties of thermal and flame retardancy are also required. Therefore, the thermal and flame retardant properties of the fibers should be improved in addition to mechanical performance.

In this thesis, firstly, polyethylene (PE) fibers were produced with a novel melt spinning line. It is aimed to improve the mechanical, thermal and flame retardant properties of the fibers by integrating nano and micro-sized additives into the melt spinning line determined in the light of the preliminary studies made with PE molds. In this context, a novel melt spinning line is designed considering a relatively low cost and environmentally friendly approach and high productivity. In this case, the traditional system was modified and named as HiPER for the high performance and functional fiber manufacturing. For the production polyethylene was preferred due to very high mechanical properties, semi-crystalline structure, costs and wide usage area. Using the novel system, the fiber was produced from linear low density polyethylene (LLDPE) polymer. To determine fiber properties, tensile testing, scanning electron microscopy (SEM), X-ray diffraction (XRD) and differential scanning calorimeter (DSC) tests were conducted. HiPER fiber exhibited 202 MPa strength and 1329 MPa elastic modulus although they were not exposed to any drawing process. This corresponds to 166% strength and 371% module increase compared to control polyethylene fibers produced under the same conditions without using the HiPER system. In addition, the elongation at break was reduced by 71% and the fibers showed more brittle structure for the HiPER fibers. Apart from the mechanical properties, it has been observed that the HiPER system increased the crystalline, amorphous and chain orientation of the fibers by effecting the internal structure.

In the second part of the thesis, various additives were used to provide flame retardant properties in addition to the mechanical performance. Three different types of flame retardant materials have been investigated, including minerals containing aluminum trihydrate (ATH), phosphorus containing additives, and nanocomposites (nanoclay and crystalline nanocellulose). The mechanical and flame retardant performances of the obtained fibers and the effects of the additives were investigated. For the detection

of thermal degradation, TG analyzes were performed. Limit oxygen index (LOI) and micro combustion calorimeter (MCC) tests were also used to determine the burning behaviors. As a result of the studies, it has been observed that the HiPER system is suitable for fiber production, and it is easy to produce performance fibers in one step. Other advantages of the novel line are that the system is environmentally friendly, does not require the use of high molecular weight polymers for high performance fiber production, and does not require a system that contains solvents that can cause harm to human health. In the preliminary studies made with the novel system, high performance fiber production was achieved at different take-up speeds. The effects of production parameters and additives on the mechanical, morphological, internal structure, thermal, and flame retardant properties of the fibers demonstrated a high potential usage with industrial-scale production of the fibers for various composite ballistic applications.



POLİETİLEN LİFLERİN MEKANİK VE ALEV GECİKTİRİCİLİK ÖZELLİKLERİNİN GELİŞTİRİLMESİ

ÖZET

Fonksiyonel polimerlerin ve mühendislik liflerinin özellikleri ve üretim yöntemleri literatürde geniş yer bulmuştur. Termoplastik polimerlerden lif üretiminde geleneksel eriyikten çekim yöntemi sıkça kullanılan bir süreç olsa da nitelikli yüksek performans lif üretimi için kullanılan polimerin moleküler ağırlığı göz önünde bulundurularak jel eğirme veya diğer çözücü destekli sistemler tercih edilmektedir. Bu tür lifler mevcut performansları doğrultusunda endüstriyel uygulamalarda çeşitli kullanımlara sahiptir ve balistik (örneğin kurşun geçirmez yelekler), otomotiv, havacılık, enerji ve elektronik gibi zorlu alanlarda gelişmiş potansiyel sergilerler. Ayrıca bu lifler kompozit uygulamalarında fiber ve kumaş formda takviye olarak kullanım potansiyeline sahiptir. Bu uygulama alanlarından özellikle kompozit malzemelerde kullanılan lifler yüksek mekanik performans sağlaması gerekirken yanmazlığın önemli olduğu havacılık ve savunma sanayi gibi uygulama alanları için ise mekanik performansa ek olarak kullanılan liflerin termal ve alev geciktiricilik özelliklerinin iyileştirilmiş olması gerekmektedir. Liflere kazandırılacak fonksiyonel özellikler için lif üretiminde kullanılan katkıların oranları ve boyutları çok önem arz ettiğinden son yıllarda geleneksel katkılar nano boyutta katkılandırmaya doğru evrilmektedir. Nano katkı kullanımı özellikle lif üretimi gibi katkı miktarının önem arz ettiği uygulamalarda geniş kullanım alanı bulmaktadır.

Bu tez çalışmasında ilk olarak yenilikçi eriyikten üretim hattı ile polietilen lifler üretilmiştir. Sonrasında ise polietilen kalıplarla yapılan ön çalışmaların ışığında belirlenen nano ve mikro boyutta katkılar eriyikten üretim hattına entegre edilerek liflerin mekanik, termal ve alev geciktiricilik özelliklerinin iyileştirilmesi amaçlanmıştır. Bu kapsamda geleneksel eriyikten üretim hattına göre yüksek üretim hızına sahip, nispeten düşük maliyetli ve çevreci bir sistem olmasından dolayı öne çıkan yenilikçi eriyikten üretim hatları ile lif üretimi araştırılmıştır. Geleneksel sistem modifiye edilerek yenilikçi eriyikten çekim sisteminin (HiPER) tasarımı ve imalatı yapılmıştır. Sistemin amacı polimerin kristalizasyonunu geciktirip, lifin iç kısmına daha fazla müdahil olmak ve makro moleküler zincir oryantasyonunu daha düzenli hale getirmektir. Sistemde kullanılmak üzere teorik olarak çok yüksek mekanik özellik gösteren, yarı kristal özelliğe sahip, ucuz ve dünyada geniş kullanım alanı bulunan polietilen seçilmiştir. Yenilikçi sistem kullanılarak linear düşük yoğunluklu polietilen (LLDPE) polimeri ile lif üretimi yapılmıştır. Tezin ikinci kısmı için ise liflere mekanik ve alev geciktiricilik özellikleri kazandırmak için çeşitli katkı malzemeleri kullanılmıştır. Fakat kullanılan mikron boyutta katkılar üretimi olumsuz etkilediğinden yüksek yüzey alanına sahip az miktarda kullanımda bile etkili olan nano boyutta katkı kullanımı tercih edilmiştir. Elde edilen liflerin mekanik ve alev geciktiricilik performansları ve katkıların liflere olan etkileri incelenmiştir. Çalışmaların sonucunda görülmüştür ki, HiPER sistemi lif üretimi için uygun olup geleneksel eriyikten çekim hattına göre oldukça kolay ve tek adımda performans lif üretimi yapılabilir. Sistemin çevreci olması, yüksek performans lif üretimi için

yüksek moleküler ağırlığa sahip polimer kullanımı gerektirmemesi ayrıca pahalı ve insan sağlığı için zarar oluşturabilecek çözücü içeren sisteme gereksinim duymaması da hattın diğer avantajları arasında yer almaktadır. Yapılan öncül çalışmaların sonuçlarına göre üretilen liflerin kompozit balistik alanında kullanılabileceği öngörülmüştür. Lif üretimi farklı sarım hızlarında ve HiPER parametreleri ile yapılmıştır. Üretim parametrelerinin ve kullanılan katkıların liflerin mekanik, morfolojik, iç yapı, termal ve alev geciktiricilik özellikleri üzerine etkileri ortaya konmuştur.

Tez çalışmasında ilk olarak polietilenden lif üretimi yapılmıştır. Yenilikçi eriyikten üretim hattının ekstüder kısmı geleneksel yöntem ile aynı sistematiğe olup beslenen LLDPE polimer granülleri ekstrüderde sıcaklığın etkisi ile eriyik hale getirilmiş ve tekli vida ile de eriyik üretim pompasına taşınmıştır. Sonrasında ise düsedan çıkmış eriyik halde bulunan lifler kılavuz yardımı ile HiPER banyo ortamına daldırılmıştır. Tam katı forma geçmemiş lifler farklı HiPER ortam parametrelerine maruz bırakılmış ve HiPER sisteminden çıkan lifler herhangi bir çekime uğramadan farklı hızlarda godetlere sarılmıştır. Lif üretimleri karşılaştırma yapılabilmesi açısından aynı koşullar altında HiPER sistemine daldırılmayan (kontrol) ve HiPER sistemi ile üretilen olmak üzere iki farklı şekilde gerçekleştirilmiştir. Polietilen lifler düşük sarım hızından liflerin çıkabileceği maksimum sarım hızına kadar üç farklı hızda toplanmıştır. HiPER sisteminde ise optimum koşulların bulunabilmesi için HiPER banyo sıcaklığı, banyo içeriği ve farklı HiPER banyo derinliklerinde çeşitli lif üretimleri yapılmıştır. Farklı ortam koşullarının ve sarım hızlarının liflere kazandırdığı mekanik ve içyapı etkilerinin ortaya koyulabilmesi için elde edilen polietilen lifler sırasıyla çekme testi, taramalı elektron mikroskobu (SEM), X-ray kırınım difraksiyonu (XRD) ve diferansiyel taramalı kalorimetre (DSC) testlerine tabi tutulmuştur. Yapılan testler sonucunda HiPER ile üretilmiş liflerde hiçbir çekime maruz kalmadıkları halde maksimum 202 MPa dayanım ve 1329 MPa elastik modülü elde edilmiştir. Bu da HiPER sistemi kullanılmadan aynı koşullarda üretilen kontrol polietilen lifleri ile kıyaslandığında %166 mukavemet ve %371 modül artışına tekabül etmektedir. Ayrıca kopma uzaması da %71 oranında düşerek HiPER sistemi ile liflerin daha gevrek bir yapı kazanması sağlanmıştır. Mekanik özelliklerin yanı sıra yapılan testler ile HiPER sisteminin liflerin içyapısını düzenleyerek kristalin, amorf ve zincir oryantasyonunu arttırdığı gözlenmiştir. Ayrıca HiPER ile üretilmiş ve sıvı azot ile kırılmış liflerin kesit görüntülerine baktığımızda UHMWPE gibi yüksek performanslı sahip liflerin gösterdiği nanofibriller içyapıya sahip oldukları görülmektedir.

Tez çalışmasının ikinci kısmında ise liflere katkılandırma yapılarak termal ve yanma davranışlarının iyileştirilmesi amaçlanmıştır. Kullanılan katkılar, ateşlemeyi başlatmamaya veya yanma işlemini başladıktan sonra geciktirmeye ve duman gelişimini engellemeye yöneliktir. Liflere alev geciktiricilik özelliği kazandırılmasının nihai amacı ise, yangın mağdurlarının sahip olduklarından sadece birkaç saniye daha fazla zaman sağlayarak kaçmalarına yardımcı olmak, insanlarda can kaybını ve yaralanmayı sınırlamak ve mülkiyeti korumaktır. Üç başlığa ayrılan mineral içerikli alüminyum trihidrat (ATH), nano kompozit katkılar nanokil, kristalin nanoselüloz ve karbon nanotüp (MWCNT) ve fosfor içerikli katkılar bu tez çalışmasında kullanılmış ve bu katkıların polietilenin mekanik, termal bozunum ve alev geciktiricilik özellikleri üzerine etkileri incelenmiştir. Ayrıca nanokil ve MWCNT nanokatıkları da belirli oranlarda birbirleri ile karıştırılarak nano katkılarla yapılan kombinasyonların polietilenin termal bozunma ve yanma davranışları üzerine sinerjistik etkileri araştırılmıştır. Katkılar çift vidalı ekstrüder kullanılarak polietilen ile harmanlanmıştır.

Belirtilen katkılar farklı oranlarda polietilen ile ilk olarak enjeksiyonda kalıplanmış ve limit oksijen indeks (LOI) ve mikro ölçekli yanma kalorimetresi (MCC) testlerine tabi tutularak polietilenin özelliklerini iyileştiren optimum katkı ve katkı oranları bulunması amaçlanmıştır. Kalıplara yapılan testler sonucunda belirlenen katkıların yenilikçi sisteme uyarlanması ise tezin son kısmını oluşturmaktadır. Lif üretiminde kullanılacak katkıların oranları ve katkı boyutları katkılandırma için önemli parametreleri oluşturduğundan mikro boyutta katkılar kullanım oranlarını düşürmek amacıyla farklı katkılar ile karıştırılmış ve nano katkılar tercih edilmiştir. Bu sebeple ATH' ın yüksek katkı gereksiniminden dolayı tek başına lif üretimi için kullanımı uygun olmadığı belirlenmiş ATH amonyum polifosfat (APP) ile karıştırılmış ve eriyikten üretim hattına entegre edilmiştir. Farklı konsatrasyonlarda ATH-APP karışımı kullanılarak farklı ortam ve sarım hızlarında lif üretimleri gerçekleştirilmiştir. Bir diğer sisteme entegre edilebilen katkı ise nanokil olmuştur. Farklı nanokil katkı oranları ve HiPER ortam koşulları kullanılarak sistem optimize edilmeye çalışılmıştır. Ayrıca liflerin eriyikten üretim hattına beslenmeden önce herhangi bir katkılandırma yapmaksızın HiPER sisteminden geçerek belirtilen özelliklerinin geliştirilmesi hedeflenmiştir. Bu sebeple Thor Kimya'dan organik fosfor temin edilmiş ve fosfor öncesinde katkılandırma yapmaksızın HiPER banyo sistemine entegre edilmiştir. Farklı HiPER banyo sıcaklıkları ve derinliklerinde lif üretimleri gerçekleştirilmiştir. Elde edilen liflerin termal bozunumlarının tespiti için (TG/DTG) analizleri, yanma davranışlarının belirlenmesi için ise limit oksijen indeks (LOI) ve MCC testleri uygulanmıştır.



1. INTRODUCTION

1.1 Purpose of Thesis

Polymeric materials have broad applications in our daily life. In this regard, polyethylene (PE) is a member of polyolefin and one of the most widely used thermoplastic polymers in various forms such as cable, packaging, automotive, film, electronics, airplane inner surface, engine, bunker gear and composite industries due to its low cost, high chemical resistance and easy handling properties. While polyethylene has a market share of 106.9 billion US\$ in 2019, it is expected to have a market share of 124.4 billion US\$ by 2024, with an annual growth rate of about 2.6% [1]. Although PE possesses high theoretical mechanical properties due to its simple aliphatic hydrocarbon structure, this polymer has high flammability. It can be easily burned under atmospheric conditions without leaving any residues. There is a need to improve the poor heat and flame retardancy performances. The flame retardant properties can be improved using suitable additives to stop or reduce the flammability of the polymeric materials. In the literature, there are many studies on flame retardant materials, but most of them are used for polypropylene with mostly film or composite forms.

Traditional melt spinning is a commonly used process in the production of fibers from thermoplastic polymers. Gel spinning or other solvent-assisted systems are preferred for the high performance fiber production, taking into account the molecular weight of the polymer.

In this thesis, polyethylene (PE), in particular linear low-density polyethylene (LLDPE), was chosen as a polymer to produce flame retardant fibers that possess adaptable physical and chemical properties. The traditional melt spinning system was modified, and the novel melt spinning approach HiPER, which is a relatively low cost and environmentally friendly system with high production speed compared to traditional melt spin line, was manufactured. Functional polyethylene fibers were obtained by this simple and novel melt spinning line (HiPER). The main idea of this

treatment system is to generate an appropriate environment where fibers reach a unique precursor. After the production of control LLDPE fibers (traditional approach) and LLDPE fibers (with HiPER), for preliminary studies, additive containing PE sheets were produced using alumina trihydrate (ATH), nanoclay, nanocellulose, carbon nanotube (MWCNT) by twin-screw extruder and injection molding. According to PE sheet analysis results, flame retardant additives such as nanoclay, ATH-APP hybrid study and micro-size organic phosphorus were adjusted to novel melt spinning line to improve mechanical, thermal, and flammability properties of fibers. The effects of production parameters and additives on the mechanical, morphological, internal structure, thermal and flame retardant properties of the fibers have been revealed by using different test methods.

1.2 Literature Review

1.2.1 Structure and properties of polyethylene (PE)

Polyethylene (PE) polymers have a wide consumption volume in the world. While polyethylene has a market share of 106.9 billion US\$ in 2019, it is expected to have a market share of 124.4 billion US\$ by 2024, with a growth rate of about 2.6% annually. It is considered the second-largest participant of the plastics industry worldwide [1]. The polyethylene molecular structure consists of a long chain backbone with carbon and hydrogen atoms that are paired with each carbon atom and connected by covalent bonds. The chain ends of PE have a methyl group and do not contain any functional groups [2], [3]. The structure of chemically pure PE polymer is alkene and formula of $C_{2n}H_{4n+2}$, n is a polymerization degree as shown in Figure 1.1. Besides the simple chemical structure of polyethylene, PE resins can be classified according to backbone chain length, and various degrees of branches. Polyethylene resin might be produced with broad density ranges which is traditionally separated as three main classes such as low-density PE (LDPE) ($0.910\text{-}0.940\text{ g cm}^{-3}$), linear low-density PE (LLDPE) ($0.915\text{-}0.94\text{ g cm}^{-3}$) and high density PE (HDPE) ($0.945\text{-}0.97\text{ g cm}^{-3}$) shown in Figure 1.1 [4]. According to density differences, PE is also sub-divisions medium density PE (MDPE) ($0.926\text{-}0.940\text{ g cm}^{-3}$), ultra low-density PE (ULDPE), and very low-density PE (VLDPE) have ($<0.915\text{ g cm}^{-3}$) range. Also, the HDPE type, which has an average of several million molecular weight, is called ultrahigh molecular weight (UHMWPE).

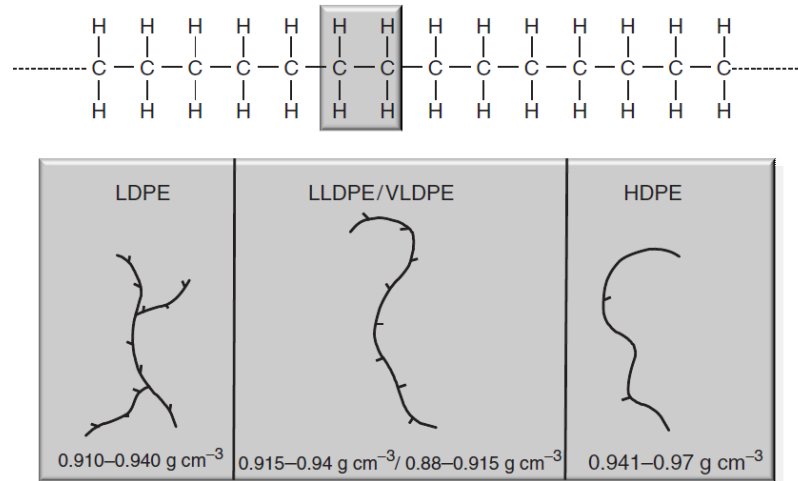


Figure 1.1: Backbone chain structure of polyethylene and various degree of branches [4].

Polyethylene (PE) is a promising material that offers high performances compare with other polymers and different materials such as glass and metal [2]. Prominent characteristic properties of PE are in general, toughness, zero moisture absorption, electrical properties, high theoretical elastic modulus, impact resistance, ease of production, chemical resistance, abrasion resistance, and low friction coefficient and low thermal resistance [2]. The chemical and physical properties of polyethylene resin are composed of its semi-crystalline nature. It is hard, flexible, and chemically inert with high electrical resistance. Chemical inertness and high electrical resistance properties are resulting from covalent bonds between C-C and C-H elements.

On the other hand, polyethylene possesses a relatively low softening point and dimensionally unstable under high stress [3]. Thus, polyethylene is generally used for short-term stress or non-stress conditions such as food packages, storage materials, and pipes. PE has a melting temperature of 130 °C and a pyrolysis temperature of 335-450 °C. Besides, polyethylene is a highly flammable polymer with a 17.4 LOI value and can quickly burn in the air [5]. In Figure 1.2, PE types and their application areas were given.

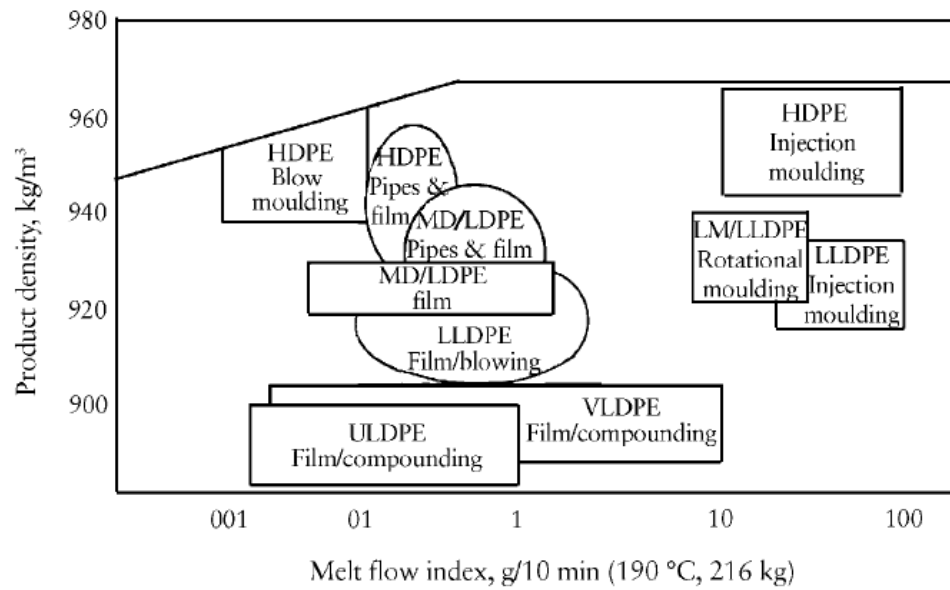


Figure 1.2 : Polyethylene types and production methods: LDPE; LLDPE; MDPE; HDPE; ULDPE; VLDPE [2].

1.2.2 Fiber production method: Melt spinning line

Melt spinning is one of the most common and convenient techniques for the production of polymeric or synthetic filaments such as polyethylene [6], polypropylene (PP) [7], polyurethanes (PU)[8], polyethylene terephthalate (PET) [9]. Hopper, extruder, spin pump (or gear pump), the spinneret, godets, and winding equipment are critical components of the melt spinning line [10] and schematic image of melt spinning line is represented in Figure 1.3. In melt spinning, granules or pellets are firstly fed from hopper to extruder. A polymer that is fed to extruder has to possess specific properties, in particular, melt flow index (MFI) with the range of 10-40 g 10min⁻¹ [10]. The extruder generally has several heating zones to melt polymer. A rotating screw is the major component of the extruder that pressurizes the molten polymer to a gear pump. The molten polymer is transported to a spin pump and passes through the melt filters to remove impurities. A filter is a critical part that prevents the blocking of the spinneret. Spinneret has lots of small orifices (0.3 to 0.8 mm) range from 1 to 150, which enables the production of multifilament in yarn [10]. The molten polymer finally exits from the spinneret holes, which has typically different geometric shapes and subject to cooling zones. As a final step, melt polymer drawing and wind are applied. Extruder capacity and heating zones, spinneret holes and shapes can be varied depending on the fabric capacity and final products. Besides take-up speeds, spin line distance, cooling conditions of spin line, extruder temperatures, a mass of molten

polymer pass through the spinneret, and spinneret hole size are the most critical factors that interact with polymer characteristics in the melt spinning [10].

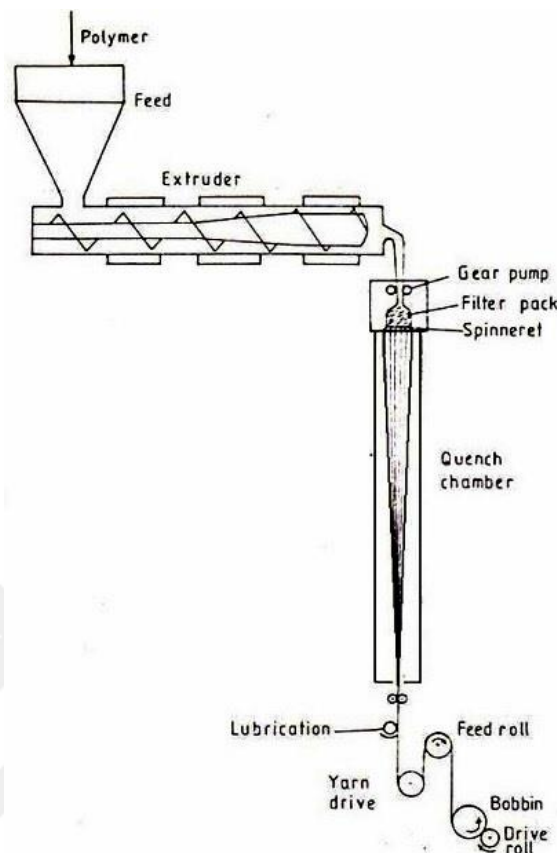


Figure 1.3: Schematic illustration of melt spinning line with main machine components [11].

The aim of the development of the melt spinning line is to reduce the cost, energy, and labor with a high production rate. Ease of processability, high production efficiency, being solvent-free, and low-cost production makes the melt-spinning technique preferable [10], among other fiber formation techniques such as dry spinning [12], and wet spinning [13]. In addition to these advantages, melt-spinning is suitable to be modified its operation and process conditions. The modification allows for changing fiber formation parameters to gain different functionalities for various end-use purposes.

In traditional melt spinning lines, the addition of polymeric is achieved after production or by the chemical addition of the raw material before feeding. The need for an additional process increases production time and expense. Thus, in addition to the conventional melt spinning line, modified melt spin lines are also used with the development integrated into this line, fibers are made to the high performance.

Polyester, polypropylene, and nylon fibers were produced with modified melt spin methods. This developed line was originally designed by Cuculo et al. in the 1990s for the production of polyester fibers with high crystallinity and orientation [14], [15]. In this system, a liquid isothermal bath (LIB) has been developed for high performance polyester fiber production. The molten fibers were immersed in the liquid bath, which is set to temperatures higher than the glassy transition temperature of PET, and then wrapped at a speed of 3000-7000 m/min [14]. After production, the fibers were subjected to hot drawing at low rates, and fibers with high orientation and crystallinity were produced [15]. The bath in the current system was translated from vertical to horizontal bath design (hIB) by Cuculo et al. [16]. It was revealed that the take-up speed and bath temperature are more important parameters for the production of PEN fibers with high modules [16]. Using this system, various production studies have been carried out with different thermoplastic polymers in order to improve the mechanical-morphological properties of the fibers and to produce high performance fibers [17]–[21]. Non-toxic bath fluids were then used in the environmentally friendly bath system called ECOB. Avci et al. [22] produced a new type of high strength and modulus polypropylene fiber in an environmentally friendly manner using an ecological isothermal bath (ECOB). The mechanical performance of fibers improved at low drawing ratios applied to the fiber with the ECOB process. In this process, the distance between the spinneret and the ECOB, the temperature of the ECOB fluid, and the drawing speeds are important parameters.

1.2.2.1 Polyethylene fibers

High performance polyethylene fibers have become a common raw material in today's technical textiles thanks to their low density, superior strength, and modulus of elasticity. Although its low thermal resistance limits its usage areas, it is used in many areas such as ballistic protection garments, sportswear, ropes, fishing nets, medical textiles, and even extraordinary sculptures and robots. Efforts to improve fiber properties and minimize their sensitivity are still ongoing [23]. Polyethylene fiber formation for general purposes has extensive applications, not only for economic reasons but also for easy processability, excellent melt dyeability, and low moisture absorption [6]. HDPE and, in particular, linear low-density PE is suitable for filament production by melt spinning technique. At the same time, ultra high molecular weight PE (UHMWPE) can only be achieved by gel spinning from dispersion or solution,

which comprised of 2 wt.% high molecular weight polymer [10]. Drawing ratios around 40-50 is applied at elevated temperatures to the gel like fibers [24]. Extrusion and drawing of UHMWPE are incredibly challenging because of ultra high melt viscosity and molecular entanglements in the fiber before drawing. Spinning of UHMWPE by gel spinning was succeeded in results and commercially high strength, high modulus PE fibers were developed, such as Dyneema and Spectra and sold in various types of coatings, films, ropes, ballistic protection [25].

Dees and Spruiell [26] also studied the structural development of linear PE monofilament by using melt spinning techniques. Subsequently, birefringence, crystallinity, crystal orientation factor, and mechanical properties of as-spun and drawn linear PE fibers were analyzed at a different take-up speed range of 50-560 m/min. These results indicated the structural development. In particular, crystallization behavior in polyethylene depends on the balance between stress and tenacity in the fiber.

Studies about melt elongation properties of linear low-density PE were also revealed by using the melt spinning technique with another article [27]. The study showed low elongation viscosity should be advantageous for the melt drawing technique. The relationship between elongation viscosity and stress was decreased with increasing temperature.

Cho et al. [28] produced linear low-density PE monofilaments from two different melt flow index values of 45 and 50 (g/10min) at elevated take-up velocities 1 to 6 km/min. The interior structure of fibers was analyzed via birefringence, WAXD, DSC, Rheovibron analyses, and tensile tests for mechanical performances. Melt spun fibers exhibited high tensile strength and modulus by increasing take-up speed, which was also proved via birefringence analysis. Moreover, with increasing, speed crystal orientation has transformed an axis into c axis orientation. They reached that maximum stress, 0.076 GPa, and initial modulus 0.605 GPa at 6 km/min.

Kolgjini et al. [29] fabricated LLDPE monofilaments by using a melt-spin line to measure mechanical, thermal, and crystalline structures of fibers. Melt-fiber like filaments were pulled throughout the water bath. Fibers were then passed through the high temperature oven. Also, Kim et al. [30] produced LLDPE fibers by using CNT with different concentrations from 0 wt% to 2wt% to improve the mechanical property and decrease the plastic deformation of the polymer.

For the case of different applications, high performance fibers, which achieved sufficient high Young's modulus and high tensile strength at low elongation at break, are required [25]. Polyethylene has unique and one of the simplest molecular configurations as $\text{CH}_2\text{-CH}_2$ and denotes one of the highest theoretical Young's modulus in crystalline form. Because of the small cross-section and linear zig-zag configuration of polyethylene structure [24]. The strain properties of polyethylene depend on the sample's molecular weight for high strain features and the sample's morphological structure for strain features [3].

In high performance heat and fire-resistant fibers, at least one of the heat resistances, chemical resistance, strength, operating temperatures, and flame retardant properties are found at high levels. One of these features or combinations of these allows filling a gap at the top end of high performance fibers [31], [32].

High performance PE fibers explained Dyneema and Spectra have been produced by the gel spinning process. Ultrahigh molecular weight commercially available PE fibers have been acquired average tensile modulus of 130 GPa and tensile strength 3.7 GPa [25]. Apart from the ultrahigh molecular weight PE, other polyethylene types such as HDPE, LLDPE have not reached the mechanical performance of UHMWPE in the conventional fiber production methods. There are limited sources in the literature about pure linear low-density PE monofilaments (without any additives) because of insufficient mechanical performances against UHMWPE.

Kolgjini et al. [29] also fabricated LLDPE monofilaments by using the melt-spin line. Cold drawn linear low-density PE filaments possessed a maximum elastic modulus of 270MPa and tensile strength of 219 MPa at maximum load.

1.2.3 Flame Retardant Polyethylene Fibers

Polymeric flammability and low thermal resistance arise as a major problem because of the organic nature of polymer materials[33]. There were fires in the USA that resulted in a loss of \$23.0 billion in 2017 [34]. Inhalation of toxic smoke and combustion gases, particularly carbon monoxide, and the injuries from the heat source are the main causes of fire deaths [33]. Thus, great economic and social damages are formed, and intensive efforts are pointed on the polymer market to produce fire retardant materials with reducing fire risk.

Burning is a chemical exothermic reaction with the sum of fuel, heat, and oxygen called the fire triangle. For polymer flammability, the first step is decomposition at elevated temperatures. The fire and fire growth stages of polymeric materials were shown in Figure 1.4. At the ignition phase, external heat is subjected to the polymer material, and heat on the polymer causes an increase in the temperature. The polymer material is continued to heat by flame source until reaching the decomposition temperature (T_d). At the decomposition temperature, chemical changes occur in polymer, and combustible and non-combustible gases, char residues, and liquid condensates are also other decomposition products [35].

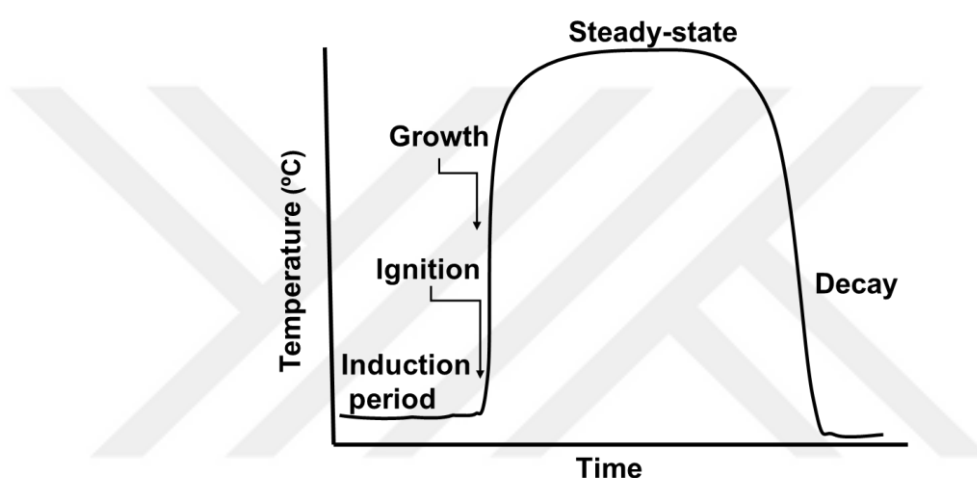


Figure 1.4 : Diagram of stages in a fire.

Mechanism of combustion and production of volatiles are occurred by partial and whole decomposition of the polymer [36]. It is resulting from the decomposition of the reaction of free radicals. Fuel and combustion gases that can react with oxygen, radiative heat transfer, flashover, smoke, energy, and light are obtained [35]. Because of thermal feedback, fuel and combustion gases cause more pyrolysis, fire enhancing, and fuel products, and the flame will continue till flammable fuel is consumed.

Flammability behavior of some important polymers is listed in Table 1.1. Polymers can be subdivided into classes based on their chemical structures. The carbon-containing polymers are one of the classes and possessing no atoms except carbon-hydrogen (C-H), and the main polymer group is a polyolefin, polyethylene, and polypropylene [4]. Oxygen-containing polymers are also second class, and celluloses, polyesters, and polyacrylics are the most important and used polymers [33]. Nitrogen-containing [37], chlorine-containing [38], and fluorine-containing [39] polymers are

other types, and all of them have different physical, chemical properties and uses according to backbone chemical structures. Moreover, these different chemical structures (C, O, N, Cl, and F) indicate different chemical reactivity, burning performance, production, and contents of smoke when they fire [33]. Aromatic rings in the polymer structure, high molecular weight, and cross-linking increase polymer flammability, whereas chain branching, double bonds, and oxygen content in polymer structure decrease polymer flame stability.

Table 1.1 : Flammability behaviors of some common polymers [40].

Inherently Flame Retardant	Less Flame Retardant	Quite Flammable
Polytetrafluoroethylene	Silicones	Polystyrene
Aromatic polyether sulfone	Polycarbonates	Polyacetal
Aromatic polyamides	Polysulfone	Acetals
Aromatic polyimides	LCP (liquid crystal polymers)	Olefins (PP, PE...)
Aromatic polyesters		Polyurethane Nylon
Aromatic polyether		
Polyvinylidene dichloride		

Overall, aromatic polymers that possess an aromatic ring in the polymer backbone exhibit greater flame resistance performance than aliphatic polymers, as shown in Table 1.1. Thus, the burning ability of the polymers depends on polymer formulations and backbone structure. These polymers, which are called less and quite flammable, can acquire highly flame retardancy with the addition of additives. Moreover, ignition, decomposition, combustion, and thermal feedback are other major parameters for fire and fire growth. Several studies indicate the polymeric material structure and pyrolysis mechanism affect the polymer stability [35], [36], [41].

1.2.3.1 Combustion mechanism

Combustion is an oxidative-gas phase reaction, which requires oxygen or air [41]. When a polymer is heated to the critical temperature combustion starts following

melting, decomposition, ignition. Before the combustion of polymer, it initially decomposes into the flammable components. Burning is an exothermic reaction, and if the polymer surface is subjected to sufficient flame and heat, a self-sustaining combustion circle is formed [41].

The commonly used polymers and their thermal temperatures, such as melting (T_m), decomposition or pyrolysis (T_d), and the ignition and the onset of the combustion (T_c) [33] are tabulated in Table 1.2. According to T_c or usually T_d values, a polymer can be classified as flammable or lower flammable. Limiting Oxygen Index (LOI) value is one of the other selective parameters for the flammability of polymer. Fibers that possess LOI value below 21.0 (natural oxygen content in air) are called “very flammable.” In contrast, fibers with between LOI 21.0-25.0 are partially flammable and higher than LOI 25.0 fibers can be called flame retardants with regards to international test standards [41], [40].

Table 1.2 : Critical temperatures to influence the flammability of polymers [41],[5].

Polymers	Melting (T_m) (°C)	Decomposition (T_d) (°C)	Ignition (T_c) (°C)	Limiting oxygen index (LOI)
Polyethylene	130	335-450	340	17.4
Polypropylene	175	320-400	520	17.5-18
Teflon	330	500-550	560	95
PVC	100-260	200-300	390	37-39
Polystrene	240	300-400	350	18.3
Nylon 6,6	260	320-400	490	24-26
Nylon 6	215	300-350	420	23-26
PET	260	280-320	440	23-25
Nomex®	380	410	500 <	28-30
Kevlar®	560	590<	550 <	29

Pure polymers are disintegrated by one or more processes such as end chain scission, random chain scission, chain stripping, and cross-linking and degraded as regard first-order kinetics. On the other hand, synthetic polymers are divided into three physical types, which reveal different combustion behavior, when heat exposed [41]. These are called thermoset, elastomers, and thermoplastics according to their degradation

behaviors. Under heat conditions, thermoset polymers cross-linked degrade to yielding char and volatiles and not melt. Unlike the thermoset polymers, thermoplastics ones initially soften and melt, then decomposed under heat and elastomers are also rubber-like materials [5], [41].

The flammability mechanism of fiber forming materials is demonstrated in Figure 1.5. There are four essential stages during the combustion. The first zone for the formation of combustion is the breaking of the weakest bonds and the formation of local degradation, which radiates combustible gases on the polymer surface. Thus, molecules pyrolysis into small molecules resulting in fuels that capable of burning with different amounts and types, depending on the polymer type [42].

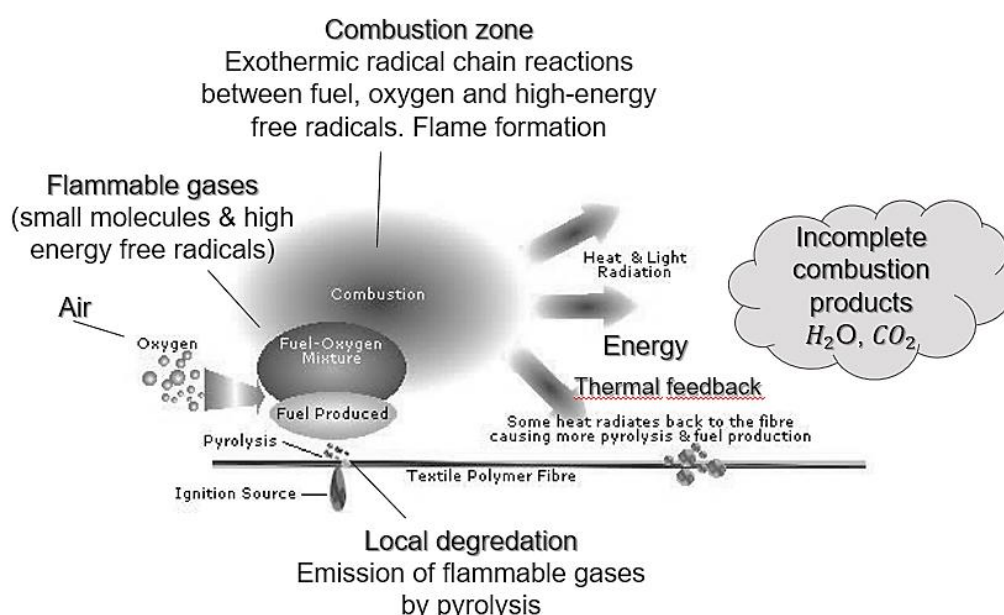


Figure 1.5 : A general schematic illustration of fire and fire growth cycles of polymers [42].

The resulting materials of pyrolysis are the main reason for flame spread. Escaping of fuel (small molecules and high energy free radicals) from the flame as smoke and mixing with oxygen in air provide a significant polymer degradation reaction. In this condition, the temperature is above ignition temperature and enough for the condensed phase reactions of the polymer [41]. These reactions of combustion will yield exothermic radical chain reactions between fuel and oxygen and high energy free radicals. Then, it creates a flame that radiates heat, light, smoke, fumes, and energy. Volatile products escape from the flame while the heavier products remain to do further reaction and ultimately degrade as char. Some of the heat radiates back to the

fiber surface, causing more pyrolysis and fuel products with the combustion cycle, as indicated schematically in Figure 1.5 [41], [42].

1.2.3.2 Thermal properties and burning behaviors of polyethylene

Semi-crystalline polymers such as polyethylene usually show a melting range instead of an exact melting point. [3]. These melting temperatures are relatively low compared to other commercial polyolefin polymers listed in Table 1.2. The branching contents, molecular weight, density, crystallinity, cooling rate, and orientation determine the melting temperatures. Various types of PEs possess different melting temperatures; for instance, high branching contents cause lower melting temperatures [3]. The thermal degradation of polyethylene and other polyolefin polymers possess the main degradation process following by initial random chain scission [41], [43]. Also, linear low-density polyethylene has melt temperatures of about 10 °C lower than comparable HDPE due to the abovementioned properties [3]. In particular, the low softening and melting points are the characteristic thermal properties of polyethylene and determine the real application areas of PE.

The heat of fusion (enthalpy) (ΔH_f) depends on the degree of crystallinity and heat of fusion of polyethylene 69 cal/g for 100% crystalline sample. The heat of fusion is principally related to the rate of polymer crystallinity, and degree of orientation, such as higher crystalline and highly oriented polymers, possess a higher heat fusion rate [3]. Besides, the thermal conductivity of polyethylene is provided by the transmission of vibrational or rotational energy due to the lack of free electrons to conduct thermal energy. Transmittance of heat is more effective in crystalline polymer, so HDPE 11-12 [(cal.cm/sec/cm².°C) x 10⁻⁴] is more conductive than other polyethylene types and heat conductivity of linear low density polyethylene is 8-10 [(cal.cm/sec/cm².°C) x 10⁻⁴] [3]. Heat capacity is also the amount of heat to increase polymer's temperature for a degree, and polyethylene has low heat capacity because of the simplicity of the polyethylene backbone [3]. Moreover, thermal expansion of linear low-density PE is 70-150 10⁻⁶in./in./°C) and high compared to other polyethylene types because of lower crystallinity [3].

Although polyethylene produces low smoke emission during the burning, it is a polymer that can be easily burned, and polymer drops can be seen while burning [44], [45]. Due to its aliphatic carbon structure, polyethylene burns quickly without any

residue and dripping. Polyethylene tends to spread the flame due to polymer dripping, and because of its higher heat release rate (HRR) value, it poses a danger in real fire situations. Also, polyethylene types possess low ignition time compared to other thermoplastic polymers [45]. PE has a very low limit oxygen index value, as shown in Table 1.2.

Thermal degradation of PE involves oxidative degradation, resulting in flammable combustion products containing several saturated and unsaturated hydrocarbons between C_2 and C_{23} [46]. The degradation starts with random chain scission into the smaller parts such as primary radicals for HDPE and secondary and tertiary radicals for LDPE due to the side chains [47]. Carbon dioxide (CO_2), water, particulate matter, and carbon monoxide (CO) are major combustion products, and some polycyclic aromatic hydrocarbons (PAHs) are also other combustion products [47].

1.2.4 Flame retardant systems

One of the most important disadvantages of polymeric materials is their low resistance to combustion, and they release large amounts of toxin gas during combustion. Flame retardant agents are additives that are used to stop or reduce the flammability of the polymer material. The general degradation and burning behavior of polymers are shown in Figure 1.6.

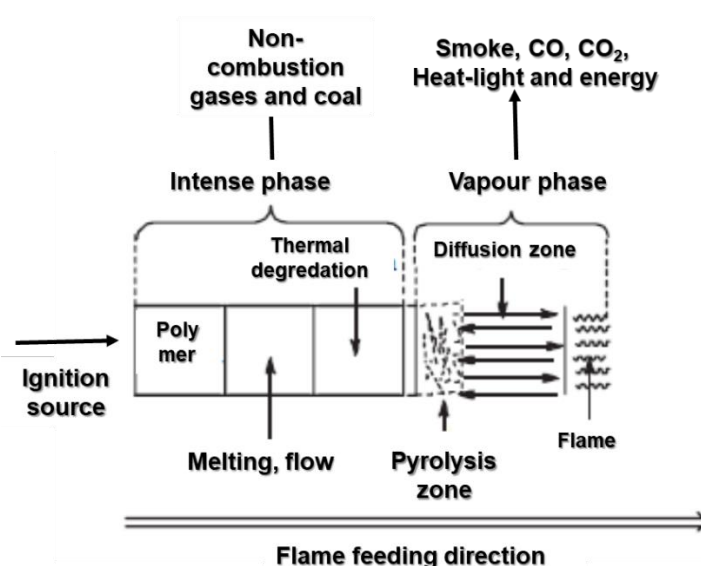


Figure 1.6 : The burning and degradation mechanism of a polymer.

Flame retardant additives are divided into different categories according to their content or mechanism of action [48]. According to the material contents, it is generally

classified as halogen-containing and halogen-free flame retardants. Halogen-containing flame retardants have an efficient impact mechanism. However, they have been banned in most countries today, as they produce harmful chemical compounds in addition to their powerful mechanism of action. Therefore, as an alternative to halogen-containing additives, intumescent and phosphorus containing additives, metal hydroxide, and nanocomposite based additives are becoming more common [49], [50]. The best known and most widely used flame retardant fibers with high mechanical and thermal properties are aramid fiber meta-aramid Nomex and para-aramid Kevlar. Nomex (DuPont) fibers do not ignite, melt, and drip. As a result of these properties, they have an important place in the fireproof and flame resistance market [51], [52].

The FR additives are activated in the solid phase after coal formation or gas phase according to the combustion mechanisms and provide features such as flame retardant to the fibers and reduction of toxic gas emissions, as shown in Figure 1.7.

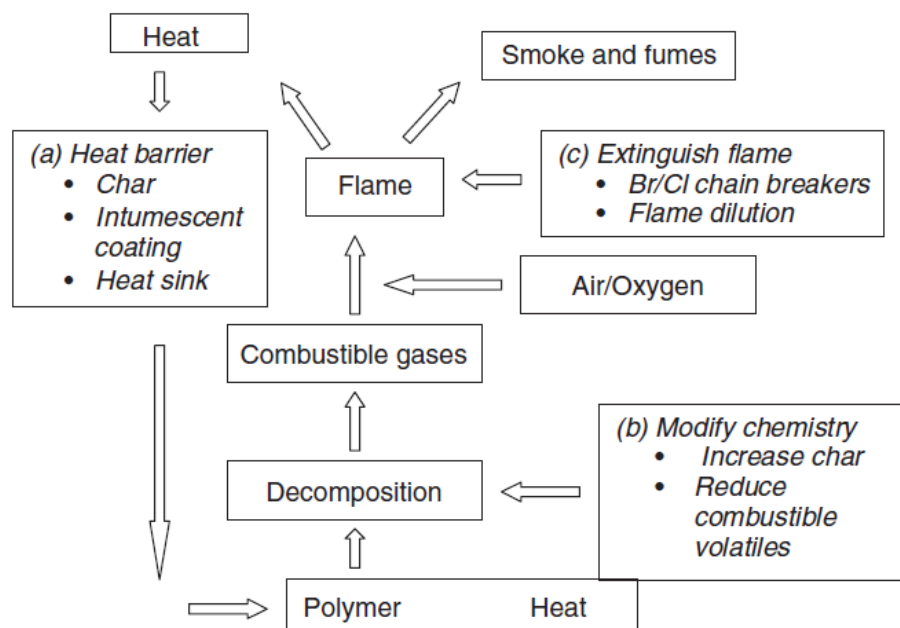


Figure 1.7 : Schematic diagram of polymer burning with the effective flame retardant systems [41].

These mechanisms can be explained in three subtitles:

Vapor phase mechanism: During the combustion process, flame retardant additives react with the vapor phase of the burning polymer to prevent the formation of free radicals at the molecular level and stop the combustion process. Inhibition of radicals

that will occur in flame and burning areas that initiate combustion areas is generally provided with antimony and halogen-based additives.

Carbonization formation in solid-phase mechanism: Flame retardant additives that form a charcoal structure react to form a carbonaceous layer on the surface of the material. With this layer, the polymer is tried to be isolated from the flammable environment effect, the decomposition reactions are slowed down and the release of combustible or non-flammable additional gases is suppressed with the barrier it creates. This method is generally achieved in non-halogen systems, for example, with the use of phosphorus and nitrogen chemistry and nanocomposite materials called halogen-free additives.

Extinguishing and cooling mechanism: Extinguishing and cooling mechanisms are dominated in hydrated minerals and halogen-free flame retardant systems. In these systems, as a result of the endothermic reaction, the water molecules in the structure are released, and the target polymer is cooled, and the combustion process is mitigated. Some hydrated inorganic minerals are added, and the heat on the material is reduced, and flammable volatiles are reduced [53].

1.2.4.1 Halogen containing flame retardants

Flame retardants with halogen content include iodine (I), bromine (Br), chlorine (Cl) and fluorine (F) elements and their compounds. The effectiveness of halogen compounds depends on the ease of halogen being released during combustion. Halogen-containing additives are effective in the gas phase. These additives dilute flammable gases and reduce their effectiveness. When halogen-containing flame retardants react with organic polymers, they usually produce diatomic inorganic compounds that possess hydrogen halogen (HX) formulation. X in the organic compound is one of the halogen compounds and is a water-soluble gas [5]. High reactive HO^* and H^* radicals act in the gas phase and react with other radicals formed during combustion like halogenated X radicals. Thanks to these effective flame retardants, less reactive radicals are formed by reducing the kinetics of combustion caused by the degradation shown in Figure 1.8.

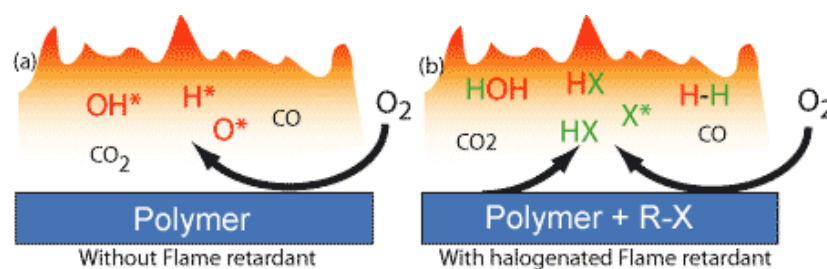


Figure 1.8 : Comparison of (a) non-FR containing, (b) FR containing burning mechanism [54].

The high heat capacity of hydrogen halides and dilution of flammable gases reduce the mass concentration of flammable gases and create a decrease in flame temperature [55]. Deca (decabromodiphenyl oxide) is one of the higher performances and cost-effective halogen containing flame retardant products. This material is used over the last decades for polyolefin, nylon, polyester, PS, PVC, and other resins. Moreover, because of the decomposition temperature, 300-310 °C, it is suitable for high temperature operations [48]. Although halogen-containing flame retardants are widely used, they pose a problem due to the toxic effect on the environment and the formation of corrosive smoke. For these reasons, their uses are restricted and banned in several countries. Weil et al. mixed 6% decabromodiphenyl oxide (deca) and 2% antimony trioxide with LDPE resin, and then the UL94 V2 ratio was obtained. To achieve the V0 ratio at UL94 for LDPE, more Deca and antimony trioxide, such as 22% and 6%, should be used, respectively [56]. The patent includes the production of flame retardant fibers and fabrics using polyolefin, especially polypropylene [57]. They preferred decabromodiphenyl oxide since it possesses low acute toxicity. The bromine content in the material is about 83-85%. Also, there is a trisisocyanate where at least one bromine for each phenyl radical group. The formulation of bromine and isocyanate was mixed with a polymer, and the blended polymer was extruded. The flame retardant was blended into the polymer with the amount of about from 3 wt% to 15 wt% during or before extrusion. Besides, there is no grey color when the fabric is dyed [57]. Also, in this patent [58], polypropylene fibers and filaments were produced using halogen containing flame retardants such as bromine and antimony oxide. The method contains mixing additives described above with anti-oxidant and low-density polyethylene (LDPE). The blended compounds were extruded and spun into fine denier, flame retardant, and color stable polypropylene fibers. Firstly, aromatic bromine compound, LDPE, and thermal antioxidant were mixed and then extruded. To form the first

compound, the extruded mixture was pelletized. Antimony oxide, LDPE, and thermal antioxidants were also mixed, extruded, and pelletized to form the second pellet. The pellets that form by step 1 and 2 were mixed, and the resulting mixture was again extruded and pelletized. Finally, pelletized granules were mixed and fed into a melt spinning line to form fibers. The spinning speeds were ranging from 200 to 1000 m/min and at 2 to 25 denier per fiber. Another example is also expressed that halogen containing additives were firstly mixed and extruded. Pellets of halogen additives were mixed with LDPE. After extrusion and pelletizing, final mixture was mixed and extruded with thermal antioxidants and polypropylene, respectively. The resulting mixture was spun by melt spinning line in accordance with example one [58].

1.2.4.2 Mineral containing flame retardants

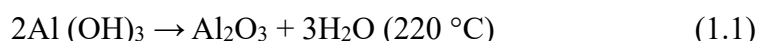
Among the flame retardants, one of the most commonly used class is mineral containing FRs and usually found in the form of micro-sized particles [59]. Mineral containing flame retardants are environmentally friendly and abundant. They provide the endothermic cooling reactions that create during combustion at temperatures of 200 °C and above. The most widely used metal hydroxide or metal oxide types are given in Table 1.3. The most commonly used varieties are aluminum trihydrate (ATH) and magnesium hydroxide ($\text{Mg}(\text{OH})_2$ or MH). The main mechanisms of ATH and MH are explained as their thermal decomposition, forming oxides (MgO and Al_2O_3), and releasing water [60]. In 2015, aluminum trihydrate had the highest share of use among halogen-free flame retardant additives, and the estimated growth rate CAGR of ATH was 5.7% in subsequent years, resulting in restriction of halogen containing FR additives [61]. They are widely used as flame retardant additives because they are inexpensive, environmentally friendly, and abundant in nature. Besides, mineral additives are used as flame retardant additives for most polymers, especially polyethylene.

Table 1.3 : Important mineral containing flame retardants and their formulations.

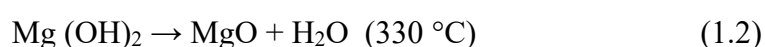
Chemical Name	Formulations
Aluminum trihydrate	$\text{Al}(\text{OH})_3$
Magnesium carbonate	$\text{Mg}(\text{CO})_3$
Magnesium hydroxide	$\text{Mg}(\text{OH})_2$
Zinc borate	$2\text{ZnO} \cdot 3\text{B}_2\text{O}_3 \cdot 3.5\text{H}_2\text{O}$
Calcium borate	$\text{Ca}_3(\text{BO}_3)_2$

ATH and Mg (OH)₂ absorb the heat of the burning polymer as a result of the endothermic reaction during combustion at 200 °C and above. In addition, during the combustion, water molecules in the structure of the additives emerge, so that the burning substance is cooled and the flammable gases are diluted. The acting mechanism of aluminum hydroxide (Eq. 1.1) and magnesium hydroxide (Eq. 1.2) are given below [62].

Aluminum trihydrate



Magnesium hydroxide



Besides, ATH forms a layer of sediment (alumina) as a result of combustion. Similar to coal layer formation, the alumina layer stops the interaction of polymers with the fire source and prevents the continuity of burning [55]. In order to improve the flame retardancy of polymers, ATH concentration might go above 40%. To obtain even higher flame retardancy in LOI and UL-94 tests, it is necessary to use additives 60% and above [53]. This situation causes production and mechanical problems for fiber products. To produce stronger FR fibers, it is necessary to reduce the amount of ATH. For this reason, phosphorus, clay, and primarily other nano-sized additives are used to provide the synergistic effects on the mineral additives [53], [63].

To provide synergistic effects of mineral containing metal hydroxides, ATH and Mg (OH)₂, Fredi et al. used fumed nanosilica with micro-sized ATH and Mg(OH)₂ for linear low-density polyethylene (LLDPE) in different concentrations. Thermal, FR, mechanical and microstructural properties of samples were analyzed [59]. Polymer additive compounds were prepared via Thermo Haake PolyLab Rheomix mixer, and then samples were hot-pressed to produce test specimens. The best results were obtained from the sample that has PE-HF-20(%)-fume nanosilica-5(%). The LOI result is 31.5 %, and the cone calorimeter pHRR result is 246 kW/m² [59].

Lujan-Acosta et al. grafted amino alcohol on the PE and mixed with ethylene-vinyl acetate (EVA) that contains polar groups for forming PE-based nanocomposites [60]. Nanoclay and metal hydroxides (ATH, MH) synergistic effects were studied in LDPE/EVA nanocomposite.

1.2.4.3 Phosphorus containing flame retardants

Flame retardants with phosphorus content are known as the second most used flame retardant additive in the world market due to lower density, environment-friendly effect, FR efficiency, and light stability [64]. All phosphorus flame retardants are separated into three main classes, such as inorganic, semi-organic, and phosphate and phosphonate esters [64]. Phosphorus containing flame retardants mentioned before can generally be described as elemental red phosphorus, inorganic phosphates, organic phosphorus-based products, and chloro-organophosphates, as shown in Figure 1.10 [55], [64].

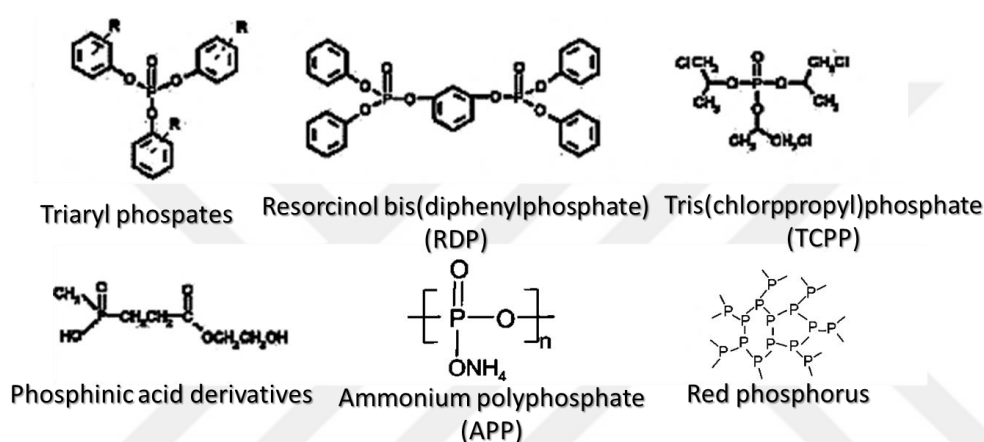


Figure 1.10: Phosphor containing fire retardants for thermoplastic polymers [65].

Water-soluble phosphorus FRs are usually used for cellulosic, organic products, and cross-linkers, whereas water-insoluble FRs are used for wide applications in thermoplastics, thermosets, coating, etc. [64]. The mechanism of action of flame retardants with phosphorus content shows activity in solid and condense phases depending on their combustion processes and chemical structures. Since they are effective in both solid and gas phases, they can provide high efficiency with low concentrations. The effect of phosphorus additives in both solid and gas phases has enabled them to be used extensively to provide flame retardant properties to the fibers [49].

To be effective in the solid phase, the additive burns, and swells, expanding and forming the coal layer covering the polymer surface. Flame retardants that form an insulation layer are called the intumescence coating layer. This mechanism is the intumescence flame retardant, and this layer protects the polymer surface by breaking

the interactions between polymer and fire. In general, phosphorus additives are known to have a significant effect on the chemical structure of polymers containing oxygen and nitrogen [55]. For the phosphorus additives to be effective in the solid phase and to form coal formation, oxygen-containing groups must be present in the polymer's chemical structure. The combination of intumescent, melamine phosphate, and viscose fibers exhibit extraordinary fire and heat resistance properties compared with individual structures [41]. Another polyethylene flammability study [66] shows that the combination of APP and LDH in the PE matrix creates char formation. Also, this combination effective in the condense phase, whereas this system does not affect the time to ignition PE. Therefore, in polyolefin such as polyethylene, phosphorus-containing additives are effective in the gas phase. In order to act in the solid phase, it is necessary to add synergistic agents that will provide coal formation [44], [67].

In gas-phase action mechanisms, it is observed that they suppress smoke better and do not produce corrosive by-products compared to halogen-containing additives [68]. Phosphorus based additives are one of the most effective inhibitors of combustion with volatile products [64].

The patent describes the disclosure of flame retardant coatings based on the carbonized and the formable foam layer [69]. Besides, to provide FR coating without using melamine, water-resistant after drying, and a small amount of NH_3 . Prepared FR coatings were applied on the steel sheet, and water resistance and insulation properties were analyzed. Also, to determine the NH_3 dry sample was placed at the system to simulate humidity in the air. Commercial materials were used in this patent, such as Pliolite, Goodyear, and Exolit AP, Clariant. Six examples were prepared, and according to fire tests, Exolit AP 422 was mixed with aliphatic urethane-acrylic hybrid, melamine polyphosphate, dipentaerythritol, TiO_2 , thickener, filler with appropriate ratios by weight. As a result of fire tests, for DIN 4102 classification, F 60 and 130 ppm of NH_3 releasing were measured [69].

1.2.4.4 Flame retardant nano-dimensional additives

There are various synthesis approaches and types of nano-sized materials used in nanocomposite reinforcements have. Nanomaterials are generally classified depending on their dimensionality instead of chemical classifications. According to the geometry of nanomaterials shown in Figure 1.11, each of them possesses different specific

nanoscale dimensions including zero-dimensional (0D), one-dimensional (1D), two-dimensional (2D) and three-dimensional (3D) materials [70], [71]. The materials with all external dimensions at the nanoscale (between 1 and 100 nm) are called 0D materials, including quantum dots, highly symmetrical dendrimers, ring of zinc oxide, and fullerenes [71]. These materials usually use in electronic, cell maker, and emulsifier applications [71]. 1D materials also possess two external dimensions at the nanoscale, and the third one is usually at the micron size. Nanotubes, nanorods, nanofibers, and nanowires are examples of 1D materials [71]. Two-dimensional materials that have only one dimension at the nanoscale include thin films, nanocoatings, and nanoplates. The last one, 3D, does not have any external nano dimension but shows nanoscale properties in internal, for example, nanocomposites and nanostructured materials [71].

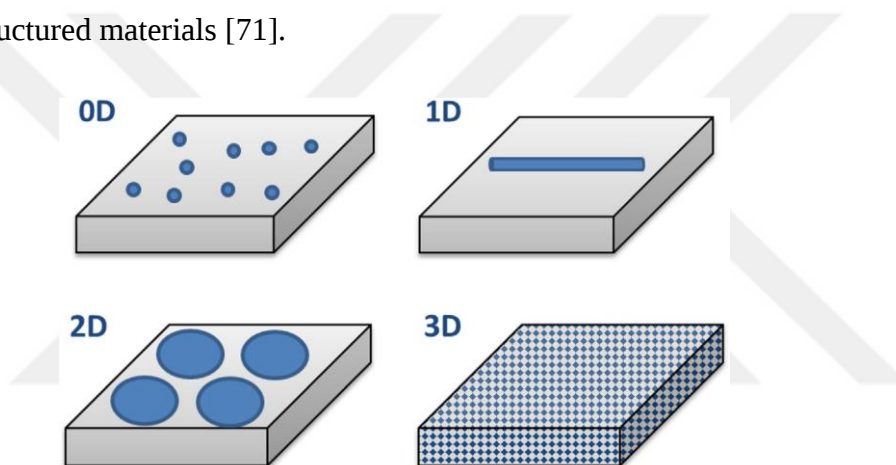


Figure 1.11 : Nanomaterials depend on dimensionality [71].

Nowadays, the additives with nanoscale have been drawn attention due to exhibit more functional properties than microscale additives when used at fewer proportions than conventional micron-size additives.

The FR properties of nano additives can be explained in two mechanisms:

- Reduction of heat release rate (HRR),
- Reduction in polymers dripping and transmit flame [48].

The enhancement studies are ongoing to develop fire, and heat properties of polymers and their nanocomposite studies seems a promising method. The grain size of the additives added into the fiber-like materials is one of the most important properties for the selection of additives in terms of producing high performance fiber and, at the same time, providing a fire retardant effect. To smooth and continuous fiber formation, a

maximum amount of 5% additive should be added to the polymer. The high efficiency of nanoparticles at low concentration makes it possible to use nanoscale additives in terms of high-performance fiber production. Therefore, as compared to the conventional additives, nano additives do not have any negative effect on the physical properties of the material in optimum conditions, as well as improving the flame retardant properties of the polymer material. However, the use of nano-additives alone in the polymer matrix as flame retardants may not be sufficient for the polymeric materials to pass flame retardant tests. Therefore, besides other conventional flammable additives, they are generally used to provide a synergistic effect that acts as a solid barrier by supporting combustion improves or coal formation. Thanks to their high surface area and volume ratio, they have a positive effect on contributing to flammability. Thus, nano additives do not dissolve into the polymer, and they are used to give a synergistic effect with other flame retardant agents. For the nonpolar polymers such as polyethylene, a compatibilizer or additive containing polar group must be mixed with the polymer to provide a homogeneous distribution of additives. Therefore, many studies have been carried out to improve homogeneous dispersion in PE-based composite materials using any compatibilizer. Lujan-Acosta et al. studied with ethylene-vinyl acetate (EVA) that contains polar groups to produce PE-based nanocomposites, and well-dispersed filler nanocomposites were obtained using EVA without any compatibilizer [60].

Recent studies for the polymer flammability have a focus on layered inorganic compounds such as organo-modified montmorillonite clay (MMT), organo-modified layered double hydroxides (LDH) and also carbon nanotubes (CNT) as filler for polymer nanocomposites [48], [66]. In 1976, Japanese firm Unitika first used clay as a flame retardant with Nylon-6 polymer [72],[73]. In the literature, it was seen that a small amount of nanoclay in the polymer enhances the flame retardant properties, in particular, lowering the peak of heat release rate [74]. The studies are stated that the addition of nanoclay increases the formation of carbon pellets as a result of the combustion of the polymer material and cuts the contact of the flame by serving as a barrier by coating the sample surface of the carbon pellet [75], [76]. In the study by Zhang et al., it was observed that the addition of nanoclay reduced the flammability of polymeric, synthetic fibers [35]. Besides, Smart et al. also improved the combustion properties and lowered the pHRR value by adding nanoclay to synthetic fibers

obtained from polypropylene (PP) [74]. The peak heat release rate (pHRR) efficiency depends on the polymeric material and nano additive types. For the polyolefin PE and PP, the reduction of pHRR is expecting about 20-50% using nano clay as a FR additive [70]. Nano additives did not improve LOI values, which is evidence for condensed phase efficiency [70]. Rather than FR additives individual use, two or more additive combinations ensure the synergistic FR mechanism as shown in Figure 1.12. To investigate the individual and combined effects of the nano additives on the FR performance, nanoclay mixed with MWCNT. After the production, Figure 1.12 demonstrates the combination of nanoclay and MWCNT decreased the heat release rate of the EVA compared with their individual results [48].

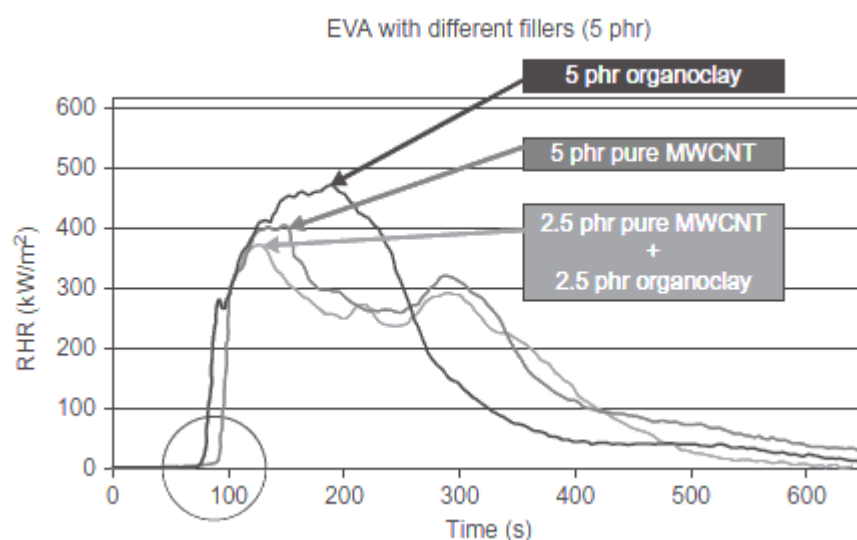


Figure 1.12 : Heat release rate results of different CNT compositions [48].

Moreover, nanocellulose can be utilized as flame retardant agents for polymers. There are limited studies about FR efficiency of nanocellulose. Its FR mechanism is based on decreasing combustion properties, such as heat release rate, dripping behaviors, and barrier effect by coating the sample surface. Mngomezulu et al. examine the thermal decomposition properties of cellulose. They demonstrated that firstly cellulose releases water absorbed at 50-200 °C and/or the moisture it has, then the depolymerization of hemicellulose between 200-370 °C and finally the separation of the glycosidic bonds of the cellulose between 340-370 °C. Mngomezulu et al. explained the decomposition of cellulose consists of the main stages mentioned above. It has also been reported that dehydrocellulose decomposes into coal and volatile substances, laevoglucosan (LVG) formation, LVG produces combustion and non-

flammable volatile substance contributes to the formation of gases, tar, and coal [77]. Lou et al., also stated that with the addition of nanocellulose into the intumescence flame retardant with the polyurethane foam as a matrix, nanocellulose increases the formation of coal during burning [78]. Besides, Liu et al., mimetic the pearl and produced nano paper by adding nanoclay on the cellulose nanofiber matrix. The resulting combustions of nanoclay-nanocellulose enhance properties of nano papers and observed that self-extinguishing and oxygen barrier layers improve the formation [79].

1.2.5 Test methods on flame retardancy

Generally, fibers with a 25% limit oxygen index (LOI) value can be classified as a flame retardant. Although the LOI test does not make sense alone during a real fire, it helps us to grade materials quantitatively. It also describes the minimum oxygen concentration that must be present in the air to continue combustion. In addition to the LOI test, the combustion reaction of all polymers, especially some high performance fibers, is evaluated using a cone calorimeter test, and their heat resistance is examined by thermal analysis (TGA) [31]. Polymeric materials can generally be exposed to temperatures above operating temperatures. But after a while, it will begin to break the polymer because of high temperature. It will also reduce the mechanical strength of polymers, especially fibers, and disrupt the current form [51].

1.2.5.1 Limiting oxygen index (LOI)

The LOI test is applied to determine the minimum amount of oxygen that should be present in the environment so that flammable materials ignite and continue burning after the ignition occurs [80]. Normally, the atmosphere contains 20.8% oxygen and 78% nitrogen. Thus, different N/O concentrations enable the determination of the burning behaviors of materials in atmospheric conditions. The schematic images of the LOI test mechanism and different sample holders depend on the form of the sample are expressed in Figure 1.13.

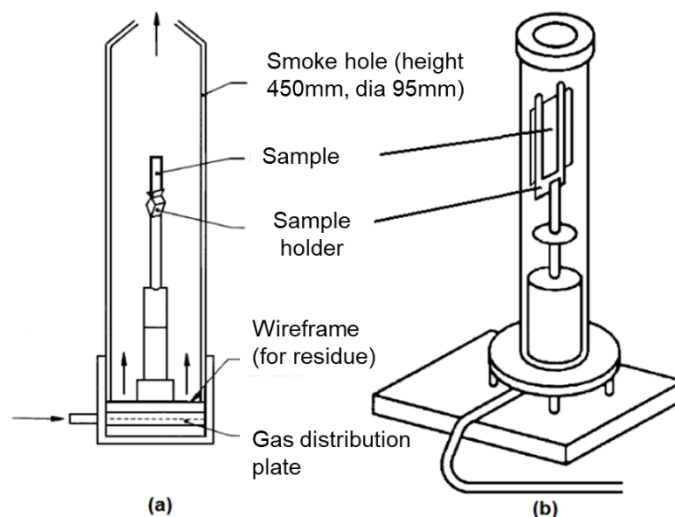


Figure 1.13 : Schematic images of LOI test samples for mold and textile products.

According to the ASTM D2863-10 standard [81], the preparation of different test sample sizes for the LOI test is defined in Table 1.4. Prepared samples continue to burn for 180 seconds, or if the burning length of the mold sample exceeds 50 mm within this period, the sample does not pass from the test.

Table 1.4 : According to ASTM D2863-10 standard sample dimensions for the LOI test.

Sample	Dimension		
	Length (mm)	Width (mm)	Thickness (mm)
Mold	100	10±0,5	4±0,25
Textile, thin film	140	52±0,5	≤10,5

LOI test enables us to classify the materials on the burning behavior. Since the oxygen content in the air is 20.8%, materials with an LOI value below 21.0% are defined as easily burning materials. When the LOI value rises above 21.0%, the combustion slows down. When the LOI value exceeds 26.0-28.0%, the materials are considered to flame retardant. Although the LOI test does not represent a real fire situation, it allows us to consider the materials quantitatively. Besides, the combustion reaction of some high performance fibers is evaluated using cone calorimetry, and heat resistance is examined by thermal analysis (TG/DTG) [31].

1.2.5.2 Microscale combustion calorimeter (MCC)

The micro combustion calorimeter (MCC) test was developed by the U.S. Federal Aviation Administration (FAA). It is based on the measurement of the combustion

temperature of products that occur during programmable heating [82]. The standard of the MCC test is ASTM D 7309 [83]. With this technique shown in Figure 1.14, micro-scale thermal analysis and flammability properties may be directly related. Besides, this test is convenient to evaluate the flammability of small scales samples such as milligram scale (usually 1-10 mg). The test sample is placed in an inert, heat-resistant pan and moved to the sample chamber inside the device. In there, the sample chamber is heated by a controlled heating program (1 K/s) under the inert atmosphere, and pyrolysis occurs. Volatiles are released after pyrolysis, and the substances combine with oxygen at 900 °C in an oxygenated combustion calorimeter. The data obtained in this contact is used to calculate the burning temperature of pyrolysis products. By way of the computer algorithm, oxygen consumption and mass flow rate are converted to specific heat release (W/g) as a function of temperature.

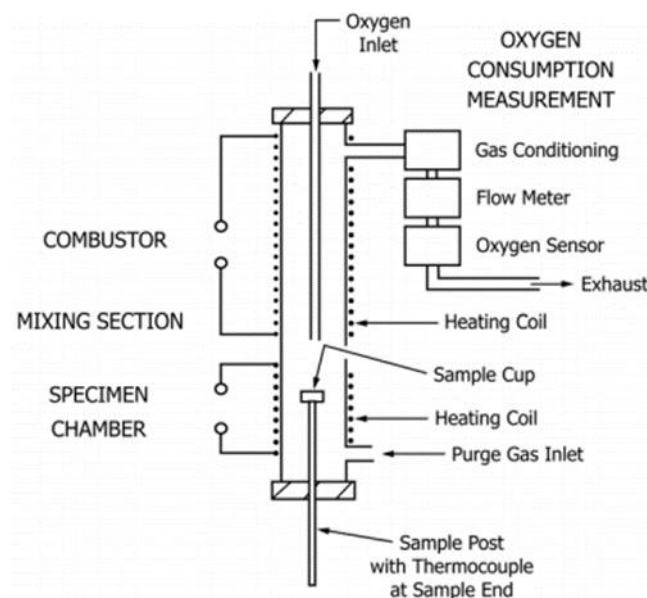


Figure 1.14 : The schematic image of micro scale combustion calorimeter [84].

As a result of the MCC test, heat release capacity (HR capacity), specific heat release rate (pHRR), and total heat release values (THR) are obtained. The peak of specific heat release rate and the temperature of the peak of pHRR are used to evaluate the fire performance of materials. The most important advantage of the MCC test is that it allows the measurement of heat release rate (HRR), which plays an important role in the case of real fire and estimation of the possible effects of the fire. High performance fibers with high heat resistance can also be exposed to temperatures above operating temperatures. However, high temperatures cause the degradation of fibers in time. This

situation decreases the mechanical performance and breaks the existing shapes of the fibers [51].

1.2.5.3 UL-94 test

UL-94 test or (ASTM D 3801 and ISO 1210) is a method that was developed by Underwriters Laboratories to evaluate the flammability of plastic materials such as electrical and electronic devices [83]. The test evaluates how long the polymeric sample burns when the 20 mm flame source is exposed to the sample for 10 seconds. Apart from determining the flammability period, the polymer's dripping behavior to cotton that is placed 300 mm below the sample is also observed. According to the sample size and shape, there are two test methods, horizontal and vertical, to determine flammability. The horizontal and vertical test methods are shown in Figure 1.15 with test dimensions. The vertical test has two times of flame first one determines the time required to sample to burn and time to extinction. The second one also determines flame extinction, char extinction, and dripping. Besides, the horizontal test flame must be at 45° angle for 30 seconds. The burning time and length of the sample are observed. In these tests, thinner samples can burn easily and more flammable. Therefore, the length of the sample has to be 125 ± 5 mm, width 13 ± 0.5 mm, and the maximum thickness of 13 mm [83].

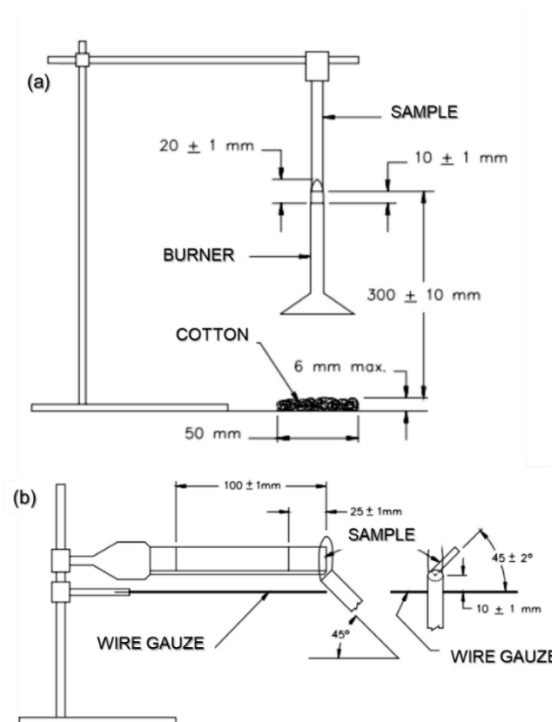


Figure 1.15 : Schematic UL-94 test methods (a) vertical, (b) horizontal [83].

After the UL-94 test, results are classified according to the standard, and samples are graded as V0, V1, and V2. A V0 classification means the lowest flammability and burning time is less than 10 seconds. However, A V1 degree is more flammable than V0 and burning time less than 30 seconds. A V2 classification also possesses the highest flammability behavior, and the burning time is less than 30 seconds. It has polymer dripping that ignites cotton under the test mechanism [83].

1.2.5.4 Cone calorimetry test

Cone calorimeter is a common test method to examine the burning behaviors of materials. The basic principle of the cone calorimeter test specified in Figure 1.16 is based on the measurement of the oxygen concentration in the flammable gases of the test sample exposed to certain heat flow ($10\text{-}100\text{ kW/m}^2$). Sample sizes are determined as $100\text{mm} \times 100\text{mm} \times 3\text{mm}$ (minimum) by the test standard (ISO 5660). Samples are placed in the device with aluminum foil trays. Thanks to the sensitive balance on the platform where the sample is placed, the mass loss in the sample can also be monitored due to the effect of combustion during the test. The heat release rate (HRR) obtained as a result of the test is expressed in kW/m^2 , and the peak and maximum values (pHRR and HRRmax) of this value are used to evaluate the burning and fire behavior of the materials. Besides, time to ignition (TTI), critical ignition heat flux, the total amount of heat released, mass loss rate, and CO/CO₂ gas concentrations are determined by the cone calorimeter test.

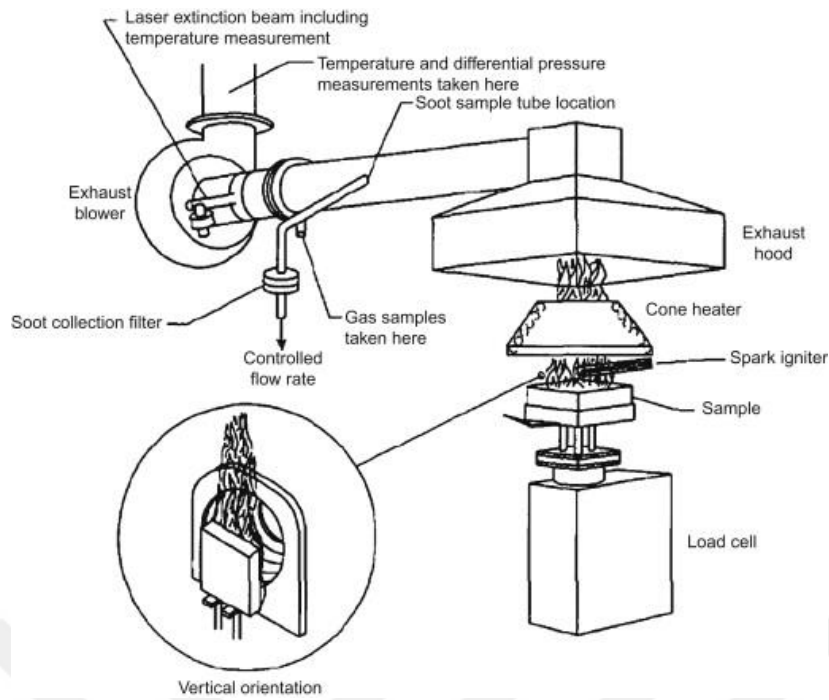


Figure 1.16 : Schematic image of the cone calorimeter test method [85].

1.2.5.5 Thermogravimetric analysis (TG/DTG)

Thermogravimetric analysis (TG/DTG) is an analysis method that provides important information about the degradation behavior of polymers under controlled conditions. In thermogravimetric analysis, polymers are analyzed in different atmospheres such as air, nitrogen and up to a certain temperature at a certain heating rate. In the analysis carried out in the air atmosphere, the temperature value with the highest mass loss during the decomposition gives the ignition temperature. Because the point where the most mass loss in the polymer structure is at this temperature value. After the test, the burning sample may leave some residue, depending on the sample composition and degradation behavior.

1.3 Hypothesis

Polyethylene, thanks to its high theoretical Young modulus, semi-crystalline morphology, cheap and wide usage area in the world, has been chosen as a polymeric material. However, its chemical structure causes low thermal resistance and flame retardant properties. The aim of the study is that to produce high strength LDPE fibers by a novel melt spinning line called HiPER and, to improve the thermal, and flame retardant properties of the fibers by integrating nano and micro-sized additives. Because the production of strong polyethylene fibers with flame resistance is not easy

with conventional spinning methods, fibers were produced via the novel melt spinning approach (HiPER). The preliminary studies made with polyethylene fibers show that the HiPER system can enable flame retardant properties without reducing the mechanical properties of polyethylene fibers.





2. EXPERIMENTAL STUDIES

2.1 Materials

In this study, for the polymer matrix, the ASPUNTM 6000 linear low-density polyethylene (LLDPE), which possesses MFI 19 g/10min and density 0.935 g/cm³, was purchased from DOW Chemical company.

For the additives, three different types of flame retardant materials have been studied, including mineral containing, phosphorus containing, and nanocomposites as shown in Figure 2.1. As the flame retardant materials, 99.95% purity aluminum trihydrate (ATH) powder with 20-25 μm grain size supplied by Entekno Industrial Technological and Nano Materials Industry Company; Cloisite-20 nanoclay powder with organic intercalated dry size <10 μm and density of 1.77 g/cm³, supplied by Feza Chemistry; nanocrystalline cellulose (CNC) with 10-20 nm width, 300-900 nm long and 1.49 g/cm³ density provided by Nanografi Industrial Company; multi-walled carbon nanotube (MWCNT) with (-COOH) functionalized >96% purity, 28-48 nm outer diameter, supplied by NANOKAR Chemicals Industry; EXOLIT AP 422 ammonium polyphosphate (APP) powder from Acar Chemistry and Industry; the second phosphorus-containing flame retardant additive organic phosphor (pentaerythritol ester of phosphoric acid, Aflammit PCO-900) from Thor GmbH (Germany) was used. For the Aflammit PCO-900 whose phosphorus content is 24 wt.%, the melting temperature has been reported as 245 °C by the manufacturer.

Thus, the functional and high performances fibers are wound on the godet only with HiPER ambient conditions, without any drawings, and almost completely amorphous state with no or very small crystalline region. The produced fibers are passed through a first modification zone (blue) which has low temperature with low viscosity. In the second zone (pink), the fibers were subjected to higher temperature and higher viscosity to manipulate the unique precursor internal structure with adding functionality to the fibers.

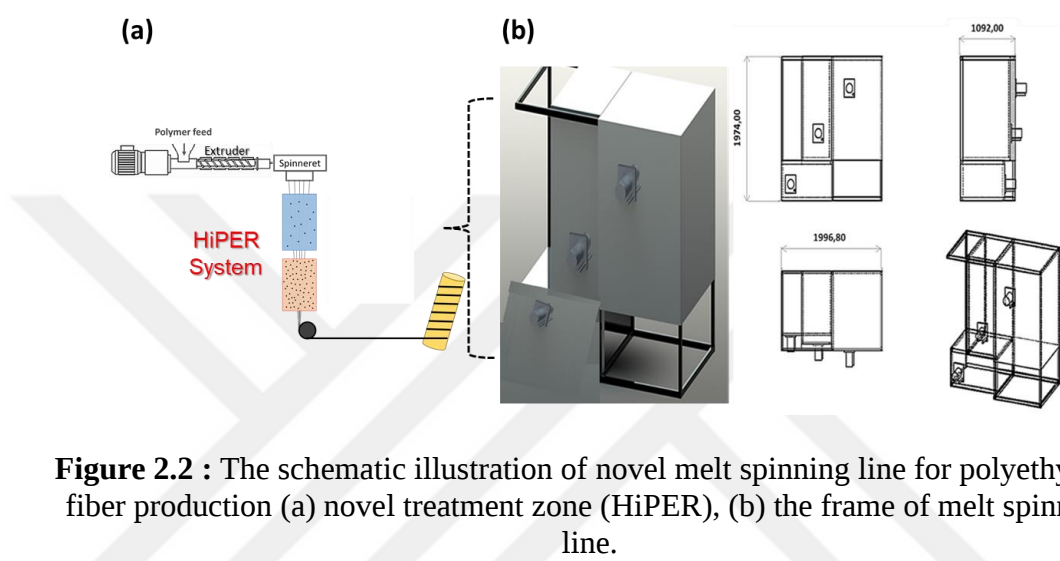


Figure 2.2 : The schematic illustration of novel melt spinning line for polyethylene fiber production (a) novel treatment zone (HiPER), (b) the frame of melt spinning line.

Modified spinning line also has totally five heating zones, namely three heating zones at the extruder, a heater at the spin pump and a heater at the spinneret. The hopper capacity that provides feeding to the extruder is 1.5 kilograms. Melt spinning line is composed of a single screw extruder, spin pump, single hole spinneret with 0.6 mm diameter, cooling unit and 3 godets. Polymer is fed manually to the hopper. The raw material (LLDPE) is gradually heated by passing through the three regions specified in the extruder. During the production, molten polymer jet ejected from the spinneret is transferred to the godets by passing through the treatment zones (HiPER) shown in Figure 2.2 (a).

2.2.2 LLDPE fiber production via HiPER system

The linear-low density polyethylene was selected to produce monofilaments. LLDPE fibers were produced by above mentioned modified melt spinning system and temperature parameters of spin line was tabulated in Table 2.1.

Table 2.1 : Temperature parameters used in the modified spinning system during production.

Extruder I (°C)	Extruder II (°C)	Extruder III (°C)	Spin Pump (°C)	Spinneret (°C)
135	165	200	190	185

The production speeds such as extruder, spin pump and take-up of produced fibers were expressed in Table 2.2. The take-up speeds were set to 400, 1000 and 2500 m/min for LLDPE fiber production and their HiPER performances were revealed in terms of mechanical performance.

Table 2.2 : Extruder, spin pump and take-up speeds of produced LLDPE fibers.

Extruder Speed (rpm)	Spin Pump Speed (rpm)	Take-up Speed (m/min)
42	50	400
25	50	1000
25	50	2500

Depending on the fiber spinnability, fibers were tried to be produce at high take-up speed. In addition, it was also tried to find optimum HiPER conditions besides high take-up speed. Process parameters were tabulated in Table 2.3.

Table 2.3 : The production conditions of LLDPE fibers.

Sample	HiPER Temperature (°C)	HiPER Length (cm)	Take-up Speed (m/min)
Control	-	-	400
HiPER-50	50	20	400
HiPER-75	75	20	400
HiPER-95	95	20	400
Control	-	-	1000
HiPER-50	50	20	1000
HiPER-75	75	20	1000
HiPER-95	95	20	1000
Control	-	20	2500
HiPER-95	95	20	2500

2.3 Enhancing the Flame Retardant Properties of LLDPE fibers

2.3.1 Preparation of flame retardant additives for LLDPE fibers

The main purpose of this thesis is to produce fire retardant performance fibers and the flow chart of experimental studies is shown in Figure 2.3. Appropriate compounds were prepared and adjusted to the melt spin line.

Additives were mixed with the polymer (linear low-density PE) by using a melt mixing process. To ensure homogeneous distribution in the prepared compositions, the polyethylene in granular form was grounded into the powder by using the Fritsch Pulverisette 14.

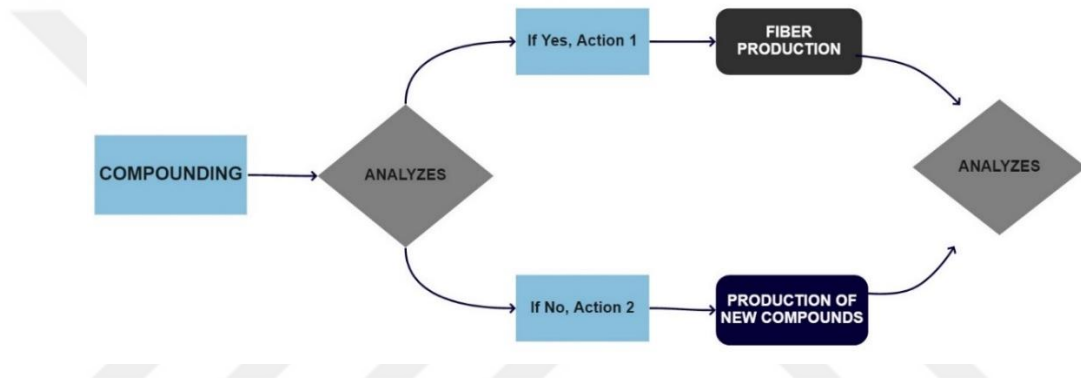


Figure 2.3 : Schematic experimental flow chart of the integration of flame retardancy mechanism to the novel melt spinning line.

The mixtures prepared in different compositions were first hand mixed with the polymer within the scope of the study. At the temperatures stated in Table 2.4 and with 100 rpm screw rotation speed compositions were blended for 2 minutes in DSM Xplore twin-screw extruder. After blending, test molds were prepared according to the LOI test standard (TS 11162-2 EN ISO 4589-2) with a pressure of 6 bar at 185 °C (80x10x4 mm). The prepared molds were conditioned overnight in the air-conditioning cabinet at 21 °C under 50% relative humidity conditions.

Table 2.4 : Compounder and molding machine parameters

Compounding Temperature (°C)	Time (min)	Screw Rotation (rpm)	Pressure (bar)
185	2	100	6

During the production of PE performance fibers, some preliminary studies have been carried out to determine the types and amounts of additives. Pure control polyethylene

molds were initially prepared. Following the preparation of PE molds without additives, polyethylene powder was firstly mixed with ATH ($\text{Al}(\text{OH})_3$), nanoclay and nanocellulose. Hence it was aimed to determine the effect of mineral and nanocomposite-based additives on the flammability of PE. Accordingly, ATH, nanoclay and nanocellulose additives were added to the polyethylene powder and concentration rates were indicated in Table 2.5, respectively. ATH and nanoclay molds were produced in four different concentrations, 10, 20, 30 and 40 wt.%. However, after preliminary FR test results nanocellulose concentrations were limited to 10 and 20 wt.% for production of nanocellulose/PE sheet.

The first molding studies were carried out to determine the polyethylene flame retardant behavior depending on the additive types. Then, best-performing additives were adjusted to the melt spinning line of linear low-density polyethylene. Molding of PE and PE-flame retardant additives is the first step to produce flame retardant polyethylene fibers. Additive ratios were determined by considering the high usage efficiency of ATH. LOI and MCC tests were applied to the samples indicated in Table 2.5 to reveal flame retardancy of PE molds. All flame retardant samples were named "PEFR" from 1 to 32.

Table 2.5 : Initial mold studies of pure PE and different types of flame retardants.

Sample	PE (%)	ATH (%)	Nanoclay (%)	Nanocellulose (%)
Control PE	100	-	-	-
PEFR-1	90	10	-	-
PEFR-2	80	20	-	-
PEFR-3	70	30	-	-
PEFR-4	60	40	-	-
PEFR-5	90	-	10	-
PEFR-6	80	-	20	-
PEFR-7	70	-	30	-
PEFR-8	60	-	40	-
PEFR-10	90	-	-	10
PEFR-11	80	-	-	20

According to LOI and MCC test results, phosphorus-based intumescence flame retardant APP was mixed with ATH to reduce ATH amount and improve the efficiency

of ATH. The aim of using ATH and APP additives ensures the synergistic effect comprising flame retardant, thermal and mechanical improvement to each other. ATH and APP powders were firstly mixed by hand and after mixing PE powder was mixed with ATH-APP by using a twin-screw extruder. For the masterbatch, ATH and APP were mixed with a different rate: 30wt.% ATH and 10wt.% APP, respectively. Extruded polymers were immersed in a water bath to cool down and then pelletized. Besides, considering the 10% additive rate-limiting in textile fibers, the total masterbatch rate for fiber production was decided as 5% by weight to determine the synergistic effect between ATH and APP. The fabricated masterbatch was fed to the melt spinning line under the conditions given in Table 2.6 in section 2.3.2.

Besides, the addition of additives to the melt mixing process, four solutions were separately prepared, such as APP, organic phosphorus, nanoclay and nanocellulose for fiber surface treatment. The purpose of this FR treatment is to reduce the negative effects of additives on the mechanical properties of the fibers and to provide flame retardancy. Four different solutions were prepared with 10 wt.% additives and solutions were mixed at 50 °C for a day in a magnetic stirrer. After a day under mentioned conditions mixed solutions were shown in Figure 2.4.

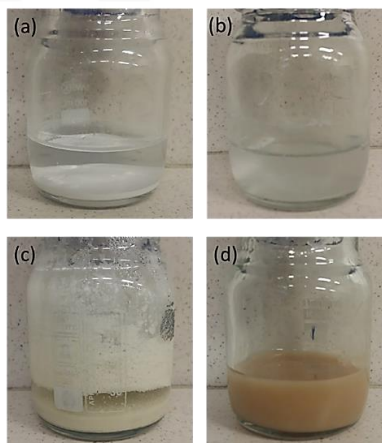


Figure 2.4 : Images of (a) APP; (b) phosphorus; (c) nanoclay; (d) nanocellulose solutions after mixing at 50 °C for a day in a magnetic stirrer.

Phosphorus-based solutions expressed in Figure 2.4 were used in a spinning bath to coat the fiber surface and results were explained in section 2.3.2.

2.3.2 Production of Flame Retardant LLDPE Fibers

After the preliminary studies for understanding the behaviors of flame retardant additives, chosen masterbatches were adjusted to the melt spinning line to produce

high performance flame retardant polyethylene fibers. Firstly, fabricated ATH-APP masterbatch granules and polyethylene granules were hand-mixed in a plastic container for pre-mixing and then granules were fed to the melt spinning line with different concentrations under the conditions expressed in Table 2.6.

Extruder temperatures in Table 2.6 were determined according to linear low-density polyethylene melting and processing temperatures. Then, LLDPE-ATH/APP masterbatch mixture was fed to the melt spinning line under the following temperatures.

Table 2.6 : Melt spinning production parameters for polyethylene masterbatch (ATH/APP) studies.

Extruder I (°C)	Extruder II (°C)	Extruder III (°C)	Spin Pump (°C)	Spinneret (°C)
135	171	200	195	190

For the polyethylene fiber spinnability, the total masterbatch amount was designated as 5 wt.%. Masterbatch doped monofilaments with different concentrations (5, 3 and 2 wt.%) were spun at different winding speeds and produced flame retardant fiber samples are indicated in Table 2.7. The take-up speeds were adjusted between 400 to 1000 m/min due to instabilities after the addition of additives. Continuous and homogeneous production could not be achieved with ATH-APP masterbatches and the produced fibers are shown in Figure 3.24.

Table 2.7 : Polyethylene/ATH-APP fibers produced at different take-up speeds and different masterbatch ratios in the melt spinning line.

Sample	PE (%)	Masterbatch (ATH-APP) (%)	Take-up Speed (m/min)
PEFR-12	97	3	400
PEFR-13	97	3	650
PEFR-14	97	3	750
PEFR-15	95	5	750
PEFR-16	98	2	1000
PEFR-17	97	3	1000

For the further studies different additive compositions were prepared and after the observations, the phosphorus-containing Aflammit PCO-900 solution shown in Figure

2.4 was used in the melt spinning line. To enhance the flame retardancy and fiber formation, polyethylene and Aflammit PCO-900 were used. In order to achieve the targeted FR effect, the concentration of organic phosphorus was also reduced considering the literature and cost, and phosphorus was used 1.5 wt.%. Working temperatures of extruder and spinning line are expressed in Table 2.8.

Table 2.8 : Melt spinning production parameters for polyethylene- phosphorus containing HiPER studies.

Extruder I (°C)	Extruder II (°C)	Extruder III (°C)	Spin Pump (°C)	Spinneret (°C)
135	165	190	190	185

Under the temperatures specified in Table 2.8, continuous fiber production was achieved. The proses parameters, such as polymer and additive content, treatment conditions and take-up speeds are specified in Table 2.9 to produce FR treated fibers. Take-up speeds of between 500 to 1000 m/min were studied. The fibers have been produced with a maximum speed of 1000 m/min so far by using with different treatment temperatures.

Table 2.9 : Polyethylene/phosphorus fibers produced at different take-up speeds and different masterbatch ratios in the melt spinning line.

Sample	PE (%)	Phosphorus Content (%)	HiPER Length (cm)	HiPER Temperature (°C)	Take-up Speed (m/min)
PEFR-18	98.5	1.5	10	50	500
PEFR-19	98.5	1.5	15	50	500
PEFR-20	98.5	1.5	10	50	750
PEFR-21	98.5	1.5	15	50	750
PEFR-22	98.5	1.5	15	25	750
PEFR-23	98.5	1.5	15	50	1000
PEFR-24	98.5	1.5	20	95	1000

After ATH-APP masterbatch studies, in order to increase FR property without decreasing the mechanical properties of the fibers, fiber production studies were carried out with nanoclay. The different compositions of nanoclay and compatibilizer (non-ionic surfactant material) were generated for fiber formation. The process parameters shown in Table 2.8 were also selected for PE/nanoclay fiber fabrication.

Fibers were produced using different take-up speeds with and without HiPER system. To obtain homogeneous and continuous fiber formation the ratios of nanoclay were selected as 1.0 and 0.5 wt.% in all composition and the production parameters of PE/nanoclay fibers are presented in Table 2.10.

Table 2.10 : Polyethylene/nanoclay fibers produced at different take-up speeds and different masterbatch ratios in the melt spinning line.

Sample	PE (%)	Nanoclay (%)	Compatibilizer (%)	HiPER Temperature (°C)	Take-up Speed (m/min)
PEFR-25	98.0	1.0	1.0	-	1250
PEFR-26	98.0	1.0	1.0	75	500
PEFR-27	98.0	1.0	1.0	75	750
PEFR-28	98.0	1.0	1.0	95	500
PEFR-29	98.0	1.0	1.0	95	750
PEFR-30	99.0	0.5	0.5	-	1000
PEFR-31	99.0	0.5	0.5	-	2000
PEFR-32	99.0	0.5	0.5	75	1000

2.4 Analyzes for Polyethylene Fibers and Molds

2.4.1 Mechanical tests

All fibers, both treated and non-treated were stored for at least 24 hours in laboratory conditions. The optical microscope images were taken from different regions of at least 10 samples in order to determine fiber diameter by Nikon Eclipse 50i polarize microscope. Then, using an Instron 4411 Universal Tensile Tester device with 50 N load cell, mechanical tests were carried out based on ASTM D3822 standard with a pulling speed of 15 mm/min and the distance between the jaws is 25.4 mm.

2.4.2 Scanning electron microscopic (SEM-EDAX) analysis

To evolve morphology and elemental analysis of the samples scanning electron microscopy (SEM) and energy dispersive x-ray analyzer (EDAX) were performed on the PE fibers. The surface of the produced fibers and the cross-sectional morphology of the broken fibers in liquid nitrogen at about -197 °C were analyzed by SEM analysis. The TESCAN VEGA 3 SEM machine was used to observe the fiber morphology.

Au/Pd was coated on the surface of the fiber to ensure the conductivity during the 165 seconds. Samples were scanned in the magnification range of 1.00 kx to 60.000 kx, and morphological images were obtained.

2.4.3 XRD analysis

Crystallization behaviors and orientation (by scanning azimuthal angle) of fibers with and without HiPER technology were examined by wide-angle x-ray diffraction (XRD) analysis. For crystallinity analysis, the RIGAKU Smart Lab x-ray diffractometer device was used. In the geometry of θ -2 θ Bragg-Brentano (monochromatic radiation $\text{CuK}\alpha$ line with $\lambda = 1.54056 \text{ \AA}$), and data between $0 - 60^\circ 2\theta$ were collected. The fibers are fixed perpendicular to the incoming beam to the glass sample holder with the double-sided tape. For the crystallinity calculation, the % crystallinity equation (Eq. 2.1) was used:

$$\text{Crystallinity (\%)} = \frac{\text{overall crystal area}}{\text{crystal and amorphous areas in total}} \times 100 \quad (2.1)$$

The Scherrer equation (Eq. 2.2) is used for to determine of crystal size [86].

$$\text{Scherer equation (L)} = \frac{k\lambda}{B \cos\theta} \quad (2.2)$$

In this equation, the crystal size is expressed by "L". The "radial" type of the angle XRD θ , Cu-2 θ is the fixed "1.54056 $\text{\AA}$ " wavelength (λ) for $\text{CuK}\alpha$ used in the Bragg Brentano geometry [87], k value for spherical crystals with cubimetric symmetry is considered "0.94" [88]. B is abbreviated as FWHM and is defined as the width taken from half the peak of the maximum height, calculated in radians in the formula (2.2).

Herman's orientation factor formula (Eq. 2.3) is used for the crystal orientation factor (fc) [86].

$$\text{Herman's orientation factor (fc)} = \frac{[(3\langle\phi\rangle)-1]}{2} \quad (2.3)$$

In the Herman orientation factor calculations are made by using the ϕ value (azimuthal angle), which is the angle between the oriented crystal axis and fiber axis obtained.

Stein and Norris equation is used for amorphous orientation factor (fa) calculation.

$$\text{Stein and Norris equation (fa)} = \frac{\Delta n - xfc\Delta n_0^c}{(1-x)\Delta n_0^a} \quad (2.4)$$

In the equation (Eq. 2.4), birefringence index (Δn) found by the determination of diffraction in the fibers by polarized microscope, the degree of crystalline (fc) calculated from the XRD result azimuthal scanned, the degree of crystallinity (x) obtained from the DSC analysis, and the intrinsic birefringence values for the crystalline and amorphous regions of the semi-crystalline polyethylene cited in the literature. Intrinsic birefringence values are used for Δn_0^c and Δn_0^a and are accepted as 0.058 and 0.048, respectively [89].

The birefringence of the fibers was determined by an Olympus BX60 polarization microscope within an immersion oil (Merck) with a refractive index of 1.515-1.517.

2.4.4 Thermal analyzes (DSC, TG/DTG)

The Universal Instrument 2000 software version of TA Instrument was used to examine the crystalline degree and thermal behaviors of fibers, such as softening, glass transition and melting temperatures. The fiber samples of about 5 mg were encapsulated in a non-volatile aluminum container and heated at 200 °C with the heating rate of 10 °C/min under nitrogen gas flow. The process was performed between 20 °C and 180 °C and heat - hold (waiting about 10 minutes to remove the thermal memory formed in the sample) - cool - hold - reheat process, respectively. The crystalline ratio of PE fibers was calculated by using the equation 2.5 [90]. In the formula, ΔH_m is the fusion heat of PE fiber produced and ΔH_{lit} is the heat of fusion of 100% crystalline PE indicated as 293 J/g from the literature [91].

$$\text{Degree of crystallinity (\%)} = 100 \times \left[\frac{\Delta H_m}{\Delta H_{lit}} \right] \quad (2.5)$$

The thermal behavior and mass loss of samples was performed by thermogravimetric analysis (TG/DTG) TA Instrument SDR Q 600 machine. In order to determine the thermal behavior of the samples, TG/DTG analysis were also performed as given in Table 2.11. About 10 mg samples are analyzed in an open alumina pan under a nitrogen atmosphere by heating, up to 800 °C with a heating rate of 10 °C/min

Table 2.11 : The tests conditions for TG/DTG test.

Sample amount	Heating rate	Burning temperature	Flowing gas	N ₂ flow rate
~9-13 mg	10 °C/min	800 °C	Nitrogen (N ₂)	100 ml/min

2.4.5 Limiting oxygen index (LOI) tests

In this study, fire behaviors of polyethylene samples under atmospheric conditions were determined by LOI test. LOI analysis was performed according to TS 11162 EN ISO 4589 standard by using LOI Test device (Concept Equipment/UK). Samples are prepared in the following dimensions:

Length: 80 mm Width: 10 mm Thickness: 4 mm.

Since the fibers cannot be tested directly by the LOI test device, fibers were prepared as bundle with the same size as the mold samples. Thus, about 0.5-1 g fibers were rolled upright position. Fiber and molds are shown in Figure 2.5 for LOI test. Samples that were conditioned under 21 °C temperature and 50% humidity at least 24 hours were tested.

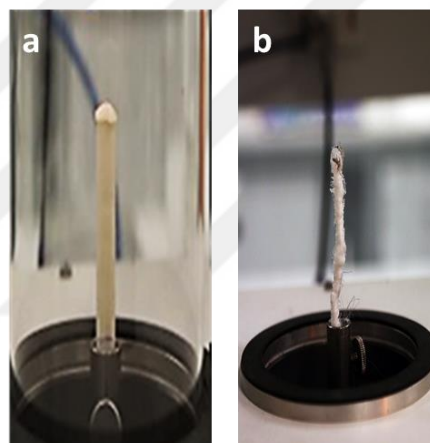


Figure 2.5 : Samples for LOI test (a) mold, (b) adjusted fiber.

2.4.6 Micro combustion calorimeter (MCC) tests

The MCC test was performed to obtain information about heat release capacity, flame resistance, ignition temperature and heat of combustion [83]. The MCC test evaluates the flammability of small-scale samples. The test sample is placed in an inert, heat-resistant pan and moved to the sample chamber inside the device. Sample chamber is heated by controlled heating program (1 K/s) under the inert atmosphere and pyrolysis occurs.

Volatiles released after pyrolysis combines with oxygen at 900 °C in an oxygenated combustion calorimeter. The data obtained in this contact is used to calculate the burning temperature of pyrolysis products. Oxygen consumption and mass flow rate are converted to specific heat release (W/g) as a function of temperature.

The MCC test was performed based on ASTM D 7309 Method A standard and test conditions are given in Table 2.12.

Table 2.12 : The test conditions for MCC test (ASTM D 7309 Method A)

Sample weight	Heating rate	Burning temperature	Loading-last temperature	O₂ flow rate	N₂ flow rate
~2.7 mg	1 K/s	900 °C	150-700 °C	20 cm ² /min	80 cm ³ /min

3. RESULTS AND DISCUSSIONS

3.1 Mechanical Properties of the LLDPE Fibers

LLDPE monofilaments were produced by novel melt spinning line (HiPER system) at different take-up speeds. The first fiber production study was observed at 400 m/min production velocity. The spinning speed was set at 400 m/min with the different HiPER temperatures such as 50, 75 and 95 °C and HiPER length was set to the 20 cm in order to observe the effect of different HiPER conditions on the LLDPE fibers. As a result of the novel productions at 400 m/min take-up speeds, the fibers obtained are shown in Figure 3.1 and Figure 3.2, normal photographs and optical microscope images, respectively.

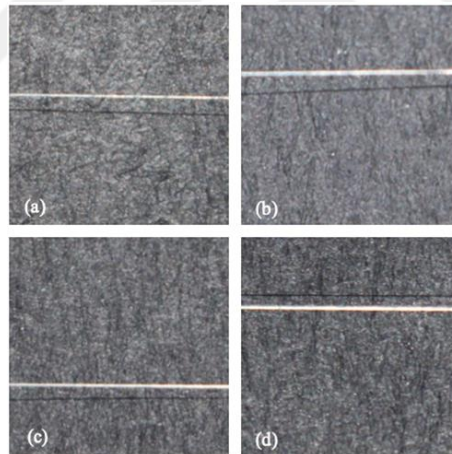


Figure 3.1 : Images of (a) control, (b) HiPER-50, (c) HiPER-75 and (d) HiPER-95 samples produced at a 400 m/min take-up speed.

The information obtained from the microscope results in Figure 3.2 show that similar fiber diameters with low standard deviations were achieved in production at different HiPER temperatures.

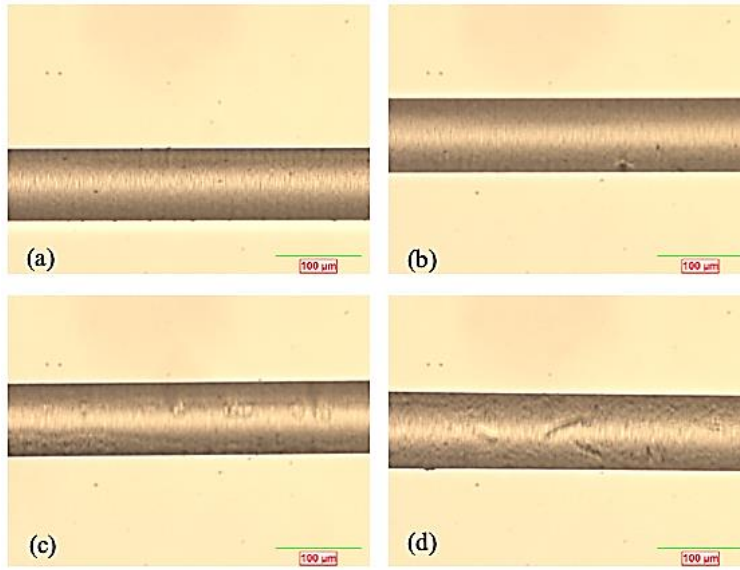


Figure 3.2 : Optical microscope images of (a) control, (b) HiPER-50, (c) HiPER-75 and (d) HiPER-95 samples produced at 400 m/min take-up speed.

In addition, strength values of fiber produced at 400 m/min take-up speed are in the range of 35-45 MPa and show similarities. However, the effect of the HiPER reflected on the elongation at the break and the modulus values. While the elongation at break was 9.55 mm/mm in HiPER 50 sample, it decreased to 8.31 in HiPER 75 and finally to 7.16 in HiPER 95 sample. Accordingly, the elastic modulus of the samples increased from 39 MPa to 60 MPa with increasing HiPER temperature.

During the further trials take-up speed was increased to 1000 m/min. Different HiPER temperatures (50, 75 and 95 °C) were studied and HiPER length was set to the 20 cm to obtain optimum HiPER condition. Produced fibers are shown in Figure 3.3 and Figure 3.4, normal photographs and optical microscope images, respectively.

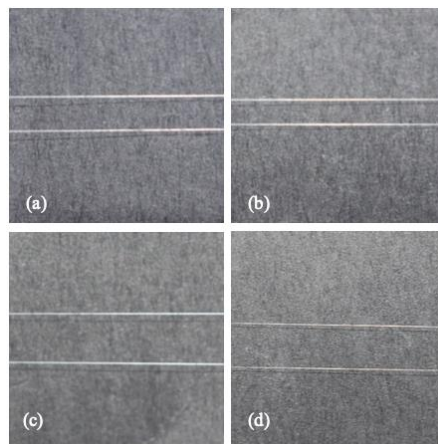


Figure 3.3 : Images of (a) control, (b) HiPER-50, (c) HiPER-75 and (d) HiPER-95 samples produced at a 1000 m/min take-up speed.

Unlike the 400 m/min take-up speed, vertical lines are observed in the fibers of the control and HiPER-50 fibers (Figure 3.4), while a linear tendency in the fiber spinning direction is observed in the HiPER-75 and 95 samples. This result probably indicates the presence of highly oriented and elongated chain structures in the direction of the fiber axis and spherulitic structures decreasing.

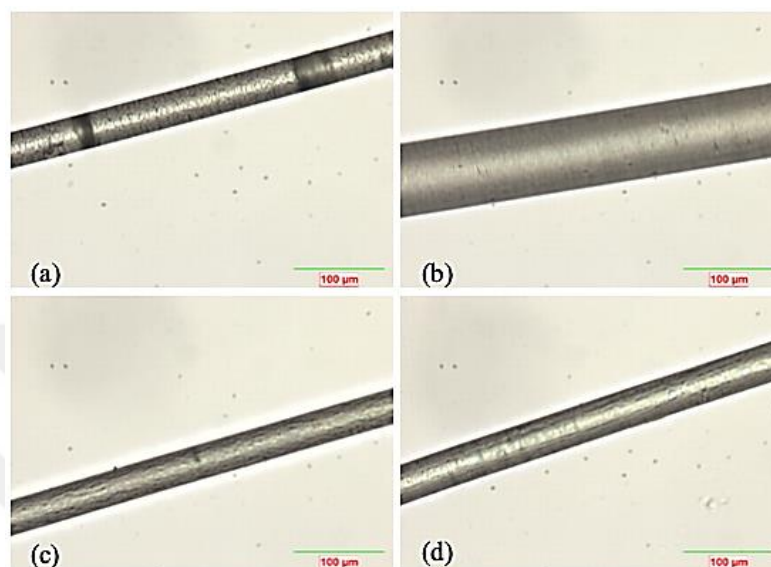


Figure 3.4 : Optical microscope images of (a) control, (b) HiPER-50, (c) HiPER-75 and (d) HiPER-95 samples produced at 1000 m/min take-up speed.

The fiber diameters of the samples of control, HiPER-75 and 95 were found 40 micrometers, while the diameters in the fibers of the HiPER-50 sample were measured as 77 ± 4 micrometers, although production was repeated more than once. Therefore, the strength of the HiPER-50 sample has the lowest result as expected compared to other fibers. Likewise, the elongation at break also had the highest value in the sample set with a value of 7.7 mm/mm. Due to the increase in HiPER temperature, the strength and modulus values were increased 128% and 92% for HiPER-75 fibers and 209% and 294% for HiPER-95 fibers, respectively when compared to the control sample.

Fibers were spun at 50 and 75 °C HiPER temperature to see effect of the HiPER temperature. In accordance with the data obtained from 400 and 1000 m/min fiber productions shown in Table 3.1, it was observed that the contribution of 95 °C HiPER temperature to mechanical performance was higher than that of 50 and 75 °C temperatures. For this reason, productions of control and HiPER 95 samples are included in ongoing LLDPE fiber formations.

It is known that by increasing the production speeds, the mechanical performance of the fibers is expected to increase. Therefore, take-up speed was increased to 2500 m/min take-up speed. HiPER fibers were formed under only 95 °C with 20 cm HiPER length at the constant take-up speed (2500 m/min). Produced fibers are shown in Figure 3.5 and Figure 3.6, normal photographs and optical microscope images, respectively.

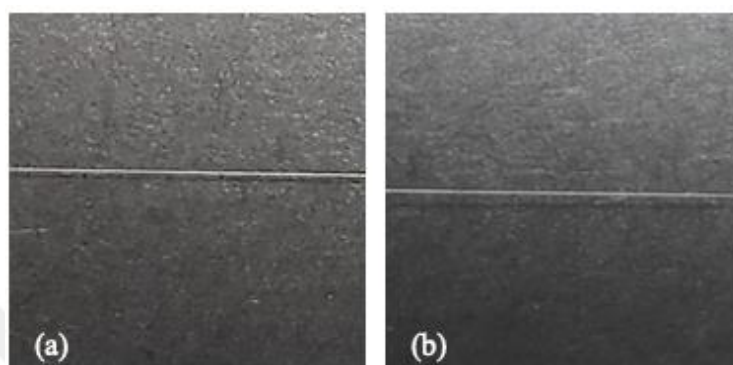


Figure 3.5 : Images of (a) control, (b) HiPER-95, samples produced at a 2500 m/min take-up speed.

In the process parameters, it was tried to produce fiber at 2700 and 3000 m/min take-up velocities, but only the control sample could be obtained. The reasons behind the production instability was thought to be that at these speeds is the increased fragility in fiber form as a result of the decrease in breaking elongation and flexibility with the increasing speed.

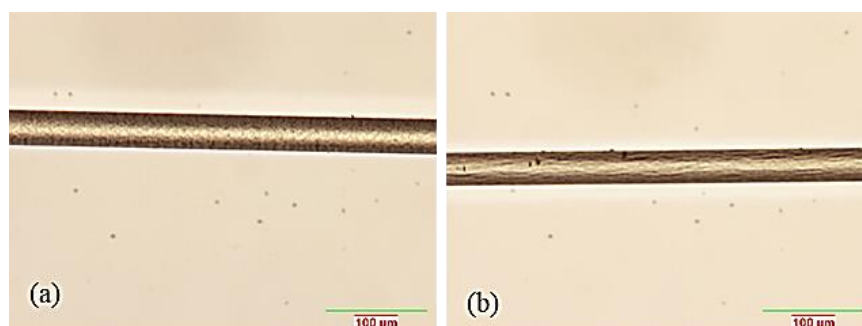


Figure 3.6 : Optical microscope images of (a) control, (b) HiPER-95, samples produced at 2500 m/min take-up speed.

The fibers obtained from the novel melt spinning line at a speed of 2500 m/min were given in Figure 3.6b, it is seen that the orientation of the fiber throughout the spinning direction in the HiPER-95 sample is more prominent while control sample is more non-uniform in terms of surface morphology. This is a sign that the internal fiber chain orientation has increased significantly and the presence of a highly oriented precursor

internal structure in HiPER-95 fiber. Table 3.1 demonstrates the mechanical test results of LLDPE fibers spun with and without HiPER system. According to mechanical test results, it is appeared that novel HiPER technology can be implemented to spin high strength high elastic modulus polyethylene fibers. As can be seen in Table 3, the highest strength and modulus values have been obtained in the fiber with HiPER-95 with a 2500 m/min take-up speed, while a HiPER length was kept 20 cm, and the distance between the spinneret and the HiPER system is 160 cm. The modulus of the fiber, which we obtained by using PE with very low molecular weight and with no drawing process, is approximately 1.33 GPa also its strength is 0.20 GPa and the elongation at break is 0.68 mm/mm. As a comparison to the literature, LLDPE fibers were produce by single hole spinneret and subjected to cold drawing possess maximum 270 MPa elastic moduli [29]. In other study, Cho et al., produced LLDPE fibers by single hole spinneret at 6 km/min take-up speed. These fibers have 76 MPa stress and 605 MPa initial moduli even though produced at high take-up speed [28]. When compared with LLDPE fibers mentioned from the literature, HiPER LLDPE fibers without any drawing process possess higher stress and elastic moduli than fibers produced from conventional spinning [28], [29].

Table 3.1 : Comparison of tensile test results of samples produced using linear low-density PE with control at 400, 1000 and 2500 m/min take-up speeds and HiPER samples with 20 cm length and 50, 75 and 95 °C temperature.

Sample	Fiber Diameter (μm)	Take-up Speed (m/min)	Tensile Strength (MPa)	Breaking Elongation (mm/mm)	Elastic Modulus (MPa)
Control	65 $\pm$ 25	400	40 $\pm$ 3	8.85 $\pm$ 0.37	39 $\pm$ 6
HiPER-50	86 $\pm$ 1	400	45 $\pm$ 3	9.55 $\pm$ 0.25	41 $\pm$ 8
HiPER-75	87 $\pm$ 3	400	35 $\pm$ 0.2	8.31 $\pm$ 0.28	55 $\pm$ 3
HiPER-95	89 $\pm$ 4	400	40 $\pm$ 5	7.16 $\pm$ 0.21	60 $\pm$ 6
Control	40 $\pm$ 2	1000	56 $\pm$ 7	3.02 $\pm$ 0.27	296 $\pm$ 57
HiPER-50	77 $\pm$ 4	1000	35 $\pm$ 4	7.65 $\pm$ 0.3	265 $\pm$ 49
HiPER-75	45 $\pm$ 3	1000	128 $\pm$ 12	1.27 $\pm$ 0.11	570 $\pm$ 130
HiPER-95	41 $\pm$ 3	1000	174 $\pm$ 26	0.61 $\pm$ 0.15	1168 $\pm$ 277
Control	35 $\pm$ 0.4	2500	76 $\pm$ 5	2.38 $\pm$ 0.18	281 $\pm$ 48
HiPER-95	34 $\pm$ 0.4	2500	202 $\pm$ 7	0.68 $\pm$ 0.07	1329 $\pm$ 202

Moreover, when compared with the control sample, the strength and modulus values of the HiPER 95 sample increased 166% and 373%, respectively in Table 3.1. The elongation at break has also decreased by 71%, resulting in a more brittle structure of the fibers.

3.1.1 Mechanical performance of FR HiPER fibers

After the production of pure LLDPE fibers with and without HiPER technology, flame retardancy properties tried to gain to LLDPE fibers. To investigate the individual and combined effects of the additives on the mechanical and flame retardant properties, various combinations of the additives were tried (ATH mixed with APP and LLDPE combined with nanoclay). For the flame retardant studies, the integration into the novel melt spinning line was achieved only with the PE/ATH/APP, PE/nanoclay studies and PE/HiPER containing phosphorus additives. However, phosphorus and nanoclay containing fiber formation studies only mechanically performed because of discontinuous and non-homogenous fiber formation with ATH/APP hybrid.

In the modified system, without any melt mixing, flame retardant property is provided to the fibers while passing through the HiPER technology during production. During production, organic phosphorus was added in the HiPER system to keep additive concentration at 1.5 wt.% and HiPER modification was carried out in the favorable production environment. In this way, functional fibers with improved thermal resistance and flame retardancy can be produced with the flame retardant additives added to the HiPER without reducing the mechanical properties of the fibers.

Phosphorus treated LLDPE fibers which is called between PEFR-18 to PEFR-24 represented in Table 2.9 with their process parameters. Fibers were spun into the phosphorus containing HiPER system. Samples were produced as control sample (without HiPER) and as treated samples with HiPER technology with HiPER lengths of 10, 15 and 20 cm and at temperatures of 25, 50, 95 °C. These treated fibers were spun at godet speeds of 500, 750 and 1000 m/min. The fibers produced by passing through an organic phosphorus-added HiPER system were examined under an optical microscope and their images are shown in Figure 3.7, Figure 3.8 and Figure 3.9.

When looking at the optical microscope images of low-density PE fibers with different take-up speeds and HiPER lengths, it is observed the droplets of phosphorus solution on the fiber surfaces. These droplets on the fiber surface of low speed production (500

m/min), have a larger structure shown in microscope images (Figure 3.7). This is clearly seen in the PEFR-19 sample obtained from HiPER length of 15 cm under 50 °C HiPER temperature (Figure 3.7b). Moreover, PEFR-18 and PEFR-19 samples have about 80 μm fiber diameters. Because of the high fiber diameter of PEFR-18 and PEFR-19 fibers, their mechanical tests were not performed and the fibers and other samples from PEFR-20 to PEFR-24 were mechanically tested shown in Table 3.2.

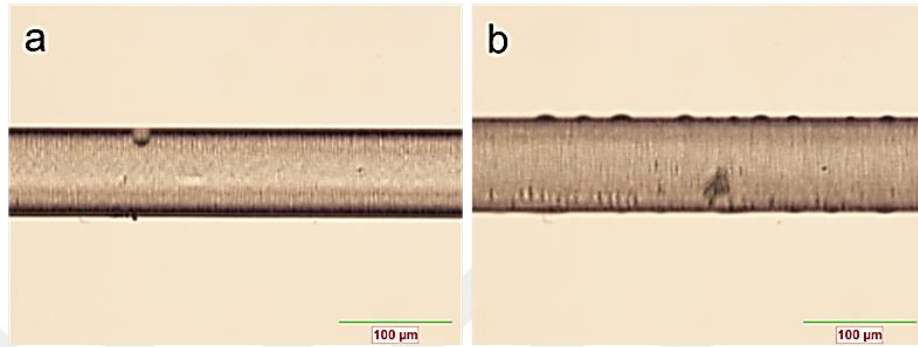


Figure 3.7 : Optical microscope images of PEFR-18 and PEFR-19 samples, respectively.

These drops, which accumulate on the surface after the phosphor treatment, are also found intensely on the fibers produced at 750 m/min and 10-15 cm HiPER length shown in Figure 3.8. As it is seen more clearly in Figure 3.8b when compared with the production at 500m/min speed (Figure 3.7), a dimensional shrinkage occurred in the drops and the spread of the drops increased in the region where they are located. Besides, HiPER treatment to the fiber at room temperature (25 °C) shown in Figure 3.8c is not effective at 50 °C.

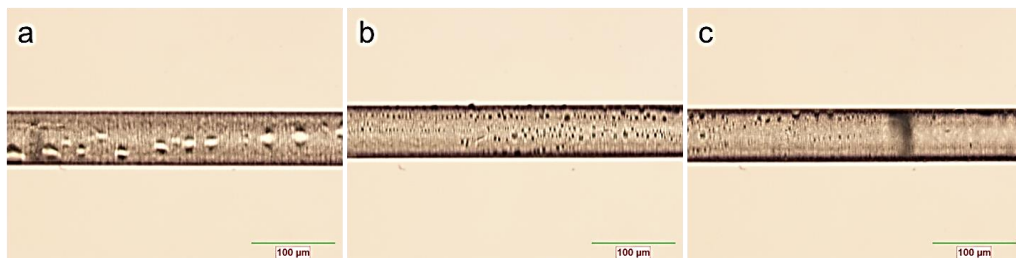


Figure 3.8 : Optical microscope images of PEFR-20,21 and 22 samples, respectively.

The PEFR-23 and PEFR-24 samples fabricated at 1000 m/min take-up speed. When the HiPER temperature was increased from 50 °C to 95 °C, as seen in Figure 3.9a and Figure 3.9b, respectively. Images similar to film coating were obtained from the drop forms on the fiber surface. It is thought that the interaction between the fibers that do not fully solidify when entering the HiPER system with the additive chemicals in the

bath with the increase in the bath temperature is considered to be better. For this reason, it can be said that the droplet like structures are dispersed more homogeneously and turned into a film form.

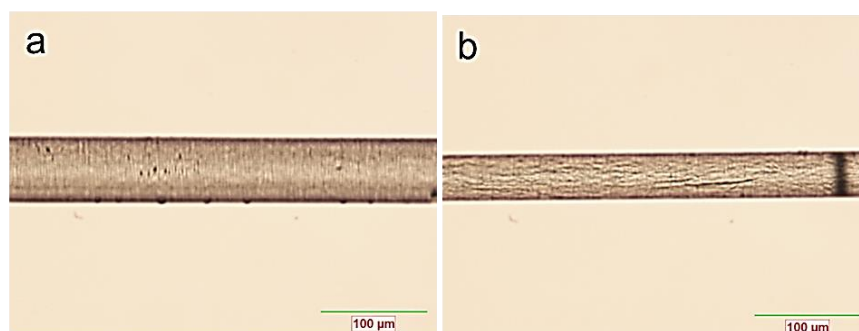


Figure 3.9 : Optical microscope images of PEFR-23 and PEFR-24 samples, respectively.

Mechanical performance of flame retardant fibers produced from LLDPE with different production parameters passed through 1.5 wt.% phosphorus/HiPER system were compared in Table 3.2. In the table, phosphorus containing flame retardant fibers are also compared with as-spun pure LLDPE fibers that were fabricated at the same take-up speed (1000 m/min).

Table 3.2 : Comparison of the mechanical performance of fibers produced from LLDPE with different production parameters passed through HiPER system containing 1.5 wt.% phosphorus and without phosphorus.

Sample	HiPER Length (cm)	HiPER Temp. (°C)	Take-up Speed (m/min)	Tensile Strength (MPa)	Breaking Elongation (mm/mm)	Elastic Modulus (MPa)
PEFR-20	10	50	750	45 ± 1	6.84 ± 0.2	105 ± 9
PEFR-21	15	50	750	43 ± 2	7.19 ± 0.3	105 ± 23
PEFR-22	15	25	750	47 ± 2	7.99 ± 0.19	94 ± 10
Control	-	-	1000	56 ± 7	3.02 ± 0.27	296 ± 57
HiPER-50	20	50	1000	35 ± 4	7.65 ± 0.3	265 ± 49
HiPER-95	20	95	1000	174 ± 26	0.61 ± 0.15	1168 ± 277
PEFR-23	15	50	1000	48 ± 3	6.5 ± 0.31	135 ± 8
PEFR-24	20	95	1000	109 ± 12	2.64 ± 0.58	226 ± 50

* Control and HiPER-50 and 95 samples are the first productions (as-spun) and are produced without HiPER technology containing phosphorus FR.

When looking at the samples of HiPER-50 produced with pure LLDPE at 1000 m/min take-up speed, there was an improvement in strength and elongation at break values in the fibers immersed in the phosphorus containing HiPER system, while a decrease in the module value was observed. HiPER-50 sample has a strength value of 35 MPa at 20 cm bath depth, whereas 48 MPa strength value was calculated in PEFR-22 sample immersed in HiPER bath containing 15 cm phosphorus. In addition, there is a significant increase compared with strength and modulus values of PEFR-23 and PEFR-24 samples when HiPER temperature increase. In addition, a decrease in the elongation at break of the fibers produced at 1000 m/min under 50 °C HiPER temperature was observed. Moreover, fibers produced at 750 m/min possess nearly same strength and modulus values. However, fabrication at room temperature (PEFR-22) cause a decrease in modulus.

PE/nanoclay fiber spinning is another flame retardant study that is analyzed mechanically. Samples from PEFR-25 to PEFR-32 shown in Table 2.10 were produced without HiPER and with HiPER that lengths are 10, 15 cm and temperatures of 75, 95 ° C at different take-up speeds. Fibers were produced with different nanoclay concentrations, 0.5 wt.% and 1.0 wt.%. Photographs and optical microscope images of fibers spun are examined Figure 3.10, Figure 3.11 and Figure 3.12, respectively. Fine bead-like structures were found in the fibers obtained from LLDPE/nanoclay. As can be seen in Figure 3.10, both the control and HiPER productions periodically observed fine bead-like structures regions in the fiber during the fiber flow.

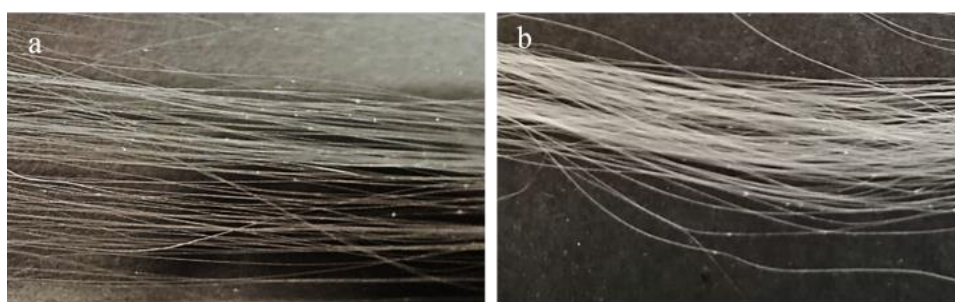


Figure 3.10 : The photographs of (a) PEFR-25 and (b) PEFR-26 samples

Apart from fine bead-like structure observations, the color difference of control and HiPER-95 fibers is quite distinct in the image shown in Figure 3.10. Although the samples passing through the HiPER have lower speed, they have gained an opaquer appearance. This opacity formed in the material is an example of the change in crystallinity.

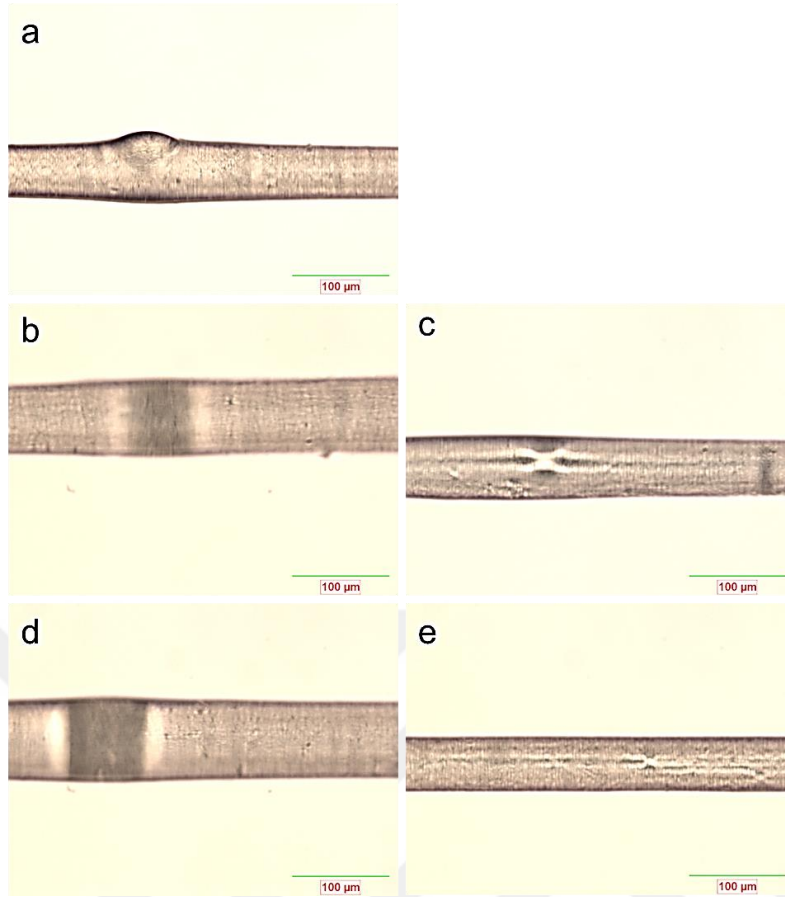


Figure 3.11 : The optical microscope images of (a) PEFR-25, (b) PEFR-26, (c) PEFR-27, (d) PEFR-28 and (e) PEFR-29.

The highest production speed was reached 1250 m/min in the control sample with a nanoclay 1 wt.% (PEFR-25). High production speed brings smaller fiber diameter. The distribution of fiber diameters is clearly noticeable in the optical microscope images in Figure 3.11.

Especially in the (PEFR-25) control sample, as seen in Figure 3.11a, nodes exceeding the surface limits of the fiber are frequently encountered. It is thought that these regions, the probable cause of which is nanoclay agglomeration, may cause breaking by weakening the cross section of the fiber under load during the tensile test. As seen in Table 3.3, while the diameters of the control sample and the elongation at break (3.57 ± 1.05) are the lowest among the given samples, their modulus were at lowest levels due to these agglomeration zones. When the polymer was passed through a 10 cm depth in the HiPER bath during the production phase, the thick band structures increased along the fiber (Figure 3.11b, d). Since the production speeds of HiPER samples were lower compared to the control sample, the HiPER fibers spun remained thicker than these samples. However, a phenomenon that we experience in low speed

HiPER works is preparing the ground for thin and thick places locally in the fiber samples. Another contribution of the production of the HiPER is that it decreases the structures similar to the knot structure seen in the control samples and probably supports the spread of this agglomeration in the fiber and on its surface. This explains the rare observation of the knot structure in HiPER samples in optical microscope examination. Although standard deviations in fiber diameters are partially high due to imperfection (knot structure), fiber diameters decreased by 16 percent for HiPER-75 and 28 percent for HiPER-95 due to the increase in production speed from 500 to 750 m/min. In Figure 3.11b, c, d and e, the effects of speed increase on fiber diameter can be seen. Based on this situation, only optical microscope examination of these samples was made and their mechanical performance was not evaluated. Based on homogeneity and high standard deviations of fibers, only optical microscope examination of these samples produced at 500 m/min take-up speed was made and their mechanical performance was not evaluated. Due to the increase in speed, the thick band regions have been replaced by thinner and frequent band formations as given in Figure 3.11c. According to Table 3.3, HiPER system is caused increase in strength and modulus values of PE/nanoclay fiber although they were produced lower take-up speed (750 m/min) than control sample (1250 m/min).

Table 3.3 : The mechanical test comparison of PEFR-25 and PEFR-29 samples which have 1.0 wt.% nanoclay content.

Sample	HiPER Length (cm)	HiPER Temp. (°C)	Take-up Speed (m/min)	Tensile Strength (MPa)	Breaking Elongation (mm/mm)	Elastic Modulus (MPa)
PEFR-25	-	-	1250	53 ± 6	3.57 ± 1.05	102 ± 23
PEFR-29	10	95	750	69 ± 5	3.47 ± 0.57	139 ± 12

Looking at the optical microscope images given in Figure 3.12 of samples produced from 0.5 wt.% nanoclay modified polymer, a more regular fiber diameter is observed in the control sample, while fluctuating across the surface of the HiPER-75 fibers obtained in half the production rate of the control sample is observed. Similar to the control samples (PEFR-25), agglomerated regions were also found in the control fibers (PEFR-31). However, by increasing production speed and decreasing nanoclay concentration, these regions are less prominent.

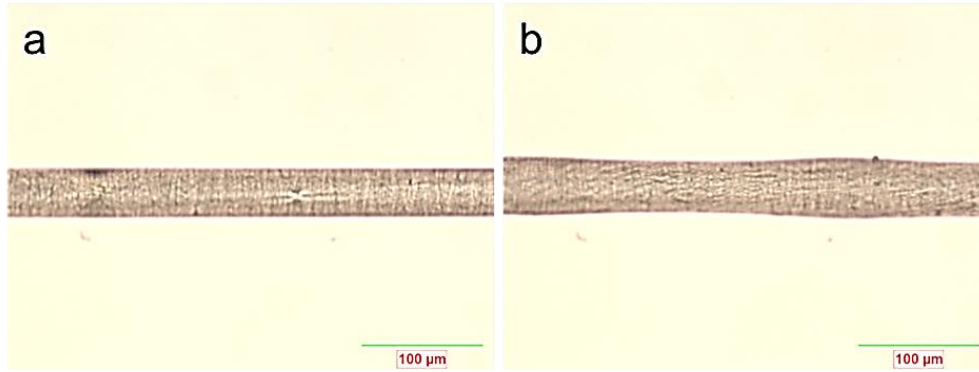


Figure 3.12 : The optical microscope images of (a) PEFR-31 and (b) PEFR-32 samples.

The increase in HiPER depth, leads to higher drag forces fiber faces. This stress-induced fiber orientation becomes more apparent. The fact that the liquid phase in the HiPER system has a higher energy compared to the air temperature supports the chain movement in the fiber. Under all these conditions, agglomeration in the HiPER fiber passing through the system is reduced to a minimum and the strength of the fiber is improved.

As in the production with 1.0 wt.% nanoclay added, in the production of 0.5 wt.% clay containing, the take-up speed of the control samples (2000 m/min, PEFR-31) was higher than the take-up speed of the samples passing through the HiPER bath (1000 m/min, PEFR-32). Depending on the difference in take-up speed, the fiber diameter of the control sample is around 40 micrometers, while the HiPER product is 49 micrometers shown in Table 3.4. Bartolomeo et al. produced polyethylene-clay nanocomposite fibers by using traditional melt spinning line and with cold drawing. After the production, nanoclay-PE fibers possess 3.0 MPa stress at yield and 60.0 MPa elastic modulus values [92].

Table 3.4 : The mechanical test comparison of PEFR-31 and PEFR-32 samples which have 0.5 wt.% nanoclay content.

Sample	HiPER Length (cm)	HiPER Temp. (°C)	Take-up Speed (m/min)	Tensile Strength (MPa)	Breaking Elongation (mm/mm)	Elastic Modulus (MPa)
PEFR-31	-	-	2000	62 ± 3	4.1 ± 0.4	133 ± 18
PEFR-32	15	75	1000	76 ± 12	4.04 ± 1.02	136 ± 27

Thus, these results provide the background for understanding the effect of nanoclay for addition to enhance mechanical properties of fibers. It can be seen that both of 1.0 wt.% and 0.5 wt.% nanoclay-PE fiber production studies possess higher mechanical performance than the literature [92]. As expected from HiPER bath production, despite the 50 percent speed drop between control production, HiPER fibers showed higher strength as 76 MPa in the tensile test (Table 3.4). Although the fiber diameters are thicker, the strength values are better and the module performances are similar in control and HiPER-75 samples. Moreover, mechanical test results provide the aspects of clay amount and 0.5 wt.% nanoclay amount seems more suitable for fiber production and possesses better mechanical performance than 1.0 wt.% nanoclay.

3.2 Morphology of LLDPE Fibers

The main purpose of SEM analysis is to reveal the effects of the HiPER system on the morphological structures of LLDPE fibers and to demonstrate the nanofibrillar structure in the cross-section of the fibers. Thus, the surface morphologies of low molecular weight LLDPE control and HiPER (different temperatures; 50, 75 and 95 °C) monofilaments by the novel melt spinning line at 400 m/min take-up speed and 20 cm HiPER length are shown in Figure 3.13. The produced fibers that are not subjected any drawing process were analyzed. In addition, the internal morphology and breaking behavior of the fibers obtained after they were broken in liquid nitrogen are given in Figure 3.14. In SEM analyzes shows (a, a') control, (b, b') HiPER-50, (c, c') HiPER-75 and (d, d') HiPER-95 samples. When looking at the SEM images of Figure 3.13, as a result of the examination of the fiber surfaces, no generally significant morphological difference was found between the control (without using HiPER) and the samples of HiPER-50 and 75. In the control, HiPER-50 and HiPER-75 samples, non-aligned lamellar microstructures were observed. However, when looking at the SEM image of Figure 3.13d, more aligned fibrillar and lamellar microstructures are seen on the fiber surface of the HiPER-95 sample. This formation is a testament to the unique internal structure to high performance fibers, as seen in the literature [25], [93]. In addition, the optical microscope images of fibers (named “ii” for all sample) were also inserted in the Figure 3.13.

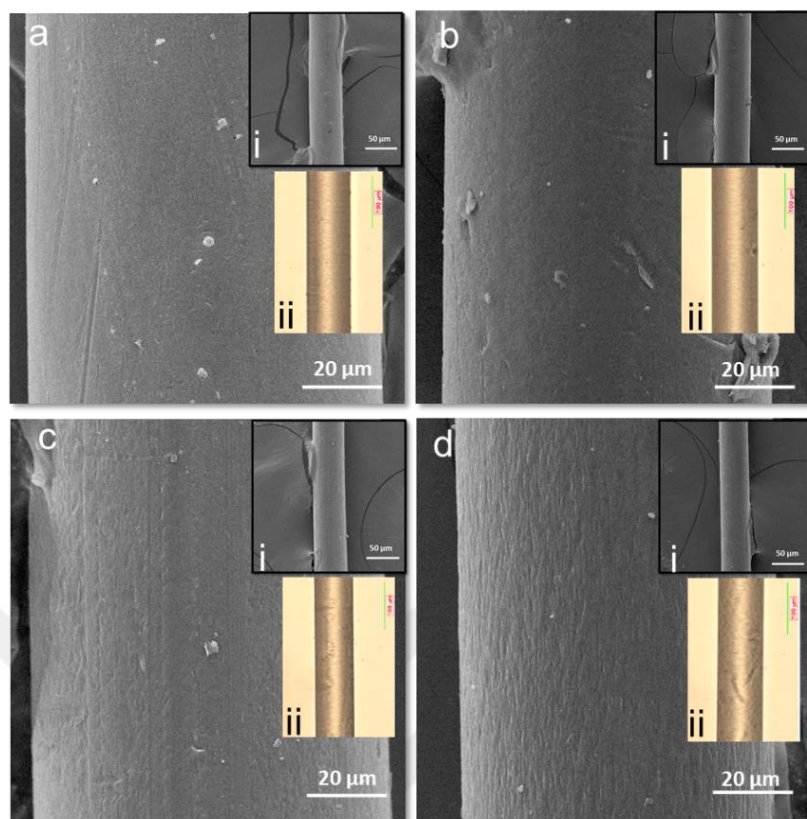


Figure 3.13 : SEM and optical microscope images of (a and ii) control, (b and ii) HiPER-50, (c and ii) HiPER-75 and (d and ii) HiPER-95 samples, respectively.

Although the untreated control sample from the samples broken in liquid nitrogen showed a brittle fracture feature, no fibrillation structure was observed in the cross section. HiPER samples showed more distinct breaking feature, especially with the increase of HiPER temperature. With the increasing temperature, microfibrillar structure development in sections increased significantly. In the samples of HiPER-50 and 75 °C (Figure 3.14b' and c') the spherulitic to fiber transition that appeared more clearly than the control sample (Figure 3.14a') was found, while the analysis images of the HiPER 95 °C sample dominated the fibrils. The appearance of spherulitic texture occurs when LLDPE fibers exhibit spherical surface morphology that gradually turns into micro and nanofibers during the transition from the HiPER [17], [94], [95]. As the temperature of the HiPER increases, the internal structure is transformed from the spherulitic structure to the micro fibrillar structure with the effect of sufficient temperature thanks to reversible friction force and high speed. Breaking mechanism of high performance fibers with microfibrillar internal structure: when the fiber breaks, the crack runs along the axis of highly oriented molecules and fibrils, and if the crack

is slightly off the axis, it joins with other cracks to eventually rupture to reach the outer axis of the fiber and form a longitudinal rupture [17].

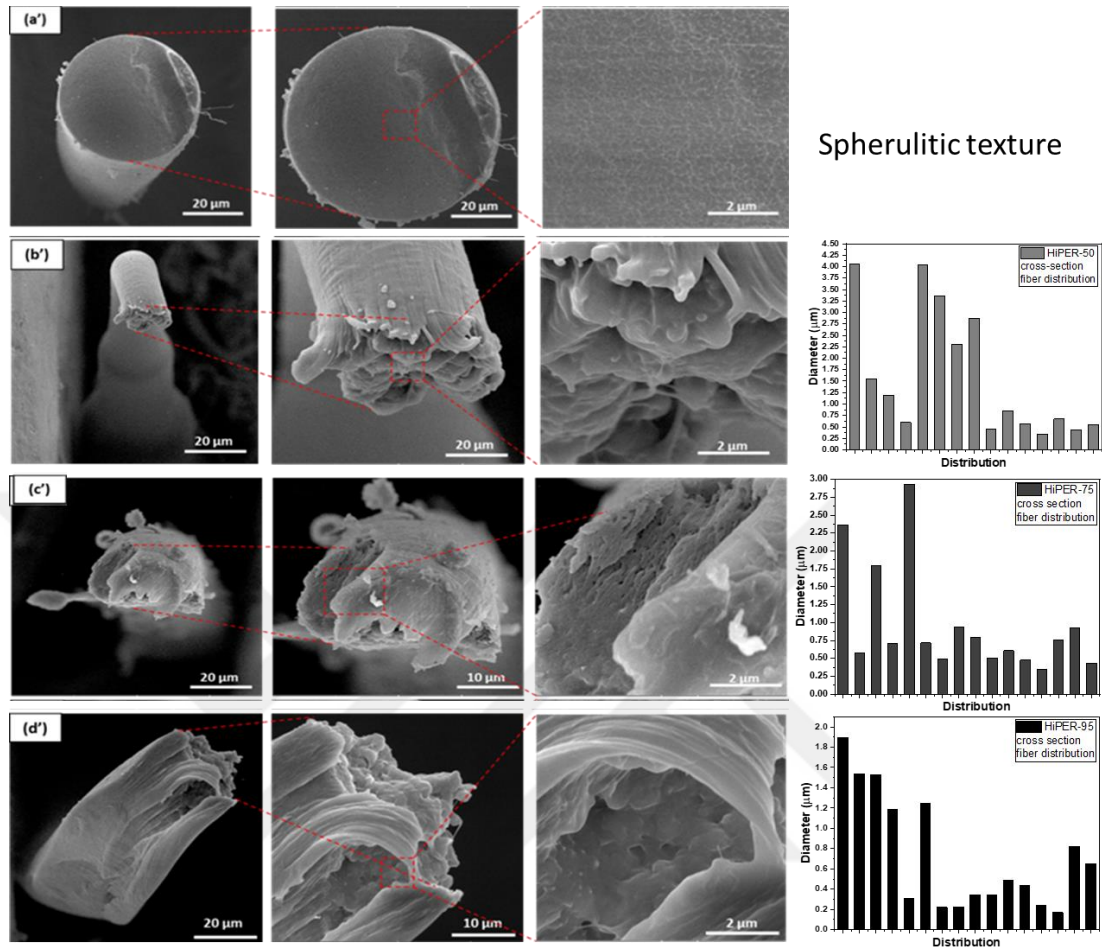


Figure 3.14 : SEM images and fibrillar structure distributions of the cross-section of the fiber (a') control, (b') HiPER-50, (c') HiPER-75 and (d') HiPER-95 samples, respectively.

On the other hand, it is the most important indicator that 50 °C forms a threshold, that is, a transition medium for the formation of fibrillar structure, when both samples break off in 50 °C samples. In the samples of HiPER-75 and 95 produced at higher temperatures after HiPER-50, microfibrillar structure is more evident shown in Figure 3.14. It can be seen that the size of fibrillar structure in the cross-section of fibers decreased when HiPER temperature is increased. While the micro fibrils distribution is seen intensely in the HiPER-50 sample, the microfibrillar structure in the samples of HiPER-75 and 95 appears to return to the nano-fibrillar structure, and the distributions of the nano-filler structure of the HiPER fibers are shown in Figure 3.14. It is also important to note that the observation of longitudinal fracture and aligned microfibrillar structure is very similar to UHMWPE fibers obtained by ultra-high

molecular weight and gel spinning method, with an average of 32 times hot-controlled drawn, even when HiPER 95 °C samples are not drawn. This fibrillated fracture type of HiPER specimens, without any hot drawing, is a property of very high performance fibers that possess very high drawn, ultra-high molecular weight, smooth orientation and high crystallinity [19], [21], [93], [96], [97].

3.2.1 Morphology and EDAX results of FR HiPER LLDPE fibers

In the flame retardant trials, the integration into the novel melt spinning line was achieved only with the PE/ATH/APP hybrid, PE/HiPER containing phosphorus and PE/nanoclay studies. Better flame retardant fiber production studies for LLDPE polymer were made with HiPER containing phosphorus and PE/nanoclay studies. Thus, only phosphorus and nanoclay containing FR studies were examined via SEM and EDAX techniques. In addition to phosphorus fiber samples, EDAX analysis of control sample was also performed to make elemental comparison and EDAX result of control sample is shown in Figure 3.15. As expected, due to the aliphatic hydrocarbon structure of PE, C is the only element of PE fiber.

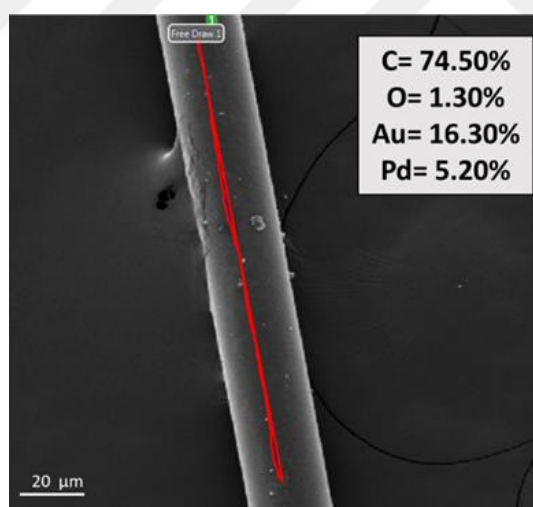


Figure 3.15 : Morphological and elemental analysis results of low-density control polyethylene fiber.

When the morphology of the PEFR-20 of the produced fibers via SEM is examined, it is seen that there is a droplet-like formation on the fiber surface demonstrated in Figure 3.16a. When the fiber surface was scanned, Au and Pd elements coming from the coating, O% (11.40%) and P (0.90%) elements from the phosphorus containing additive, and 19.40% C from the PE were found on the treated fiber, whereas on the control PE sample shown in Figure 3.15, only carbon is determined from the fiber.

Therefore, looking at the results of EDAX, it is seen that the fiber surface is relatively covered with phosphorus while passing through the HiPER system.

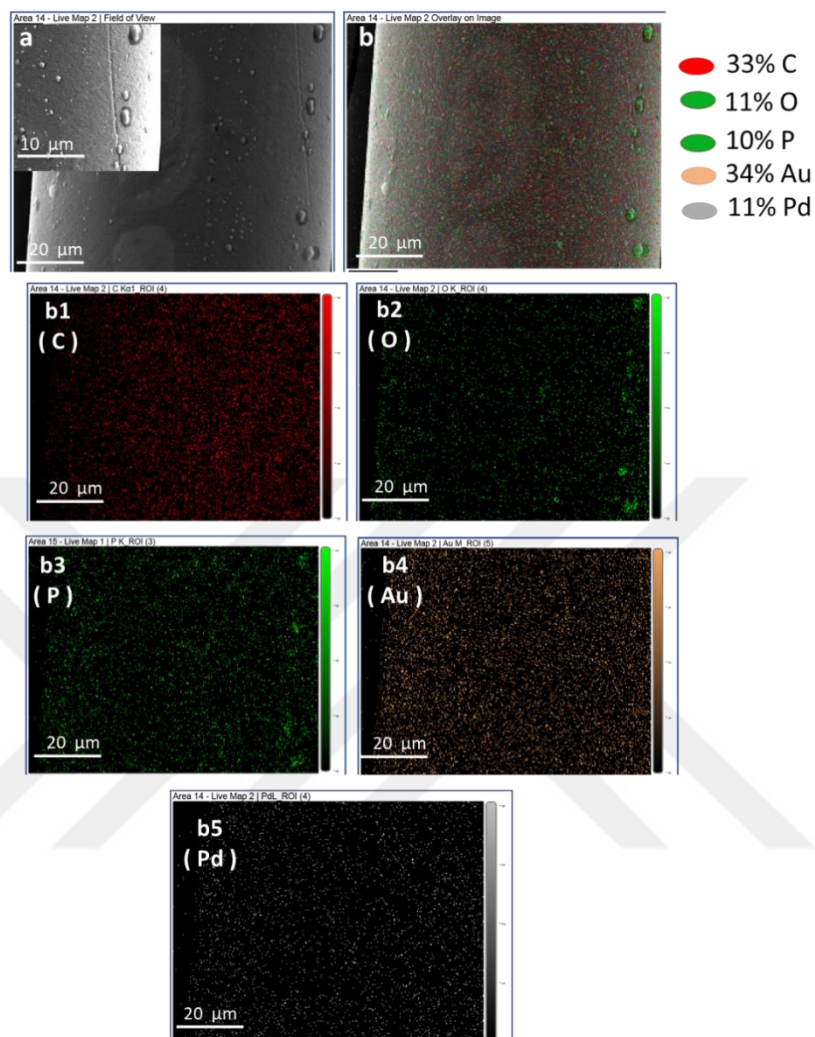


Figure 3.16 : Morphological and elemental analysis results of PEFR-20 fiber, phosphorus bath with a concentration of 1.5 wt.%. (a) SEM; (b) EDAX full color distribution; (b1) C (carbon); (b2) O (oxygen); (b3) P (phosphorus); (b4) Au (gold); (b5) Pd (palladium) distributions.

The EDAX result of the fibers produced with nanoclay (PEFR-25) is shown in Figure 3.17. Looking at the EDAX result, unlike pure PE fibers, silicium (Si) element was determined besides all other elements, such as C, O, Au and Pd in nanoclay added LLDPE fibers.

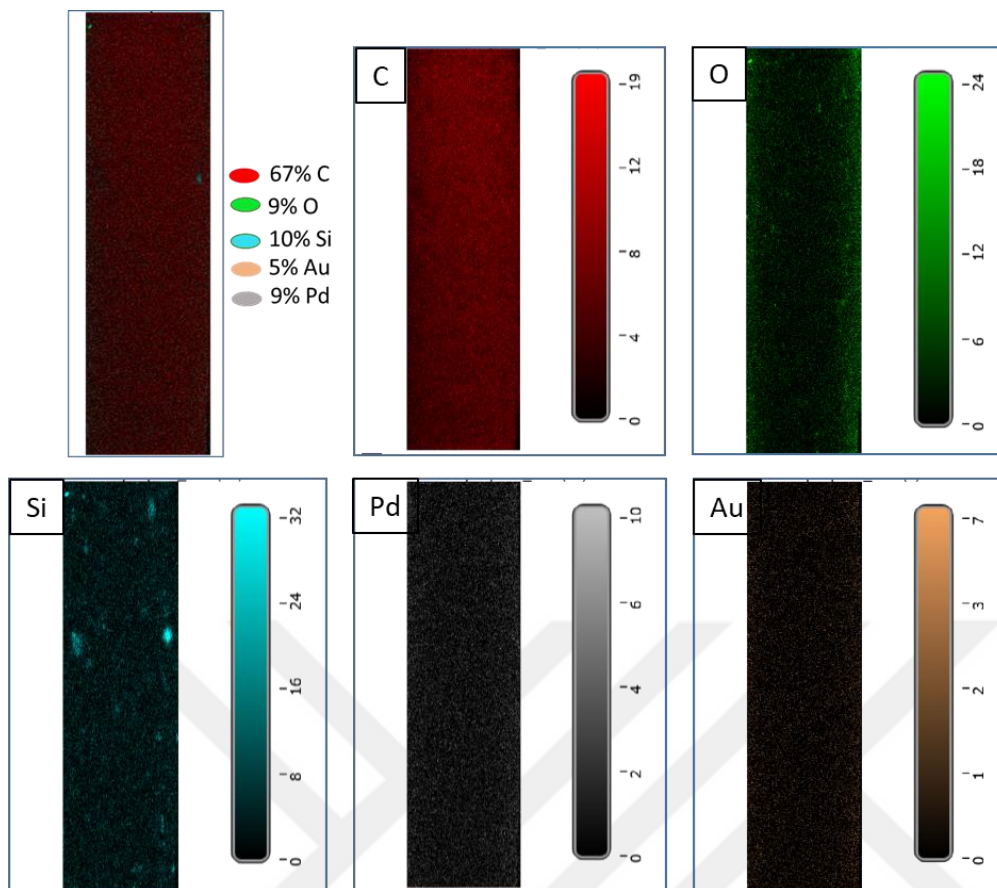


Figure 3.17 : Morphological and elemental analysis results of PEFR-25 fiber, that containing nanoclay with a concentration of 1.0 wt.%. (a) SEM-EDAX full color distribution; C (carbon); O (oxygen); Si (silicium); Au (gold); Pd (palladium) distributions.

3.3 Crystalline Structure via Wide Angle X-Ray Analysis

XRD analysis was performed on pure LLDPE fibers to obtain degree of crystallinity, amorphous-crystal orientation factors and crystal size of LLDPE fibers. The main purpose of this analysis is to reveal the effects of the HiPER system on the crystal structures of LLDPE fibers. Thus, because of the limited possibilities, only the fibers which are produced by novel melt spinning line at 400 m/min take-up speed were performed by XRD analysis. XRD graphics of samples of low molecular weight PE fibers produced with a take-up speed of 400 m/min are given in Figure 22. As expected, high characteristic sharp peaks corresponding to the crystalline region and low-density peaks corresponding to the amorphous region emerged from the characteristic XRD peaks of the control LLDPE. As a result of the comparisons made in the literature, it was seen that the strong diffraction peak $2\theta = 21.620^\circ$ (110), two weak diffraction peaks $2\theta = 23.904^\circ$ (200) and $2\theta = 36.03^\circ$ (020) show that LLDPE has orthorhombic

crystal lattice structure [98]–[101]. As seen in Figure 3.18, the same characteristic XRD peaks were observed in three different LLDPE samples except for HiPER-95 that do not show (020) peak.

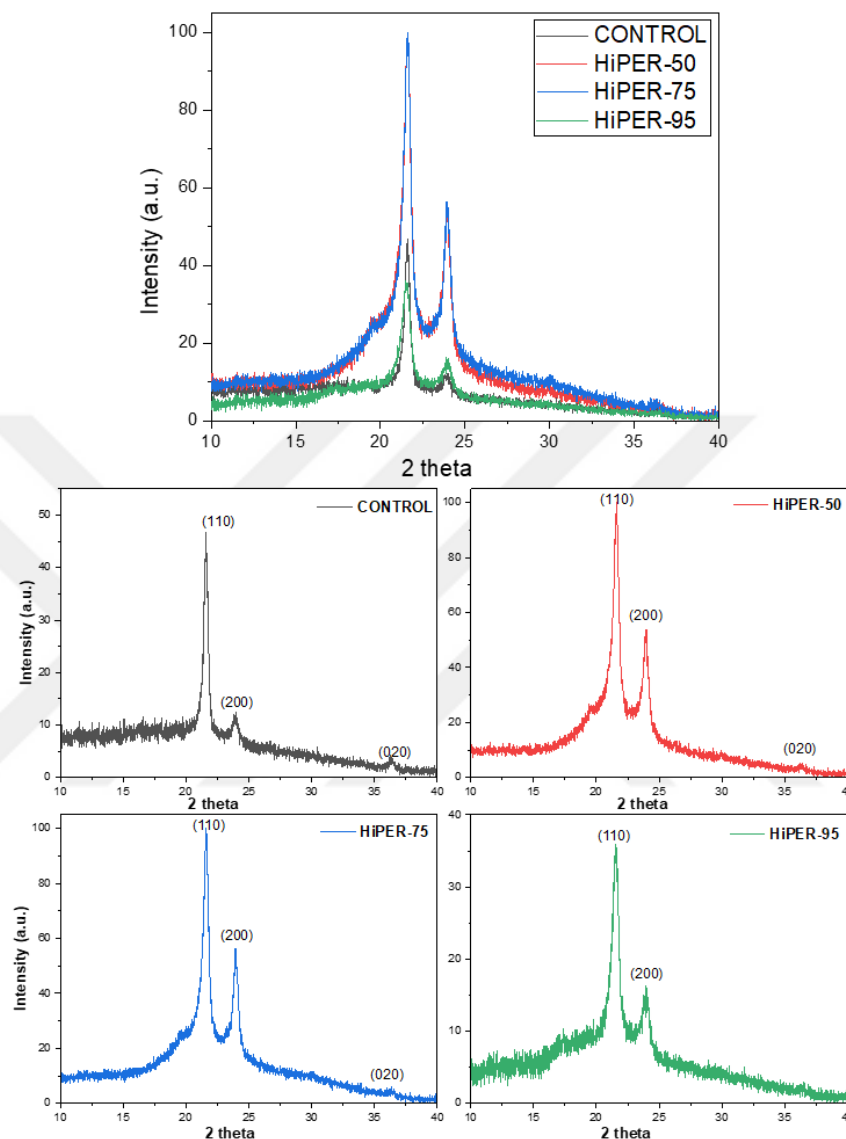


Figure 3.18 : The appearance of the characteristic XRD peaks of the control, HiPER-50, 75 and 95 samples produced from low molecular weight PE.

The percent crystallinity values obtained in Table 3.5 were calculated using the Origin 2018 software program to remove the amorphous background below the peaks in the XRD graphics indicated in Figure 3.18. The areas under the peaks are proportional to the scattering intensity of the XRD, and as indicated from these areas, the amorphous regions were removed and percent crystallinity and crystal sizes were determined. Table 3.5 demonstrates the information about crystallinity, crystalline (fc) -

amorphous (f_a) orientation, chain orientation (Δn) and crystal size produced using LLDPE polymer with a take-up speed of 400 m/min.

Table 3.5 : Comparison of degree of crystallinity, crystal-amorphous orientation factor, chain orientation and crystal sizes for low molecular weight PE polymer at 400 m/min take-up speed at 50, 75 and 95 °C bath temperatures and control fibers.

Sample	Crystallinity (%)	(Δn)	(f_a)%	f_c (110) (%)	f_c (200) (%)	Crystal size (Å) L_{110}	Crystal size (Å) L_{200}
Control	36.461	5	35	31	39	190	147
HiPER - 50	40.874	6	61	52	64	164	132
HiPER - 75	42.086	8	48	43	-	89	79
HiPER - 95	44.403	18	38	40	42	85	54

In the literature, it has been seen that the crystallinity values for LLDPE is generally in the range of 40% to 70%. Different crystallinity values were obtained under different HiPER conditions we produced. Samples produced at 400 m/min production speed exhibit crystallinity values lower the control sample. Here, it is understood that the precursor inner structure formed (low crystallinity and high orientation as much as possible) is not fully especially in HiPER samples due to low speed. In addition, as bath temperature increased in HiPER samples, XRD peaks became stronger and more sharpened so crystallinity value increased. Here, with the increase in temperature, macromolecular chain mobility in the fiber's inner-structure has increased, which has caused to increase the crystallization by promoting molecular chain relaxation and rearrangement [87], [102]. Then, when the new crystalline regions that started to form in the fibers came out of the HiPER bath, they suddenly solidified before they could grow due to the sudden temperature difference and cooling effect. Thus, fibers with small crystal size and high degree of crystallinity were formed compared to the control sample Table 3.5. In addition, it was observed that the crystal sizes decrease when the temperature increased. This situation intersects with the theorem that the crystal size decrease while crystallinity increases [17]. Table 3.5 demonstrates that the increase in HiPER temperature at temperatures above 50 °C reduces amorphous and crystalline orientation factor values. However, the chain orientation increases with HiPER temperature increase, as well. The value of (Δn) given in Table 3.5 gives us the result

of chain orientation in the fiber. Looking at (Δn) of LLDPE fibers produced at 400 m/min a take-up speed, (Δn) value is seen as 5. Besides, the fibers produced at different HiPER temperatures at the same take-up speed, it is seen that as the temperature increases, the fiber orientation increases and (Δn) values of the control sample increases to 3.6 times at 95 °C.

In other words, before reaching the ecological HiPER bath, the molecular chains in the fibers that do not have a full solid form become mobile due to the effect of the hot HiPER environment and reversible friction force. In addition, the chains reach a more regular orientation with the precursor form, which is also obtained with the effect of high speed. Crystallization takes place from a certain orientation, and then, from the HiPER to the fiber spinning, very high orientation fibers with high crystallinity value are formed, with relatively small size crystal structures relative to the control sample [87], [102]. The unique precursor form obtained with this HiPER technology differs greatly from the internal morphology of all other polymeric fibers, resulting in a high strength increase.

3.4 Thermal (DSC, TG/DTG) Properties

According to DSC results of the produced fibers, the onset of melting temperature and melting temperature (T_m) are determined by heating curves, while the cooling curve is determined the temperature of starting to solidify and the crystallization temperature (T_c). The temperature values of fibers produced at 400 m/min and 2500 m/min with and without HiPER system are summarized in Table 3.6.

Table 3.6 : DSC temperature values of control, HiPER-50, 75 and 95 fibers.

DSC	Sample	Peak Temp. (°C)	Sample	Peak Temp. (°C)
First heating	Control-400	126	Control-2500	129
	HiPER – 50-400	127		
	HiPER – 75-400	124-126	HiPER - 95-2500	129
	HiPER – 95-400	124-127		

As can be seen in Table 3.6 and Figure 3.19, it is observed that the temperature of the onset of melting and T_m temperature of the control samples produced at 400 m/min

remain the same for the first heating and final heating, while the temperature of the onset of melting to decrease as the HiPER temperature increases for HiPER productions. When looking at the DSC graphs shown in Figure 3.19, while the first heating and the second heating demonstrate the endothermic peak as expected; and cooling shows exothermic peak [90]. In addition, it is observed that 2 endothermic peak values are obtained for the first heating in HiPER-50 and 75 samples shown in Figure 3.19. It can be interpreted the formation of two endothermic peaks as the temperature of the bath increases, new crystalline regions or folded chain lamellar structures are formed with lower melting temperature and less crystallinity. While a single endothermic peak is obtained in all samples for second heating, seen that the HiPER samples increases the T_m to 127 °C by shifting the melting temperature 1 °C. Looking at the cooling data, at the control sample and HiPER-50, it is observed that the crystallization start temperature is 119 °C, while HiPER-75 and 95 samples begin to crystallize earlier. It is seen that the T_c peak value does not change as the HiPER temperature increases.

Besides, for the fibers produced at 2500 m/min, the melting peak temperature for all first heating samples is 129 °C; cooling is 104 °C and final heating is 127 °C. Also, the onset temperature increased in second heating. As seen in the first heating graphics shown in Figure 3.19 of the fibers produced at 2500 m/min speed, the peaks became sharper when the control samples were passed through the HiPER bath. This situation was also observed in cooling and second heating DSC curves.

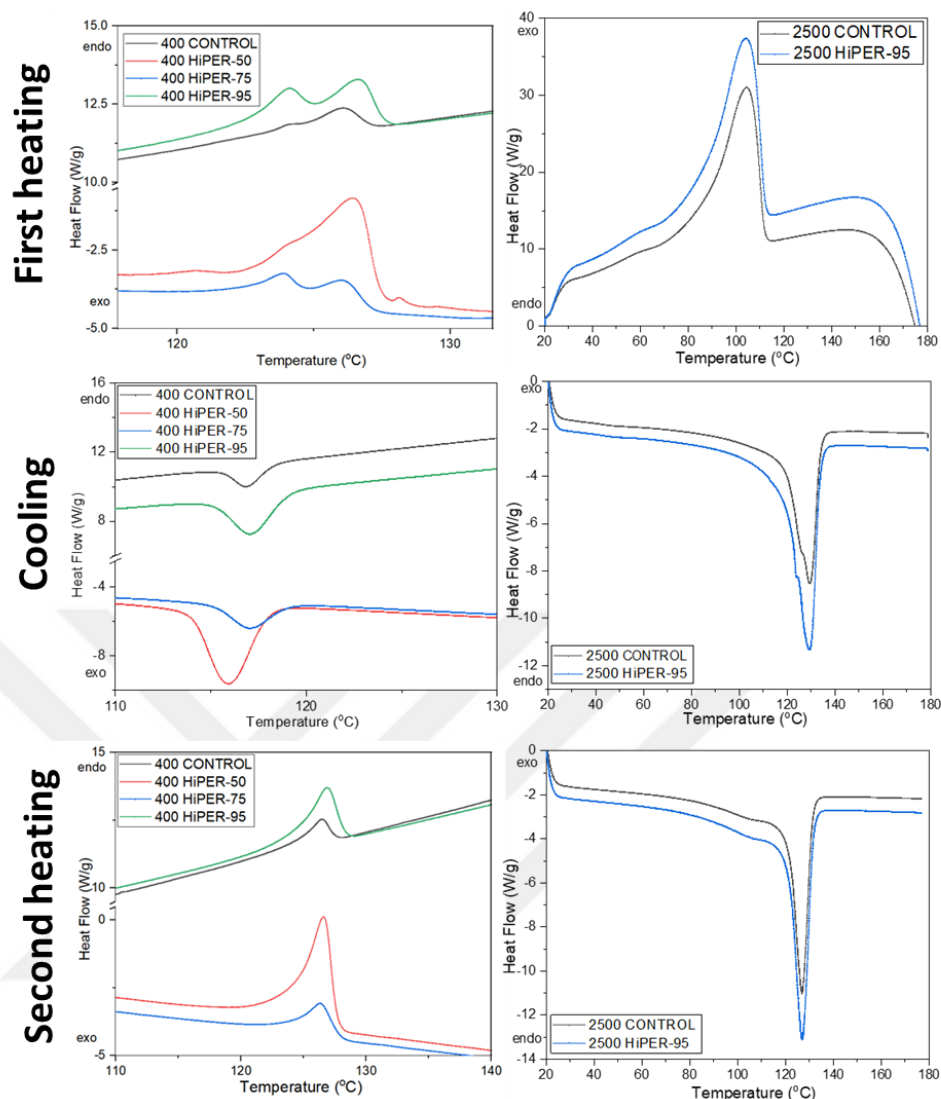


Figure 3.19 : Control produced with take-up speed of 400 m/min (a, b and c) and 400 m / min (d, e and f) of draft, HiPER 50, 75 and 95; heat warming (3-fold shooting, 90 ° C) control (L-K), initial heating of HiPER 50, 75 and 95 samples; comparison of cooling and final heating DSC results.

Table 3.7 demonstrates the degree of crystallinity values of fibers produced at 400 m/min and 2500 m/min take-up speeds. For the fibers produced at 400 m/min, from the control sample to HiPER-95, the first heating crystallinity value increased by 18.5%. Also, when we look at the cooling and second heating crystallinity values, it is seen that HiPER-50 sample reaches the highest crystallinity values.

Looking at the first heating values of the fibers produced with the take-up speed at 2500 m/min, the crystalline ratios of HiPER-95 and control samples were found to be 40% and 47%, respectively, and the crystallinity of the HiPER95 sample passed through the bath decreased by 15% compared to the control sample. When looking at the second heating values, it is seen that it has the same trend as the first heating the

crystalline ratios of HiPER-95 and control samples were found as 46% and 52%, respectively. The crystallinity of the HiPER-95 sample passed through the HiPER bath decreased by 10.2% compared to the control sample. At the speed of 2500 m/min is reached, crystalline drop decreases in the fibers passing through the bath. While an increase in crystallinity values of fibers produced with 400 m/min take-up speed from control to HiPER sample, the crystalline values of the fibers produced at 2500 m/min decrease from the control to the HiPER sample as expected in the study. Crystallinity increase in fibers produced with 400 m/min take-up speed can be interpreted the unstable inner structure of fibers due to low production speed and test conditions of DSC that examine the internal structure changing at increasing temperatures.

Table 3.7 : DSC temperature values of control, HiPER-50, 75 and 95 fibers produced.

DSC	Sample	Degree of crystallinity (%)	Sample	Degree of crystallinity (%)
First heating	Control-400	24	Control-2500	47
	HiPER – 50-400	28		
	HiPER – 75-400	33	HiPER-95-2500	40
	HiPER – 95-400	32		
Cooling	Control-400	23	Control-2500	51
	HiPER – 50-400	28		
	HiPER – 75-400	27	HiPER-95-2500	40
	HiPER – 95-400	26		
Second heating	Control-400	20	Control-2500	52
	HiPER – 50-400	30		
	HiPER – 75-400	28	HiPER - 95-2500	46
	HiPER – 95-400	26		

3.4.1 Thermal properties of FR HiPER fibers

DSC analysis was only performed for as-spun fibers that have not any flame retardant additives and the aim is determination of their T_m , T_c temperatures and degree of crystallinity values. The fibers that have phosphorus and nanoclay containing additives were examined by TG/DTG analysis in order to determine temperatures value at which 10% mass loss occurs, residue amount at 600 °C and at the maximum mass loss temperatures (T_{DTGmax}). The TG/DTG values of control and phosphorus containing fibers such as $T_{10\%}$ (°C), residue at 600 °C (%) and T_{DTGmax} (°C) are indicated in Table 3.8. When looking at the TG/DTG results, it is seen that pure LLDPE fibers do not possess any residue at 600 °C. Also, some residues observed in phosphorus treated fibers, PEFR-19, PEFR-23 and PEFR-24 at 600 °C. As a result, the flammable additive reduces the $T_{10\%}$ temperature and the peak value of the DTG curve. For the PEFR-23 and 24 samples $T_{10\%}$ temperature is lower than the control sample so phosphorus additives were decomposed before polymer, LLDPE. However, maximum mass loss temperatures (T_{DTGmax}) were indicated the similar temperatures.

Table 3.8 : The TG/DTG values of control and phosphorus containing fibers.

Sample	$T_{10\%}$ (°C)	Residue at 600 °C (%)	T_{DTGmax} (°C)
Pure PE	450	0	479
PEFR-18	452	0	472
PEFR-19	451	2.4	469
PEFR-20	452	0	476
PEFR-21	451	0	472
PEFR-22	452	0.1	472
PEFR-23	447	1.9	478
PEFR-24	443	3.0	478

The TG/DTG curves of control and phosphorus containing samples are shown in Figure 3.20 and Figure 3.21. For TG curve, it is observed that the degradation occurred in one step between about 400-500 °C.

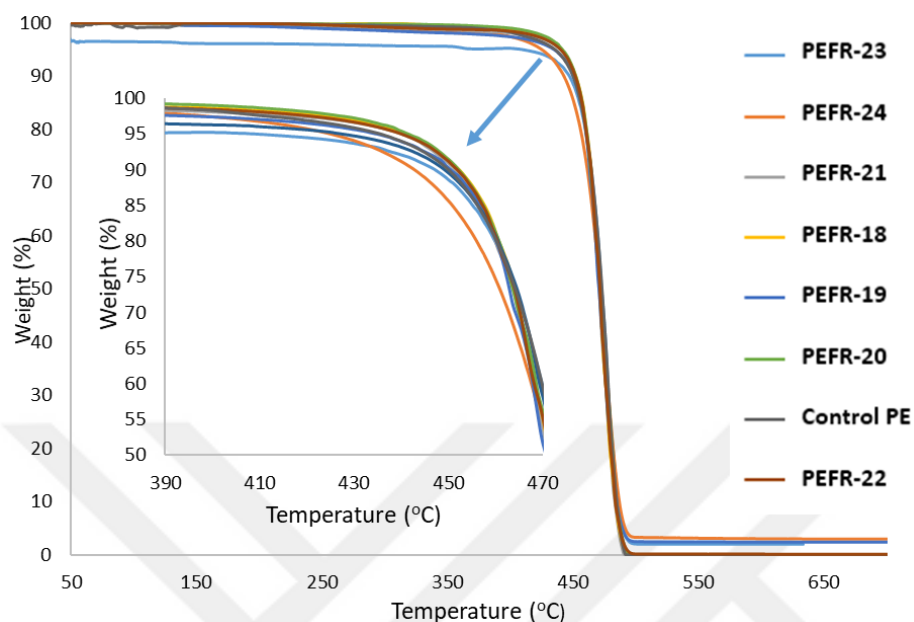


Figure 3.20 : The TG curves of control and phosphorus containing samples.

Compared with the control sample, PEFR-24 sample began to decompose earlier, leaving more residue after the test. The temperature at which the maximum mass loss rate of the control sample was seen was also the similar. Moreover, PEFR-23 and PEFR-24 samples were decreased $T_{10\%}$ values and there was no change in T_{DTG} values and residue formation was observed at the end of the analysis at 600 °C. It has been concluded that it will have an effect on the gas phase since it degrades before the polymer, and also increases the thermal degradation resistance of LLDPE in the solid phase by forming residues.

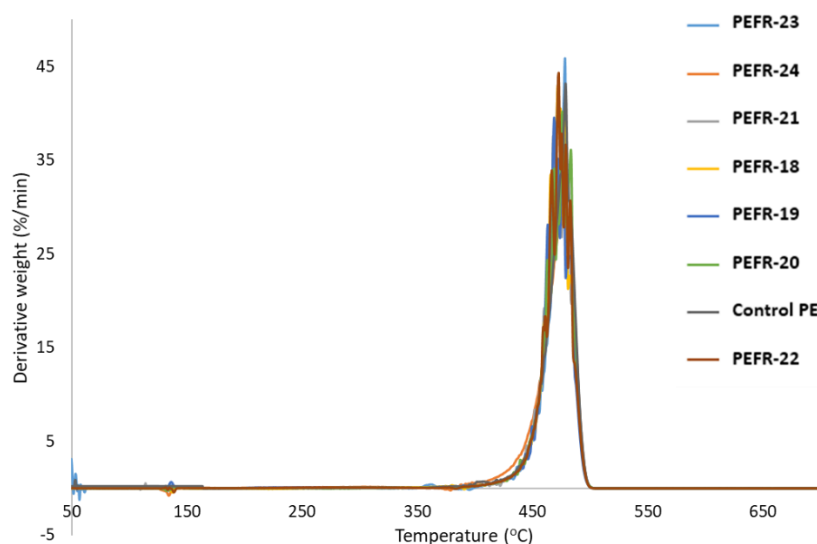


Figure 3.21 : The DTG graphs of control and phosphorus containing samples.

The TG/DTG values of nanoclay containing fibers such as $T_{10\%}$ (°C), residue at 600 °C (%) and T_{DTGmax} (°C) are indicated in Table 3.9. Nanoclay caused an increase in degradation temperature $T_{10\%}$, whereas created residue after burning at 600 °C. In addition, nanoclay additives decreased the maximum degradation temperature (T_{DTGmax}) of samples compared with control sample in Table 3.8. Also, it is seen that nanoclay content effects the amounts of residue after burning shown in PEFR-26, 27 and 29 samples and residue is proportional to the amount of nanoclay. Moreover, it can be interpreted samples that have higher HiPER temperatures provides more residue after burning.

Table 3.9 : The TG/DTG values of nanoclay containing samples.

Sample	$T_{10\%}$ (°C)	Residue at 600 °C (%)	T_{DTGmax} (°C)
PEFR-25	453	0	471
PEFR-26	454	2.07	470
PEFR-27	454.5	3.09	471
PEFR-28	453	0.2	470
PEFR-29	452	2.33	475
PEFR-30	445	0.36	475
PEFR-31	454.4	0.26	473
PEFR-32	455	1.25	476

In addition, when fibers containing 1.0 wt% nanoclay, called PEFR-25 produced without HiPER technology at 1250 m/min take-up speed are examined, no residue are achieved compared to the other samples produced by HiPER technology. Thus, it can be said that combination of nanoclay and HiPER system enhance the residue amounts of polyethylene fibers. Also, the TG/DTG curves of nanoclay containing samples are shown in Figure 3.20 and Figure 3.23. It is observed that the degradation occurred in one step between about 400-500 °C for all samples. In Figure 3.22 demonstrates only PEFR-30 sample decreased the degradation temperature $T_{10\%}$.

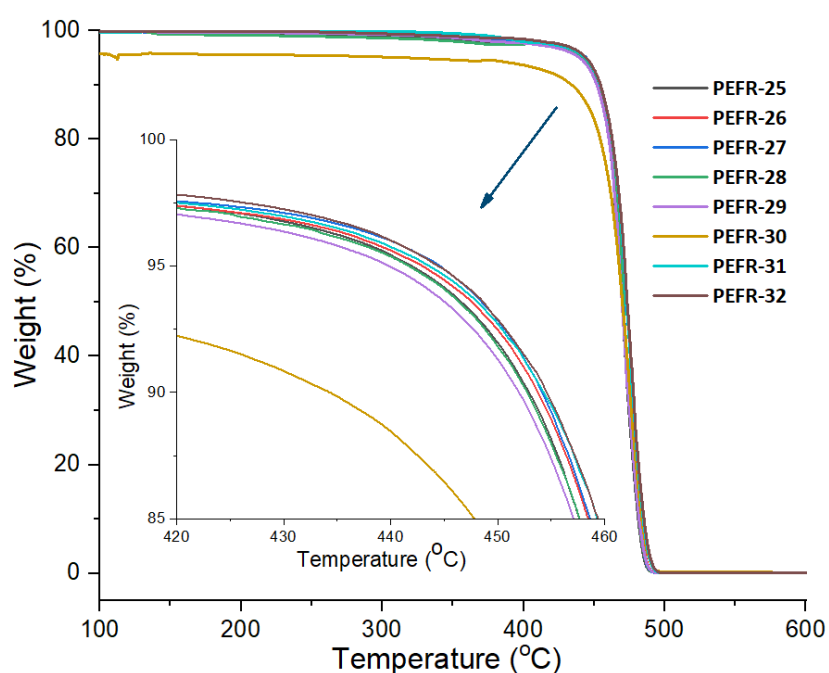


Figure 3.22 : The TG curves of nanoclay containing samples.

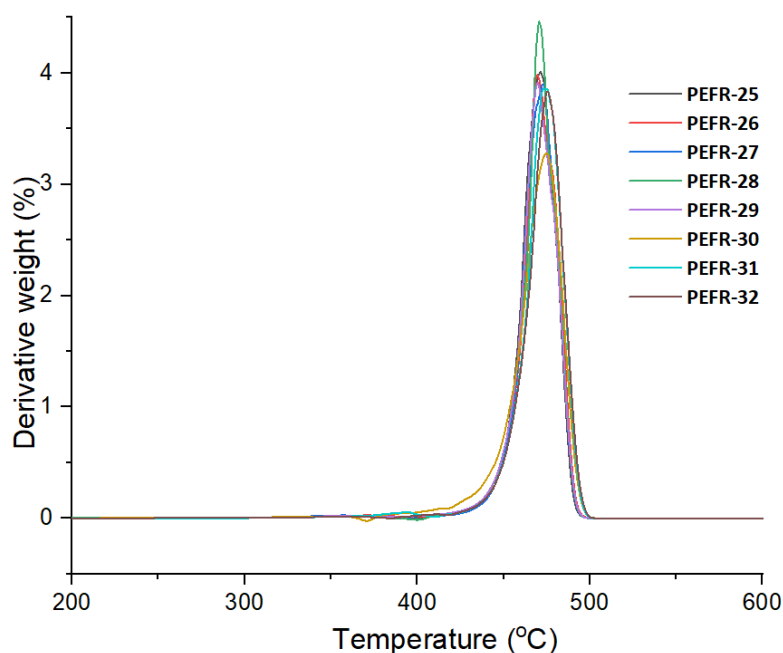


Figure 3.23 : The DTG graphs of nanoclay containing samples.

It has been concluded that nanoclay will have an effect on the thermal degradation resistance of LLDPE in the solid phase by forming residues. It is thought that the samples containing nanoclay rather than phosphorus-added samples will provide stronger thermal resistance thanks to the coal formation. Therefore, combination of nanoclay and HiPER technology enhance the coal formation of the polyethylene fibers.

3.5 Limiting Oxygen Index (LOI) Test

Limit oxygen index (LOI) test was applied to sheets containing 10%, 20, 30 and 40% ATH; 10%, 20, 30 and 40% nanoclay and 10% and 20% nanocellulose in terms of determine the burning behaviors of additives in room conditions before feeding additives to the novel melt spinning line. LOI test results belong to different compositions of ATH, nanoclay and nanocellulose sheets are represented in Table 3.10. According to the table, it is seen that increase in the amount of additives only increase the LOI results of ATH molds, while increase in amount of additives causes to decrease in LOI test results of nanoclay and nanocellulose. Therefore, the best FR

performances are indicated for more than 40% ATH and less than 10 wt.% nanoclay and nanocellulose.

Table 3.10: Comparison of LOI test results belongs to different compositions of ATH, nanoclay and nanocellulose sheets.

Sample	PE (%)	ATH (%)	Nanoclay (%)	Nanocellulose (%)	LOI (%)
Control PE	100	-	-	-	19.8
PEFR-1	90	10	-	-	19.91
PEFR-2	80	20	-	-	20.91
PEFR-3	70	30	-	-	21.3
PEFR-4	60	40	-	-	22.17
PEFR-5	90	-	10	-	20.30
PEFR-6	80	-	20	-	19.29
PEFR-7	70	-	30	-	19.71
PEFR-8	60	-	40	-	20.65
PEFR-10	90	-	-	10	19.30
PEFR-11	80	-	-	20	18.67

Looking at the LOI results of the samples prepared with ATH, it was seen that adding 10% ATH increases the burning time. While the mold produced only with PE is extinguished in 75 seconds, the burning time decreases to 75 seconds, 30 seconds and 4 seconds, with the addition of 20% and more ATH additives. In addition, adding ATH in the specified amounts has been shown to reduce the amount of burning samples. It was observed that adding 40% ATH with the sample produced only from PE increased the LOI result by 2%. As it can be understood from the work done by Beyer et al., with the addition of ATH, the LOI value was found to be around 25% and it was stated that it would only be possible with the addition of 65% ATH to achieve better performance [62].

Although there is no change in LOI value in composite structures using nanoclay, adding nanoclay extended the burning time of the samples. Combustion distance was shortened in the same time period compared to samples made with ATH. Although the addition of nanoclay has no effect on the LOI result, it is worth noting that nanoclay improves the burning behavior and melt drip feature of the polymeric material. On the other hand, since composite materials containing nanocellulose exceeded the burning

time and burning length standard, they could not get a good positive result from the LOI test. However, when looking at the samples produced with nanoclay and ATH, coal formation and flameless dripping were observed in the burning polymer compare with the addition of nanocellulose.

After the production of pure (control) LLDPE fibers with traditional and HiPER technology, flame retardancy properties tried to add to LLDPE fibers. Masterbatch and LLDPE polymers were fed into the system to investigate the effect of masterbatch granules containing 30%ATH-10% APP additive to the fibers produced by the novel melt spinning line. The purpose of the hybrid study prepared using ATH and APP additives is to provide synergistic effects to each other in terms of flame retardant, thermal and mechanical properties as seen in the literature. There is no coal formation in the flame retardant mechanism of ATH and for 25% and above LOI value, amount of 65% and above ATH is required. In addition, in studies using only ATH additive, drip formation is observed in the polymer [55]. It is aimed to improve the negative features of ATH by adding APP. When APP is added in sufficient amounts, it has coal formation, reduces the burning time of polymers and prevents drip formation [103]. The first flame retardant study with PE/ATH/APP masterbatch were added to the novel melt spinning line at 5%, 3% and 2% concentrations. Fibers were tried to spin with different take-up speeds. The same polymer (LLDPE) and masterbatch form (ATH-APP) was used in all samples, only the rate used was changed. Fibers called from PEFR-12 to PEFR-17 represents the fibers with ATH-APP masterbatch study demonstrated in Table 2.7. Figure 3.24 shows the images of some fibers produced with 5%, 3% and 2% concentrations of masterbatch additive. In polymer-masterbatch studies, homogeneous and continuous production has not been achieved. Because of the fiber diameter, size and amount of additives are important parameters. Thus, to provide flame retardancy ATH/APP masterbatch study resulted in failure to fiber spinning as shown in Figure 3.24.

In all three hybrid works shown in Figure 3.24, since the fibers are very brittle, it has been very difficult to immerse them in the HiPER bath and not achieve to wind at the godet.

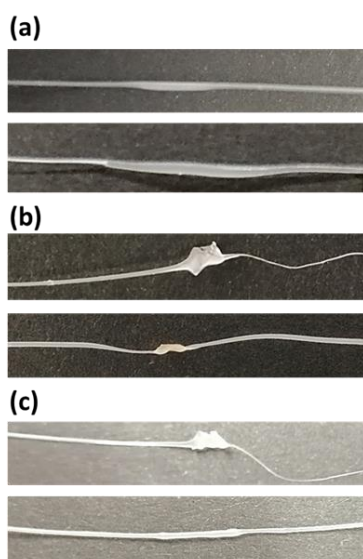


Figure 3.24 : The appearance of the discontinuous fibers obtained as a result of the LLDPE/ATH-APP hybrid fiber study at different contribution rates (a) 5%; (b) 3%; (c) 2%.

In the fibers produced with the ATH-APP mixture fed in granular form into the polymer, additives were observed in agglomerations when the polymer flow from the spinneret and a continuous homogeneous fiber spinning was not achieved. Because of the discontinuous and non-homogenous fiber spun only LOI test was achieved for ATH-APP containing fibers. Table 3.11 demonstrates the amount of 2% is not enough for ATH-APP masterbatch study to gain flame retardancy. Moreover, considering the LOI test results, the LOI value, which was approximately 19% for pure polyethylene, was increased to 20% with the effect of masterbatch and high take-up speed. Additives reduced the burning rate and burning length in all samples.

Table 3.11 : LOI results of ATH-APP masterbatch studies in different production parameters.

Sample	PE (%)	Masterbatch (ATH-APP) (%)	Take-up Speed (m/min)	LOI (%)
PEFR-12	97	3	400	18.80
PEFR-13	97	3	650	19.80
PEFR-14	97	3	750	19.50
PEFR-15	95	5	750	19.30
PEFR-16	98	2	1000	18.60
PEFR-17	97	3	1000	20.00

In addition, there was some increase in LOI when the winding speed increased. This situation is thought to be caused by increased fiber molecular orientation and increased crystallinity with increasing take-up speed. However, there was some decrease in the LOI value of the sample with 5% masterbatch rate. It was evaluated that this is due to the fact that the flammable material is not homogeneously distributed.

Table 3.12: LOI results in different production conditions of the control and fibers containing 1.5% phosphorus.

Sample	HiPER Length (cm)	HiPER Temperature (°C)	Take-up Speed (m/min)	LOI (%)
Control PE	-	-	1000	19.80
PEFR-18	10	50	500	21.50
PEFR-19	15	50	500	21.20
PEFR-20	10	50	750	21.3
PEFR-21	15	50	750	21.5
PEFR-22	15	25	750	21.2
PEFR-23	15	50	1000	21.50
PEFR-24	20	95	1000	21.50

When looking at Table 3.12, the LOI value of pure PE is seen as 19.8%. When looking at the samples passed through 95 and 50 °C HiPER bath produced at 1000, 750 and 500 m/min fiber take-up speeds, maximum 21.5% LOI value is observed in all productions, while for other samples LOI values are decreased. In addition, PEFR-32 sample passed through the phosphor bath at room temperature has the lowest LOI result. It can be concluded that the minimum HiPER temperature for high LOI is 50 °C.



Figure 3.25 : Burning behaviors of fibers containing 1.5% phosphorus during the LOI test.

According to the LOI test result, the flame retardant additive (organic phosphorus) reduced the flammable rate. It increased the LOI value. Images of the samples before LOI test are presented in Figure 3.25. In order to show the combustion rate and low flame height, the images of some samples when their LOI value is set to 21.6 are shown in Figure 3.25. It can also be seen from the figure that smoke is not released during burning. It was observed that after the fire source was withdrawn, the flame did not grow and self-extinguished.

3.6 Micro Scale Combustion Calorimeter Test Results

Micro combustion calorimeter test was initially applied to the sheets containing 10%, 20, 30 and 40% ATH; 10%, 20, 30 and 40% nanoclay and 10% and 20% nanocellulose in terms of determine combustion properties such as the heat releasing rate (HRR), pHRR (W/g), heat release capacity (HRC, J/gK) and total heat releasing (THR, kJ/g) values before feeding additives to the novel melt spinning line. MCC test results

belong to different compositions of ATH, nanoclay and nanocellulose sheets are represented in Figure 3.26.

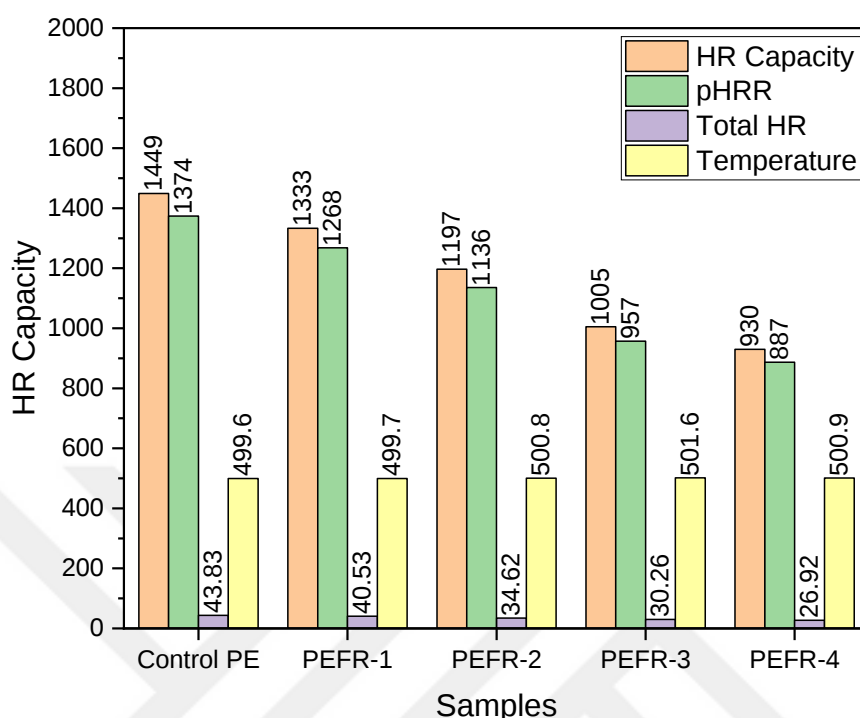


Figure 3.26 : MCC test results of control PE and ATH sheet studies in different compositions.

When looking at the results of MCC, it was seen that the amount of ATH had a positive effect on the HRR result and decreased the HR capacity. As the amount increased, HRR result decreased by 35%. In addition, the HR capacity of 1449 (J/gK) of PE decreased to approximately 930 (J/gK) with the addition of 40% ATH. The heat emission temperature of 499 °C does not change with the addition of ATH. The total heat release value, which was 43.83 (kJ/g), decreased by 38% with the addition of ATH and became 26.92 (kJ/g). In the study by Nazare et al., shows PHRR and total heat release value decrease with the addition of ATH [104].

On the other hand, looking at the Figure 3.27, adding nanoclay did not affect the HR capacity and peak of heat release rate of PE, and we even see that the HRC and pHRR values of PE increased until 40% nanoclay was added. However, the addition of nanoclay has been shown to reduce the total heat release from 43.83 (kJ/g) to 32.48 (kJ/g) compared to control PE. In addition, Smart et al., added nanoclay to synthetic

fibers obtained from polypropylene (PP) and results showed nanoclay improved their combustion properties and lowered the pHRR values.

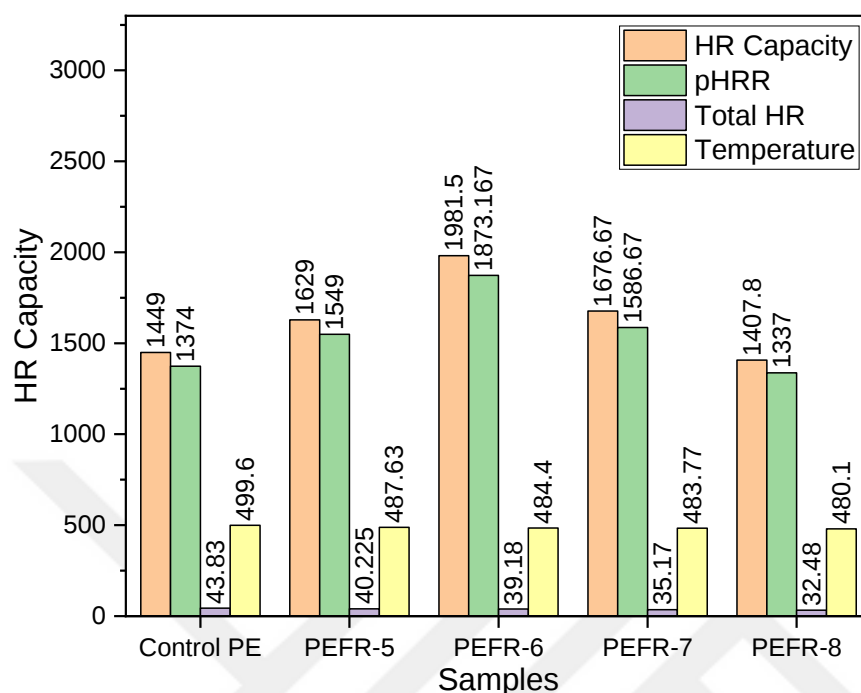


Figure 3.27 : MCC test results of control PE and nanoclay sheet studies in different compositions.

When looking at the MCC results of samples produced using 10% and 20% nanocellulose, the addition of nanocellulose had a positive effect by reducing the rate of heat release. HR capacity of 1149 (J/gK) for control PE has decreased to 1136 (J/gK) with the addition of 20% nanocellulose. Moreover, addition of nanocellulose decreased the total heat release of polyethylene from 43.83 (kJ/g) to 36.15 (kJ/g). Likewise, the peak of heat release value decreased as nanocellulose was added. When compared with nanoclay and ATH samples, PEFR-1 to PEFR-8, coal formation and flameless dripping were observed with addition of nanocellulose during the burning of polymer.

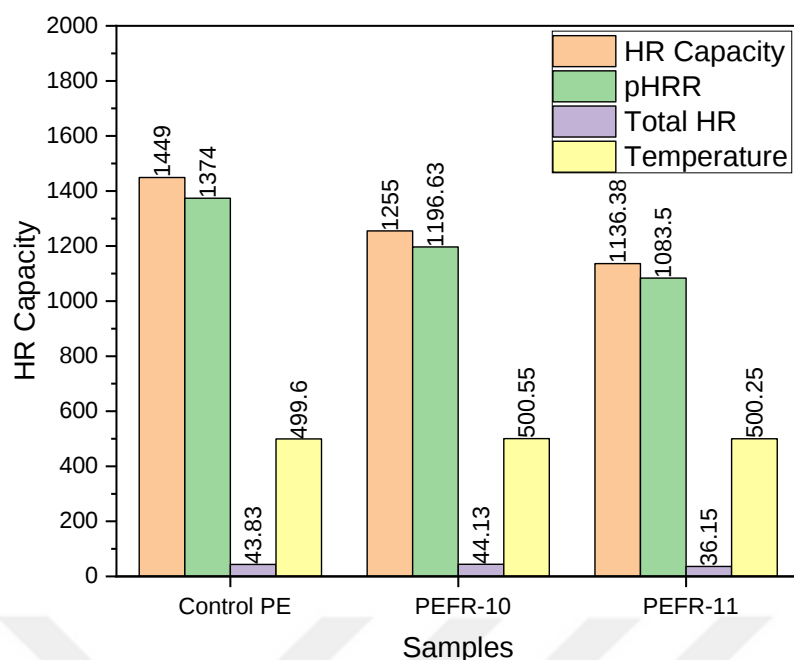


Figure 3.28 : MCC test results of control PE and nanocellulose sheet studies in different compositions.

The MCC results of the phosphorus containing fibers is shown in Figure 3.29. When we look at the figure, we see that the best results belong to the PEFR-20, PEFR-21, PEFR-23 and PEFR-24. In these samples, significant improvements were observed in heat release capacity and pHRR values compared to control. When we look at the control PE that does not have phosphorus additive given in Table 3.13, the pHRR was found to be 1523 (W/g) and the heat release capacity was found to be 1559 (J/g). When looking at the MCC test result made with the control sample, it was observed that the heat release rate of the samples passing through the HiPER system contains phosphorus generally improved. However, it is seen that the best results belong to the samples produced at 50 °C HiPER temperature and 15 cm HiPER length at 750 and 1000 m/min take-up speeds, respectively, encoded as PEFR-21 and PEFR-23. Looking at the decrease in the amount of heat release, the best result belongs to PEFR-21 samples and 22.45%, 23% and 18% decrease was observed in HR capacity, pHRR, THR values, respectively.

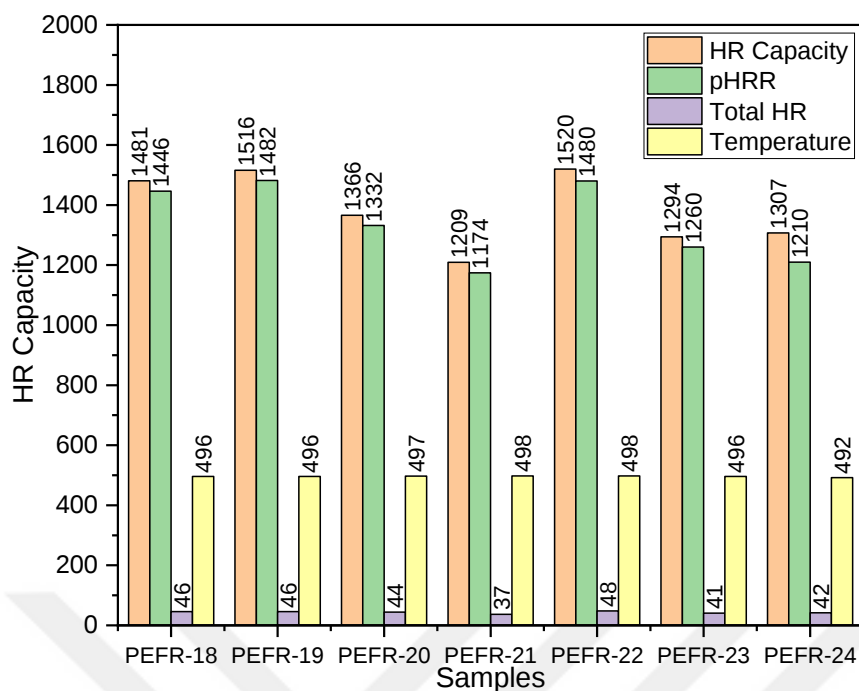


Figure 3.29 : MCC test results for LLDPE fibers with a concentration of 1.5% phosphorus with different process parameters.

Table 3.13 demonstrates that the peak temperature varies between 490-500 °C and the lowest temperature is given by the sample PEFR-24 with 492 °C. A decrease in peak of heat release rate was also observed in all samples passed through the HiPER system compared to the control sample.

Table 3.13 : MCC test results for control LLDPE and LLDPE fibers with a concentration of 1.5% phosphorus.

Sample	HR capacity (J/gK)	pHRR (W/g)	Total HR (kJ/g)	Peak Temperature (°C)
Control PE	1559	1522.5	45.2	499.05
PEFR-18	1481	1445.5	46.35	495.5
PEFR-19	1516	1482	45.5	496.35
PEFR-20	1366	1332	44	496.65
PEFR-21	1209	1173.65	37.4	498.65
PEFR-22	1520	1480	47.55	498.45
PEFR-23	1294	1259.5	41.45	496.4
PEFR-24	1307	1209.5	42.05	491.8

The MCC results of the nanoclay containing fibers is shown in Figure 3.30. MCC results show that the addition of nanoclay reduces the HR capacity of all samples

except the PEFR-25 sample and PEFR-28 has the better HR capacity, 1391 (J/gK) than other samples. Moreover, nanoclay decrease pHRR values of all samples. When we look at the peak temperatures, it is seen that the peak temperature varies between 495-500 °C and the lowest temperature is given by the PEFR-28 sample with 496 °C.

Moreover, when looking at the Figure 3.27, which is sheet form and has different nanoclay concentrations between 10.0 wt.% to 40.0 wt.%, sheets reached the minimum 1337 W/g pHRR value. However, PE fibers produced with nanoclay and HiPER technology possess lower pHRR value, 1269 W/g than pure PE sheet. Therefore, it has been found that lower nanoclay concentrations are more effective than 10 wt.% and higher concentrations.

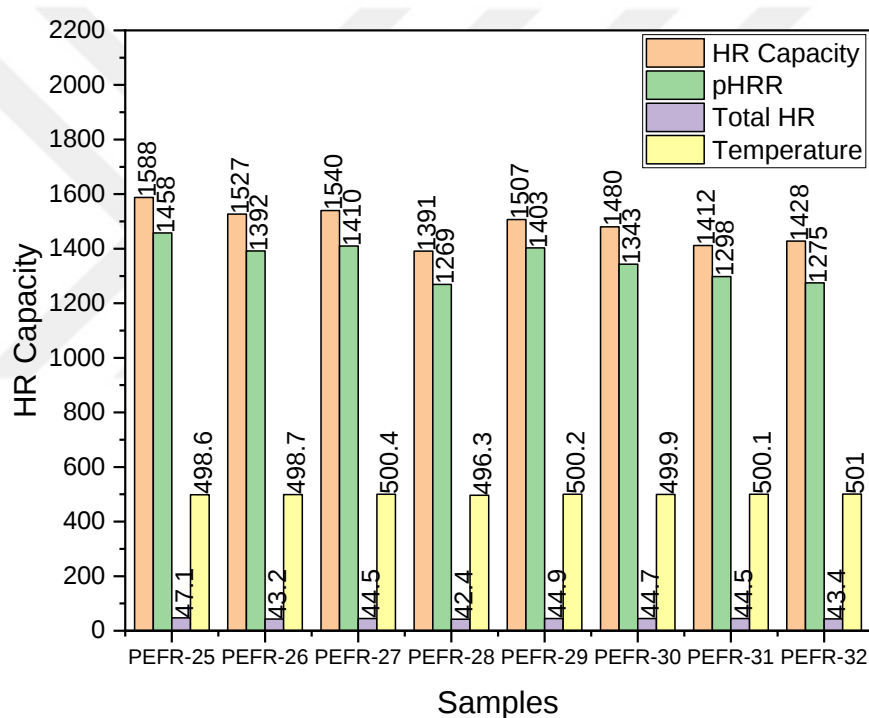


Figure 3.30 : MCC test results for LLDPE fibers with containing of nanoclay additive at different process parameters.

Table 3.14 demonstrates MCC results and based on the data the best sample is PEFR-28, which achieve the best enhanced combustion properties. The PEFR-28 sample contains 1.0% nanoclay and was produced at 95 °C HiPER temperature and 500 m/min take-up speed. However, the samples, PEFR-31 and PEFR-32 which have 0.5 wt.% nanoclay possess higher pHRR and HR capacity values following the PEFR-28 sample. It can be said that lower nanoclay amount was homogenously distributed in polyethylene fibers and caused to the better combustion properties.

Table 3.14 : MCC test results for LLDPE fibers with containing of nanoclay additive.

Sample	HR capacity (J/gK)	pHRR (W/g)	Peak Temperature (°C)	Total HR (kJ/g)
PEFR-25	1588	1458	498.6	47.1
PEFR-26	1527	1392	498.7	43.2
PEFR-27	1540	1410	500.4	44.5
PEFR-28	1391	1269	496.3	42.4
PEFR-29	1507	1403	500.2	44.9
PEFR-30	1480	1343	499.9	44.7
PEFR-31	1412	1298	500.1	44.5
PEFR-32	1428	1275	501	43.4

In addition, when fibers containing 1.0 wt% nanoscale, called PEFR-25 produced without HiPER technology at 1250 m/min take-up speed are examined, lower MCC results are achieved compared to the other samples produced by HiPER technology. Thus, it clearly said that combination of nanoclay and HiPER technology create the positive synergistic effect and found out the better flame retardancy combustion properties. When compared with control PE, nanoclay enhance the combustion properties of PE fibers, such as pHRR and HR capacity values. These results investigate the combined effects of nanoclay and HiPER technology on the flame retardancy and combustion properties of LLDPE fibers.

4. CONCLUSIONS AND RECOMMENDATIONS

The works presented in this thesis and their results were listed below:

- The traditional melt spinning system was modified and the novel melt spinning system (HiPER) was designed and manufactured.
- For use in this system, polyethylene, linear low density (LLDPE), as a polymeric source was chosen.
- Fiber productions were carried out in two different ways, which were not immersed in the HiPER system (control) and produced with the HiPER system, under the same conditions for comparison.
- The effects of production parameters and additives on the mechanical, morphological, internal structure, thermal and flame retardant properties of the fibers have been revealed.
- As a result of the mechanical test, maximum 202 MPa strength and 1329 MPa elastic modulus were obtained in the fibers produced with HiPER-95 system at 2500 m/min take-up speed, although they were not exposed to any drawing process. This corresponds to 166% strength and 371% module increase compared to control polyethylene fibers produced under the same conditions without using the HiPER system (control). In addition, the elongation at break was reduced by 71% and fibers were gained more brittle structure with HiPER.
- HiPER specimens were performed nano-fibrillated fracture type, without any hot drawing, and this fibrillated structure is a property of very high-performance fibers.
- Apart from the mechanical properties, it has been observed that the HiPER system increases the crystalline, amorphous and chain orientation of the fibers by regulating the internal structure of them.
- In addition, this thesis aims to improve the flame retardant properties of polyethylene, mostly by adding less than 10 wt.% of additives through the

modified melt spinning line. Because, the amount and size of additives are dominant and essential factors for the fiber formation with adjusting parameters of the melt spin line.

- Accordingly, three different types of flame retardant materials have been studied, including minerals containing, phosphorus containing, and nanocomposites such as aluminum trihydrate (ATH), nanoclay, crystalline nanocellulose and carbon nanotube (MWCNT) and phosphorus containing additives, respectively.
- Looking at the LOI test, the maximum LOI value was reached as 21.5 LOI in the fibers passed through the phosphorus bath.
- In addition, when fibers containing 1.0 wt% nanoclay, called PEFR-25 produced without HiPER technology at 1250 m/min take-up speed are examined, no residue are achieved compared to the other samples produced by HiPER technology. Thus, it can be said that combination of nanoclay and HiPER system enhance the residue amounts of polyethylene fibers.
- Lower MCC results are achieved in control sample, PEFR-25 compared to the other samples produced by HiPER technology. Thus, it clearly said that combination of nanoclay and HiPER technology create the positive synergistic effect and found out the better flame retardancy combustion properties regards to pHRR and HR capacity values.
- As a result of the studies, it has been observed that the HiPER system is suitable for strong fiber production at speed close to the conventional melt spinning line.
- Preliminary studies with the novel system have predicted that ballistic clothing may be produced with functional fibers produced with this novel system related to sufficient mechanical performance and thermal resistance.

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CURRICULUM VITAE



Name Surname : Beyza Nur Gunaydin

Place and Date of Birth : Uskudar/Istanbul, 06.05.1994

E-Mail : beyza.tpkrn@gmail.com

EDUCATION :

- **B.Sc.** : 2017, Istanbul Commerce University, Faculty of Engineering, Jewellery Engineering
- **M.Sc.** : 2020, Istanbul Technical University, Institute of Science and Technology , Nano Science and Nano Engineering

PROFESSIONAL EXPERIENCE AND REWARDS :

- 2018-2020 Geliştirilen Çevre Dostu Yöntem ile Yeni Nesil Yüksek Performanslı ve Fonksiyonel Polietilen Bazlı Fiberlerin Geliştirilmesi, 1003 TÜBİTAK (Project Resarcher)
- 2017 Undergraduate Graduation with the Honor of Faculty 3rd Degree
- 2017 Undergraduate Graduation with the Honor of Department 1st Degree

PUBLICATIONS, PRESENTATIONS AND PATENTS ON THE THESIS :

- **Gunaydin, B.N., Seyhan, A., Polat., Y., Kilic, A., Demir, A., Avci, H., 2020:**” Improving flame retardancy of PE with halogen-free materials”, International Fiber and Polymer Research Symposium, January 24-25, 2020 Bursa, Turkey pp. 79-80.