ANKARA YILDIRIM BEYAZIT UNIVERSITY

GRADUATE SCHOOL OF NATURAL AND APPLIED SCIENCES

DESIGN, PRODUCTION AND FIRE CHARACTERIZATION OF FLAX FIBER REINFORCED SHAPE MEMORY POLYMER COMPOSITES with FLAME RETARDANT PROPERTY

M.Sc. Thesis by

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M.Sc. THESIS EXAMINATION RESULT FORM

We have read the thesis entitled **"DESIGN, PRODUCTION AND FIRE CHARACTERIZATION OF FLAX FIBER REINFORCED SHAPE MEMORY POLYMER COMPOSITES with FLAME RETARDANT PROPERTY"** completed by **BAHADIR AYDAŞ** under the supervision of **Asst. Prof. Dr. MEHEMET FATİH ÖKTEM** and we certify that in our opinion it is fully adequate, in scope and in quality, as a thesis for the degree of Master of Science.

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ABSTRACT

Natural fibre reinforced polymer composites have been widely used instead of synthetic fibre reinforced composite applications in recent years due to their environmentally friendliness, low cost and ease of availability. It is highly preferred especially in the automotive, marine and aviation sectors.. The material used in these areas must be flame retardant as well as having superior mechanical and chemical properties.

In this study, it is aimed to increase the flame retardancy of the shape memory polymer matrix composites produced with natural flax fibre by using polydopamine and titanium dioxide nano powders. Dopamine hydrochloride was polymerized in tris - hydrochloride acid buffer solution and flax fibres were coated with dipping and blending method with polydopamine. 1.5% titanium dioxide was used to increase the flame retardancy of the polymer matrix. The coating and nano powder distribution were characterized by scanning electron microscopy. The fire behaviours of composites were examined by horizontal and vertical burning and limiting oxygen index tests. Thermal analyses were carried out by thermogravimetric method. Both vacuum assisted oven and hot press process were tried for curing and hot press was chosen as feasible application resulting homogenous and fully saturated wet fibre surface.

As a result of this study, the polydopamine coating reduced the flame spread rate by 52%. When titanium dioxide combined with polydopamine was used, the flame spread rate decreased by 74.73%. According to the limiting oxygen index test result, it was observed that the polydopamine coating increased the minimum amount of oxygen required for combustion to 23%, and when using polydopamine together with titanium dioxide to 24%.

Keywords: Natural fibre reinforced polymer composite, polydopamine, flame retardancy, shape memory polymer composite

KETEN ELYAF TAKVİYELİ YANGIN GECİKTİRİCİ ŞEKİL HAFIZALI POLİMER KOMPOZİTLERİN TASARIM, ÜRETİM VE YANGIN KARAKTERİZASYONU

ÖZ

Doğal elyaf takviyeli polimer kompozitler çevre dostu, düşük maliyetli ve kolay elde edilebilir olmasından dolayı son yıllarda sentetik elyaf takviyeli kompozit uygulamalarının yerine yaygın olarak kullanılmaya başlanmıştır. Özellikle otomotiv, denizcilik ve havacılık alanlarında oldukça fazla tercih edilmektedir. Bu alanlarda kullanılan malzemenin üstün mekanik ve kimyasal özeliklerin yanı sıra yangına dayanıklı olması gerekmektedir.

Bu çalışmada doğal keten elyaf kullanılarak üretilen şekil hafızalı polimer matrisli kompozitlerin, polidopamin ve titanyum dioksit nano tozları kullanılarak yangın dayanımının artırılması amaçlanmıştır. Dopamin hidroklorid tris – hidroklorik asit tampon çözeltisinde polimerize edilmiş ve doğal elyaflar daldırma ve karıştırma yöntemi ile polidopamin kaplanmıştır. Polimer matrisin yangın dayanımını artırmak amacıyla %1,5 titanyum dioksit kullanılmıştır. Yapılan kaplama ve nano toz dağılımı taramalı elektron mikroskobu ile karakterize edilmiştir. Kompozitlerin yangın davranışı yatay ve dikey yanma testleri ve sınırlayıcı oksijen index testi ile incelenmiştir. Termal analizler Termogravimetrik analiz yöntemi ile yapılmıştır. Hem vakum destekli fırın, hem de sıcak pres yöntemleri kürleştirme için denenmiş ve sıcak pres yöntemi homojen ve tam doymuş ıslak fiber yüzeylerin elde edilmesi açısından seçilen uygun yöntem olmuştur.

Bu çalışmanın sonucunda polidopamin kaplama alev yayılım hızını % 52 oranında azaltmıştır. Polidopamin ile birlilte titanyum dioksit kullanıldığında alev yayılım hızı %74,73 oranında azalmıştır.Sınırlayıcı oksijen index test sonucuna göre, polidopamin kaplama yanma için gerekli minimum oksijen miktarını %23'e, polidopamin ile birlikte titanium dioksit kullanıldığında %24'e yükselttiği görülmüştür.

Anahtar Kelimeler: Doğal fiber takviyeli polimer kompozit, polidopamin, yangın geciktirici, şekil hafızalı polimer kompozit

CONTENTS

NOMENCLATURE

Abbreviations

C	Carbon
Cl	Chloride
CO	Carbon monoxide
Cu	Copper
Fe	Iron
g	Gram
h	Hour
H	Hydrogen
HCl	Hydrochloric acid
H_2O_2	Hydrogen peroxide
H_2SO_4	Sulfuric acid
$KMnO_4$	Potassium permanganate
M	Molar
mg	Milligram
ml	Milliliter
N	Nitrogen
Na	Sodium
$NaNO_3$	Sodium Nitrate
NaOH	Sodium Hydroxide
Ni	Nickel
nm	Nanometer
O_2	Oxygen
P	Phosphorus
rpm	Round per minute
Si	Silicon
SiO_2	Silicon dioxide
T_{trans}	Transition temperature
Ti	Titanium
TiO_2	Titanium dioxide
wt	Weight

Acronyms

APP	Ammonium polyphosphate
DAP	Diammonium phosphate
DTG	Differential thermogravimetric analysis
EDS	Energy dispersive spectroscope
GO	Graphene oxide
LOI	Limiting oxygen index
PDA	Polydopamine
PU	Polyurethane
SEM	Scanning electron microscopy
SMA	Shape memory alloy
SMC	Shape memory ceramic
SMM	Shape memory material
SMP	Shape memory polymer
TGA	Thermogravimetric analysis
UL	Underwriters laboratories

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CHAPTER 1

INTRODUCTION

Composite materials have become an indispensable part of many sectors today. This material group, which is used in many areas, continues its development. Today, composite materials have a wide range of applications from healthcare to space and aviation, from automotive to military equipment, and accelerated its development with advancement of technology [1]**.** Expectations from these materials can be short listed as high performance and long expected life in the field where they are used. In this respect, composite materials are superior materials that exploit the properties of each constituent and have quite different manufacturing technologies than the traditional materials**.** To make a general definition, composite is a material composed of two or more components which are combined at macroscopic level. The components of a composite material are distinguishable at the macro level which makes them separable from metal alloys. One of the constituent components is the matrix and the other is the reinforcement. Composite materials are generally formed by placing superior properties of reinforcing material in the matrix material, which alone will exhibit lower properties in the field of application. Here, the fibre placed in the interior is the part that physically supports the load to a great extent, while the matrix absorbs the external effect and transmits it to the fibre and maintains the position of the reinforcing material. While this mechanism works, parts of this material system exhibit superior performance while retaining their physical and chemical properties [2]. Some features of composites include high strength, light weight, design flexibility, corrosion resistance, easy workability and so on [3]**.**

The use of composite materials in a wide variety of fields enables easier identification of the properties that need to be developed. The properties that need to be improved during the lifecycle and post-processing disposal are obvious. The development of these materials should be need-based and sufficient. From this point of view, the orientation towards environmentally friendly materials increased without any disruption in the usage process. Composites produced by combining organic and

environmentally friendly materials are a great advantage for the environment and human health both in terms of usage process and after-use disposal processes. [4] **,** [5]**.** Referring to the ongoing studies in this direction, it can be seen that natural fibres are one of the important reinforcing materials in composite materials. The use of natural fibre reinforcement material has increased considerably especially in polymer matrix composites. This minimizes environmental damage both during and after use. [6]**.**

Polymers and polymeric composites can exploit many advantages when using natural fibres. The main reasons for widespread use of polymers are low cost, light weight, easy to form, specific stiffness, strength and, excellent resistance to corrosion. [7]**,** [8]**.** In addition to these advantages, polymers have a disadvantage such as easy flammability [9]**.** Generally, these hydrocarbon-based materials are indispensable components of composite materials despite their low fire resistance. For this reason, many studies have been made to increase the fire resistance of polymer materials [10]**.** While increasing the combustion resistance of composite materials with polymer matrix, harm to the environment and human health should not be ignored. Halogen-based substances have been used extensively in previous studies as fire retardants and successful results have been obtained, but the combustion gases of these materials are highly toxic and very harmful to the environment. In addition, considering that polymer matrix composites are used in a wide range of applications in daily life, the harm that such materials can cause to human and environment, even if they do not burn quickly, should be taken into consideration. In order to avoid this situation, the fibre, matrix and flame retardant additives of the composite material produced must be biocompatible, biodegradable and nontoxic. [11]**.**

In this respect, it is aimed to produce environmentally friendly, non-toxic, degradable in nature, fire resistant composite material which does not harm human health in daily use. The production of natural composites with shape memory polymer matrix by coating polydopamine to flax fibre is not available in the literature. In addition, the flame retardant property of the flax fibre is supported by the addition of TiO_2 to the matrix material. In this study, Scanning Electron Microscopy (SEM) to investigate surface morphology, Thermogravimetric Analysis (TGA) for examination of thermal properties, Limiting Oxygen Index (LOI) and vertical and horizontal fire tests were used to investigate flame retardant properties. The main purpose of this study is to

contribute to the literature by producing composite material containing natural fibres and additives with improved flame retardant properties by hot press production method.

CHAPTER 2

LITERATURE REVIEW

2.1 Flame Retardancy

Combustion is a multi-step event involving chemical and physical processes [12]**.** Flammable materials must pass through the ignition phase before burning and emitting heat, and this phase is the critical phase required to spread the fire. However, to start the ignition, there must be a gas release from the combustible material. The occurrence of flammable gases by chemical decomposition due to the heat of the flammable material is called pyrolysis [13].When the polymer materials are exposed to a sufficiently high temperature, the covalent bonds break with this external energy and pyrolysis starts. With this starting phase, flammable gases are released, and the spread of flammable gases continues until combustion begins. Combustion occurs based on the amount of oxygen in the environment, the temperature reached and the type of flammable gases [14]**.** Depending on these parameters, the amount of heat generated due to partial or complete combustion varies and results in a change in pyrolysis rate. The reason for the change in pyrolysis ratio due to the type of combustion is that the heat generated during the combustion increases the amount of pyrolysis by contributing to the leading heat source [15]**.** Components that are necessary for fire are shown in figure 2.1 named as fire triangle.

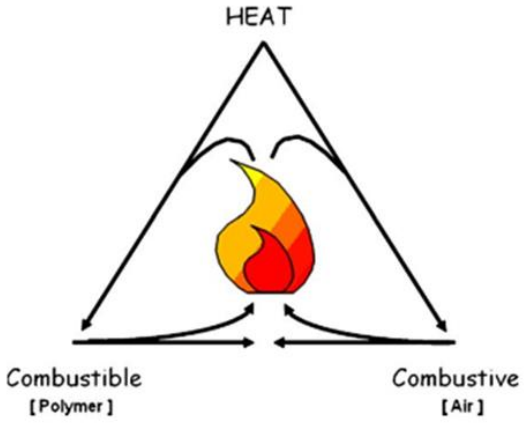

Figure 2.1 Fire Triangle [16]**.**

Although the most important factor in the degradation of the bonds in the polymers is the heat, the degradation also depends on various factors. These factors are mainly macromolecular structure, environmental conditions, and additive materials. In macromolecular structure, functional groups, molecular weight, branching and amorphous amount of structure affect the degradation process. In addition, the amount of moisture in the environment also affects decomposition [17]**.**

The first step of the combustion process of polymers is pyrolysis and second step is ignition. With increasing the temperature polymer chains start scission. Scission of polymer chains causes gas emission to the environment. The ignition of the polymers takes place when the flammable gas density attains the needed minimum flammability grade by thermal degradation of the macromolecules. This may be by outer or auto-ignition, and the combustion continues as the temperature is above the gas phase ignition temperature [18]**.**

After pyrolysis and ignition, combustion process proceed with flame spreading by way of other polymer bonds scission and gassing through flameout by internal or external effects [19]. The mechanism belonging to the fire process is shown in Figures 2.2. and 2.3.

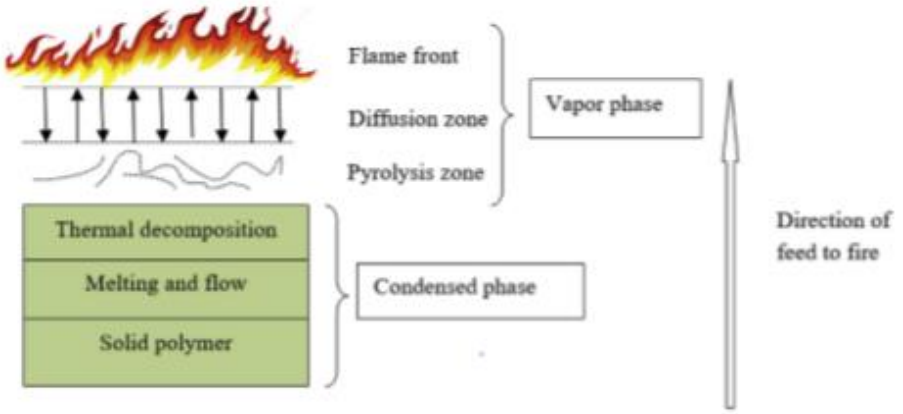

Figure 2.2. Fire Mechanism [19] **.**

In general, heat, fuel and O_2 are required for combustion to take place. Burning continues until these components are exhausted. Any effect on the material can be described as flame retardant in order to slow down or delay the burning of materials and reduce the risk of fire against these components required for combustion. The main purpose of flame retardant systems is to delay ignition in polymeric materials, slow down or stop flame propagation speed and pyrolysis. Systems that function on polymer materials in this way are called flame retardant systems [20].

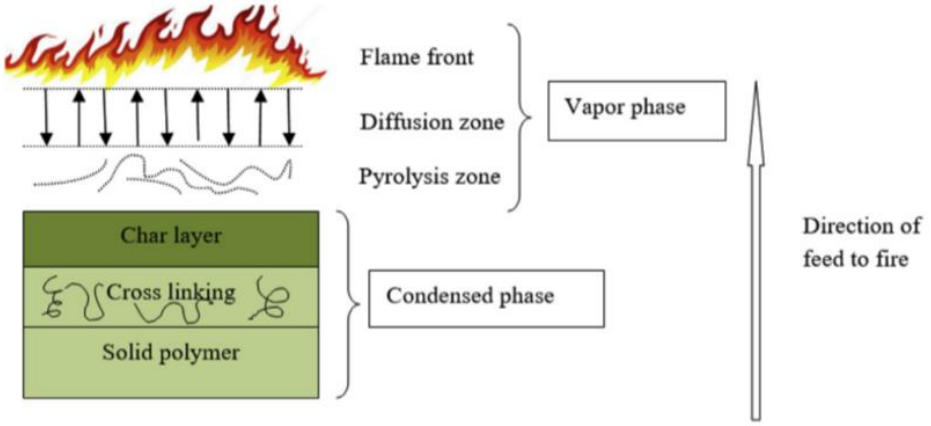

Figure 2.3 Fire Mechanism with char layer [19].

2.1.1 Flame Retardant Additives

With the development of technology, materials with new versatilities and higher performances are needed to improve the material for an intended application. From this point of view, a feature of polymer composite materials that needs to be developed is their low fire resistance. Many studies have been conducted in order to improve the flame retardant properties of polymer composites. The main purpose in these studies is to increase the fire resistance of these materials, thus creating new materials operating in higher temperatures. Recyclable and environmentally friendly composites are the primary goal of many studies. Therefore, additives that do not harm human health must be used in flame retardant systems [21] [22] .

Creating a flame retardant effect by using flame retardant additives is one of the methods used in production and design of the flame retardant polymer composite materials. It produces effective results by adding nano or micro powders to the composite system from outside or by covering the fibre with these flame retardant additives [23].

In this study author studied with biocompatible flame retardant additives to produce flame resistant flax fibre SMP matrix composite. These additives are named as dopamine hydrochloride and TiO_2.

Besides that, we can classify flame retardant additives primarily in six groups and each group has different ways to increase flammability time or reducing of fire spreading rate. These flame retardants are mineral flame retardants, halogenated flame retardants, P-based, N-based, Si-based flame retardants and nanometric particles. Mineral-based flame retardant additives have advantages like endothermically decomposition and high temperature action. Halogenated flame retardants effect according to the types of halogen in additive materials. P-based flame retardants are used in polymer synthesis stage and this group has many types of P such as phosphates, phosphonates, phosphinates, red P and phosphine oxides. N and Si-based flame retardant additives effect the resistance of fire correlatively with their chemical component due to thermal resistance variation [16].

2.1.1.1 Dopamine Hydrochloride

Nature-friendly materials have increased their importance in recent years with the limitations brought by international regulations. For this reason, components of composite materials made of natural and biocompatible components became uttermost importance. With these developments, the use of halogen-containing materials has decreased and research and studies on non-toxic biological materials have increased [24]. This situation has also accelerated for flame retardant composite materials. The gases produced by flame retardant composites originating from chemical materials during the fire pose a great danger in this respect. Bio molecules such as lignin, plantal materials, and some protein varieties have been examined and studied as flame retardant composite components in the studies conducted in accordance with these regulations and restrictions [25][26] [27]**.**

PDA, which has an important place among these studies, is an insoluble biopolymer. This biomaterial produced by autoxidation of catecholamine neurotransmitter dopamine is used as a multi-purpose coating material in many studies. In addition, it has an important place in flame retardant composite materials with its predisposition to the formation of char layer and its radical scavenging feature. Char layer formation acts as a protective layer during combustion. It prevents the transmission of heat by creating a wall between the heat generated by combustion and the material. It also has a preventive role in the emergence of gases that are fuel to fire by slowing or completely preventing the ongoing pyrolysis process [28] [29].

Dopamine hydrochloride is completely a natural and biocompatible material produced by scientists inspired by a protein contained in mussels. This material is polymerized to obtain PDA. PDA has become popular in coating applications with its good adhesion to various surfaces. In addition, PDA has good fire resistance in addition to the advantages it provides in the coating process. For this reason, PDA coating process is highly preferred in the production of composites that are natural, environmentally friendly and harmless to human health [30].

In the literature, many studies can be seen exploiting these emerging advantages. Especially with PDA being a biocompatible material, the possibility of toxic gas

emission during the fire is eliminated. Ellison et al. [31] coated the flexible PU foam PDA by dipping method and examined the fire resistance and the amount of heat release. In the absence of a flame retardant additive, the PU foam that melts completely in the torch test retains the surface and shape integrity by delaying pyrolysis with PDA coating as shown in Figure 2.4. In addition, the results of the cone calorimetry tests indicated that the heat release rate of the PDA coated sample decreased to about 67%. It was revealed in this study that the catechols in dopamine have a strong radical scavenging effect and help the formation of char layer, contributing to the flame retardant behaviour of PU.

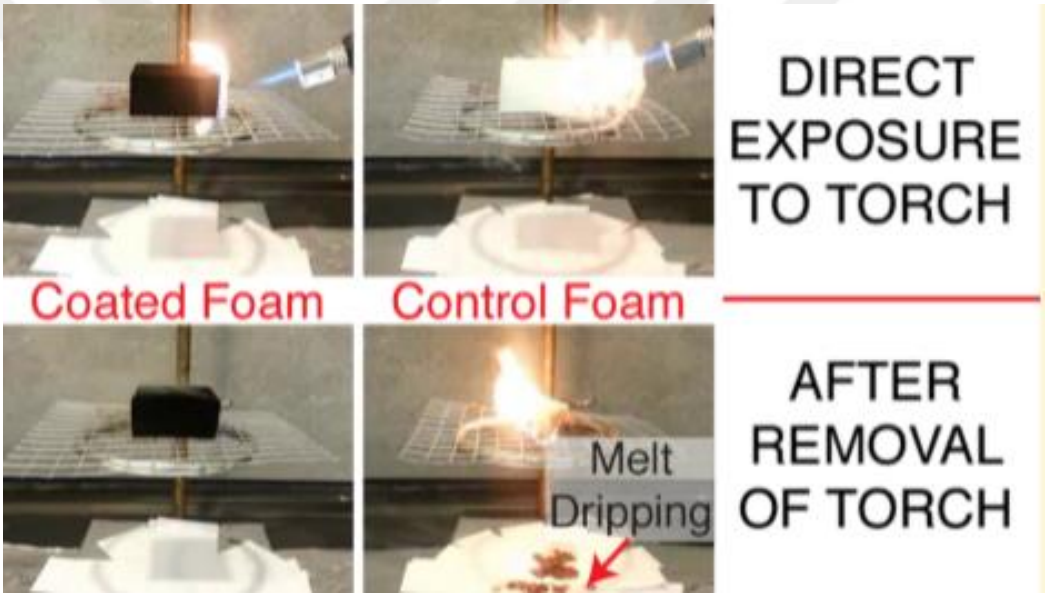

Figure 2.4 Fire behaviours of PDA coated and un-coated polyurethane based foams [31].

In another study, Wu et al. [32] produced 60 micron graphene / PDA composite film and single GO film and compared the results by carrying out thermal conductivity, fire resistance and micro combustion calorimeter test. As a result of this study, the GO film showed lower thermal conductivity in the in-plane direction. In the micro combustion test, the graphene/PDA composite film did not show any degradation below 500 ^{o}C, and the GO film showed degradation at 165 ^{o}C. Finally, as shown in Figure 2.5, the composite film containing PDA showed superior fire resistance behaviour.

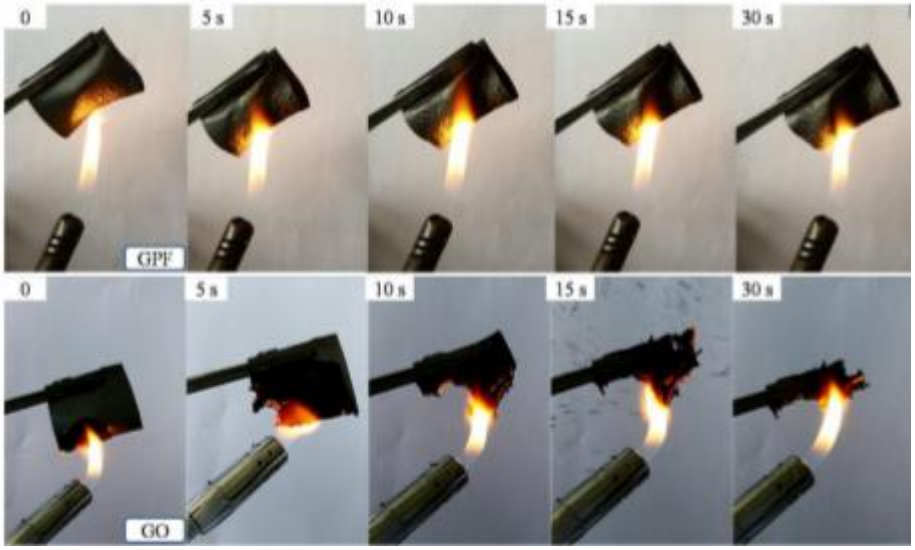

Figure 2.5 Comparison of graphene/PDA composite film and GO film [32].

Mao et al. [33] designed a cellulosic composite material with porous structure and investigated fire behaviour of porous cellulosic sponges in another study. While the burning rate was measured as 10.3 mm/s in the reference sample, this value was measured as 0 mm/s in the PDA doped sample. In addition, PDA-containing sample LOI value was 29.5% and a significant decrease was observed in heat release values.

2.1.1.2 Graphene Oxide

Graphene was produced in 2004 in the form of single and several layered graphene flakes using adhesive tape, produced by the exfoliation of graphite. Graphene is basically a nanoparticle where regular carbon atoms are sp^2 hybridized in a hexagonal structure. It is a single-layer and an atom-thick structure that is the basic building block of all carbon allotropes. Graphene, which has a unique molecular structure with its two-dimensional structure having a single atom thickness and strong bond structure between molecules, has very good electrical, electrochemical, thermal, optical and mechanical properties [34] [35].

The development of graphene with different functional properties and different sizes is especially important in polymer composite studies. Polar groups on the graphene

surface improve compatibility with the polymer surface. The types of graphene obtained by the oxidation method are more suitable for surface formation as it bonds due to functional groups in graphene-based composite production [36]. The structure of graphite and graphene are shown in Figure 2.6.

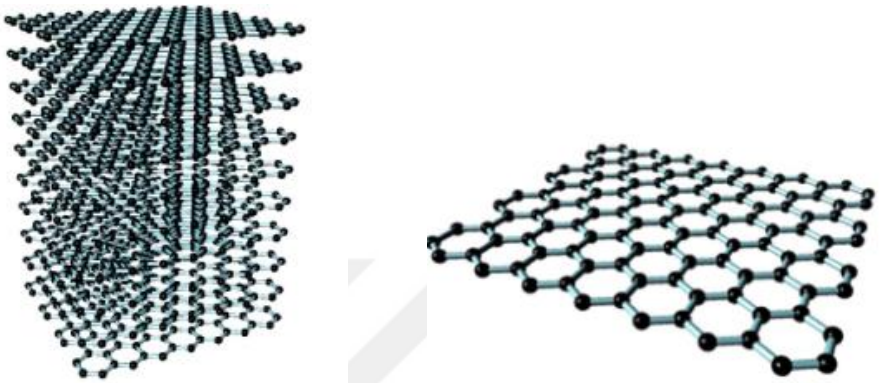

Figure 2.6 Graphite and graphene structure [37].

Thin layers of GO have recently emerged as a new carbon-based nanoscale material, providing an alternative path to graphene.

Unlike graphene, GO is a 2-dimensional material containing O_2 and H atoms in its structure [36]. It is an oxidized form of graphene, with functional O_2 groups located on the Sp^2 plane, and is synthesized by the Brodie, Staundenmaier, Offeman, and Hummers methods. The degree of oxidation in these methods, which is based on the oxidation of graphite with strong acids and oxidants, depends on the type of reaction, the reaction conditions and the properties of the graphite [38].

All physical properties of GO and graphene can be changed by removing functional groups from the surface. GO, which contains functional O groups, is hydrophilic and soluble in water, but graphene is hydrophobic and insoluble in water. The most widely known and used GO production method today is the Modified Hummer's Method [39]. GO structure can be seen in Figure 2.7.

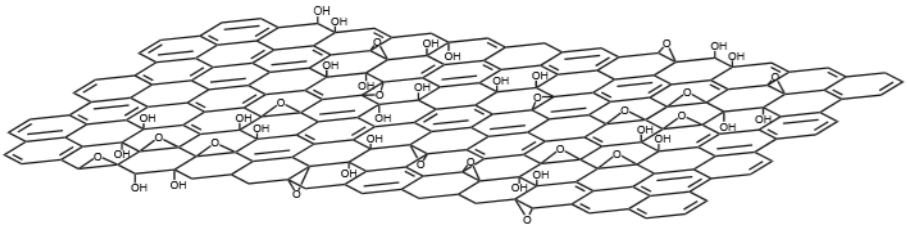

Figure 2.7 GO structure [36].

In the Modified Hummer's Method, powdered graphite pieces are put into the beaker inside the ice bath. Then $NaNO_3$ and high concentration H_2SO_4 are added and mixed. $KMnO_4$, a strong oxidizing agent, is added to the mixed solution after the mixture temperature is below 50 ^oC after one hour and mixed for 2 hours. When the temperature is fixed to 40 ^oC, deionised water is added, and mixing is continued. At the last stage, H_2O_2 is added to the mixture, and it is observed that the graphite particles in the mixture change colour from black to brown. GO material is obtained in the consistency of mud. After mixing, the GO sludge is obtained until the pH becomes neutral and is washed with deionised water and centrifuged. Depending on the type of solvent desired to be used, the same process can be repeated, and the exchange of solvent is performed to dissolve the GO in the desired solvent. It is possible to produce faster and greater amount of graphene than other methods with chemical reduction reactions of GO produced by Modified Hummer's Method. The primary reason for using this method frequently is that its cost is much lower than other methods. Substances used in production are dangerous and toxic gases are released during production. The resulting GO sludge is very acidic and must be studied carefully throughout production. [40] [41].

2.1.1.3 Titanium Dioxide

TiO_2 has three different polymorphic structures; anatase, rutile and brookite. Anatase and rutile have tetragonal microstructures and brookite has orthorhombic microstructures. As can be seen in the Figure 2.8, all three TiO_2 structures are composed of TiO_6 octahedral chains where each Ti^{4+} ion is surrounded by six O^{2-} ions.

Brookite is a structure mostly found only in minerals. Anatase and rutile structures are generally used as photocatalysts. Ti-O bond lengths are shorter than rutile and Ti-Ti bond lengths in anatase are longer than rutile. The bond structures of two molecules are different because of these variations [42] [43] [44].

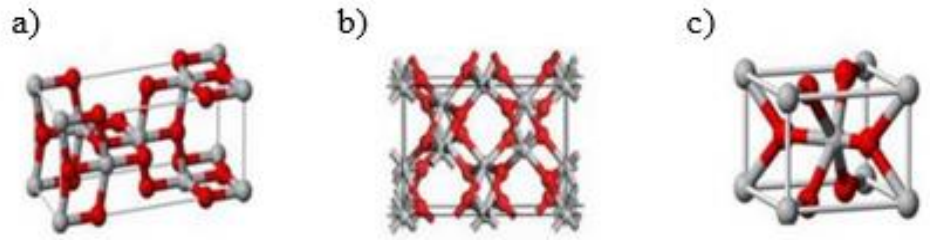

Figure 2.8 TiO_2 semiconductor crystal forms a) anatase b) brookite c) rutile [45].

TiO_2 is widely used in many areas due to its physical and chemical properties and new application areas are being investigated. It is used in the removal of resistant organic materials in wastewater due to its photocatalytic activity, and in the production of energy in solar panels due to its photovoltaic feature. Due to its electronic properties, it is also used in energy storage devices such as in lithium batteries and supercapacitors, sensors, transparent conductive film production, and biomedical devices [46]. Since TiO_2, which is used in paint and coating materials, plays a role of photocatalyst in the decomposition of organic pollutants adhering to the surfaces, it has been widely used in the field of architecture. The photocatalytic cleaning feature of TiO_2 is also used in the fabric industry, which does not hold dirt and prevents the production of bacteria. In addition, various researches have been conducted on the use of TiO_2 in dental implants and drug delivery [47] [48].

In addition to all these features, TiO_2 nanoparticles have excellent thermal stability. In the recent years, studies on the use of these nanoparticles with polymer materials have increased. Polymers, due to their structure, emit high heat and toxic gases through dense smoke production. This creates high fire risks. For this reason, efforts to improve fire retardant properties of polymer matrix composites have gained acceleration. Although halogen-containing flame retardant additives have a positive effect on fire

resistance, their use as flame retardant brings harm for human health and environment. Therefore, halogen-free flame retardants are becoming increasingly important [49].

The flame retardant effect of TiO_2 nanoparticles used in polymer materials is as follows; TiO_2 nanoparticles dispersed in the polymer matrix form the surface layer that comes into contact with the flame as the polymer matrix melts during combustion. This layer, which has high thermal stability, combines with the char layer formed by the polymer material during combustion. Thanks to this combination, a stronger thermal insulating wall is formed. Thus, as the heat transfer travels less into the inner parts of the material, a barrier is formed between the flammable gases that may be caused by the pyrolysis of the polymer with the flame [50].

Li et al. [51] in their study, examined flame retardant properties by adding two types of TiO_2 nanoparticles, rutile-type and anatase-type, to the silicone acrylate coating. In the study, the char layer formed by TiO_2 nanoparticle varieties was examined with SEM and is as shown in Figure 2.9. As can be seen in the images, honeycomb char layer is formed in rutile-type TiO_2 add-on material. This layer prevents heat transfer to the lower part and protects it from fire. However, this honeycomb char layer was not clearly seen in the anatase-type TiO_2 additive structure.

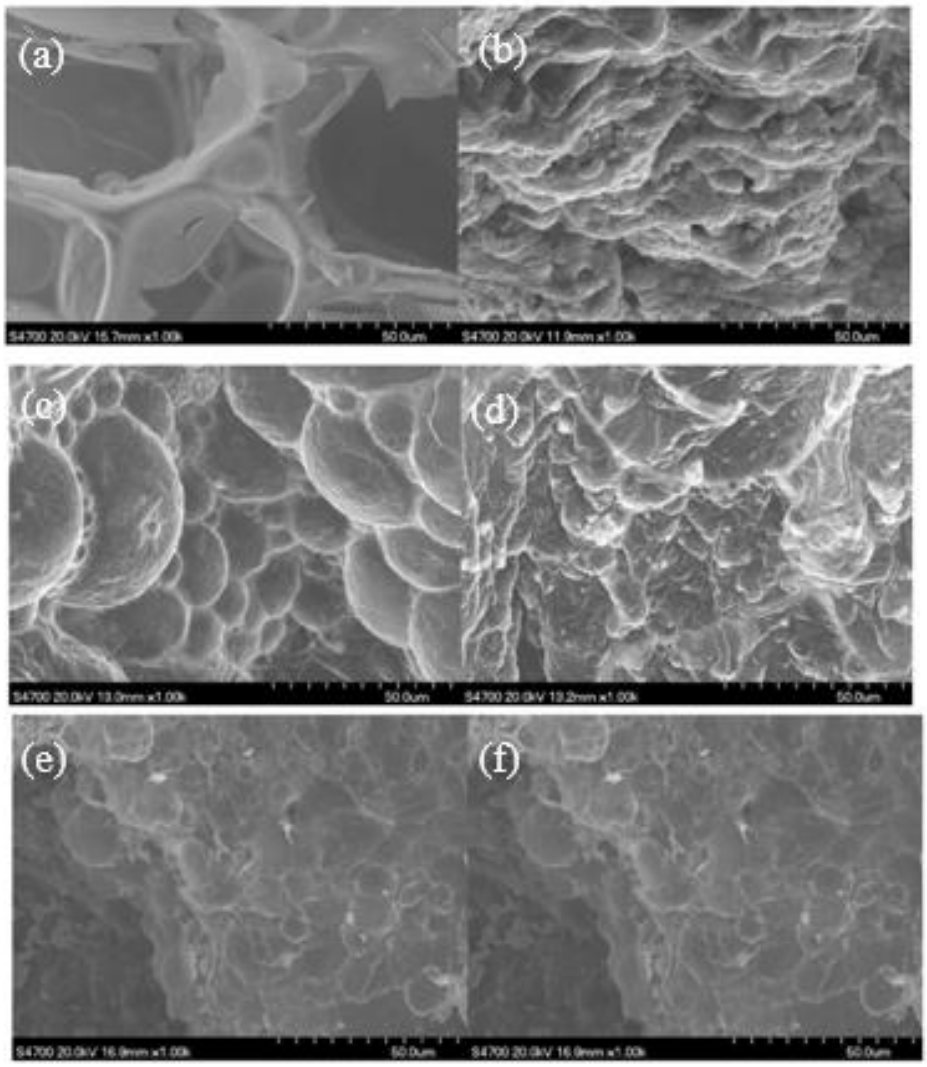

Figure 2.9 SEM images of before and after burned TiO_2 coated materials. a) Reference sample before burning, b) Reference sample after burning, c) Rutile-type TiO_2 coated material before burning, d) Rutile-type TiO_2 coated material after burning, e) Anatase-type TiO_2 coated material before burning, f) Anatase-type TiO_2 coated material after burning [51].

In another study, Chen et al. [52] aimed to improve the flame retardant properties of thermoplastic PU, which has a wide range of applications. By using Masterbatch melt blending technique, homogeneous distribution of TiO_2 particles in the polymer was achieved.

In addition, ammonium polyphosphate, an effective natural flame retardant, was used in the study. As a result of combustion experiments, with the formation of nano-sized Ti-O-Ti network, an effective char layer has been formed and heat and smoke emissions have decreased. In this study, TiO_2 particles showed a supportive effect to char layer that formed by thermoplastic PU and APP.

Mahr et al. [53] produced TiO_2 and SiO_2 inorganic wood composites by using sol-gel method and examined their flame retardant behaviour. In their studies, cone calorimeter and O_2 index tests were carried out. According to the results, CO and other toxic gas emissions decreased due to the protective layer formed during combustion. In addition, the flame spread rates have decreased. Considering the O_2 index test results, the flame retardancy of the composite structure containing TiO_2 is higher than that of the composite structure containing SiO_2.

Costa et al. [54] investigated the flame retardant effects by covering bio macromolecules on natural fibres. In addition to whey protein and casein nano-TiO_2 was used in the study. The aim here was to examine the synergistic relationship between biomacromolecules and nano-TiO_2 in terms of fire resistance. Due to the increasing interest in natural fibres, one of their weaknesses, the flame retardancy feature is aimed to be developed by using environmentally friendly components. According to the results of the study, nano-TiO_2 powders helped to maintain the stabilization of biomacromolecules on the fabric during combustion as a specific binder. In this way, flame retardancy increased and flame spread rate decreased on the used natural fibres as can be seen in Figure 2.10.

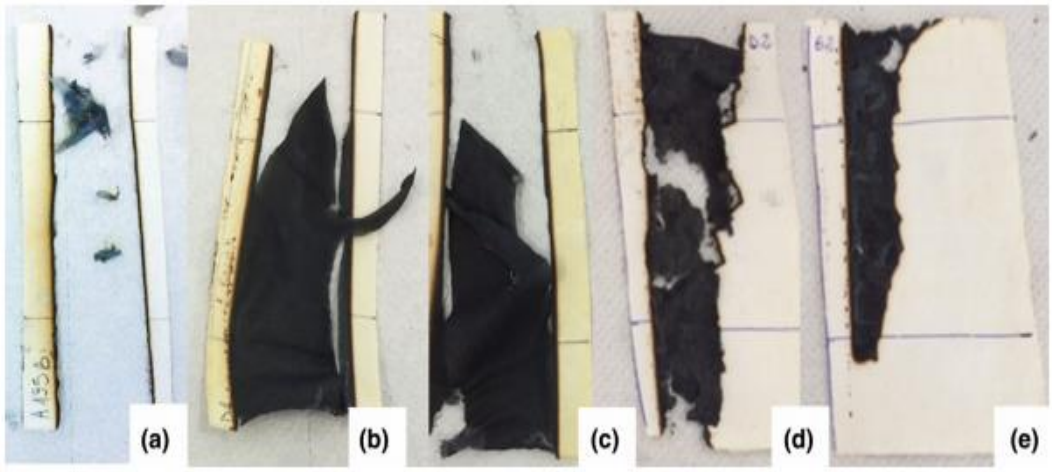

Figure 2.10 Flammability test results of cottons, **a)** untreated cotton, **b)** casein+whey protein treated cotton (4 layers), **c)** casein + whey protein treated cotton (8 layers), **d)** casein + whey protein + TiO_2 treated cotton (4 layers), **e)** casein + whey protein + TiO_2 treated cotton (8 layers) [54] .

2.2 Natural Fibres

Natural fibres have attracted the attention of scientists and researchers in recent years due to having novel properties than fibres created with traditional reinforcement materials. In the past few years, much research has been done on the development of natural fibre composite materials. Natural fibres are originated from vegetable and animal fibres according to the sources from which they are obtained. It is usually necessary to undergo some pre-treatments such as cleaning, sorting, chemical modification, etc. after it is obtained. These types of fibres have usage areas in textile industry such as yarn making and woven fabric. In infrastructure studies, it is used as a reinforcing phase in concretes and composite materials in order to provide sound insulation. Since natural fibres are obtained from animal and plant sources, they are renewable, and their most important advantage is they are environmentally friendly. Natural fibres are low-density, high specificity and low cost fibres. Unlike other reinforcing fibres, they are biodegradable and non-corrosive. It is possible to use natural fibres as reinforcing materials for industrial applications. Natural fibres that are widely used worldwide can be listed as: jute, flax, hemp, corn, cotton, ramie, sisal, pineapple, bamboo, etc. [55] .

Although natural fibres are widely used in military and civil applications, they have some drawbacks as well. They can easily ignite, and the flame can spread rapidly on the fibre. This phenomenon restricts the usage area of natural fibres, which is subject to be improved. The average thermal decomposition temperature of cellulose structures in the air environment is between 300 °C to 400 °C. Studies are aimed to increase the decomposition temperature and to decrease the rate of flame propagation. Advantages and disadvantages of natural fibre composites are summarized in the table 2.1 [56] .

Table 2.1 Advantages and disadvantages of natural fibre composites [55] .

Advantages	Disadvantages
High specific stiffness, strength, and low density	Lower durability than synthetic fibre composites
A renewable resource that requires little energy in its production	High moisture absorption
Low cost and hazards in manufacturing processes	Lower thermal durability than synthetic fibre composites
Low emission of toxic fumes when subjected to heat and during incineration at end of life	Limiting matrix options
Less abrasive damage to processing equipment compared with that of synthetic fibre composites	High flame propagation rate

2.3 Polymer Matrix Composites

Polymers have become an indispensable part of our daily life in many areas. Easy processing and low cost of these materials are among their most important advantages. For this reason, research on polymer material know-how goes on with high pace. One of the emerging areas in the polymer matrix composite research is to develop composite with high flame retardant capability. In addition, the development of

biocompatible materials has accelerated thanks to the advancements in polymer science. The proposed research aims to develop a composite material with improved flame resistance that does not have any harmful constituent to human health. From this perspective, it is necessary to use a biocompatible polymer matrix [19].

With the improvements in polymer science, important steps have been taken regarding the development of smart polymers. An important member of this class of materials known as SMMs are SMPs.

In this study, SMP, which has many applications from the health to the aerospace industries, will be used as the matrix material of the composite material. The SMP that will be used is a PU based biocompatible polymer.

2.3.1 Shape Memory Polymer

SMMs are the material types that can change their original shape with right stimulus, and they can recover their permanent shape when the stimulus is not active. Types of stimulus can be temperature, water, light, or magnetic field. This ability is called as the Shape memory effect. Shape memory effect shows itself in three ways; the material should be able to return to its original shape when the right stimulus is applied after the shape change, the material should be able to retain its mechanical properties when it returns to its original shape and the material should be able to follow the sequence of shape change when the shape changing stimulus is applied but the number of following the sequence of shape change is limited. SMMs are mainly classified as SMAs, SMPs and SMCs as shown in the Figure 2.11. Three types of SMAs have been developed based on their main alloying element and their usage areas can vary from aerospace to medical applications. These alloys are classified as Ni – Tİ based (Nitinol), Cu – based and Fe – based materials. Nitinol SMAs are the most used and studied amongst the SMAs because of their biocompatibility and high performance properties. Especially biocompatibility of nitinol allows these materials to be exploited in biomedical applications as invasive surgery materials and stents. Good machinability and low cost make the Cu – based alloys attractive in shape memory applications. Compared to nitinol and Cu – based alloys, Fe – based alloys are much

weaker and are generally used for one – time – processes due to their relatively lower cost. Generally SMAs have progressed in the field of thermo – responsive applications [57].

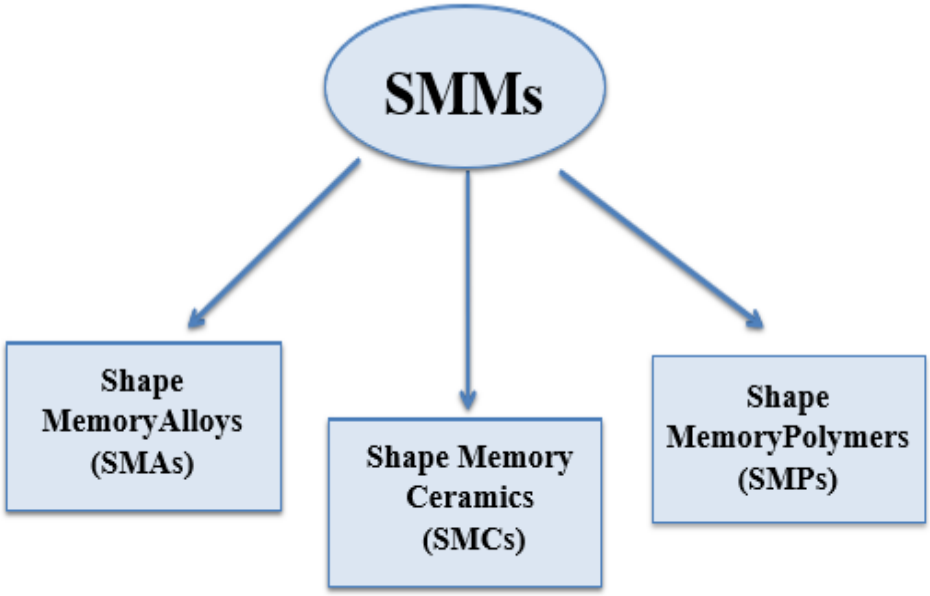

Figure 2.11 Types of Shape Memory Materials.

Polymer materials have many advantages such as being lightweight, elastic, durable, high corrosion resistant, biocompatible, and electrical resistivity, therefore they are first choice in great number of applications. This material group has a crucial polymer type called as SMP. SMPs are the polymer groups that can change their permanent shape with right stimulus to temporary shape which is determined before. They are also emerging materials that can be fabricated into complicated shapes. SMPs have the ability to keep memory of their permanent shape even after long time deformation [58]. While the permanent shape is obtained during production process, temporary shape is determined with a process called as programming. After production and programming steps, SMPs just need essential stimulus to transform. Shape memory property is not an inherent property in polymers; for this reason, SMPs need essential stimulant. Shape memory property consist of morphology and particular production process combination [2]. As shown in the Figure 2.12 shape memory phenomenon

occur with martensitic transformation in SMAs, instead a dual-segment system; cross-links and switching segments create shape memory mechanism in SMPs. While cross-links determine permanent shape, switching segments and transition temperature fix temporary shape [59].

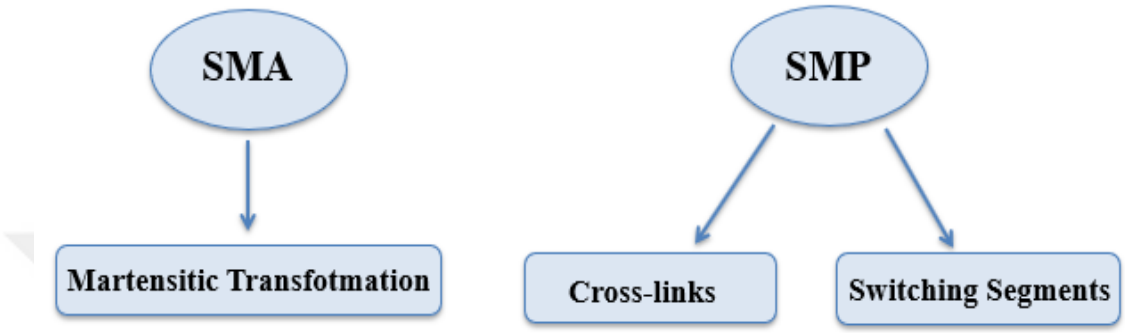

Figure 2.12 Shape memory phenomenon occurring types according to material classification.

SMPs have several advantages compared to SMAs such as; good shape recoverability, easy processing, programmability, low density, controllability of recovery behaviour, low cost and tailoring of many properties. SMPs are generally triggered thermally however if SMP contain proper active fillers it can be stimulated electrically, magnetically or electromagnetically as well [60].

We can list the thermomechanical cycle of thermo-responsive SMPs with following steps as shown in the Figure 2.13, being the first step of manufacturing of the SMP into original shape without any deformation. Next step is heating the SMP above the T_{trans} and deformation of the SMP by using an external force, then cooling below T_{trans} to eliminate constraint and obtain temporary pre-deformed shape. When required, heating of the pre-deformed SMP above T_{trans}, one can witness the recovery of the SMP towards its first shape [59].

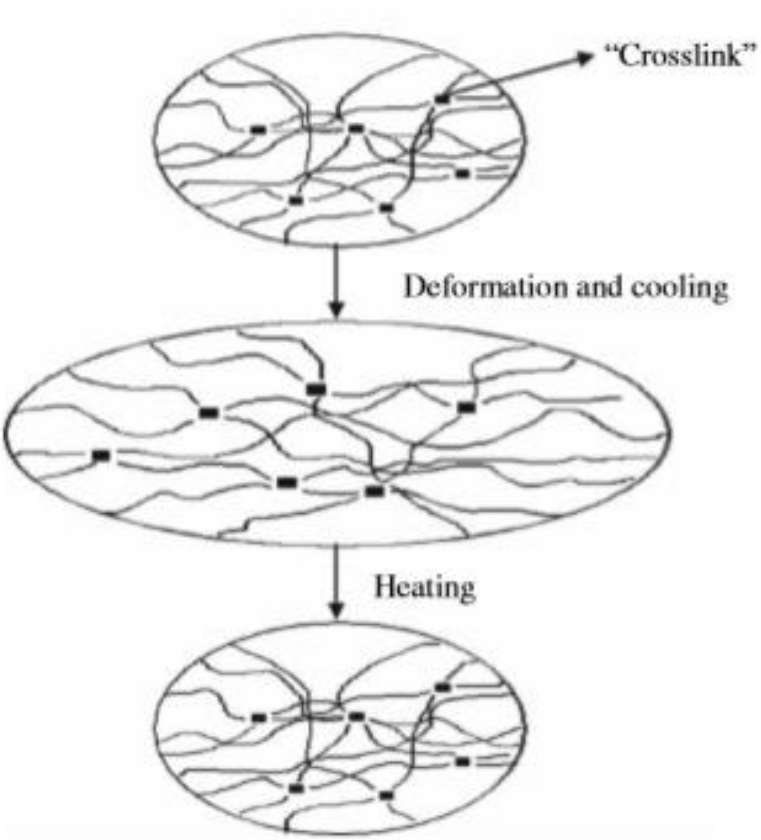

Figure 2.13 Mechanism of Shape Memory Effect of SMPs [59].

Several properties of SMPs can change during shape change such as mechanical, surface, optical, shape and permeability by keeping them in memory. These changes can be achieved by environmental influences such as temperature, electric field, light, magnetic field, chemical solution, and ion. Because of these properties, shape memory polymers have a widespread application area such as biomedical devices, space vehicles, textile, energy, electronic engineering, and civil engineering [61].

The biocompatibility feature is crucial so that any material can be used therapeutically on the human body. From the point of shape memory polymers, polyurethane-based materials draw attention to biocompatibility. Another feature that allows SMPs to be used in medical applications is the ability to adjust the glass transition temperature. Moreover, the polyurethane shape memory polymer material is also advantageous with low thrombogenic effect [62].

CHAPTER 3

EXPERIMENTAL PROCEDURE

The composite samples that were used in this study were produced in Ankara Yıldırım Beyazıt University laboratories. Hot press method was used as composite plate production method. During the characterization stages, SEM examination, thermal analysis and UL-94 burning tests were performed in Ankara Yıldırım Beyazıt University laboratories. LOI test, which is another burning characterization test, was performed in Ankara Gazi University laboratory.

In this study, natural fibres treated with diammonium phosphate after cleaning process, were coated with PDA to form a polymer matrix composite. Then, the change in the decomposition temperature and minimum O_2 content required for combustion, burning behaviour, and the surface morphology after coating of the composite material were examined.

3.1 Preparation of Samples

3.1.1 Chemical Cleaning and Alkaline Treatment

Flax fibre was used as natural fibre in the flame retardant composite material produced in the study. Fibres were cleaned to improve the quality of the PDA coating. This process also removes impurities between the fibre and the matrix by cleaning the fibre surface. In order to carry out this process, the fibres were kept in deionized water for 30 minutes. The fibres that were left to dry for 24 hours at room temperature were then kept in a deionized water-NaOH solution in a 5:1 ratio for 4 hours. After these processes applied to all fibre samples, the fibres were left to dry at room temperature again.

Another application in the study is that the fibres are treated with DAP. At this stage, 10% deionized water-DAP solution was used. In this process applied at room

temperature, the fibres were kept in solution for 10 minutes and dried at room temperature for 24 hours. Treated flax fibres can be seen in Figure 3.1.

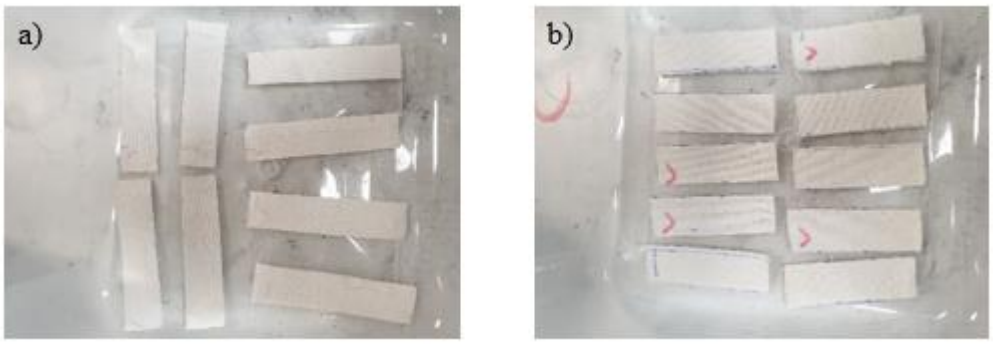

Figure 3.1 Treated flax fibres with DAP a) for UL-94, b) for LOI.

3.1.2 PDA Coating

PDA was obtained by polymerizing of dopamine hydrochloride (Sigma Aldrich) to coat the fibres. For the polymerization process, tris-HCl buffer solution as shown in the Figure 3.2 (pH 8.5) was used. For preparing the 1 M 500 ml tris-HCl buffer solution, 420 ml deionized water was first placed in the beaker. Then 60.56 g of tris hydroxymethyl aminomethane were added to the water and mixed with a magnetic stirrer until a transparent appearance was achieved. Then HCl was added to balance pH to 8.5. Stirring was continued until pH stabilization was achieved. 20 ml deionized water was added to complete the solution by 500 ml. Finally, the pH was measured again, and the mixing process was terminated.

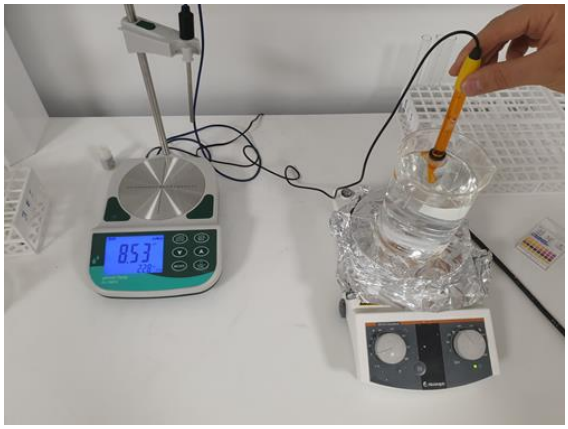

Figure 3.2 Tris- HCl buffer solution pH measurement.

Coating was carried out with PDA tris-HCl buffer solution containing 2 mg/ml PDA. Then, the cleaned fibres were immersed inside the solution and the mixing process was continued for 24 hours. PDA solution became getting dark colour during coating process and these steps can be seen in the Figure 3.3. The masses of the PDA coated fibres were measured before and after the process. Masses of the samples are shown at Table 3.1. After the, coating processes were completed, fibres were washed with deionized water and removed from non-adherent substances on the surface. Then coated fibres were dried at room temperature (see Figure 3.4).

Table 3.1 Masses of the samples before and after PDA coating.

Sample Types	UL-94 SMP Matrix Samples	UL-94 SMP+TiO_2 Matrix Samples	LOI SMP Matrix Samples	LOI SMP+TiO_2 Matrix Samples
Mass Before Coating	6.46 g	6.31 g	6.36 g	5.84 g
Mass After Coating	6.27 g	6.42 g	5.28 g	5.65 g

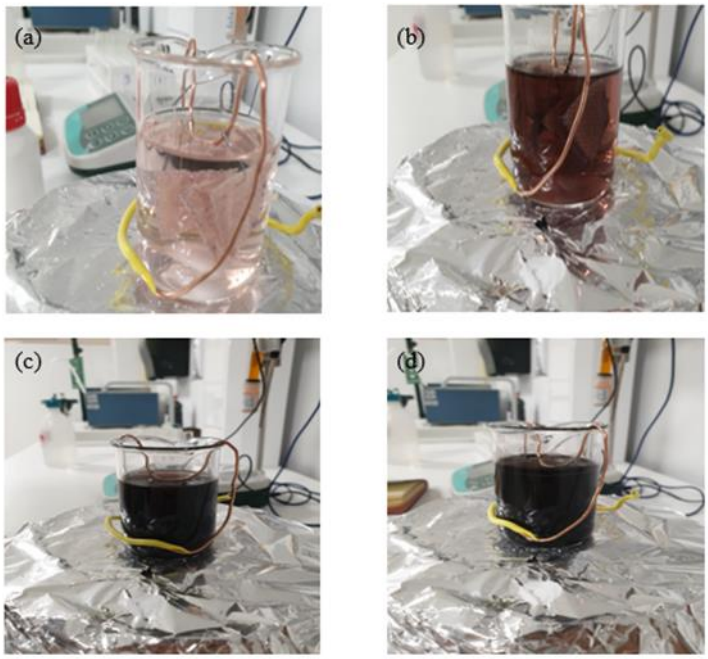

Figure 3.3 PDA – Tris-HCl buffer solution after a) 30 seconds, b) 15 minutes, c) 3 hours, d) 24 hours.

Figure 3.4 PDA coated flax fibres.

3.1.3 Composite Plate Production by Hot Press Method

The composite plates were produced in the next step from the natural fibres that were cleaned, and PDA coated. In this process, hot plates are employed for curing of the polymer and pressure is also applied. SMP MP 3510 (SMP Technologies Inc., JAPAN) was applied to the fibres homogeneously on each layer with a brush before pressing. SMP MP 3510 properties shown in Table 3.2. Then, curing was carried out under 0.4 tons pressure and at 70 ^{o}C for 4 hours. Hot press process machine (MSE Technology LPM4SH20) can be seen in Figure 3.5.

Figure 3.5 Hot Press machine.

SMP MP 3510 was used as matrix material for reference and PDA coated samples, and TiO_2 (Nanografi Nano Technology, Rutile Type, 45 nm) added SMP was used for PDA coated flame retardant composite plates. The components of pure SMP were mixed with the Speed-Mixer dual asymmetric centrifuge device at 3000 rpm for 2 minutes and applied to the fibres. 1.5% TiO_2 was added to the SMP, and the nano

powders were dispersed with ultrasonic probe (Ultrasonics, Ultrasonic Processor) for 30 minutes.

Table 3.2 Properties of SMP MP 3510 in glass region [63].

Item	Unit	SMP MS 3520 Properties
Hardness	Shore D	78
Tensile strength	MPa	53
Elongation	%	10-30
Bending modulus	MPa	1550
Bending strength	MPa	63
Specific gravity		1.20
Glass transition temperature	^{o}C	35

Figure 3.6 Speed Mixer dual asymmetric centrifuge device.

Then, hardener was added to the mixture and it was mixed for 2 minutes at 3000 rpm and applied to the fibres. Speed Mixer and ultrasonic probe devices can be seen in Figures 3.6 and 3.7.

Figure 3.7 Ultrasonic Probe.

Samples sizes were 130 mm x 13 mm x 2.5 mm for UL-94 tests and 80 mm x 10 mm x 2.5 mm for LOI tests.

3.2 Characterization Methods

3.2.1 Microstructural Analysis

PDA coated surfaces of fibres and TiO_2 reinforced polymer matrix were examined with SEM (Hitachi SU5000, see Figure 3.8). Before the microstructural analysis gold was coated with sputter coater for 20 seconds to fibre sample surfaces and 12 second to polymer surface to increase the conductivity of samples (Leica EM ACE200, see Figure 3.9) In the examination, the surfaces of the reference samples were compared with the PDA coated sample surfaces. In addition, the DAP effect on the fibre surface and the distribution of TiO_2 in the polymer were investigated. Char layers that formed on the surfaces of the samples after combustion were examined.

Figure 3.8 Hitachi SU5000 Scanning Electron Microscope.

Figure 3.9 Sputter coater.

3.2.2 Thermal Characterization

TGA / DTG (Hitachi STA 7300, see Figure 3.10) analysis were performed to observe the decomposition temperature of the samples and the change in their mass with increasing temperature.

Figure 3.10 Hitachi STA 7300 TGA / DTG device.

3.2.3 Fire Characterization

LOI and UL-94 tests were carried out to get information about the fire behaviour of samples. In the LOI test, the minimum amount of O_2 needed to burn the material was investigated. In this test, the amount of O_2 required for combustion of PDA coated samples compared to uncoated samples was examined. LOI test device can be seen in Figure 3.11.

Figure 3.11 LOI test device.

Flame spread behaviours of materials were observed by UL-94 test. In the horizontal UL-94 test, while these behaviours were observed, the flame propagation rate and how far it progressed was examined. In vertical UL-94 test, dripping behaviour of the material during combustion was examined. UL-94 test device was designed by our research team and can be seen in Figure 3.12.

Figure 3.12 UL-94 test device.

CHAPTER 4

RESULTS AND DISCUSSION

4.1 Scanning Electron Microscope Analysis

Flax fibres have been used as fibre in my study, where the author has been working on the design, production and fire characterization of composites with natural fibre reinforced flame retardant. Flax fibre was used as a reinforcing material and PU based SMP was used as a matrix material. After cleaning the fibres used in the production of composite plates, they were immersed in DAP solution and the first flame retardant treatment took place. Dopamine Hydrochloride and TiO_2 served as flame retardant in the polymer matrix composite material. Also DAP is a known flame retardant [64]. PDA was obtained by polymerizing of dopamine hydrochloride in Tris-HCl buffer solution. When the literature studies were taken into consideration, the fibres were immersed in PDA-Tris HCl buffer solution and mixed at room temperature for 24 hours and PDA coated fibres are given in Figure 3.4. Studies in the literature, it was observed that the flame retardant properties of the materials increased significantly with the PDA coating process [31]. In another literature study, TiO_2 slowed the progression of the flame during combustion and created a layer that prevents heat transfer to the next layer [65]. For this reason, 1.5 % TiO_2 was used in the matrix material. In addition, PDA is a completely non-toxic and biocompatible material, creating a flame retardant system that does not pose any harm to the environment [31].

SEM surface images of flax fibres before and after PDA coating are shown in Figure 4.1. Figure 4.1a shows fibres without cleaning and DAP treatment. Figure 4.1b shows the fibres cleaned and exposed to DAP treatment. Figure 4.1 c shows PDA coated fibres. Cleaning and DAP processes have removed unwanted materials such as hemicellulose, lignin and pectin from the surface of the fibre. It has also transformed the fibre surface into a rough form that makes it more conducive to the coating. Thanks to this rough surface, the coating is more efficient than, as well as an increase is made in interfacial bonding between the fibre surface and the polymer matrix in composite formation.

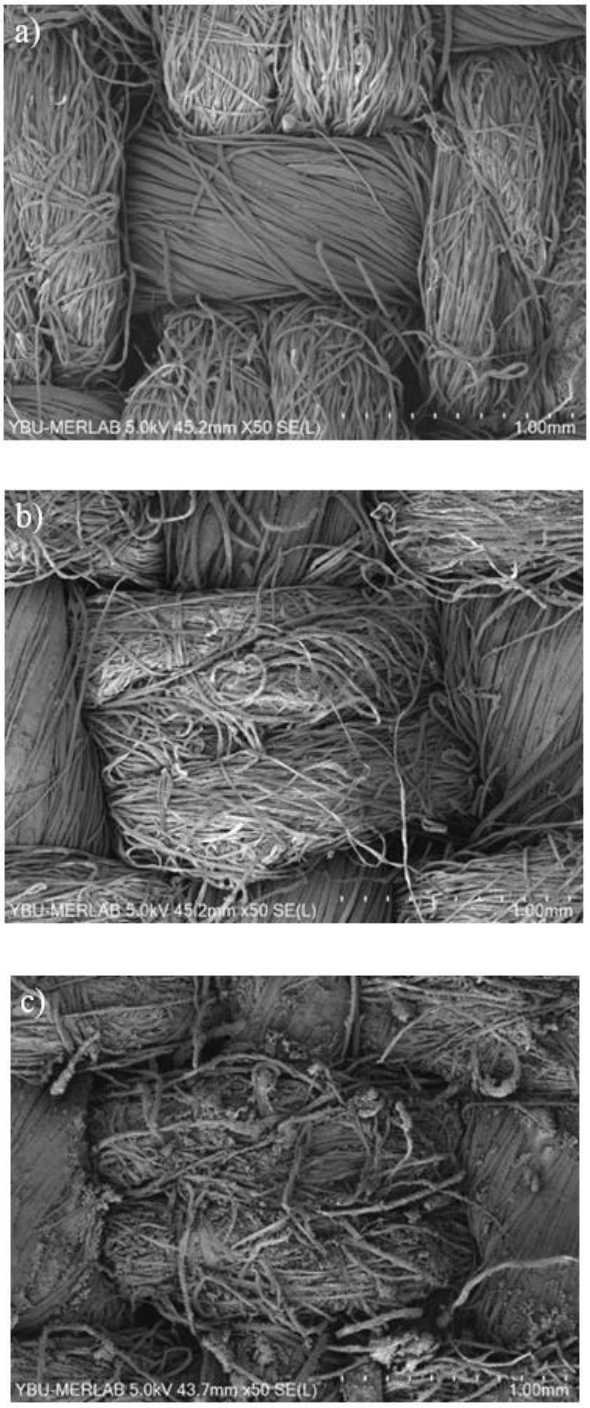

Figure 4.1 SEM surface images of a) un-treated b) DAP coated c) PDA coated fibre surfaces.

In this study, PDA coating was applied to flax fibres for the first time in the literature by dip-coating and mixing method. PDA nanoparticles, inspired by mussels, provide double function thanks to catechol and amine groups, which produce free radical and

radical scavenging activity. While these radicals are highly adhesive, PDA has increased the thermal stability and flame retardant properties of the coated materials. In addition, the reactive radical scavenging feature of PDA showed that a good surface coating can be made, especially for complex surface morphologies (see Figure 4.2). The colour change of flax fibres to dark colour showed that PDA was successfully coated.

Figure 4.2 Flax fibre surface coated with PDA.

SEM images of PDA coated flax fibres are presented in Figure 4.3. As seen here, a regular PDA growth was obtained without any significant change in the fibre structure and surface of the flax fibres.

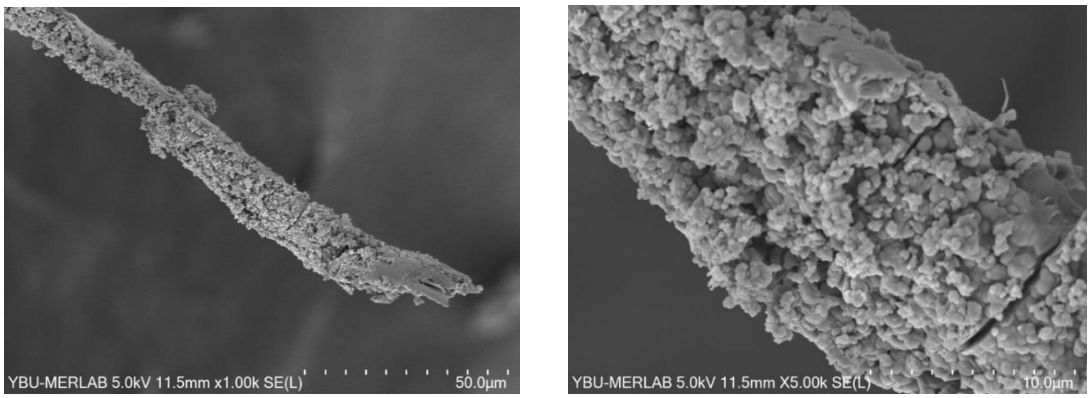

Figure 4.3 PDA growth on the fibres.

PDA also shows a homogeneous and conformal coating structure. PDA nanoparticles grew in solution and adhered to the smooth PDA film formed on the fibre. This has been achieved thanks to the high adhesiveness of the PDA. Figures 4.4, 4.5 and 4.6 shows pure flax, DAP treated flax and PDA coated flax fibres respectively.

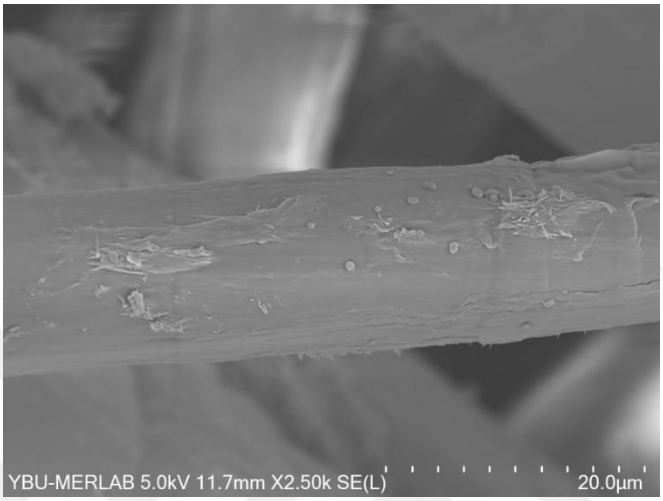

Figure 4.4 SEM image of pure flax fibre.

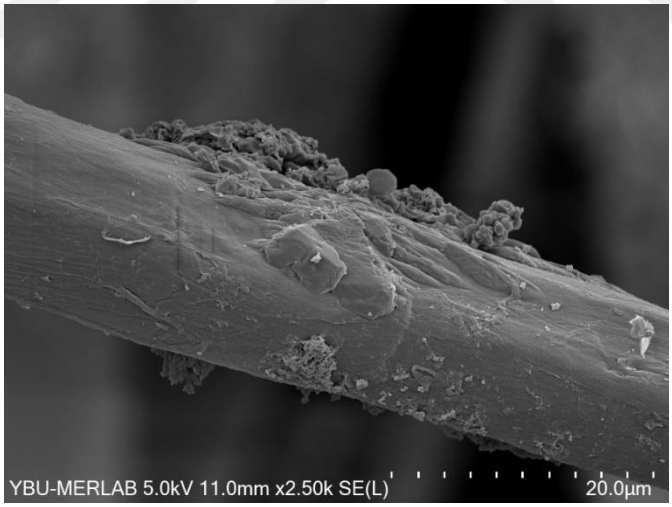

Figure 4.5 SEM image of DAP treated flax fibre.

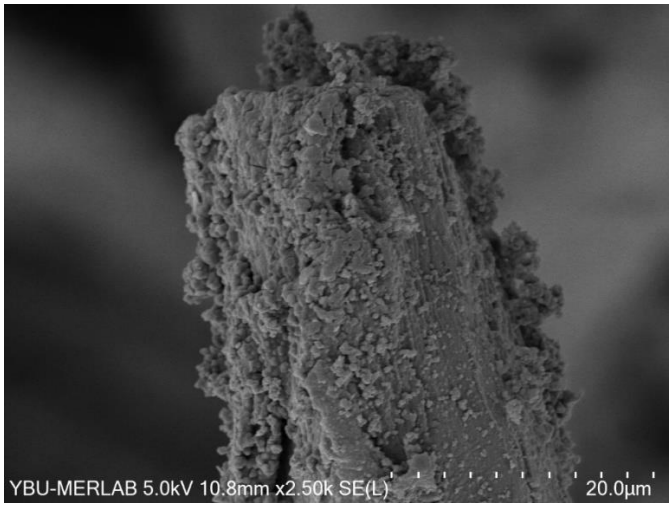

Figure 4.6 SEM image of PDA coated flax fibre.

Growth continued during the PDA coating on the fibre surface. These growing surface structures formed an integrated coating layer with PDA accumulation. Figure 4.7 shows accumulation of the PDA on the end point of the fibre.

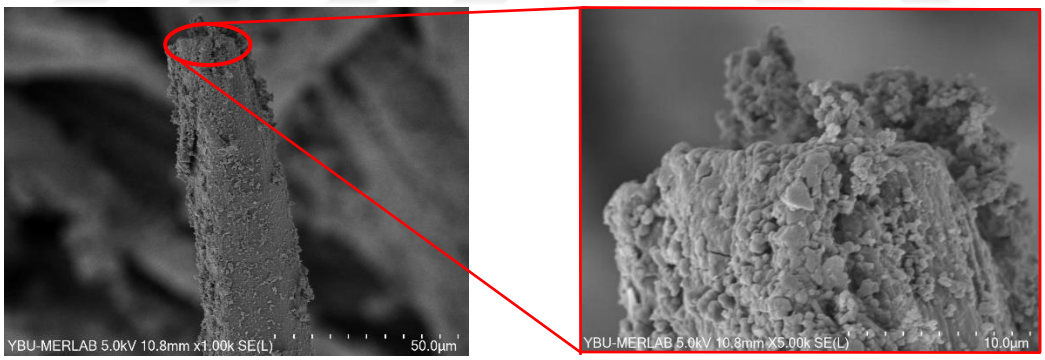

Figure 4.7 PDA accumulation on end point of the fibre.

Surface morphology was examined after burning in order to observe the damage on natural fibres. When PDA coated fibres are compared before and after burning, it is seen that there is no significant change in coating and fibre structure. Although the overall structure of the composite contracted due to the effect of combustion, the fibres tended to preserve their structure. In Figure 4.8, SEM images of PDA coated fibres before and after burning are given.

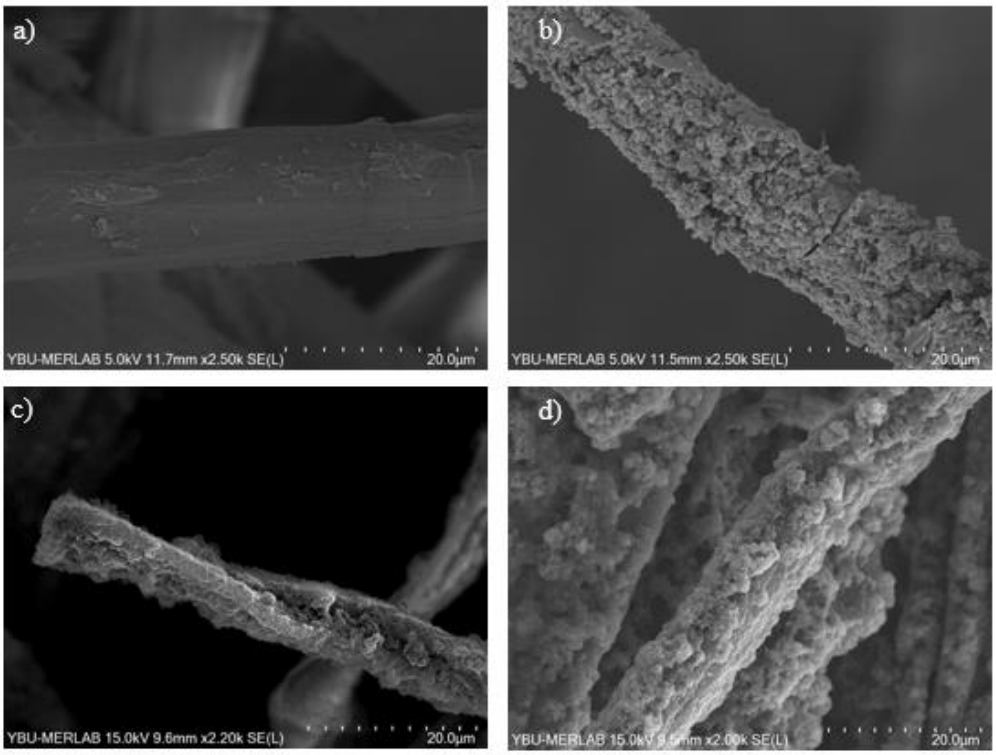

Figure 4.8 SEM images of a) non-coated flax fibre before burning, b) PDA coated flax fibre before burning, c) PDA coated flax fibre composite after burning, d) PDA coated flax fibre TiO_2 reinforced polymer composite after burning.

Figure 4.9 shows the SEM images of the PDA coated fibre composites after burning. The images clearly show that the fibres and the PDA coating on the fibre surface retain their structure.

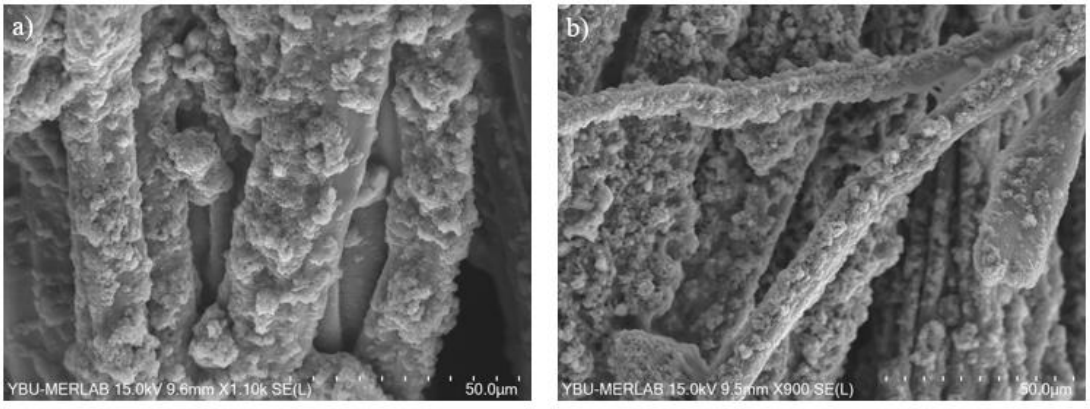

Figure 4.9 SEM images of a) PDA coated fibre polymer matrix composite after burning, b) PDA coated fibre TiO_2 reinforced polymer matrix composite after burning.

Ellison et al. [31] in their study examined PDA coating on PU foam, PDA showed that the coating forms a layer after combustion, protecting the foam surface at a cellular grade. Considering these results, it is seen that the same mechanism functions in PDA coated flax fibres. The SEM image obtained after combustion as a result of the work on the PU foam and the SEM image after the combustion of the structure formed on the flax fibre surface are given in figure 4.10. The char layer formed on the surface after combustion is very similar to the PDA coating structure and it is seen that the PDA coating structure is preserved. In addition to preserving the flax fibre structure of this layer, the flame spread rate has decreased due to the radical scavenging feature of the catechols.

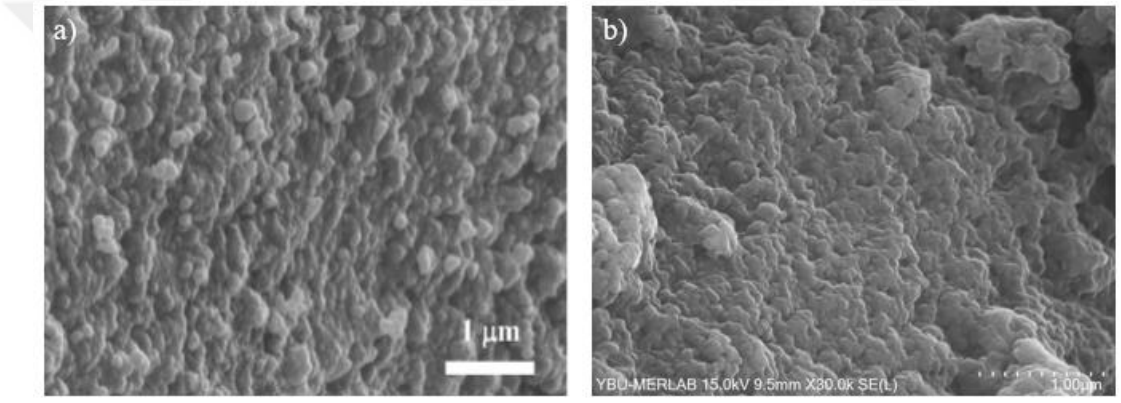

Figure 4.10 SEM images of a) PDA coated PU foam surface after combustion [31], b) PDA coated flax fibre composite surface after burning.

The dispersion of TiO_2 in the polymer matrix is given in Figure 4.11. Figure 4.11a shows pure polymer and Figure 4.11b shows TiO_2 reinforced polymer matrix. As seen in the SEM images, TiO_2 showed a homogeneous distribution in the polymer matrix. This indicates that the flame retarding effect of TiO_2 will be observed in the whole material, not locally.

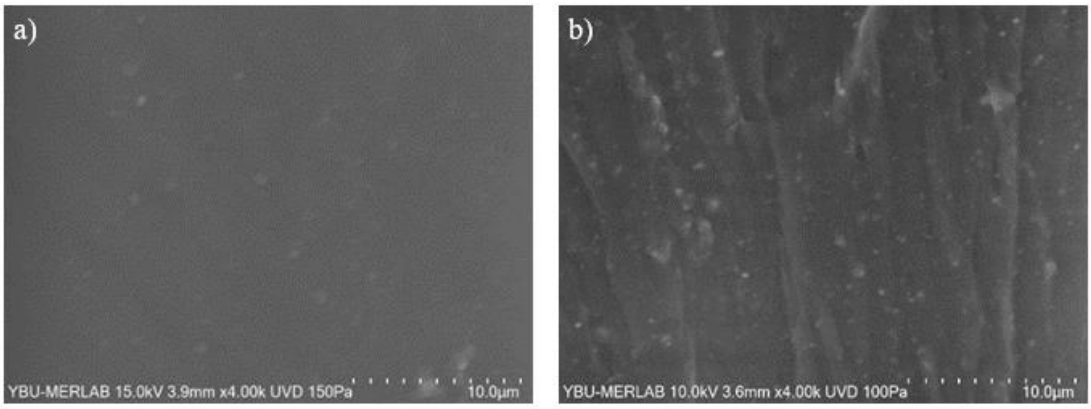

Figure 4.11 SEM images of a) pure polymer matrix b) TiO_2 reinforced polymer matrix.

4.2 Energy Dispersive X-Ray Spectroscopy (EDS) Analysis

The elements and their proportions in the composites were examined by Energy Dispersive Spectrometer. EDS map sum spectrum of pure flax fibre is shown in Figure 4.12.

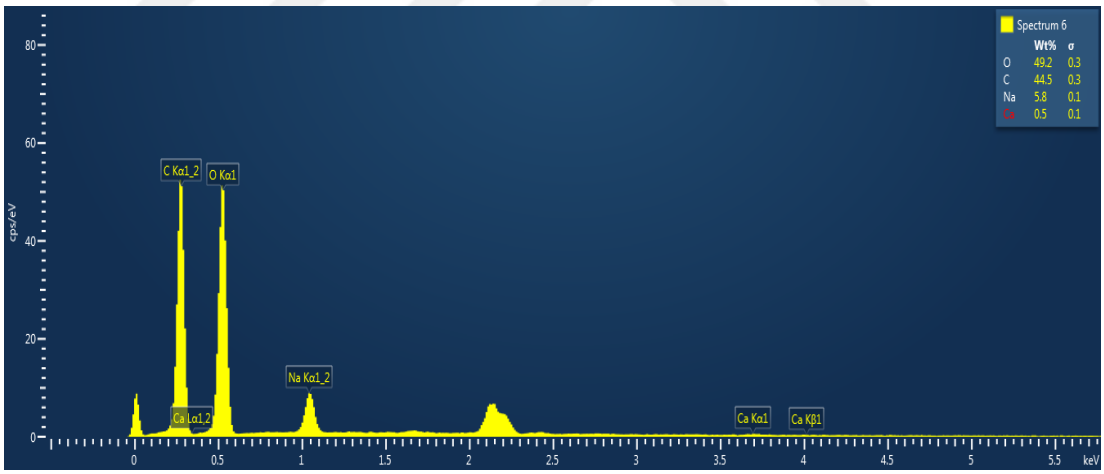

Figure 4.12 EDS map sum spectrum of pure flax fibre.

The effect of cleaning with NaOH applied before flax fibre coating is clearly seen in Figure 4.12. Figure 4.13 shows the EDS map sum spectrum of DAP treated flax fibre. The results of the analysis support the DAP coating process applied on the fibre.

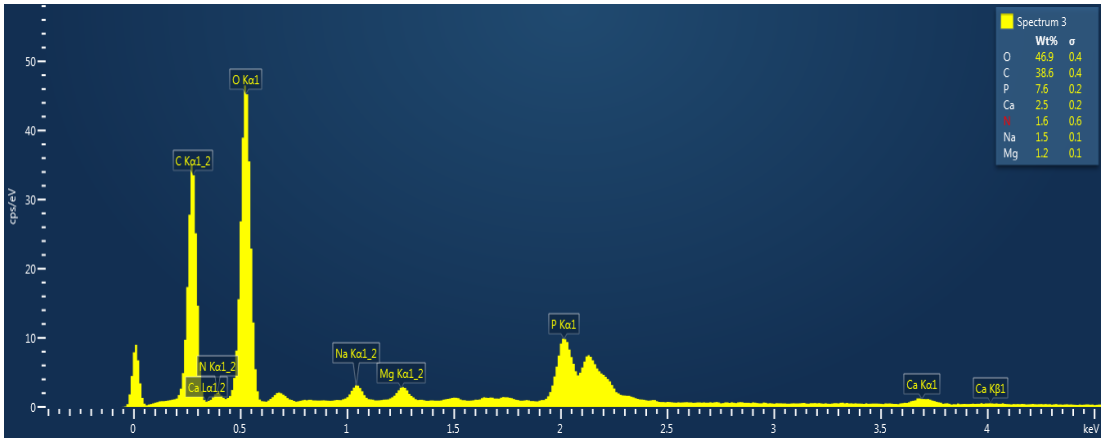

Figure 4.13 EDS map sum spectrum DAP treated flax fibre.

Figure 4.14 shows the EDS map sum spectrum of PDA coated flax fibres. According to the distribution on the flax fibre, the Cl element originating from dopamine hydrochloride is clearly visible. As a result of this analysis, it supports that the PDA is coated on the fibre surface.

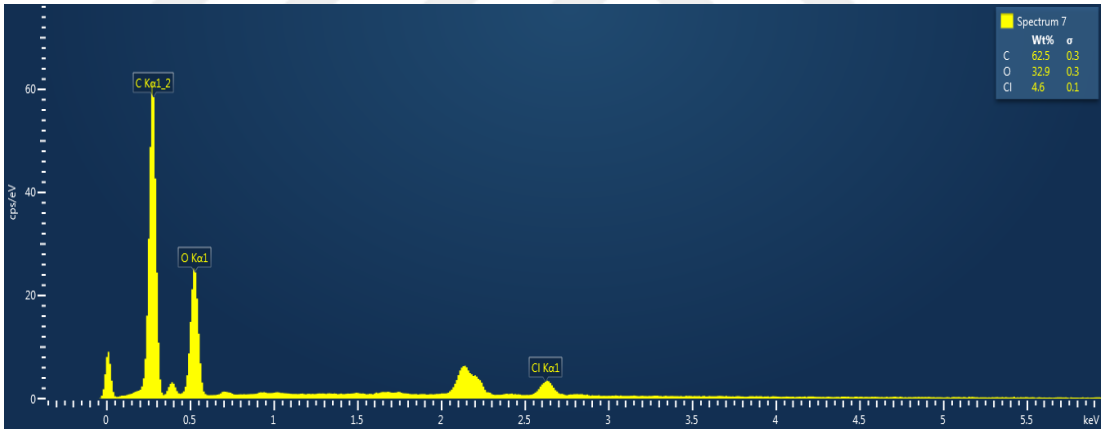

Figure 4.14 EDS map sum spectrum PDA coated flax fibre.

4.3 TGA / DTA Analysis

TGA / DTA method was used for thermal analysis of samples. The analysis took place in a N atmosphere and an upper temperature of 520 ^{o}C. Fibre and polymer were analysed separately to correctly interpret the effect of PDA and TiO_2 on the thermal behaviour of the composite. As a result of the study, the result of the TGA / DTA

analysis of the pure SMP is given in Figure 4.15. DTA curve in the TGA / DTA diagram of pure SMP, it is seen that the endothermic peak value is 304.7 ºC. As it can be understood from the TGA curve, the polymer had a high rate of weight loss in the temperature increase up to this peak. This temperature can be specified as the temperature at which the material degrades. In addition, pure SMP sample lost % 81 weight in the 35-520 ºC temperature range.

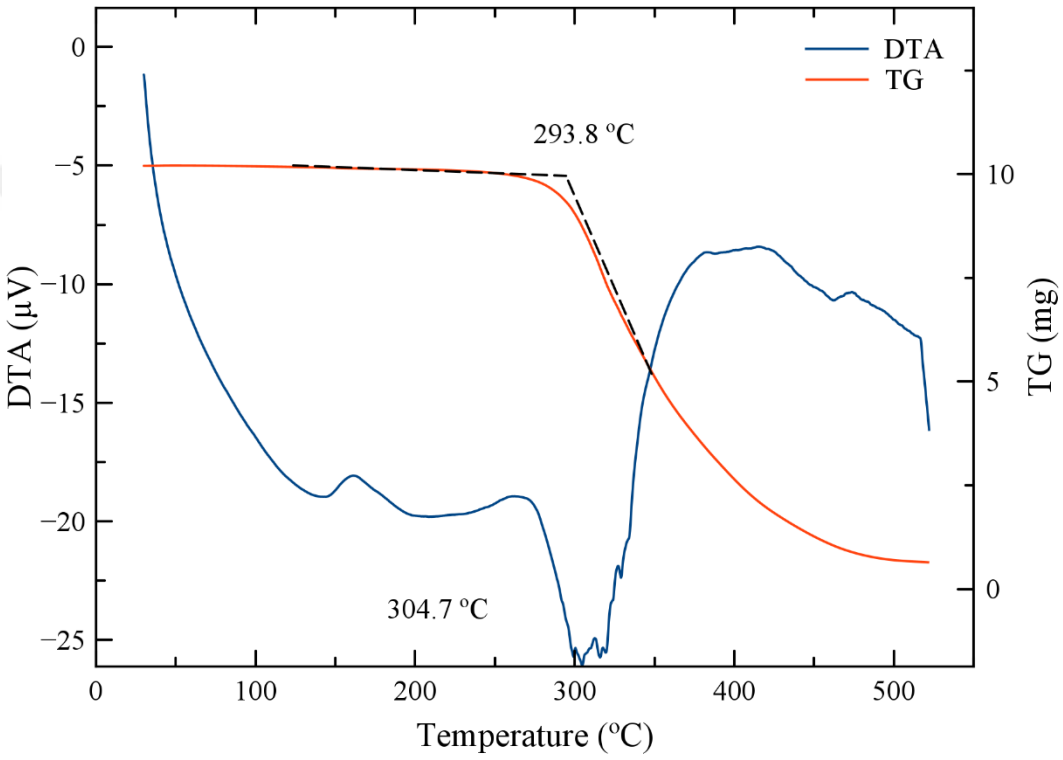

Figure 4.15 TGA / DTA analysis of pure SMP.

Alghamdi et al. [66] in their study with TiO_2 reinforced polypropylene, they showed the effect of TiO_2 on the decomposition temperature by increasing the decomposition temperature from 350 ºC to 420 ºC. In the TGA / DTA diagram given in Figure 4.16, the results of TiO_2 reinforced shape memory polymer can be seen. As seen in the TGA / DTA diagram of the TiO_2 reinforced polymer, the endothermic peak value is at 341.1 ºC. Compared to pure polymer, TiO_2 reinforced polymer appears to have an increase 12% in decomposition temperature. TiO_2 can maintain its structure without degradation up to much higher temperatures. Figure 4.17 shows the TiO_2 TGA / DTA

diagram. As seen on the TGA / DTA diagram, TiO_2 did not show any significant degradation behaviour in the 35 - 520 ^oC temperature range. Weight loss of TiO_2 reinforced polymer is 2%.

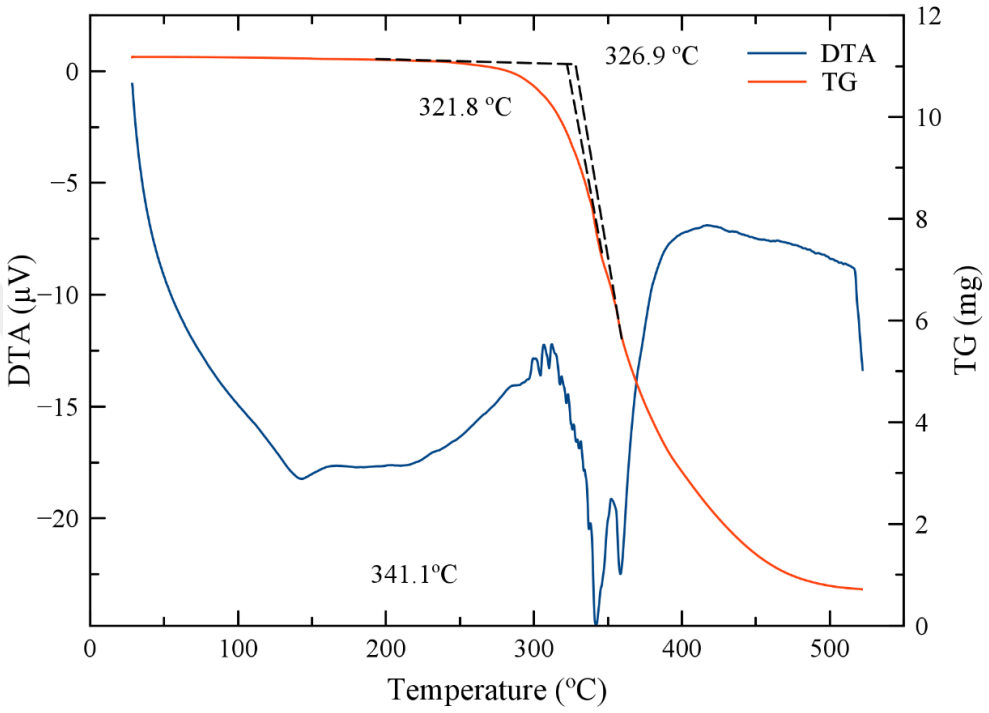

Figure 4.16 TGA / DTA analysis of TiO_2 reinforced shape memory polymer.

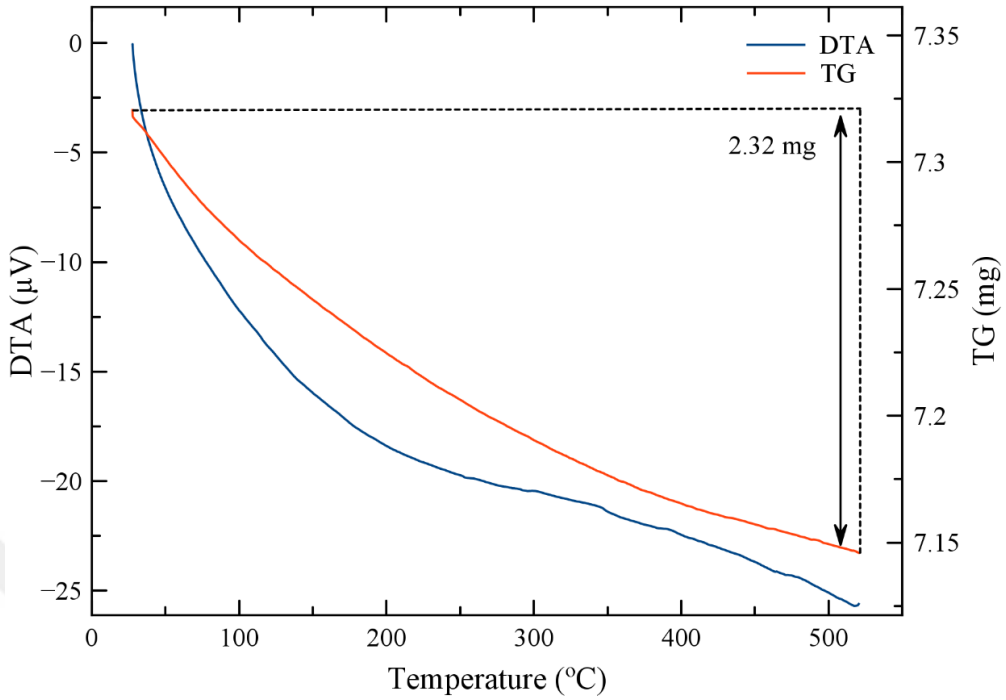

Figure 4.17 TGA / DTA analysis of TiO_2.

Pure flax and PDA coated flax were examined to observe the behaviour of the natural fibre used in the composite plate when exposed to heat. Figure 4.18 shows the thermal analysis results of pure flax fibre. In TGA / DTA analysis of uncoated flax fibre, endothermic peak value is seen at 361.8 °C. With the TGA curve, this temperature value is supported by high weight loss and degradation. Weight loss rate in uncoated fibre is 82%.

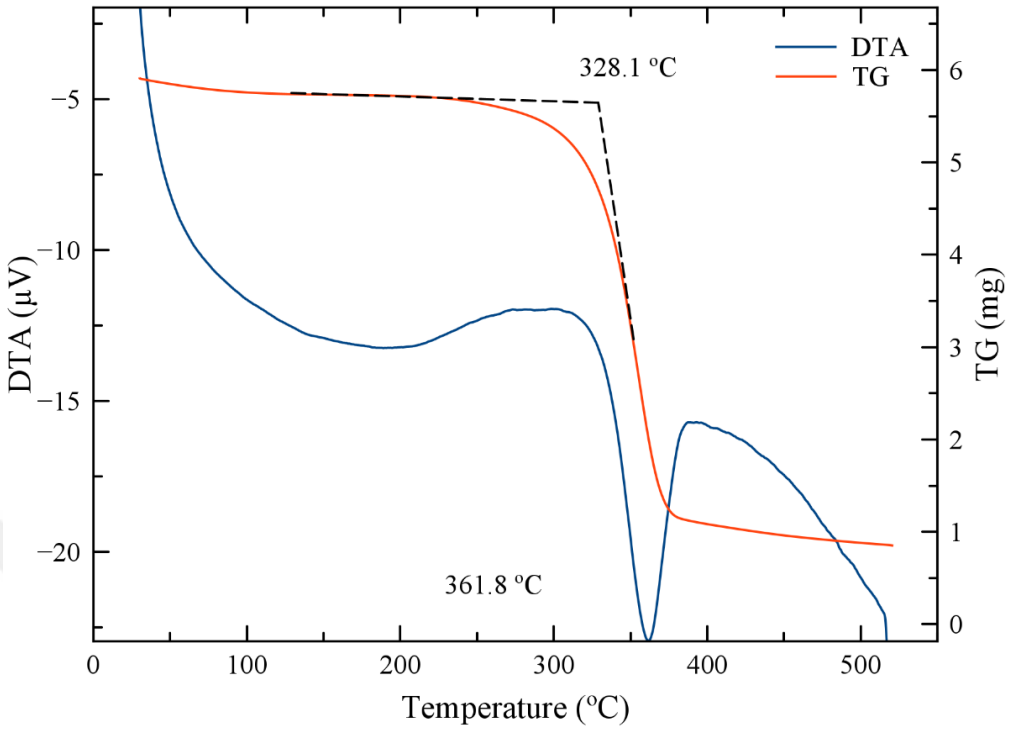

Figure 4.18 TGA / DTA analysis of pure flax fibre.

Finally, figure 4.19 shows the TGA / DTG results of PDA coated flax fibre. When we examine the TGA / DTA analysis of PDA coated flax fibre, it is seen that there are significant endothermic peaks at two points. These points are the intervals in which high weight losses occur in time. Based on this, the decomposition temperatures can be determined as 252 °C and 346 °C.

Dai et al. [67] stated in their study that dopamine is a source of carbon. It is understood that any PDA coated surface will form a carbon layer when exposed to a certain temperature. This carbon layer forms a thermal insulation wall on the material. Ellison et al. [68] in their study found out, this carbon char layer formed by using PDA and GO showed that it is an effective flame retardant system. The remarkable part in these analysis results is that the first endothermic peak value of PDA coated flax fibre is lower than the uncoated flax fibre endothermic peak value. The reason for this situation is that PDA has a polymeric structure and shows a lower temperature carbonization behaviour. Considering the results, while PDA forms a carbon layer at low

temperature, there is no significant change in the decomposition temperature of flax fibre. Another remarkable point here is the amount of weight loss. Although PDA coated fibre gave the first endothermic peak at lower temperature, the weight loss rate was lower than uncoated flax fibre. Uncoated flax fibre has 82 % weight loss, while PDA coated flax fibre has a weight loss of 75 % between 35 – 520 ºC temperatures. Based on the SEM images in Figures 4.9, and 4.10 and the mass loss quantities of burning tests and thermal analysis, the PDA were decomposed at low temperature and formed a protective layer on the flax fibre. PDA layer reduced the amount of fibre degradation and mass loss.

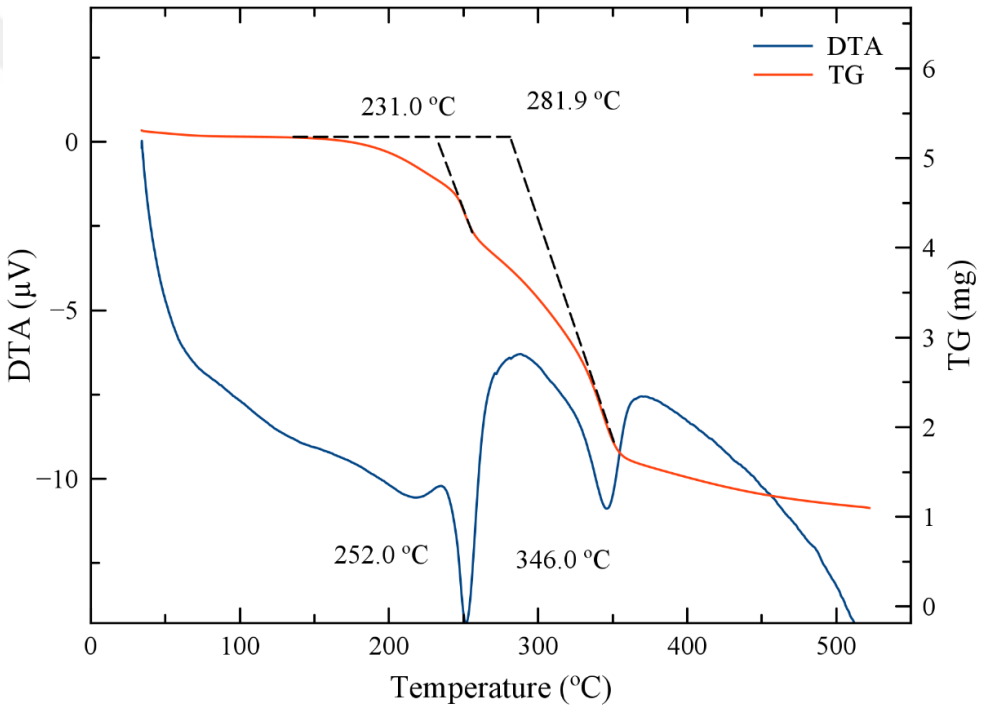

Figure 4.19 TGA / DTA analysis of PDA coated flax fibre.

4.4 Fire Test Analysis

4.4.1 UL-94 Test Analysis

UL-94 vertical and horizontal burning tests were carried out to examine the fire behaviour of the samples. Combustion tests were carried out according to the ASTM D-3801 vertical burning test standard and ASTM D-635 horizontal burning test standard. In the vertical combustion test, the samples were exposed to the flame for 10

seconds at a height of 20 mm flame source and 90º angle. Cotton was placed under the sample during combustion. During the combustion, the burning time of the sample and the dripping are examined. It is also noted whether the broken pieces ignite the cotton.

The vertical burning test apparatus and reference sample (non-coated fibre with only polymer matrix) are shown in figure 4.20. The reference sample burned for 59 seconds from the first contact with the flame. At the end of combustion, spontaneous quenching did not occur and the sample fell on the cotton as a whole piece and ignited the cotton.

Figure 4.20 Vertical fire test setup and reference sample.

The composite plate consisting of PDA coated fibre and polymer matrix burned for 105 s in vertical burning test. Despite the long burning period, no dripping took place on the cotton and the sample was self-extinguished. It is also seen in figure 4.21 that the sample examined after combustion preserves its physical structure much more than the reference sample. The fact that the burning time is long and the appearance is preserved after burning indicates that the flame progresses much more slowly and that the PDA forms a protective layer during the burning. The part related to the examination of the burning rate is described in the horizontal burning test results. According to the results of vertical burning test, it is seen as an advantage that there is no dripping and the structure is protected more than the additive-free sample.

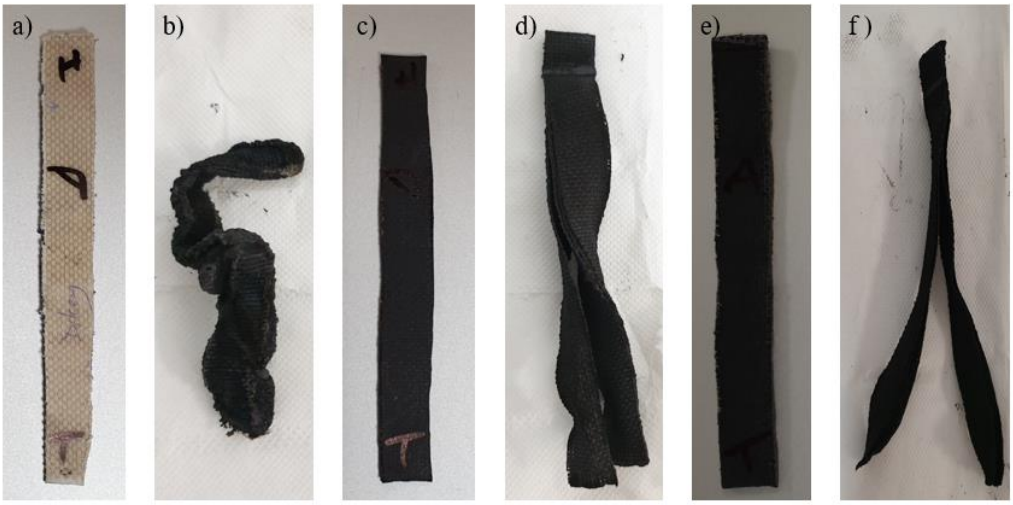

Figure 4.21 Physical appearance of the a) reference sample before burning, b) reference sample after burning, c) PDA coated fibre - pure polymer matrix composite sample before burning, d) PDA coated fibre - pure polymer matrix composite sample after burning, e) PDA coated fibre - TiO_2 reinforced polymer matrix composite before burning, f) PDA coated fibre – TiO_2 reinforced polymer matrix composite after burning.

As with the polymer matrix composite consisting of PDA coated fibres, the PDA coated fibre TiO_2 reinforced polymer matrix composite plates have long burning times and spontaneous extinction without dripping. The sample burned for 101 seconds. Thanks to the presence of TiO_2 in the polymer matrix, the flame penetrated the interior of the material less and was effective in protecting the structure together with the PDA. The effect of the protective layer formed by TiO_2 is understood from the fact that the mass loss in the sample before and after the test is less than that of other samples. The change in the masses of the samples as a result of the vertical burning tests is given in table 4.1.

Table 4.1 Mass loss quantities of samples before and after vertical burning tests.

Sample Types	Mass of before burning	Mass of after burning	Mass loss	Mass loss (%)
Non-coated fibre polymer matrix composite	4.46 g	0.80 g	3.66 g	82.06
PDA coated fibre polymer matrix composite	4.99 g	1.51 g	3.48 g	69.73
PDA coated fibre TiO_2 reinforced polymer matrix composite	5.03 g	1.55 g	3.48 g	69.18

In the horizontal burning test, the rate of flame spread on the materials was examined. In order for the material to be considered successful as a result of this test, the flame spread rate must be less than 76 mm / min. This classification is valid when the thickness of the samples is less than 3 mm and the samples in this study provide this requirement. Low flame spread rate is very important to prevent the fire from spreading in a short time.

In the horizontal combustion test, the sample was placed on the test apparatus parallel to the ground. The flame was applied to the sample for 30 seconds from a distance of 20 mm at an angle of 45^o. The propagation rate of the flame was noted depending on the time by paying attention to the 25 mm and 75 mm limits previously marked on the sample. The 75 mm limit marked on the material is expected to burn for more than 60 seconds.

The test setup of the non-coated fibre polymer matrix composite was given in figure 4.22. The time to reach the limit of 75 mm from the moment the material was exposed to the first flame is 48 seconds. When the calculation is made with this period, the propagation rate of the flame is 95 mm/min. According to these results, the flame spread rate of the non-coated fibre polymer matrix composite is quite high and it failed according to the horizontal burning test standard.

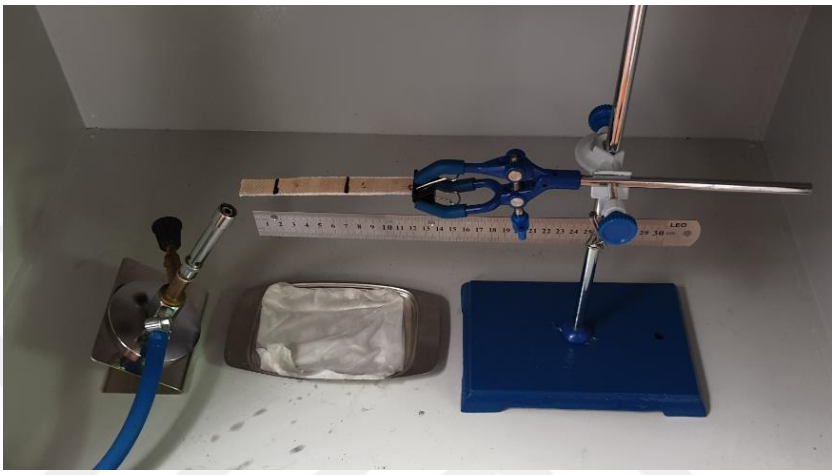

Figure 4.22 Experimental setup of horizontal burning test of non-coated fibre polymer matrix composite plate.

In the horizontal burning test results of polymer matrix and TiO_2 reinforced polymer matrix composite plates consisting of PDA coated fibres, considerable improvement has been observed compared to the reference sample. Flame spread rate decreased significantly in both samples. The flame propagation behaviours of the samples are given in Figure 4.23.

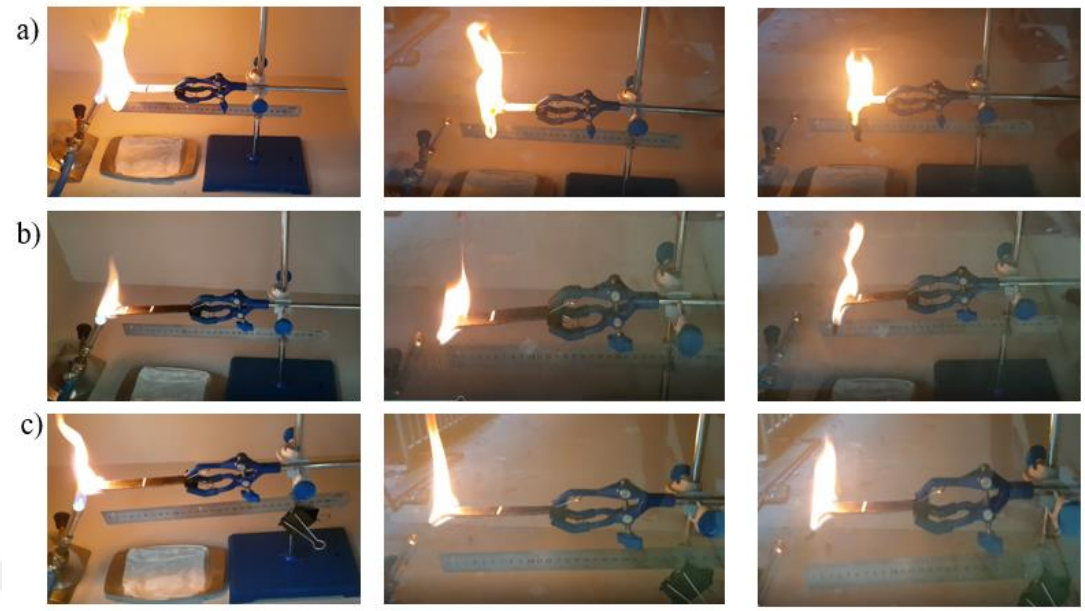

Figure 4.23 Flame propagation of the a) non-coated fibre polymer composite plate, b) PDA coated fibre polymer matrix composite plate, c) PDA coated fibre TiO_2 reinforced polymer matrix composite plate after 20 s, 50 s and 80 s.

Considering the results, 75 mm part burned in 100 s in PDA coated fibre polymer matrix composite plate. According to this combustion performance, the flame spread rate is 45.6 mm/min. In PDA coated fibre TiO_2 reinforced polymer matrix composite plate, this part burned in 190 s. The flame spread rate is calculated as 24 mm/min. Horizontal combustion test results are given in Table 4.2. In consequence of these results, both samples are successful according to the horizontal burning test standard.

Table 4.2 Horizontal combustion test result of the samples.

Samples	Flame spread time to 75 mm boundary	Flame spread rate (mm/min)	Improvement in flame spread	Pass test successfully
Non-coated fibre polymer matrix composite	48 s	95	-	-
PDA coated fibre polymer matrix composite	100 s	45.6	52 %	X
PDA coated fibre TiO_2 reinforced polymer matrix	190 s	24	74.73 %	X

4.4.2 LOI Test Analysis

LOI testing is a type of test that allows us to observe the flammability of materials. In the LOI test, the minimum amount of O_2 required to burn the material is determined. In this test, the sample in the O_2-N atmosphere is placed vertically in the chimney in the experimental setup. O_2 and N gases are introduced from the bottom part into the flue to adjust the O_2-N content of the atmosphere. The material in this atmosphere is ignited from the top and the burning behaviour is observed. If the burning takes more than 30 seconds in the specified environment, the amount of O_2 is reduced to a lower level. In the O_2-N atmosphere where the combustion takes less than 30 seconds, the limit O_2 amount is determined.

In the study, composite plate consisting of non-coated fibre polymer matrix was the most flammable material with 20% limit amount O_2 in LOI test. This amount was

followed by a polymer matrix composite plate consisting of PDA coated fibres with 23% O_2 content. According to the results of the experiment, the most resistant materials to fire in the same atmosphere were PDA coated fibre TiO_2 reinforced polymer matrix composite plates. The minimum amount of O_2 required for combustion is 24%.

PDA prevents the growth of the flame thanks to the protective layer it forms on the main material immediately after being burned. In this mechanism, it minimizes the interaction of the flame with the fibres and reduces the fuel required for fire. With the images in the Figure 4.10, it has been proved that the fibre retains their structure after burning. From this point of view, in composites consisting of PDA coated fibres, the flame shows a much weaker character during combustion. Despite the material ignition, more O_2 was needed than the O_2 present in the atmosphere, since the burning time was less than 30 seconds. As a result, composite samples produced with PDA coated fibre burned shorter duration in the atmosphere than the uncoated samples, according to the LOI test, and required more O_2 to continue the combustion.

In view of the TiO_2 reinforced polymer matrix, in addition to the flame retardant effects of the PDA coating, the protective layer formed by TiO_2 contributed to maintaining stability. While a protective layer is formed by the PDA on the inside, a layer with TiO_2 is formed as a result of the melting and burning of the polymer matrix on the outside. This outer layer helps maintain thermal stability while creating a strong thermal insulation wall. In this way, the heat travels less to the inner parts of the material and the amount of flammable gas expected to be produced by the components decreases and the transition to the outer parts becomes difficult. For this reason, TiO_2 reinforced PDA coated fibre composite showed the best performance in LOI test [51].

CHAPTER 5

CONCLUSIONS AND FUTURE WORK

5.1 Conclusions

In this study, the design, production, and fire characterization of natural fibre reinforced flame retardant polymer matrix composites were investigated. The results obtained at the end of the study are as follows:

1. In SEM examinations, it was seen that PDA was coated on the fibre surface with a regular distribution. In the images taken with different magnifications, it was seen that the PDA was coated to the intermediate parts and end points of the fibres. PDA could be successfully observed on the fibre surface after combustion. PDA formed a protective layer during combustion and served as a barrier in the passage of heat. In this way, it delayed the progression of the heat to the interior and served as a flame retardant. PDA coating process is successful when it is done by dipping and mixing method in tris-HCl buffer solution for 24 hours at room temperature.

After the 1.5 % TiO_2 nano powders added to the polymer matrix were dispersed in the A component of the polymer with an ultrasonic probe for 30 minutes, the polymer A and B components were mixed at 3000 rpm for 2 minutes. According to the SEM images of the cured polymer after this process, TiO_2 nano powders provided a homogeneous distribution in the polymer matrix.

2. EDS analysis was performed to determine the elemental ratio. According to EDS analysis results, 5.8 wt % Na was seen in pure flax fibre content. This is because the natural fibres were washed in NaOH solution for cleaning before composite production.

According to EDS analysis of DAP treated flax fibre, besides C, O and Na elements, P element ratio of 7.6 wt % was observed.

Finally, according to the results of EDS analysis of PDA coated fibre, it was observed that there was 4.6 wt % Cl element on the fibre surface. This is because PDA is in the

form of dopamine hydrochloride before polymerization. The source of the element Cl is PDA.

According to the results of the EDS analysis, the rates of the expected element types were determined as a result of the works performed at different stages.

3. Thermal analysis were carried out to investigate the effect of TiO_2 and PDA, which are used in the production of flame retardant composite material with natural fibre, on the decomposition temperature and mass loss rate. In these analyses, polymer matrix and fibre were analysed separately to obtain correct results. 1.5 wt% TiO_2 nano powder was added to the polymer matrix. The pure polymer matrix gave an endothermic peak at 304.1 ^oC. In the TiO_2 reinforced polymer matrix, this value increased to 341.1 ^oC. As a result of this analysis, it is clear that TiO_2 nano powder increases the decomposition temperature. The 1.5 wt% TiO_2 nano powder addition caused an approximate 35 ^oC increase in the decomposition temperature of SMP.

When we examined the effect of PDA on the decomposition temperature, we found that there was no increase. PDA formed the first endothermic peak at 252 ^oC and flax fibre degraded at 346 ^oC. The remarkable result in this analysis is the decrease in the mass loss rate. Non-coated flax fibre lost 82% mass as a result of analysis in the same range, while PDA coated fibre suffered 75% mass loss. PDA coating reduced the mass loss rate of the fibre by 7% and provided an advantage in this regard.

4. PDA and TiO_2 effects and fire behaviour of natural fibre reinforced composite were examined in horizontal and vertical burning tests. In the vertical burning test, the sample was placed on the test device perpendicular to the ground. The sample was then ignited by a flame source at a distance of 20 mm for 10 seconds. In addition, cotton was placed under the sample. After the sample ignited, the burning time and the dripping during the burning were examined. Finally, the masses of the samples were measured after combustion. As a result of the test, the PDA uncoated sample burned completely in 59 seconds and fell onto the cotton in one piece and the cotton ignited. Composite specimen with PDA coated fibre polymer matrix burned for 105 seconds and extinguished spontaneously without any dripping or rupture. The PDA coated fibre TiO_2 reinforced polymer matrix composite burned for 101 seconds and extinguished spontaneously without dripping and part breakage.

As a result of the vertical burning tests, the mass loss rates of the samples were examined. Mass loss rate in non-coated fibre composite was 82.06 %, 69.73 % in PDA coated fibre polymer matrix composite and 69.18% in PDA coated fibre TiO_2 reinforced polymer matrix composite. According to these results, PDA coating and TiO_2 nano powder insert showed flame retardant properties. Increasing combustion times gradually indicate that the rate of flame spread decreases and the rate of mass loss decreasing gradually shows that the structure of the material is preserved during combustion.

In the horizontal combustion test, it is seen more clearly that the flame spread rate decreases. Samples were placed in the test device parallel to the floor and were exposed to the flame at a 45^o angle and a distance of 20 mm for 30 seconds. In this test examining the propagation rate of the flame on the sample, the burning time was recorded. The test specimens were marked according to ASTM - D635 horizontal burning tests standard. The fact that the flame can take the distance of 75 mm in more than 60 seconds means that the samples are acceptable. In the non-coated sample, this distance burned in 48 seconds. Therefore, the reference sample was not successful in the test. PDA coated fibre polymer matrix composite sample exhibited 100 seconds; PDA coated fibre TiO_2 reinforced polymer matrix composite sample showed 190 seconds burning performance. According to these results in the horizontal burning test, the reference sample showed 95 mm / min, the PDA coated fibre polymer composite sample 45.6 mm / min and the PDA coated fibre TiO_2 reinforced polymer matrix composite sample showed 24 mm / min burning speed. Flame retardant composite samples met the test standard <76 mm / min. Thanks to the PDA and TiO_2 protective layer, the flame propagation rate has decreased.

5. The LOI Test determines the minimum amount of O_2 required for the burning of the composites produced in the study. The flame retardant effect was clearly seen in the LOI test with the effect of PDA and TiO_2. The amount of O_2 required to burn the polymer matrix composite material consisting of non-coated fibres for 30 seconds was determined as 20 %. In PDA coated fibre polymer matrix composite, this value increased to 23 %. PDA coated fibre TiO_2 reinforced polymer matrix composite required a minimum of 24 % O_2 for 30 seconds of burning. As can be seen from the

results, the minimum amount of O_2 required by the composites to continue burning has increased thanks to PDA and TiO_2.

5.2 Future Work

- The mechanical properties of the composites produced can be examined.
- Different amounts and durations of coating can be applied to examine the effect of PDA coating on the fibres on burning.
- The smoke produced during combustion should be analysed.
- Micro combustion and heat release rate tests should be performed on the composites produced.

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TOPICS OF INTEREST

- Polymer Composites
- Flame Retardant Composites
- Shape Memory Polymers