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GRADUATE SCHOOL OF NATURAL AND APPLIED SCIENCES

CARBON BASED HEATING ELEMENTS AND THEIR PRACTICAL APPLICATIONS

M.Sc. THESIS

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Department of Materials Science and Engineering

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Thesis Advisor: Asst. Prof. Dr. Mustafa EROL

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KARBON BAZLI ISITMA ELEMANLARI VE PRATİK UYGULAMALARI

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Ahmet YAVAŞ, a **M.Sc.** student of **IKCU Graduate School Of Natural And Applied Sciences**, successfully defended the thesis entitled "**CARBON BASED HEATING ELEMENTS AND THEIR PRACTICAL APPLICATIONS**", which he prepared after fulfilling the requirements specified in the associated legislations,

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To my family,

FOREWORD

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ABBREVIATIONS

CF	: Carbon Fiber
CNT	: Carbon Nanotube
PAN	: Polyacrylonitrile
PDMS	: Polydimethylsiloxane
PET	: Polyethylene Terephthalate
EVA	: Ethylene-vinyl Acetate
Zn	: Zinc
ZnO	: Zinc Oxide
IR	: Infrared
Al_2O_3	: Alumina
PE	: Polyethylene
PS	: Polystyrene
PA	: Polyamide
UK	: United Kingdom
L_c	: Crystallite Height
L_a	: Crystallite Width
SEM	: Scanning Electron Microscope
XRD	: X-Ray Diffraction
TGA	: Thermal Gravimetric Analysis
EDS	: Energy Dispersive Spectroscopy
ATR	: Attenuated Total Reflection
CNT	: Carbon Nanotube
W/m.K	: Watt/meter.kelvin
g/cm^3	: gram/cubic centimeter
GPa	: Gigapascal
PTC	: Positive Temperature Coefficient
NTC	: Negative Temperature Coefficient
E/A_0-CF	: Epoxy and 0% Alumina Coated Carbon Fiber
E/A_1-CF	: Epoxy and 1% Alumina Coated Carbon Fiber
E/A_5-CF	: Epoxy and 5% Alumina Coated Carbon Fiber
E/A_{10}-CF	: Epoxy and 10% Alumina Coated Carbon Fiber
LTTA	: Long-term Thermal Aging
UL	: Underwriters Laboratories
PV	: Polymer Variation Test Method Program
RTI	: Relative Thermal Index

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CARBON BASED HEATING ELEMENTS AND THEIR PRACTICAL APPLICATIONS

ABSTRACT

Carbonaceous materials have attracted a tremendous amount of attention during the last decades due to their outstanding properties for a variety of applications. Among them, carbon fibers are state of the art materials with excellent physical, mechanical, electrical, thermal and chemical properties. Especially the thermal and electrical properties of carbon fibers combined with other prominent characteristics enable them to be employed as an effective heating element. Regarding to this motivation, in this study, it is mainly aimed to fabricate carbon fiber based heating elements and to evaluate them as fabric based heating elements with heat retention. With this regard, initially, alumina powders (Al_2O_3) with varying concentrations (0 wt%, 1 wt%, 5 wt%, and 10 wt%) were added in to epoxy based resins. A continuous coating equipment was designed and utilized to deposit Al_2O_3/epoxy composite films on carbon fibers. Alumina with its superior thermal properties most particularly heat retention abiliy was chosen to increase heating performance of the heating element. After that, structural, morphological and thermal properties of coated carbon fiber samples were characterized by X-ray diffraction (XRD), scanning electron microscope (SEM), and thermal gravimetric analysis (TGA), respectively. Electrical and heating properties of the coated carbon fiber samples were also investigated and this investigation was performed using a multimeter and an experimental setup consisting of a thermal camera and a 60-V DC power supply, respectively. Additionally, thermal aging characteristics of the heating element were tested to estimate the service life-time. Heating fabrics designed and developed by means of this research were applied as plain heaters in a midibus of Anadolu Isuzu Automotive Industry and Trade Inc. (TURKEY) in the scope of the project (1010 STZ 2016). The performances of the fabrics, as a part of the Santez Project, were evaulated in the PhD thesis supervised by Assoc. Prof. Dr. Vollan Kırmacı who is the manager of the project. Finally, two different carbon fiber based heating fabrics for comparison, with and without Al_2O_3/epoxy film, were prepared to act as plain heaters under 12V potential. The results pointed out that carbon fiber based heating fabric modified by Al_2O_3/epoxy film exhibited improved heating performance thanks to the synergistic effects between carbon fiber and alumina structure.

KARBON BAZLI ISITMA ELEMANLARI VE ONLARIN PRATİK UYGULAMALARI

ÖZET

Son birkaç on yıl içinde karbon içerikli malzemeler sahip oldukları üstün özellikleri sayesinde çeşitli uygulamalar için çok büyük bir miktarda ilgi görmüştür. Onların arasında, muhteşem fiziksel, mekanik, elektriksel, termal ve kimyasal özellikleriyle karbon fiberler teknoloji harikası malzemelerdir. Özellikle termal ve elektriksel özelliklerinin diğer seçkin karakteristikleriyle birleşmesi karbon fiberlerin etkili bir ısıtma elemanı olarak kullanılmasını mümkün kılmaktadır. Bu motivasyonla bağlantılı olarak bu çalışmada ana olarak karbon fiber bazlı ısıtma elemanlarının üretilmesi ve onların kumaş bazlı ısıtma elemanı olarak değerlendirilmesi amaçlanmaktadır. Bu kapsamda ilk olarak değişen konsantrasyonlarda (0%, 1%, 5%, and 10%) alumina tozları (Al_2O_3) epoksi bazlı reçineye eklenmiştir. Özel bir sürekli kaplama ekipmanı tasarlanmış ve karbon fiberlerin üzerine Al_2O_3/epoksi kompozit filmleri depozit etmede kullanılmıştır. Üstün termal özellikleri ve bilhassa ısı tutma kabiliyetinden dolayı alümina ısıtma elemanının ısıtma performansını artırmak için seçilmiştir. Daha sonra kaplanmış karbon fiber örneklerinin yapısal, morfolojik ve termal özellikleri sırasıyla X ışını difraksiyonu (XRD), taramalı elektron mikroskobu (SEM) ve termal gravimetrik analiz (TGA) yöntemleriyle karakterize edilmiştir. Ayrıca kaplanmış karbon fiber örneklerinin elektriksel ve ısıtma özellikleri araştırılmış ve bu araştırma sırasıyla bir multimetre ve bir termal kamera ile 60V doğru akım güç kaynağı içeren bir deneysel düzenek kullanılarak gerçekleştirilmiştir. Ek olarak, ısıtma elemanının termal yaşlanma karakteristikleri servis kullanım ömrünü tahmin etmek için test edilmiştir. Bu araştırma vasıtasıyla tasarlanan ve geliştirilen ısıtma kumaşları proje (1010 STZ 2016) kapsamında Anadolu Isuzu Otomotiv Sanayi ve Ticaret A.Ş.'nin bir midibüsünde düzlemsel ısıtıcılar olarak uygulanmıştır. Projenin bir bölümü olarak kumaşların performansları, proje yöneticisi Doç. Dr. Volkan Kırmacı danışmanlığındaki doktora tezinde değerlendirilmiştir. Son olarak, karşılaştırma amacıyla Al_2O_3/epoksi film içeren ve içermeyen iki farklı karbon fiber bazlı ısıtma kumaşı, 12V potansiyel altında yüzey ısıtıcısı olarak kullanılması için hazırlanmıştır. Sonuçlar, Al_2O_3/epoksi filmi ile modifiye edilmiş karbon fiber bazlı ısıtma kumaşının, karbon fiber ile alümina yapısının sinerjistik etkileri sayesinde gelişmiş ısıtma performansı sergilediğini göstermiştir.

1. INTRODUCTION

Carbonaceous materials are of crucial importances in human life. They have represented a great asset in many industries from time immemorial. Since then, carbonaceous materials have diversely used: charcoals to warm up, flaky graphites as powder for pencil leads, graphite electrodes while making steel, carbon blacks in reinforcing tires, carbon rods in developing primary batteries because of being electrically conductive and graphite fluorite to improve their performance, slim graphite flakes for advanced computers and control panels, carbon fibers in aircraft and space systems, carbon nanotubes, fullerenes and graphene in nanotechnology, etc. [1;2].

From past to present, the element carbon has been known with its diversity. Carbon has various derivatives namely polymorphs or allotropes in contradistinction to most of elements. Carbon derivatives such as graphite, graphene, diamond, carbon fiber, fullerene, etc. consist entirely of carbon atoms, however they possess various structures and properties. Having a three dimensional (3D) structure, the diamond is one of the hardest material. Nevertheless, the graphite with two dimensional (2D) structure is quite soft that it is often used as a lubricant. Likewise, the graphite has good electrical conductivity, can be higher than metallic copper with doping, whereas the diamond is totally insulator. In addition, carbon nanotubes and buckminsterfullerene C60 have respectively one-dimensional (1D) and quasi-zero-dimensional structure, and they have various application area in nanotechnology [1;3].

Among these carbon derivatives, carbon fiber (CF) is a promising carbonaceous material which is widely studied and used in applications because of its unique properties such as splendid mechanical properties at room and relatively high temperatures, low density and light weight, high thermal and chemical stability, high electrical and thermal conductivity, low linear coefficient of thermal expansion and great creep resistance [2;4-6]. Especially in recent years, an increasing number of researchs on carbon fibers (CFs) have been explored and their application areas including aerospace, military, automotive, medical, energy generation, construction, etc. have increasingly expanded thanks to most particularly being suitable for mass production today [2;5;7-9].

Having low and high temperature applications, heating elements can be divided into two categories. Low temperature applications are generally applied to household usage like water heaters, plain heaters, and thermoelectric devices etc. while high temperature applications are related to industrial requirements including metal melting, ceramic sintering, and refractory. Heating elements are composed of electrothermal materials which are some sort of electrical resistance that can easily and efficiently transform electric energy into heat energy via joule heating namely resistive heating. Traditionally, metal and metal alloys having high melting temperatures and preferred resistances are used in these kind of heating elements. Some metallic alloys which are Kanthal (Fe-Cr-Al Alloy), Cupronickel, and Nichrome (80/20 Ni-Cr Alloy) with their trade names are main ones. Metal based heating elements generally show several disadvantages such as non-uniform heating, higher densities, high power consumption, intolerance to acid or base, relatively short lifetimes, and rigidities in contrast to their moderate thermomechanical stabilities [10-14]. Over the last few decades, carbon-based composite materials have been widely investigated and studied so as to overcome these drawbacks instead of traditional heating elements. Having distinct and tunable properties like low cost, accessibilty and processability, low density, good recyclability, combining ability with other materials, good electrical and thermal properties, carbon based materials such as carbon nanotubes (CNTs), graphite, graphene, carbon black, carbon fiber or their hybrids are promising materials in a variety of applications including heat-related applications [12;14;15]. In this direction, it is reported that there are many different studies on carbon based composite heating elements as summarized in Table 1.1.

Table 1.1 : Some reported studies on carbon based composites with different filler and matrix types.

Carbonaceous Material (Filler) heating element	**Matrix form**	**Application**	**References**
Graphite and Carbon nanotube	PET	Plain heater for commercial vehicles	[12]
Carbon nanotube	PDMS	Not reported	[14]
Carbon nanotube	PAN based carbon fiber	Not reported	[16]
Chopped carbon fiber	Cement	Smart floor heating	[17]
Carbon nanotube	PDMS	Not reported	[18]
Carbon fiber	Epoxy resin and glass fabric	Composite mold as heating element	[19]
Chopped carbon fiber	Epoxy resin	Not reported	[20]
Graphene	Epoxy resin	Not reported	[21]
Graphite nanoplatelets	PET and EVA	Wearable and smart electronics as heater	[22]
Graphene oxide platelets	Natural rubber latex	Not reported	[23]

Table 1.2 (continue) : Some reported studies on carbon based composites with different filler and matrix types.

Carbonaceous Material (Filler) heating element	Matrix form	Application	References
Graphite flakes and Carbon blacks	Polystyrene	Plain heater	[24]
Graphite	Polyethylene glycol	Plain heater	[25]
Carbon fiber	Epoxy resin	Not reported	[26]
Carbon black	Epoxy resin	Not reported	[27]
Carbon fiber	Epoxy based resin	Not reported	[28]

According to the table, it can be seen that various carbonaceous materials as filler have generally been embedded in different polymer matrices to produce composite heating element in film or bulk forms. Among all carbon based materials, CF has been studied a lot more due to relatively low cost compared to the past, being available mass production, and outstanding characteristics. Graphite also has similar properties. However, CF with greater mechanical properties has been preferred more rather than graphite [5;9;29].

As mentioned above, carbon derivatives have usually been utilized as filler material in composite films in literature. There are also a very few studies reported in which carbon fiber is used as main material (matrix) on heating element. For instance, Chien et al. [30] developed nanostructured zinc oxide (ZnO)-coated CF filaments to investigate their thermal properties for infrared (IR) heater. Likewise, a study of CF coated metallic zinc (Zn) powder on joule heating has been reported by Jonathan et al. [31]. Nevertheless, no other studies and applications of carbon fiber coated materials other than Zn and/or ZnO as a heating element have been founded as far as the literature survey done.

Within scope of this thesis, the main purpose is to produce alumina (Al_2O_3) coated CF to be employed a heating element in that the exact study has not been worked on before to the extent literature survey. In this context, an authentic carbon fiber coating equipment firstly were designed and all coating operations were carried out by using this equipment. Then, all obtained final samples were characterized by several characterization techniques including XRD, SEM and. TGA for structural, morphological and thermal properties, respectively. Besides, electrical, heating and thermal aging properties of the samples were investigated with using the experimental setups. In the light of these results, obtained final products were evaluated and the most effective one were chosen to be used in various heating applcations. In this direction, alumina coated and uncoated heating fabrics containing CF filaments were designed to be employed in heating applications. Then, their heating performances were also tested.

2. THEORETICAL BACKGROUND

2.1 Heating Elements

Heating elements are commonly utilized in various domestic and industrial applications such as; toasters, hair dryers. deicing, home improvement, furnaces, space heating, plain heaters, electric blankets, and seat heating. Heating elements are developed as wire or strip shape and they can also be taken preferred shapes by bending. Metallic form of heating elements are most common one. However, non-metallic materials like silicide and carbide are also favorable in fabricating heating elements. Any of these materials mentioned above are required to have some desirable properties including high melting temperature, atmosphere stability, thermal and mechanical shock resistance, constant temperature coefficient of resistivity, and ease of forming for utilization as a heater [11;32;33].

The materials of heating elements can withstand up to maximum 2000°C for operating temperatures. However, the resistance of each material varies in this temperature range for a certain atmosphere. To give an examle, having an operating temperature up to 1500°C in air (oxidizing), a metal can be utilized at most 1150°C in a reducing atmosphere [11;33].

2.1.1 Resistive heating (Joule heating)

The electrical power P *in* association with the flow of a current I under a voltage difference V is specified by

$$P = VI \tag{2.1}$$

This power is dissipated in the form of heat due to the resistance of material and this phenomenon is called as resistance heating. In addition, the principle on conversion of electrical energy into thermal energy is known as Joule effect (Joule's Law). This is why the resistive heating is also referred to as joule heating. The units of P, V and, I are respectively watts (W), volt and, ampere. Based on Ohm's law (Equation 2.2) which indicates the direct proportionality of voltage (V) and current (I) in a resistance (R),

$$V = IR \tag{2.2}$$

equation 2.1 can be explained as

$$P = I^2 R \tag{2.3}$$

and as

$$P = V^2 / R \tag{2.4}$$

As a result of Ohm's and Joule's Law, the relationship between electrical energy (input) and thermal energy (output) has been clarifed. From this point forth, resistive heating can procure undesired heat as well as and desired heat generation. Because of Joule's Law, resistive heating arises from the presence of any electric current passes through a resistive material. Therefore, the design of heating systems should be made by taking into account this phenomena and the risk of overheating, even melting, On the other hand, the amount of heat generated can be controlled by the internal resistance of the heating element as well as the applied electric current and voltage. That is to say, so as to achieve a desired high power value (heat amount), both voltage and current should not be too small (equation 2.1) and their values depend on the resistance. If the values of resistance of the materials used in heating elemetns is small, the values of voltage will also be small since V = IR. On the contrary, when the resistance is large, the current will be small since I = V/R. Accordingly, an intermediate resistance value is optimal to obtain a desired high power [32;34;35].

Additionally, resistance of the material applied to an electric field depends on both electrical resistivity which is characteristic property for all materials.

$$R = \rho \frac{L}{A} \tag{2.5}$$

As for equation 2.5, the resistance of the heating element is proportional to its length (L), and inversely proportional to its cross-sectional area (A). Moreover, the the electrical resistivity (ρ) for the material is a function of temperature.

Measuring the ability of materials to permit electrical current to flow, the electrical conductivity (σ_e) which is also an inherent material property and a function of temperature is identified as the reciprocal of resistivity. This relation is given by equation 2.6 [11;34].

$$\sigma_e = \frac{1}{\rho} \tag{2.6}$$

Table 2.1 : Electrical conductivities (at room temperature) of some materials [11].

Metals and Alloys	*Conductivity σ_e (Ω.m)$^{-1}$	Non Metals	*Conductivity σ_e (Ω.m)$^{-}$
Silver	$6.3\text{x}10^7$	**Graphite**	10^5
Copper (cp)	$5.8\text{x}10^7$	**Germanium**	2.2
		Silicon	0.43
Gold	$4.2\text{x}10^7$	**Polyethylene (PE)**	10^{-14}
		Polystyrene (PS)	10^{-11}
Aluminum (cp)	$3.4\text{x}10^7$	**Diamond**	10^{-11}

Table 2.1 shows the electrical conductivities of some engineering materials. It can be seen that each material possess different conductivities and accordingly they are classified as conductor, insulator and semiconductor regarding to their conductivity values. It is clearly seen that why pure metals are utilized in heating elements thanks to their highest conductivities. With the very low conductivities, some materials in the table including polyethylene (PE), polystyrene (PS), and diamond are electrical insulator. Having the conductivitiy values smaller than metals but much greater than insulators, graphite, germanium, and silicon are semiconductors [11].

2.1.2 Types of heating elements

As summarized in resistive heating, the basic principle of heating with heating elements is based on transformation of electrical energy to thermal energy in which an electrical current passes through a chosen resistance material or element then transfers its generated heat by conduction, convection and/or radiation to the material

(Figure 2.1.).With this phonemena, heating enviroment is also heated together with heating element [36].

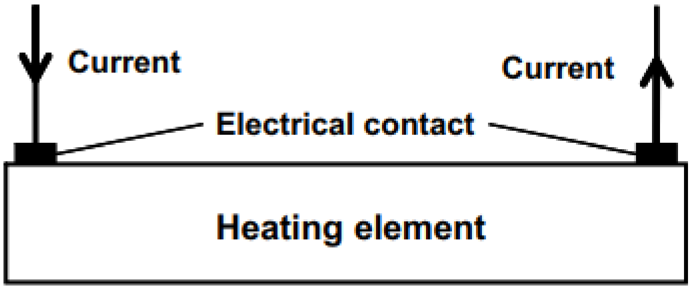

Figure 2.1 : The basic representation of a heating element [32].

Materials to be used as heating elements consist of metal and metal alloys, ceramics, sheathed elements, graphite, composites (polymer matrix composites, cement matrix [37].

2.1.2.1 Metallic heating elements

Conventionally, the heating materials is designed by the utilization of functional materials in the various form. For instance, metals used as a coil supply the necessity of a long length of metal wire by virtue of the low resistivity of metals. Metallic elements are generally used in the form of wire, strip, tape or coil. Having these mentioned shapes, heating materials require to be admissible ductility in the production process. Besides, there are a few potential points to be considered such as, decreasing life-time of heating material because of decreasing cross-section of the material used by progressive oxidation of surface or reduction of mechanical properties in a given service temperature and so. Practically, an optimal thickness of the heating element for suitable life-time is decided for each application. Metal compositions for the use of heating applications depend on service temperature desired, resistivity of the material, the temperaure coefficient of resistance, corrosion resistance, mechanical properties, machinability, and cost [36;37].

The dominant metallic heating elements based on metals and alloys for domestic and industrial applications nickel-chromium, iron-nickel-chromium, and iron-chromium-aluminium alloys. Among these, nickel-chromium alloy known as nichrome with common composition of 80% nickel and 20% chromium has been prevalently used thanks to its attractive properties such as, low cost, high resistivity compared to many other metals, oxidation resistance at elevated temperatures [32;36]. In general, having higher maximum element temprerature (1425°C in comparison with 1250°C for nichrome), longer life-time (2-4 times), higher surface load, higher resistivity, lower density and, no spalling oxide (which may occur contamination and also originate short circuit or failure of elements), the iron-chromium-aluminium alloys with commercial name as kanthal have better properties compared to nickel-chromium based alloys in terms of performance and life-time. However, they can not easily manufactured as nickel-chromium alloys [36;38].

All alloys mentioned above form an adherent non-spalling, self-sealing oxide layers on the surface of the alloy. Further oxidation is restricted by diffusion of reacting species through this oxide layer. The iron-chromium-aluminium alloys depend on an alumina film occuring on the surface and, a chromium oxide film as for the nickel-iron-chromium alloys. Moreover, The some exotic metals including platinum, tantalum and, molybdenum are utilized for specific applications like vacuum works in elevated temperatures. Some examples of these materials with applications and some characteristics is illustrated by table 2.2 [36].

On the other hand, sheathed heating elements are considered within metallic elements in which sheathed elements are based on protecting the elements used from the environment conditions in working area with the utilization a proper insulation layer covering the element from an outer sheath. For instance, several domestic appliances employed as heating materials including cooker rings, immersion heaters and kettle elements are manufactured with using magnesium oxide powders which separate the helical element coils from copper, stainless steel or nickel based alloy sheath material.

Similarly, in many industrial applications such as cartridge heaters, radiant panels and immersion heaters, mineral insulated elements are also utilized. Thin strip or band heaters are convenient utilizing a mica insulation between the element and the sheath. Other industrial appliances having more importance operate a protective and thermally conductive metallic or ceramic sheath insulated from the heating elements by an air space formed by appropriate ceramic supports and spacers. As forementioned, the choice of materials for employing in any of these applications should be attentively made referring to the thermal, electrical and mechanical properties, corrosion or degredation resistance and so [36].

2.1.2.2 Non-metallic heating elements

Metal based heating elements having a temperature limit around 1400°C are commonly utilized up to approximately 1300°C for reliable service conditions. These elements lose their strength over time and their service life-time relatively short. For this reason, one of the non-metallic heating elements based on ceramic material such as, silicon carbide, molybdenum disilicide, lanthanum chromite and hot zirconia which possess satisfying electrical conductivity to be employed as heating elements are widely used.

These ceramic based materials enable to be performed as heating elements up to 1700-1800°C service temperature. However, ceramic heating elements have some differences from metal based ones in many respects. The most important point to be paid attention is that they are deprived of formability. Therefore, ready-made forms which are in a fixed form such as rods, hair pins are useful for these heating elements. For example, the furnaces are designed by use of ready-made forms.

The silicon carbide and molybdenum disilicide elements which rely on a protective, self-sealing silica layer throughtout the surface are in tendency to be brittle. Thus, they should be carefully handled. Even so, these elements are sutibale for much higher temperatures and can witstand higher surface loadings in air compared to traditional metallic elements. Besides, some of them can possess unusual temperature coefficients of resistance. For instance, having a negative temperature coefficient (NTC) (α) up to approximately 788°C, silicon carbide possesses a positive temperature coefficient (PTC) of resistance above this temperature. Figure 2.2 illustrates resistiviy of some materials in relation to that.

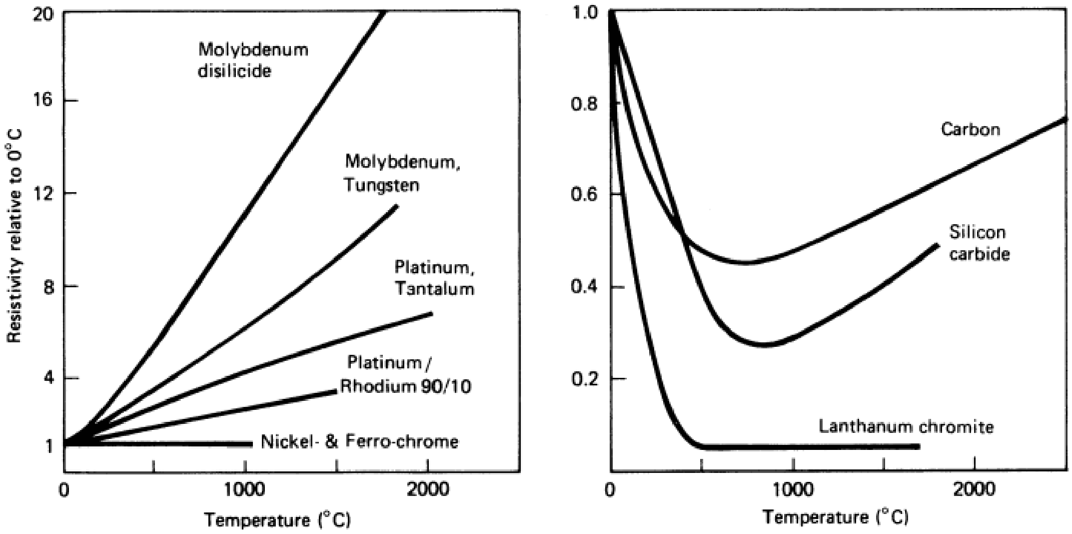

Figure 2.2 : Resistivity (relative to 0°C) of some resistance materials [36].

Consider that the values depicted in the figure are only given with the intention of illustration. The actual resistivity may vary with respect to purity, grain size and type of production. Once again, form of element, working resistance, support, insulation and the other parameters should be taken into consideration alongside selection of element.

Graphite is another common nonmetallic element material for the purpose of heating element and note that it has to be employed in the oxygen-free mediums [33;36].

Table 2.2 : Materials for resistance-heating elements [36].

Material	ϴ(°C)	$\rho(10^{-8}/m)$	$\alpha(10^{-3}/K)$	Principal application
Nickel based alloys[1] 80 Ni/20 Cr	1200	108	+14	Furnaces, resistance heaters, mineral insulated elements for domestic and industrial use
60 Ni/15 Cr/bal Fe	1150	111	+18	Firebar and convector heaters. Domestic and furnace application up to 1100°C
35 Ni/20 Cr/bal Fe	1100	104	+29	Some domestic appliances and general heating equipment at moderate temperature.

Table 2.3 (continue) : Materials for resistance-heating elements [36].

Material	Θ(°C)	$\rho(10^{-8}/m)$	$\alpha(10^{-3}/K)$	Principal application
20 Ni/25 Cr/bal Fe	1050	95	–	Terminal blocks
22 Cr/5.3 Al/bal Fe	1375	139	–	Industrial furnaces
22 Cr/4.8 Al/bal Fe	1300	135	4.7	Furnaces for moderate temperatures, appliances
Exotic metals Platinum	1300	10.58	3.92	Laboratory furnaces, small muffle furnaces
90 Pt/10 Rh	1550	18.7	–	
60 Pt/40 Rh	1800	17.4	–	
Molybdenum[2]	1750	5.7	4.35	Vacuum furnaces, inert atmosphere furnaces
Tantalum[2]	2500	13.5	3.5	Vacuum furnaces
Tungsten[2]	1800	5.4	4.8	Incandescent lamps, vacuum and inert atmosphere furnaces
Nonmetallic materials Graphite[2]	3000	1000	-26.6	Vacuum, inert gas, reducing-atmosphere furnaces
Molybdenum disilicide	1900	40	1200	Glass industry, ceramic kilns, metal heat treatment, plus laboratory furnaces
Silicon carbide	1650	1.1×10^5	–	Furnaces for heat treatment of meals, ceramic kilns, conveyer furnaces
Lanthanum chromite	1800	2100	–	Laboratory furnaces and special ceramic kilns
Zirconia[3]	2200	–	–	Laboratory furnaces and special ceramic kilns

Θ, Maximum element operating temperature; ρ, electrical resistivity at 20°C; α, mean temperature coefficient of resistance at 20°C
1: Approximate compositions.
2: Not be used in atmosphere containing oxygen, oxides of carbon, water vapor, etc.
3: Becomes sufficiently conducting at temperatures in excess of 1000°C.

Composites are created by combining at least two different materials with a separate interface between them to constitute a single substance. These materials having different physical and chemical properties are commonly classified as matrix and dispersed phase (reinforcement). Although matrix and reinforcement possess different properties, the combination of them forms a composite with outstanding properties compared to the parent material [39].

Among the composite materials, polymer matrix composites attract great interest in many applications due to its low density, load-adapted rigidity and strength and ease of manufacture. In these composites, particles and/or fibers (usually glass or carbon fibers) are embedded in a polymer matrix. Polymer matrix composites are dominant materials utilized in heat-related applications in which electrically conductive phase (additives or fillers) are used. Carbon materials such as carbon black and carbon fiber, metallic materials including aluminum flakes, stainless steel fibers, metal coated materials, metal particles and conjugated conducting polymers are used in polymer composites as a conductive phase, thus makes the polymer composite suitable for usage as a heating element. Lastly, polymer matrix composite heating elements have relatively low temperature limit because of its thermal properties. The majority of the studies given in the table 1.1 are related to polymer matrix composites in which various polymer resins are used as a matrix material [11;39-41].

Additionally, cement matrix composites are also employed in heating applications. Traditional concrete has electrical conductivity, whereas its resistivity is too high for joule heating to be useful. This high resistivity can be diminished with using severel electrically conductive additives including discontinuous carbon fibers or steel fibers, and graphite or other carbon materials. Also, alkaline slag binder can be used to reduce it. Nevertheless, among these, the best procedure to adjust the resistivity is to utilize a conductive admixture at a volume fraction beyond the percolation threshold [37].

In comparison with other materials, carbon has come to the forefront during the recent years due to its superior properties such as high resistivity, great temperature resistance, ability to radiate heat, and its usability in fiber shape. For this reason, carbon and its derivatives are applicative for heating elements. These carbon based materials have been extensively studied in heating applications as carbon based polymer composites or carbon-carbon composites. Some forms of carbon heating elements are continuous and discontinuous carbon fiber, unwoven carbon fiber mats, woven carbon fiber fabrics, carbon black, flexible graphite and other nanostructured carbon materials [14;18;32;41-43]. Similarly, some studies in which carbon materials used are listed in the table 1.1.

2.2 Carbon Fiber

2.2.1 Historical perspective

The history of carbon fibers (CFs) dates backs about thousands of years. CFs have been fabricated unintentionally by using natural cellulosic fibers like cotton or linen for a long time. The first CFs made purposively have been recorded in 1879 by Thomas Edison in which he carbonized cotton yarn to obtain a incandescent lumb filament. However, this workout could not be wholly accomplished and he consequently revised his effort with using a tungsten wire instead of the fiber. Thereafter, revival of interest for CFs lasted until 1950s. Large-scale production of CFs started in this year when synthetic rayons as textile materials including cloth and felt were carbonized to manufacture CFs for high temperature applications. Following that, the development of high performance fibers from polyacrylonitrile (PAN) in the 1960s in Japan and the UK led to a commercial breakthrough. Having simpler production process and higher carbon output with %50 compared to rayon with %30, PAN based fibers are more efficient and economic. At around the same times with development of CFs from PAN, pitch based fibers attained prevalently from petroleum, asphalt, coal tar, and PVC were introduced in Japan and the U.S.. Although it has a very cheap precursor, pitch based fibers are ordinarily inferior to PAN based fibers in terms of its properties [3;5].

2.2.2 General information for structure and properties

Carbon fibers have an atomic structure similar to graphite and formed entirely of carbon atoms. Perfect graphite composed of graphene sheets in which carbon layers are aligned in a hexagonal crystal system along three dimensional order as shown in figure 2.3.

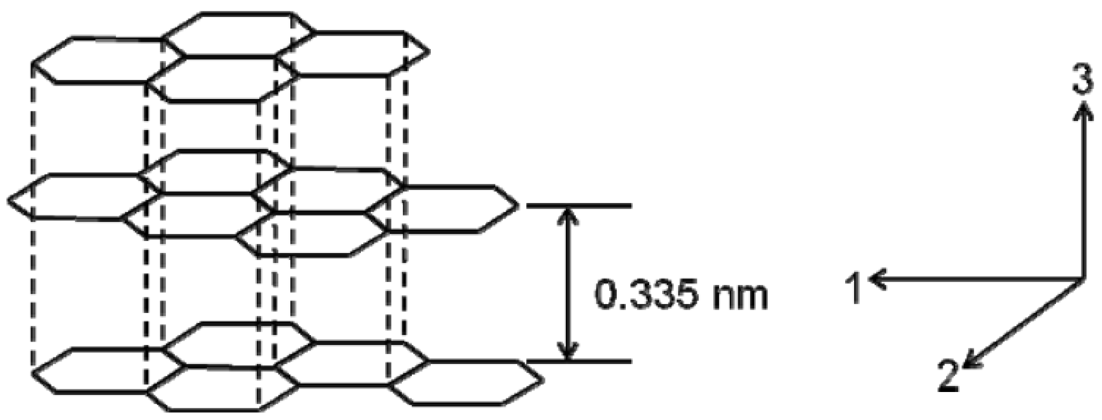

Figure 2.3 : Structure of graphitic crystals and crystal directions [2].

However, CFs can be also in hybrid or turbostratic which is two dimensional structure as well as graphitic one. In graphitic hexagonal periodicity, graphene sheets are arranged in parallel to each other in an orderly manner. The atoms in a sheet are covalently bonded each other via sp^2 bonding, whereas there is a relatively weak Van der Waals forces between the sheets. Among the two graphene layers, d-spacing (d_{002}) is around 0,335 nm for a single graphitic crystal shown in the figure 2.3. Calculated elestic values of these crystals have been reported that C_{11} (a direction), C_{33} (c direction) and C_{44} (parallel to the planes or shear planes) are respectively 1,060 GPa, 36.5 GPa, and 4.5 GPa [2;5].

Carbon fibers have commonly turbostratic structure because of stacking parallel graphene sheets as an arbitrary displacement. In this structure, it has been stated that interplanar d-spacing may go up to 0,344 nm due to irregular stacking and presence of sp3 bonding. The interplanar spacing of CFs tends to increase at higher manufacturing temperatures compared to perfect graphite. For instance, an investigation carried out by Johnson and Watt [44] demonstrated that turbostratic crystallites have Lc (crystallite height) of at least 12 layer planes and La (crystallite width) of 6–12 nm in a PAN based CF processed at 2500°C. These crystallite parameters increase with the heat traetment temperature. In general, a perfect graphite-like crystalline order can only be sighted in pitch-based CFs and vapor grown CFs. As for turbostratic structure, it may be observed in CFs formed by other precursors like PAN. Figure 2.4, 2.5 and 2.6 demonstrate the examples of SEM (scanning electron microscope) microstructures of PAN based CFs, pitch based CFs, and rayon based CFs, respectively [2;5].

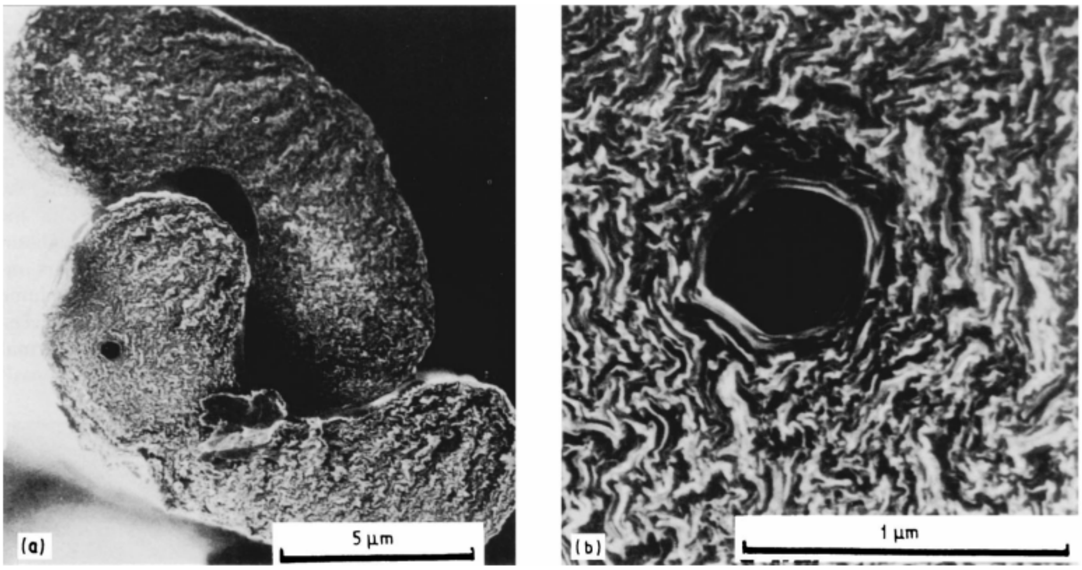

Figure 2.4 : Scanning electron micrographs of PAN based carbon fibers: (a) low and (b) high magnification [5].

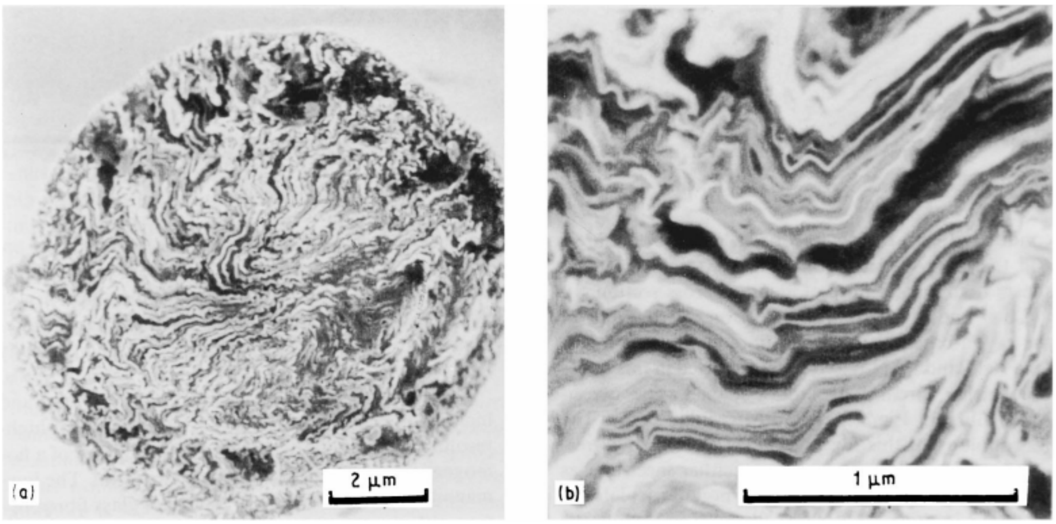

Figure 2.5 : Scanning electron micrographs of pitch based carbon fibers: (a) low and (b) high magnification [5].

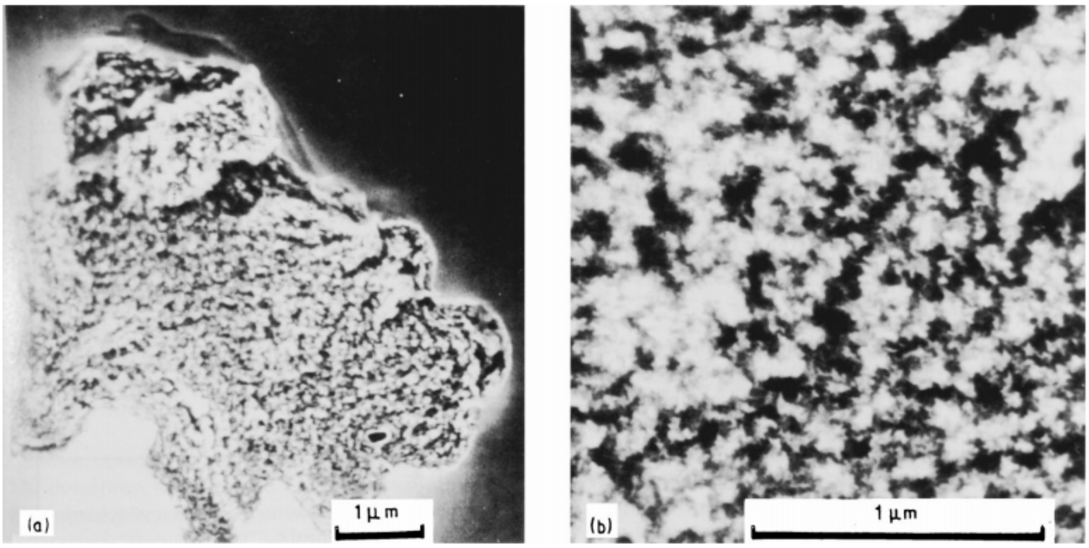

Figure 2.6 : Scanning electron micrographs of rayon based carbon fibers: (a) low and (b) high magnification [5].

The carbon fiber microstructure changes regarding the precursors and manufacturing conditions. There are a variety of representative models for microstructures have been recommended. For instance, according to Wick's model [45] the graphite sheets are arranged as parallel to the fiber direction while stacked irregularly in the transverse direction. Another study for microstructure model of CFs based on PAN based CFs. In this study, it was reported a branched microfibrillar structure in which many of the fibrils lined up in the fiber longitudinal direction. The width of these fibrils is around 10 nm [2] Several microstructures from the pitch based CFs such as radial, flat-layer and, onion-skin having transverse texture proposed by Edie et al. [46]. These microstructures are given in figure 2.7.

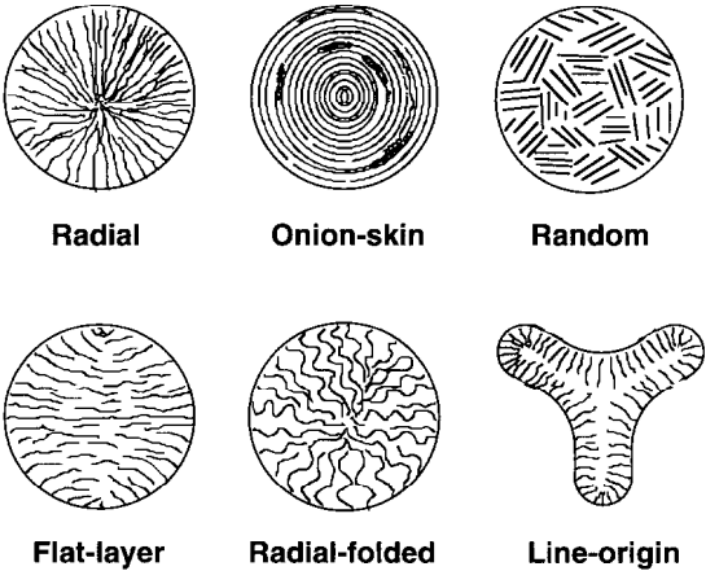

Figure 2.7 : Microstructures of pitch based carbon fibers [46].

Noted that fiber properties is directly associated with microstructure of fibers. CFs have high electrical and thermal conductivity through the fiber direction, since they possess high content of delocalized π electrons and graphene sheets in CFs are parallelly aligned through the fiber axis. The thermal conductivity of CFs varies within a wide range depending upon fiber precursor and fiber structure. Having highest degree orientation, especially pitch based CFs have highest value of thermal conductivity along the axis direction. It can be more than 1000 W/mK which is almost three times of copper that is one of the best metal conductor. On the other side, PAN based CFs possess lower thermal conductivity compared to pitch based CFs due to their more obvious isotropic structure. Therefore, they can only have a thermal conductivity coefficient up to 125 W/mK at room temperature. Electrical conductivity of CFs is also able to compete with metals. In general, pitch based CFs with a high orientation demonstrate a greater electrical conductivity than PAN based CFs [1-3;29;47].

Otherwise, thermal expansion coefficent of CFs measured through the longitudinal direction is quitely low and negative which is in the range of $-0.5x10^{-6}$/K and $-2.0x10^{-6}$/K at room temperature, once more due to high crystalline arrangement. These values increase slowly with a temperature rise [2;3].

In company with their low density of 1.7 – 2.0 g/cm^3 , CFs have excellent strength to weight ratio making them great candidate for many application. High modulus and strength of fibers stem from high crystallinity and great alignment of crystals in the axis direction. It should be noted that tensile strength and tensile strain decrease while elactic modulus increases. As an outstanding value, tensile strength of CFs may be around 5 GPa and over depending precursor type, processing conditions and fiber structure, and this value makes the CFs almost five times stronger than steel. Moreover, compressive strength of CFs is low because of weak Van der Waals bonding between the graphene sheets and their fibrillar structure [1-3].

Apart from all mentioned properties, CFs have high corrosion resistance, chemical and biological inertness, fatigue resistance, and nonflammability features. Also, a general reduction in their cost during the recent years makes the CFs unique and most desirable material nowadays [1;29].

2.2.3 Precursor types

As mentioned above, CFs are produced from three main precursors which are PAN (polyacrylonitrile), pitch manufactured from petroleum or coal tar, and rayon which is a cellulose based textile material. In addition, several alternative precursors for CFs have been studied over the years such as lignin, silk chitosan, eucalyptus tar pitch and synthetic polymers. Further, vapor grown CF were also produced from gaseous hydrocarbons [29].

2.2.3.1 PAN (polyacrylonitrile) based carbon fibers

Among the all commercial precursors for carbon fiber production, PAN precursor with molecular formula $[C_3H_3N]_n$ is the most favored one which has over 90% usage today.This widespread utilization of PAN is owing to being most suitable precursor to obtain high performance CFs (in comparison with pitch or rayon) with its higher melting point and greater carbon yield which is over 50% of the initial precursor mass. Having the greatest tensile strength and a wide range of elastic modulus compared to other precursor based CFs, PAN based CFs can also be fabricated in a variety of tows. Considering the processing and purifying the pitch precursor to form fiber, they are more expensive than fiber produced from PAN precursor. PAN with relatively high carbon yield can be provided that a thermally stable, highly oriented molecular order in a low heat treatment temperature. Additionally, PAN precursor has fast pyrolysis rate without evolving its main structure [1-3;48]. Its molecular structure were given in figure 2.8.

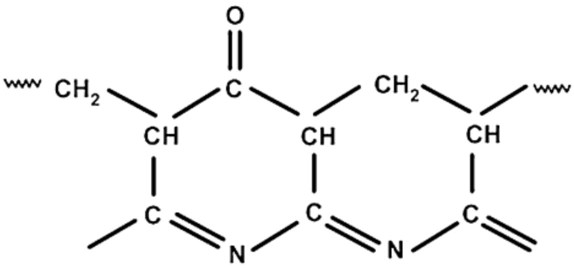

Figure 2.8 : The molecular structure of PAN [48].

In particular, the studies in recent years demonstrate that PAN based CFs have been extensively used in a wide range of areas including textile industry, composite technology, and other structural applications [48].

Processing conditions of PAN precursor to obtain CFs have a few steps listed in table 2.3.

Table 2.4: Processing steps of PAN precursor [49].

Processing steps of PAN precursor
• Polymerization of PAN
• Spinning of fibers
• Thermal stabilization
• Carbonization
• Graphitization
• Surface treatment

Regarding this, initially, acrylonitrile plastic powder is combined with another plastic in which methyl acrylate or methyl methacrylate are generally utilized. After, they are reacted with a catalyst by the addition polymerization method through suspension or solution polymerisation process to compose a PAN plastic.

Subsequently, the plastic formed is spun into fibers by a few methods. In one of these methods, the plastic is combined with spesific chemicals and pumped through tiny jets into a chemical bath or quench chamber in which the plastic condences and solidifes into fibers. Further method, the plastic mix is heated and pumped through tiny jets into a chamber in which the solvents evaporate and a solid fiber forms in time. The spinning is crucial, since the internal atomic structure of the fiber is taken shape during this step. Thereafter, the fibers are washed and stretched to obtain the requested fiber diameter. The stretching process ensures the proper alignment of the molecules within the fiber, and the formation of the tightly bonded carbon crystals after carbonization step.

Following the spinning, the chemical structure of fibers have to be transformed from their linear atomic bonding to a ladder bonding that is thermally more stable in advance of carbonization process. This process named as thermal stabilization is carried out by heating the fibers in air up to around 200–300°C for 30–120 min. With this treatment, the fibers gather up oxygen molecules from the air and regulate their atomic bonding model again. The chemical reactions in thermal stabilization are complicated and include many steps in which some of them take place simultaneously. In addition, a temperature rise occurs due to these chemical reactions, and it have to be controlled to prevent overheating of the fibers.

Subsequent to thermal stabilization step, the fibers are heated to ≈1000–3000°C for certain minutes in a furnace containing a gas mixture through carbonization and graphitization process. The mixture must be without oxygen in terms of avoiding the fibers from burning in high temperatures. Also, the gas pressure inside the furnace must be higher than the outside air pressure, and the inlet and outlet zones of fibers to furnace must be isolated to prevent oxygen entrance. Heating the fibers provides the loss of their noncarbon atoms as well as a few carbon atoms in a variety of gases form which are water vapour, ammonia, carbon monoxide, carbon dioxide, hydrogen, and nitrogen. After the noncarbon atoms are removed, tightly bonded carbon crystals occur and these crystals have a more or less parallel alignment through the axis direction of the fiber. Apart from the all these, the process named as carbonization occurs around 1000-1500°C in which carbon yield is between 50% and 55%, and circular structure of the fiber is provided. Also, a significant amount of gases products is expelled. As for graphitization, it is carried out at higher temperatures that is up to 3000°C. At the end of this process, the carbon yield of the fiber is over 99% and tensile modulus of the fiber is also increased.

In the sequel of carbonization and graphitization processes, the surface properties of fibers are not well to bond with other materials utilized in composite structure. To fill this deficiency and obtain better fiber surface in terms of bonding properties, their surface is oxidized slightly. The oxygen atoms added to the surface with oxidation maintains better chemical bonding and also etches and roughens the surface for better mechanical bonding. This process is carried out by exposing the fibers in gases or liquid products such as; air, carbon dioxide, ozone, sodium hypochlorite, nitric acid. The fibers may also be coated by electrolytically to make the fibers the positive terminal in a bath contaning several electrically conductive materials. In the surface treatment, the process should be carefully perfomed to prevent the fiber from surface defects such as pits which could induce fiber failure.

CFs produced at the end of several steps mentioned above are often coated to utilize in composites. With this coating process, the better interaction between the fiber surface and the matrix and, also the protection the CFs from a damage during winding or weaving are provided. This coating process called sizing are performed by using compatible coating materials including epoxy, polyester, nylon, urethane, and others [3;29;48;49].

2.2.3.2 Pitch based carbon fibers

There are two kinds of pitch used for fiber production which are natural pitch and synthetic pitch. Natural pitch is obtained from petroleum and coal tar comprised of fused aromatic rings. In general, although coal pitch have more aromatic rings than petroleum, petroleum pitch is utilized more, because coal pitch having a high carbon particle content induces filament breakage in due course of extrusion and thermal tretament. Pitch precursors can be made up of higher than 80% carbon and its composition changes depending on source and processing conditions. Natural pitch precursors are optically divided into two categories as isotropic and anisotropic that is also known as mesophase pitch.

Pitch precursor has several advantages such as having lower material cost, higher char yield, higher degree of orientation compared to PAN. Pitch based fibers with graphite-like structure (Figure 2.9) due to great degree of orientation possess higher elastic modulus and better thermal and electrical properties throughout the fiber direction. But, especially some processing steps including pitch purification, mesophase formation and fiber spinning cause considerably cost increase to obtain high performance CFs.

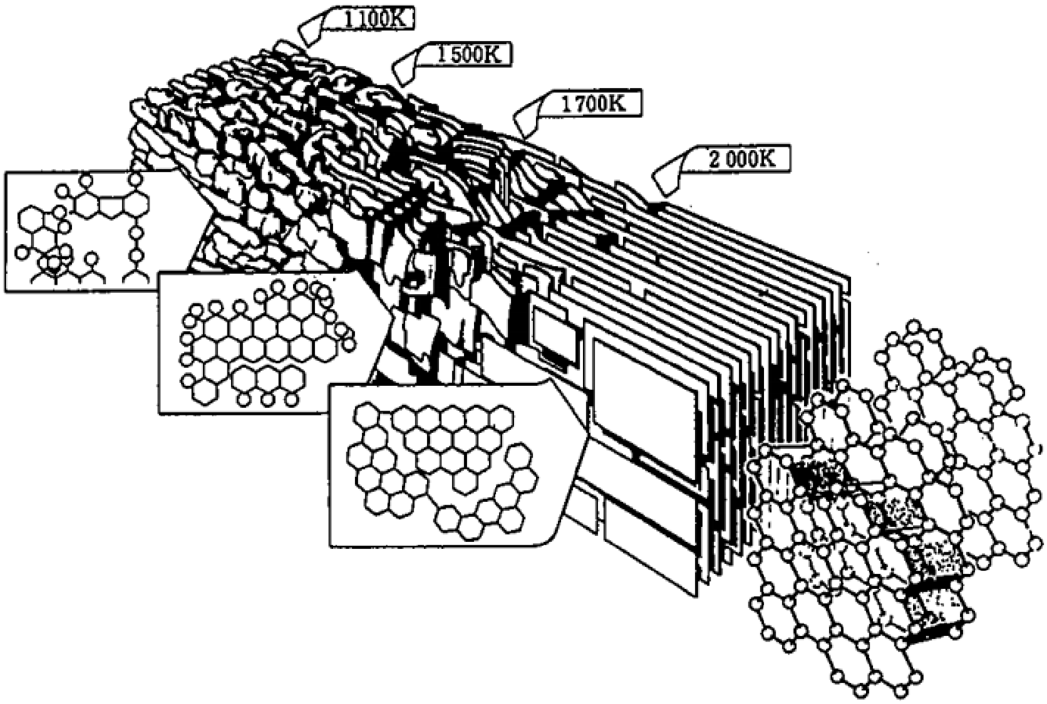

Figure 2.9 : A representation of a change from mesophase to graphite-like structure in carbonization and graphization steps [47].

Both isotropic and anisotropic (mesophase) pitches are utilized in CF production. Isotropic pitches which are petroleum and coal tar are used to produce low elastic modulus and low strength for general purpose with low cost. However, the mesophase pitches are commonly preferred to achieve high performance fibers. Having a significant amount of anisotropic phase (liquid crystalline phase) and a istropic phase, mesophase pitch is obtained by the pyrolysis of petroleum or coal tar pitch in which they are heated at 350–500 °C in an inert atmosphere. Then, they are needed to be subjected to the given temperatures for hours or even days to achieve requested amount of mesophase.

The production of CFs from the pitch precursors have some differences as well as similarities considering the processing of PAN. Among these, the pitch preparation step is the foremost. In this operation before spinning, pitches used are subjected to purification process to eliminate the impiruties. Because these impiruties cause a decrease in tensile strength of CFs produced. Besides, thermoplastic pitch is transformed to a thermoset form during stabilization to be undergone high temperature carbonization process. Table 2.4 demonstrates the list of production steps of CFs from pitch precursor.

Table 2.5 : Processing steps of pitch precursor [29].

Processing steps of pitch precursor
• Pitch preparation • Spinning • Thermosetting • Carbonization • Graphitization • Surface treatment

Furthermore, the synthetic pitches have been drawn an high interest during the recent years. As these pitches have a higher purity and also stabilization process of them can take place faster at a determinated temperature [2;29;47].

2.2.3.3 Rayon based carbon fibers

Cellulose based materials including rayon, cotton, flax, sisal, and linen are also used in CF production. Among these cellulosic materials, rayon has been predominantly utilized and investigated for commercial applications. Several types of rayon for fibers are available. However, highly polymerized viscose rayon is the most suitable one given molecular structure in figure 2.10.

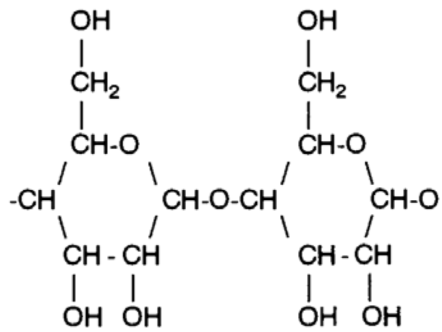

Figure 2.10 : The molecular structure of viscose rayon [3].

It can be seen that molecular structure of rayon having chemical formula $(C_6H_{10}O_5)_n$ has many heteroatoms (O and H) which must be expelled. Furthermore, many carbon atoms are lost due to the formation of volatile carbon oxides during pyrolysis. After all, the total weight loss reach up to ~70% in the thermal decomposition step and, carbon yield for rayon based CFs are only between 10% and 30%. Besides, the processing cost of them are high and physical properties are limited. Accordingly, the utilization of rayon based CFs are commercially limited.

The processing steps of rayon to obtain CFs is similar to PAN and pitch precursor. They have three main step which are;

- Low temperature decomposition/oxidation
- Carbonization
- Graphitization

Elastic modulus of rayon based CFs can be higher than 500 GPa with a medium tensile strength of about 2.5 GPa [2;3;29].

3. EXPERIMENTAL STUDIES

3.1 Materials

Within the scope of this thesis, PAN based CFs, alumina (Al_2O_3) powder and, epoxy based polymer resin materials were utilized to produce carbon based heating element. Among these materials, the main material is the carbon fiber (Figure 3.1). Each CF filament contains a sheaf of individual fiber in which total number of this fiber is approximately 12000. CF filaments utilized were commercially supplied from DowAksa(Turkey). Having a superior elastic modulus and strength, CF is also both thermally and electrically great conductor and a non-flammable material as mentioned before.

Figure 3.1 : The carbon fibers.

Epoxy resin as a thermoset polymer have been extensively used in various application including coatings, adhesives, sealants, insulation materials in power equipment and heavy apparatus, encapsulation of electronic circuit elements and a matrix resin for composites, under favour of their perfect electrical insulation properties, beneficial heat and chemical stability, and suitable manufacturing process [50]. Epoxy resin used in the scope of the thesis was purchased from Akkim Chemistry Inc. İzmir Turkey. This resin is a milky water-based polymer emulsion.

Alumina is the one of the refractory materials which are capable to retain the heat directed to them. They also accumulate and withstand to high temperatures. Besides, alumina has lower cost compare to other important refractory materials such as MgO, BeO, adn ZrO_2 [51]. Because of these, alumina was chosen as a coating material for heat retention in the scope of this thesis and the alumina powder used in this study, which have a purity over 99% and have a particle size 50 µm in the range of 65-80% and <45µm in the range of 10-25%, was supplied from Eti Alüminyum A.Ş. It must also be noted that this alumina powder used is a residuum obtained from production of aluminum. Consequently, by depositing Al_2O_3/epoxy films on CFs to produce fabric based plain heaters, a residual material was employed – with an environmental friendly approach – as a functional additive in a composite material.

3.2 Method

3.2.1 Design and application of carbon fiber coating equipment

In the scope of this thesis, a CF coating equipment (Figure 3.2) was designed. CF coating process was carried out by using this equipment.

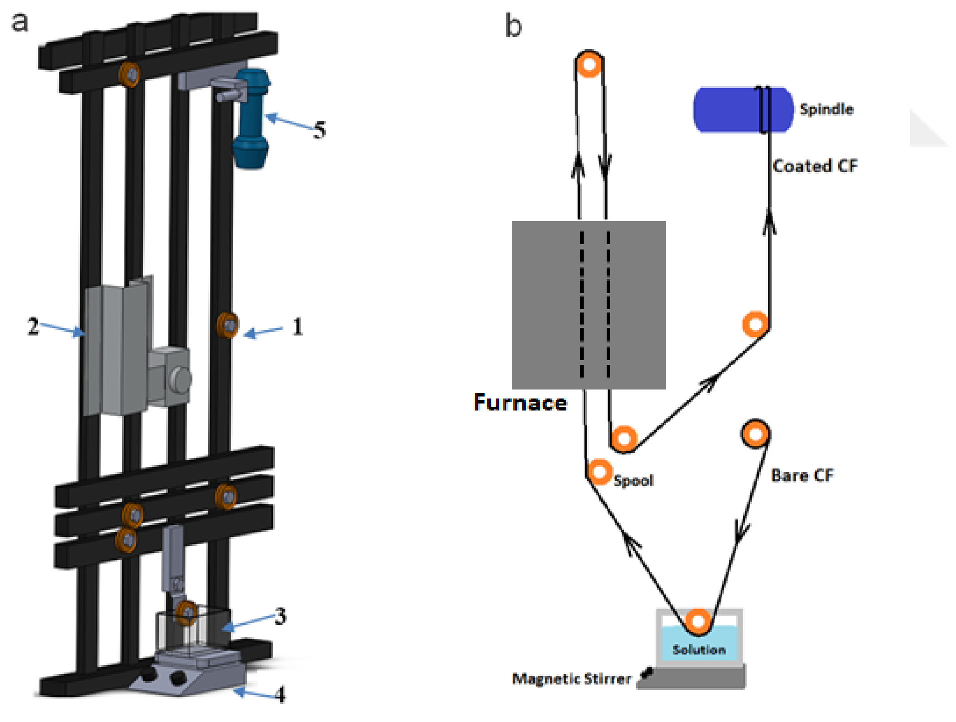

Figure 3.2 : a) The carbon fiber coating equipment **b)** The schematic representation of the coating process.

In this coating equipment, spools (1) were used for movement of CFs. CFs were firstly applied on the left spool, then all CFs were put on the other spools. A furnace

(2) was put on the equipment for drying and curing of a coating solution. The coating solution (3) was prepared in different ratios of alumina powder and epoxy resin material, then was placed on the magnetic stirrer (4). The magnetic stirrer helps to stir the solution by created magnetic field. The final spool (5) is the spindle which is utilized in rolling CFs coated with epoxy and alumina powder (E/A-CF).

3.2.2 Coating application

Subsequent to the coating equipment design, the preparation of the coating process was started. The half of the first spool was positioned the way that into the coating solution. Coating solutions were prepared with four different ratios and these ratios were given in table 3.1. The epoxy resin used in each coating solution was 500 g. Initial application was done with pure epoxy resin without alumina powder and then 1%, 5%, 10 % ratios of alumina powder (Al_2O_3) was added into the epoxy, respectively. Subsequently, the furnace was heated up around 210°C and the speed adjustment (~0.06 m/s) was done. Later, the coating process was begun. Firstly, CFs on the first spool were immersed into the coating solution then move through the furnace for drying. The coating process was repeated for each solution as listed in table 3.1.

Table 3.1 : The ratios of coating solutions.

Solutions	Weight of Al_2O_3 (g)
E/A_0	0
E/A_1	5
E/A_5	25
E/A_{10}	50

3.3 Characterization of Samples

3.3.1 Morphological, structural and thermal characterization

Several characterization methods were carried out to investigate morphological and structural properties of samples prepared by coating before and after the coating process. X-Ray Diffraction (XRD) and Scanning electron microscopy (SEM) analyses were done on the alumina powder (Al_2O_3). SEM and XRD analyses were also done on the coated CFs. Additionally, Thermal Gravimetric Analysis (TGA) was used to determine the structural degradation temperature of bare CFs.

3.3.1.1 X-Ray diffraction (XRD)

X-Ray Diffraction analysis is a common analytical technique used in determining structural phases of materials for all kinds of materials such as powders and crystals. Also, XRD can provide information about the unit cell determination of materials so crystallite structures can determine. XRD analysis depends on constructive interference X-Rays and crystalline sample [52].

The crystallinity and phase structure of the samples were characterized via X-Ray diffractometer (Thermo Scientific ARL K-Alpha) Cu-Kα irradiation (λ = 1.54 Å) scanning between 2θ of 10° and 70°. These analyses were performed by a scanning speed 0.1 and during 600 seconds.

3.3.1.2 Scanning electron microscopy (SEM)

Scanning Electron Microscopy (SEM) is a one of the basic types of electron microscopes which is a powerful method for the investigation of surface structures of materials. The specimens desired to observe can be displayed in various magnification in the range of 10 and 100000 times depending on the instrument utilized. In brief, SEM generates an image by means of signals created via a high-energy beam of electrons passing through the specimen. The types of signals produced by the SEM is made up of secondary electrons (SE), back-scattered electrons (BSE) and characteristic X-rays which provides the viewer the impression of three dimensions [11;53].

In the scope of this thesis, the microstructural observation of alumina powder and CF samples (bare CF, E/A_0-CF, E/A_1-CF, E/A_5-CF and E/A_{10}-CF) were carried out by using the Zeiss Sigma 300 VP instrument operating at a few accelerating voltage with several magnifications. EDS (Energy Dispersive Spectroscopy) analysis which is a method of SEM providing chemical elemental composition of materials was also done to obtain chemical elemental composition of coated CF samples.

3.3.1.3 Thermal gravimetric analysis (TGA)

TGA is a commonly used technique in determining thermal behaviour of materials. In this technique as a principle, the mass of the specimen analyzed is monitored against time or temperature while the temperature of the specimen is programmed.

The thermal data obtained via a software program as a plot of mass loss or percent loss versus time or temperature can be used in interpretting thermal behaviour of the given material [11].

The thermal analysis of the bare CF was studied under N_2 flowing with the help of Perkin Elmer STA 8000 instrument in order to obtain information about the thermal behaviors of the it. Thermal data were analyzed using a software program supplied with the instruments. In this experiment, heating regime was regulated as 10 °C/min from 25 ^{o}C to 1000 °C under nitrogen atmosphere.

3.3.2 Electrical properties

The CF as a main component of this thesis are considered to be resistive heating element. For this reason, the resistance of the CF have crucial importance. As mentioned before, the resistance of the heating element is proportional to its length so the resistance values of CF are associated with length of fiber used as a heating element. So as to determine this relationship, the resistance measurements of CF with various lengths of fiber in the range of 10 cm and 100 cm with 10 cm intervals (10, 20, 30, 40, 50, 60, 70, 80, 90, and 100 cm) were carried out using a multimeter.

3.3.3 Heating properties

Surface temperature and heat retention of a heating element are two main significant factors in achieving effective heating. In this direction, The heating behaviors of coated CF samples were characterized using the experimental setup depicted in figure 3.3 containing a thermal camera (Santech ST-980 80x80 pixels) and a 60-V DC electrical power supply (Sunline PS 605D). All prepared samples (bare CF, E/A_0-CF, E/A_1-CF, E/A_5-CF and E/A_{10}-CF) were connected to the electrical power supply with a connector, and the temperature distributions and variations on the samples were monitored using the thermal camera.

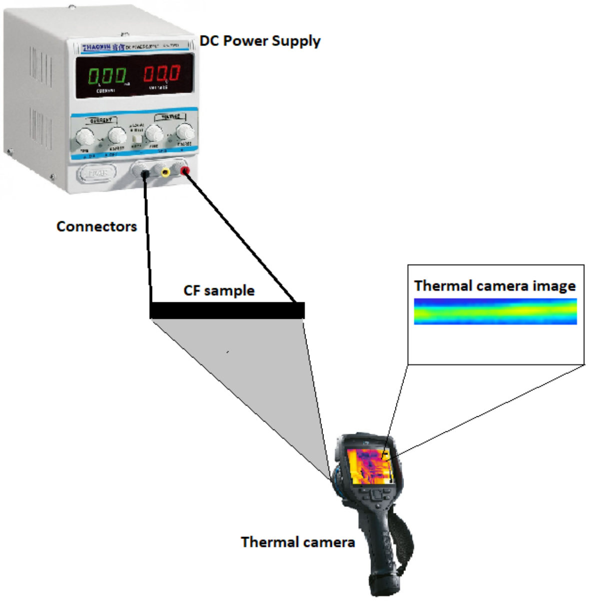

Figure 3.3 : The schematic illustration of the experimental setup.

On the point of determining the heating potential of the bare CF, a sample of bare CF with 20 cm length were used to measure maximum service temperature at the end of 10 minutes. This experiment was performed under several voltage values between 1.2 and 20.4 with 1.2 intervals. Temperature changes against time for each test were recorded via thermal camera and then the obtained values were plotted to present and interpret the heating characteristics of the bare CF.

Following this, another experiment was carried out in order to evaulate and compare each other the heating performances of the coated CF samples. According to former results obtained from the investigation heating potential of the bare CF, three potential values and once again 10 minutes as voltage and time parameters were chosen. Each sample (E/A_0-CF, E/A_1-CF, E/A_5-CF and E/A_{10}-CF) was placed to the experimental setup, respectively and all measurements during the experiment were recorded. Besides, so as to observe heat retention potential of samples especially for Al_2O_3 coated ones alongside maximum service temperature, temperature measurements against time after the power interruption at the end of 10 minutes were continued via the thermal camera until the temperature of the sample used dropped to room temperature.

3.3.4 Thermal aging properties

Long term thermal aging (LTTA) properties for materials have been introduced by UL (Underwriters Laboratories) with Polymer Variation Test Method Program (PV Standards). One of the these standarts is UL 746B which provides accelerated aging and life projections of materials.

Thermal performance of a material are affected by severel conditions such as creep, thermal softening and failure (change in appearance, weight, dimension, or other properties including electrical, thermal, physical, etc.). therefore, a relative thermal index (RTI), which is a indicator for the material's ability to retain a particular property (thermal, electrical, etc.) when exposed to elevated temperatures for an extended period of time, is established for certain property of a material [54-56].

UL 746B standard for the thermal aging characteristic of material depends on the Arrhenius equation. According to this equation (equation 3.1), material properties such as tensile and elongation of the polymer insulation change with time and temperature in parallel with a reaction rate (K).

$$K = A\exp(-E/RT) \tag{3.1}$$

in which

K = specific reaction rate
A = constant
E = activation energy of the reaction
R = gas constant
T = temperature

By taking the natural log of both sides, the equation becomes,

$$\log(time) = \text{constant} + (1/2.303) * (\text{E/RT}) \tag{3.2}$$

or

$$\log(time) = a + b/T \tag{3.3}$$

Hence, log(time) becomes a linear relationship with temperature. Thus, this equation can be utilized to project thermal aging properties of a material at a longer time with obtained experimental results over short periods [54-56].

The approach utilized to project thermal aging properties of CF depends on certain increase in resistance with time and temperature. In this context, the thermal aging properties of CF were analyzed utilizing a thermal aging setup (Figure 3.4) which is made up of a multimeter, a heating oven, a computer, and CF filaments by referring UL 746B standard [55].

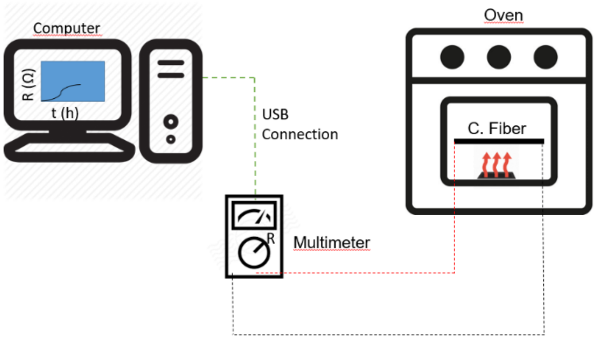

Figure 3.4 : The thermal aging setup of CF.

Within scope of the UL 746B standard, the requirement of at least three different temperatures which must be lower than structural degradation temperature of the material used is stated. Therefore, temperature values will be operated were determined with regard to TGA results of the CF. Following this, the initial resistance (R_i) of identical three CF filaments with a 100 cm length were measured by the multimeter at ambient temperature. Later, each samples were put into the oven at three different temperatures determinated. Time for a 25% increase in resistance ($t_{1.25Ri}$) were chosen as an end point (an indicative as RTI) of the experiment for each temperature (Figure 3.5a). Finally, as addressed in the UL 746B, obtained time and temperature data were recorded and used in creating a curve of log $t_{1.25Ri}$ versus inverse temperature (1/°C) for the estimation service life-time of CF under desired temperature as shown in figure 3.5b.

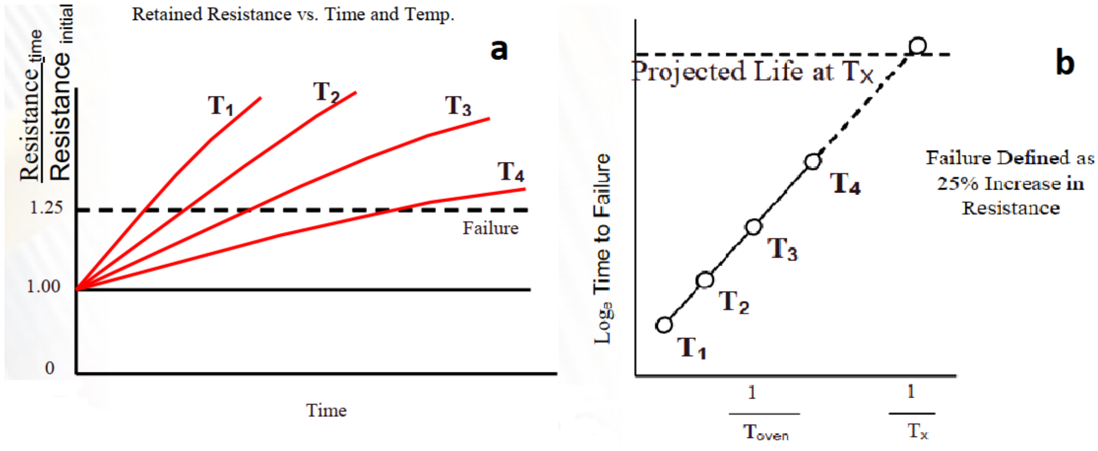

Figure 3.5 : a) The representation of time and temperature data for 25% resistance increase and **b)** a final curve of service life time ($\log t_{1.25Ri}$) versus inverse temperature by given UL 746B standard [55].

3.4 Applications

Within scope of this thesis, one of the main purposes is the application of carbon based heating elements. Based on this purpose, a prototype study as a flexible heating fabric based heating element to be used in various applications were designed with using CF filaments. This design is made up of several components including a polyester fabric, CF filaments, silver plated wires as fabric matrix, and electrical input terminal. In this context, a polyester fabric of 120x60 cm dimensions was woven by a conventional weaving process with 7 CF filaments with 107 ∓ 3cm at 7 cm intervals. CF filaments were aligned in horizontal direction, whereas the silver plated wires were vertical in order to maintain a parallel resistance circuit. A schematic representation of this design and an image of the final product with components were shown in figure 3.6. Furthermore, alumina coated polyester fabric were also produced so as to increase heating performance of the heating element. The coating ratio of alumina on polyester fabric were determined according to best performance among the E/A_1-CF, E/A_5-CF and E/A_{10}-CF samples.

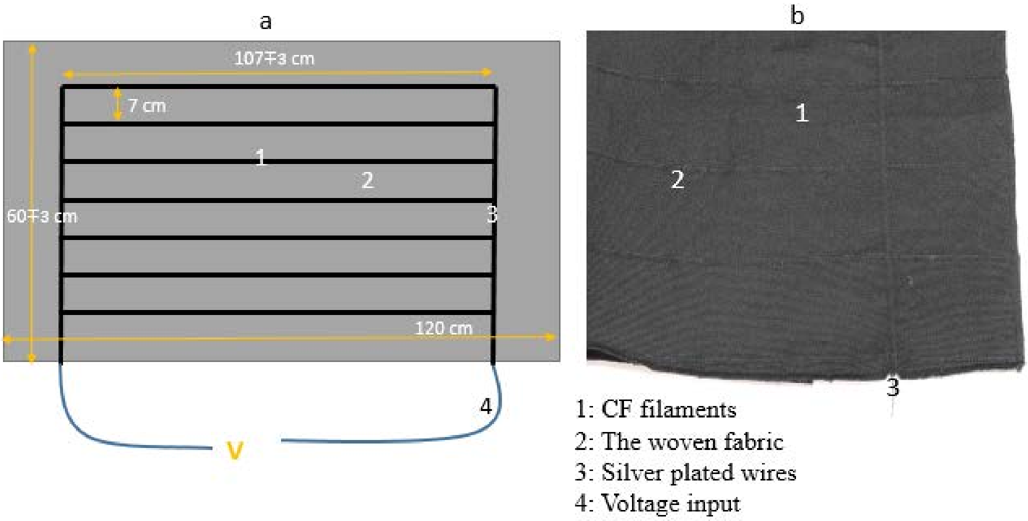

Figure 3.6 : a) The schematic representation of the desing of woven fabric based heating element **b)** The image of final product of woven fabric.

Subsequent to design and fabrication of heating fabrics, heating behaviors of the fabrics were evaulated. Therefore, an experimental setup given in figure 3.7 were established including the samples, a electrical power supply with a connector, and a thermal camera (Santech ST-980 80x80 pixels) to monitor the temperature distributions and variations on the samples. Following this, the uncoated and coated samples were respectively connected to the electrical power supply under constant potential value. Each sample at room temperature were heated at this certain potential for 30 minutes and obtained temperature values with correponding time values were recorded via the thermal camera. After, the electrical power were interrupted but recording the temperature and time values were continued until the temperature of the samples dropped the room temperature so as to observe heat retention perfomance of each sample. All obtained values were plotted to present and interpret the heating and heat retention potential of the samples.

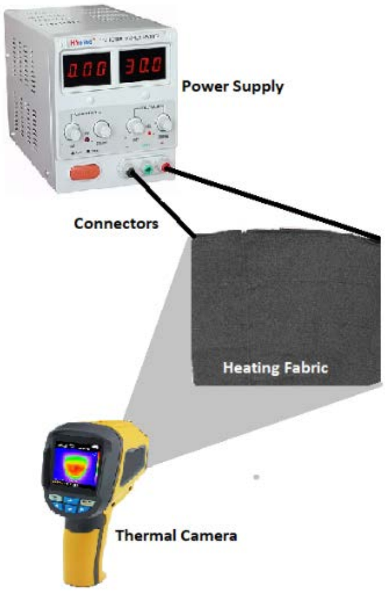

Figure 3.7 : The schematic illustration of the experimental setup.

Additionally, in the SANTEZ project (1010 STZ 2016), the fabrics that are developed without Al_2O_3/epoxy modification were employed as plain heaters on a midi-bus produced by Anadolu Isuzu Automotive Industry and Trade Inc. In the scope PhD thesis of Hayri Eren under the supervision of Volkan Kırmacı.

4. RESULTS AND DISCUSSION

4.1 Phase Analysis

Crystalline structure and phases of the samples were determined by examining the x-ray diffraction (XRD) patterns. XRD analyses were applied onto the alumina powder, bare CF and coated samples named as E/A_0-CF, E/A_1-CF, E/A_5-CF and E/A_{10}-CF, respectively.

XRD patterns of these samples were given in figure 4.1. Al_2O_3 has a structurally complex oxide which is made up of a few phases including metastable ɣ- and Ɵ-Al_2O_3 and stable α-Al_2O_3 phase. α-Al_2O_3 particles used in this study exhibit peaks at 2Ɵ angles of 25.57, 35.14, 37.76, 43.33, 46.16, 52.53, and 57.47 corresponding to the (d_{012}), (d_{104}), (d_{110}), (d_{113}), (d_{024}), and (d_{116}) spaces, respectively (JCPDS file no. 88-0826). It can be seen in the figure that these peaks indicated with 1 are responsively convenient to literature [57;58].

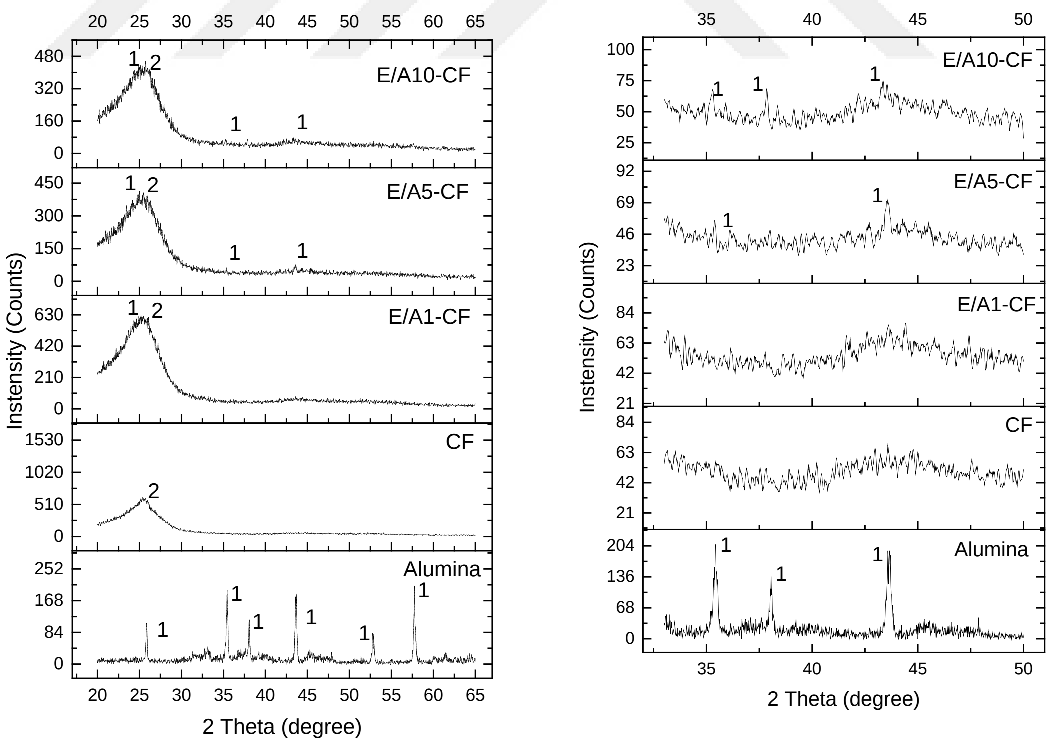

Figure 4.1 : XRD analyses of the alumina and the coated samples (E/A_0-CF, E/A_1-CF, E/A_5-CF and E/A_{10}-CF).

As for bare CF and coated samples, according to these XRD patterns, the characteristic peaks at around 25° diffraction angles marked with 2 which are assigned to disordered graphitic 002 plane belongs to the CF (JCPDS 41-1487) [4;59]. As the most significant result, it can be seen that insensities of the characteristic peaks of the alumina in the coated samples became clear with increasing coating percentage of alumina. At this point, severel peaks at 25.57°, 35.14°, 37.76°, and 43.33° indicating the existence of alumina particles were clarified with increasing alumina content. It seems to obvious these peaks especially for E/A_5-CF and E/A_{10}-CF samples because of having more alumina. Furthermore, these results are consistent with the literature [60].

4.2 Microstructure and Morphology Analysis

Microstructure which is a structure of any kind of material determined by some microscopic techniques can highly influence the physical properties of the material such as strength, toughness, ductility, hardness, corrosion or wear resistance, thermal behavior, and so on [11].

On the purpose of examine and determine the microstructures of the materials used including alumina powder and bare CF, and also the coated samples produced including E/A_0-CF, E/A_1-CF, E/A_5-CF and E/A_{10}-CF, SEM photographs at various magnifications were taken. Also, EDS (Energy Dispersive Spectroscopy) analysis was performed to obtain elemental structure and especially to observe the existence of alumina due to aluminum in coated CF samples.

Firstly, SEM images of the alumina powder and bare CF sample were given in figure 4.2 and figure 4.3, respectively. As observed from the figures, the microstructural morphology of the bare CF have a smooth surface and alumina powders possess circular-like morphology. These SEM morphologies are also convenient to the literature [30;60].

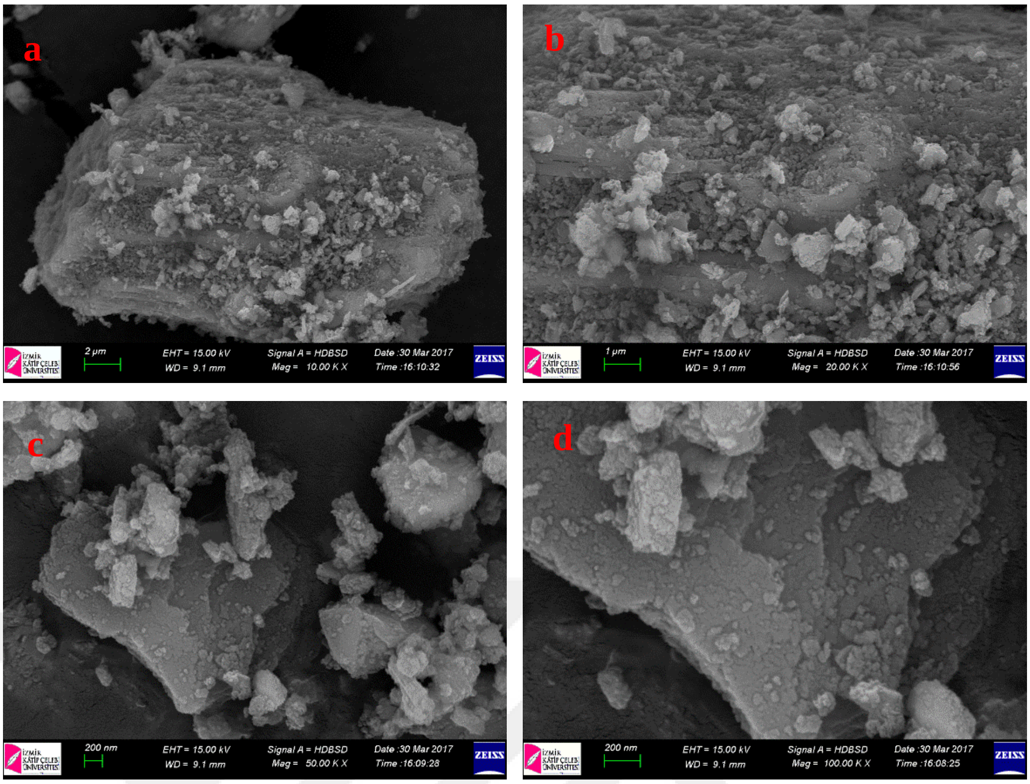

Figure 4.2 : SEM images of alumina powder in different magnifications a) 10.000X b) 20.000X c) 50.000X d) 100.000X.

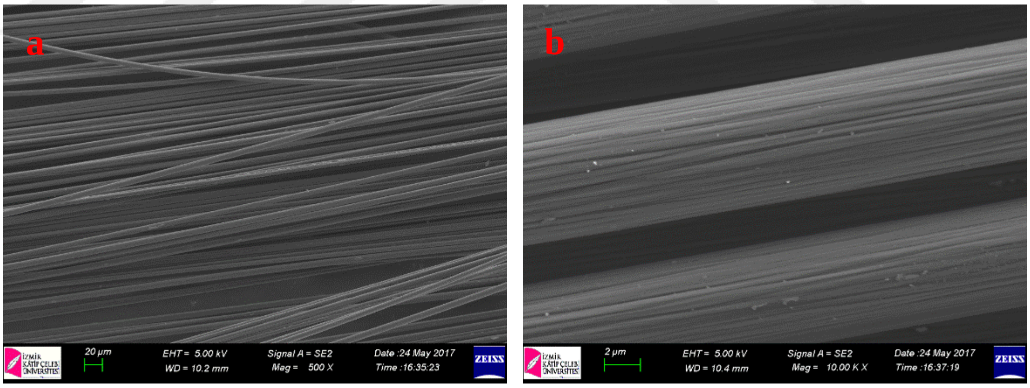

Figure 4.3 : SEM images of bare CF in a) 500 X and b) 10.000X magnifications.

After, SEM images of coated samples which are E/A_0-CF, E/A_1-CF, E/A_5-CF and E/A_{10}-CF were given in figure 4.4, 4.5, 4.6, and 4.7, respectively.

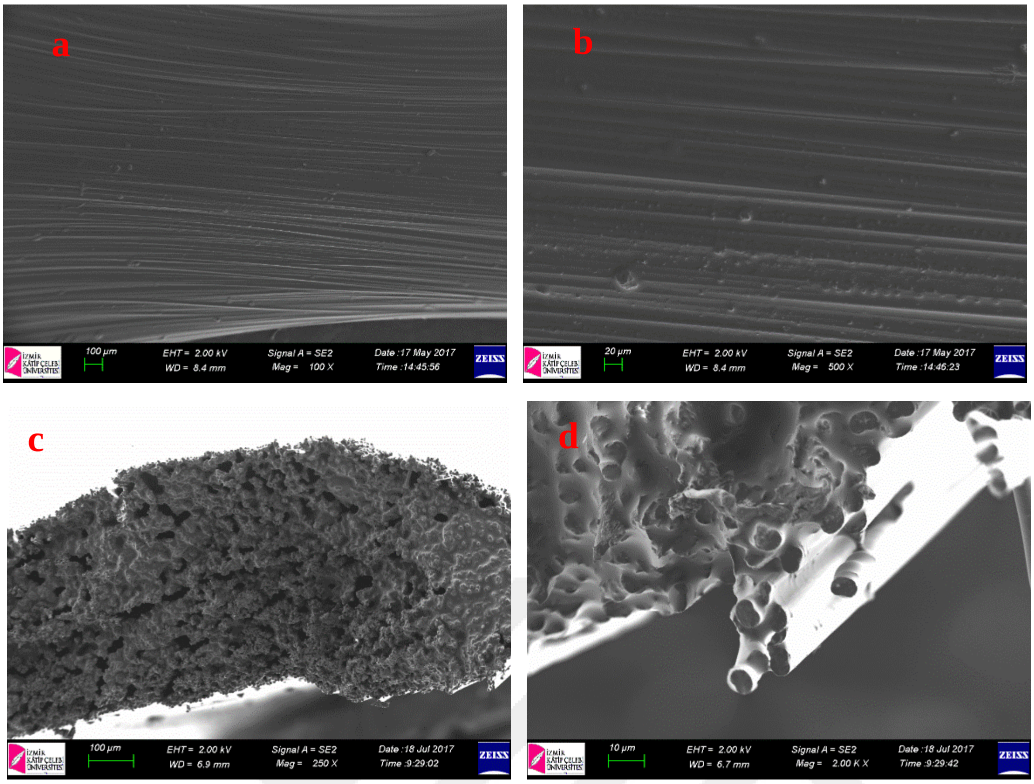

Figure 4.4 : SEM images of E/A_0-CF in several magnifications a) 100X, b) 500X, c) 250X and d) 2000X.

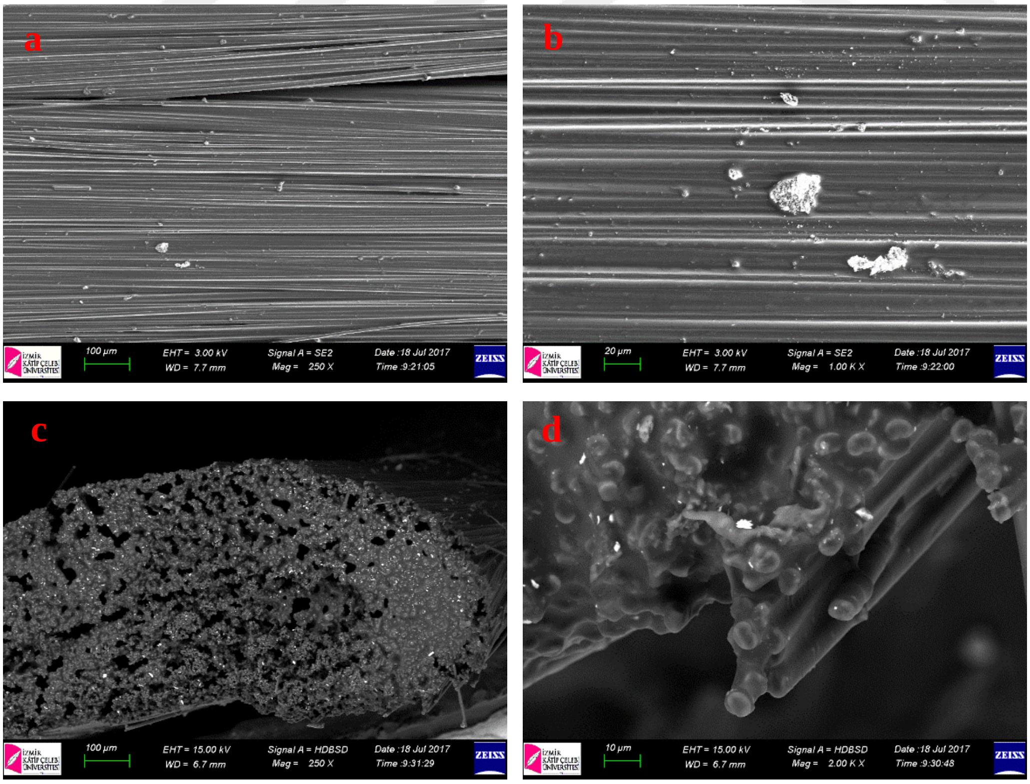

Figure 4.5 : SEM images of E/A_1-CF in several magnifications a) 250X, b) 1000X, c) 250X and d) 2.000X.

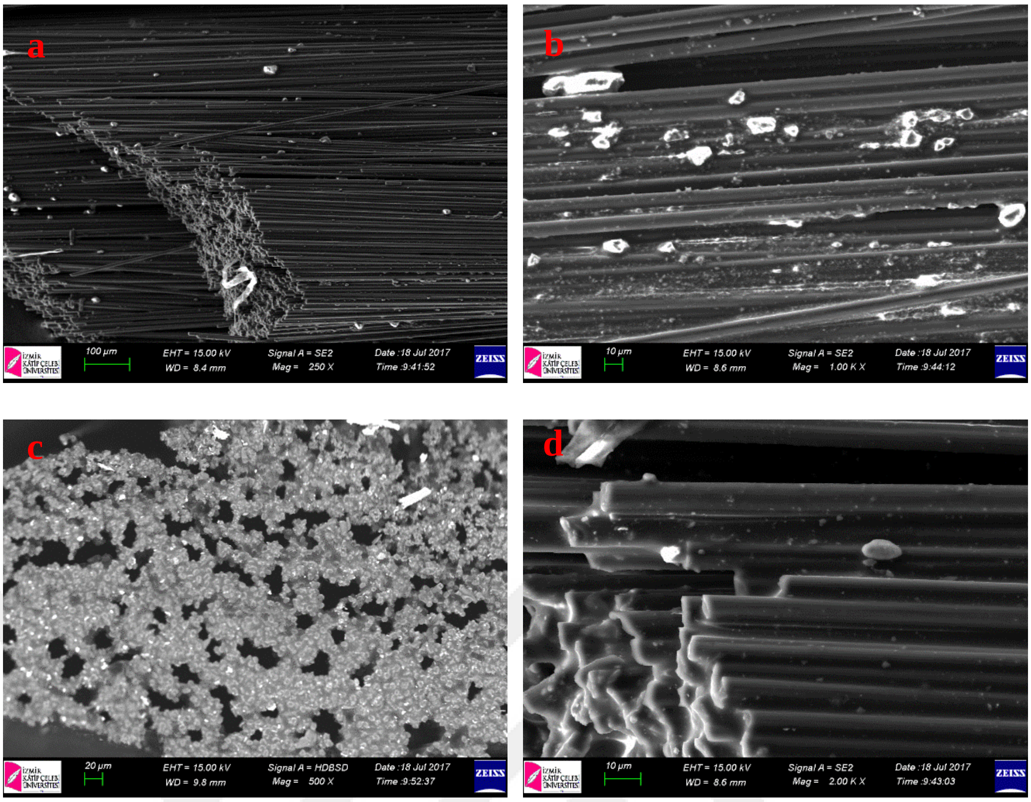

Figure 4.6 : SEM images of E/A_5-CF in several magnifications a) 250X, b) 1000X, c) 500X and d) 2000X.

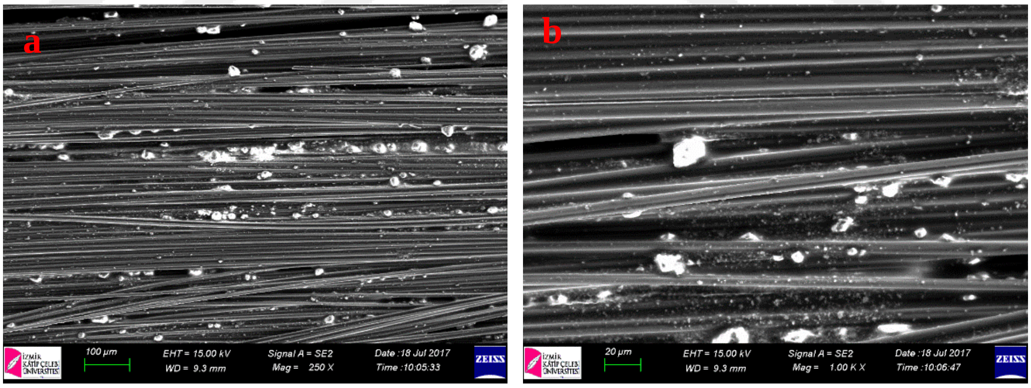

Figure 4.7 : SEM images of E/A_{10}-CF in several magnifications a) 250X, b) 1000X, c) 500X and d) 2000X.

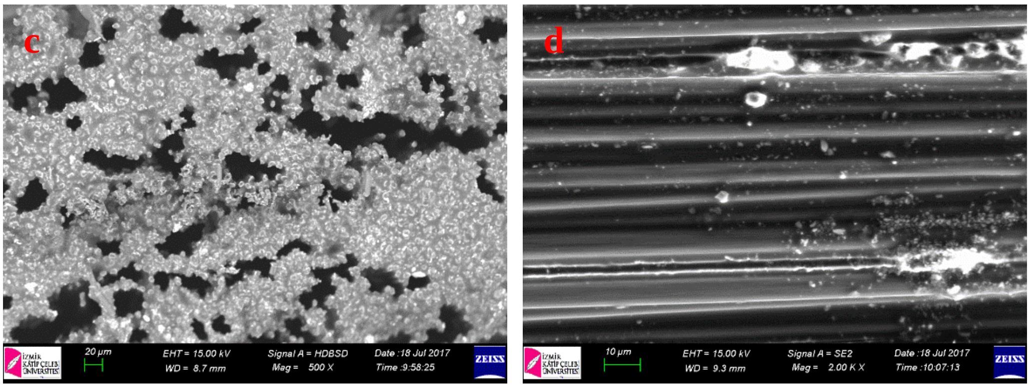

Figure 4.7 (continue) : SEM images of E/A_{10}-CF in several magnifications a) 250X, b) 1000X, c) 500X and d) 2000X.

Regarding to these images, it is clear that epoxy coating surrounding CFs with homogeneous structure for each sample was succesfully carried out and these results are compatible with the studies on epoxy coating over CF filaments in the literature [61;62]. Also, it can be seen from figure 4.5, 4.6, and 4.7, E/A_1-CF, E/A_5-CF and E/A_{10}-CF samples consist of alumina on their surfaces but E/A_5-CF and E/A_{10}-CF samples have higher quantity of alumina and their alumina dispersion on the surface are more homogeneous compare to E/A_1-CF. Additionally, E/A_0-CF sample has still smooth structure on its surface in spite of epoxy addition (Figure 4.4) to the contrary other samples. Because, the presence of alumina in E/A_1-CF, E/A_5-CF and E/A_{10}-CF samples created rough structures on their surfaces. The obtained results match with the study performed by Hsieh et al. [60] based on carbon fiber filaments decorated with alumina layer.

As for the result of EDS analyses, EDS images of E/A_1-CF, E/A_5-CF and E/A_{10}-CF samples used in determining elemental structure of the samples were given in figure 4.8. Also, obtained results with regard to these images were listed in table 4.1.

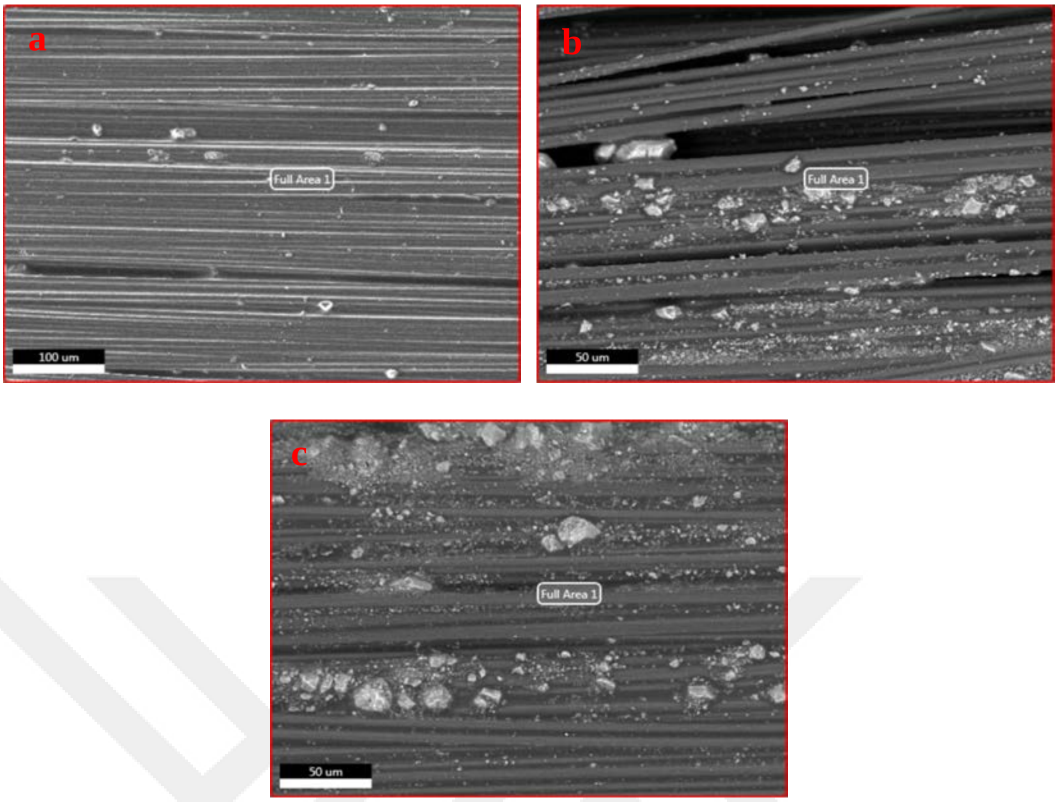

Figure 4.8 : EDS images of alumina coated CF samples a) E/A_1-CF b) E/A_5-CF c) E/A_{10}-CF.

Table 4.1 : EDS data of alumina coated CF samples.

Sample	**% Weight**		
	Carbon	Oxygen	Aluminum
E/A_1-CF	76.87	21.87	0.88
E/A_5-CF	68.33	26.09	5.58
E/A_{10}-CF	67.56	25.27	7.17

According to the table, EDS analyses confirmed the atomic composition of the samples being made of aluminum, oxygen and carbon for the three cases. The aluminum and oxygen content revealed the presence of alumina while carbon content is due to carbon fiber. Besides, as the coating ratios of alumina on CF's increase, aluminum amount also increased.

4.3 Thermal Analysis

From the TGA curve, it is possible to determine the thermal characteristics of the materials. Thermal stability of the CF was illustrated by thermo-gravimetric analysis (TGA). The TGA curve of the CF was represented in figure 4.9.

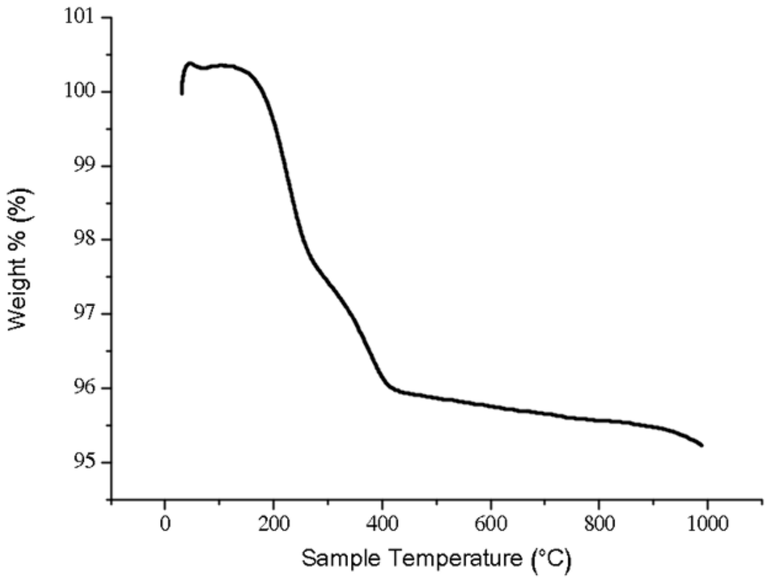

Figure 4.9 : TGA curve of the CF.

Within the scope of this analysis, as it can be seen from the curve, CF exhibits a high thermal stability in which it has maximum weight loss around 5% (residual weight 95%) even at 1000°C. Besides, considering the degredation profile, its structural degradation temperature is around 450°C. Similar TGA result of CF with the study of Farhad et al. [63] were obtained.

4.4 Electrical Properties

Electrical properties of the CF are the most important parameters for heating element and its applications. Fiber length versus resistance measurements were afforded using a multimeter. The relation between them were plotted as a curve with using obtained results and this curve was given in figure 4.10.

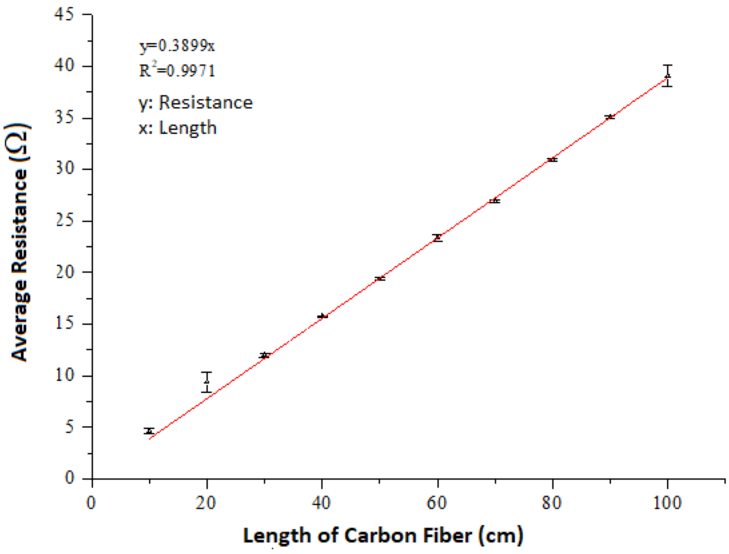

Figure 4.10 : The relation between length and resistance of the CF.

With regard to the curve, a linear function as y=0.3899x was obtained with R^2=0.9971 where x, y, and R denotes length of the CF, corresponding resistance, and mean square errors, respectively. In conclusion, as it might be understood that the resistance of the heating element is directly proportional to length so it is clear that this heating element act as a ideal resistor having linear resistance. In literature, similar linear relation between resistance and length of CF were determined by the study of Eddib and Chung [64].

4.5 Heating Performance

Heating and heat retention performance tests of the bare CF, E/A_0-CF E/A_1-CF, E/A_5-CF and E/A_{10}-CF samples were performed by using the experimental setup as mentioned previously in chapter 3.

Initially, on the purpose of investigating the heating potential of the bare CF with respect to maximum service temperature with varying potential values, the relation between maximum service temperature and potential, and also the relation between resistance of the CF sample and potential were shown on a curve by using obtained results. This curve were given in figure 4.11.

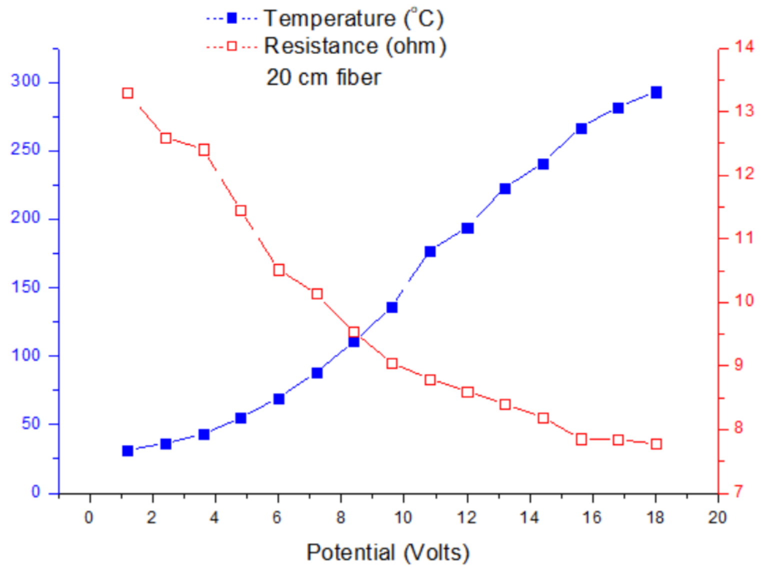

Figure 4.11 : Temperature and resistance variation of 20 cm carbon fiber with varying potential values.

As it might be seen from the figure, maximum service temperature are inversely proportional to resistance of the CF with changing potentials. In other words, as the potential increases, the service temperature increases whereas the resistance decreases. This proves that CF has a negative temperature coefficient (NTC) up to around 300°C. On the same point, it is clear that service temperature of the CF sample can reach up to approximate 300°C by adjusting suitable potential value.

Thereafter, in order to evalulate and compare of heating and heat retention performances of the coated samples (E/A_0-CF, E/A_1-CF, E/A_5-CF and E/A_{10}-CF), as previously mentioned, three potential values were chosen as 2V, 4V, and 6V with regard to obtained results from the curve in figure 4.11. Subsequently, three different charts were created for each potential value (2V, 4V, and 6V) and demonstrated in figure 4.12, figure 4.13, and figure 4.14, respectively.

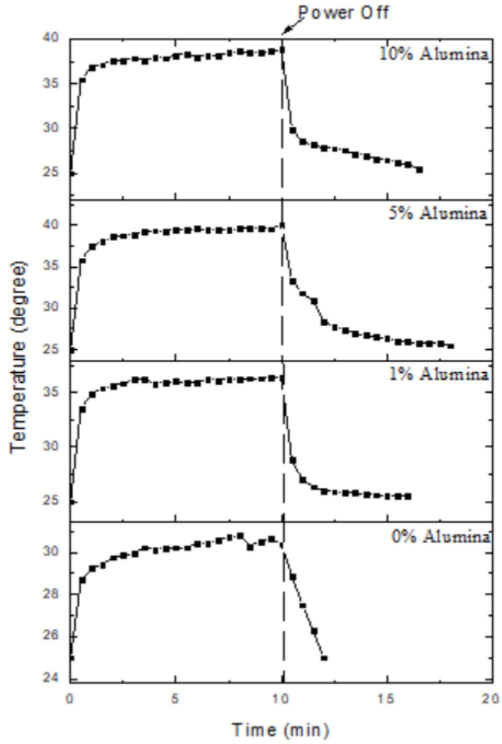

Figure 4.12 : Heating and heat retention performance of the E/A_0-CF, E/A_1-CF, E/A_5-CF and E/A_{10}-CF samples with 20 cm lengths for 2V.

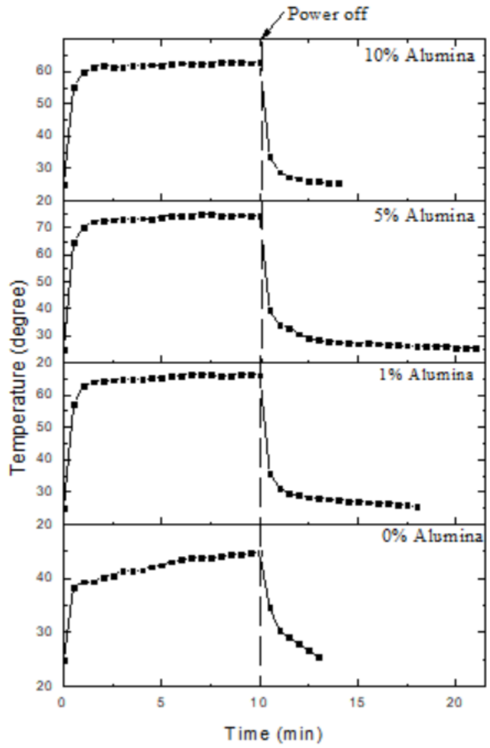

Figure 4.13 : Heating and heat retention performance of the bare CF, E/A_1-CF, E/A_5-CF and E/A_{10}-CF samples with 20 cm lengths for 4V.

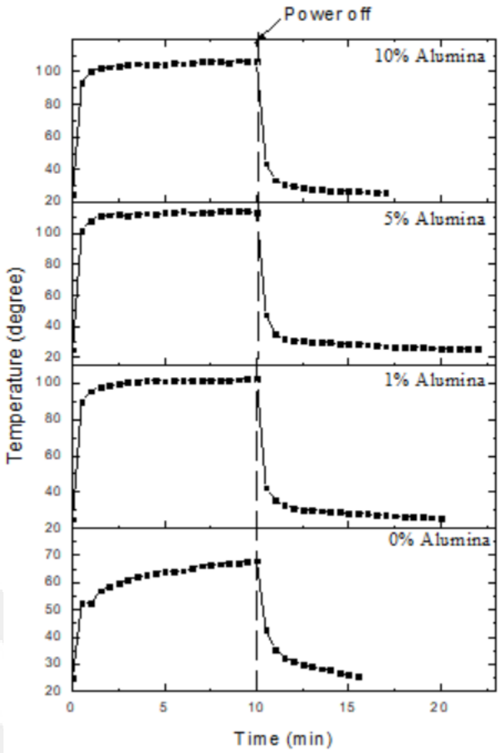

Figure 4.14 : Heating and heat retention performance of the bare CF, E/A_1-CF, E/A_5-CF and E/A_{10}-CF samples with 20 cm lengths for 6V.

In line with these results (Figure 4.12, Figure 4.13, and Figure 4.14), as the potential values increased from 2V to 6V, maximum temperatures of the samples increased with for all experiments. However, the sample without alumina (E/A_0-CF) shows lower heating potential compare to other samples consisting of alumina because its maximum temperature remained lower in all experiments. Altough maximum temperature values of the E/A_1-CF, E/A_5-CF, and E/A_{10}-CF samples at the end of 10 minutes are close to each other, E/A_5-CF reached higher temperatures so it has best heating potential.

Furthermore, as it might be understood from the all charts, the heat retention rate of E/A_0-CF sample are quite low rather than the other samples. After power interruption, its temperature decreased rapidly. On the other hand, the other samples retained heat within them for a longer time thanks to containing alumina. Nevertheless, all samples possess different heat retention rates. Among them, E/A_5-CF has best heat retention performance as such in heating potential.

In literature, similar studies related to heating and heat retention properties of carbon based materials have been reported. Hsieh et al. carried out a study on ZnO nanoparticles onto CFs forming a composite filament for infrared heater. They investigated heating rate and maximal heating temperature of CF filaments under fixed 25 V potential and reported that ZnO-coated CF heater could reach to 184 °C as the maximum temperature and its heating rate were 28 °C/min [30]. Similarly, another study based on different wear comfort properties of ZrC/graphite and Al_2O_3/graphite-embedded, heat-storage woven fabrics were examined by Hyun and Seung [65]. They also used ceramic particles onto PET filaments which were spun on the pilot spinning equipment and compared to regular PET/PA woven fabric in terms of heat storage and release properties. In sum, they reported that surface temperatures the Al_2O_3 and ZrC-embedded fabrics were greater than the regular PET/PA fabric and the heat-retention rates of the ceramic-embedded fabrics were also more than two times higher than the regular PET/PA fabric, which showed the good heat-storage and release properties of the ZrC/graphite and Al_2O_3/graphite embedded fabrics. Basic principles of these studies in terms of measured heating properties are in common with our study.

Additionally, a ($\Delta T/\Delta t$) table were formed so as to prove numerically heat retention rate of samples for all potential values. In order to calculate the heat retention by means of delta T/delta t, final temperature after power interruption were firstly substracted from maximum temperature reached after 30 minutes, then obtained value were divided by elapsed time after power interruption. Obtain results were given in table 4.2.

Table 4.2 : ($\Delta T/\Delta t$) ratios for 2V, 4V, and 6V for all samples.

Samples	***2V***	***4V***	***6V***
E/A_0-CF	2.70	6.43	7.73
E/A_1-CF	1.83	5.08	7.69
E/A_5-CF	1.80	4.47	7.35
E/A_{10}-CF	2.06	9.32	11.52

With regard to the table, the smaller values for each potential mean better heat retention performances. In this case, this values are parallel with figure 4.13, 4.14, and 4.15 as mentioned before. In that, E/A_5-CF has smaller values in all potentials which means that its heat retention potential are better than other samples.

In conclusion, taking into account all of results, E/A_5-CF is the best sample in terms of heating performance compare to other samples.

4.6 Thermal Aging Performance

Within scope of the UL 746B standard, accelerated thermal aging test was carried out using the thermal aging setup given in figure 3.3. As mentioned previously, three aging estimation temperatures, lower than the structural degradation temperature obtained through TGA, were decided as 400°C, 350°C, and 300°C. The durations for a 25% increase in resistance ($t_{1.25Ri}$) for each temperature were obtained and given in table 4.3. As it can be seen in the table, the duration for a 25% increase in resistance goes up majorly with decreasing temperature.

Table 4.3 : The duration for a 25% increase in resistance.

Temperature (°C)	400	350	300
$t_{1.25Ri}$ (h)	33	83	360

So as to evaluate the thermal aging properties of each CF sample, a curve of log $t_{1.25Ri}$ versus inverse temperature (1/°C) for the estimation aging-time of CF under different temperatures was created by using the time and the temperature data recorded up to %25 increase in resistance. Obtained curve was given in figure 4.15.

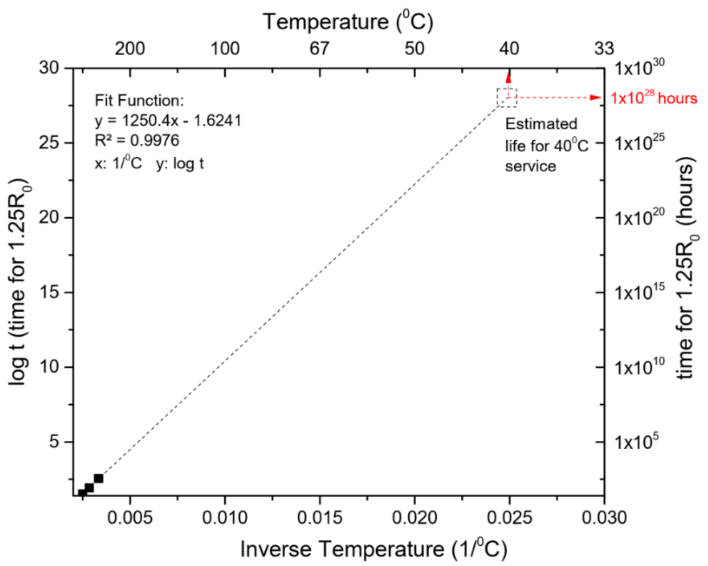

Figure 4.15 : The estimated aging-time of CFs under different temperatures.

With regard to this curve, a linear function as y=1250.4x – 1.6241 was obtained with R^2=0.9976 where x, y, and R denotes inverse temperature, log $t_{1.25Ri}$ and mean square errors, respectively. Consequently, it can be understood that the aging-time of CFs at relatively low temperatures increase extremely. By extrapolating the function, the estimated aging-time of CFs at 40°C were calculated as 10^{28} hours (1.15x10^{24} years). Furthermore, aging time of CFs are approximately between 10^{20} and 10^{30} hours in the service temperatures ranging from 30°C and 60°C desired in the scope of this thesis. Besides, the aging-time in any of service temperature for a desired application can be estimated by this function. As a result, a linear relation between temperature and aging time were obtained as stated the UL 746B standard [55;56].

4.7 Applications

On the purpose of putting into practice the CF based heating elements, two different fabric based heaters which are 5% alumina coated and uncoated were designed and tested. For the coated fabric, coating ratio of alumina were determined as 5% because E/A_5-CF sample demonstrated best heating performance compare to E/A_1-CF and E/A_{10}-CF samples. The results belonging to these heating fabrics as temperature versus time graphs with their thermal camera images against time were given in figure 4.16 and 4.17.

According to the tables, a slighly higher temperature (57.9°C) were observed in the 5% alumina coated fabric at the end of 30 minutes compare to uncoated fabric (56°C). Subsequent to the power interruption after 30 minutes, it was also observed that there is a remarkable difference in terms of heat retention between 5% alumina coated and uncoated fabrics. The temperature of uncoated fabric were decreased to around room temperature (25.8°C) within 10 minutes whereas the temperature of 5% alumina coated fabric were decreased to same temperature within 20 minutes. Thus, it might be said that 5% alumina coated fabric demonstrates significantly better heat retention potential. Likewise, its heating performance is also better. Additionally, this results mentioned can be seen from the images in the tables.

As mentioned before, a similar study including an application on heating properties of ZrC/graphite and Al_2O_3/graphite-embedded, heat-storage woven fabrics for garments has been reported by Hyun and Seung [65]. They investigated heat storage and release properties of these woven PET fabrics. They observed that both surface temperatures and heat retention rates of the Al_2O_3 and ZrC-embedded fabrics were better than regular PET/PA fabric thanks to ceramic particles and graphite as carbon based material as likely our study.

Finally, the fabrics developed in this thesis were used and tested in a midi-bus of Anadolu Isuzu Motor Company as a PhD thesis. The fabrics were applied to floor, side walls, roof and the seats of the vehicle. The performance of the fabrics were recorded through numerous thermocouples for varying outside temperatures. The comfortable heating was accomplished with at least 40 % yield, if compared to classical heating with hot water flow and heat fan based systems. Design, development and applications of fabric based plain heaters were succesfully achieved as aimed in the proposal of SANTEZ project (1010 STZ 2016) which is a combination of MSc thesis of Ahmet Yavaş and PhD thesis of Hayri Eren conducted under the supervision of Mustafa EROL and Volkan Kırmacı, respectively.

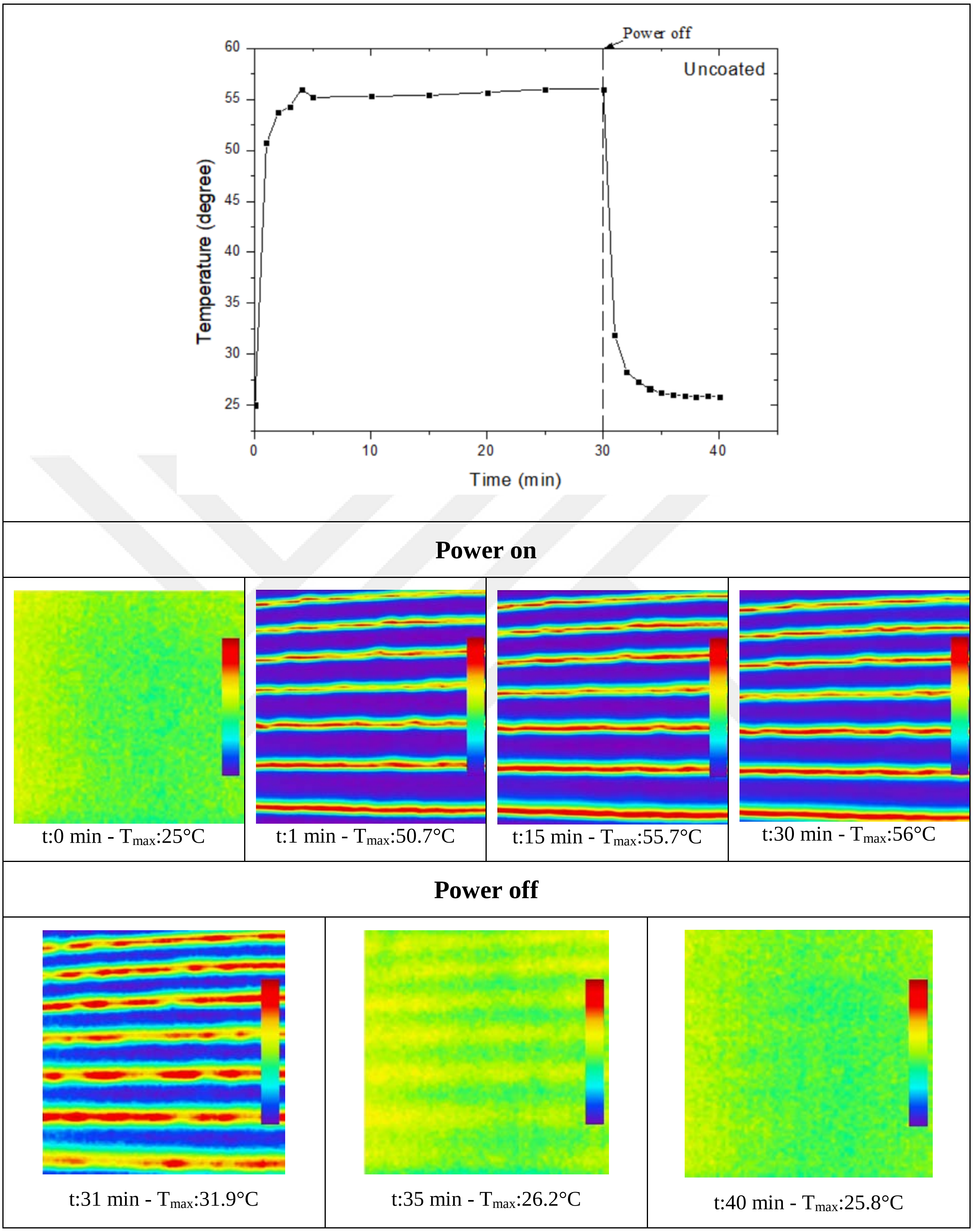

Figure 4.16 : The temperature versus time graph of uncoated fabric based heater and its thermal camera images as power on and power off.

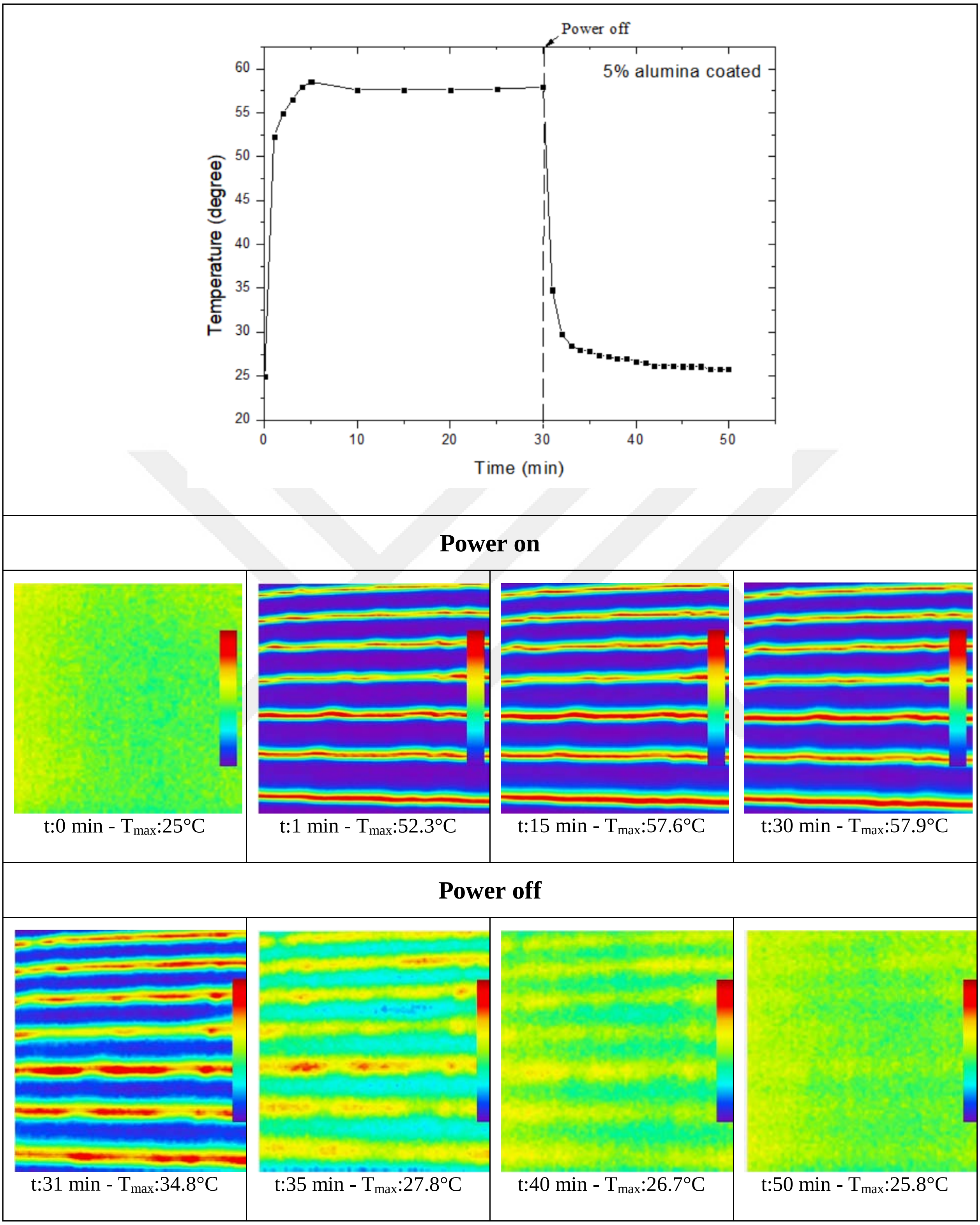

Figure 4.17 : The temperature versus time graph of 5% alumina coated fabric based heater and its thermal camera images as power on and power off.

5. CONCLUSIONS AND FUTURE PLANS

In conclusion, the production and practical applications of carbon based heating elements was successfully afforded as titled in the thesis.

Within this scope, prior to production process, a special continuous coating equipment was successfully designed. After, coating processes of samples was successfully carried out with desired compositions by using this design. All the structural data obtained from XRD analysis for the alumina and coated point out that; the XRD patterns of the alumina are in good agreement with literature and alumina powders with various concentrations were deposited on CF samples in epoxy matrix without any structural change. In the coated CF samples, relatively homogeneous dispersions in terms of alumina, especially for E/A_5-CF and E/A_{10}-CF samples, were observed in the SEM analyses. Besides, it is clear that epoxy matrix were successfully obtained for all samples considering SEM results. Within the scope of TGA analysis, it was proven that CF exhibits a high thermal stability and its structural degradation temperature were determined as around 450°C. The obtained structural degradation temperature are well enough and even higher than the desired service temperatures for the CF based heating element.

Electrical properties of the CF are one of the most important parameters for heating element and its practical applications. With regard to fiber length versus resistance measurements, it was detected a directly proportional relation between them proving that the CF based heating element behaves as a ideal resistor having linear resistance.

Heating performances of the samples are crucial from the point of obtaining effective heating elements. On this point, an investigation on the heating potential of the bare CF were firstly performed using varying potentials. It was observed that maximum temperature can reach up to 300°C with increasing potential which is more higher than desired temperature value for heating applications. However, relatively low temperatures (30-60°C) are sufficient for heating purpose in the scope of this thesis. Therefore, 2V, 4V, and 6V as the potential parameters for the subsequent heating performance measurements were determined in order to provide these temperatures. It must also be noted that CF has a NTC according to resistance versus potential measurements. Subsequently, on the point of determining heating and heat retention performances of coated samples, E/A_5-CF sample demonstrated the best performance among all samples according to all measurements performed under 2V, 4V and, 6V potentials. Its both maximum temperature values and heat retention time values are higher compare to other samples. Regarding this, this concentration were used in fabric based heaters for applications.

As for thermal aging tests, service life-time of the CF under relatively high temperatures were estimated by using UL 746B accelarated thermal aging test. The obtained results clearly indicate that CF has an outstanding thermal aging property. Especially under service temperatures (between 30°C and 60°C) desired in the scope of this thesis, its aging-time range are approximately between 10^{20} and 10^{30} hours.

In this thesis, one of the main purpose is putting into practice obtained heating elements. Within this scope, two applications on heating purpose were carried out. These are 5% alumina coated and uncoated fabric based heaters designed and produced by us. It must be noted that 5% alumina coated fabric based heater demonstrated better performance in terms of heating and, heat retention after power interruption. In particular, its heat retention potential are significantly higher compare to uncoated fabric thanks to alumina particles.

As denoted in the title of the thesis; carbon based heating elements were successfully produced and performed in some applications on the purpose of putting into practice them. The obtained results indicate that this study which has some innovations for the heating applications. Hence, the produced fabric based heater can be easily adapted and used into the present heating applications. This high potential of the results can also be transferred into industrial scale of production.

REFERENCES

[1] Ahmadijokani, F., Shojaei, A., Arjmand, M., Alayi, Y., & Yan, N. (2018). Effect of short carbon fiber on thermal, mechanical and tribological behavior of phenolic-based brake friction materials. *Composites Part B:Engineering.* https://doi.org/10.1016/j.compositesb.2018.12.038

[2] Alloys, R. H., & Furnaces, I. (1992). Resistance heating alloys. *Materials & Design,* 13(2), 113–114. https://doi.org/10.1016/0261-3069(92)90133-3

[3] An, J., & Jeong, Y. G. (2013). Structure and electric heating performance of graphene / epoxy composite films. *European Polymer Journal,* 49(6), 1322–1330. https://doi.org/10.1016/j.eurpolymj.2013.02.005

[4] Arai, Y. (1993). Structure and properties of pitch-based carbon fibers. *Nippon Steel Technical Report*. https://doi.org/10.1007/BF01410948

[5] Athanasopoulos, N., Koutsoukis, G., Vlachos, D., & Kostopoulos, V. (2013). Temperature uniformity analysis and development of open lightweight composite molds using carbon fibers as heating elements. *Composites Part B: Engineering*, 50, 279–289. https://doi.org/10.1016/j.compositesb.2013.02.038

[6] Bajpai, P. (2013). Update on Carbon Fibre. Smithers Rapra Technology Ltd. Retrieved from www.polycomposite.ir

[7] Beggs, K. M., Randall, J. D., Servinis, L., Krajewski, A., Denning, R., & Henderson, L. C. (2018). Increasing the resistivity and IFSS of unsized carbon fibre by covalent surface modification. *Reactive and Functional Polymers*, 129(June 2017), 123–128. https://doi.org/10.1016/j.reactfunctpolym.2017.06.016

[8] Bhatt, P., & Goe, A. (2017). Carbon Fibres: Production, Properties and Potential Use. Material Science Research India, 14(1), 52-57, https://doi.org/10.13005/msri/140109

[9] Chand, S. (2000). Carbon fibers for composites. *Journal of Materials Science*, 35(6), 1303–1313. https://doi.org/10.1023/A:1004780301489

[10] Chien, A. T., Cho, S., Joshi, Y., & Kumar, S. (2014). Electrical conductivity and Joule heating of polyacrylonitrile/carbon nanotube composite fibers. *Polymer (United Kingdom)*, 55(26), 6896–6905. https://doi.org/10.1016 j.polymer.2014.10.064

[11] Chu, K., & Park, S.-H. (2016). Electrical heating behavior of flexible carbon nanotube composites with different aspect ratios. Journal of Industrial and Engineering Chemistry, 35, 195–198. https://doi.org/10.1016/jiec.2015.12.033

[12] Chu, K., Yun, D.-J., Kim, D., Park, H., & Park, S.-H. (2014). Study of electric heating effects on carbon nanotube polymer composites. Organic Electronics, 15(11), 2734–2741. https://doi.org/10.1016/j.orgel.2014.07.043

[13] Chung, D. D. L. (2004). Self-heating structural materials. Smart Materials and Structures, 13(3), 562–565. https://doi.org/10.1088/0964-1726/13/3/015

[14] Chung, D. D. L. (2010). Composite Materials. (B. (Manchester M. S. C. Derby, Ed.) (Second). London: Springer London. https://doi.org/10.1007/978-1-84882-831-5

[15] Eddib, A. A., & Chung, D. D. L. (2018). Electric permittivity of carbon fiber. Carbon. https://doi.org/10.1016/j.carbon.2018.11.028

[16] Edie, D. D. (1998). The effect of processing on the structure and properties of carbon fibers. *Carbon,* 36(4), 345–362. https://doi.org/10.1016/ S0008-6223(97)00185-1

[17] El-Tantawy, F., Kamada, K., & Ohnabe, H. (2002). In situ network structure, electrical and thermal properties of conductive epoxy resin-carbon black composites for electrical heater applications. *Materials Letters*, 56(1–2), 112–126. https://doi.org/10.1016/S0167-577X(02)00401-9

[18] Erol, M., & Celik, E. (2013). Graphite-flake carbon-black-reinforced polystyrene-matrix composite films deposited on glass-fiber woven fabrics asplane heaters. *Materials in Technologies*, 47(1), 25–28.

[19] Flueckinger, C. (2015). PV Standards and Long Term Thermal Aging (LTTA). *3rd ATLAS/NIST Workshop on PV Durability*.

[20] Fosbury, A., Wang, S., Pin, Y. F., & Chung, D. D. L. (2003). The interlaminar interface of a carbon fiber polymer-matrix composite as a resistance heating element. *Composites Part A*: Applied Science and Manufacturing, 34(10), 933–940. https://doi.org/10.1016/S1359-835X(03)00208-2

[21] Fu, L., Huang, A., Gu, H., & Ni, H. (2018). Properties and microstructures of lightweight alumina containing different types of nano-alumina. *Ceramics International,* 44(15), 17885–17894. https://doi.org/10.1016j.ceramint.2018.06.261

[22] Guo, R., Cao, W., Mao, X., & Li, J. (2016). Selective Corrosion Preparation and Sintering of Disperse α-Al2O3 Nanoparticles. *Journal of the American Ceramic Society*, 99(11), 3556–3560. https://doi.org/10.1111/jace.14403

[23] Hambach, M., Möller, H., Neumann, T., & Volkmer, D. (2016). Carbon fibre reinforced cement-based composites as smart floor heating materials. *Composites PartB: Engineering*, 90,465–470. https://doi.org/10.1016/ j.compositesb.2016.01.043

[24] Hsieh, C. Te, Tzou, D. Y., Huang, Z. S., Hsu, J. P., & Lee, C. Y. (2017). Decoration of zinc oxide nanoparticles onto carbon fibers as composite filaments for infrared heaters. *Surfaces and Interfaces*, 6, 98–102. https://doi.org/10.1016/j.surfin.2016.12.001

[25] Hsieh, C. Te, Tzou, D. Y., Huang, Z. S., Lee, C. Y., & Chang, J. K. (2016). High performance infrared heaters using carbon fiber filaments decorated with alumina layer by microwave-assisted method. J*ournal of the Taiwan Institute of Chemical Engineers*, 59, 521–525. https://doi.org/10.1016/j.jtice.2015.08.017

[26] Huang, X. (2009). Fabrication and properties of carbon fibers. *Materials*, 2(4), 2369–2403. https://doi.org/10.3390/ma2042369

[27] Jayaraman, T., Murthy, A. P., Elakkiya, V., Chandrasekaran, S., Nithyadharseni, P., Khan, Z., … Ashokkumar, M. (2018). Recent development on carbon based heterostructures for their applications in energy and environment: A review. *Journal of Industrial and Engineering Chemistry,* 64, 16–59. https://doi.org/10.1016/j.jiec.2018.02.029

[28] Jiang, H., Wang, H., Liu, G., Su, Z., Wu, J., Liu, J., … Zhou, W. (2017). Nanoplatelets for Wearable / Smart Electronics and Deicing Devices, 699(2), 1049–1056.

[29] Johnson, W., & Watt, W. (1967). Structure of High Modulus Carbon Fibres. *Nature,* 214, 597–598. https://doi.org/10.1002/jps

[30] Jones, P. L., Taylor, S., Nakai, S., & Jennings, J. (2003). Electroheat and Materials Processing. *Electrical Engineer's Reference Book: Sixteenth Edition*, 1–38. https://doi.org/10.1016/B978-075064637-6/50009-5
[31] Katunin, A., Hufenbach, W., Kostka, P., & Holeczek, K. (2010). Frequency dependence of the self-heating effect in polymer-based composites. *Journal of Achievements in Materials and Manufacturing Engineering*, Vol. 41, n, 9–15.
[32] Kim, H. A., & Kim, S. J. (2018). Wear comfort properties of ZrC/Al2O3/graphite-embedded, heat-storage woven fabrics for garments. *Textile Research Journal*, 1–14. https://doi.org/10.1177/0040517518770681
[33] Kim, H. S., Park, N. K., Lee, T. J., Um, M. H., & Kang, M. (2012). Preparation of nanosized α - Al2O3particles using a microwave pretreatment at mild temperature. *Advances in Materials Science and Engineering*, 2012. https://doi.org/10.1155/2012/920105
[34] Kim, M., Sung, D. H., Kong, K., Kim, N., Kim, B. J., Park, H. W., … Kim, S. G. (2016). Characterization of resistive heating and thermoelectric behavior of discontinuous carbon fiber-epoxy composites. *Composites Part B: Engineering*, 90, 37–44. https://doi.org/10.1016/j.compositesb.2015.11.037
[35] Kim, T., & Chung, D. D. L. (2003). Carbon fiber mats as resistive heating elements. *Carbon,* 41(12), 2436–2440. https://doi.org/10.1016/S0008-6223(03)00288-4
[36] Kimura, T., & Yasuda, S. (1986). Self-temperature-control plane heaters by graphite-polyethylene glycol mixed systems. *Journal of Applied Physics*, 59(3), 960–962. https://doi.org/10.1063/1.336571
[37] Kong, K., Deka, B. K., Kim, M., Oh, A., Kim, H., Park, Y. Bin, & Park, H. W. (2014). Interlaminar resistive heating behavior of woven carbon fiber composite laminates modified with ZnO nanorods. *Composites Science and Technology*, 100, 83–91. https://doi.org/10.1016/j.compscitech.2014.06.006
[38] Kou, Y., Zhou, W., Li, B., Dong, L., Duan, Y. E., Hou, Q., … Dang, Z. M. (2018). Enhanced mechanical and dielectric properties of an epoxy resin modified with hydroxyl-terminated polybutadiene. *Composites Part A: Applied Science and Manufacturing,* 114, 97–106. https://doi.org/10.1016/j.compositesa.2018.08.016
[39] KV, K., Katti, P., Kumar, S., & Bose, S. (2017). Assessing the interfacial properties in carbon fiber/epoxy nanocomposites: From 'interlayers' to 'interconnects.' *Nano-Structures and Nano-Objects,* 12, 194–209. https://doi.org/10.1016/j.nanoso.2017.10.009
[40] Laboratories, U. (2009). *UL 746B Polymeric Materials* – Long Term Property Evaluations.
[41] Lu, M., Xiao, H., Liu, M., Li, X., Li, H., & Sun, L. (2018). Improved interfacial strength of SiO2coated carbon fiber in cement matrix. *Cement and Concrete Composites,* 91(January), 21–28. https://doi.org/10.1016j .cemconcomp.2018.04.007
[42] Marshall, I. H. (1988). High-performance fibre composites. *Composites*, 19(2), 166. https://doi.org/10.1016/0010-4361(88)90730-6
[43] Moulson, A. J., & Herbert, J. M. (2003). Electroceramics: Materials, Properties, Applications. *(A. J. Moulson & J. M. Herbert, Eds.) (Second).* England: John Wiley & Sons Ltd.
[44] Mustafa, E. (2013). *Production And Industrial Applications Of Heat Releasing*

Electronic Nanocomposite Materials For Heating Systems. Dokuz Eylül University.
[45] Olakunle, O., & Oluwabunmi, A. (2015). Towards Sustainable Burnt Bricks Production in Akure, Ondo State - Nigeria. *International Journal of Biological and Physical Sciences* Accepted Date, 3(2), 15–17. Retrieved from https://www.watchpub/ijbps/index.htm
[46] Ordonez-Miranda, J., & Yang, R. (2015). Effect of a metallic coating on the thermal conductivity of carbon nanofiber-dielectric matrix composites. *Composites Science and Technology*, 109, 18–24. https://doi.org/10.1016/j.compscitech.2015.01.010
[47] Park, H. K., Kim, S. M., Lee, J. S., Park, J. H., Hong, Y. K., Hong, C. H., & Kim, K. K. (2015). Flexible plane heater: Graphite and carbon nanotube hybrid nanocomposite. *Synthetic Metals,* 203, 127–134. https://doi.org/10.1016/ j.synthmet.2015.02.015
[48] Pierson, H. O. (1993). Handbook of Carbon, Graphite, Diamond and Fullerenes. *Handbook of Carbon, Graphite, Diamond and Fullerenes,* 25–69. https://doi.org/http://dx.doi.org/10.1016/B978-0-8155-1339-1.50008-6
[49] Qian, X., Zhi, J., Chen, L., Zhong, J., Wang, X., Zhang, Y., & Song, S. (2018). Evolution of microstructure and electrical property in the conversion of high strength carbon fiber to high modulus and ultrahigh modulus carbon fiber. *Composites Part A: Applied Science and Manufacturing*, 112(April), 111–118. https://doi.org/10.1016/j.compositesa.2018.05.030
[50] Quan, J., Colorado, H. A., Yeh, P. C., & Yang, J. M. (2016). Hybridized ZnO nanostructures on carbon-fiber through combustion synthesis induced by joule heating. *Ceramics International,* 42(11), 13053–13060. https://doi.org/10.1016/j.ceramint.2016.05.085
[51] Rahaman, M. S. A., Ismail, A. F., & Mustafa, A. (2007). A review of heat treatment on polyacrylonitrile fiber. *Polymer Degradation and Stability,* 92(8), 1421–1432. https://doi.org/10.1016/j.polymdegradstab.2007.03.023
[52] Reale Batista, M. D., & Drzal, L. T. (2018). Carbon fiber/epoxy matrix composite interphases modified with cellulose nanocrystals. *Composites Science and Technology,* 164, 274–281. https://doi.org/10.1016/j.compscitech.2018.05.010
[53] Sakr, M., & Liu, S. (2014). A comprehensive review on applications of ohmic heating (OH). *Renewable and Sustainable Energy Reviews*, 39, 262–269. https://doi.org/10.1016/j.rser.2014.07.061
[54] Sarles, S. A. (2006). Controlled Resistive Heating of Carbon Fiber Composites. *Virgin Tech,* 18–60.
[55] Shekar, H. S. S., & Ramachandra, M. (2018). Green Composites: A Review. Materials Today: Proceedings, 5(1), 2518–2526. https://doi.org/10.1016/j.matpr.2017.11.034
[56] Smith, M. (2017). New developments in carbon fiber. *Reinforced Plastics,* 00(00), 1–4. https://doi.org/10.1016/j.repl.2017.07.004
[57] Speakman, S. A. (2013). Introduction to X-Ray Powder Diffraction Data Analysis. *Center for Materials Science and Engineering at MIT*.
[58] Stability Testing of Self-Regulating Heating Cables and New High Temperature Heating Cable Solutions. (2018.). Retrieved from www.thermon.com
[59] Stadtländer, C. T. K.-H. (2007). Scanning electron microscopy and transmission

electron microscopy of mollicutes: challenges and opportunities. Modern Research and Educational Topics in Microscopy, (2018), 122–131. Retrieved from http://pdf-release.net/external/1716339/pdf-release-dot-net-pp122-131.pdf

[60] Wang, S., Chen, Z. H., Ma, W. J., & Ma, Q. S. (2006). Influence of heat treatment on physical-chemical properties of PAN-based carbon fiber. *Ceramics International,* 32(3), 291–295. https://doi.org/10.1016/j.ceramint.2005.02.014

[61] Weinmann, M., & Aldinger, F. (2003). Precursor-Derived Ceramics. *Handbook of Advanced Ceramics: Materials, Applications, Processing and Properties* (Vol. 1–2). https://doi.org/10.1016/B978-012654640-8/50007-9

[62] White, W. M. (2005). *Chapter 9. In Isotope Geochemistry* (pp. 358–414). https://doi.org/10.1016/B978-0-12-086450-8.50014-8

[63] Xia, Y., Yu, X., Sheng, C., Liang, C., Huang, H., Gan, Y., … Zhang, W. (2017). N991 / MWCNTs / PEO composite fi lms with nano SiO 2 particles as fi ller for advanced flexible electric heating elements. *Materials Research Bulletin,* 90, 273–279. https://doi.org/10.1016/j.materresbull.2017.03.014

[64] Yurddaskal, M., Doluel, E. C., Kartal, U., Koksalar, A., & Celik, E. (2018). Graphene and carbon black filled conductive nanocomposite films for heating element applications. *Journal of Materials Science:* Materials in Electronics, 0(0), 0. https://doi.org/10.1007/s10854-018-0026-9

[65] Zhan, Y., Meng, Y., & Li, Y. (2017). Electric heating behavior of flexible graphene/natural rubber conductor with self-healing conductive network. *Materials Letters,* 192, 115–118. https://doi.org/10.1016/j.matlet.2016.12.045

CURRICULUM VITAE

1. **Adı Soyadı:** Ahmet YAVAŞ
2. **Doğum Tarihi:** 28/05/1991
3. **Ünvanı:** Araştırma Görevlisi
4. **Öğrenim Durumu**

DERECE	ALAN	ÜNİVERSİTE	YIL
Yüksek Lisans	Malzeme Bilimi ve Mühendisliği ABD.(İngilizce)	İzmir Katip Çelebi Üniversitesi	2018
Lisans	Metalurji ve Malzeme Mühendisliği (Türkçe)	Dokuz Eylül Üniversitesi	2014

5. **İş tecrübesi**

ÜNVAN	ALAN	KURUM	YIL
Araştırma Görevlisi	Malzeme Bilimi ve Mühendisliği ABD	İzmir Katip Çelebi Üniversitesi	2016 - Bugün
Metalurji ve Malzeme Mühendisi	AR-GE	Teknobim Nanoteknolojileri Araştırma Geliştirme Dezenfektan San.Tic.Ltd.Şti	2014 - 2015

6. **Yayınlar**

A- Uluslararası bilimsel toplantılarda sunulan ve bildiri kitaplarında (proceedings) basılan bildiriler

1. Kırmacı Volkan, Erol Mustafa, Eren Hayri, **Yavaş Ahmet** (2018). Electrical Heating System Performance Evaluation of A noval heating system in a public transport vehicle. International Conference on Heat Transfer and Fluid Flow (Iser-Internatıonal Society for Engıneers and Researchers), (Tam metin bildiri), (Kontrol No: 4385711)
2. **Yavaş Ahmet**, Kırmacı Volkan, Erol Mustafa, Eren Hayri (2018). An investigation on Carbon Fibers as flexible heating elements. International

Congress on Mathematic, Engineering and Natural Sciences-IV, (Tam metin bildiri), (Kontrol No: 4385766)

3. **Yavaş Ahmet**, Güler Saadet, Erol Mustafa (2018). Synthesis of ZnO Nanostructured Photocatalysts via Electrochemical Anodization. 2nd International Students Science Congress, (Tam metin bildiri), (Kontrol No: 4385758)
4. Başalan Emine, Erol Mustafa, Sancakoğlu Orkut, Dikici Tuncay, **Yavaş Ahmet**, Çelik Erdal (2017). Formation of TiO2 Nanotube Layers Through Magnetron Sputtering and Electrochemical Anodization. The International Porous and Powder Materials Symposium and Exhibition (PPM 2017), (Özet bildiri), (Kontrol No: 3719895)
5. Erol Mustafa, Kırmacı Volkan, Eren Hayri, **Yavaş Ahmet**, Duran Hüseyin, Öztürk Yavuz (2017). Yolcu Taşımacılığı Yapan Taşıtlarda Işınımla Isıtmasısteminde Kullanılan Tekstil Kumaşının Tasarımı. 1st International Turkish World Engineering and Science Congress, (Tam metin bildiri), (Kontrol No: 3719929)
6. **Yavaş Ahmet**, Dikici Tuncay, Erol Mustafa (2017). Synthesis of ZnO Nanostructures through Electrochemical Anodization. The International Porous and Powder Materials Symposium and Exhibition Symposium (PPM2017), (Özet bildiri), (Kontrol No: 3719909)
7. Kırmacı Volkan, Erol Mustafa, Eren Hayri, **Yavaş Ahmet** (2018). An experimental study on fabric based heaters as an innovative approach for vehicle heating. International Congress on Mathematic, Engineering and Natural Sciences-IV, (Tam metin bildiri), (Kontrol No: 4385770)

7. Projeler

1. 1010 STZ 2016 Yolcu Taşımacılığı Yapan Taşıtlarda Işınımla Isıtma Sisteminin Tasarımı İmalatı ve Performans Deneylerinin Yapılması, Sanayi Bakanlığı (SAN-TEZ) Projesi, Yürütücü: Kırmacı Volkan, Bursiyer: **Yavaş Ahmet**, Bursiyer: Eren Hayri, Araştırmacı: Erol Mustafa, 01/07/2016 (Devam Ediyor)

8. Başarılar / Ödüller

1. Dokuz Eylül Üniversitesi Metalurji ve Malzeme Mühendisliği 3.65 GNO ile Mühendislik Fakültesi **ikinciliği**
2. Dokuz Eylül Üniversitesi Metalurji ve Malzeme Mühendisliği 3.65 GNO ile bölüm **birinciliği**