FABRICATION AND CHARACTERIZATION OF CERAMIC FIBERS FROM PRECERAMIC POLYMERS

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by
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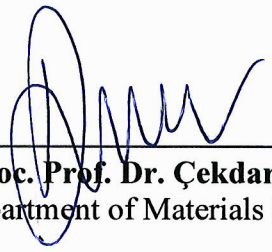

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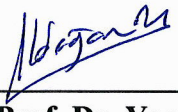

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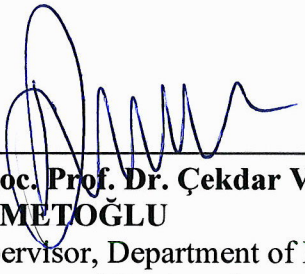

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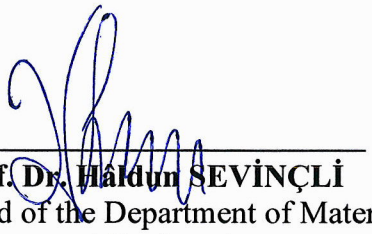

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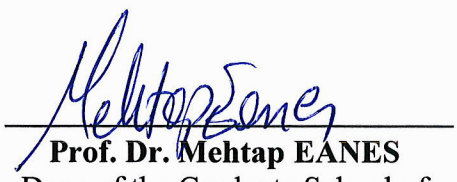

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ABSTRACT

FABRICATION AND CHARACTERIZATION OF CERAMIC FIBERS FROM PRECERAMIC POLYMERS

Ceramic fibers which are classified as oxide and non-oxide fibers are preferred to use in applications which are carried out at high temperature since they have high strength, low thermal expansion, corrosion, and oxidation resistance. Non-oxide fibers are generally produced using preceramic polymers by the spinning method. The production of ceramic materials using preceramic polymers by spinning method is more advantageous than other methods since the production of complex materials could be achieved at lower temperatures. The preceramic polymer family is basically classified as polysiloxane, polysilazane and polycarbosilane. In this thesis, it was aimed to obtain ceramic fiber in the most economical way. In this context, a spinning device was designed and made. Additionally, polysiloxane which is the most economical preceramic polymer was used to produce ceramic fiber. Polysiloxanes were spun by melt spinning. Obtained fibers were cured by different methods. As a result of pyrolysis, 65-130 μm thickness SiOC fibers were achieved.

ÖZET

PRESERAMİK POLİMERLERDEN SERAMİK FİBERLER ÜRETİMİ VE KARAKTERİZASYONU

Oksit ve oksit olmayan lifler olarak sınıflandırılan seramik liflerin, yüksek dayanıma, düşük ısıl genleşmeye, korozyona ve oksidasyona karşı dirence sahip oldukları için yüksek sıcaklıkta gerçekleştirilen uygulamalarda kullanılması tercih edilir. Oksit olmayan fiberler genellikle eğirme yöntemiyle preseramik polimerler kullanılarak üretilir. Eğirme yöntemi ile preseramik polimerler kullanarak seramik malzeme üretmek diğer yöntemlere kıyasla daha avantajlıdır çünkü karmaşık yapılı malzemeler daha düşük sıcaklıklarda üretilebilir. Preseramik polimer ailesi temel olarak polisiloksan, polisilazan ve polikarbosilan olarak sınıflandırılır. Bu tezde, seramik elyafın en ekonomik şekilde elde edilmesi amaçlandı. Bu bağlamda, bir eğirme cihazı tasarlandı ve yapıldı. Ayrıca; seramik elyafı üretmek için en ekonomik preseramik polimer olan polisiloksanlar kullanıldı. Polisiloksanlar eriyik (melt) eğirme yöntemiyle elde edildi. Fiberler farklı yöntemlerle kürlendi. Piroliz sonucunda 65-130 μm kalınlığında SiOC fiberler elde edildi.

Dedicated to my family…

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LIST OF ABBREVIATIONS

PDC	Polymer Derived Ceramic
MK	Poly (methy-silsesquioxane)
PHMS	Polymethylhydrosiloxane
PDMS	Polydimethylsiloxane
CVD	Chemical Vapor Deposition
ABS	Acrylonitrile Butadiene Styrene
RT	Room Temperature
SEM	Scanning Electron Microscopy
TGA	Thermogravimetric Analysis
XRD	X-ray Diffraction
EDX	Energy Dispersive X-ray
ICDD	International Centre for Diffraction Data

CHAPTER 1

INTRODUCTION

1.1. Motivation

Fibers are hair-like materials that are stretched pieces either continuous or discrete and are generally defined as long chains of molecules of organic or inorganic structure.[1] Because of their high tensile, low bending and torsional rigidities, low density and high specific surface area, they show superiority in many high technology applications. And thus, fibers are seen as a promising material for various industrial application. [2]

Ceramic fibers are useful materials since they could be used as reinforcement fibers for metals, plastics, and ceramics.[3-4] Yajima et al. are the first to show that organosilicon polymers can be used to produce high-strength SiC-based fibers. The first of commercially available polymer-derived fibers based on Yajima et al methods are Nicalon and Tyranno fibers.[5-6]

This thesis consists of two main steps which are design and made of the spinner device and spinning of polysiloxane.

1.2. The Structure and Scope of the Thesis

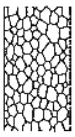
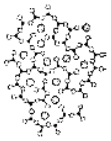
The first Chapter; introduction includes the structure, classification and production methods of the fibers. The materials and methods are given in Chapter 2. The experimental results and discussion of results are given in Chapter 3 and the brief summary of this study are given in Chapter 4.

1.3. Classification of Fibers

The fibers are made up of chain molecules at the molecular level. The characteristic properties of the fibers such as flexibility, strength, tenacity, modulus,

toughness, thermal and chemical resistance are determined by the orientation and bond type of the molecules that create these chains.[7] For example: According to the atomic or molecular structure of the fibers, they are classified as crystal, semi-crystalline or amorphous. The crystal structure provides hardness and high strength to the fibers, while the amorphous structure provides flexibility and reactivity.[2] The structure of some fibers are given in Table 1.1 and a comparison of the mechanical properties of fibers with respect to their structure is given in Figure 1.1.

Table 1.1. Structure and properties of some fibers (Source: Krenkel, 2008).[7]

Fiber type	Polyester polyamide	Aramide fibers from LC phase	Carbon	Ceramic (crystalline)	Ceramic (amorphous) glass
Structure					
	1D linear 2 phases	1D linear 1 phase	2D layered	3D isotropic	3D isotropic
Bond type	1D covalent, hydrogen bonds (PA), dipole-dipole (PES), van der Waals	1D covalent, hydrogen bonds, van der Waals	2D covalent, van der Waals	3D covalent/ ionic	3D covalent/ ionic
Crystallinity	Medium	Paracyrstalline	Paracrystalline	Polycrystalline	Amorphous
Orientation	Medium	Very high	High	None	None

The covalent and ionic bonds in the structure of the fibers have the highest energy and they show one (1D), two (2D) or three-dimensional (3D) orientation. It determines the fiber's mechanical strength and modules. The mechanical property is directly proportional to the bond energy therefore, the mechanical property increases. However, if only the bond energy is considered, it is expected that the tensile strength and modulus values of ceramic materials containing 3D covalent and ionic bonds must be the highest. As shown in Figure 1.1, carbon fibers have the highest tensile strength and modulus values. While ceramic fibers are isotropic without molecular orientation, but carbon fibers have 2D covalent bonds with high orientation.

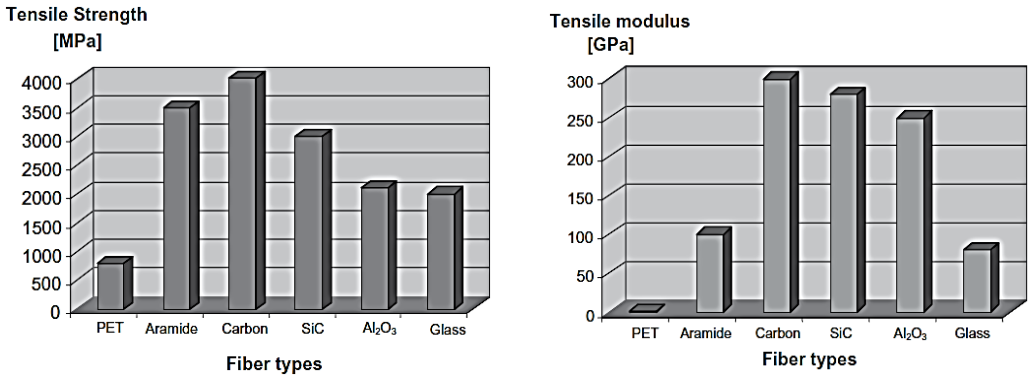


Figure 1.1. Tensile strengths (averages) of different fiber types (Source: Krenkel, 2008).[7]

Morphology is another factor which has an effect on the physical properties of the fiber. Important factors are uniformity of the diameter along the fiber, porosity, cross-section and structural defects, as well as surface properties such as roughness and surface energy. Finally, the manufacturing process of the fiber is highly effective on structure formation and physical properties.

The fibers can be classified based on the production source as shown in Figure 1.2.

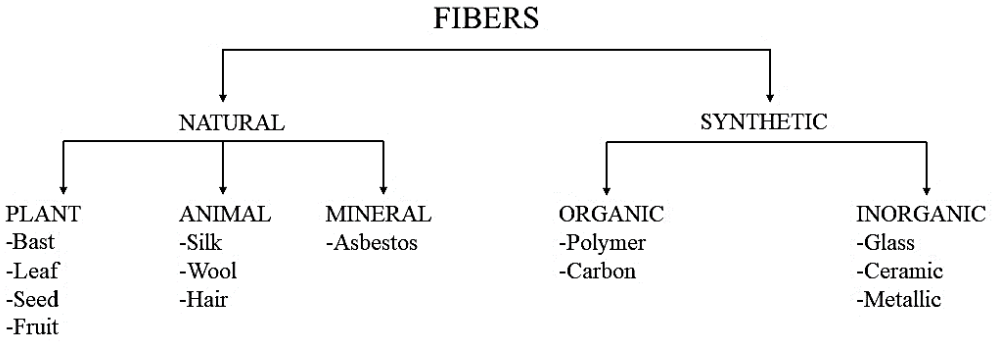


Figure 1.2. Classification of natural and synthetic fibers
(Source: Jawaid and Khalil, 2011).[8]

Whereas natural fibers such as cotton, jute, silk,kenaf and hemp were used until the first years of the 20th century, there was a tendency to synthetic or man-made fibers in the 1890s due to the need.[9]

1.3.1. Natural Fibers

Natural fibers originated from animal, vegetable or mineral are known and used for centuries. According to the literature, in general, animal fibers have lower strength and modulus, however, they have higher elongation than vegetable fibers. Mineral fibers are expensive and brittle, and thus, they are less preferred.

Natural fibers are used as reinforcing materials today due to their advantages. For instance, they are a renewable resource and can be obtained with low energy and cost. Additionally, they are environmentally friendly and biocompatible. Moreover, they cause high CO2 emissions.[10] However, it has some disadvantages such as low strength, especially impact, failure to adapt to changing weather conditions, poor fire and moisture resistance.[8, 11]

1.3.2. Synthetic Fibers

In 1664, the famous British scientist Robert Hooke proposed the idea that artificial silk can be produced by imitating silkworm. Silkworms produce fiber by the hardening of the liquid in the air environment, which is extracted by pressing through a small hole. He claimed that artificial fibers could be produced by this way.

In 1842, the English weaver Louis Schwabe designed a machine based on Robert Hooke's thought.[12] Glass fiber was obtained by removing the liquid from the hole with pressure with the help of this device and hardening in the air environment. However, it was not found suitable because it was intended to be used in the textile field. In this process, fiber sources in nature have gained great attention from scientists and it was thought that cellulose could be used as a fiber source by dissolving in an appropriate solvent.

In 1846, the scientist Friedrich Schonbein found that nitrocellulose can be obtained by dissolving cellulose in nitrite acid. In 1855, George Audemars discovered that nitrocellulose solidifies in the air and has a filament structure that can wrap around a

spool. Nitrocellulose fibers were purposed to use commercially because they are soft and flexible. Yet they are flammable, so their usage in the textile field has prevented.

In 1884 Count Hilaire de Chardonnet obtained artificial fibers using a solution of nitrocellulose. In 1890 Besancon also built a factory and started to produce 'Chardonnet silk'.[13]

Between 1928 and 1932, W.H. Carothers et al. produced completely synthetic fibers. The first commercially completely synthetic fiber was successfully produced from adipic acid and hexamethylene diamine and it was called nylon 66.

After that, other synthetic fibers, namely polycaprolactone, polyacrylonitrile, polyvinyl alcohol, poly (ethylene terephthalate), and polypropylene were produced in 1939, 1949, 1950, 1953, and 1957, respectively.[14]

1.3.2.1. Inorganic Fibers

Fibers made from organic polymers used for traditional industrial uses such as textiles, households. Besides, inorganic fibers were produced as well as organic fibers. Inorganic fibers have high temperature resistant with high tensile strength and modulus values. The first produced inorganic fibers are asbestos and glass.[15] In the following years, oxide and non-oxide ceramic fibers were also produced.[16]

1.3.2.1.1. Ceramic Fibers

Ceramic fibers are used in many fields due to their high temperature resistance against oxidation. They are used as reinforcing materials for automotive engine parts, aircraft and space machinery, structural members in furnaces and they can also use as a filter for high temperature applications. [17]

The ceramic fibers are divided into two groups which are non-oxide fibers such as SiC (silicon carbide), BN (boron nitride), Si-B-N-C (silicon-boron-nitride-carbide), Si-Ti-C-O, SiOC(Silicon oxycarbide) and oxide fibers, such as Al_2O_3 (aluminum oxide, including single crystal alumina), Al_2O_3+ZrO_2 (alumina zirconia mixtures), YAG (yttria-alumina-garnet), $3Al_2O_3$-$2SiO_2$ (mullite). Whereas non-oxide fibers have a low resistance to oxidation, and superior strength and frictional resistance; oxide fibers have high resistance to oxidation and low frictional resistance.[8, 18]

a.) Polymer Derived Ceramic (PDC) Fibers

Non-oxide ceramic fibers generally are produced from preceramic polymers; polysilane, polycarbosilane, polysilazane, polycarbosilazane, polyborosilazane and polysiloxane.[19] The first non-oxide ceramic fibers SiC were produced using polycarbosilanes by Yajima in 1957 and commercial production of Nippon Carbon triggered the interest in this field.

Table 1.2. Commercial fibers manufactured from preceramic polymers (Source: Council, 1998).[19]

Company	Fiber	Spin Method	Cure Method	Ceramic Composition
NCK[a]	CG-NICALON	Melt	Air oxidation	Si-C-O
	HI-NICALON	Melt	Electron beam	SiC+C
	HI-NICALON	Melt	Electron beam	SiC
Ube[b]	TYRANNO	Melt	Air oxidation	Si-C-O-Ti
		Melt	Electron beam	Si-C-Ti
	TYRANNO-Z	Melt	Air oxidation	Si-C-O-Zr
		Melt	Electron beam	Si-C-Zr
MER/UM[c]	_____	Solution Dry	Thermal + chemical	SiC
3M/UF[d]	_____	Solution Dry	Thermal + chemical	SiC+C or SiC
DCC[e]	SYLRAMIC	Melt	Air oxidation	SiC+ TiB_2
Bayer[f]	_____	Melt	Chemical	Si-N-B-C-O or Si-N-B-O

[a] Nippon Carbon Company; Tokyo, Japan, [b] UBE Industries, Ltd.; Tokyo, Japan, [c] MER Corporation; Tucson, Arizona, and University of Michigan, [d] 3M Corporation; Minneapolis, Minnesota, and University of Florida, [e] Dow Corning Corporation; Midland, Michigan, [f] Bayer Company; Leverkusen, Germany.

The preceramic polymers are more advantageous than conventional ceramics because the final properties of ceramics such as composition, optical, thermal, magnetic and electrical properties can be adjusted via pyrolysis conditions. Figure 1.3 shows the steps of obtaining ceramic fiber.

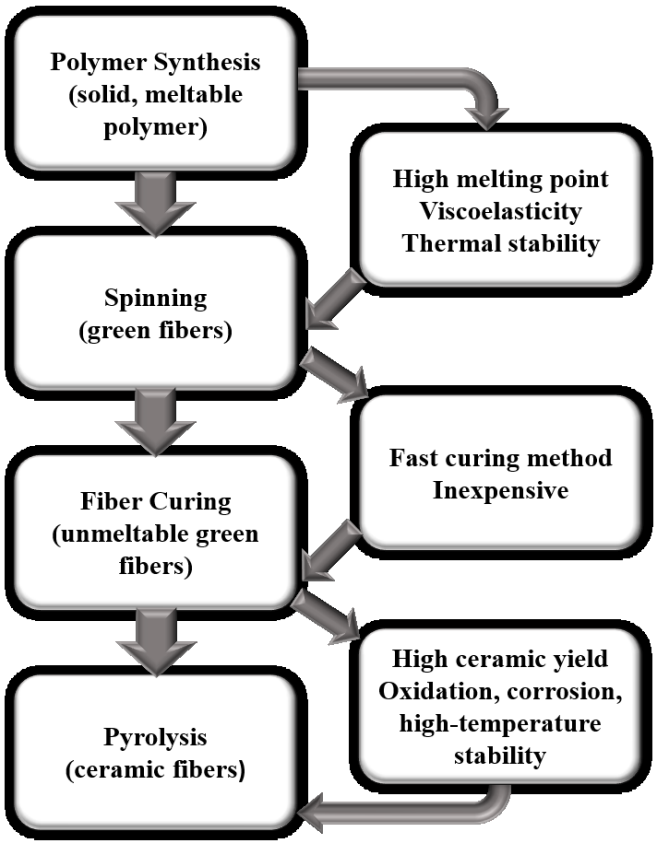


Figure 1.3. Typical process sheme for conversion of polymeric precursor to ceramic fiber (Source: Motz and Bordia, 2009).[18]

Polymer derived from ceramics (PDCs) is a precursor used in the production of advanced ceramic materials containing elements such as C, N, B in the Si-based backbone which is called as polymer based ceramic.[13, 20] A general formula of the precursor organosilicon polymer is shown in Figure 1.4.

Preceramic polymers molecular structure and chemistry greatly affects the final ceramic products composition, microstructure and phase distribution,[21] categorized as binary systems, such as Si-C, Si-N, ternary systems, such as Si-O-C, Si-C-N, and quaternary systems such as Si-B-C-N, Si-B-O-C.[22]

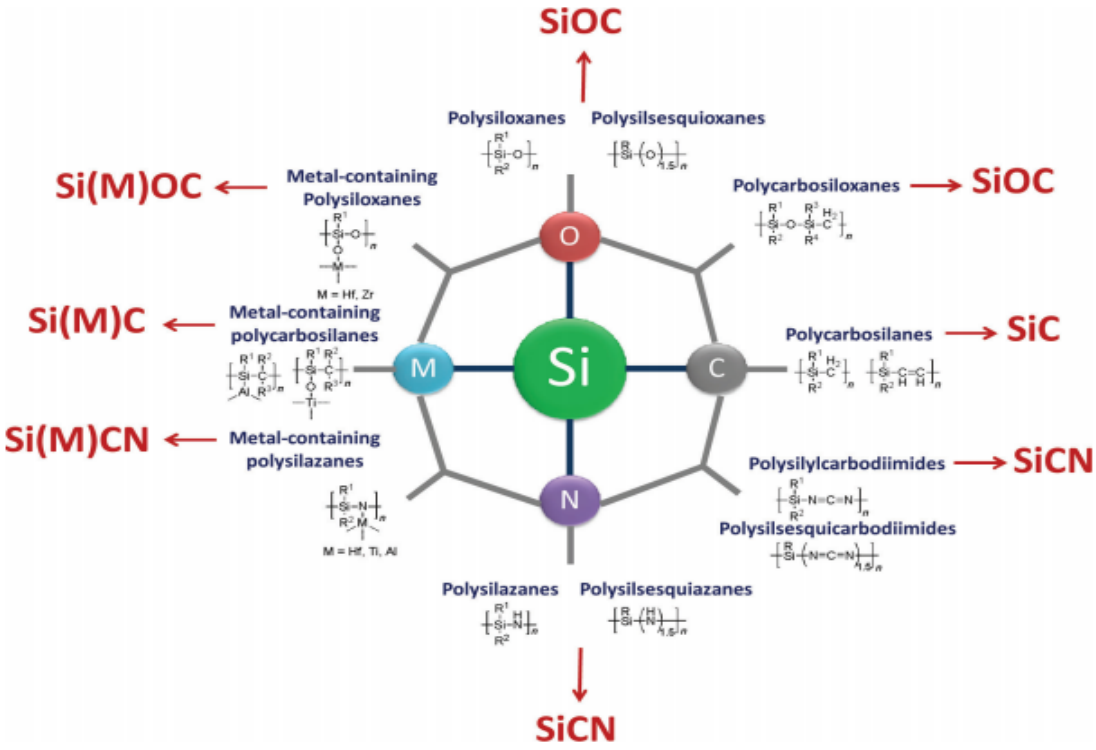


Figure 1.4. Forms of preceramic polymers containing silicon
(Source: Mera and Ionescu, 2002).[23]

The conversion of preceramic polymers to ceramics takes place in three main steps:

i.) Preceramic polymer synthesis

ii.) Crosslinking with curing process

iii.) Converting to ceramics by pyrolysis process

The temperature ranges in which these steps take place are shown in Figure 1.5. Crosslinking is an important step in ceramic production. During crosslinking, preceramic polymers are converted from an organic form to inorganic form and the structure becomes thermoset. Thus, the loss of low molecular weight compounds is prevented during ceramicization. Additionally, ceramic yield increases and the material ensures to retain its shape. Thanks to the usage of a catalyst, ceramic yield could be enhanced and curing could be obtained at lower temperatures. In the curing process, in addition to thermal oxidation, the methods such as radiation and e-beam curing (usually performed in vacuum) are used. [24] However, penetration is limited in these methods, they are appropriate for low-sized samples such as fiber.

The pyrolysis process begins with the decomposition of organic particles from the structure, so the structure turns to inorganic from organic state. This decomposition is called as mineralization or ceramization and occurs between 400-800 ° C.

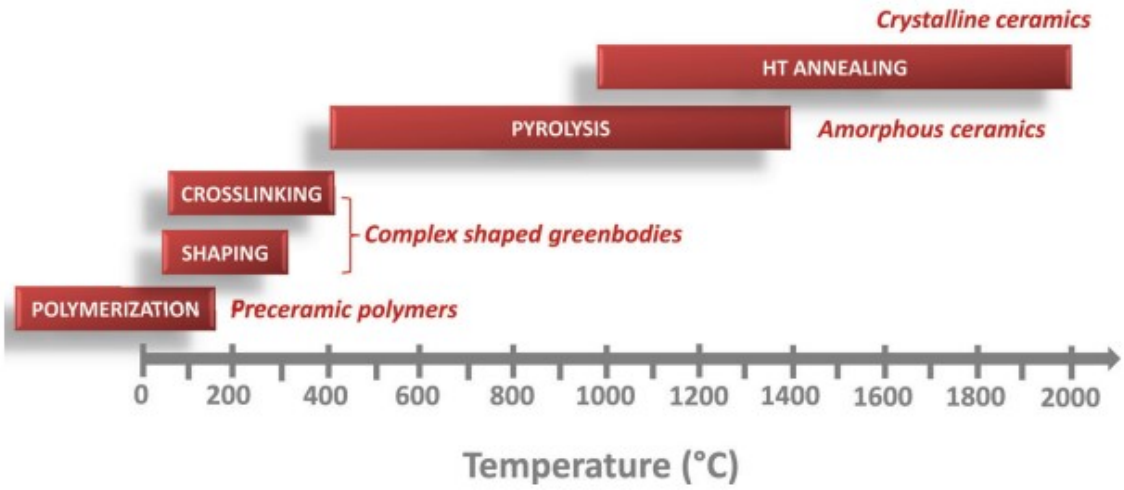


Figure 1.5. Based on the temperature, thermal decomposition of polymers to ceramics (Source: Mera and Ionescu, 2002).[23]

1.) Silicon Oxycarbide (SiOC)

Silicon is a compound formed by bonding with carbon and oxygen atoms simultaneously and its molecular formula is SiOxC4-x ($0 \leq x \leq 4$). In SiOC production, poly (organosiloxanes) and poly (organosilsesquioxanes) precursors are widely used, [RR'SiO] n and [$RSiO_{1.5}$] n, respectively. R and R' represent the hydrocarbon groups such as H, OH, methyl, vinyl, phenyl, Oet.[22]

Poly(organosiloxane) is preferred in SiOC production due to its superior chemical and physical properties as well as easy availability and low cost. Polysiloxane exists in different forms such as silicone oils (fluids), silicon elastomer (rubbers) and silicone resin depending on the backbone structure, degree and type of crosslinking. Silicone oils have a linear or cyclic structure with respect to functional side chains and end groups of the structure, which are connected to the backbone of silicon and oxygen atoms. Some silicone oils are shown in Figure 1.6.

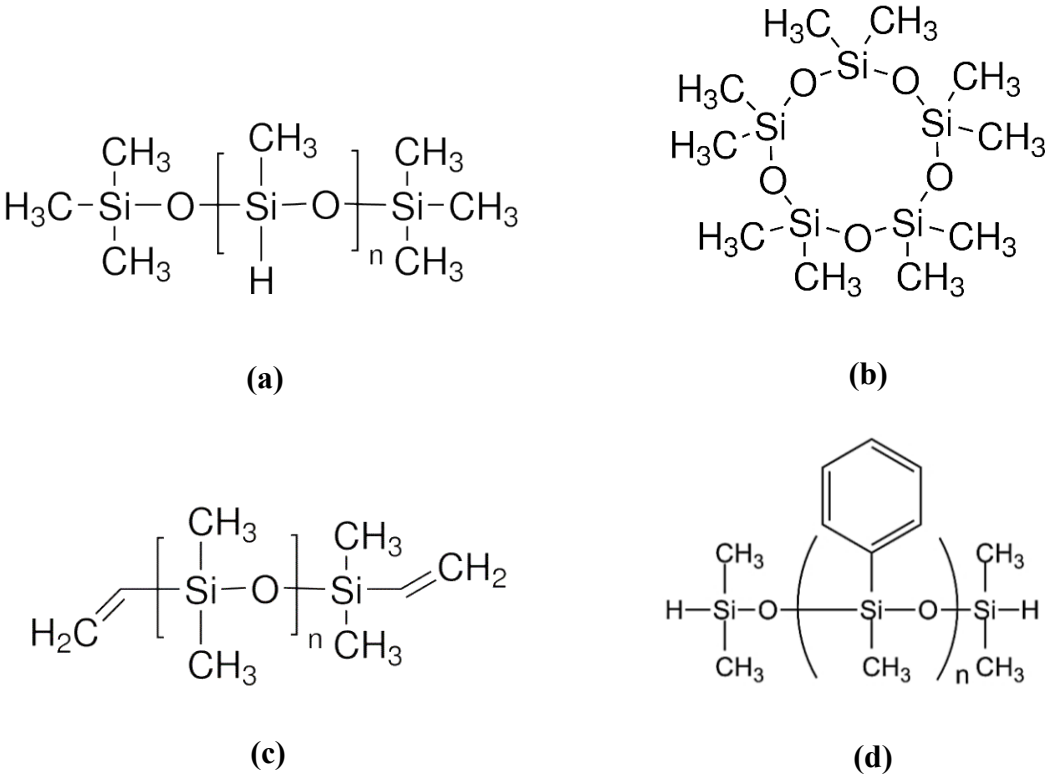


Figure 1.6. Structure of some silicone oils; (a) polymethylhydrosiloxane, (b) D5, decamethyl-cyclo-pentasiloxane, (c) vinyl-terminated polydimethylsiloxane, (d) polyphenylmethylsiloxane. (Source: Vakifahmetoglu et al, 2016).[22]

Silicone resins is a solid form of polysiloxane which is called as poly (organo silsesquioxanes). It is a highly branched polymer compared to silicon oils and elastomer. Therefore, the ceramic yield is high.

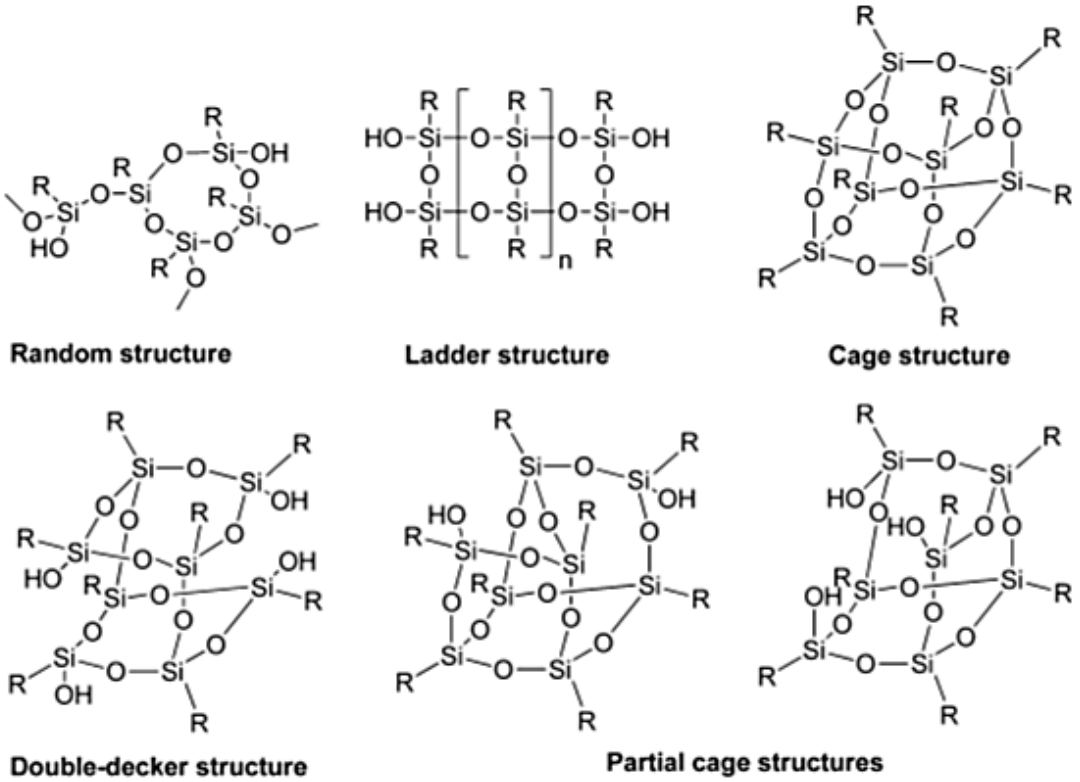


Figure 1.7. Chemical structure of poly (organosilsesquioxanes)
(Source: Zhu and Chen, 2013).[25]

Poly(methyl-silsesquioxane) (MK) is widely used because of its their easy availability and low cost.

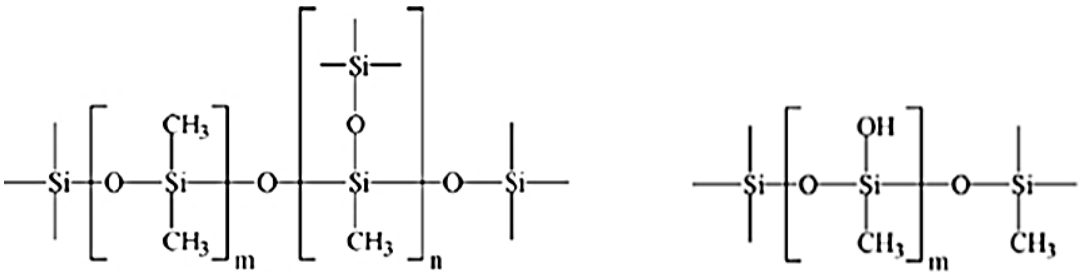


Figure 1.8. Network units of (a) MK (PMS) and (b) Structural units containing OH-.[26]

Table 1.3. Properties of some polysiloxanes used in this thesis.
(Source: Vakifahmetoglu et al, 2016).[22]

Commercial Chemical Name and Chemical Formula	Polymethyl hydrosiloxane (PHMS) $(CH_3(H)SiO)_n$	Polydimethyl siloxane (PDMS) $(C_2H_6OSi)_n$	MK: Poly (methyl-silsesquioxane) (PMS) $(CH_3O_{1.5}Si)n$
Form	Liquid	Liquid	Solid (Powder)
Organo Groups R, R'	$-CH_3$	$-CH_3$	$-CH_3$
Cross-linking Groups O-R, O-R'	-H	$-H_2C=CH_2$	-OH, $-OC_2O_5$
Melting Point (range)	0	0	35-55 °C
Thermal Decomposition	>350	>380	>350 °C
Colour	Clear colorless	Clear colorless	White

The crosslinking of polysiloxanes and polysilsesquioxanes prepolymers is achieved during curing by condensation or hydrosilylation (addition) reaction of the functional groups (Si-H, Si-OH or Si-vinyl functionalities) of these prepolymers. The hydrosilylation reaction is carried out by the addition of silicon hydride to the unsaturated carbon-carbon bond (vinyl or other alkenyl functionality) or by the free radical initiation technique, which results in no by-product.

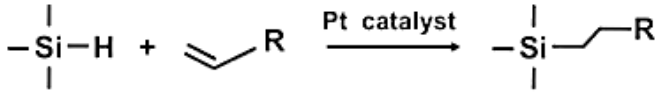


Figure 1.9. Reaction scheme of the hydroslylation reaction
(Source: Pantano et al, 1999).[27]

The condensation reaction is that Si-OH functional group leads to Si-O-Si bond formation in the presence of organometallic catalyst such as zinc acetylacetonate, zinc octoate, stannous (tin) octoate, tin diacetate, etc. The reaction causes the formation of by-products such as water, alcohols, and acids.

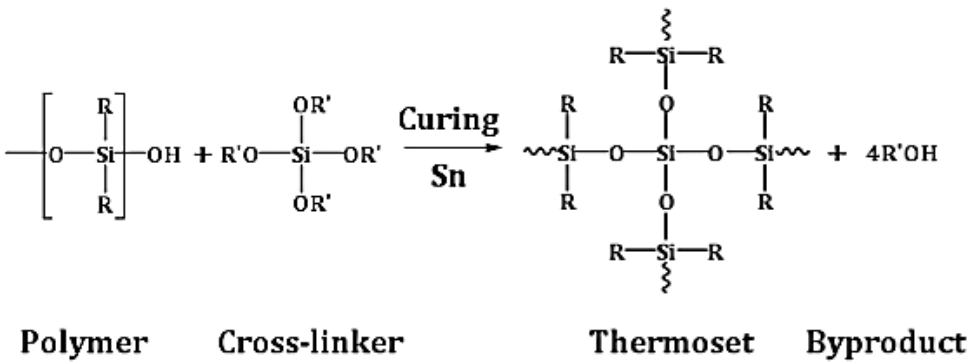


Figure 1.10. Reaction scheme of the condensation reaction
(Source: Vakifahmetoglu et al, 2016).[22]

After curing, during the pyrolysis process, SiOC is found in the form of SiCxO2(1-x) + yCfree. SiCxO2(1-x) and yCfree refer to amorph structure and free carbon phase, respectively. X and y values are determined based on the composition of the preceramic polymers and pyrolysis conditions (temperature and atmosphere).[23]

1.4. Conversion of the Preceramic Polymer to Fiber

The production methods of non-oxide ceramic fibers are very limited**.** It can be produced by Chemical Vapor Deposition (CVD) and extrusion (spinning) methods. The CVD method is less preferred because it is more complex and the thickness and flexibility of the obtained ceramics are limited. Extrusion (spinning) method is widely used.

1.4.1. Spinning Process

The spinning method is a technique developed by inspiring from spiders and silkworms. The spinning method is mainly based on adjusting the viscosity of material

for spinning, the formation of liquid jets by pressure for the flowing of material through small holes (nozzles) and the solidification of jets. It is then turned to the fibers by drawing by means of a bobbin or spool. Fibers can be obtained in a wide range of thicknesses (millimeter to nanometer range).

The first experiment of this technique was made by dissolving cellulose nitrate (celluloid) in alcohol / ether solution. The solvent was evaporated to produce the fiber.

Spinning technique is classified as wet, dry and melt spinning based on jet formation and solidification. The thickness of fibers obtained by this method depends on the concentration of material, nozzle diameter, draw speed and distance etc.

In the following years, the electrospinning method was developed to produce nano sized fibers with lower thickness.[28].

a.) Wet Spinning: The material is dissolved in an appropriate solution. It passes through the nozzles with pressure and then, the fibers are wrapped around a spool in an appropriate coagulation bath where the material is coagulated and the solvent is removed. The composition of the bath is the most important parameter in this method since it affects the morphology of the fibers. [29]

b.) Dry Spinning: Dry spinning method is similar to wet spinning method. The material is dissolved in the appropriate solvent as in the wet spinner method and it is spun with pressure. However, unlike the wet spinning method, the solvent is evaporated using heat instead of a coagulation bath. After the evaporation of solvent, fibers are obtained. [29]

c.) Melt spinning: The difference between the other methods and melt spinning is that the material is melted without using a solvent and then, it is spun. The solidification of the molten material takes place either by temperature difference during spinning or by blowing cold air. The spinning without using any solvent has some advantages, for instance, there is no need for an extra process to remove the solvent and it saves time.[6, 30]

d.) Electrospinning: Electrospinning is the extraction of material dissolved in the appropriate suitable solvent under electrostatic forces.[31]This technique consists of 3 main components; high voltage supply, syringe pump and grounded collector. Factors affecting fiber thickness are concentration, viscosity,[32] molecular weight,[33] surface tension,[34]

electrical conductivity,[35] dielectric constant[36], evaporation temperature of solvent[37] used, applied voltage,[38] spinning distance, flow rate[39] and ambient conditions.[40]

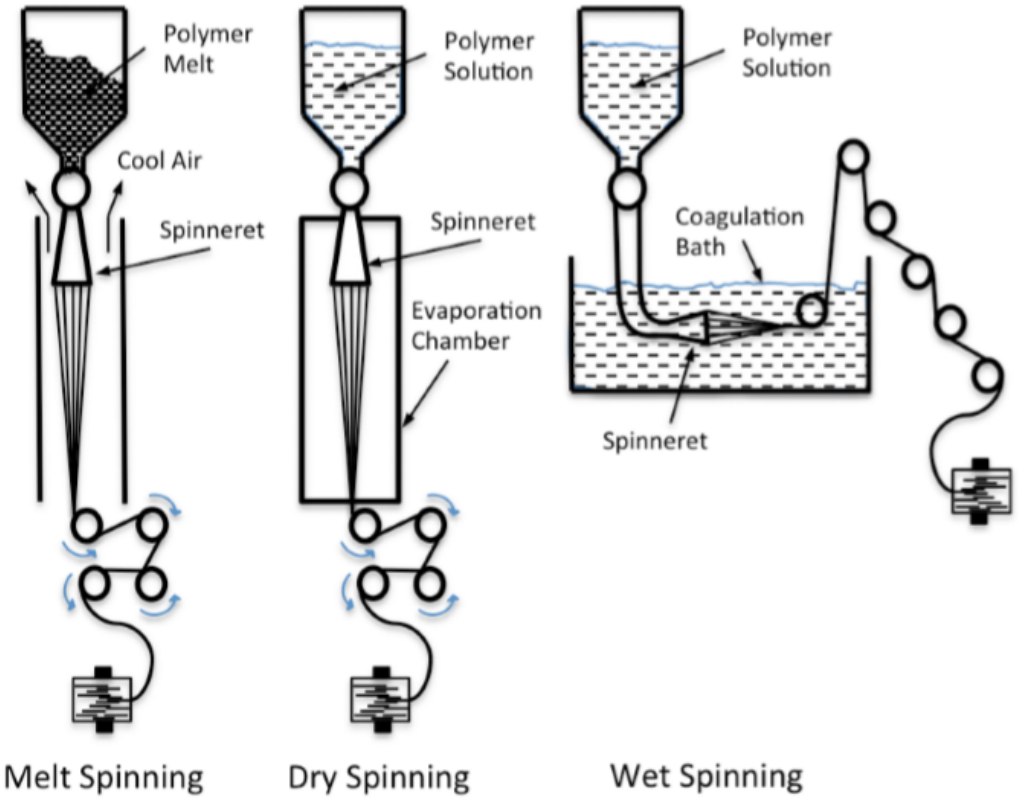


Figure 1.11. Schematic illustration of traditional techniques for fiber spinning (Source: Dallmeyer and Kadla, 2014).[41]

CHAPTER 2

EXPERIMENTAL

2.1. Materials

Poly(methyl) silsesquioxane (Silres MK Powder, CAS: 68554-70-2) was supplied from Wacker Chemie AG, Germany. Two types of polysiloxanes which are vinyl-terminated polydimethylsiloxane (PDMS, MW ~ 62700, 10000 cSt CAS: 68083-19-2) and a linear polyhydromethylsiloxane (PHMS, MW ~2100-2400, 30-45 cSt CAS: 63148-57-2) were supplied from Gelest Inc (Tully-town, PA). 2,4,6,8-Tetramethyl-2,4,6,8-tetravinylcyclotetrasiloxane, (TMTVS 97%, CAS: 2554-06-5,) was supplied from Alfa Aesar, USA. Tin(II) 2-ethylhexanoate (CAS: 301-10-0) and platinum-divinyltetramethyldisiloxane complex 2% in xylene (CAS: 68478-92-2) were supplied from Sigma Aldrich. Photo-curable siloxane of proprietary composition TEGO RC 711 was supplied from Evonik Industries, Germany and a photo-initiator Irgacure 819 was supplied from Ciba Specialty Chemicals, Switzerland.

2.2. Equipment

Spinning devices are generally used in the textile industry. These devices are large scale, complex and costly. For this reason, the laboratory scale spinning device was designed by DVL ARGE Engineering and Trade Company. As shown in Figure 2.1, spinner device consists of 5 parts which are syringe, syringe pump, spool, heater and vertical stage.

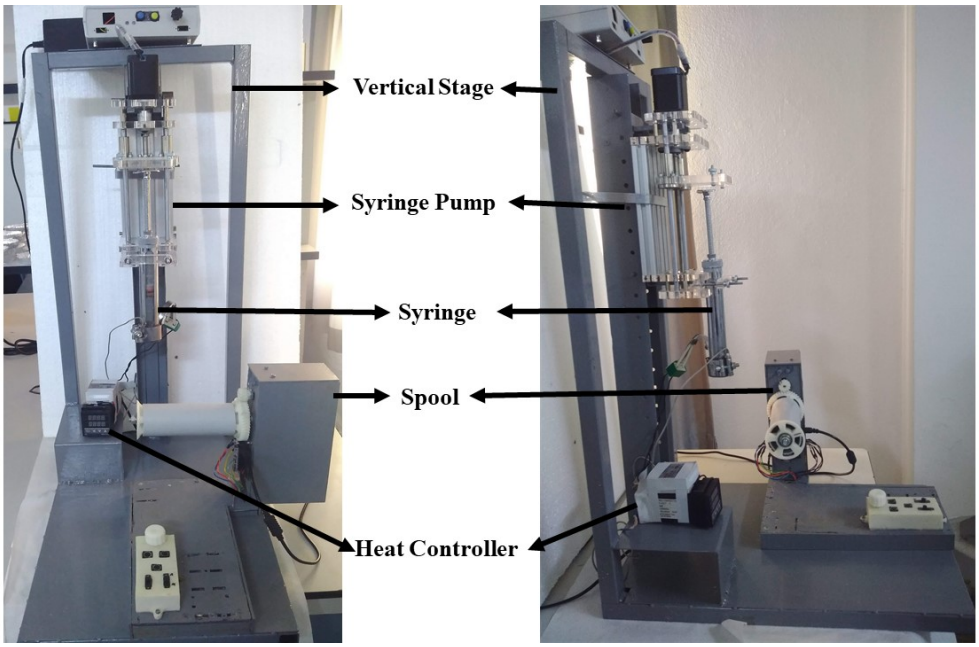


Figure 2.1. Melt spinner.

2.2.1. The Syringe

As shown in Figure 2.2, the used syringe has a volume of 50 ml, dimensions of 21 * 3 cm and durability up to a maximum of 280 ° C.

Figure 2.2. The used syringe.

2.2.2. The Syringe Pump

The syringe pump and control panel are shown in Figure 2.3. The syringe is placed in the first part to apply pressure. The other part is the control panel which enables us to adjust the speed and direction of the applied pressure.

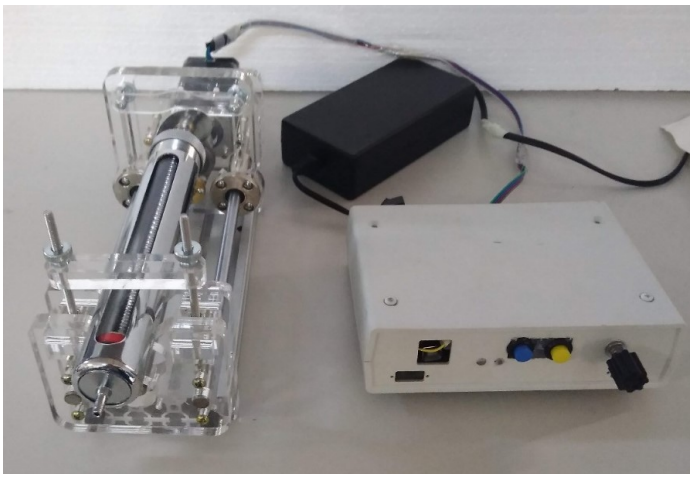


Figure 2.3. a) The syringe pump, b) Control panel.

The place of syringe can be adjusted according to the size of used syringe. The blue key on the control panel is the on/off key, and the yellow key is used to set the pressure direction. The properties of the motor (Model Number: 17HS4401) are 1.8 step angle (degree), current of 1.7 A and its dimensions of 42x42x40.

2.2.3. The Spool

As shown in Figure 2.4, the wheels of the spool were produced with 3D printer using acrylonitrile butadiene styrene (ABS) polymer. 12 V DC Gear motor (EBOWAN brand) was used and its torque is 30 kg.cm.

Figure 2.4. The Spool.

2.2.4. The Heat Controller

The resistance shown in Figure 2.5**.** is wrapped around the syringe. The thermocouple is placed between the syringe and resistance. The temperature is also set on the control panel. The limit of temperature is maximum of 400° C.

Figure 2.5. The heat controller.

2.2.5. The Vertical Stage

A scaffold was designed for spinning in the direction of gravity. As shown in Figure 2.6, it was drawn via AutoCAD program and made in the metal studio in the IZTECH. The height of the syringe pump is adjustable.

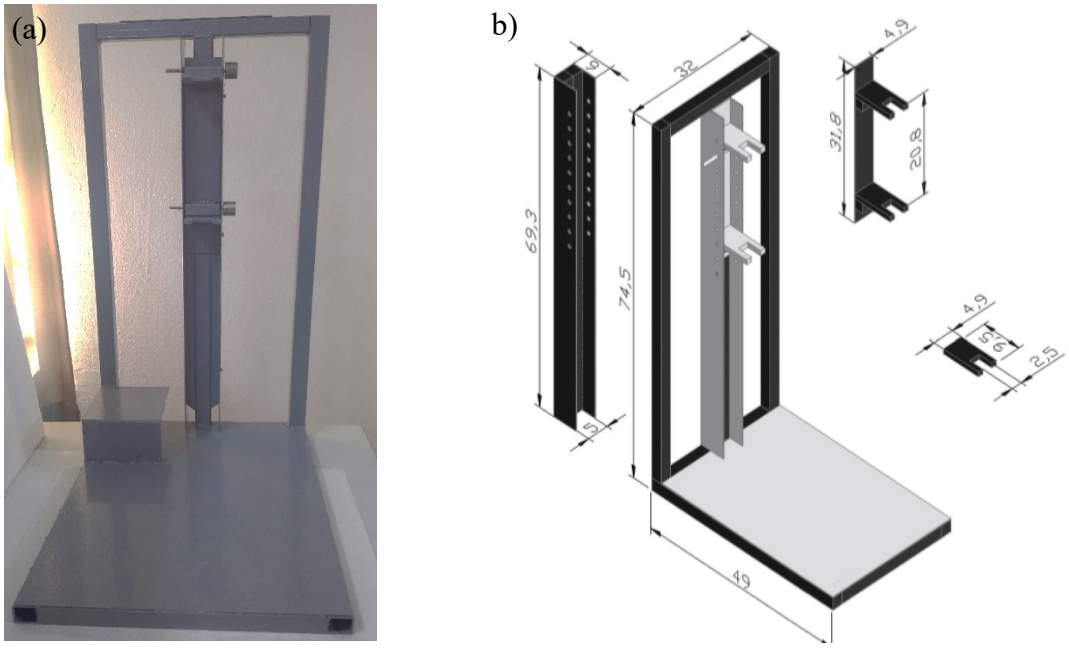


Figure 2.6. a) The vertical stage, b) 3D AutoCAD drawing.

2.3. Methods

Fibers were produced by different curing methods at different spinning temperatures.

2.3.1. Spinning and Curing of Polysiloxanes

A set of experiments were carried out in the presence of polysiloxane resins MK as a preceramic precursor.

In a first set of experiments, MK resin was cured in an oven at 250 °C for 24 h. Si-OH groups in the structure of the silicone resin were cross-linked by condensation at 250 °C. The cured MK was ground in a mortar and hence, the cured MK was obtained in powder form.

As given in Table 2.1, the cured and as received MK were mixed in certain weight percent (wt%) to accelerate the curing process and spun at the temperature range of 90 and 250°C. The batches inserted into an oven and temperature was increased to 200 °C.

Table 2.1. Spinning parameters

Batches	Temperature (°C)	Cured MK (wt%)	As received MK (wt%)
F1-100MK-AS	90	0	100
F1-95MK-5CMK-AS		5	95
F1-90MK-10MK-AS		10	90
F1-75MK-25MK-AS		25	75
F2-100MK-AS	120	0	100
F2-95MK-5CMK-AS		5	95
F2-90MK-10MK-AS		10	90
F2-75MK-25MK-AS		25	75
F3-100MK-AS	150	0	100
F3-95MK-5CMK-AS		5	95
F3-90MK-10MK-AS		10	90
F3-75MK-25MK-AS		25	75
F4-100MK-AS	180	0	100
F4-95MK-5CMK-AS		5	95
F4-90MK-10MK-AS		10	90
F4-75MK-25MK-AS		25	75
F5-100MK-AS	200	0	100
F5-95MK-5CMK-AS		5	95
F5-90MK-10MK-AS		10	90
F5-75MK-25MK-AS		25	75

(cont. on next page)

Table 2.1. (Cont.)

F6-100MK-AS	220	0	100
F6-95MK-5CMK-AS		5	95
F6-90MK-10MK-AS		10	90
F6-75MK-25MK-AS		25	75
F7-100MK-AS	250	0	100
F7-95MK-5CMK-AS		5	95
F7-90MK-10MK-AS		10	90
F7-75MK-25MK-AS		25	75

According to the experimental results, the most homogenous fiber was found to be F1-100MK-AS and then, it was cured by a different method. In this method, baths containing dibutyltin dilaurate and tin (II) 2-ethylhexanoate metallic catalysts were prepared to cure the fibers shown in Figure 2.7. In order to use the catalysts more economically, dibutyltin dilaurate and tin (II) 2-ethylhexanoate were diluted in DMF and water. MK is insoluble in water and DMF. They were mixed to become a homogeneous solution by a magnetic stirrer for 30 minutes. Obtained F1-100MK-AS fiber was immersed in the baths. This step is necessary to avoid melting during high temperature ceramization process.

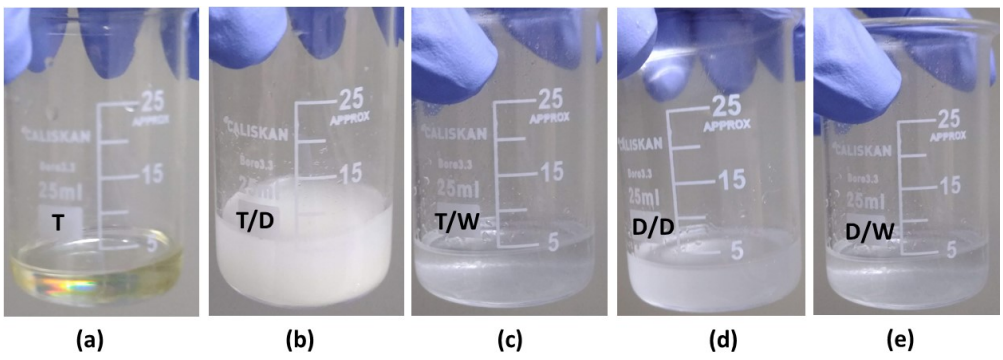


Figure 2.7. Curing baths a) 100 wt% tin (II) 2-ethylhexanoate catalyst, b) 5 wt% tin (II) 2-ethylhexanoate catalyst in DMF, c) 5 wt% tin (II) 2-ethylhexanoate catalyst in water, d) 5 wt% dibutyltin dilaurate catalyst in DMF, e) 5 wt% dibutyltin dilaurate catalyst in water.

In the second set of experiments were carried out with MK and catalyst tin (II) 2-ethylhexanoate. They were mixed into a glass beaker at the given amounts given in Table 2.2. The mixture was spun at 90 °C.

Table 2.2. Parameters of the second experiment

Spinning Temperature (°C)	**As received MK (g)**	**Catalyst tin (II) 2-ethylhexanoate (µL)**
90	1	50
90	1	25

In a third set of experiments, the commercially available polysiloxane oil PHMS, a cyclic TMTVS, catalyst Pt were used. The catalyst Pt (0.05 wt%) was diluted in xylene solution containing of catalyst. Preceramic mixture was prepared using PHMS and TMTVS in a beaker and the used amounts were given in the Table 2.3. The preceramic mixture was mixed by a magnetic stirring at room temperature (RT) for 3 min at 300 RPM. After that, xylene solution containing 0.05 wt% catalyst Pt was added into the mixture. The blend was mixed for 1 min.

Table 2.3. Parameters of the third experiment.

PHMS (g)	**Cyclic TMTVS (µl)**	**Catalyst Pt (µl)**
1 g	100	200

In a fourth set of experiments, liquid photocurable siloxane of TEGO RC 711, photo initiator Irgacure 819 and MK were used. Photocurable preceramic blend was prepared using TEGO RC 711 and Irgacure 819. They were mixed by a magnetic stirring at RT for 15 min. Then, MK was added into the solution. Blend was mixed for 10 minutes in the amounts given in the Table 2.4. The prepared mixture was spun at 80 °C.

The obtained fibers with photocurable siloxane were cured for 2h under UV of 365 nm wavelength in nitrogen ambient.

Table 2.4. Parameters of the fourth experiment.

Spinning Temperature (°C)	TEGO RC 711 (g)	Irgacure 819 (g)	MK (g)
80	0.5	0.045	1.5

2.3.2. Conversion Process from Polysiloxane to SiOC

Cured fibers were pyrolyzed at 1000 °C with a heating rate of 2 °C/min in a tabular furnace (PROTERM PTF 16/75/450, Ankara, Turkey) had alumina tube and 2h dwell time at the maximum temperature under Ar flow (2 L/min).

2.4. Characterization

The morphology of the preceramic polymers and SiOC fibers were investigated by Scanning Electron Microscopy (SEM; Quanta 250, FEI, Hillsboro, OR, USA) and cross-sections and surfaces of them were analyzed via energy dispersive X-ray (EDX) spectrometer attached SEM. Before analysis, samples surfaces were coated with ~10 nm Au (Emitech K550X sputter coater, Qnorum Technologies, UK). Phase analysis of the ceramic fibers was analyzed by the Philips X'Pert Pro instrument (2θ, from 10° to 90°and the scan step; 0.005 °/second). The polymer-to-ceramic conversion was determined by differential thermal analysis/thermal gravimetry (DTA/TG). The analysis was carried out with a STA 8000 Perkin Elmer Diomand TGA instrument under nitrogen flow using a heating rate of 5 °C min^{-1} up to the maximum temperature of 1000 °C.

CHAPTER 3

RESULTS AND DISCUSSION

In the first set of experiments, although as received MK was mixed with cured MK, when the temperature of the oven was reached to the melting temperature of MK, the shape of fibers was not conserved and thus, they melted as shown in Figures 3.1-3.7.

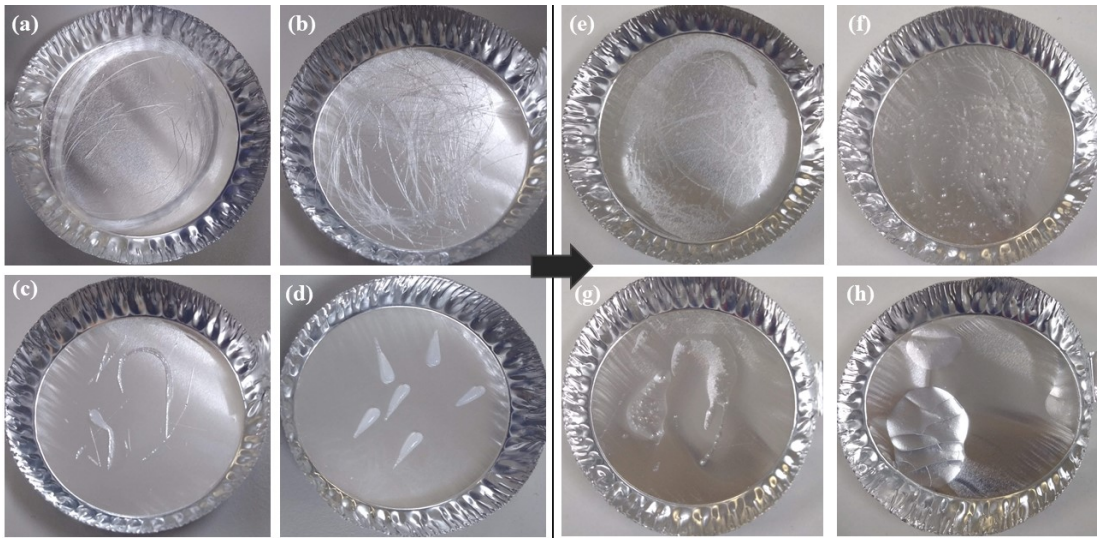


Figure 3.1. Before oven curing a) F1-100MK-AS, b) F1-95MK-5CMK-AS, c) F1-90MK-10CMK-AS, d) F1-75MK-25CMK-AS, after oven curing (@200°C/ 24h), e) F1-100MK-OC, f) F1-95MK-5CMK-OC, g) F1-90MK-10CMK-OC, h) F1-75MK-25CMK-OC.

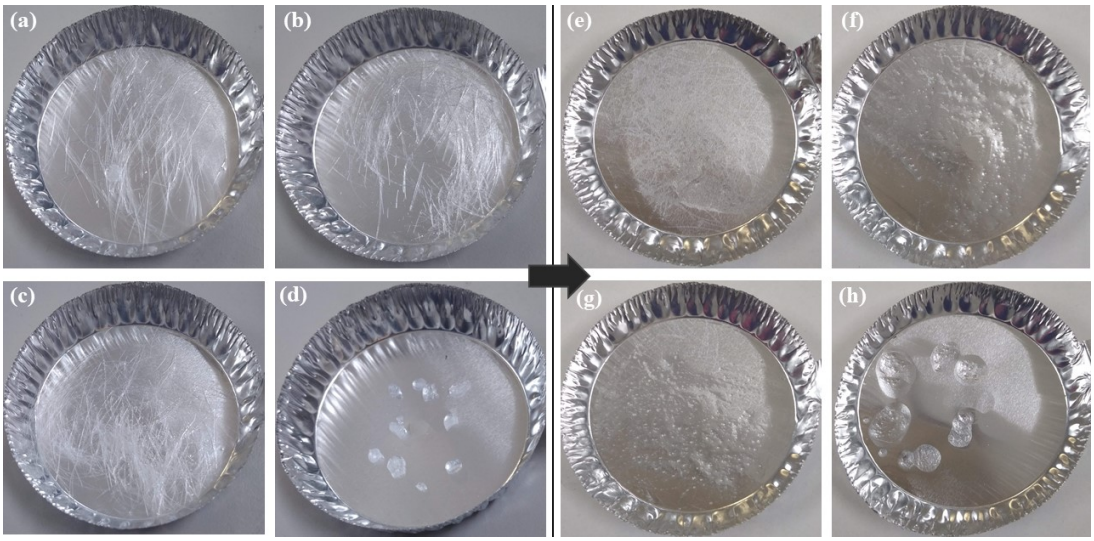


Figure 3.2. Before oven curing a) F2-100MK-AS, b) F2-95MK-5CMK-AS, c) F2-90MK-10CMK-AS, d) F2-75MK-25CMK-AS, after oven curing (@200°C/ 24h), e) F2-100MK-OC, f) F2-95MK-5CMK-OC, g) F2-90MK-10CMK-OC, h) F2-75MK-25CMK-OC.

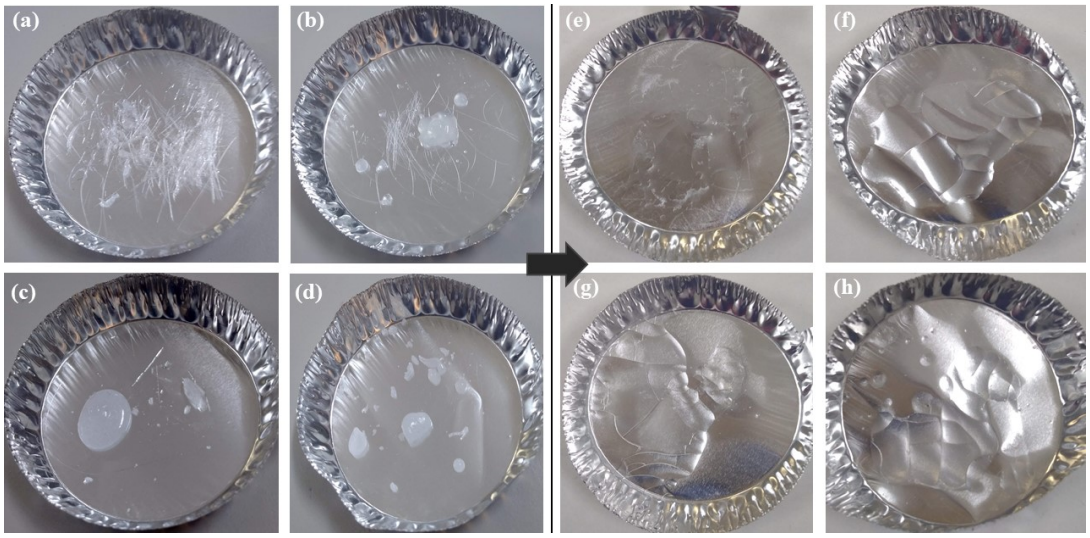


Figure 3.3. Before oven curing a) F3-100MK-AS, b) F3-95MK-5CMK-AS, c) F3-90MK-10CMK-AS, d) F3-75MK-25CMK-AS, after oven curing (@200°C/ 24h), e) F3-100MK-OC, f) F3-95MK-5CMK-OC, g) F3-90MK-10CMK-OC, h) F3-75MK-25CMK-OC.

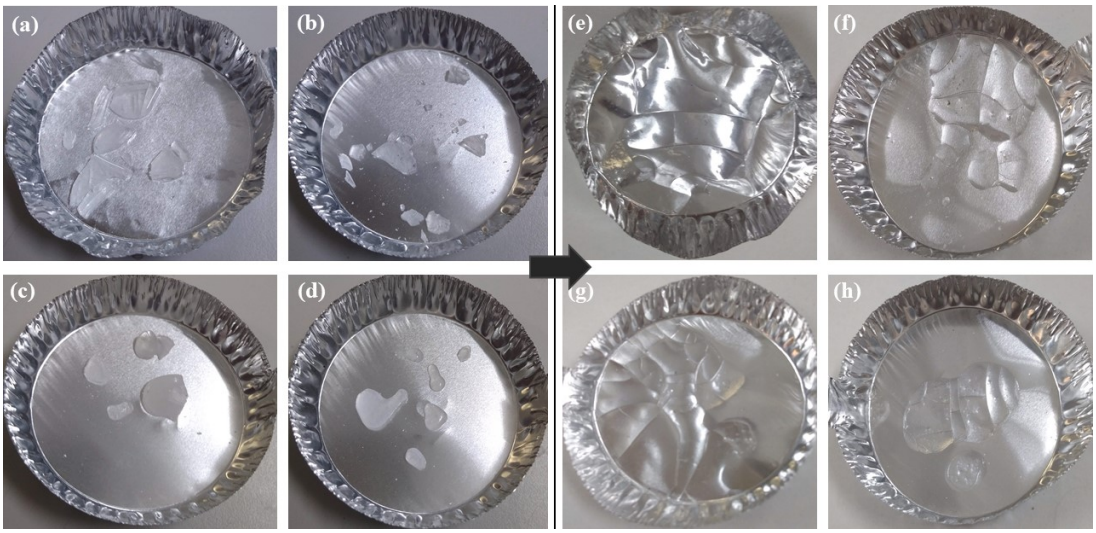


Figure 3.4. Before oven curing a) F4-100MK-AS, b) F4-95MK-5CMK-AS, c) F4-90MK-10CMK-AS, d) F4-75MK-25CMK-AS, after oven curing (@200°C/ 24h), e) F4-100MK-OC, f) F4-95MK-5CMK-OC, g) F4-90MK-10CMK-OC, h) F4-75MK-25CMK-OC.

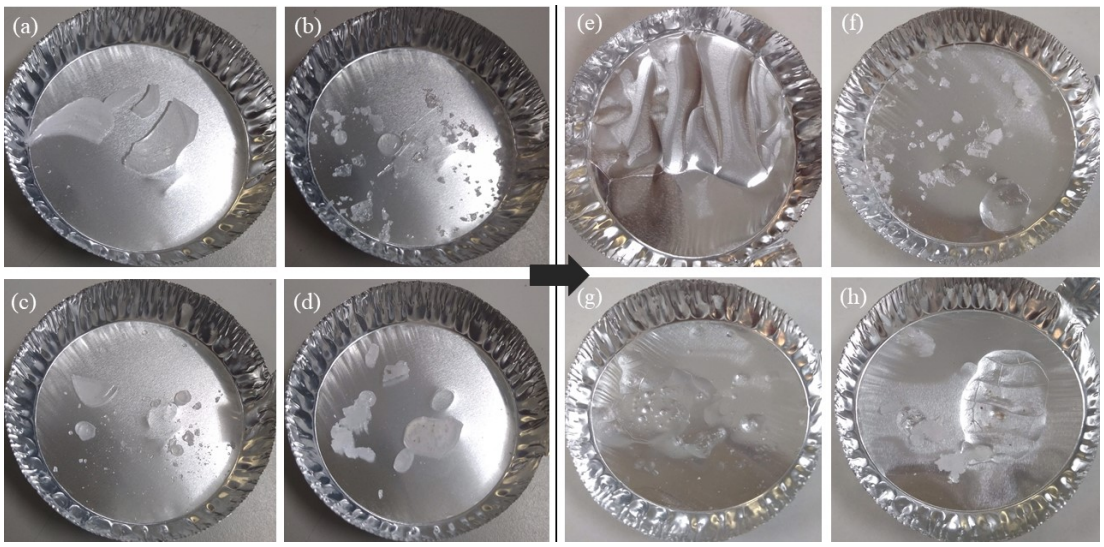


Figure 3.5. Before oven curing a) F5-100MK-AS, b) F5-95MK-5CMK-AS, c) F5-90MK-10CMK-AS, d) F5-75MK-25CMK-AS, after oven curing (@200°C/ 24h), e) F5-100MK-OC, f) F5-95MK-5CMK-OC, g) F5-90MK-10CMK-OC, h) F5-75MK-25CMK-OC.

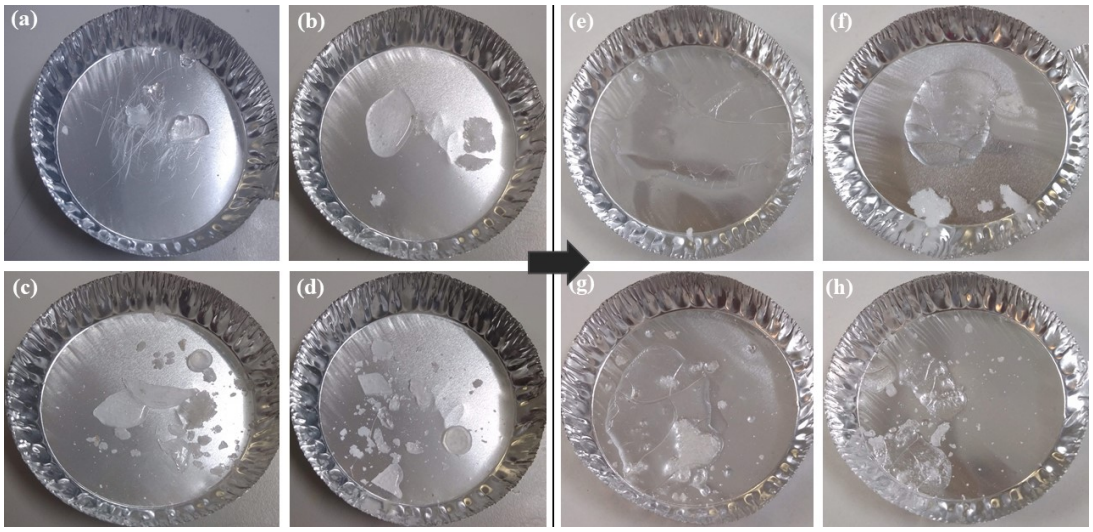


Figure 3.6. Before oven curing a) F6-100MK-AS, b) F6-95MK-5CMK-AS, c) F6-90MK-10CMK-AS, d) F6-75MK-25CMK-AS, after oven curing (@200°C/ 24h), e) F6-100MK-OC, f) F6-95MK-5CMK-OC, g) F6-90MK-10CMK-OC, h) F6-75MK-25CMK-OC.

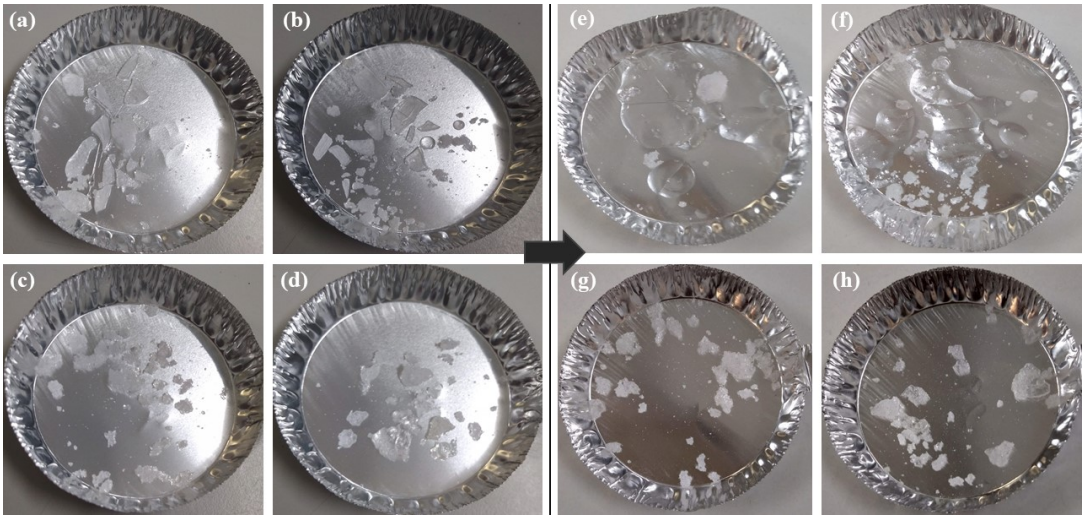


Figure 3.7. Before oven curing a) F7-100MK-AS, b) F7-95MK-5CMK-AS, c) F7-90MK-10CMK-AS, d) F7-75MK-25CMK-AS, after oven curing (@200°C/ 24h), e) F7-100MK-OC, f) F7-95MK-5CMK-OC, g) F7-90MK-10CMK-OC, h) F7-75MK-25CMK-OC.

The fibers could not conserve their shape as a result of heat curing, so the curing was achieved in the pools prepared with catalyst and the fibers were pyrolyzed.

As a result of pyrolysis, the form of dense fibers was obtained in the 100 wt% tin (II) 2-ethylhexanoate catalyst in bath and 5 wt% tin (II) 2-ethylhexanoate catalyst in DMF bath. However, the cured fiber in the DMF bath (F1-100MK-AP2) is more brittle than the cured fiber in the tin (II) 2-ethylhexanoate bath (F1-100MK-AP1).

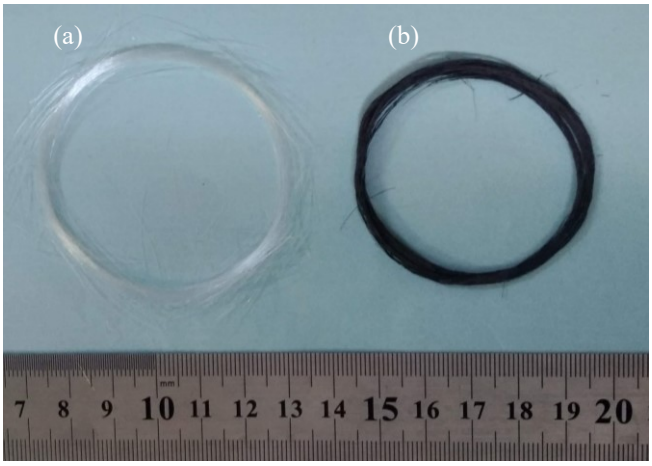


Figure 3.8. Before curing, a) F1-100MK-AS after pyrolysis (AP), b) F1-100MK-AP1.

In a second set of experiments, fiber could not be produced because the MK and catalyst tin (II) 2-ethylhexanoate mixture was cured at the spinning temperature. The mixture was pellet in the syringe. Although the experiment was repeated by reducing the amount of catalyst, the production of fiber could not be achieved.

In the third set of experiments, spin could not be achieved because the viscosity of the mixture prepared from preceramic polymers was low. The viscosity of mixture and solidification temperature are important parameters for spinning.

In the fourth set of experiments, it was observed that the fibers could not conserve their shape during curing under UV since there is a temperature increase due to UV irradiation. The experiment was repeated by reducing the curing time to half an hour and keeping the other parameters as constant with the previous experiment. However, the fibers could not conserve their shape even the curing time reduced to half an hour and they melted.

2.5. Morphological Properties of Fibers

Before curing and after pyrolysis morphology of dense fibers were analyzed by SEM**.** Figure 3.9 shows SEM F1-100MK-AS (before curing) fabricated by melt spinner and the fiber is about 55 µm in size. It was observed that the outer surface of the fiber is smooth, however, bubbles form on the inner surface due to the applied heat during the spin. These bubbles in the structure are formed due to the condensation of Si-OH bonds by the effect of applied heat.

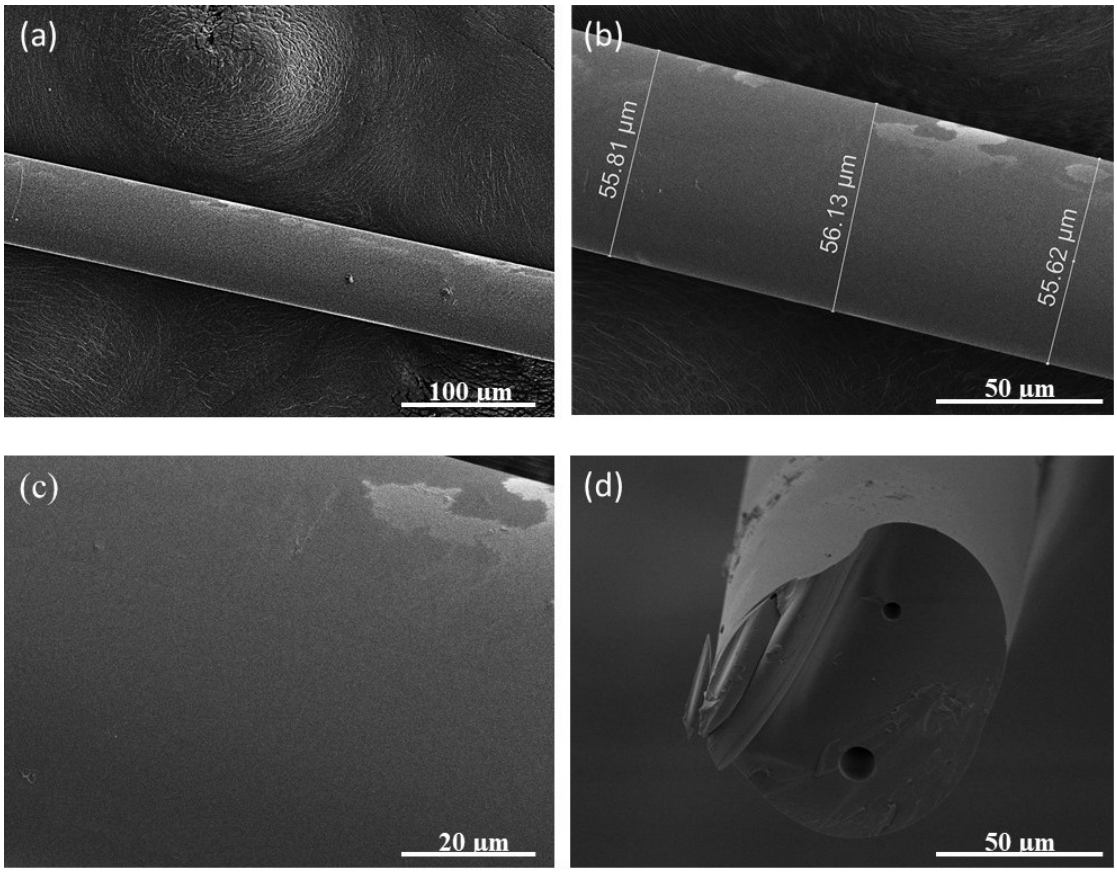


Figure 3.9. SEM image of FI-100MK-AS a-c) outer surface, d) cross-sectional area.

After pyrolysis, the morphology of the fibers has changed considerably as shown in Figure 3.10. The thickness of the fiber increased to 65-70 µm and spheres of 2-5 µm were formed on the surface.

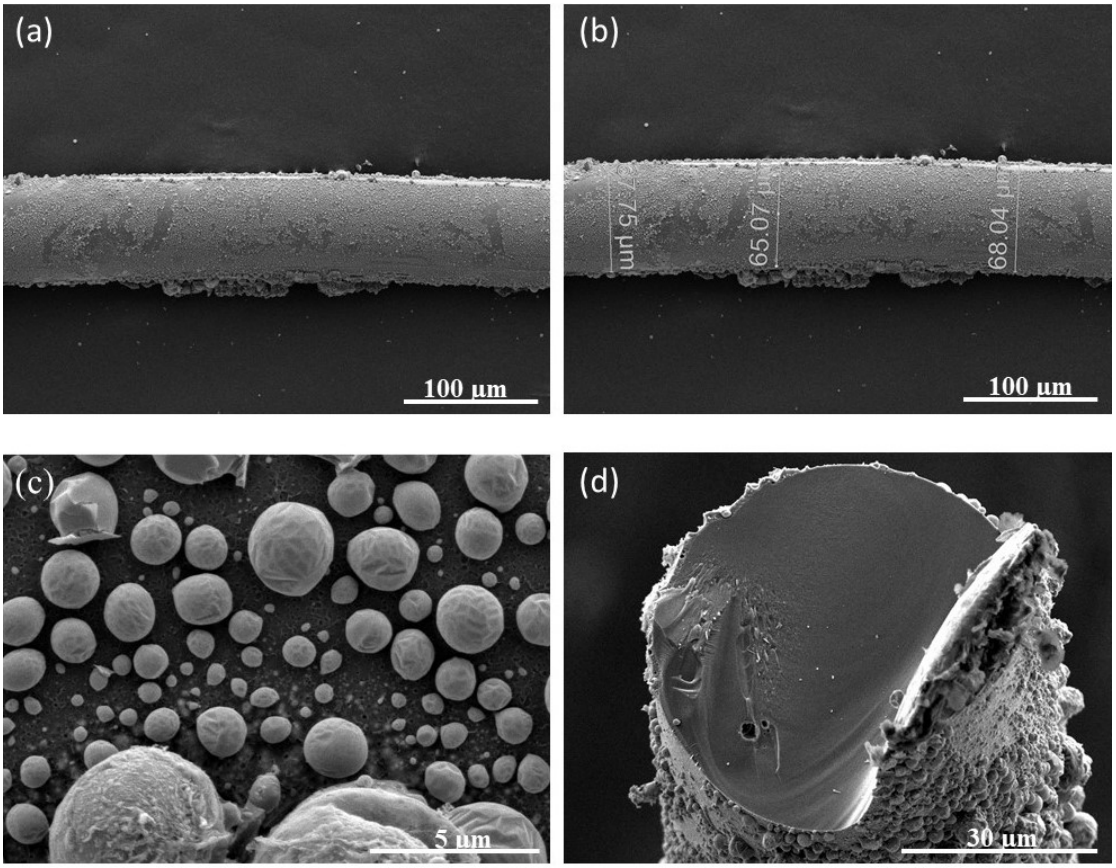


Figure 3.10. SEM image of 1000 °C pyrolyzed FI-100MK-AP1 (4h curing 100 wt% tin in bath), a-c) outer surface, d) cross-sectional area.

As shown in Figure 3.11, the thickness of the fiber increased to 120-130 µm and spheres of 2-4 µm formed on the surface. In order to investigate the spheres formed on the surface, an energy dispersive X-ray (EDX) spectrum analysis was performed.

EDX spectrum analysis was performed to determine the elemental composition of the cross-section and surface of the fiber. As shown in Figure 3.12. a) spectrum 1 analysis was used to determine the chemical composition of the surface. As a result of the analysis, the conversion of MK to SiOC was confirmed. As shown in Figure 3.12. b), Spectrum 2 analysis was performed to identify the chemical composition of the spheres formed on the surface. The result of analysis came out that the spheres formed on the surface were tin which is used in the bath prepared to cure the fibers.

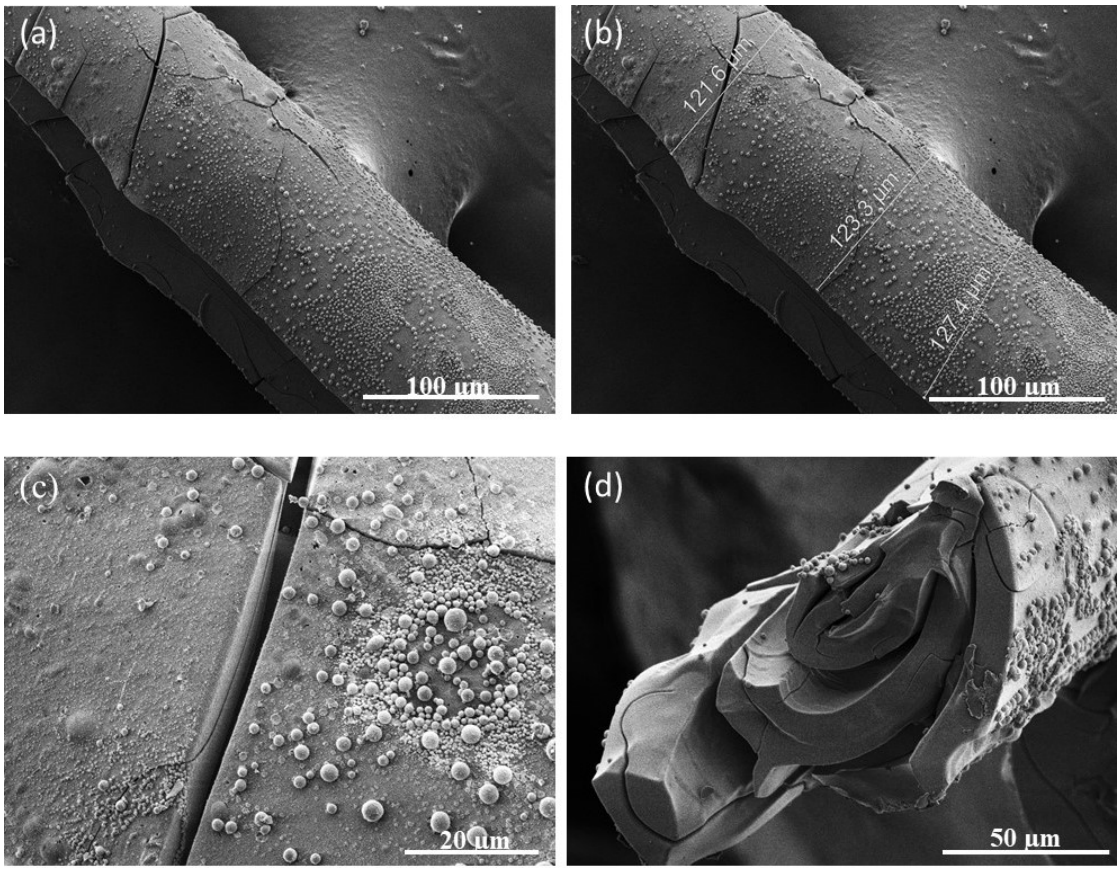


Figure 3.11. SEM image of 1000 °C pyrolyzed FI-100MK-AP2 (4h curing 5 wt% tin (II) 2-ethylhexanoate in DMF bath) a-c) outer surface, d) cross-sectional area.

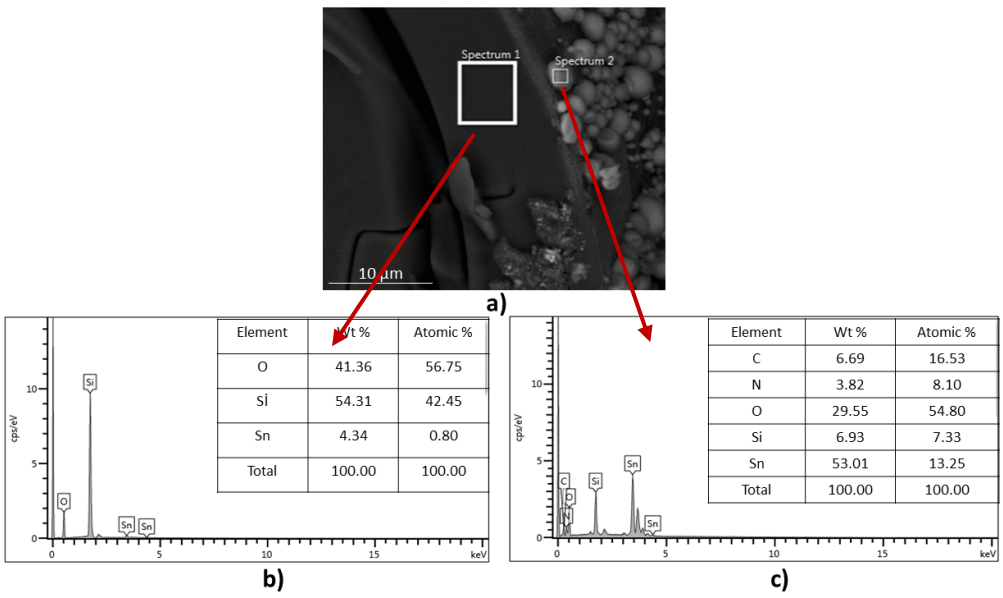


Figure 3.12. SEM image of F1-100MK-AP2, a.) image of cross-sectional area, EDX analysis of, b) spectrum 1, c) spectrum 2.

2.6. Structural Properties of Fibers

The pyrolytic conversion from the preceramic polymer to ceramic and the amount of catalyst tin (II) 2-ethylhexanoate which did not decompose during pyrolysis were investigated by thermal gravimetric analysis.

Based on the curve shown in Figure 3.13, the MK preceramic polymer had a mass loss starting from ≈230°C which is a result of the polycondensation reactions during cross-linking, with release of gaseous by-products. At temperatures higher than ≈350°C, there is an almost continuous mass loss due to the ceramization decomposition reactions, which ends at ≈800°C. Additionally, the MK shows a ceramic yield of 85 wt% at 1000°C.

Based on the curve shown in Figure 3.13, the metallic catalyst tin (II) 2-ethylhexanoate remains 21 wt% at 1000°C.

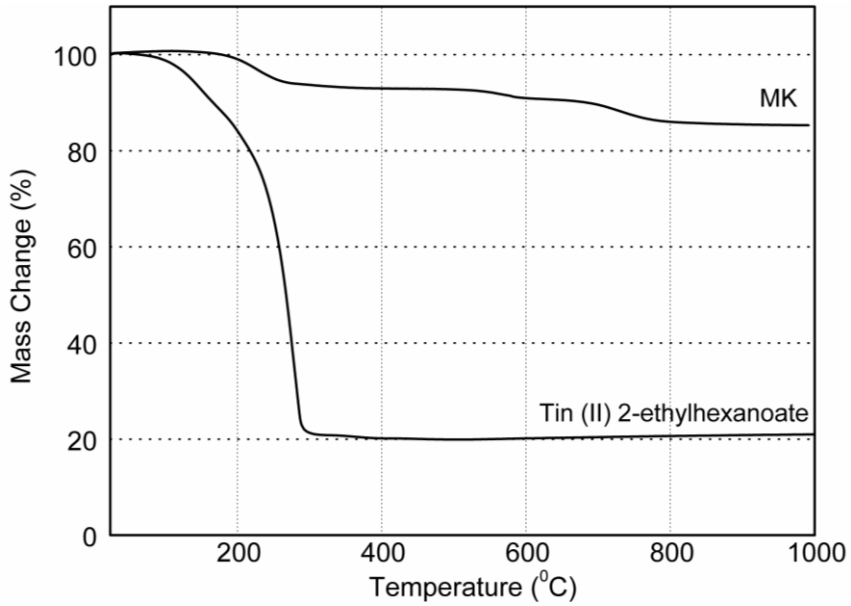


Figure 3.13. TGA curves for the as received MK and catalyst tin (II) 2-ethylheanoate.

X-ray diffraction analysis was performed to confirm the EDX analysis result. As shown in the Figure 3.13, metallic tin gave a perfect match with the calculated pattern. (ICDD No: 86-2264). As a result, EDX analysis results are in line with XRD analysis results. The remaining 21wt% of tin was observed as crystals in the structure at 1000 °C.

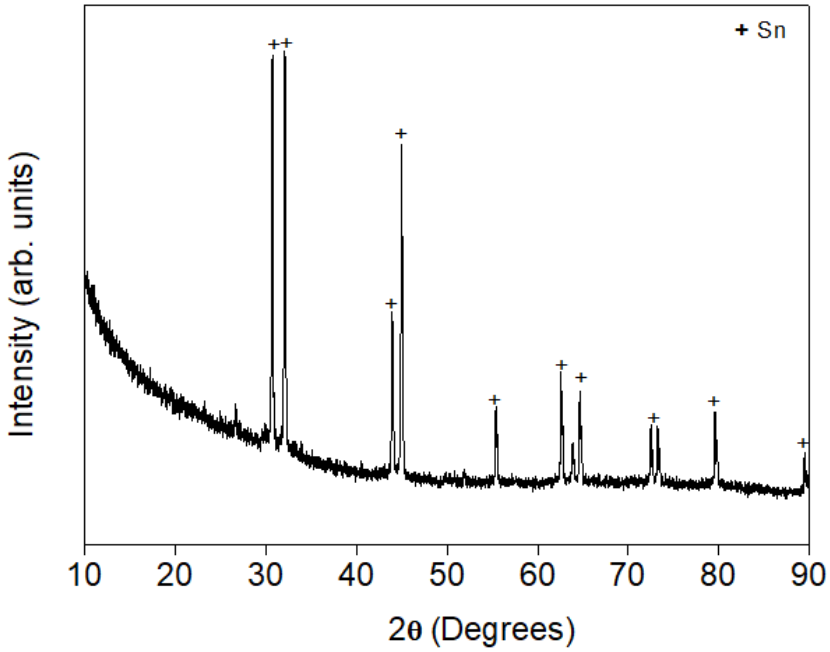


Figure 3.14. X-ray diffraction patterns of the F1-100MK-A1.

CHAPTER 4

CONCLUSIONS

In this thesis, the melt spinner device was designed and made for the production of ceramic fiber from polysiloxane which is the most economical preceramic polymer. After that, spinning of different preceramic polymers was attempted.

Fibers (about 55 μm thickness) were obtained from the polysiloxane polymer MK. They were cured by different methods such as temperature, UV and catalyst and were pyrolyzed. As a result of pyrolysis, 65-70 μm thickness SiOC fibers were achieved. The unexpected increase in the thickness of the fibers is due to the fact that the catalyst did not decompose during pyrolysis. Because the catalyst used (tin (II) 2-ethylhexanoate) is metallic, it did not decompose at 1000°C and the surface of the fiber coated in the form of spheres of 2-5 μm thickness.

In future studies, different polysiloxanes and curing methods can be developed to produce ceramic fibers with more homogeneous and smoother surface morphology. Thus, the usage area of the produced ceramic fibers can be increased.

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