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SYNTHESIS AND CHARACTERIZATION OF POLYCAPROLACTONE NANOCOMPOSITE FIBER WITH TITANIUM DIOXIDE ADDITIVES

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ABSTRACT

Nanotechnology can control the atomic, molecular, and supramolecular levels of matter. As the size of a particle goes down to nano-size, materials exhibits good characteristics in terms of electronics, optic, thermal, magnetic and fotocatalysis properties. The nano composite fibers comprise of finely dispersed flakes of the second phase inorganic material with nylon or polyester type fiber forming polymers. Nano-fiber based materials obtained by the method of electrospining in the interest of the outstanding features has increased due to the common application areas of filtration, composites, medicine. In this research, we produced nano composites at 0.50 1, 2, and 4 % ratio using polycaprolactone (PCL) and titanium dioxide (TiO2). Energy Dispersive X-Ray Spectroscopy (EDS) and Scanning Electron Microscopy (SEM) were used to analyze titanium dioxide nano fibers.

Keywords: Electrospinning, Nanofiber, Polycaprolactone, Titanium dioxide

1. INTRODUCTION

Nanotechnology is a technology that deals with the numbers and transactions of the metric in the billion. With a wider narrative, the material is engineered at the atomic molecular dimension and new and different properties are made more obvious. It is the development of functional materials and systems for controlled production of nano-sized physical, chemical and biological phenomena. [1] The properties possessed by a material vary when the size of the material in one or more directions is reduced at the nanometer level. For example, ceramics, normally fragile, can easily deform and shape when the grain size is reduced to nanometer. Gold size shows red color in 1 nm. Composite materials reinforced with nanosized powders achieve much higher performance values. New products can be obtained in various fields (medicine, electronics, defense, textile, etc.) by taking advantage of the superior features that nanotechnology has achieved. [2] In 1930s Carothers group synthesized a polymer called Polycaprolactone (PCL). [3]

Polycaprolactone polymer (PCL) is a synthetic polymer used as a suture material in clinical applications approved by the Food and Drug Administration (FDA). PCL has both biocompatibility and slow degradability, which promotes bone growth. [4] It is nontoxic, has low immunogenicity, and is extensively applied in tissue engineering for many years. [5] PCL is a biodegradable polymer with a ring-opening polymerization of caprolactone. [6] PCL can be biodegradable by living organisms in the external environment, for example by fungi and bacteria. However, they cannot be biodegradable in animal and human body due to lack of suitable enzyme. [7]

Titanium dioxide (TiO_2) is a naturally occurring titanium oxide. Also known as titania, titanium IV oxide or titanium oxide. [8] Titanium dioxide is known as a research material. Among the reasons for to use as a research material is biocompatibility, electrical, physical and optical properties and the balance of its chemical structure. [9] There are three mineral forms of titanium dioxide. These forms

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are anatase, brookite and rutile, respectively. The anatase type TiO_2 is often used as a fotocatalysis property under UV irradiation. Rutile type of TiO_2, which is another form, is mainly used as white pigment in paints. TiO_2 is a versatile material which is used in many fields such as cosmetics, industry in many products. For example, in sunscreen lotions, paint pigments, toothpastes, solar cells, electrochemical electrodes, capacitors are also used as a food coloring agent. [10]

In this paper, TiO_2 was obtained using sol gel production method. This method is a technique by which a lot of materials can be produced by preparing the solution, gelling and removing the solvent from the system. In sol-gel production method, there are three different ways to obtain the end product. First one; gelation of a solution of colloidal powders. Second one; Hydrolysis and polycondensation of alkoxide or nitrate precursors. Then drying the gels. Last one; Hydrolysis and polycondensation of alkoxide precursors followed by aging and drying under ambient atmospheres. The purpose of the Sols function is to show the distribution of colloidal particles in the liquid. Colloids consist of solid particles with a diameter of 1-100 nm. [11]

Electrospinning is a simple and versatile method for producing various nanofibres from polymer. [12] Electrospinning is an old technique but still impressive. It was first observed by Rayleigh in 1897. It was then examined by Zeleny in 1914 as an electrospray and patented by Formhals in 1934. [13] Electrospinning is a worldwide production method. It is a highly preferred method because of the size, shape, flexibility, completeness and cost of the products in many scientific and technological applications compared to other technical products. The electrospinning method allows scientists to produce fibers in beaded or non-beaded tissue forms in the micro- and nano-size range. These nanofibers are produced by a directed jet of a polymeric solution with the aid of electrostatic force. The polymer jet is not affected by rigidity due to the interaction of the charged particles with the electrostatic field, and is placed in an amount of capillary before collecting in the grounded collector. The solvent evaporates during this process. Depending on the types of collectors, solidified fibers in an alignment or in the form of nonwoven fibers are obtained from these processes. [4] Different variables have been discussed during the electrospinning process. When these variables are not specified, some variables cause direct fiber formation and high quality nano fibers to fail during processing. In various literature researches, these study parameters are classified under many different subheadings such as process parameters, solution parameters and environmental conditions. [14]

Table 1. Parameter of Electrospinning Process [6]

Process Parameters	**Solution Parameters**	**Environmental Conditions**
Flow Rate	Viscosity/ Concentration	Temperature
Electric field strength	Conductivity	Humidity
Distance between tip and collector	Solution tension	Air velocity
Needle tip design	Polymers molecular weight	
Collector composition and geometry	Dipole moment	
NA	Dielectric constant	NA

Nano Composite fibers consist of nano or polyester-type fiber forming polymers and finely dispersed nano-sized particles consisting of a second-phase inorganic material and at least one dimension of one of the phases being below 100 nm.[1, 16] In nanocomposites due to their high area / volume ratios, the interfacial areas at which the matrix materials and reinforcing materials are in contact with each other have better properties than those of conventional composites.[1] This involves obtaining biphasic fibers with other refinement properties such as physical strength, high mechanical strength, electrical conductivity and /or thermal stability.[16] Because of these properties, nanofibers and nano-fiber based materials become increasingly popular and important R & D studies in the industry.[17]

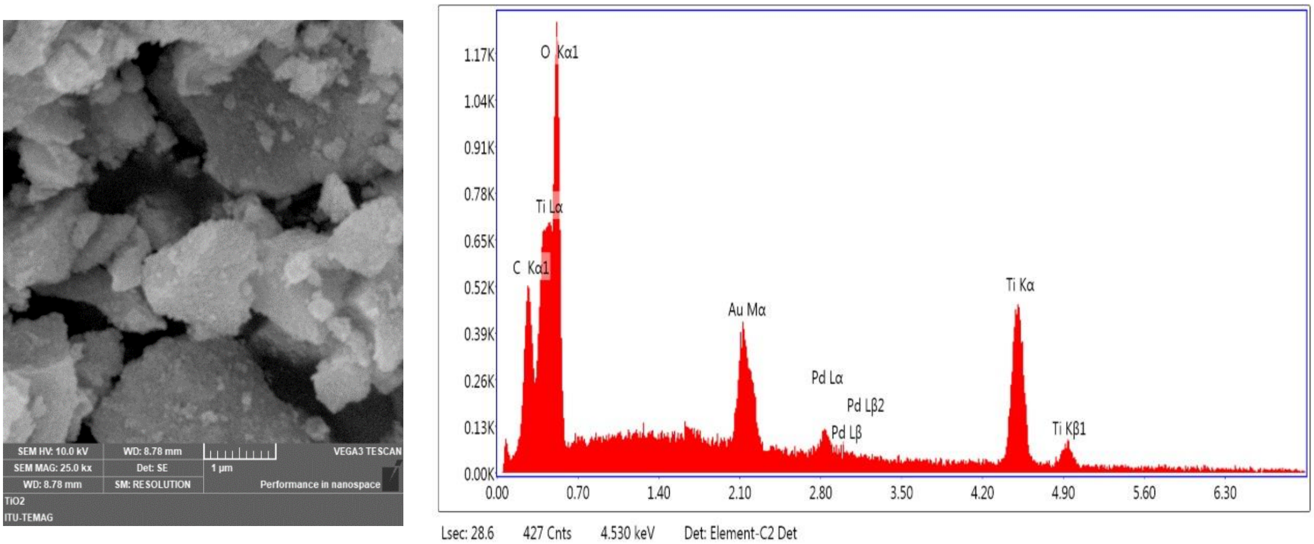
2. MATERIALS AND METHOD

2.1. Materials

This research was done using PCL and TiO_2 particles. PCL was obtained Sigma Aldrich (M.W.: 80000). In order to get composite fibers, Istanbul Commerce University (ICU) Nanotechnology Lab is use TiO_2 polymeric solution. PCL dissolve using chloroform and acetonitrile. Chloroform for analysis ($CHCL_3$) (M.W.: 119,38 g/mol) and Acetonitrile (CH_3CN) (M.W.: 41,05 g/mol) were obtained Merck, Germany. TiO_2 particles are obtained by sol-gel method. 2-Propanol anhydrous 99,5 % (C_3H_8O) (M.W.: 60.10 g/mol) and Titanium (IV) Butoxide (≥97,0 %) ($C_{16}H_{36}O_4Ti$) (M.W.: 340,32 g/mol) were obtained Sigma Aldrich which are necessary for this process.

2.2. Method

The first step is the fabrication of the TiO_2 particles by using sol gel method. Isopropanol and Titanium (IV) Butoxide chemicals are used to prepare TiO_2 particles. These chemicals are stirred for about 10 minutes and then a 10 % HCl solution is added to dropwise using a pipette. Once the gel has formed, it is dried at 80 ° C for 24 hours or until it has completely solidified. After drying, the powdering process begins. The resulting amorphous TiO_2 particles are annealed at 550 ° C for 2 hours. TiO_2 was analyzed by using Scanning Electron Microscopy (SEM, TESCAN at ITU-TEMAG Lab, ISTANBUL) with 25.0 K X magnification SEM-EDS results were also demonstrated in order to demonstrate the purification of TiO_2.The results of this analysis shown in figure 1.



(a) Morphology of TiO_2 by SEM (b) Elemental analyze of TiO_2 by SEM-EDS.

Figure 1.: Characterization of TiO_2 (a) Morphology of TiO_2 by SEM (b)Elemental analyze of TiO_2 by SEM-EDS

Other step is preparation of the polymeric solution. PCL was dissolved in solvents chlorofom and acetonitrile at ratio of 85:15. Electrospinning was used to fabricate PCL nanofibers. PCL incorparated with TiO_2 different concentrations of 0.50, 1, 2 and 4 wt % electrospinning was performed under various conditions. The prepared solutions were mechanically stirred at 300 rpm and 50 ° C for 24 hours. Each prepared polymeric solution is poured into a 10 ml plastic syringe and and placed into the electrospinning device NE 200 NanoSpinner. The flow rate of the polymer solution from the syringe was controlled by means of a programmable syringe pump. Nanofiber was electrospun at ~25KV with flow rate of 1 ml/hr. Collector was fixed at ~25 cm far from the nozzle to collect the nanofiber mesh. Figure 2 shows the schematics of an electrospinning process.

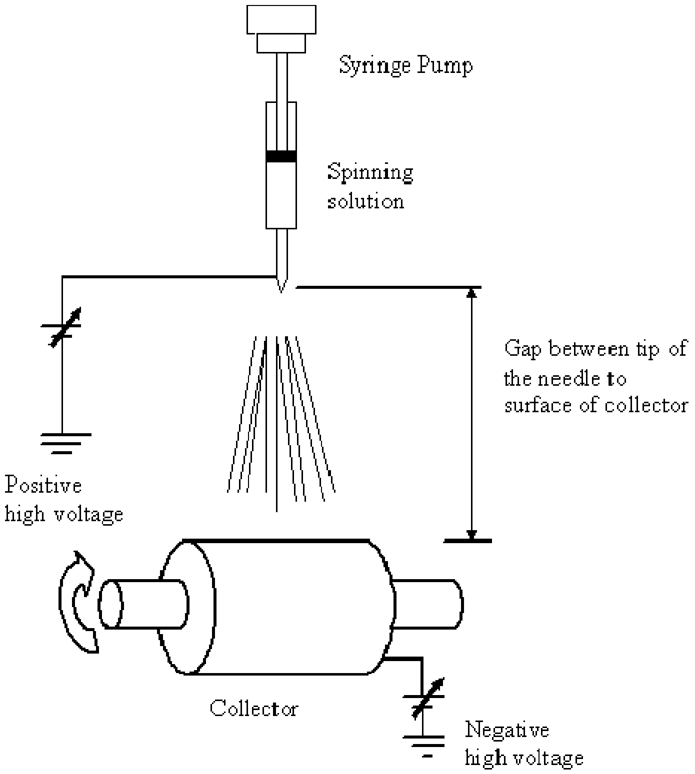
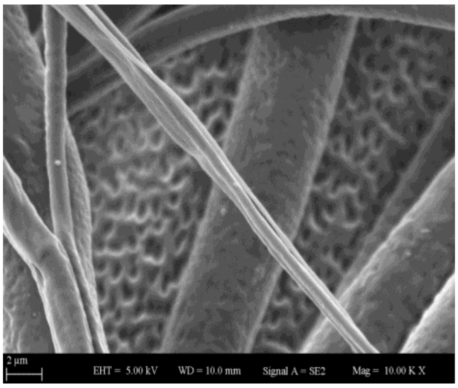


Figure 2. Schematic view of an electrospinning process [18]

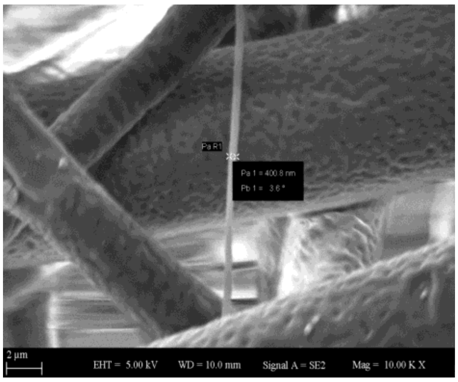
3. RESULTS AND DISCUSSION

TiO_2 – PCL nanocomposites fibers surfaces were coated with Au-Pd in order to ensure the conductive surface and the morphologies of the TiO_2 – PCL nanocomposite fibers were observed by using Scanning Electron Microscopy (SEM, ZEISS SIGMA at Yıldız Technical University Center Lab, Istanbul). SEM-EDS results were also demonstrated in order to observe chemical composition of the composites. TiO2 - PCL nanocomposite fibers coated on fibers were shown in SEM images in Figure 3. TiO_2 – PCL nanofibers were achieved and tested. In Figure 3 shows the estimated fiber sizes of TiO_2 - PCL nanocomposite fibers by looking at the SEM images.

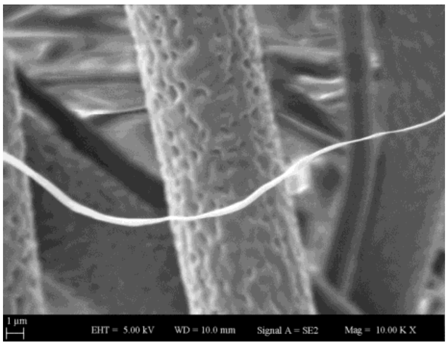
(a)Pure PCL



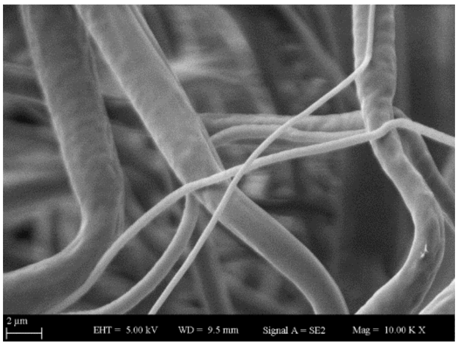
(b) % 0.50 TiO_2



(c) % 1 TiO_2



(d) % 2 TiO_2



(e) % 4 TiO_2

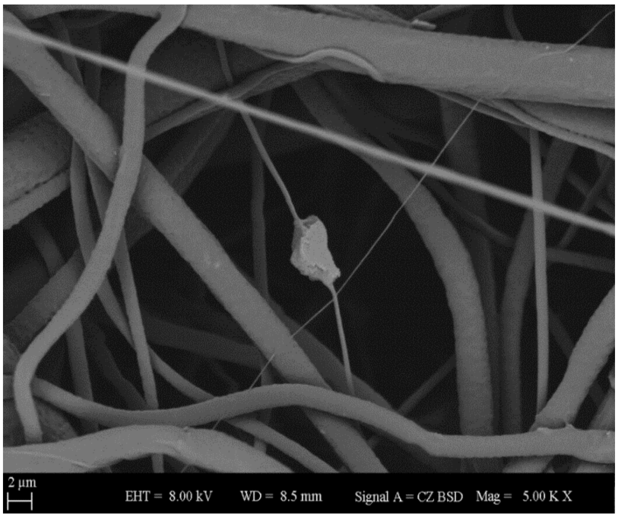


Figure 3. SEM images of TiO_2 – PCL nanofibers with different concentrations of TiO_2: a, Pure PCL; b, % 0.50 TiO_2; c, % 1 TiO_2; d, % 2 TiO_2; e, % 4 TiO_2.

TiO_2 - PCL nanocomposites fibers produced in all ratios are demonstrated in figure 3 by SEM image. All figures were observed with 10.00K X magnification, except figure 3 (e) which possesses 5.00 K X magnification.

Thickness measurements of all produced TiO_2 doped PCL nanocomposite fibers were made. In the figure, the graphic shows the thickness values of nanofibers.

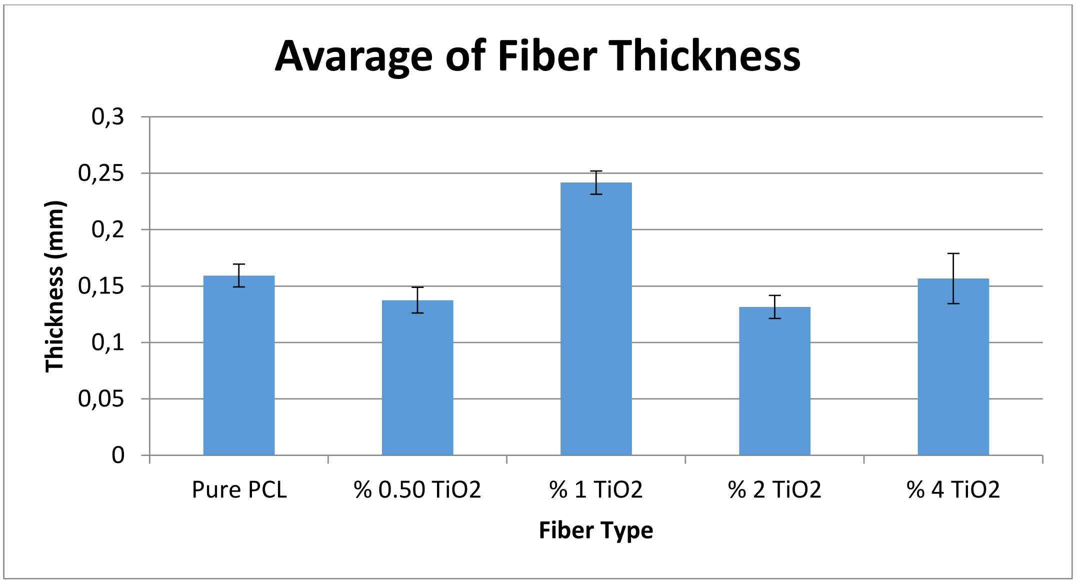
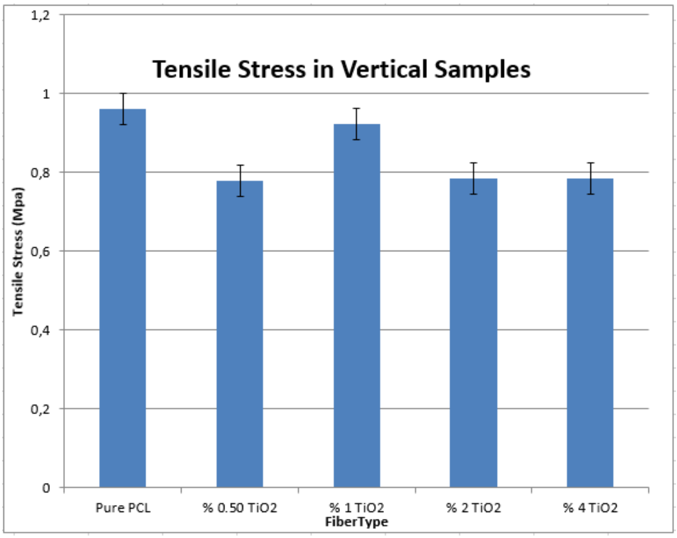
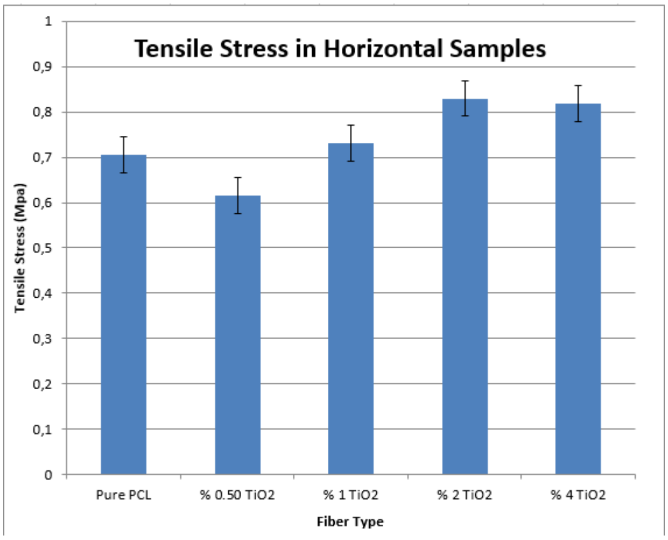


Figure 4. Avarage of Fiber Thickness TiO_2 - PCL nanocomposites fibers

Tensile testing was performed with Instron 4411 on TiO2 - PCL nanocomposite fibers. With 50 Newton load, 30mm / min shrinkage was performed. Samples were taken both horizontally and vertically. Figure 5 shows the values of both applications.



a) Tensile Stress in Vertical Samples TiO_2 - PCL nanocomposites fibers



b) Tensile Stress in Horizontal Samples

Figure 5. Tensile Stress in Vertical and Horizontal Samples TiO_2 - PCL nanocomposites fibers

TiO_2 was added to the fibers and TiO_2 - PCL nanocomposite fibers were produced and tested by SEM and SEM-EDS methods. These fibers were measured with ImageJ software. As shown in the literature, the average diameter of these nano fibers appears to increase with the addition of TiO_2 particles to the nano fibers [19 - 20]. The average diameter values of our study are shown in Figure 6.

In this study, the values in the other diameters other than nanofiber containing 1% TiO_2 in fiber diameters are close to each other. This may be because the polymeric solution has reached an optimum level.

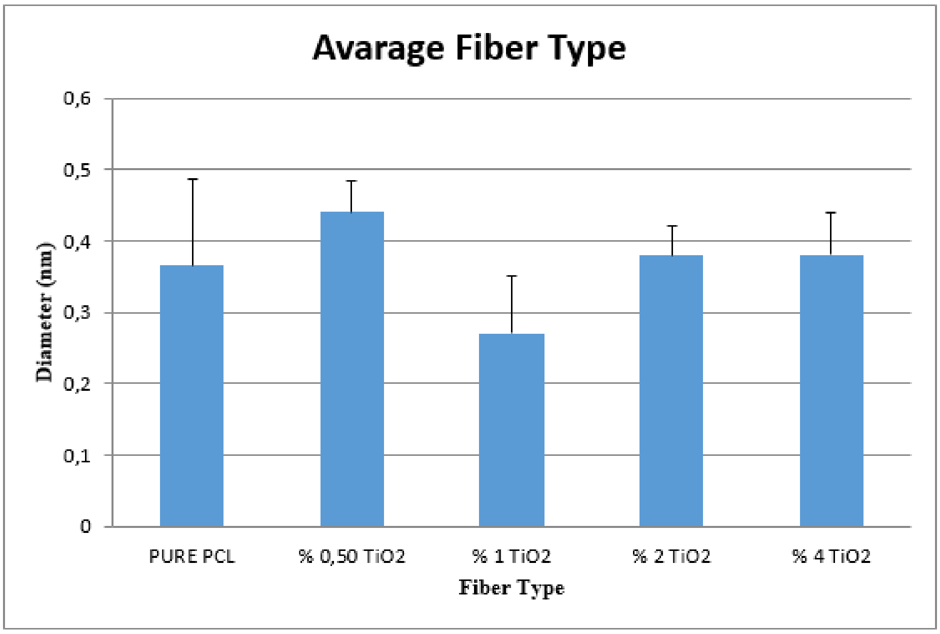


Figure 6. Average fiber diameter of PCL fibers with different concentrations of TiO_2

4. CONCLUSION

Polycaprolactone (PCL) nanocomposite fibers were obtained by electrospinning under various spinning conditions. In addition, TiO_2 additives were added to the polymeric solutions to produce nanocomposite fibers and add new properties. These fibers are characterized using SEM and TiO_2 particles are analyzed by using EDS. These nanofibers tested under tensile testing. Observed data shows that increased the percentage of TiO_2, increased tensile strength. Produced nanocomposite fibers can be used in various industrial applications. For example, it is used in many fields such as self-cleaning or non-wetting fabric in the textile industry, as an antibacterial surfactant in the biomedical field, in the military and electronic products.

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