
EFFECT OF ETHYLENE OXIDE, AUTOCLAVE AND ULTRA VIOLET STERILIZATIONS ON SURFACE TOPOGRAPHY OF PET ELECTROSPUN FIBERS

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Abstract: The aim of this study to investigate the effects of different sterilization methods on electrospun polyester. Ethylene oxide (EO), autoclave (AU) and ultraviolet (UV) sterilization methods were applied to electrospun fibers produced from polyethylene terephthalate (PET) solutions with concentrations of 10, 15 and 20 wt.%. The surface characteristics of the fibers were examined by scanning electron microscope (SEM), atomic force microscope (AFM), surface pore size studies and contact angle measurements. Differential scanning calorimetry (DSC) tests were carried out to characterize the thermal properties. Fourier Transform Infrared spectroscopy (FTIR) tests were performed to analyze the micro structural properties. SEM studies showed that different sterilization methods made significant changes on the surfaces of the fibers depending on the PET concentration. Although the effects were decreased with the increasing polymer concentration, the fiber structure was damaged especially with the EO sterilization. The contact angle values were decreased with the UV sterilization method the most.

Keywords: Electrospun fiber, Polyester, Sterilization, Characterization

Etilen oksit, Otoklav ve Ultra Viyole Sterilizasyonlarının PET Elektroçekim Liflerin Yüzey Topografisi Üzerine Etkisi

Öz: Bu çalışmanın amacı farklı sterilizasyon metodlarının elektroçekim polyester lifleri üzerindeki etkisini incelemektir. PET lifleri; ağırlıkça %10,15 ve 20 oranında polietilen tereftalat (PET) içeren çözeltilerden elektroçekim yöntemiyle üretilmiş ve etilen oksit (EO), otoklav (AU) ve ultraviyole (UV) ile sterilize edilmiştir. Üretilen yüzeylerin yüzey karakterizasyonu taramalı elektron mikroskobu (SEM), atomik kuvvet mikroskobu (AFM), yüzey gözeneklilik boyutu analizleri ve temas açısı ölçümleriyle gerçekleştirilmiştir. Yüzeylerin termal özellikleri Diferansiyel taramalı kalorimetre (DSC) testleri; mikro yapısal özellikleri Fourier Transform Infrared spektroskopisi (FTIR) ile araştırılmıştır. SEM çalışmaları farklı sterilizasyon yöntemlerinin, polimer konsantrasyonuna bağlı olarak büyük değişikliklere neden olduğunu göstermiştir. Artan polimer konsantrasyonu ile yöntemlerin etkileri azalma gösterse de, lif yapısı -özellikle EO sterilizasyonunda oldukça zarar görmüştür. Temas açısı değerlerinde UV sterilizasyonu sonrası büyük düşüş görülmüştür.

Anahtar Kelimeler: Elektroçekim lif, Poliester, Sterilizasyon, Karakterizasyon

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1. INTRODUCTION

Among various application areas of electrospun fibers, currently, medical applications are one of the most promising areas. The surfaces, produced by electrospinning can be used as scaffolds, wound dressings or drug delivery systems due to their 3D structure (Yoshito et al. 2003, Zong et al. 2005, Li et al. 2006, Greiner and Wendorff 2007, Sill ve Recum 2008). Electrospun surfaces may be favorable for cell culture studies, bioreactors and tissue engineering applications because of their unique properties like, high porosity, small pore size, large surface area and small diameter. Electrospinning has been shown to be a potentially significant technique, with an ability to produce a range of scaffolds from wide range of materials with different surface properties (Yoshito et al. 2003, Zong et al. 2005, Li et al. 2006, Greiner and Wendorff 2007, Sill ve Recum 2008).

All biomaterials in medical applications as they are implanted within the body or placed in contact with corporeal fluids must be sterilized otherwise microorganisms may cause deleterious effects (Marreco et al. 2004). Therefore, sterilization is required for every material or device made available for medical use, however the efficacy of this sterilization must be approved as these sterilization treatments may adversely affect material properties such as mechanical behavior, surface energy, surface topography. These changes must be carefully analyzed as they affect biomaterial's performance (Holy et al. 2000, Marecco et al. 2004, Badylak et al. 2009).

There are many sterilization methods reported in the literature including ethylene oxide sterilization, autoclave (steam) sterilization, dry heat, ultraviolet (UV) and gamma radiation, immersion in alcohol aqueous solutions at different concentrations (Block 2001, Rutala and Weber 2001, Dimitrievska et al. 2011). Although there are many researches about the effects of sterilization methods on medical materials such as devices, films and fabrics, there are not enough studies about sterilization effects on electrospun fibers (Nair 1984, Hayashi et al. 2006, Mendes et al. 2007).

The development of high performance electrospun biomaterials to be used in medical applications requires control and analyze of medical material's morphology, topography, surface chemistry after sterilization. The aim of this study is to investigate the effects of different sterilization methods on electrospun polyester. Therefore most used sterilization methods (EO, AU and UV sterilizations) were applied to electrospun polyethylene terephthalate (PET) surfaces. After sterilization, surface topography changes were analyzed by SEM, AFM, contact angle tests and surface pore size measurements. FTIR was studied to understand the chemical changes and DSC studies were performed to understand the biomaterial's bulk properties.

2. MATERIALS AND METHODS

2.1. Materials

In this study commercially available PET pellets (textile grade) with a viscosity of 0.645 Poise were used in order to produce electrospun material. PET solutions with different concentrations were prepared by the dissolution of PET pellets in trifluoroacetic acid (TFA) (50 wt. %) and dichloromethane (DCM) (50 wt. %) solvents. The TFA/DCM system appears to be a good solvent for PET (Lopes-da-Silva et al. 2009, Duzyer et al. 2011, Khansari et al. 2013). All chemicals were commercially available from Sigma-Aldrich and used as received without any further purification.

2.2. Methods

2.2.1. Electrospinning Process

PET fibers were produced by an electrospinning device (Inovenso NanoSpinner24) in the Laboratories of Uludag University, Textile Engineering Department (Bursa, Turkey) (Figure 1). During electrospinning PET polymer solution is extruded from a needle resulting a jet flowing towards a collector.

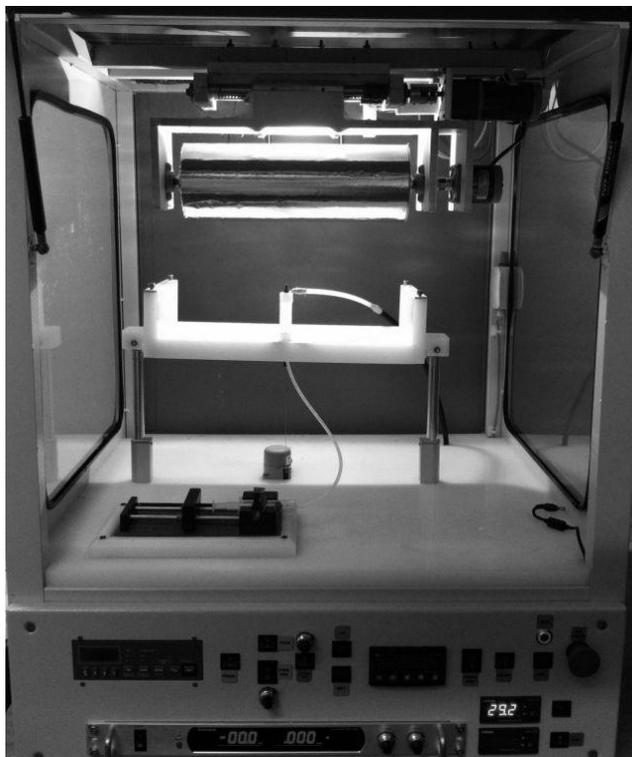


Figure 1:
Electrospinning setup

In this study the jet flows upward from the surface of a pendant drop of fluid toward a rotating drum. The main aim of this research is to produce electrospun fiber mats to be used in medical applications. The fiber dimensions such as diameter and diameter variations along the fiber length are very important as they affect the performance of the material. Therefore in this study three different electrospun fiber mats were produced with different fiber diameters. There are many electrospinning parameters that alter the fiber diameter such as polymer concentration, voltage, the distance between the collector and the needle, flow rate and collector speed. However some of these parameters are strongly depends on each other such voltage and the distance. Many researchers showed the polymer concentration as one of the most important parameter in terms of fiber diameter (Theron et al. 2004, Tan et al. 2005, Thompson et al. 2007).

In this study three different polymer concentration were chosen to produce different fiber diameter. Table 1 shows the spinning parameters. All experiments were carried out in air at room conditions.

Table 1. Electrospinning parameters of PET fibers

Concentration (wt.%)	Voltage (kV)	Distance (mm)	Flow Rate (ml/h)	Collector Speed (rpm)
10	10	10	1	250
15	10	10	1	250
20	10	10	1	250

Increasing polymer concentration alters the viscosity of the solution which affects the spinnability of the polymer-solvent system. Viscosity measurements were performed by a Brookefield viscosimeter at 100 rpm (Uludag University, Bursa-TURKEY). Temperatures of the solutions with different PET concentrations were 19°C, approximately (Table 2).

Table 2. Viscosity measurements of the solutions with different concentrations

Material (PET)	Viscosity (cP)
10% wt.	38.40
15% wt.	115.20
20% wt.	278.40

2.2.2 Sterilization Process

All medical materials should be sterilized before application. There are many researches about sterilization of medical materials produced by conventional methods. However, there isn't enough information about sterilization of electrospun fiber mats. Therefore, most common sterilization methods namely; ethylene oxide (EO), autoclave (AU) and ultraviolet (UV) sterilizations were applied to the electrospun fiber mats produced from different concentrations of PET solutions. All the sterilizations were carried out according to the standard procedures used in the sterilization unit of the Medical Faculty of Uludag University.

1. *Ethylene oxide sterilization:* Ethylene oxide is a colorless flammable and poisonous gas attacks the cellular proteins and nucleic acids of microorganisms.

Before sterilization, the samples were preconditioned in a room for 24 h. After preconditioning, PET electrospun fiber mats were treated by ethylene oxide for 4 hours at 55°C. After treatment, samples were left at room conditions for 4 hours to remove any remaining EO gas and to allow absorbed gas to evaporate.

2. *Autoclave sterilization:* The samples were sterilized in a Class B type autoclave (Dentsan). The procedure was as follows:

121°C – 1.1 bar (65 min.) - Vacuum I (4 min.)- Vacuum II (4 min.)- Vacuum III (4 min.)- Sterilization (15 min.)- Drying (10 min.)- Vacuum IV (4 min.)

3. *UV sterilization:* The samples were first rinsed with ethylene alcohol and then with phosphate buffered saline (PBS) solution for 3 times. Afterwards, the samples were sterilized in a laminar flow sterile cabinet (Thermo, Hera guard, model HPH) under UV light for 1 hour ($\lambda=254$ nm). The procedure was repeated for both sides of the samples.

2.2.3 Characterization of the Electrospun Fiber Mats

Depending on the sterilization method, the treatment results in surface topography changes. Surface roughness can be altered leading to surface energy changes. Therefore SEM, AFM and contact angle measurements were carried out to understand surface changes.

The surface morphologies of the electrospun fiber mats sterilized by different methods were evaluated by scanning electron microscopy (SEM) using Carl Zeiss Evo 40 (Uludag University, Bursa,TURKEY) and JEOL 840JXA model scanning electron microscopes (TUBITAK MAM, Gebze-TURKEY). Fiber orientation in the mat, fiber diameter changes, fiber evenness, fiber surface roughness and pore size of the electrospun fiber mats were evaluated. The surfaces were coated with a thin conducted gold layer prior to SEM observations. Fiber thickness measurements were carried out during SEM analysis on the image. 20 measurements were performed for each sample and average values were recorded.

Surface pore size of the electrospun fiber mats were measured using Image J software. SEM images of the electrospun fiber mats were installed on the software and threshold images of the samples were obtained. The darker areas, which represent the pores, were calculated. 10

measurements were performed for each sample and average values were recorded (Heyderkan et al. 2008, Yang et al. 2009).

Atomic force microscopy (AFM) analyses were performed in order to understand surface topography of the samples. The analyses were carried out by a PARKSISTEM AFM (TUAM, Afyon-TURKEY). The samples were cut rectangular and $5 \mu\text{m}^2$ areas were scanned for each sample in non-contact mode.

The fiber diameter was measured by an Electronic Digital Micrometer. 10 measurements were performed for each sample and average values were recorded.

In order to understand the effect of sterilization methods on wettability, contact angle measurements were carried out. The contact angle of the electrospun fiber mats were measured using KSV-The Modular CAM 200 contact angle measurement system (Uludag University, Bursa-TURKEY). A distilled water drop was dispersed on each sample using a micropipette; the image of each drop was captured by the camera connected with a computer based image capture system. The images were captured as quickly as possible after water droplet was placed onto the sample surface and photographed in less than 1 s.

Different sterilization method can cause a chemical modification on the material surface and can cause the new functional groups generated (Weiss et al. 1997, Costa et al. 1998, Rai et al. 2013). Many researchers showed chemical modifications after sterilization (Weiss et al. 1997, Costa et al. 1998, Rai et al. 2013). Therefore, FTIR analyses were carried out to understand the changes. FTIR spectra were recorded on a Perkin-Elmer 2000 spectrometer (BUTAL, Bursa-TURKEY), using attenuated total reflectance (ATR) technique on the mat surface at in the $650\text{-}4000 \text{ cm}^{-1}$ wavenumber range. 128 scans were taken at a resolution of 4 cm^{-1} . 3 spectra were recorded for each sample and average spectrum was given.

DSC analysis was performed on a Sapphire model test machine by Perkin Elmer (BUTAL, Bursa-TURKEY). The samples were ramped from room temperature to $300 \text{ }^\circ\text{C}$ with a scanning rate of $10 \text{ }^\circ\text{C}/\text{min}$. For each sample 3 scans were recorded. DSC graphs are given as recorded with no further modification.

3. RESULTS AND DISCUSSION

3.1. SEM and AFM Studies

The morphology of the samples was investigated by SEM and AFM studies. Fiber diameter, fiber evenness and fiber surface topography changes were analyzed.

Figure 2 shows the physical conditions of the electrospun PET mats before and after sterilizations, Figure 3 shows the SEM micrographs and Figure 4 shows the AFM images of the samples sterilized by different sterilization methods. Rectangular specimens were cut out of the electrospun fiber mats. The surfaces were soft and paper-like before sterilizations. Visible changes were observed especially with EO and AU sterilizations at lower polymer concentrations. The surfaces became brittle and convoluted due to the unbalanced surface tension with EO sterilization. Because of the heat treatment in AU sterilization, the surfaces became brittle (Figure 2).

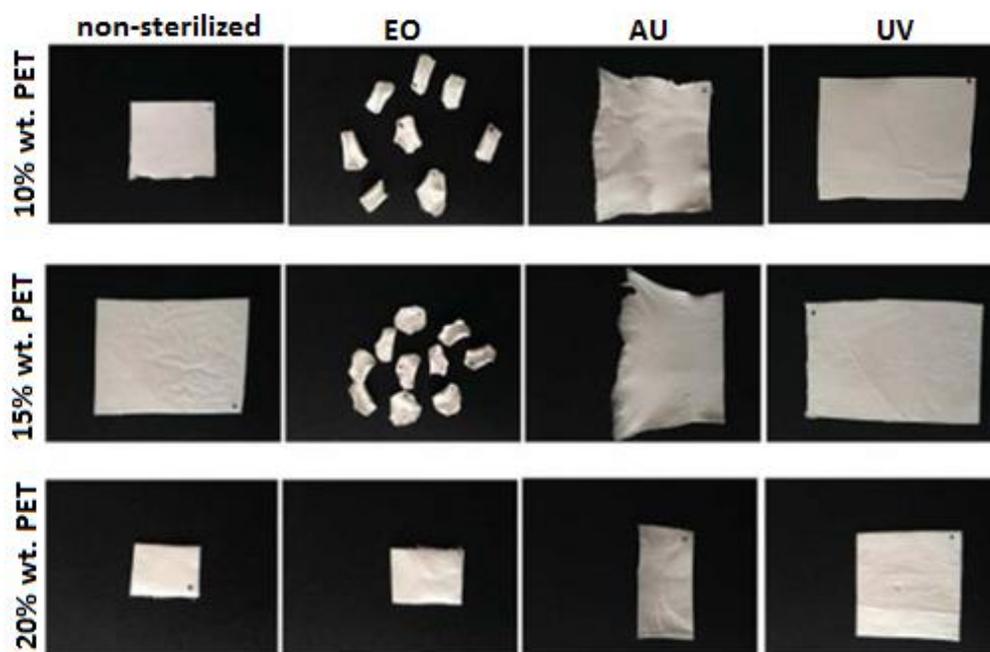


Figure 2:
Physical conditions of the electrospun PET mats before and after sterilizations

Electrospun samples formed nonwoven surfaces with different diameters and were placed randomly in the electrospun fiber mat depending on the polymer concentration.

It was also observed that, with the increasing polymer concentration, fibers with larger diameters and fewer defects were produced because of the increasing viscosity of the polymer solutions (Doshi and Reneker 1995, Fong et al. 1999, Huang et al. 2003, Shenoy et al. 2005). Increasing polymer concentration causes an increase in viscosity resulting more chain entanglements. Higher number of entanglements between the polymer chains resist stretching in applied electric field (Lopes-da-Silva et al. 2009, Greenfeld and Zussman 2013). Changing polymer concentration alters the solution viscosity and also the solution surface tension. At low viscosities surface tension is very dominant and controls the fiber formation and diameter. At higher concentrations, higher viscosities and lower surface tensions are obtained resulting larger and more uniform fibers (Deitzel et al. 2001)

The SEM and AFM images also showed that electrospun PET fibers were not parallel aligned in the mat and PET fibers electrospun from 10% wt. solution had a non-uniform cross-section along the fiber length. With the increasing polymer concentration, it was observed that the fiber cross-section became more uniform. Although thicker fibers were produced from 20% wt. solution, fiber diameters were mostly uniform along the fiber length (Figure 3-4).

The SEM and AFM images of the electrospun fiber mats (Figure 3-4) demonstrated different reactions in response to the sterilization techniques. Samples exposed to UV appeared to have no visible changes to their structure. In contrast, especially at lower polymer concentrations, EO and AU sterilized mats exhibited small nodule like structures, particularly at the fiber junctions and molten surface appearance along with roughened areas.

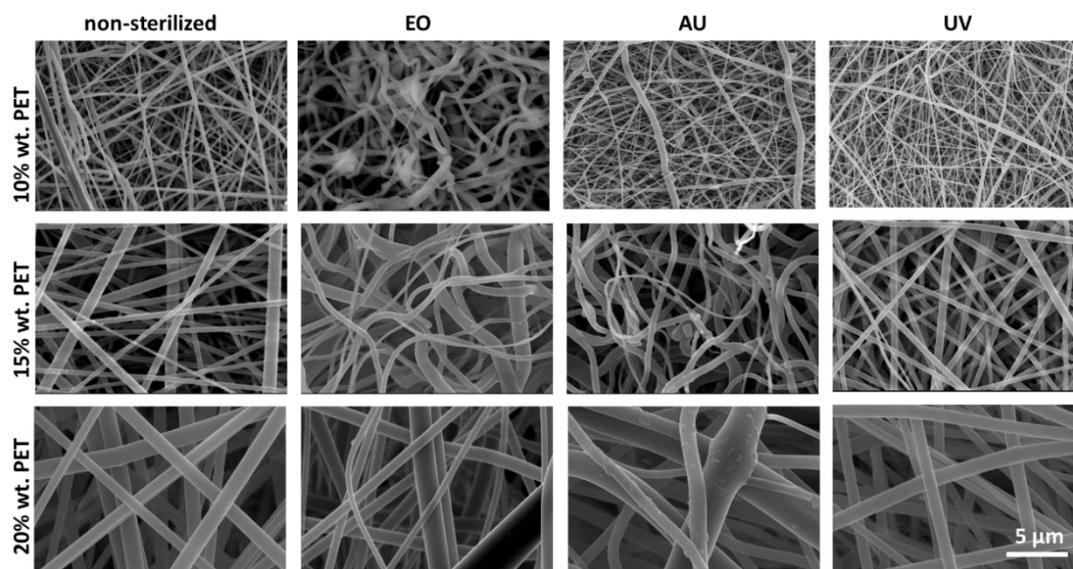


Figure 3:
SEM micrographs of the electrospun PET fibers before and after sterilizations (The scale bar in the set is 5 μm for all the images).

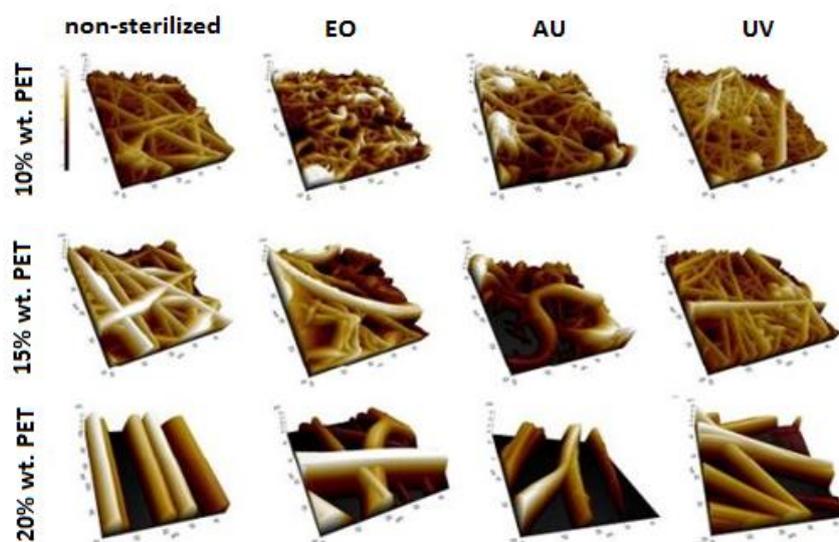


Figure 4:
AFM images of the electrospun PET fibers before and after sterilizations.

The SEM and AFM images showed that EO and AU sterilization methods gave damage to the surfaces and different sterilization methods changed the thicknesses of the electrospun fiber mats depending on the polymer concentration (Table 3). EO sterilization affected the surfaces the most. This may be attributed to the unstable three-membered ring of ethylene oxide as it was reported in literature (Nair 1995). The effect of EO sterilization was less intense with the increasing fiber concentration.

AU sterilization affected the fiber thickness due to the effect of high temperature during sterilization. The effect of short heat treatment on the conventional PET fibers involves microstructural changes such as molecular arrangement in their amorphous regions (Cho et al. 2007).

Many researchers showed shifts in T_g and T_m towards lower temperatures with decreasing fiber diameter (Nair 1995, Deitzel et al. 2001, Cho et al. 2007, Greenfeld and Zussman 2013). Therefore, electrospun fibers would be more affected by heat compared to that of bulk versions. During AU sterilization the samples were subjected to higher temperatures therefore the molecular orientation might be destroyed during the application of the heat. On the other hand, EO and UV sterilizations did not affect the fiber mat thicknesses significantly (Table 3).

Surface pore size and distribution plays key role in medical materials. The surface pore sizes of PET fiber mats were examined. Figure 5 and Table 3 show the threshold images of the SEM micrographs and surface pore sizes of PET fiber mats. For the fiber mats produced from 10% wt. PET solutions, surface pore sizes of the mat were increased with EO and AU sterilizations. UV method didn't affect the surface pore size of the mat. With the increasing polymer concentration, surface pore sizes of the UV sterilized fiber mats were decreased.

Table 3. Diameters and fiber mat thickness values of the samples

Material		Diameter (µm)	CV% Diameter	Mat Thickness (mm)	CV% Mat thickness	Pore Size (µm ²)	CV% Pore size
10 wt% PET	Non-sterilized	0.66	46.97	0.110	5.44	5.287	37.62
	EO sterilized	0.91	20.88	0.103	1.85	10.810	33.95
	AU sterilized	0.94	34.47	0.204	0.72	17.809	23.45
	UV sterilized	0.66	45.76	0.119	1.17	5.346	29.42
15 wt% PET	Non-sterilized	0.87	27.59	0.220	2.00	24.439	41.25
	EO sterilized	1.88	42.55	0.275	0.52	17.215	59.31
	AU sterilized	1.46	21.37	0.406	0.39	16.186	36.48
	UV sterilized	1.34	25.37	0.224	0.60	13.155	16.62
20 wt% PET	Non-sterilized	2.36	27.80	0.420	1.02	52.154	52.39
	EO sterilized	2.92	77.81	0.400	0.36	51.014	81.21
	AU sterilized	2.33	37.39	0.596	0.27	62.641	62.30
	UV sterilized	2.48	16.61	0.438	0.51	23.990	59.46

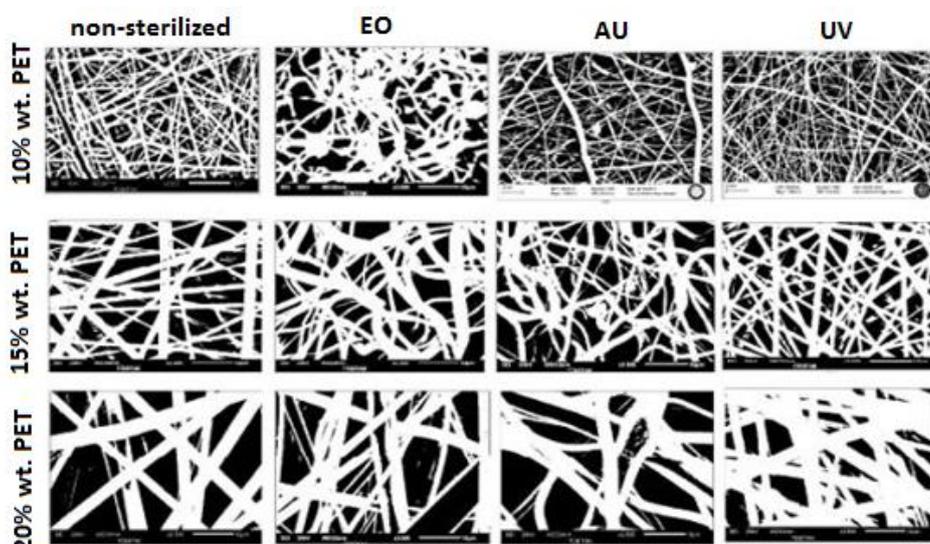


Figure 5:

Threshold images of the electrospun PET fiber mats before and after sterilizations.

3.2. Contact Angle Measurements

The contact angle (CA) measurements of the samples before and after sterilization are shown in Table 4. CA is a quantitative measure of surface characteristics of the fibers like adhesion, wettability and absorption (Duzyer et al. 2011). CA varies according to the surface roughness, pore size and shape of the structures on the surface (Darmanin and Guittard 2013).

CA values showed a slight increase with increasing polymer concentration which also results an increase in fiber diameter. Higher fiber diameter results twisted bundles like structure resulting even higher CA values. However this increase in CA value is not very pronounced. The results showed that samples show super hydrophobic structure as all samples have contact angle values above 90° due to formation of 3D rough surfaces. Different sterilization methods also gave high contact angle values; however, a significant reduction in CA was recorded with UV method due to changes of surface pore size.

Table 4. Contact angles of the electrospun fiber mats produced from different concentrations and sterilized by different methods

Material (PET)	Contact Angle ($^\circ$)
10% wt.(non-sterilized)	132.71
10% wt.(EO sterilized)	122.90
10% wt. (AU sterilized)	127.41
10% wt. (UV sterilized)	97.05
15% wt. (non-sterilized)	140.02
15% wt. (EO sterilized)	122.67
15% wt. (AU sterilized)	124.12
15% wt. (UV sterilized)	115.21
20% wt. (non-sterilized)	141.71
20% wt. (EO sterilized)	109.02
20% wt. (AU sterilized)	136.12
20% wt. (UV sterilized)	112.53

3.3. DSC Studies

Thermal analysis of electrospun samples was performed by differential scanning calorimetric analysis. Table 5 shows the corresponding data obtained from the samples from different solutions and sterilized by different methods.

For a typical PET, DSC thermograms show 3 important peaks. First peak is an endothermic peak which indicates the glass temperature of the fiber. Second peak is an exothermic peak indicating the cold crystallization temperature followed by an endothermic peak which gives the melting temperature of the fiber (De Clerk et al. 2003, Duzyer et al. 2011).

The DSC thermograms of the non-sterilized samples and sterilized by different methods were shown in Figure 6-8. For non-sterilized samples, DSC thermograms followed a typical pattern expected for PET (De Clerk et al. 2003, Duzyer et al. 2011).

Each peak was analyzed by means of different sterilization methods. It was seen that T_g values were changed slightly with the increasing polymer concentration. Also, higher T_g values were obtained with the sterilization methods which includes heat (EO and AU sterilizations).

The presence and the size of the T_c peaks indicate the remaining crystallizable molecular chains in the structure (Duzyer et al. 2011). This peak was not seen for the electrospun fibers sterilized by AU. AU sterilization was performed around 120°C. Therefore, the crystallizable molecular chains in this region were thought to be crystallized during the sterilization. Therefore, no pronounced cold crystallization peak was seen.

The cold crystallization peak was obvious for the other sterilization methods. The position of the peak was not changed with different polymer concentrations. However, ΔH_c values were slightly different depending on the polymer concentration. ΔH_c value is correlated to the amount of crystallizable molecules. Increasing polymer concentration increases viscosity and molecular entanglements.

A single melting endotherm was observed for each sample around 250-260°C. The position of the melting point was not changed. Generally, small differences were observed in ΔH_m values.

Table 5. DSC data of the electrospun fiber mats sterilized by different methods

Material (PET)	T_g (°C)	T_c (°C)	ΔH_c (mj/mg)	T_m (°C)	ΔH_m (mj/mg)
10% wt.(non-sterilized)	58	114	-21.4	256	41.3
10% wt.(EO sterilized)	57	94	-21.2	253	65.7
10% wt. (AU sterilized)	57	-	-	257	42.4
10% wt. (UV sterilized)	50	121	-21.2	255	44.8
15% wt. (non-sterilized)	60	118	-33.4	255	53.8
15% wt. (EO sterilized)	59	91	-28.8	242	51.4
15% wt. (AU sterilized)	61	-	-	257	40.1
15% wt. (UV sterilized)	60	120	-19.1	256	34.7
20% wt. (non-sterilized)	75	122	-29.9	256	49.2
20% wt. (EO sterilized)	74	127	-27.5	255	40.1
20% wt. (AU sterilized)	78	-	-	255	31.1
20% wt. (UV sterilized)	61	124	-27.4	256	50.2

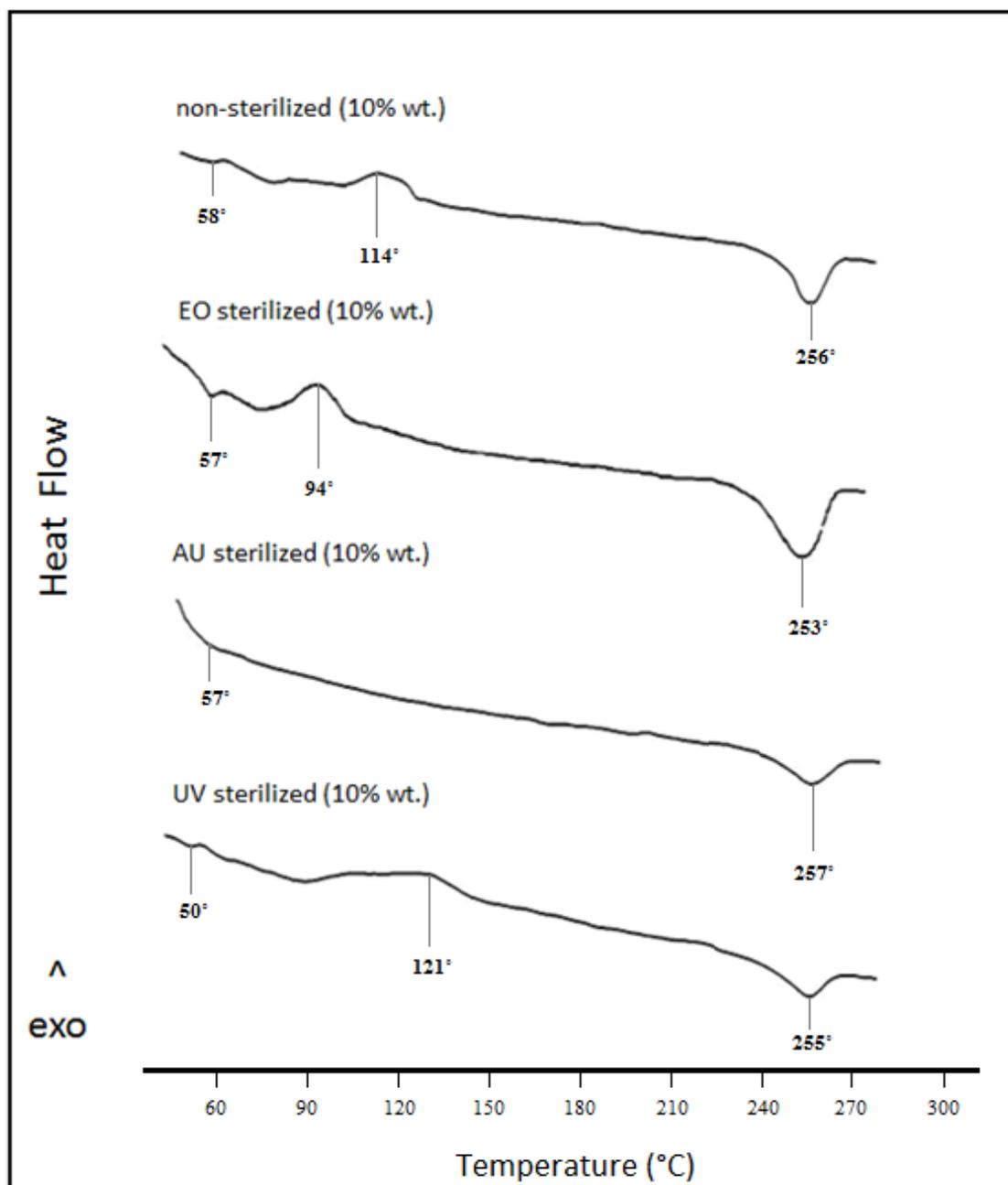


Figure 6:
DSC thermograms of electrospun fiber mats produced from 10% wt. PET solutions sterilized by different methods

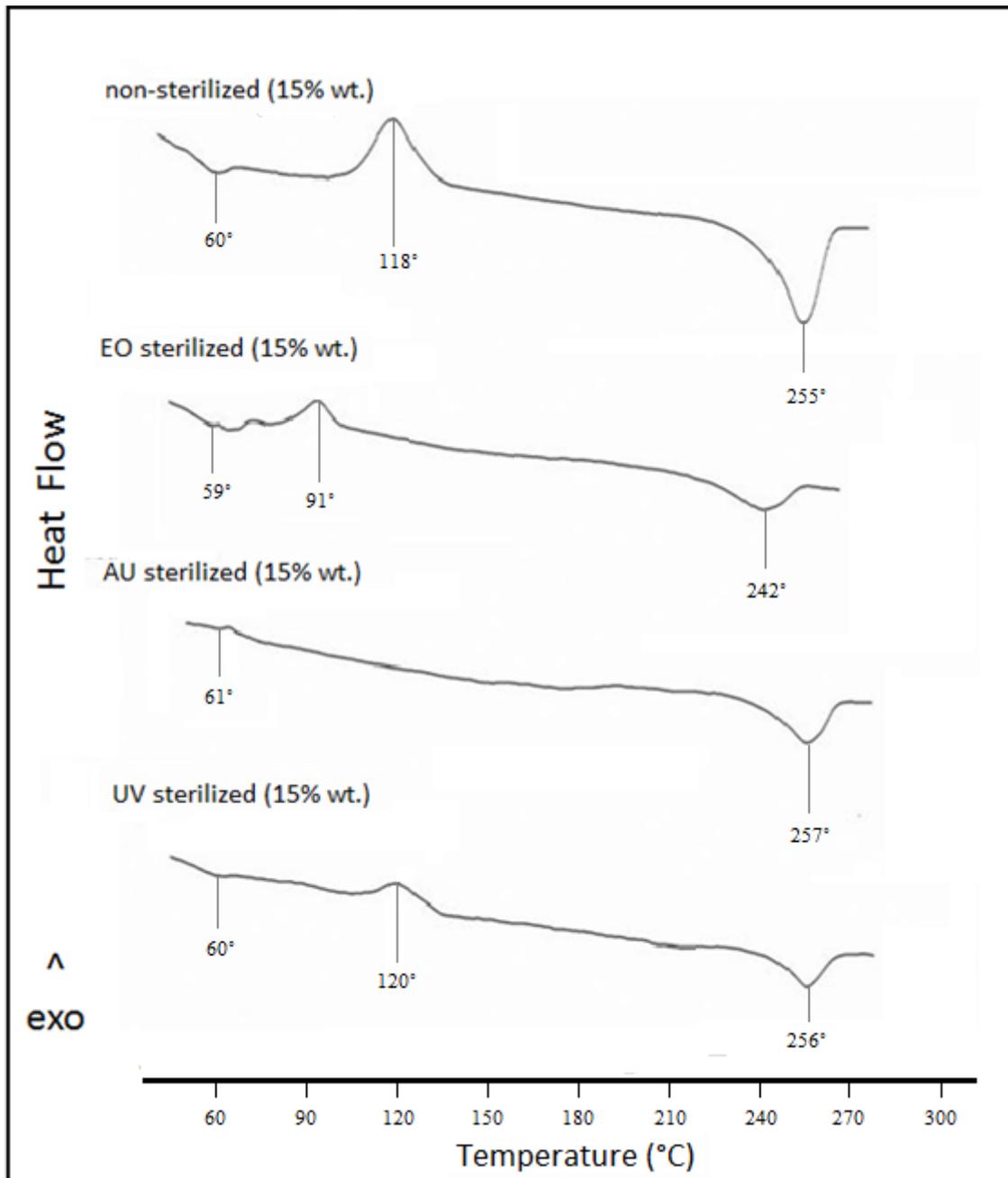


Figure 7:
DSC thermograms of electrospun fiber mats produced from 15% wt. PET solutions sterilized by different methods

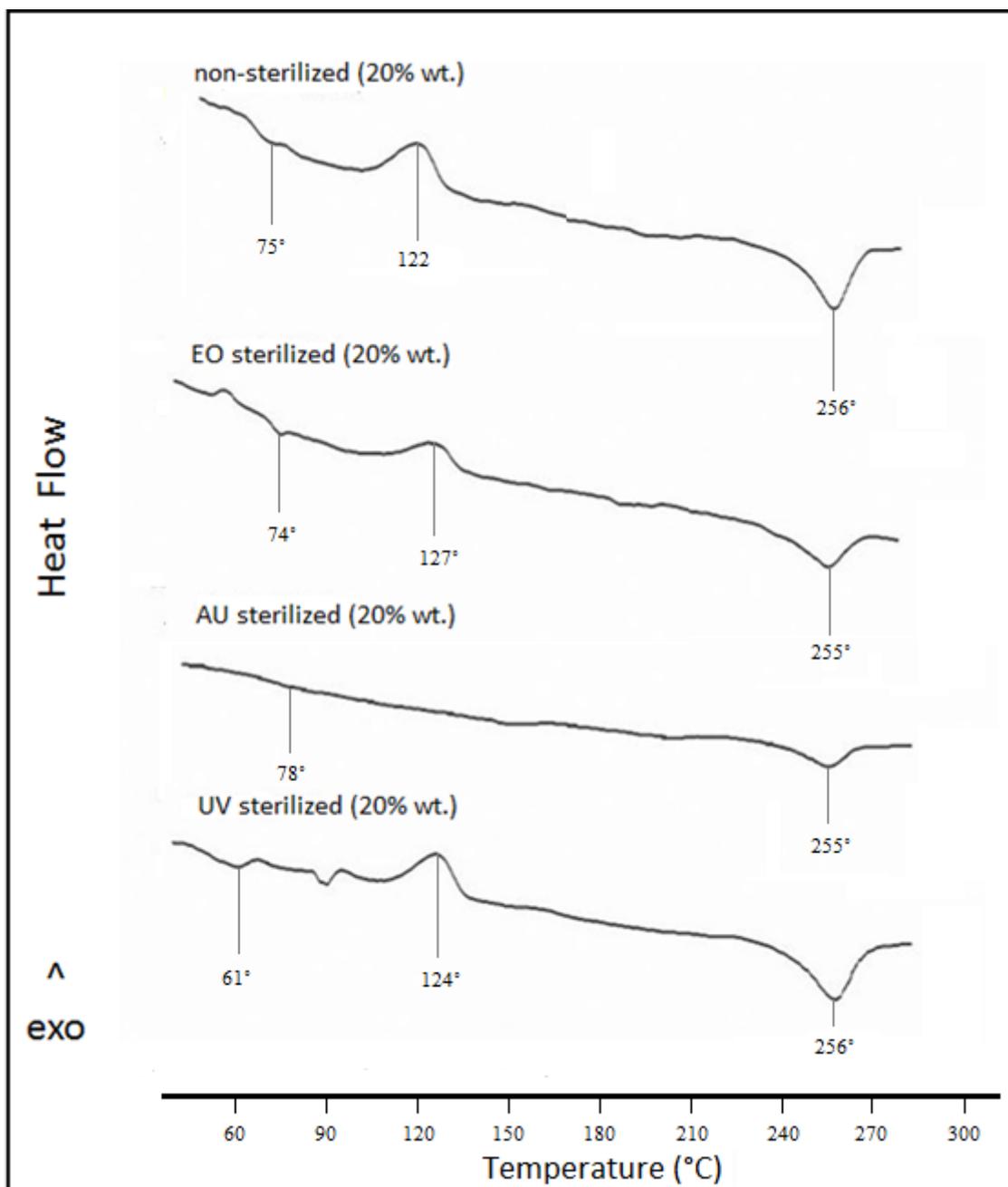


Figure 8:
DSC thermograms of electrospun fiber mats produced from 20% wt. PET solutions sterilized by different methods

3.4. FTIR Studies

Figure 9-11 show FTIR spectrums of the samples produced from 10, 15 and 20% wt. PET solution, respectively. The main absorption bands in the IR spectra of PET have been assigned as follows, the band at $3100-2800\text{ cm}^{-1}$ is attributed to aromatic and aliphatic -C-H bond stretching, at 1720 cm^{-1} to the ester carbonyl bond stretching, at $1470-1350\text{ cm}^{-1}$ to the bending and wagging vibrational modes of the ethylene glycol segment, at 1235 cm^{-1} to the ester group stretching, at 1090 cm^{-1} to the methylene group and at 1016 and 725 cm^{-1} to aromatic bands. Many of the medium and weaker bands have been attributed to chain configurations and are

sensitive to whether the sample is amorphous, oriented, or crystalline. Differences are due to the configuration of the ethylene glycol group (cis/trans isomers) and also the phenylene carbonyl bond (cis–trans isomers) (Chen et al. 2013).

FTIR results showed that there were not significant changes on the main peaks. The small changes at 1720 cm^{-1} band and the band at $3100\text{-}2800\text{ cm}^{-1}$ were observed with the application of different sterilization methods. Therefore, it was concluded that sterilization methods, where higher temperatures are applied to the samples, might be effective on the molecular orientation and the fine structure of the fibers. Especially temperatures near or higher than T_g might cause rearrangement of the molecules.

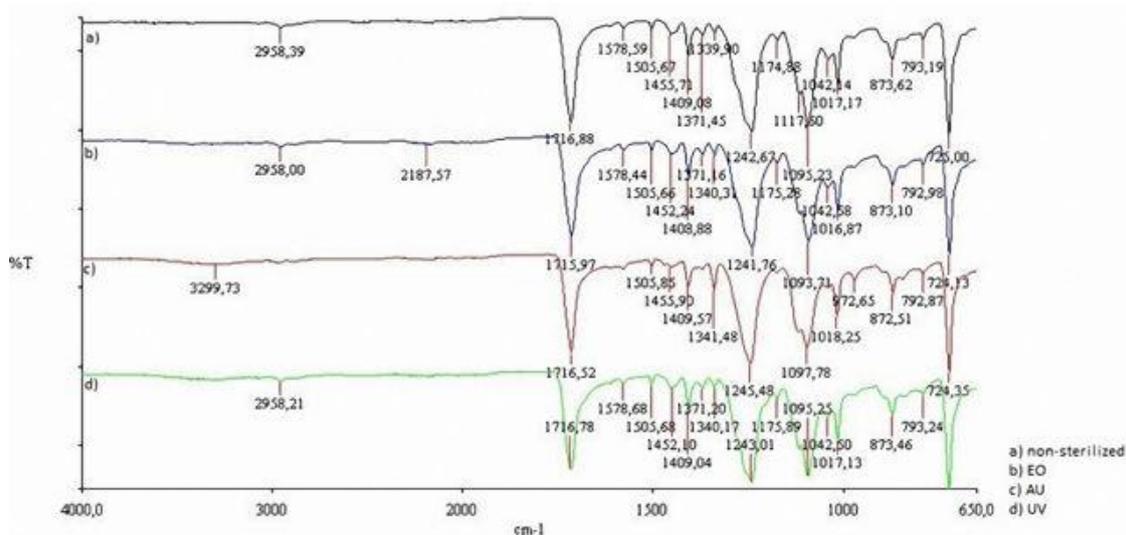


Figure 9:

FTIR spectrums of electrospun fiber mats produced from 10% wt. PET solutions sterilized by different methods

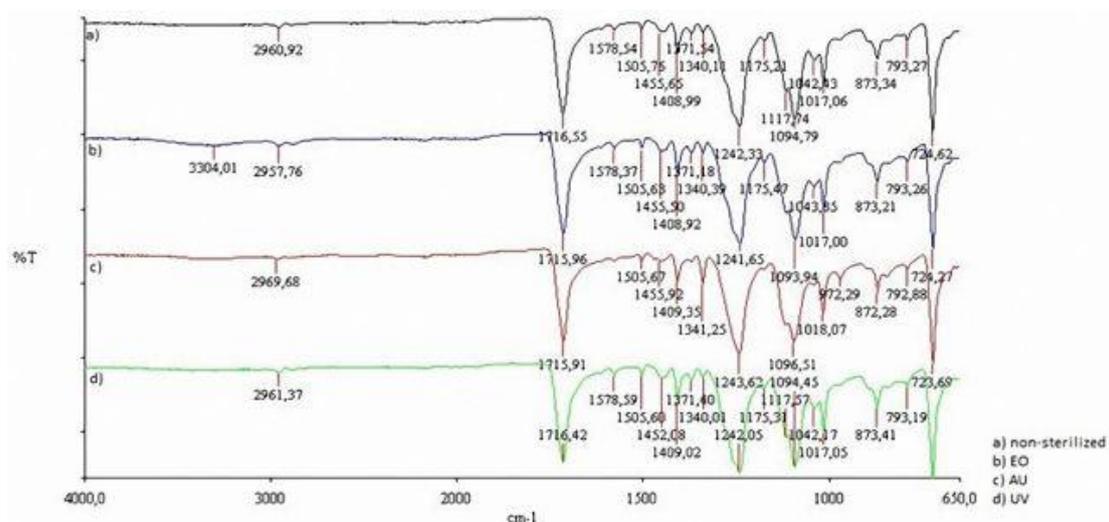


Figure 10:

FTIR spectrums of electrospun fiber mats produced from 15% wt. PET solutions sterilized by different methods

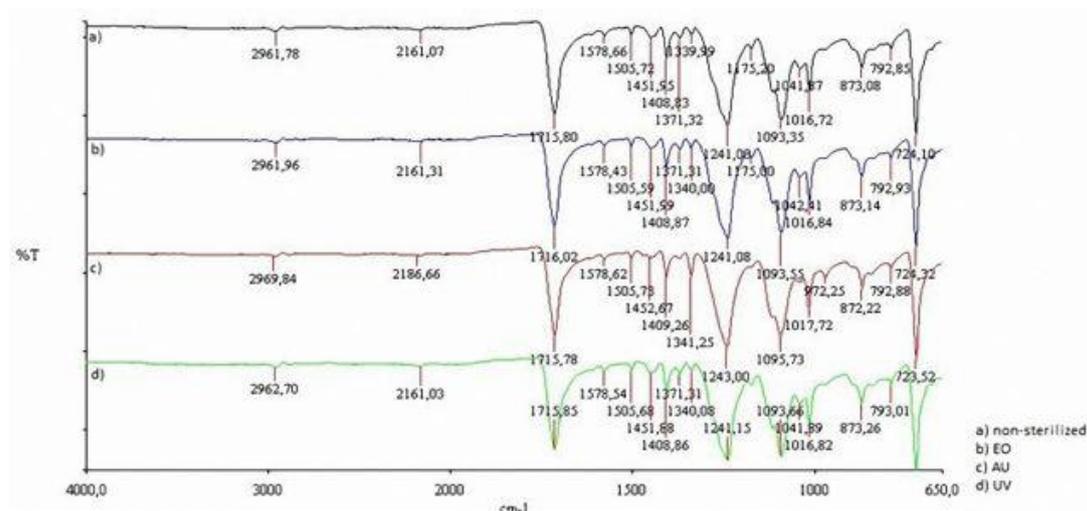


Figure 11:

FTIR spectrums of electrospun fiber mats produced from 20% wt. PET solutions sterilized by different methods

4. CONCLUSION

EO, AU and UV sterilization methods were applied on electrospun PET fibers produced from different polymer concentrations. After sterilization, SEM, AFM and contact angle measurements were carried out to understand the changes on surface properties. It was seen that EO and AU sterilizations affected the surfaces at lower concentrations, where UV sterilization doesn't affect the surfaces at all. The effect of EO and AU sterilization became less clear with the increasing polymer concentration.

EO and AU sterilizations include temperature above T_g values of the electrospun fiber mats. At temperatures above glass transition temperatures, molecules would have enough energy to move. Also polymeric materials are known to be sensitive and affected by heat applications. Therefore, sterilizations which involve heat caused changes in structure and surface topography. Also, due to the three-membered ring and activity of ethylene oxide, the surfaces might be affected for EO sterilization.

Contact angle values increase depending on the polymer concentration. The results show that with the decreasing fiber diameter, the samples get super hydrophobic structure due to formation of 3D rough surfaces. Different sterilization methods also affect the surface properties of the samples. The contact angle values decreased with the different sterilization methods as sterilization technique affected the roughness and surface pore size formation.

Single melting peak was observed for each sample by DSC analyses. The position of the melting peak didn't change for each sample. For the electrospun mats sterilized by AU, no cold crystallization peak was observed. Cold crystallization indicated the remaining crystallizable molecular regions present in the fiber structure. During AU sterilization, molecules can rearrange themselves due to higher temperatures. Therefore no crystallization peak was observed for AU sterilized samples.

FTIR results showed that there were not significant changes on the formations and positions on the peaks. However some small changes were observed on peak intensities and widths. Therefore, it was concluded that sterilization methods don't have major impacts on the chemical changes. Sterilization methods which include heat are more effective on the molecular orientation.

5. ACKNOWLEDGMENT

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