(REFEREED RESEARCH)

EFFECTS OF DIFFERENT STERILIZATION METHODS ON POLYESTER SURFACES

FARKLI STERİLİZASYON YÖNTEMLERİNİN POLİESTER YÜZEYLER ÜZERİNE ETKİLERİ

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ABSTRACT

The aim of this study is to investigate the effects of different sterilization methods on polyester surfaces. Therefore, ethylene oxide (EO), autoclave (AU) and ultraviolet (UV) sterilization methods were performed on two groups of polyester surfaces. In the first part, the effects of different sterilization methods on polyethylene terephthalate (PET) nanofibers produced by electrospinning with different concentrations were investigated. In the second part, the effects of different sterilization methods on PET fabrics were investigated. The effects of the different sterilization methods on surface properties of PET surfaces were examined by scanning electron microscope (SEM) studies and contact angle measurements. The changes in mechanical properties were investigated by Instron studies. It was seen that different sterilization methods affected the nanofibers significantly depending on the polymer concentration. This effect was less clear for the PET fabrics. It was concluded that UV sterilization gave less damage to the nanofibers.

Key Words: Sterilization, Electrospinning, Nanofiber, Polyethylene terephthalate, Characterization.

ÖZET

Bu çalışmanın amacı farklı sterilizasyon yöntemlerinin polyester yüzeyler üzerine etkilerini incelemektir. Bu amaçla, iki grup polyester yüzey üzerine etilen oksit (EO), otoklav (AU) ve ultraviyole (UV) sterilizasyon yöntemleri uygulanmıştır. İlk kısımda, farklı konsantrasyonlarda elektro çekim (elektrospinning) yöntemi ile üretilen polietilen tereftalat (PET) nanolifler üzerine farklı sterilizasyon yöntemlerinin etkisi araştırılmıştır. İkinci kısımda, PET kumaş üzerine farklı sterilizasyon yöntemlerinin etkileri incelenmiştir. Farklı sterilizasyon yöntemlerinin yüzey özellikleri üzerine etkileri taramalı elektron mikroskobu (SEM) ve temas açısı ölçümleri ile incelenmiştir. Mekanik özelliklerdeki değişiklikler Instron çalışmaları ile incelenmiştir. Polimer konsantrasyonuna bağlı olarak, farklı sterilizasyon yöntemlerinin nanolifleri belirgin olarak etkilediği görülmüştür. Bu etki PET kumaşlar için daha azdır. UV sterilizasyon yönteminin nanoliflere en az hasarı verdiği sonucuna varılmıştır.

Anahtar Kelimeler: Sterilizasyon, Elektrospinning, Nanolif, Polietilen tereftalat, Karakterizasyon.

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1. INTRODUCTION

Today's one of the most important issue in health care is microorganisms which are spread from patient to patient by many ways such as the equipment used in surgery, staff and other materials used for patient care. There are many textile materials that can be used inside or outside of the human body, such as scaffolds, implants and wound dressings. Therefore, sterilization and disinfection of the equipment and materials used in surgery and hospitals play key role (1).

In literature, sterilization is defined as the destruction or removal process of all forms of microbial life present on the surface, such as microorganisms, fungi, bacteria (2,3). This process can be either physical or chemical and sometimes both, depending on the type of the microorganisms and the type of the material used in surgery and other materials used for patient care.

Etyhlene oxide and autoclave sterilizations are the most commonly used methods in hospitals. Ethylene oxide can easily diffuse into the material to be sterilized and is effective at low temperatures. However, it remains ethylene oxide residues and the unstable three-membered ring of the ethylene oxide can react with various functional groups including sulfhydryl, amino, carboxyl and hydroxyl groups of proteins and nucleic acids (4).

Autoclave sterilization can be used as an alternative method to the ethylene oxide sterilization. It involves high temperature, steam and pressure in the process. Therefore, the disadvantage of the process is the hydrolysis of the polymer during sterilization (4).

An alternative to those methods summed up below can be ultraviolet sterilization since it does not involve any heat or mechanical treatment and is also eco-friendly.

Polyethylene terephthalate (PET) is a linear polymer and is widely used in medical applications such surgery sutures, medical gowns, hospital sheets in the form of yarns and fabrics because of its characteristics including biostability, non-allergenic and non-toxic properties (5).

With arising applications of nanofibers, PET nanofibers can also be used in medical applications such as scaffolds or drug delivery systems in the form of nanofiber mats. Among various methods, electrospinning is one the most commonly used method to produce nanofibers in recent years since it is simple and allows a wide range of polymers to electospun. The method involves using electrical charges to produce nanofibers. In the electrospinnnig process a high voltage is applied to the polymer solution or melt held at the tip of a capillary. When the voltage overcomes the surface tension of the polymer solution, a charged polymer jet ejects from the tip and moves towards to the charged collector. During the travel of the jet, the solution evaporates and leaves a dry fiber on the collector surface (6-7). These nonwoven surfaces consist of nanofibers find many applications in medical. Since these materials have to be sterilized before application, most appropriate method has to be chosen in order not to give any damage to the material properties.

Considering these conditions, the aim of this study is to investigate the effects of different sterilization methods on electrospun polyester nanofibers and polyester fabrics. Since, PET surfaces can be used in the medical field as nanofiber mats or woven fabrics depending on the application area, the effect of ethylene oxide (EO), autoclave (AU) and ultraviolet (UV) sterilization methods were investigated in both forms. From this point of view, this study consists of two parts. In the first part, the effects of different sterilization methods on polyethylene terephthalate (PET) nanofibers produced by electrospinning with different concentrations were investigated. In the second part, the effects of different sterilization methods on PET fabrics were investigated.

2. MATERIALS AND METHODS

2.1. Materials

In this study commercially available PET pellets and plain weave 100% polyester (PET) fabric were used. PET solutions with different concentrations (10, 15 and 20 wt.%) were prepared by the dissolution of PET pellets in trifluoroacetic acid (TFA) (50 wt.%) and dichloromethane (DCM) (50 wt.%) solvents. All chemicals were commercially available from Sigma-Aldrich and used as received without any further purification.

2.2. Methods

PET nanofibers were produced by an electrospinning device (Inovenso NanoSpinner24) in the Laboratories of Uludag University, Textile Engineering Department (Bursa, Turkey).

The jet flows upward from the surface of a pendant drop of fluid toward a rotating drum (Figure 1). Table 1 shows the spinning parameters of the produced nanofibers. All the experiments were carried out in air at room conditions.

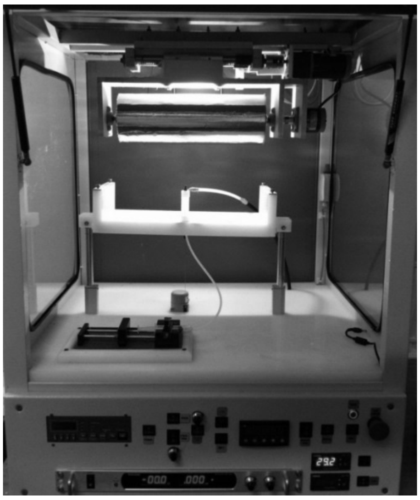

Figure1. Electrospinning setup

The surface morphologies of the fabrics and the nanofibers sterilized by different methods were evaluated by a Carl Zeiss Evo 40 (Uludag University, Bursa,TURKEY) and a JEOL 840JXA model scanning electron microscopes (TUBITAK MAM, Gebze-TURKEY).

The contact angle of the fabrics and electrospun nanofiber mats were measured using a 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.

Table 1. Electrospinning parameters of nanofibers

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

Mechanical characteristics of the PET fabrics and nanofiber mats were evaluated by Instron Universal Testing Machine (Model No. 4301) in the Laboratories of Uludag University, Textile Engineering Department (Bursa, Turkey).

Sterilization Methods: Before cell culture studies, fabrics and nanofibers should be sterilized. Although there are many researches about sterilization of fabrics, there isn't enough information about sterilization of nanofiber mats. Therefore, most common sterilization methods namely; ethylene oxide (EO), autoclave (AU) and ultraviolet (UV) sterilizations were applied to the nanofiber mats produced from different concentrations of PET. 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: PET fabric and nanofiber mats were treated by ethylene oxide for 4 hours at 55°C. After treatment, samples were left at room conditions for 4 hours.

2. Autoclave sterilization: The samples were sterilized in a Class B type autoclave (Dentsan) The procude 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 3 times. Afterwards, the samples were sterilized in a laminar flow sterile cabinet (Thermo, Hera guard, model HPH) under UV light for 1 hour. The procedure was repeated for both sides of the samples.

3. RESULTS AND DISCUSSION

3.1 PET Nanofiber Mats

The morphology of the nanofiber mats were investigated by SEM studies (Figures 2-4). Nanofibers formed nonwoven surfaces with different diameters and were placed randomly in the nanofiber mat depending on the polymer concentration. With the increasing polymer concentration, nanofibers with larger diameters and fewer beads were produced because of the increasing viscosity of the polymer solutions. Table 2 shows the diameter distribution and coefficient of variation (CV) of the nanofibers. SEM images also showed that PET nanofibers were not exactly aligned in the mat and PET nanofibers electrospun from 10% wt. solution had a non-uniform cross-section along the fiber length. With the increasing polymer concentration, 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.

Different sterilization methods made significant changes on the surfaces of the nanofibers. Among all sterilization methods, UV method gave less damage to the surfaces for all concentrations and 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 [4]. For the nanofibers produced from 10% wt. solution, agglomeration of the fiber bundles was observed with EO sterilization. For the nanofibers produced from 15% wt. solution, the effect of ethylene oxide sterilization was quite decreased; fiber uniformity was disturbed along the length. For the nanofibers produced from 20% wt. solution, effect of EO sterilization was less intense compared to the nanofibers produced from 10% wt. solution. For autoclave sterilization which includes high temperature and pressure, diameter along the fiber length was not uniform in lower concentrations (10% wt. and 15%wt.). As a result, stiffer handle was obtained. Moreover, as the fiber diameter decreased, the effect of sterilization method on the fiber surface was more pronounced.

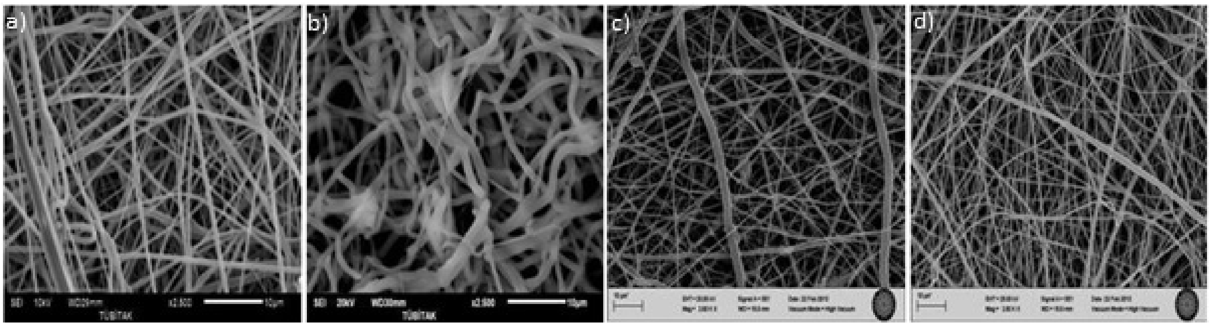

Figure 2. SEM micrographs nanofibers produced from 10% wt. PET solution, a) non-sterilized, b) EO, c) AU, d) UV sterilized, respectively

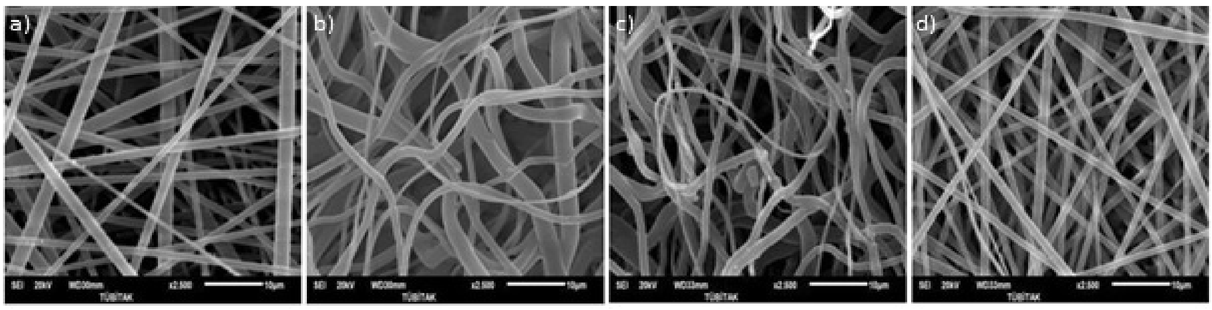

Figure 3. SEM micrographs of nanofibers from 15% wt. PET solution a) non-sterilized, b) EO, c) AU, d) UV sterilized, respectively

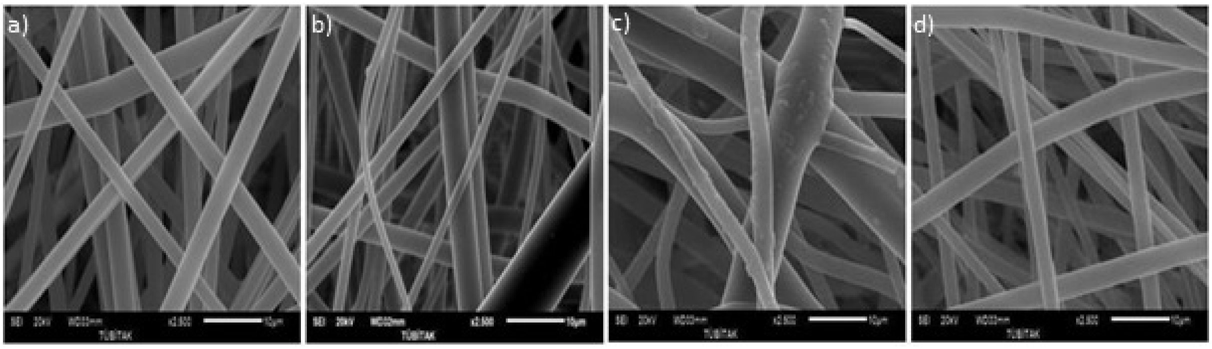

Figure 4. SEM micrographs of nanofibers produced from 20% wt. PET solution, a) non-sterilized, b) EO, c) AU, d) UV sterilized, respectively.

Table 2. Diameters of the nanofibers

Material (PET)	Diameter (μm)	CV (%)
10% wt.(non-sterilized)	0.66	46.97
10% wt.(EO sterilized)	0.91	20.88
10% wt. (AU sterilized)	0.94	34.47
10% wt. (UV sterilized)	0.66	45.76
15% wt. (non-sterilized)	0.87	27.59
15% wt. (EO sterilized)	1.88	42.55
15% wt. (AU sterilized)	1.46	21.37
15% wt. (UV sterilized)	1.34	25.37
20% wt. (non-sterilized)	2.36	27.80
20% wt. (EO sterilized)	2.92	77.81
20% wt. (AU sterilized)	2.33	37.39
20% wt. (UV sterilized)	2.48	16.61

Contact angle of the surfaces are one of the most important properties in order to understand the surface characteristics of the fibers like adhesion, wettability and absorption.

Table 3 shows the contact angles of the nanofiber mats.

Table 3. Contact angles of the nanofiber mats

Material (PET)	Contact Angle (°)
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

For nanofiber mats, the results show that contact angle values change depending on the polymer concentration. As the fiber diameter decreases, the nanofiber mats become super hydrophobic. Different sterilization methods also affect the surface properties of the nanofibers. The contact angle values were decreased with the different sterilization methods. It was seen that there was a decrease in contact angles with UV sterilization. A decrease in contact angles after UV sterilization was recorded. This decrease did not follow a regular regime with the increasing polymer concentration and it was not a significant change.

In order to understand the mechanical behavior of the PET nanofiber mats, tensile tests were performed. The results are given in Table 4. Nanofibers produced from 20% wt. PET solutions gave the highest modulus and lowest elongation at break. Young modulus and the elongation values of the nanofiber mats were changed with different sterilization methods. This change was more significant especially with autoclave sterilization. AU sterilization resulted in a decrease in both modulus and elongation at break values. The decrease in modulus was attributed to the stiffer structure of the surfaces.

Table 4. Tensile results of nanofiber mats

Material	Young Modulus (MPa)	Elongation at Break (%)
10% wt.(non-sterilized)	137.4	104.68
10% wt.(EO sterilized)	218.1	99.12
10% wt. (AU sterilized)	125.7	36.83
10% wt. (UV sterilized)	132.8	121.72
15% wt. (non-sterilized)	154.7	99.35
15% wt. (EO sterilized)	148.7	62.86
15% wt. (AU sterilized)	79.68	32.08
15% wt. (UV sterilized)	124.8	84.87
20% wt. (non-sterilized)	224.1	55.95
20% wt. (EO sterilized)	222.5	53.37
20% wt. (AU sterilized)	85.3	23.12
20% wt. (UV sterilized)	219.6	78.52

3.2 PET Fabrics

The structure of the PET fabrics sterilized by different methods was investigated by SEM studies. Figure 5 shows the micrographs of the single fibers and Figure 6 shows the SEM micrographs of the fabrics. SEM images show that, different sterilization methods didn’t make any significant change on the surface of the PET fabrics.

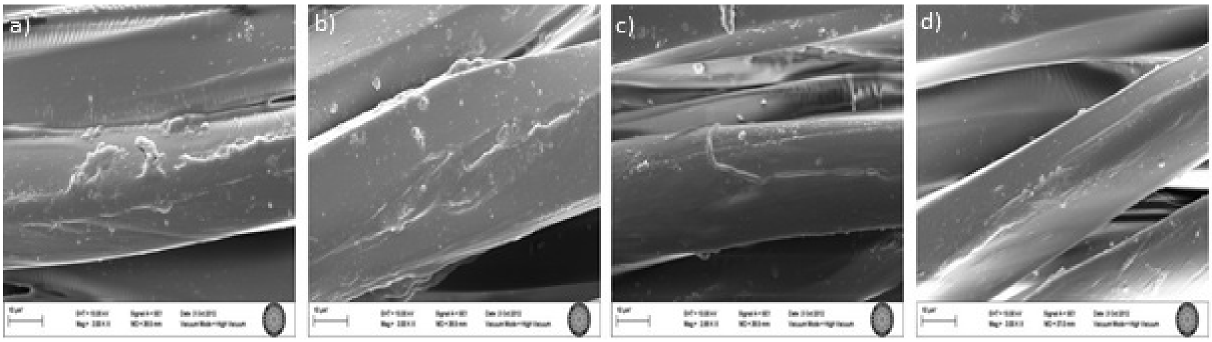

Figure 5. SEM micrographs of single fiber of PET fabric sterilized by different methods, a) non-sterilized, b) EO, c) AU, d) UV sterilized, respectively

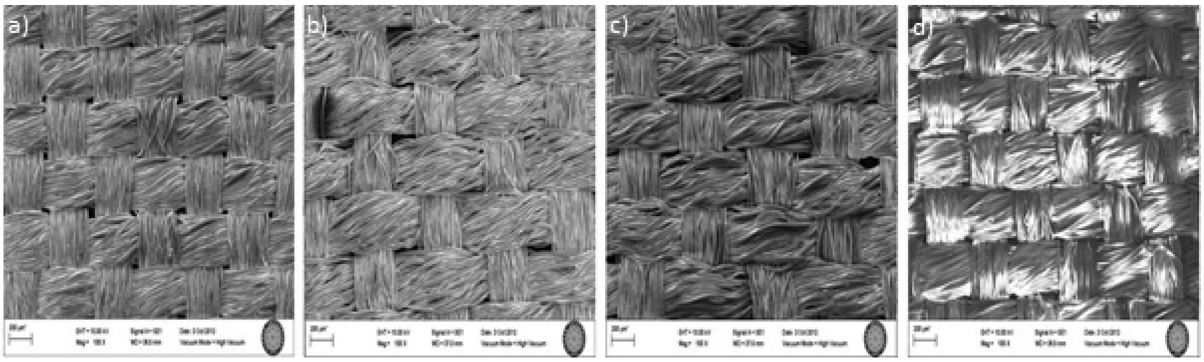

Figure 6. SEM micrographs PET fabric sterilized by different methods, a) non-sterilized, b) EO, c) AU, d) UV sterilized, respectively

Results of the contact angle measurements are given in Table 5. The highest contact angle was observed with UV sterilization.

Table 5. Contact angles of the PET fabric sterilized by different methods

Material	Contact Angle (°)
non-sterilized fabric	54.71
EO sterilized fabric	69.23
AU sterilized fabric	77.28
UV sterilized fabric	115.19

Instron tests were also performed on PET fabrics sterilized with different sterilization methods. Table 6 shows the Young modulus and elongation at break values of the fabrics. Young modulus increased and the elongation at break decreased with different sterilization methods.

Table 6. Tensile results of PET fabrics sterilized by different methods

Material (PET)	Young modulus (MPa)	Elongation at Break (%)
non-sterilized fabric	358.34	31.97
EO sterilized fabric	429.14	23.59
AU sterilized fabric	428.64	26.45
UV sterilized fabric	422.38	27.13

4. CONCLUSION

Conventional PET fabrics and nanofibers are widely used in many medical applications. PET fabrics are mostly used as hospital sheets and surgical gowns, while PET nanofibers can be used as implants, scaffolds or drug delivery systems. In order to use these materials in medical applications, all must be sterilized otherwise microorganisms may cause deleterious effects. Understanding the effects of sterilization is very beneficial to choose the most appropriate method. Therefore SEM studies, contact angle measurements and mechanical analysis were performed on nanofiber mats and fabrics sterilized by EO, AU and UV methods.

For nanofiber mats, SEM images showed that PET nanofibers were not exactly aligned in the mat and had a non-uniform cross section along the fiber length at lower concentrations. With the increasing polymer concentration, the fiber cross-section became more uniform and thicker fibers were obtained. Among all sterilization methods, UV method gave less damage to the surfaces for all concentrations and EO sterilization affected the surfaces the most. For PET fabrics, it was concluded that sterilization methods did not have a significant effect on surface properties.

The contact angle values of both nanofiber mats and fabrics changed with the different sterilization methods. For nanofiber mats, it was seen that there was a decrease in contact angles with UV sterilization which did not follow a regular regime with the increasing polymer concentration. For the sterilized fabrics, the highest contact angle was observed with UV sterilization.

Nanofibers produced from 20% wt. PET solutions gave the highest modulus and the lowest elongation at break. It was also seen that the modulus and the elongation at break decreased with the AU sterilization. For PET fabrics, Young modulus increased and the elongation at break decreased with different sterilization methods.

It is crucial to choose the most appropriate method as they affect both mechanical and surface properties. In this study, UV sterilization method is suggested since it is a suitable sterilization for nanofiber surfaces.

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