

The effect of UV irradiation on the electrospun PCL/TiO₂ composites fibers

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ABSTRACT: The effect of UV irradiation and micro- and nano-TiO₂ as well as titanate nanotubes (TiNT) on the phase morphology and thermal properties of the electrospun PCL composite fibers was investigated. Polycaprolactone (PCL)/TiO₂ (micro- and nano-TiO₂ as well as titanate nanotubes) composite fibers were prepared by electrospinning a polymer solution. The PCL and PCL/TiO₂ composite fibers were exposed to UV light at irradiation times of 5 and 10 days. After UV irradiation the crystallinity of the electrospun PCL/TiNT composite fibers increased because of the large specific surface area of TiNT. The thermal stability of the PCL/TiNT electrospun composite fibers increased due to the formation of crosslinking structure after UV irradiation. The SEM analysis suggests that after UV radiation the fibers showed high degree of degradation due to the high number of fibers breakages and fibers surface voids. The results of FTIR spectroscopy confirmed that the TiO₂ particles enhance the degradation process because of their photocatalytic activity. © 2016 Wiley Periodicals, Inc. *J. Appl. Polym. Sci.* **2016**, *133*, 43539.

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INTRODUCTION

Most conventional plastics are nonbiodegradable, and their increasing accumulation in the environment has been a threat to the planet. To reduce the amount of waste, attention has been focused on the development of biodegradable polymers. The aliphatic polyesters have been the subject of increasing focus because of their biodegradability and biocompatibility. Poly(ϵ -caprolactone) (PCL) is aliphatic polyester which is one of the earliest polymers synthesized by the Carothers group in the early 1930s with good mechanical and thermomechanical properties.¹ PCL is a hydrophobic, semicrystalline, biocompatible polymer. It has good solubility, a low melting point, and exceptional blend-compatibility. PCL is widely used in different biomedical applications, such as tissue engineering, drug delivery, and medical devices. Some of its properties can be modified/improved by the addition of fillers or other polymers.^{2,3} The degeneration intermediates or metabolism products are small molecules nontoxic to the human body. So, PCL-based materials have potential applications in biomedicine. Since the past 2 decades, immobili-

zation of titanium dioxide (TiO₂), a popular photocatalyst, on different substrates has been drawing a lot of attention because it eliminates the need of costly post-treatment separation processes. Considering the various substrates that have been tried for supporting TiO₂ photocatalysts, polymer substrate seems to be very promising due to its several advantages such as flexible nature, low-cost, chemical resistance, mechanical stability, low density, high durability, and ease of availability. Nanometer dimension TiO₂ nanoparticles have been recently proposed as attractive filler materials for biodegradable polymer matrices as it enhances cell attachment and proliferation on the composite surfaces.⁴ TiO₂ has also shown to be biocompatible with blood and tissue, making it suitable for blood compatible coating on biomedical implants like artificial bone and dental implants.⁵

Electrospinning is the process of nanofibers formation under electrical field, where polymer solution or melt is being stretched by electrostatic forces.⁶ Usually the nanofiber diameter prepared by this technique ranges between few nanometres to few microns. Randomly deposited electrospun nanofibers form interconnected

fibrous structures (mats) with small inter fibrous pores, high porosity, and high surface area.⁷ The physical configuration of the electrospun fibrous structures is easily controlled by set of processing parameters (e.g., electrical voltage, needle tip to collector distance, flow rate), polymer solution characteristics (e.g., concentration, viscosity, surface tension, electrical conductivity) and environment condition (e.g., temperature, humidity).⁸ Apart from physical structure control, the process offers versatile chemical compositions preparation (e.g., bicomponent fibers) and additional functionalization of the electrospun fibrous mats. These possibilities have raised the interest in the exploration of electrospun materials in many application fields including: biomedicine,⁹ electronics and energy conservation,¹⁰ chemistry,¹¹ environment protection,¹² and specialty textiles.¹³ In electrospun materials, TiO₂ has been widely explored for solar to electrical energy conversion devices,¹⁴ photodegradation of toxic dyes,¹⁵ and hydrogen generation.¹⁶

In this study the aim was to enhance polymer degradation process by the incorporation of TiO₂ photocatalyst fillers. Thus, polycaprolactone was electrospun into fibers with the addition of nano- and micro- TiO₂ as well as TiO₂ nanotubes. Prepared electrospun fibers were further evaluated for their morphological and chemical structure, thermal properties and thermal stability before and after UV irradiation.

EXPERIMENTAL

Materials

The polymer used as matrix was PCL (Polycaprolactone 440744-500G, average M_n 70,000 – 90,000 g mol^{-1} by GPC, $M_w/M_n < 2$, density 1.145 g mL^{-1} at 25 °C). Titanium dioxide (TiO₂) technical micro powder (denoted as mTiO₂, particles 500, density 3,9 g cm^{-3}) and TiO₂ nano powder (denoted as nTiO₂, particles 21 nm, density 4,26 g cm^{-3} , commercial grade Aeroxide P25) were used as fillers and both were supplied by Sigma-Aldrich, Germany. The organic solvents used were tetrahydrofuran and *N,N*-dimethylformamide.

TiO₂ nanotubes (TiNT) were synthesized by hydrothermal treatment of TiO₂ in concentrated NaOH. 6 g of TiO₂ powder were added into 10M aqueous NaOH solution and the mixture was heated in a closed PTFE vessel at 120 °C for 20 h. This yielded TiNT dispersed in a strongly alkaline solution. The TiNT suspension was washed with water till the pH value reached around 10 and freeze-dried.¹⁷

Preparation of PCL Fibers by Electrospinning

PCL fibers and PCL/TiO₂ composite fibers were produced by electrospinning. Neat PCL fibers were prepared from polymer solution concentration of 14% (w/w) by dissolving the polymer in THF/DMF mixture (1:1 w/w) at room temperature with vigorous stirring for 3 h. 0.5 wt % of each filler TiO₂ (micro and nano particles) as well as TiNT was added to the solution and further homogenized by stirrer and ultrasonic homogenizer for 5 h and 15 min, respectively. The electrospinning conditions were as follows: solution flow rate of 1 mL/h, electrical voltage of 18 kV and needle tip to collector distance of 15 cm.

UV Irradiation

UV irradiation of the electrospun fibers was investigated in air at a temperature of 40 °C, using a low-pressure mercury lamp

unit (ultraviolet chamber Suntest; Heraeus Suntest CPS xenon light lamp) which emits radiation $\lambda = 290$ nm. Irradiation times were 5 and 10 days.

Experimental Techniques for Characterization of Materials

Differential Scanning Calorimetry (DSC). Thermal properties of the electrospun fibers were studied by Differential Scanning Calorimetry with DSC Instrument Mettler Toledo 822^e, under nitrogen atmosphere. Differential scanning calorimetry (DSC) belongs to the group of thermal techniques by which polymer materials phase transitions of I and II order can be easily determined. Samples (9 – 11 mg) were heated from the room temperature to 120 °C and hold isothermally for 10 min to eliminate the effects of the thermal history during material processing. Afterwards, the samples were then cooled to –100 °C and reheated to 120 °C. Tests were run with heating/cooling rate of 10 °C/min and cooling was provided by the Liquid Nitrogen Cooling Accessory (LNCA). Temperatures of phase transitions and enthalpies were determined from the second DSC heating cycle.

Thermogravimetry (TG). The thermal stability of the electrospun fibers was studied using TG analyzer Q 500, TA Instruments. Samples of the nominal size of 10 mg were analyzed in the temperature range from 25 °C to 700 °C, by heating rate of 10 °C/min in nitrogen.

FTIR Analysis. The chemical structural changes of the electrospun fibers after UV irradiation were carried out by Fourier-Transform Infrared Spectrometer on a Perkin-Elmer Spectrum One with an Attenuated Total Reflection Accessory (ATR). Measurements were done for PCL samples before and after exposure to UV irradiation for 5 and 10 days, in the range from 4000 to 400 cm^{-1} , with resolution of 4 cm^{-1} .

Scanning Electron Microscope (SEM). Scanning Electron Microscope Tescan Vega 3 Brno, Czechoslovakia, was used to investigate the morphology of the electrospun fibers before and after exposure to the UV irradiation for 5 and 10 days. The specimens were coated with gold by means of vapour deposition. SEM micrographs were collected at magnifications of 500 \times and 7000 \times .

RESULTS AND DISCUSSION

Results of Differential Scanning Calorimetry

In this paper, DSC technique was used to determine the influence of the addition and types of fillers (TiO₂) as well as UV irradiation on the glass transition temperature (T_g), melting temperature (T_m), crystallization temperature (T_c) and degree of crystallinity (χ_c) of electrospun PCL/TiO₂ composite vs. DSC thermograms obtained for the electrospun PCL fibers and electrospun PCL/TiO₂ composite fibers after the second cycle of heating and cooling before (all investigated PCL composites) and after 5 days of UV exposure (neat PCL, PCL/mTiO₂, PCL/nTiO₂ and PCL/TiNT composite fibers) are shown in Figure 1(a,b), respectively, while the values obtained from DSC thermograms are tabulated in Table I.

The degree of crystallinity (χ %) was calculated by using eq. (1):

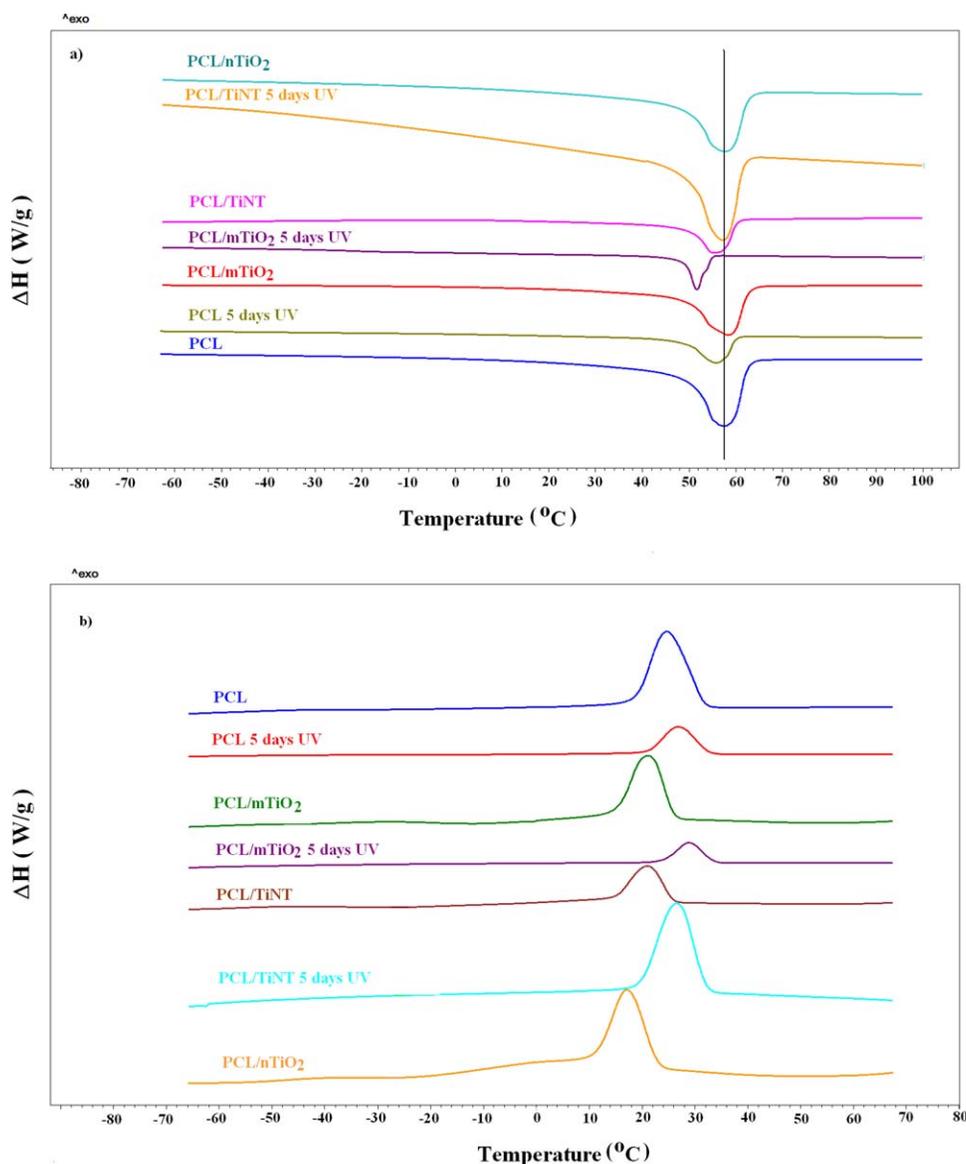


Figure 1. DSC heating curves (a) and cooling curves (b) for electrospun PCL fibers and electrospun PCL/TiO₂ composite fibers before and after UV irradiation. [Color figure can be viewed in the online issue, which is available at wileyonlinelibrary.com.]

$$\chi_c = \left(\frac{\Delta H_m}{\Delta H_m^0 \times \left(1 - \frac{\%w_{TiO_2}}{100}\right)} \right) \times 100 \quad (1)$$

where ΔH_m is the enthalpy of the melting peak, ΔH_m^0 is the heat of melting of purely crystalline PCL, considering these values as 142, 0 Jg⁻¹,^{18,19} w is the weight fraction of TiO₂ in the sample.

Table I. Thermal Properties of Electrospun PCL Fibers and Electrospun PCL/TiO₂ Composite Fibers before and after UV Irradiation

Electrospun fibers	T_g (°C)	T_m (°C)	T_c (°C)	ΔH_m (Jg ⁻¹)	ΔH_c (Jg ⁻¹)	χ_c (%)
PCL	-64.3	57.5	24.9	55.64	46.77	39.2
PCL 5 days UV irradiation	-64.5	55.6	26.9	61.67	52.58	43.4
PCL + 0,5% m TiO ₂	-63.8	58.4	21.2	35.57	40.60	26.4
PCL + 0,5% m TiO ₂ 5 days UV irradiation	-68.0	51.5	28.9	35.47	70.05	26.3
PCL + 0,5% n TiO ₂	-64.0	57.4	17.4	44.09	69.08	32.7
PCL + 0,5% TiNT	-65.2	55.2	21.1	38.31	40.17	28.4
PCL + 0,5% TiNT 5 days UV irradiation	-64.5	56.8	27.0	53.37	52.71	39.6

Polycaprolactone is semicrystalline polymer with amorphous and crystalline phase; the amorphous phase provides the elastomeric properties whereas crystalline phase imparts dimensional stability and order to the molecular array PCL structure. The ordered arrangements of the amorphous and crystalline phases, as well as the degree of crystallinity are strongly influenced by the electrospinning process parameters. The DSC thermograms recorded during the second scan after heating and cooling of the electrospun PCL fibers before UV irradiation displayed the glass transition temperature T_g and the melting endotherm at T_m [Figure 1(a)].

Electrospun PCL fibers showed a phase transition at -64.3 °C, which was attributed to the glass transition temperature (T_g) and a melting process located between 40 °C and 66 °C with a T_m at 57.5 °C,²⁰ related to a crystalline phase. Moreover, during the cooling scan [Figure 1(b)] one exothermic crystallization peak were obtained at 24.9 °C associated to the crystallization temperature T_c , attributed to the crystalline phase of PCL. From Table I, we can see that the T_c of UV irradiated electrospun PCL fibers is shown to increase by about 2 ° compared to the T_c of unirradiated electrospun PCL fibers. The increase in T_c of UV irradiated electrospun PCL fibers suggests that UV irradiation affects the crystallization of electrospun PCL fibers. The highest crystallinity was found for the electrospun PCL fibers after UV irradiation. It is clear that T_g of the electrospun PCL fibers remains at the same temperature while the melting temperature (T_m) decreases after 5 days of UV irradiation due to the formation of less well-ordered crystalline structure after UV irradiation. After UV irradiation, the crystallinity of the electrospun PCL fibers increased due to thickening of the crystallites during UV irradiation.

The addition of micro TiO_2 particles in the neat PCL slightly increased T_g compared to the neat electrospun PCL fibers which may be result of placement of mTiO_2 particles in the amorphous phase of PCL, resulting in the decrease of the molecular mobility of the amorphous phase and an increase in free volume.²¹ Due to the interaction between the polymer and TiO_2 particles the T_g can moves because of the H-bonds and van der Waals interactions between the hydrophilic TiO_2 and polar PCL.²² The degree of crystallinity decreased for the electrospun PCL/ mTiO_2 composite fibers and also the T_m , related to the electrospun PCL fibers melting was shifted to higher temperature by the presence of mTiO_2 . The endothermic peak related to the melting of crystalline phase of electrospun PCL fibers was broadened, furthermore the weak peak as a shoulder at a temperature higher than the T_m at $58, 4$ °C was observed, which could be attributed to the presence of crystalline regions at various degrees of crystals perfection.

After 5 days of UV irradiation the T_g of the electrospun PCL/ mTiO_2 composite fibers was shifted to the lower temperature ($-68, 0$ °C) compared to the unirradiated electrospun PCL/ mTiO_2 composite fibers ($-63, 8$ °C) as well as electrospun PCL fibers ($-64, 3$ °C). This behaviour can be explained that during the photodegradation process the carbonyl groups in the PCL can absorb UV light and produce free radicals^{23,24} resulting in mobility of the amorphous phase to the lower temperature. As

Table I shows, the addition of nTiO_2 and TiNT particles in the neat PCL had almost no effect on the T_g and T_m . The addition of nTiO_2 and TiNT in the neat PCL promotes an increase in the disorder of the crystalline phase, decreasing the degree of crystallinity from 39.2% to 32.7% and 28.4% , respectively. This phenomena was probably caused by the reduction of the diffusion of the PCL chains to the growing crystalline lamella and disruption of the regularity of the chain structures in PCL.

When the electrospun PCL/ TiNT composite fibers were irradiated for 5 days the T_g values increased. This behavior can be attributed to a reduction in the polymer chain mobility. Furthermore, the TiNT presence increased the T_m , T_c and the crystallinity degree values. It can be concluded that the UV irradiation accelerates the degradation and because of the large specific surface area of TiNT network structure can be formed which increases the crystallinity. Furthermore, degradation of the ester linkages by the UV irradiation resulting in the polymer chains cleavage and formation crystalline domains.

TG Analysis

In order to determine the thermal stability of the electrospun PCL fibers and the PCL/ TiO_2 composite fibers, i.e. the influence of the micro- and nano- TiO_2 as well as the TiNT on the neat PCL thermal stability, thermogravimetric analysis were performed on the electrospun fibers before and after five days of UV irradiation. Generally, the thermal stability is observed by temperature change at which a degradation or weight loss starts. If this temperature, in the presence of filler, shifts to higher value compared to the neat polymer, it will suggest improved thermal stability of the polymer/filler composites. However, the filler particles do not have necessary influence on the improvement of the thermal stability of the polymer matrix. For example, the filler might slow down the degradation process due to strong interactions with the polymer chains or the chains of the formed radicals, thus restricting the polymer chain movement and inhibiting the reaction of propagation. According to literature²⁵ the PCL degradation involves hydrolytic chain scission of the ester ($\text{C}=\text{O}$) group resulting in a random arrangement of the PCL chain. Apart from the degradation of the polyester group, PCL involves slow degradation of five hydrophilic repeating $-\text{CH}_2-$ groups.

Figures 2 and 3 show the TG and DTG curves, respectively, of the neat electrospun PCL fibers before and after UV irradiation. The neat electrospun PCL fibers displayed a one step degradation process with decomposition temperature ($T_{5\%}$) at $344, 3$ °C and maximum decomposition temperature (T_{max}) at $387, 5$ °C (Table II). After 5 days of UV irradiation thermal stability of the electrospun PCL fibers decrease (the ($T_{5\%}$) shifts from 344.3 °C to 303.9 °C). This behaviour was expected since the UV irradiation results in the polymer chain scission and the formation of radicals which are further involved in the propagation degradation. The process of degradation ends at a temperature lower (431.0 °C) than the one of neat electrospun PCL fibers (453.4 °C). The residue at 700 °C is greater after UV radiation which is a result of the crosslinking structure formed by the influence of the UV light. The addition of the micro- TiO_2 particles resulted in insignificant improvement of the

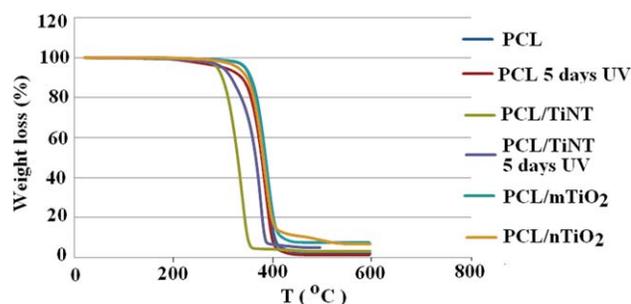


Figure 2. TG curves of the electrospun PCL fibers and PCL/TiO₂ composite fibers before and after UV irradiation. [Color figure can be viewed in the online issue, which is available at wileyonlinelibrary.com.]

thermal stability and the lowest improvement was in the case of the PCL/TiNT composite fibers. This can be explained by the formation of TiNT agglomerates which resulted in formation of inhomogeneous structure with lower thermal stability. After five days of UV irradiation of the PCL/TiNT electrospun composite fibers the thermal stability is evidently greater due to the formation of crosslinking structure after UV irradiation which explains the increase of the residue. The obtained result does not suggest a photocatalytic activity of the TiNTs.

Morphology of the Electrospun Composite Fibers

The morphological structure of the electrospun PCL and PCL/TiO₂ composite fibers before and after UV irradiation (of 5 and 10 days) was observed by scanning electron microscope. SEM micrographs of the electrospun PCL before and after UV irradiation of 5 and 10 days are given in Figure 4(a–f), respectively. The electrospun PCL fibers [Figure 4(a,b)] show cylindrical shape with only few random beads deformations. Figure 4(c,d) showed that when the electrospun PCL fibers were exposed to UV irradiation of 5 days breakage of the fibers was observed.

After 10 days of UV irradiation, Figure 4(e,f), finer fibers with random junctions were observed. Figure 5(a,b) shows the morphology of the electrospun PCL/n-TiO₂ composite fibers. The fibers were cylindrical and relatively uniform, similar to the neat electrospun PCL fibers.

SEM image for m-TiO₂ particles is shown in Figure 6. The morphology of electrospun PCL/m-TiO₂ composite fibers is

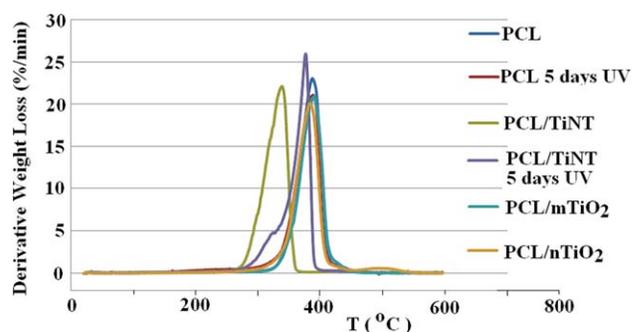


Figure 3. DTG curves of the electrospun PCL fibers and PCL/TiO₂ composite fibers before and after UV irradiation. [Color figure can be viewed in the online issue, which is available at wileyonlinelibrary.com.]

given in Figure 7(a,b). The images clearly show the relatively uniform distribution of the micro particles, but with random agglomerations along the fibers lengths as well. After 5 days of UV radiation, Figure 7(c,d), the fibers showed high degree of degradation due to the high number of fibers breakages and fibers surface voids. After 10 days of UV irradiation the fibrous structure of the PCL was degraded entirely, as seen in Figure 7(e,f) it disappeared, thus leaving behind the agglomerated m-TiO₂ particles.

The SEM images of the electrospun PCL/TiNT composite fibers are given in Figure 8. Due to the size of the TiNT as in case of the PCL/nTiO₂ fibers, the TiNT could not be observed easily along the fibers.

Generally these fibers were relatively uniform with nano and micro fibers diameters, Figure 8(a,b). After 5 days of UV irradiation there was no significant change in the fibers morphology unlike in case of the 10 days of UV radiation exposure where the fibers breaking process was clearly initiated. The fibers increase in fineness and junction formation suggested degradation of the PCL fibers.

The SEM analysis suggests that the mTiO₂ acts as a photocatalyst, i.e. it accelerates the chemical reaction of degradation which was observed with the PCL fibers disappearance after UV irradiation exposure. This result suggests that in air any alkyl radicals will react with oxygen and formed hydroperoxides which can contribute to auto-catalytic reaction.

Table II. TGA Results

Electrospun fibers	$T_{5\%}^a$ (°C)	T_{max}^b (°C)	T_f^c (°C)	W^d (%)	Residue at 700 °C (%)
PCL	344.3	387.5	453.4	97.6	2.4
PCL 5 days UV irradiation	303.9	388.1	431.0	96.8	3.2
PCL + mTiO ₂	345.9	389.1	429.3	91.5	8.5
PCL + nTiO ₂	330.7	383.4	478.0	92.9	7.1
PCL + 0,5% TiNT	288.6	338.7	349.3	96.0	4.0
PCL + 0,5% TiNT 5 days UV irradiation	300.1	376.6	384.6	94.4	5.6

^a $T_{5\%}$, temperature at which 5% weight loss occurs from the TG curve.

^b T_{max} , temperature of maximum rate of decomposition from the DTG curve.

^c T_f , final degradation temperature.

^d W , weight loss from the TG curve.

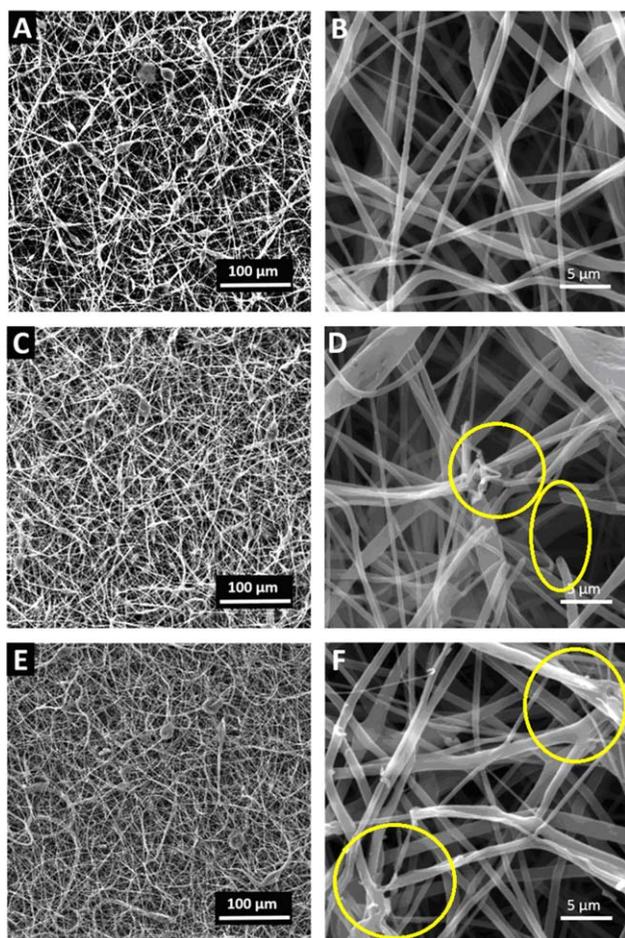


Figure 4. SEM images of the electrospun PCL before: (a) and (b), after 5 days: (c) and (d) and 10 days: (e) and (f) of UV irradiation exposure. Scale bars of 100 μm and 5 μm . [Color figure can be viewed in the online issue, which is available at wileyonlinelibrary.com.]

Results of Fourier Transformed-Infrared Spectroscopy (FTIR)

In order to characterize the possible structural changes of electrospun PCL fibers and electrospun PCL/TiO₂ composite fibers during the exposure to UV irradiation, Fourier transform infrared spectroscopy (FTIR) investigation was performed. The FTIR spectra of electrospun PCL fibers and electrospun PCL/TiO₂ composite fibers before and after UV irradiation are shown in Figures 9–12. Figure 9 shows FTIR spectra of the electrospun

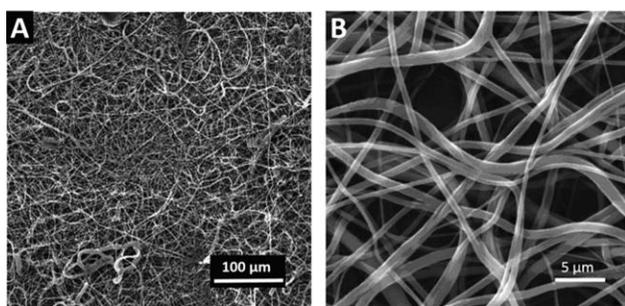


Figure 5. SEM images of the electrospun PCL with 0, 5% nTiO₂ (a) scale bar of 100 μm and (b) 5 μm .

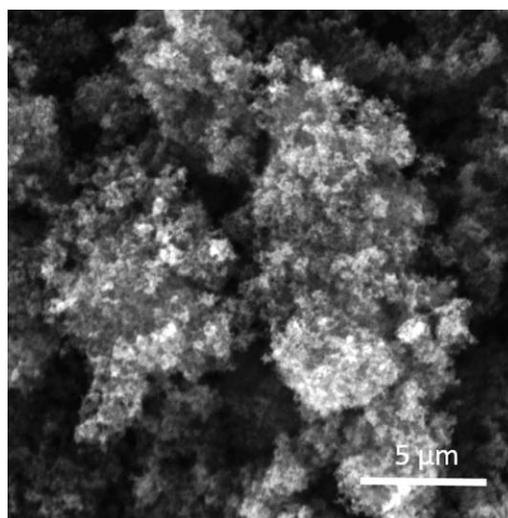


Figure 6. SEM image of the mTiO₂ particles. Scale bar of 5 μm .

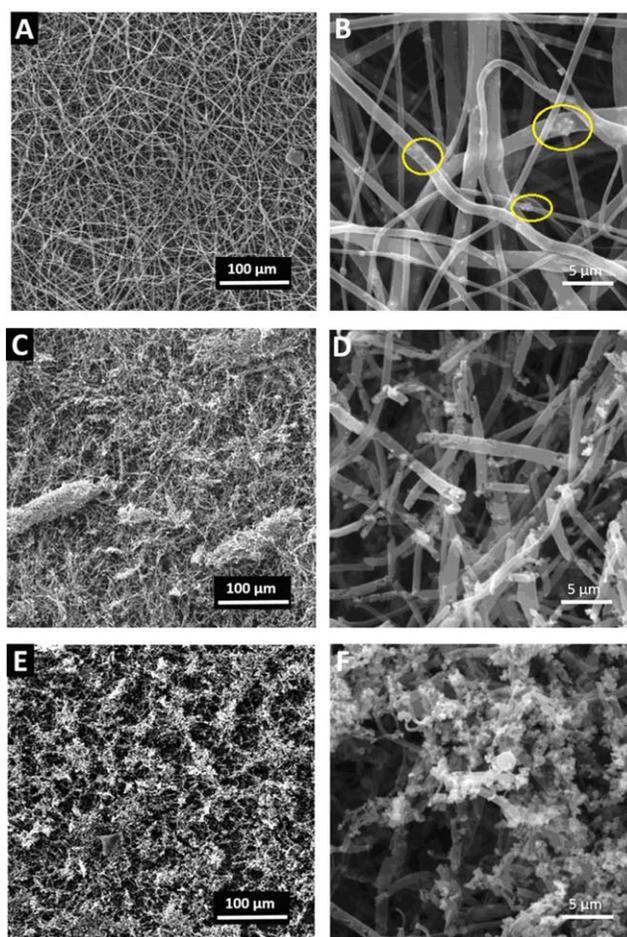


Figure 7. SEM images of the electrospun PCL with 0, 5% of mTiO₂ before: (a) and (b), and after 5 days: (c) and (d), and after 10 days: (e) and (f), of UV radiation exposure. Scale bars of 100 μm and 5 μm . [Color figure can be viewed in the online issue, which is available at wileyonlinelibrary.com.]

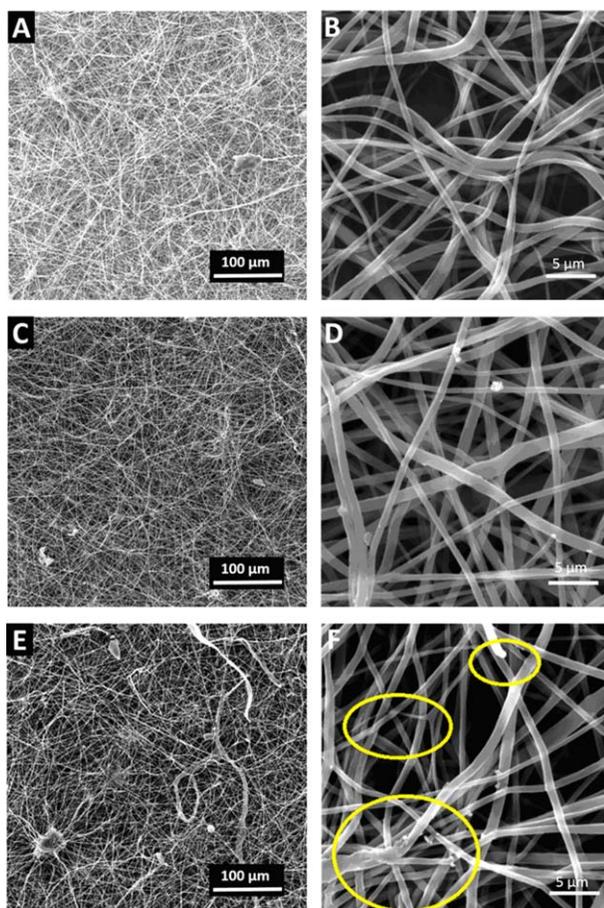


Figure 8. SEM images of the electrospun PCL with 0, 5% TiNT before: (a) and (b), and after 5 days: (c) and (d), and after 10 days: (e) and (f), of UV radiation exposure. Scale bars of 100 μm and 5 μm . [Color figure can be viewed in the online issue, which is available at wileyonlinelibrary.com.]

PCL fibers before and after 5 and 10 days of UV irradiation. There are four main common peaks in the spectra, the alkyl C—H group at 2943 and 2860 cm^{-1} , the stretching vibration peak of the ester carbonyl (C=O) group in the amorphous phase at 1722 cm^{-1} and the C—O stretching vibration peak at 1219 cm^{-1} .²⁶ The peak at 1293 cm^{-1} corresponds to the crystalline phase of electrospun PCL fibers (C—C and C—O) and peak at 1166 cm^{-1} corresponds to (CH₂) deformation.²⁷ UV irradiation had caused changes in the IR spectrum of the electrospun PCL fibers after UV exposure using a high UV irradiation directly to the fibers surface. This was observed as a relative decrease in intensity of the band at 1722 cm^{-1} (carbonyl stretching group), the change was attributed to a change in polymer crystallinity resulting from irradiation. The FTIR spectra of the electrospun PCL/m TiO₂ and electrospun PCL/TiNT composite fibers before and after 5 and 10 days of UV radiation are shown in Figures 10 and 11. The intensity of the absorption bands of all electrospun fibers after 10 days of UV irradiation decreased compared to no irradiated composite fibers and neat PCL fibers. The results indicate that UV degradation is further supported by the photocatalytic activity of the TiO₂ filler which enhances the degradation process. The FTIR spectra of the electrospun PCL/n TiO₂ composite fibers before UV irradiation are shown in Figure 12. The FTIR spectra of the electrospun PCL/n TiO₂ composite fibers after UV irradiation are not shown because there had been a complete degraded in a very short time.

CONCLUSIONS

The effect of UV irradiation and micro- and nano- TiO₂ as well as titanate nanotubes (TiNT) on the thermal properties and morphology of the electrospun PCL fibers and PCL/TiO₂ composite fibers has been investigated. Composites consisting of a PCL-based matrix system and micro- and nano-TiO₂ as well as TiNT were produced by electrospinning.

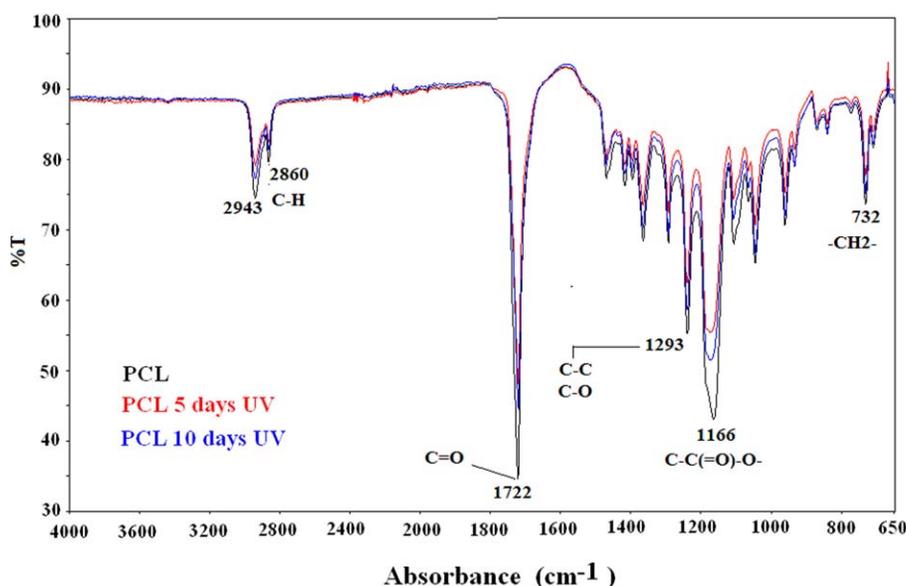


Figure 9. FTIR spectra for the electrospun PCL fibers before and after 5 and 10 days of UV irradiation. [Color figure can be viewed in the online issue, which is available at wileyonlinelibrary.com.]

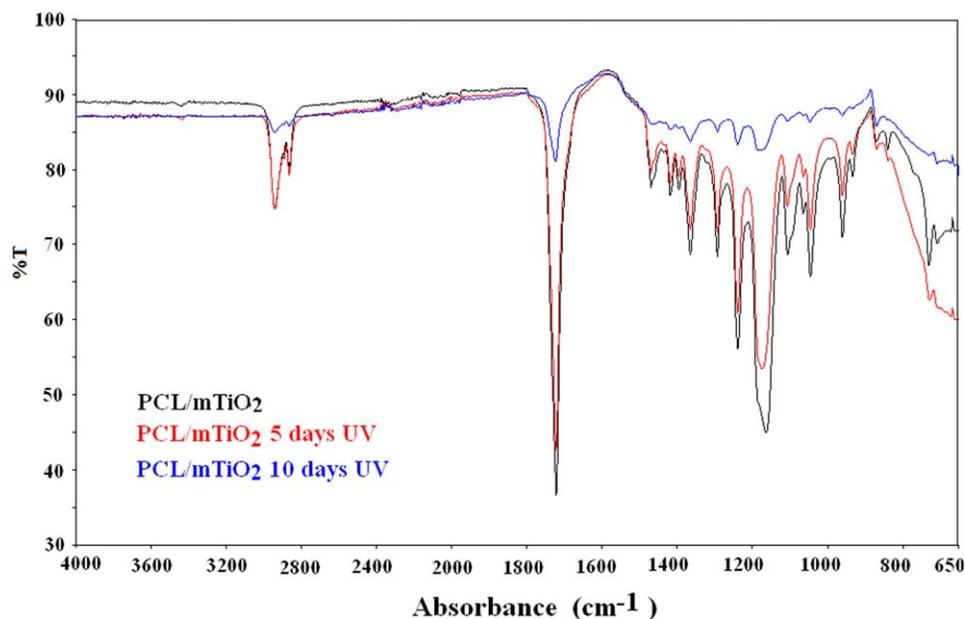


Figure 10. FTIR spectra for the electrospun PCL + 0, 5% mTiO₂ composite fibers before and after 5 and 10 days of UV irradiation. [Color figure can be viewed in the online issue, which is available at wileyonlinelibrary.com.]

The addition of micro TiO₂ (mTiO₂) particles in the PCL slightly increased T_g compared to the neat PCL due to the placement of mTiO₂ particles in the amorphous phase of PCL. While the nano TiO₂ (nTiO₂) and Ti nanotubes (TiNT) had no effect on the T_g and T_m compared to the neat PCL. After UV irradiation, the T_g of the electrospun PCL/TiNT composite fibers shifted to higher temperatures due to the lower mobility of the amorphous phase of PCL. The irradiated electrospun PCL/TiNT composite fibers showed an increase in the crystallinity degree (χ_c), melting (T_m) and crystallization (T_c) temperature.

Thus, it can be concluded that the UV radiation accelerates the decomposition of electrospun composites.

The slight improvement of thermal stability of electrospun PCL/TiO₂ composites fibers was obtained with the addition of micro- and nanoparticles of TiO₂ as well as with Ti nanotubes and the lowest improvement was in the case of the PCL/TiNT composite fibers because of TiNT particles agglomeration and formation of inhomogeneous structure of the electrospun fibers. The results obtained from the SEM analysis proved that the mTiO₂ particles act as a photocatalyst and accelerates the

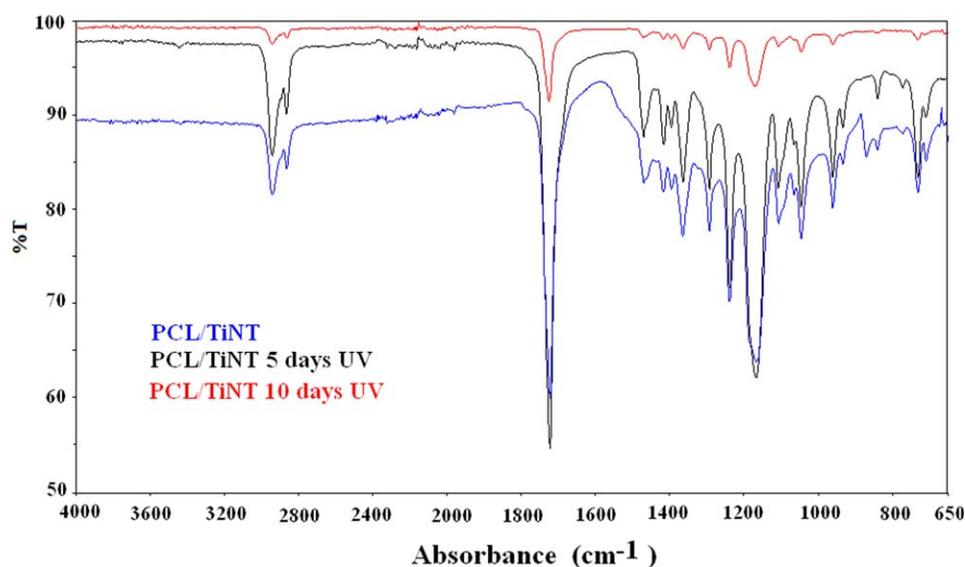


Figure 11. FTIR spectra for the electrospun PCL + 0, 5% TiNT composite fibers before and after 5 and 10 days of UV irradiation. [Color figure can be viewed in the online issue, which is available at wileyonlinelibrary.com.]

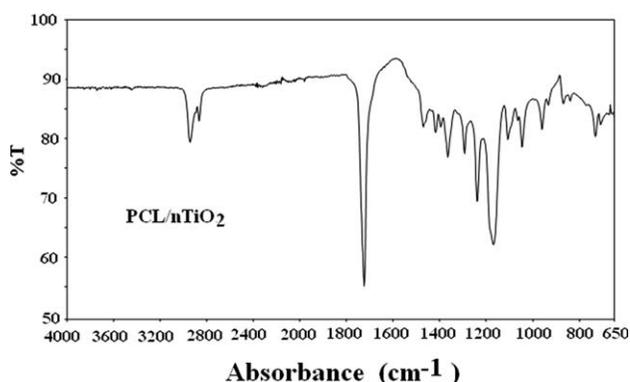


Figure 12. FTIR spectra for the electrospun PCL + 0, 5% nTiO₂ composite fibers before UV irradiation.

chemical reaction of degradation as a result of the photocatalytic activity of mTiO₂. On the SEM micrographs of the electrospun PCL/TiNT and PCL/nTiO₂ composite fibers ribbon form fibers were visible and the fibers diameter is not the same over the entire surface of electrospun composites fibers. In the electrospun PCL/TiNT composite fibers after 5 days of UV irradiation insignificant changes in the structure of the fibers were obtained which indicate on the lesser degradation process in these composites. The results obtained by FTIR-ATR spectroscopy indicate on UV degradation, which is further supported by the photocatalytic activity of the TiO₂ filler which accelerates the process of composite degradation.

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