Effect of Micro and Nano TiO$_2$ on UV Degradation behavior of TiO$_2$ Reinforced Polycaprolactone Composites

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Received: April 14, 2017   Revised: July 23, 2017   Accepted: August 4, 2017

This paper is dedicated to Prof. Mirjana Metikoš-Huković on the occasion of her 80th birthday

Abstract: In this work the influence of micro and nano titanium dioxide (TiO$_2$) particles on the properties of polycaprolactone (PCL) based composites before and after UV radiation was investigated. The neat PCL and PCL / TiO$_2$ micro and nanocomposites were radiated for 120 and 240h. DSC analysis showed that the melting temperature ($T_m$) decreased while the crystallization temperature ($T_c$) and degree of crystallinity ($\chi_c$) increased when the composites were exposed to UV radiation. DMA analysis showed that the glass transition temperature ($T_g$) increased after UV irradiation. The addition of fillers leads to an increase in the initial weight loss (5 wt %) which decreases by time of exposing the samples to UV radiation. SEM showed that the addition of micro and nano TiO$_2$ promote UV degradation of polymer matrix after 120 and 240 h degradation. The results of FTIR spectroscopy confirmed that the micro and nano TiO$_2$ enhance the degradation process because of their photocatalytic activity. The PCL / TiO$_2$ microcomposites showed higher changes in all investigated properties after UV radiation compared to the PCL / TiO$_2$ nanocomposites.

Keywords: particle-reinforced composites, nanocomposites, thermal properties, thermomechanical properties, UV radiation.

INTRODUCTION

The resistance to UV light is an important factor for outdoor applications of polymeric materials. Aliphatic polyesters are biopolymers in which repeating units are bonded via ester linkages. They represent an interesting alternative to synthetic non biodegradable polymers for a short life range of applications. PCL is a linear, hydrophobic, and semicrystalline polyester and biodegradable polymer. Its physical properties and commercial availability make it very attractive, not only as a substitute for non biodegradable polymers of commodity applications, but also as a specific material in medicine and agricultural areas. PCL can be prepared by either the ring-opening polymerization of ε-caprolactone using a variety of anionic, cationic, and co-ordination catalysts or via free radical ring-opening polymerization of 2-methylene-1,3-dioxepane.⁴

When biodegradable polyesters are exposed to the environment, photodegradation, biodegradation and hydrolytic degradation, take place. From the literature, PCL undergoes a two-stage degradation process. The first stage is the non-enzymatic hydrolytic chain scission of ester groups and the second stage is intracellular degradation of PCL.⁵ In recent years titanium dioxide, TiO$_2$, has been studied extensively because of its significant structural, physical, optical, chemical, and electrical properties. It is effectively used in optical filters, antireflective coatings, and photocatalysts.⁶ The photocatalytic mechanism of TiO$_2$ has been reported⁷ as follows: the reaction of e$^-$ with O$_2$ and h$^+$ with H$_2$O likely yields O$_2^*$, HOO$^*$ and HO$. These O$_2^*$, HOO$^*$ and HO$^*$ accelerate the photodegradation of polymer matrices. The active oxygen species described above begins the degradation reaction by attacking neighbouring polymer chains. The degradation process extends into the...
polymer matrices through the diffusion of the reactive oxygen species. The photodegradation of the biodegradable PCL polymer is well known; however, very little is known about the photodegradation of PCL composites reinforced with microparticles and especially nano sized particles of filler TiO$_2$ which has photocatalytic effect during UV irradiation.

Furthermore, there is not a systematic study on the effect of UV radiation on the surface properties of PCL / TiO$_2$ micro and nanocomposites. Accordingly, the main objective of this work was to investigate behaviour of PCL / TiO$_2$ micro and nanocomposites under UV radiation regarding morphology and thermal properties. Compared to similar works this work is unique since it focuses on PCL / TiO$_2$ micro and nanocomposites opposite of the neat PCL.

**EXPERIMENTAL**

The PCL (Polycaprolactone 440744-500G, average molecular mass $M_m$ of 70,000–90,000 g mol$^{-1}$ by GPC, $M_m/ M_w < 2$, density 1.145 g mL$^{-1}$ at 25 °C); titanium dioxide (TiO$_2$) technical micro powder (denoted as mTiO$_2$; particles 0.1 μm to several μm) and TiO$_2$ nano powder (denoted as nTiO$_2$; particles 21 nm, commercial grade Aerioxide P25) were supplied by Sigma-Aldrich, Germany. A laboratory Brabender mixer was applied to prepare PCL / TiO$_2$ micro and nanocomposites with 1.0 wt % of the TiO$_2$ micro and nanoparticles. The temperature in mixer was 120 °C and a screw speed 60 min$^{-1}$; time of mixing was 7 minutes. The reinforced composites were obtained by compression moulding at 140 °C using a laboratory hydraulic press Daek Model 44-226.

A low-pressure mercury lamp unit (ultraviolet chamber Suntest; Heraeus Suntest CPS xenon light lamp) was used for UV radiation of PCL / TiO$_2$ micro and nanocomposites for 120 and 240 h in air at a temperature of 40 °C. The lamp emits radiation $\lambda$ =290 nm. Exposed samples were removed from the chamber and evaluated with different techniques.

Differential scanning calorimetry (DSC) measurements were performed in three cycles (two heating and one cooling scans) from 25 to 190 °C, at 10 °C min$^{-1}$ in the atmosphere of nitrogen at a flow rate of 40 mL min$^{-1}$. Samples with a mass of 10.0 ± 0.5 mg were first heated from 25 °C to 190 °C at a heating rate of 10 °C min$^{-1}$ and held for 10 minutes to eliminate material’s thermal history. Then, the samples were cooled with liquid nitrogen from 190 °C to –100 °C at the cooling rate of 10 °C min$^{-1}$ and finally, they were reheated again to 190 °C. The cell constant was calibrated using a standard indium sample. Degree of crystallinity $\chi_c$ was calculated by using the Equation (1):

$$\chi_c = \frac{\Delta H_m}{\Delta H_m^0 \times (1 - \frac{\omega_{TiO_2}}{100})} \times 100$$  \hspace{1cm} (1)

where $\Delta H_m$ is the experimental melting enthalpy obtained by DSC measurement and $\Delta H_m^0$ is the enthalpy of melting of purely crystalline PCL, considering these values as 142.0 J g$^{-1}$.[6,7]

The viscoelastic properties (loss, $E''$, and storage modulus, $E'$) as a function of temperature for the neat PCL and PCL micro and nanocomposites before and after UV irradiation were determined by dynamic mechanical analysis (DMA). DMA was done by using TA DMA model 983 over a temperature range –100 °C to 120°C, the heating rate was 3 °C min$^{-1}$ and at the frequency of 1 Hz. The dimensions of specimens were 20 mm × 10 mm × 1 mm. All the samples were cooled to –100 °C using liquid nitrogen.

Thermal degradation was evaluated using a TA Instruments Q500 system analyser under the following conditions: weight 10.0 ± 0.5 mg; nitrogen atmosphere (60 mL min$^{-1}$); heating rate 10 °C min$^{-1}$; temperature range 25 °C to 600 °C. The obtained thermal degradation temperatures were: the temperature at which 5 % weight loss occurs ($T_{5\%}$), the temperature of maximum rate of decomposition ($T_{max}$), and the final degradation temperature ($T_f$).

The dispersion morphology of the filler in the PCL matrix was examined by a field emission scanning electron microscope, FEG QUANTA 250 SEM FEI. Samples were graphite-sputtered using the QUORUM equipment. SEM analysis was performed at different magnifications, from 200× to max 100 000×. Fracture surfaces of neat PCL and composites were determined by SEM Tescan Vega TS 5136 MM, equipped by EDS Bruker. The samples were fractured in liquid nitrogen and then sputtered coated with gold / platinum to avoid excessive charging during imaging.

Structural changes, including the interchange in position and intensity of the characteristic bands before and after UV treatment, were obtained at room temperature in reflection mode by attenuated total reflectance (ATR) with a FT-IR spectrometer (Perkin Elmer FT-IR Spectrum One). The scanned wave number range was 4000–450 cm$^{-1}$.

**RESULTS AND DISCUSSION**

**Differential Scanning Calorimetry (DSC) Before and After UV Radiation**

The results of DSC analysis of unexposed and UV exposed neat PCL and PCL / TiO$_2$ micro and nanocomposites are summarized in Table 1. From Table 1 it is clearly seen that the melting temperature ($T_m$) of crystalline phase of PCL...
found at 57.4 °C, while the crystallization (T_c) of PCL obtained at 27.7 °C. The degree of crystallinity (χ_c) of the neat PCL was 41.73%. Compared with the neat PCL before UV radiation the (χ_c) slightly increased after UV radiation (Table 1) due to an increase in the crystalline fraction during UV irradiation.[18] In the process of photodegradation the carbonyl group selectively absorbs energy and results in the cracking of the chain in the PCL and in the formation of free radicals. Further decomposition of the primary radicals results in the formation of the gas products CO and CO_2, other possibility is formation of crosslinking. Table 1 show that the addition of TiO_2 micro and nanoparticles in PCL slightly increased the T_m, indicating that the interaction between PCL and TiO_2 particles occurred. On the other hand, the irradiated samples showed wider endothermic peaks and lower melting temperatures, this behaviour are due to an increase in the crystalline fraction during UV radiation (Table 1) due to an increase in the crystalline fraction during UV irradiation.[19] Sadi, et al.[19] were investigated the effect of UV radiation on PHB samples. Their results also showed that T_m decreased in PHB samples because of the scission reactions which can occur at the lamellar surfaces. These scission reactions increase the surface free energy of the crystals and decrease of the T_m. The addition of TiO_2 micro and nanoparticles in the PCL had no effect on the crystallization temperature, which means that TiO_2 particles do not act as nucleating agents in the course of cooling. The radiation led to an increase in the T_c of neat PCL and all PCL / TiO_2 micro and nanocomposites (Table 1). After UV irradiation the degree of crystallinity (χ_c) of PCL / TiO_2 micro and nanocomposites increased, especially in composites reinforced with TiO_2 nanoparticles (Table 1).

Dynamic Mechanical Analysis (DMA) Before and After UV Radiation

Figure 1 and Table 1 show the temperature dependence of loss modulus (E’’) for the neat PCL and PCL reinforced with TiO_2 micro and nanoparticles before UV irradiation and after exposed to UV radiation for different periods of time. The loss modulus curves show that the transition from the glassy to the viscoelastic state takes place in the temperature range of ~80 °C to 20 °C, while the glass transition temperature in the E’’ curve (T_g) related to the mobility of the amorphous phase of the neat PCL was ~54.1 °C.

According to results shown in Table 1, it can be observed that the PCL submitted to UV radiation of 120 h and 240 h presented an increase in T_g of about 4 °C and 10 °C, respectively, when compared to the neat PCL. DMA measurements of samples before and after UV radiation confirmed that the changes in the structure resulting from the degradation process affected the mobility of the amorphous phase and its interaction with the crystalline phase.[11] The T_g increase for the UV radiated PCL is possibly related to a reduction in local segmental mobility as due to photooxidative crosslinking. The presence of TiO_2 nanoparticles in PCL / TiO_2 microcomposites before UV radiation lead to increased T_g for about 3 °C compared with that of the neat PCL.

Changes in loss modulus after 120 h and 240 h of UV radiation are reflected in the reduction of peak heights in the field of T_g, peak width and shift the temperature peak maximum (i.e. T_g) to higher temperatures with the addition of 1.0 wt.% of TiO_2 microparticles, due to decreased mobility of the amorphous phase of PCL.

Based on the decrease of the T_g it can be concluded that with the addition of TiO_2 microparticles some interaction between the PCL and TiO_2 microparticles exist which reduces the mobility of the amorphous segments in the PCL. The T_g values in Table 1, show that the addition of TiO_2 nanoparticles slightly shifted T_g to lower temperature prior to UV radiation, which indicates that TiO_2 nanoparticles affects the relaxation process of PCL chain segments but the interaction between PCL and TiO_2 nanoparticles is not strong. After 120 h of UV radiation, the T_g of the PCL / TiO_2 nanocomposite shifted to higher temperatures for about 12 °C compared to the same unexposed composite. Accordingly, the T_g increased due to the reduced mobility of the statistical coil chain segments in the amorphous region. [11] While, after 240 h of UV radiation, the T_g of PCL / TiO_2 nanocomposite moved to a lower temperature (~50.2 °C). This behaviour is clarified by photodegradation in the amorphous region of PCL and by

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**Table 1.** Thermo-mechanical (DMA) and thermal (DSC) properties of the neat PCL and PCL / TiO_2 micro (m) and nanocomposites (n).

<table>
<thead>
<tr>
<th>Samples</th>
<th>T_g DMA[5] / °C</th>
<th>T_m[m] / °C</th>
<th>T_t [m] / °C</th>
<th>ΔH_m[m] / J g⁻¹</th>
<th>χ_c[m]</th>
<th>E''[m] / °C</th>
</tr>
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<tr>
<td>PCL</td>
<td>–54.1</td>
<td>57.4</td>
<td>27.7</td>
<td>58.67</td>
<td>41.7</td>
<td>0.60</td>
</tr>
<tr>
<td>PCL 120 h UV</td>
<td>–50.7</td>
<td>57.3</td>
<td>29.2</td>
<td>60.02</td>
<td>42.7</td>
<td>0.63</td>
</tr>
<tr>
<td>PCL 240 h UV</td>
<td>–44.7</td>
<td>56.3</td>
<td>28.0</td>
<td>60.42</td>
<td>43.0</td>
<td>0.57</td>
</tr>
<tr>
<td>PCL+1% m TiO_2</td>
<td>–51.6</td>
<td>58.4</td>
<td>27.4</td>
<td>57.38</td>
<td>40.8</td>
<td>0.62</td>
</tr>
<tr>
<td>PCL+1% m TiO_2</td>
<td>–50.4</td>
<td>55.5</td>
<td>28.7</td>
<td>52.82</td>
<td>37.6</td>
<td>0.63</td>
</tr>
<tr>
<td>PCL+1% m TiO_2</td>
<td>–48.7</td>
<td>55.3</td>
<td>28.5</td>
<td>57.11</td>
<td>40.6</td>
<td>0.76</td>
</tr>
<tr>
<td>PCL+1% n TiO_2</td>
<td>–57.0</td>
<td>58.0</td>
<td>27.4</td>
<td>55.19</td>
<td>39.3</td>
<td>0.56</td>
</tr>
<tr>
<td>PCL+1% n TiO_2</td>
<td>–45.3</td>
<td>55.4</td>
<td>28.3</td>
<td>57.48</td>
<td>40.9</td>
<td>0.49</td>
</tr>
<tr>
<td>PCL+1% n TiO_2</td>
<td>–50.2</td>
<td>55.6</td>
<td>29.2</td>
<td>66.14</td>
<td>47.1</td>
<td>0.67</td>
</tr>
</tbody>
</table>

[T_g: glass transition temperature from DMA.
T_m: melting temperature.
T_t: crystallization temperature.
ΔH_m: melting enthalpy.
χ_c: degree of crystallinity.
E'': storage modulus at 25 °C]
higher separation between the amorphous and crystalline phases, causing a greater mobility of the amorphous phase segments. Based on the storage modulus \(E'\) curves of the neat PCL and PCL / TiO\(_2\) micro and nanocomposites before and after UV radiation (Figure 2) for each composite, \(E'\) decreased with the increasing temperature. The storage modulus is much greater than the loss modulus, and the deformation during the periodic power save much more than it is lost. According to Ferry\[13\] in the transition from the glassy state in viscoelastic effect of cyclic loading parts of macromolecules are becoming increasingly mobile and much of the energy is lost as heat, the storage modulus decreases rapidly while the loss modulus rises sharply. From the DMA results shown in Figure 2 and Table 1 it is evident that with the addition of TiO\(_2\) micro and nanoparticles value of the storage modulus in the glassy

![Figure 1](image1.png)  
**Figure 1.** Plot of loss modulus \(E''\) of (a) neat PCL and (b) PCL / TiO\(_2\) micro- and (c) nanocomposites before and after UV radiation.

![Figure 2](image2.png)  
**Figure 2.** Plot of storage modulus \(E'\) of (a) neat PCL and (b) PCL / TiO\(_2\) micro- and (c) nanocomposites before and after UV radiation.
state before UV radiation increases for the PCL / TiO$_2$ microcomposites while decreases (except after UV radiation of 240 h) for the PCL / TiO$_2$ nanocomposites compared to the neat PCL. The fall in the value of storage modulus can be attributed to the difficulty of the stress transferring from the polymer matrix to the inorganic TiO$_2$ particles.

In the case of PCL / TiO$_2$ micro and nanocomposites increases of $E'$ at 25 °C (Table 1) were observed after longer time of irradiation (240 h) by ca.18 % and 10 %, respectively.

**Thermal Stability Before and After UV Radiation**

Figures 3–5 present the TG and DTG curves of the neat PCL and PCL / TiO$_2$ micro and nanocomposites before and after UV radiation. The data obtained from TGA thermograms are presented in Table 2. The degradation of all samples before and after UV radiation involves one main decomposition step obviously corresponding to PCL decomposition. In the inert atmosphere, the thermal degradation of PCL takes place via the ester pyrolysis reaction with the random rupture of the polyester chains to form CO$_2$, H$_2$O, and carboxylic acid.$^{[14]}$ At 365.5 °C started the decomposition of the neat PCL, and 98.4 % of the decomposition occurred at 426.2 °C (Table 2). The onset temperature of the degradation, evaluated at the point where 5 % degradation occurs.

The addition of 1.0 wt.% of TiO$_2$ micro and nanoparticles in PCL matrices increased the 5% loss temperature ($T_{5\%}$) compared to neat PCL. This means that the presence of TiO$_2$ micro and nanoparticles improved PCL thermal stability. When the PCL and PCL / TiO$_2$ micro and nanocomposites were exposed for 120 h and 240 h to UV irradiation, the $T_{5\%}$ increased slightly (Figure 3a, 4a and 5a). The obtained result for $T_{5\%}$ may be due to degradation of PCL by UV radiation, also crosslinking of the polymer may occur after UV radiation. According to results PCL / TiO$_2$ micro and nanocomposites have a higher durability to thermal degradation compared to the neat PCL. The thermal degradation increase as the time of UV radiation increases.

The explanation for this behaviour is that a better dissipation of heat inside the composite may be accomplished with higher thermal diffusivity of TiO$_2$ particles and the burning of the composites a delay.$^{[15]}$ The addition of TiO$_2$ microparticles resulted in better thermal stability than addition of TiO$_2$ nanoparticles. This behaviour

![Figure 3](image3.png)  
**Figure 3.** (a) TG and (b) DTG curves of the neat PCL before and after UV radiation.

![Figure 4](image4.png)  
**Figure 4.** (a) TG and (b) DTG curves of PCL / TiO$_2$ microcomposites before and after UV radiation.
suggests on the aggregation of TiO\(_2\) nanoparticles in the composites. The maximum decomposition temperature (\(T_{\text{max}}\)) of the neat PCL was at 408.6 °C, while the \(T_{\text{max}}\) of PCL increased with addition of TiO\(_2\) micro and nanoparticles and after UV radiation (Figure 3b–5b, Table 2).

Based on measured residuals at 600 °C before and after UV radiation, shown in Table 2, it was evident that the residue of unexposed PCL was 1.4 %, while the residues of the unexposed PCL / TiO\(_2\) micro and nanocomposites were the same. This behaviour for the neat PCL may be relate to the formation of crosslinked structures during the sample preparation by compression moulding. The residue of 1.4 % for PCL / TiO\(_2\) micro and nanocomposites before UV radiation was partially due to the content of TiO\(_2\) micro and nanoparticles (1 mas %) and partially for the crosslinked structures formed during the sample preparation. The residues at 600 °C in the PCL / TiO\(_2\) micro and nanocomposites increased with an increase of the irradiation time. The reason for this higher residue after UV radiation may be the presence of crosslinked macromolecules that these PCL composites contained.

**PCL and PCL Micro- and Nanocomposites Morphology Before and After UV Radiation**

Morphological structure and dispersion of fillers in polymer matrix is the most important for final properties of polymer composites. The SEM images in Figure 6 show the neat PCL and PCL reinforced with TiO\(_2\) micro and nanoparticles before UV radiation. The SEM images of the neat PCL shows granular structure (Figure 6a). TiO\(_2\) nanoparticles are randomly distributed and very well dispersed in PCL matrix, due to good compatibility of matrix and filler (Figure 6c).\[16,17\]

Addition of TiO\(_2\) microparticles into the PCL matrix shows tendency some of particles to agglomerate and form TiO\(_2\) micro spheres, due to the influence of the surface hydroxyl groups (Figure 6b). The SEM images of surface of the neat PCL and PCL micro and nanocomposites after UV radiation are shown in Figures 7 and 8.

The SEM images reveal that UV degradation of neat PCL leads to formation of gaps, which are more pronounced and interconnected with higher degradation time (Figure 7). Microparticles of TiO\(_2\) intensify UV degradation of large size agglomerates of TiO\(_2\), especially after 240 hours of irradiation (Figures 8a, 8b). While the addition of TiO\(_2\) nanoparticles to PCL matrix more efficiently promotes UV decomposition with regards to TiO\(_2\) microparticles (Figures 8c, 8d).

![Figure 6](image-url1).

**Figure 5.** (a) TG and (b) DTG curves of PCL / TiO\(_2\) nanocomposites before and after UV radiation.

![Figure 6](image-url2).

**Figure 6.** SEM images of (a) PCL; (b) PCL / TiO\(_2\) microcomposites, and (c) PCL PCL / TiO\(_2\) nanocomposites, before UV radiation.
Figure 7. SEM images of PCL after UV radiation: after (a) 120 h; (b) after 240 h.

Figure 8. SEM images after UV radiation of PCL / TiO₂ microcomposites: after (a) 120 h and (b) after 240 h; and PCL/TiO₂ nanocomposites: after (c) 120 h and (d) after 240 h.
Figure 8d shows that after 240 hours of UV radiation almost completely polymer matrix is decomposed, while TiO\(_2\) nanoparticles remained and formed filler network [18]. Such morphological analysis is in correlation with DMA results and higher \(E'\) at 25 °C for PCL/TiO\(_2\) nanocomposites after 240 hours of UV radiation (Table 1, Figure 2). Figure 9 shows SEM analysis of fractured surfaces of the neat PCL and PCL / TiO\(_2\) micro and nanocomposites before and after UV radiation.

SEM microphotographs of fractured surface of PCL / TiO\(_2\) microcomposites (Figure 9d) and PCL / TiO\(_2\) nanocomposites (Figure 9g) before UV radiation show rough structure with shrouded particles, especially TiO\(_2\) nanoparticles due to strong interactions with polymer matrix. After UV...
radiation, it can be seen plastic fracture for the neat PCL (Figures 8b, c) especially after 120 hours of exposure (Figure 9b). The fractured surface of PCL / TiO₂ microcomposite (Figures 9 e, f) shows lower degradation of polymer matrix in relation to the PCL / TiO₂ nanocomposite (Figures 9 h, i), and consequently more ductile behaviour of polymer matrix during deformation.

**ATR-FTIR Analysis Before and After UV Radiation**

Figure 10a presents the ATR-FTIR spectra of the neat PCL before and after 120 h and 240 h of UV irradiation. The peaks which appear at 2941 cm⁻¹ and 2860 cm⁻¹ are attributed to stretching of C–H bonds; the carbonyl stretching absorption at about 1730 cm⁻¹,[19] the absorption band at 1469 cm⁻¹ attributed to the axial symmetric deformation of CH₂; band at 1292 cm⁻¹ assigned to the backbone C–C (=O)–O the stretching vibration of the crystalline phase of PCL; the absorption band at 1160 cm⁻¹ related to the axial deformation of C–C(=O)–O and the absorption band at 728 cm⁻¹ related to the (CH₂)–stretching vibration.

Ti–O–Ti bond in TiO₂ is identified with peaks below 700 cm⁻¹.[20] The ATR-FTIR spectra of PCL / TiO₂ micro and nanocomposites, both unexposed and UV exposed are shown in Figure 10b and 10 c, respectively. The ATR-FTIR spectra showed that after UV radiation the intensity of the PCL peaks gradually decreased with an increasing time of UV radiation. This decrease in intensity was probably due to the photodegradation of PCL by UV radiation. Moreover, existence of TiO₂ micro and nanoparticles in the irradiated PCL / TiO₂ micro and nanocomposites led to the changes resulting from some characteristic functional groups of PCL that was probably due to the photocatalytic degradation and no existence of intermolecular interaction. As could be seen from the results, the PCL / TiO₂ microcomposites showed higher changes in the intensity of IR absorption peaks than the PCL / TiO₂ nanocomposites.

**CONCLUSION**

This study considers the effect of TiO₂ micro and nanoparticles on UV degradation behavior of TiO₂ reinforced

<table>
<thead>
<tr>
<th>Samples</th>
<th>T₅% / °C</th>
<th>Tmax / °C</th>
<th>Tf / °C</th>
<th>Weight loss / %</th>
<th>Residue / %</th>
</tr>
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<tbody>
<tr>
<td>PCL</td>
<td>365.5</td>
<td>408.6</td>
<td>426.2</td>
<td>98.4</td>
<td>1.4</td>
</tr>
<tr>
<td>PCL 120 h UV</td>
<td>374.6</td>
<td>414.6</td>
<td>439.2</td>
<td>97.4</td>
<td>1.6</td>
</tr>
<tr>
<td>PCL 240 h UV</td>
<td>379.9</td>
<td>414.2</td>
<td>429.7</td>
<td>98.8</td>
<td>1.8</td>
</tr>
<tr>
<td>PCL+1%mTiO₂</td>
<td>375.1</td>
<td>413.6</td>
<td>435.3</td>
<td>98.6</td>
<td>1.4</td>
</tr>
<tr>
<td>PCL+1%mTiO₂ 120 h UV</td>
<td>378.1</td>
<td>412.7</td>
<td>431.0</td>
<td>97.2</td>
<td>2.4</td>
</tr>
<tr>
<td>PCL+1%mTiO₂ 240 h UV</td>
<td>378.6</td>
<td>412.9</td>
<td>432.5</td>
<td>96.1</td>
<td>3.5</td>
</tr>
<tr>
<td>PCL+1%nTiO₂</td>
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<td>413.1</td>
<td>437.3</td>
<td>98.6</td>
<td>1.4</td>
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<tr>
<td>PCL+1%nTiO₂ 120 h UV</td>
<td>373.8</td>
<td>413.2</td>
<td>434.4</td>
<td>97.9</td>
<td>1.9</td>
</tr>
<tr>
<td>PCL+1%nTiO₂ 240 h UV</td>
<td>373.2</td>
<td>412.2</td>
<td>431.9</td>
<td>97.4</td>
<td>2.4</td>
</tr>
</tbody>
</table>

(a) T₅%: temperature at which 5% weight loss occur from the TG curve.
(b) Tmax: temperature of maximum rate of decomposition from the DTG curve.
(c) Tf: final degradation temperature.
polycaprolactone composites under UV radiation for 120 and 240 h. The DSC analysis showed that $T_m$ was decreased during UV radiation, suggesting a decrease of the lamellae thickness and an increase of less ordered crystals. The irradiation led to an increase in the $T_c$ and degree of crystallinity ($\chi_c$) of the neat PCL and all PCL / TiO$_2$ composites, especially of composites with TiO$_2$ nanoparticles due to an increase in the crystalline fraction during UV radiation. The DMA results suggested that the addition of TiO$_2$ micro and nanoparticles did not affect the $T_g$ prior to UV radiation. After 240 h of UV irradiation, the $T_g$ of PCL / TiO$_2$ micro and nanocomposites was moved to a lower temperature. This behaviour could be explained by photodegradation in the amorphous region of PCL and by the higher separation between the amorphous and crystalline phases, which caused a greater mobility of the amorphous phase segments. The storage modulus of the PCL / TiO$_2$ micro and nanocomposites increased after UV radiation. Morphology of the prepared composites was characterized by scanning electron microscopy. While the PCL / TiO$_2$ nanocomposites exhibited very well dispersion of the filler, the PCL / TiO$_2$ microcomposites contained TiO$_2$ agglomerates. After UV radiation, especially after 240 h of irradiation in composite with TiO$_2$ microparticles almost completely polymer matrix is decomposed, while TiO$_2$ nanoparticles remained and formed filler network. TGA results showed that PCL / TiO$_2$ micro and nanocomposites had a higher resistance to thermal degradation compared to the neat PCL, and it appeared to increase as the time of UV radiation increased. The increase of the degradation temperature was probably due to crosslinking of the polymer after UV radiation. TiO$_2$ micro and nanoparticles in irradiated PCL / TiO$_2$ composites led to the changes of some characteristic functional groups of PCL that was probably due to the photocatalytic degradation. The PCL / TiO$_2$ microcomposites showed higher changes of the intensity of IR absorption peaks than the PCL / TiO$_2$ nanocomposites.

**Funding.** This study was funded by University of Zagreb, Croatia (grant no. 110001/2013). The authors declare that they have no conflict of interest.

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