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Characterization of Biodegradable Polycaprolactone Containing Titanium Dioxide Micro and Nanoparticles

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Abstract**—**Composites based on a biodegradable polycaprolactone (PCL) containing 0.5, 1.0 and 2.0 wt % of titanium dioxide (TiO_2) micro and nanoparticles were prepared by melt mixing and the effect of filler type and contents on the thermal properties, dynamic-mechanical behaviour and morphology were investigated. Measurements of storage modulus and loss modulus by dynamic mechanical analysis (DMA) showed better results for microfilled PCL/TiO_2 composites than nanofilled composites, with the same filler content. DSC analysis showed that the T_g and T_c of micro and nanocomposites were slightly lower than those of neat PCL. The crystallinity of the PCL increased with the addition of TiO_2 micro and nanoparticles; however, the χ_c for the PCL was unchanged with micro TiO_2 content. The thermal stability of PCL/TiO_2 composites were characterized using thermogravimetric analysis (TGA). The initial weight loss (5 wt %) occurs at slightly higher temperature with micro and nano TiO_2 addition and with increasing TiO_2 content.

Keywords**—**Morphology, polycaprolactone, thermal properties, titanium dioxide.

I. Introduction

BIOPOLYMERS are usually divided in three groups, depending on the production process and sources [1]. The first class is the polymers directly extracted from biomass (e.g. polysaccharides, proteins, lipids). The second type is the polymeric materials produce by classical synthesis using either renewable biobased monomers (such as poly (lactic acid)) or based monomers (such as polycaprolactones). Finally, the third kind consists of the polymeric materials produced by microorganisms and genetically-modified bacteria (for instance the polyhydroxyalkanoates). One of the most promising candidates of the above biopolymers is polycaprolactone (PCL), produced from renewable resources and readily biodegradable. PCL is one of an important group of thermoplastics and has recently received much attention because of its flexibility and biodegradability, applying in food packaging, tissue engineering, dressing for wound, and drug delivery [2], [3]. However, some shortcomings such as high cost, low melting temperature and low mechanical properties restrict widespread industrial use of PCL. In order to improve the physical properties of polymer, inorganic particles were usually used to improve some properties of the polymer. The promise of these new composites is controllable combination of the properties of the polymer (flexibility, toughness, and easy processing) and the properties of filler (hardness, durability and thermal stability) [4]. Titanium and its alloys are increasingly used in due to their excellent mechanical properties, and good biocompatibility. Titanium dioxide (TiO_2) is an inert and cheap material, and its well-known non-toxicity (even in nanometric scale) for human related applications allows it's used as an additive in cosmetics, pills or toothpaste [5], [6]. Organo-inorganic composites materials that combine attractive of dissimilar oxide and polymer components are not simply physical blends, but they can be broadly defined as complex materials containing both organic and inorganic constituents intimately mixed [6]-[8]. The scale of mixing or, in other words, the degree of homogeneity, would influence or even command the ultimate properties of the composites. In this paper we report the effect of titanium dioxide micro and nanoparticles on the thermal properties, dynamic-mechanical behaviour and morphology of PCL/TiO_2 composites.

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II. Experimental

A. Materials

The PCL (Polycaprolactone 440744-500G, average M_n 70 000-90 000 $gmol^{-1}$ by GPC, $M_w/M_n<2$, density 1.145 g/mL at 25°C) was supplied by Sigma-Aldrich, Germany. Titanium dioxide (TiO_2) technical micropowder (denoted as $mTiO_2$, particles 100 nm to several μm) and TiO_2 nanopowder (denotaed as $nTiO_2$, particles 21 nm, commercial grade Aeroxide P25) also supplied by Sigma- Aldrich, Germany were used as the filler.

B. Sample Preparation

Composites with 0.5, 1.0 and 2.0 wt% of the TiO_2 micro and nanoparticles were prepared by using a laboratory Brabender mixer at temperature of 120°C with a screw speed of 60 min^{-1}, total time of mixing was 7 min. Final specimens for all investigations (size 40 mm x 12mm x1.5 mm) were obtained by compression molding of extruded materials using a laboratory hydraulic press Dake Model 44-226 at 140°C.

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C. Testing Methods

1. Dynamic Mechanical Analysis (DMA)

Dynamic mechanical measurements were carried out on a DMA 983 Dynamic Mechanical Analyser (TA Instruments, USA). The samples were cooled to -90°C and then heated to 90°C at a frequency of 1 Hz with a constant heating rate of 3°C/min. The samples length between the clamps was approximately 40 mm. All the samples were cooled to -90°C using liquid nitrogen.

2. Differential Scanning Calorimetry (DSC)

Thermal behavior of the PCL/TiO_2 composites was studied using a DSC Mettler Toledo 822e differential scanning calorimeter in a nitrogen atmosphere. In the first heating and cooling scans, the samples were heated from 25 to 120°C at a cooling rate of 10°C/min and held at that temperature for 10 min in order to eliminate any previous thermal history. Then, the samples were cooled with liquid nitrogen (flow rate 40mL/min) from 120 to -100°C at a cooling rate of 10°C/min; this was followed by reheating to 120°C for the second heating run. The crystallization and melting parameters were recorded from the cooling and reheating scans. The cell constant was calibrated using a standard pure indium sample. The crystallinity percentage (χ_c) of PCL and their composites was calculated through a comparison of the heat of fusion of the composites to the heat of fusion of the completely crystalline polymer as an external standard:

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

where ΔH_m is the enthalpy of fusion per gram of the samples recalculated for the PCL mass, $\Delta H°_m$ is the enthalpy of fusion per gram of 100% crystalline PCL and $\%w_{TiO2}$ is weight of the used filler. For $\Delta H°_m$, was used 142.0 J/g [9] [10]. Glass transition temperature (T_g) was taken as the midpoint of the specific heat increment.

3. Thermo Gravimetric Analysis (TGA)

In order to study thermal degradation of neat PCL as well as their composites, PCL/TiO_2 micro and nanocomposites, thermogravimetric analysis (TGA) has been carried using a TA Instruments Q500 system analyzer, USA, by the non-isothermal thermogravimetry. Samples of approximately 10 mg were placed in alumina crucibles and tested with a thermal ramp over a temperature range of 25 to 600°C, at a heating rate of 10°C/min in nitrogen and oxygen atmosphere (60 mL/min). The thermal degradation temperatures taken into account were temperature at which 5% weight loss occur ($T_{5\%}$), temperature of maximum rate of decomposition (T_{max}), final degradation temperature (T_f).

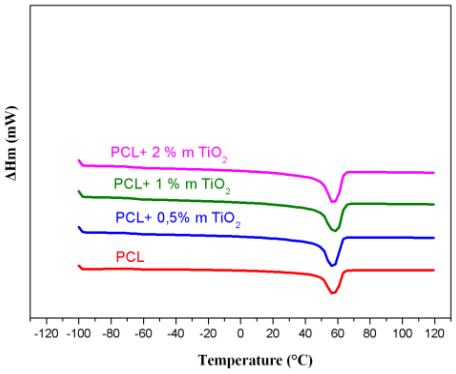
4. Scanning Electron Microscopy (SEM)

The samples phase structure was observed by SEM microscope (VEGA Plus TS 5135, Tescan), previously ultrathin sections of samples were prepared with ultramicrotome Leica and vacuum-coated with a Pt film using a Vacuum sputter coater, SCD 050, Balzers.

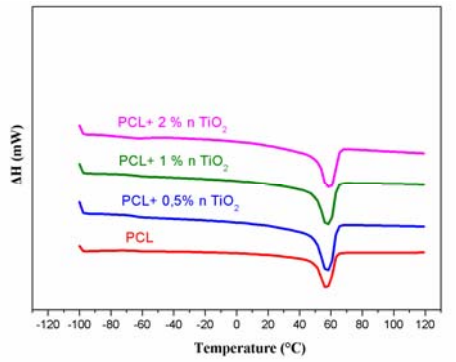
III. Results and Discussion

A. Thermal Properties (DSC)

DSC measurements were performed to characterize the glass transition (T_g), melting and crystallization behavior of the neat PCL and PCL/TiO_2 micro and nanocomposites. The DSC curves obtained from the second run by scanning from -90 to 90°C are shown in Fig. 1. In all PCL/TiO_2 composites, two phase transitions were observed, that is T_g due to the amorphous phase of PCL and melting of the crystalline phase of PCL located at higher temperature.



(a)



(b)

Fig. 1 DSC heating curves of (a) PCL/mTiO_2 and (b) PCL/nTiO_2 composite

Table I shows a summary of the thermal parameters obtained from the DSC thermograms. A slight shift of T_g to the lower temperature in the PCL/TiO_2 micro and nanocomposites were observed which is may be due to the higher mobility of the amorphous phase of PCL because of a higher degree of phase separation between the amorphous and crystalline phase in PCL containing TiO_2 micro and

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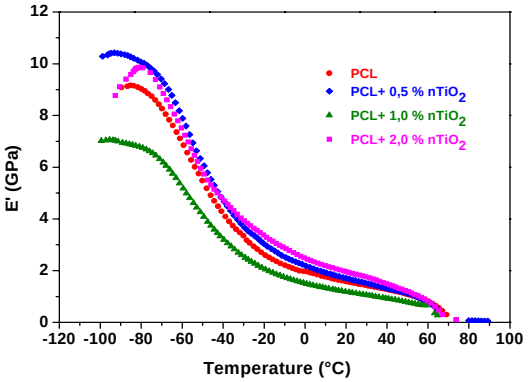
nanoparticles [11], [12]. With the increase of content of TiO_2 particles the T_g was unchanged. The melting point of the PCL/TiO_2 composites is found to slightly increase with the increase of TiO_2 micro and nanoparticles. When the content of TiO_2 micro and nanoparticles increases the T_c of the composites decreases, only in PCL/TiO_2 composites prepared with 2 wt% of TiO_2 particles T_c increased. The data presented in Table I indicate that the crystallinity of PCL in PCL/TiO_2 composites was higher than that of neat PCL. The increase of content of TiO_2 microparticles does not affect on the crystallinity of PCL.

TABLE I
THERMAL PROPERTIES OF THE NEAT PCL AND PCL/TiO_2 MICRO AND NANOCOMPOSITE

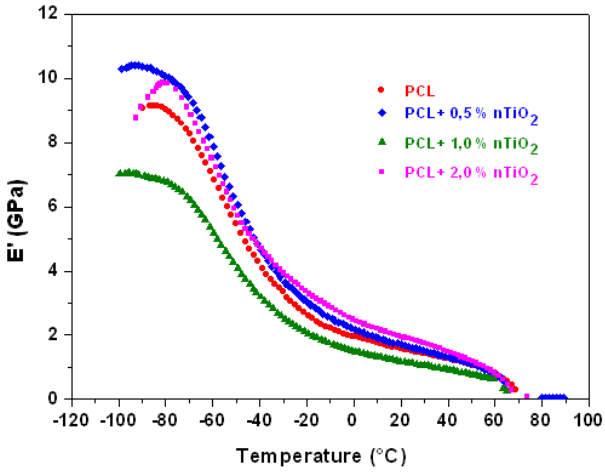
Sample	T_g (°C)	T_m (°C)	T_c (°C)	χ_c (%)	$E'_{25°C}$ (GPa)
PCL	-64,6	56,9	28,2	22,2	1,501
PCL + 0,5 % mTiO$_2$	-65,9	56,7	27,8	26,7	1,583
PCL + 1,0 % mTiO$_2$	-66,1	58,5	27,4	26,8	1,589
PCL + 2,0 % mTiO$_2$	-66,0	57,3	29,6	26,8	1,855
PCL + 0,5 % nTiO$_2$	-65,6	57,7	28,3	26,1	1,614
PCL + 1,0 % nTiO$_2$	-66,1	58,2	27,4	27,6	1,448
PCL + 2,0 % nTiO$_2$	-66,0	57,1	29,7	24,6	1,856

B. Dynamic Mechanical Analysis (DMA)

To investigate the effect of the TiO_2 particles on the viscoelastic properties of PCL/TiO_2 composites, DMA measurements were performed in the temperature range from-90 to 90°C. Fig. 2 shows the temperature dependence of the storage modulus (E') for PCL/TiO_2 composites. The dynamic-mechanical results show slight increases of E' of composites by the addition of TiO_2 micro and nanoparticles and increased with TiO_2 content (Table I). The increase in the E' indicate that the addition of TiO_2 particles can induce reinforcement effects.



(a)

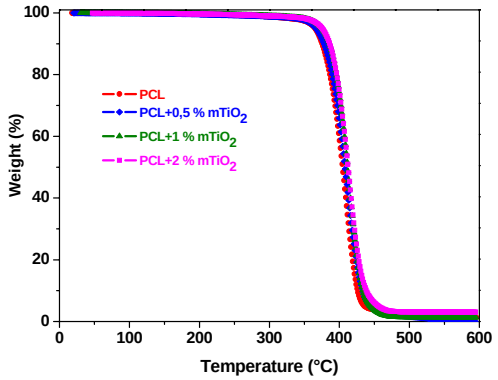


(b)

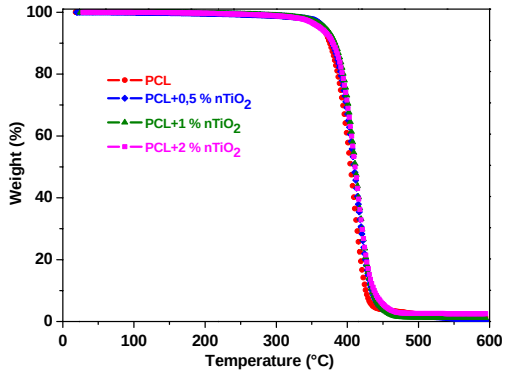
Fig. 2 Plot of storage modulus (E') of (a) PCL/mTiO_2 and (b) PCL/nTiO_2 composite

C. Thermo Gravimetric Analysis (TGA)

One step degradation was occurred for neat PCL and PCL/TiO_2 micro and nanocomposites in nitrogen atmosphere (Figs. 3 (a) and (b)). The characteristic thermal degradation temperatures are reported in the Table II. The thermal stability of the PCL is improved by the presence of TiO_2 microparticles and with TiO_2 content as shown by increase of $T_{5\%}$ (Fig. 3 (a), Table II). In the case of PCL/TiO_2 nanoparticles (Fig. 3 (b), Table II) the addition of nTiO_2 does not significantly affect on the thermal stability. According to Fukushima et al. [13] thermal degradation of PCL in inert atmosphere take place through the rupture of the polyester chain via ester pyrolysis reaction with the release of CO_2, H_2O and formation of carboxylic acid groups.



(a)



(b)

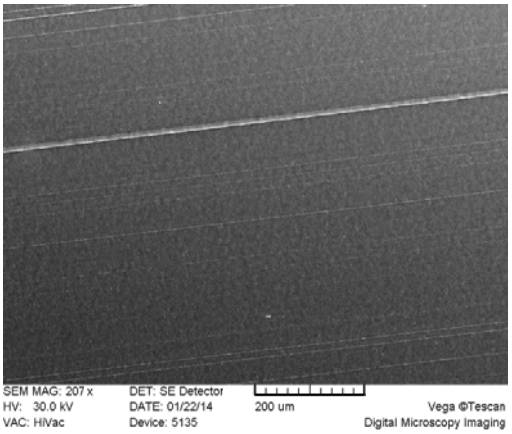
Fig. 3 TG curves of (a) PCL/mTiO$_2$ and (b) PCL/nTiO$_2$ composite

TABLE II
RESULTS OF TGA MEASUREMENT FOR THE NEAT PCL AND PCL/TIO$_2$ MICRO AND NANOCOMPOSITE

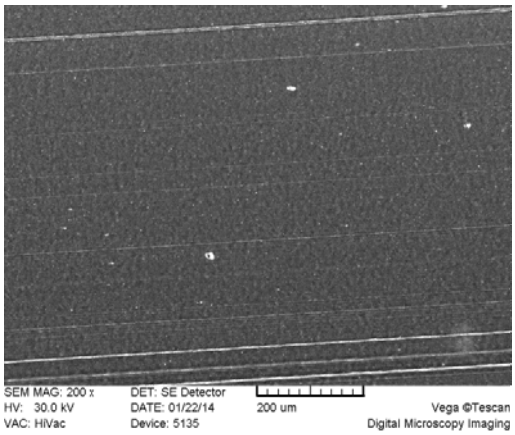
Sample	$T_{5\%}$ (°C)	T_{max} (°C)	T_{end} (°C)	Δm (%)
PCL	365,5	410,2	426,9	98,13
PCL + 0,5 % mTiO$_2$	366,7	411,9	434,5	99,00
PCL + 1,0 % mTiO$_2$	375,1	414,5	434,5	98,00
PCL + 2,0 % mTiO$_2$	376,0	414,3	436,5	96,52
PCL + 0,5 % nTiO$_2$	367,3	413,4	440,0	99,00
PCL + 1,0 % nTiO$_2$	368,2	414,4	437,8	98,36
PCL + 2,0 % nTiO$_2$	361,6	413,1	443,0	96,85

D. Scanning Electron Microscopy (SEM)

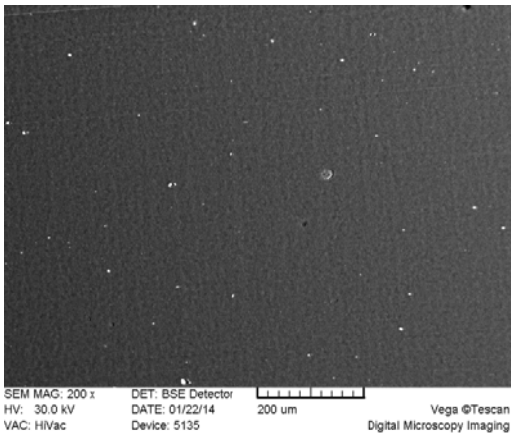
The Fig. 4 shows the SEM micrographs of neat PCL and PCL/TiO$_2$ composites with 2 wt % of TiO$_2$ particles. It is observed from the micrograph that the TiO$_2$ microparticles were better dispersed through the PCL matrix, only some small aggregates are present in PCL/mTiO$_2$ composite (bright surface in Fig. 4 (b)). However in the case of PCL/nTiO$_2$ composite more aggregates were formed (bright surface in Fig. 4 (c)).



(a)



(b)



(c)

Fig. 4 SEM micrographs of the neat PCL (a), PCL/mTiO$_2$ (b) and PCL/nTiO$_2$ (c) composite

IV. CONCLUSION

The thermal and morphology properties of the neat PCL and PCL/TiO$_2$ micro and nanocomposites were investigated by differential scanning calorimetry (DSC), dynamic mechanical analysis (DMA), thermogravimetric analysis (TGA) and scanning electron microscopy (SEM). The results from the DMA measurements show that the storage modulus (E') slight increased by the addition of TiO$_2$ micro and nanoparticles and with TiO$_2$ content. The DSC results indicated that the slight shift of T_g to the lower temperature in the PCL/TiO$_2$ micro and nanocomposites may be due to the higher mobility of the amorphous phase of PCL. The crystallinity of PCL in PCL/TiO$_2$ composites was higher than that of the neat PCL. According to the TGA results the thermal stability of the PCL is improved by the presence of TiO$_2$ microparticles compared to the TiO$_2$ nanoparticles. It was shown that the TiO$_2$ microparticles were better dispersed through the PCL matrix than TiO$_2$ nanoparticles.

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