PREPARATION AND CHARACTERIZATION OF POLY (ε-CAPROLACTONE)/TiO$_2$ MICRO-COMPOSITES

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Based on XRD results, the study of crystallization of the PCL/TiO$_2$ MCs showed that TiO$_2$ MPs have significant influence on crystallization behaviour of poly (ε-caprolactone) in the PCL/TiO$_2$ MCs. The FTIR spectra indicated that the C=O of PCL shifted when TiO$_2$ MPs was added, indicating that some Van der Waals bonding between the alkyl groups of TiO$_2$ and the ester group of PCL were formed. In comparison with the pure PCL, TGA data indicated an enhancement of thermal stability of PCL/TiO$_2$MCs. SEM results confirmed the surface of TiO$_2$ MPs has sufficient compatibility with PCL through the link of the coupling agent between TiO$_2$ MPs and PCL, which can reduce the aggregation of TiO$_2$ MPs and improve dispersity. Transmission electron microscope (TEM) studies were performed to provide evidence for the micrometric dispersion of the TiO$_2$ MPs into PCL matrix on microscale.

1. Introduction

Nowadays a great interest of many leading scientists in the world is attracted by perspective high performance hybrid organic-inorganic polymer composites materials because of their multiple applications. Typically, for the composites (including hybrid composites) preparation the different dispersed substances, like clays, CaCO$_3$, alumina, silica, TiO$_2$ and others could be used. The polymer/TiO$_2$ composites are one of the most widespread due to their multifarious application fields, such as high refractive thin films, photo catalysts, and composite solid polymer electrolytes for Li-batteries or solar cells. Basic methods of the polymer/TiO$_2$ composites preparation could be presented as follows: (1) formation of polymer materials with introduced fine dispersed commercial TiO$_2$, (2) self-made relatively stable TiO$_2$ sol preparation followed by incorporation into polymer matrix [1].

PCL is a semicrystalline polymer with a low melting point of around 60°C and a glass transition temperature of about -60 °C [2]. Polycaprolactone (PCL) is non-toxic synthetic aliphatic polyesters in biomedical applications are especially used as drug delivery devices, because when inside of the body they are completely degradable. As a type of polymer, PCL is susceptible to be degraded by many types of bacteria [3, 4]. Micro-sized additives are used as an effective strategy to alter and enhance the properties of PCL [5]. Various types of filler, like clay, carbon nanotubes, silica, hydroxyapatite and TiO$_2$ have been incorporated into PCL to prepare MPs [6-10].

In this study, TiO$_2$ micro-particles were surface modified by Propionic acid and n-hexylamine at the first and then were used for fabricating microcomposites by the solvent casting

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processwhich is relatively simple to scale up at industrial production. The influence of TiO_2 micro-particles on thermal and morphological properties was assessed by thermogravimetric, Fourier transform-infrared spectrometer, X-ray diffraction, scanning electronic microscope and transmission electron micrograph respectively.

2. Experimental

2.1 Materials

TiO_2 powder with mean particle size in a length range 74-160 nm provided by BDH or GPR Corp. (England). Poly (ε-caprolactone) (PCL) was purchased from Solvay caprolactone and used without further purification (England). Propionic acid and n-hexylamine were purchased as analytical grade reagents from HMBG, Hamburg, Acros, New Jersey, USA, respectively and used without further purification. Other chemical reagents were obtained as analytical grade and used without further purification.

2.2 Preparation of TiO_2MPsModified by Propionic Acid and n-Hexylamine

Propionic acid and n-hexylamine were used as agents of surface modification of TiO_2 micro-particles. This combination was very useful to obtain a stable colloidal solution of TiO_2 micro-particles in chloroform. The addition of an essential quantity (3, 5, 7, 10, 15 wt %) of TiO_2 was added in excess amount of propionic acid (50 ml). After stirring as slurry for2 h at room temperature, the precipitated solid was collected by centrifugation and washed as solid to remove the extra propionic acid five times with ethyl acetate. The TiO_2 micro-particles treated by propionic acid and without drying were added to methanol (50 g). In addition, the mixture was sonicated for 1h. The precipitated solid was easily dispersed into methanol. After wards, excess amount of n-hexylamine (50 ml) was added to the solution. The mixture was stirred for 1 hour; the precipitated solid was collected by centrifugation and washed as solid to remove the extra n-hexylamine five times with ethyl acetate. The wet of precipitated solid was placed in (55 ml) of chloroform.The colloidal solution in which surface modified TiO_2 micro-particles were well dispersed was obtained. Solid-part weight of surface modified micro-particles in solution was checked before hand by evaporation drying method. Solid-part weight ratio in solution was controlled to 20 wt%.

2.3 Preparation of PCL/TiO_2 MPs Films

The 3.0 g of PCL was dissolved in to the 55 mL of chloroform. The contents of surface modified TiO_2 were controlled by changing PCl weight ratio from 3, 5, 7, 10, and 15 wt.% to prepare the PCL/TiO_2 MPs films, respectively. Both solutions were mixed by stirringuntil became homogeneous under room temperature. Every solution was cast on to the Petri dishes, respectively and dried in evacuated desiccators for a week to remove the solvent. Afterward, the films were peeled form Petri dishes.

2.4 Characterization Methods

Adsorption of organic species on the TiO_2 MPs was studied by Fourier transform-infrared spectrometer (FT-IR spectrum 100 series, USA) using the following preparative procedures. The spectrum was collected in the range from 4000 to 500 cm^{-1}.The X-ray powder diffraction pattern was recorded using a X-ray diffractometer (XRD: Model PW 3040 MPD X́ Pert Panalytical PH14PS,) using Cu Ka (λ=1.540562Å) radiation. The dispersion morphology of the particles on PCL matrix was observed using scanning electron microscope (LEO1455 VPSEM, Germany). Thermal analyses of the PCL/TiO_2 MPs hybrid films were performed by a (TGA/SDTAB51[e], METTLER TOLEDO, Switzerland).The morphology analysis was performed on transmission

electron micrograph (TEM) analyzer (Hitachi H-7100, Japan). The measurements were carried out under a nitrogen atmosphere at heating rate of 10 °C/min from room temperature to 800 °C.

3. Results and discussion

3.1 Infrared Spectroscopy

The FT-IR spectra of pure TiO_2 MPs, Poly (ε-caprolactone) (PCL) and PCL/TiO_2 MCs films are shown in Figure 1. The broad bands in the region of 450-720 cm^{-1} are ascribed to TiO_2 vibration absorption [11]. The characteristic absorption bands are also given of PCL in Table 1. The characteristic absorption bands at 2942 and 2865 cm^{-1} are related to C-H stretching vibration of hydrocarbon of PCL. The band at 1721 cm^{-1} is ascribed to the stretching vibration of carbonyl groups (C=O) of PCL [12]. The characteristic absorption bands in the range of 1165–1468 cm^{-1} are attributed to the deformation of –CH_2– of PCL interpenetrated in the inorganic network.
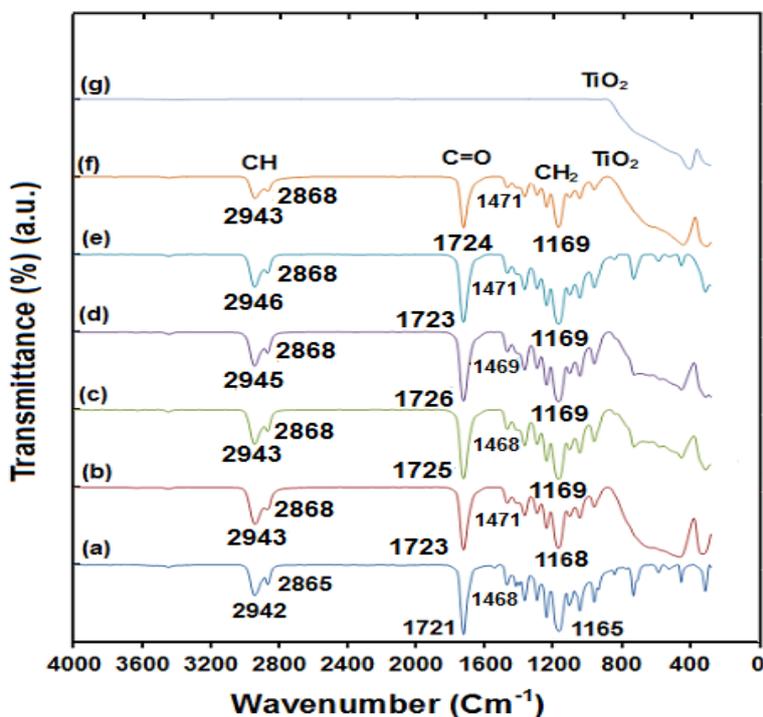
Fig. 1. FT-IR spectra of PCL (a), PCL/TiO_2 MCs at 3, 5, 7, 10 and 15 wt.% (b-f), respectively.

Table 1. Band assignments of FT-IR spectra to PCL.

Wavenumber (cm^{-1})	Band Assignment
2942, 2865	Stretching C–H
1721	C=O
1165-1468	Deformation CH_2

The PCL/TiO_2 MPs (15 wt.%) also displays the same characteristic bands similar to PCL polymer. Nevertheless, the corresponding wave numbers peaks of pure PCL shifted from 2942, 2865, 1721, 1468, and 1165 cm^{-1} to 2943, 2868, 1724, 1471, and 1169 cm^{-1} in the PCL/TiO_2 MCs films for 15 wt.% of TiO_2. This displacement was probably caused by the formation of Van der Waals action existing between TiO_2 and carbonyl groups (C=O) of PCL [12]. It is suggested that

these alkyl groups are present at the surface of titanium oxide network. These alkyl groups potentially form Van der Waals bonding interactions with the carbonyls of PCL chains [13].

3.2 Crystalline Structure

XRD curves in Figure 2 demonstrate the MCs materials were subjected to wide angle X-ray diffraction (XRD) measurement. The strong and sharp crystalline peaks at 21.37° and 23.67° are attributed to the [110] and [200] crystallographic planes of PCL, crystal, respectively. In the PCL/TiO$_2$ (15%) MCs film materials, the indices of PCL crystal did not alter while the intensity of diffraction peaks was significantly decreased. The broad amorphous halos increased with increasing the content of inorganic component, which suggested the formation of micro-crystallisable PCL in the MCs.

As observed, the crystallinity of PCL decreased with increasing the content of inorganic component in the PCL/TiO$_2$ MCs system. Especially when the content of TiO$_2$ reached 15 wt % in the MCs, the sharp crystalline peaks of PCL were no longer observed. That is to say, PCL exists in the amorphous form in the MCs. It is thus proposed that the inorganic networks confine the crystallization of PCL in MCs film system. It should be mentioned that no diffraction peaks were observed for crystals of TiO$_2$, indicating that the inorganic component is micro-crystalline in the microcomposites [14].
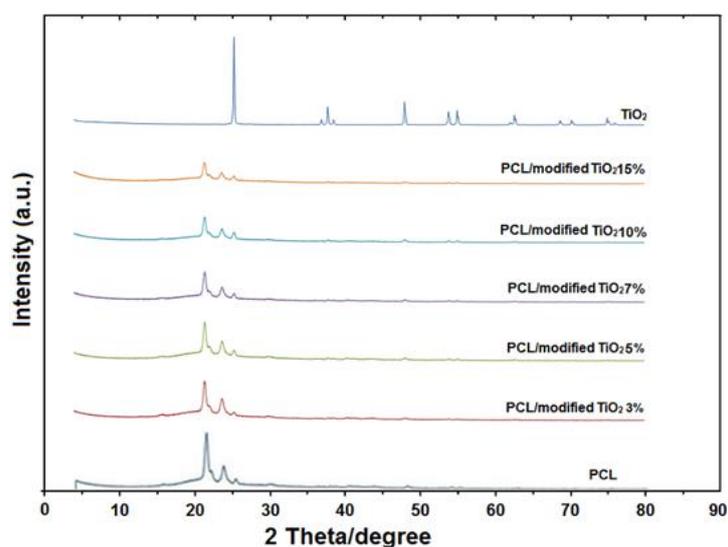
Fig. 2.XRD patterns of PCL, PCL/TiO$_2$ MCs at 3, 5, 7, 10 and 15 wt.%, and TiO$_2$ MPs respectively.

3.3 Thermogravimetric Analysis

Based on Fig. 3, TGA thermograms of weight loss is shown as a function of temperature for pure PCL and different percents of PCL/TiO$_2$ MCs (3, 5,7, 10 and 15 wt%) under a nitrogen atmosphere at the heating rate of 10 °C/min in the temperature ranging from room temperature to 800 °C. As indicated in Table 2, the thermal degradation data of the PCL and PCL/TiO$_2$ MCs comprises the temperature of 5 and 10% weight loss (T$_5$ and T$_{10}$ wt %) with char yield at 800 °C.

According to the Figure 3, the temperature of polymer decomposition for PCL/TiO$_2$ MCs obviously shifts to a higher temperature range than that of pure PCL, indicating the enhancement of thermal stability of MCs. The char yield of pure PCL at 800 °C is 0%, whereas those of the PCL/TiO$_2$ MCs at 800 °C are in the range of 8–21%, increasing with the increase of TiO$_2$ MPs content in the PCL. Due to compatibility role of TiO$_2$ MPs in the polymer matrix, these thermal behaviours of MCs lead to a higher decomposition temperature. Because of high thermal stability

of TiO_2 MPs, the incorporation of TiO_2 MPs can improve the thermal decomposition rate of the PCL/TiO_2 MPs [14, 15].
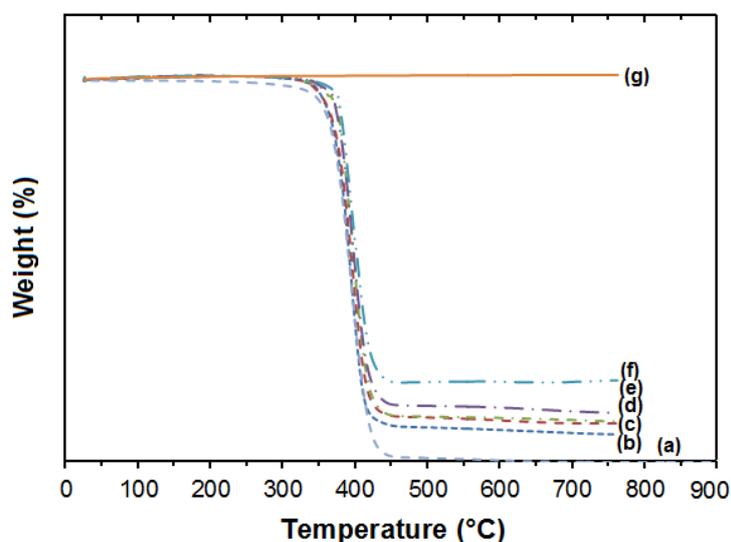
Fig. 3.TGA thermograms of PCL (a), PCL/TiO_2 MCs at 3, 5, 7, 10 and 15 wt.% (b-f), and TiO_2 MPs respectively.

Table 2. Effect of TiO_2 MPs content on thermal stability of polymer microcomposites.

Sample content	$T_{5\%}$	$T_{10\%}$	Residue	Char
PCL	0	350	362	0
PCL/TiO_2 MCs	3	355	369	8
PCL/TiO_2 MCs	5	355	369	12
PCL/TiO_2 MCs	7	369	377	13
PCL/TiO_2 MCs	10	369	377	15
PCL/TiO_2 MCs	15	374	380	21

3.4 Surface Morphology Study

The SEM images in Figs. 4(a-f) show surface morphology of PCL, TiO_2 and PCL/TiO_2 MCs filled with 3, 5, 7 and 10 wt%, respectively. Morphological studies were done with SEM, confirming the formation of MCs. It is revealed that the dispersion of MPs in the polymer matrix plays an important role in the properties of MCs. Therefore, SEM was applied to explore the morphology of films to examine the dispersion of the TiO_2 MPs into the PCL matrix. For PCL/TiO_2 MCs, low content of TiO_2 particles are good separated and randomly distributed in PCL matrix. This can be explained that surface modification by PPA and HEA can improve the compatibility between TiO_2 MPS and polymer matrix, which can solve the appearance of strong aggregation between TiO_2 particles. It can also be observed that the TiO_2 MPs are wrapped into the PCL matrix, which indicates that strong interfacial interaction between the matrix and the MPs [13, 15]. But, at high content of TiO_2 MPs can be seen that the particles tendency to agglomerate intensified because of no surface modification is performed on the TiO_2 MPs, thus decrease compatibility between the TiO_2 MPs and PCL matrix, which results in the decrease of interfacial interaction between the matrix and the MPs and distribution of TiO_2 in matrix reduce. Thus, extensive TiO_2 can lead to the formation of a network [16, 17].
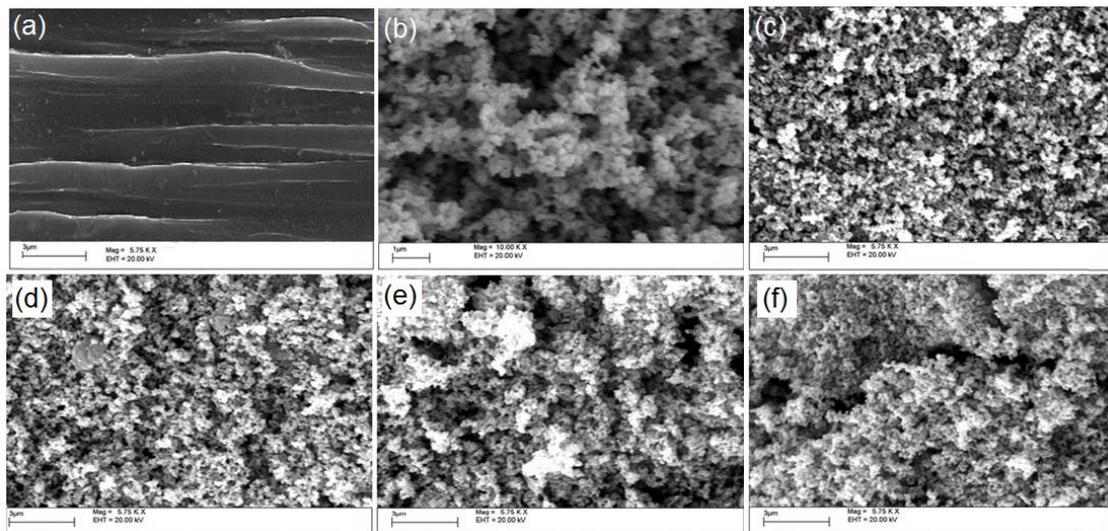
*Fig. 4.SEM micrographs for PCL (a), TiO₂ (b) and PCL/TiO₂ MCs at 3, 5, 7,
and 10 wt.% (c-f) respectively.*

3.5 Transmission Electron Microscopy

The transmission electron microscope (TEM) micrographs of the pure TiO_2 MPs and the PCL/TiO_2 MCs filled with 3 and 5wt% is respectively indicated in Figure 5. Although not fully investigated; careful imaging at quite high magnification by TEM technique can provide a good evaluation about particle size and morphology [16]. From Figure 5, it can be deduced that the MPs have some aggregation. In contrast, Figures 5(b-c) of PCL/TiO_2 MCs with diameter of about 117 nm. It is observed from the TEM images that the surface modification by PPA and HEA leads to finer dispersion and distribution of modified TiO_2 MPs. Based on this, the result proved that the phenomenon of TiO_2 MPs agglomeration reduced effectively because of improved compatibility between TiO_2 MPs and PCL matrix by the introduction of surface modification [15, 18].
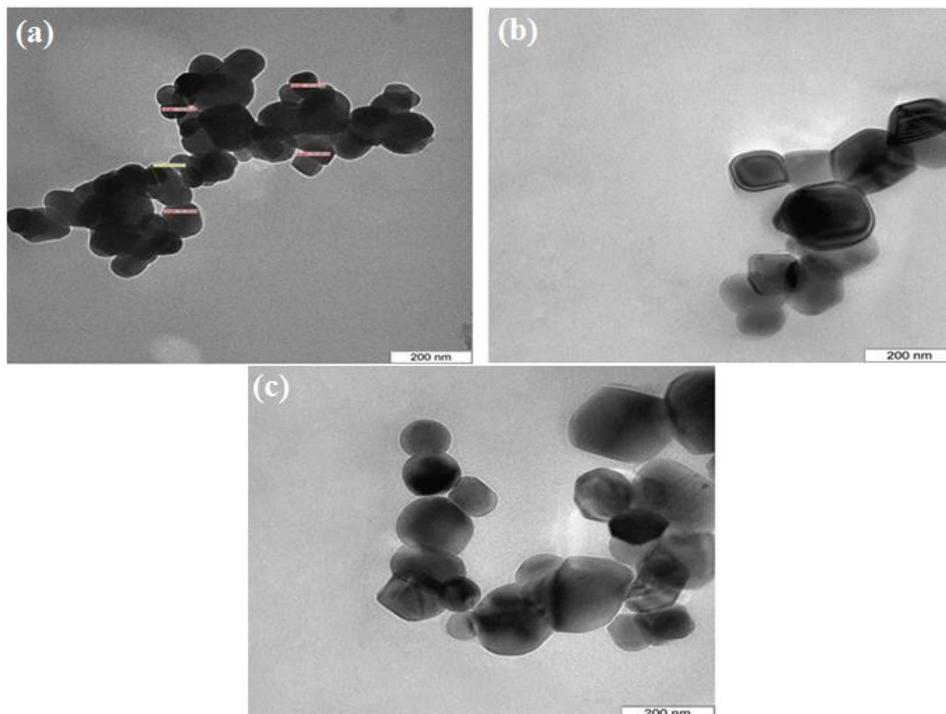
Fig. 5. Transmission electron micrographs for TiO₂ (a), PCL/TiO₂ MCs for 3 and 5wt % (b-c).

4. Conclusion

XRD indicates that the interaction exist between TiO_2 particles and PCL molecule. Based on FTIR results of PCL/TiO_2 MCs system, the interaction between TiO_2 network and PCL matrix is due to the formation of Van der Waals bonding. By increasing MPs contents, the TGA measurement revealed an enhancement of the thermal stability of the PCL/TiO_2 MCs by increasing TiO_2 MPs content. Based on SEM results, the PCL/TiO_2, after surface modification of TiO_2 by PPA and HEA increased the interfacial interaction between the TiO_2 MPs and PCL matrixes. TEM results showed that the TiO_2 MPs agglomeration is improved because of the compatibility between TiO_2 MPs and PCL matrix with surface modification of TiO_2 by PPA and HEA. Meanwhile, maximum Young's modulus and tensile strength values occurred at about 1 wt% TiO_2 for PCL/TiO_2 MCs. Above this 1 wt%, it is proposed that excess titanium oxide MPs may cause separation between the organic and inorganic phases, so reducing compatibility between the titanium oxide network and PCL matrix. In the case of PCL/TiO_2, the elongation at break decreased to some extent for all of the tested PCL/TiO_2 MCs films, compared with the pure PCL film.

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