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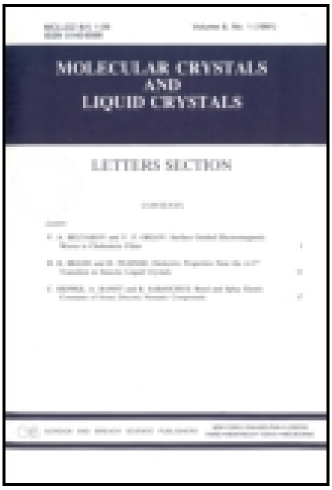

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A Facile Esterification Reaction Towards the Synthesis of Poly(methyl methacrylate)/Titanium Dioxide Nanocomposites

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A Facile Esterification Reaction Towards the Synthesis of Poly(methyl methacrylate)/ Titanium Dioxide Nanocomposites

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Poly(methyl methacrylate)/titanium dioxide (PMMA-g-TiO_2) nanocomposites were prepared by the direct esterification reaction under mild conditions. Initially, the surface of titanium dioxide nanoparticles (TiO_2 NPs) was modified by 3-glycidoxypropyl trimethoxysilane in order to prepare epoxy functionalized TiO_2 NPs. The nanoparticles were refluxed in ethanol solution of HCl to convert the epoxy groups into alkyl-hydroxyl units. Subsequently, PMMA chains were attached to the surface of TiO_2 NPs by the esterification reaction between alkyl-hydroxyl units at the nanoparticle surface and carboxylic acid terminated PMMA. Fourier transformed infrared spectrometry confirmed the presence of PMMA groups grafted on the surface of TiO_2 NPs. X-ray diffraction and X-ray photoelectron spectroscopy revealed the existence of the grafted PMMA of the nanocomposites. An improved thermal property of the nanocomposites was observed by thermogravimetric analysis while transmission electron microscopy images confirmed well dispersed nanocomposites in chloroform due to the functionalization of PMMA brushes.

Keywords: TiO_2 nanoparticles; poly(methyl methacrylate); grafting to; esterification reaction

1. Introduction

In the past decades much effort has been devoted to investigate polymer/inorganic nanocomposites, which have received some interests in many areas, such as diagnosis, environment separation, ceramic and electrophoretic display [1, 2]. With the introduction of inorganic components, the performance of polymers will be greatly enhanced with respect to mechanical, electronic, thermal and especially optical properties. PMMA, a kind of commercial polymer plastic, has high strength, outstanding outdoor weathering properties, good optical transparency and excellent dimensional stability due to rigid polymer chains [3, 4]. These properties of PMMA provide significant importance for biomedical material, dental, and surgical applications, and an important engineering material for electronics, optical communication [5, 6]. Recently, attention to titanium dioxide nanoparticles has grown interest

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due to its unique photocatalytic properties, along with its applications as food industries [7, 8]. However, it is difficult to disperse inorganic nanoparticles in non-polar polymers due to the incompatibility and nanoparticles tend to strongly aggregate which reducing the mechanical properties of the resultant nanocomposites materials [9, 10]. Many methods have been explored to improve the dispersibility of inorganic nanoparticles in polymer such as sol-gel blending technique, in situ polymerization process, in situ forming nanoparticles process and polymer encapsulation technologies [11–13]. Considering the above aspects, PMMA encapsulated TiO$_2$ would overcome the prevailing bottlenecks to adapt with their potential applications.

In the present work, PMMA chains were attached to the surface of TiO$_2$ NPs by the esterification reaction in a facile manner.

2. Experimental Details

2.1 Materials

TiO$_2$ nanoparticles, 3-glycidoxypropyl trimethoxysilane (GPS), tetrahydrofuran (THF), toluene, ethanol, hydrochloric acid (HCl), N,N'-dicyclohexylcarbodiimide (DCC), 4-dimethylaminopyridine (DMAP) were used as received. All chemicals were purchased from Aldrich, Korea. Carboxyl-terminated poly(methyl methacrylate) (PMMA-COOH, $M_n = 12.700$ g/mol, PDI $= 1.34$) was synthesized by reversible addition-fragmentation chain transfer (RAFT) polymerization of methyl methacrylate as reference [14].

2.2 Preparation of Epoxy Groups Modified TiO$_2$ Nanoparticles

3.0 g of TiO$_2$ NPs was charged in 50mL of dry toluene and the suspension was ultrasonicated for 20 min. Then, 3 mL of GPS was added quickly and the suspension was refluxed at 110°C for 8 h under nitrogen atmosphere. The modified TiO$_2$ NPs were centrifuged, washed several times with toluene and dried under vacuum at 40°C for 24 h.

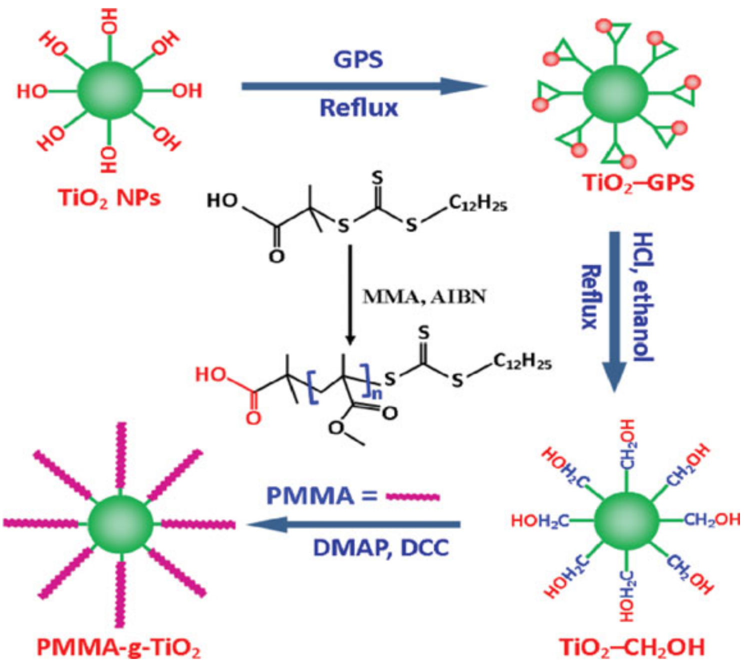
2.3 Synthesis of PMMA-g-TiO$_2$ by Esterification Reaction

The hydroxyl-functionalized TiO$_2$ NPs (TiO$_2$-CH$_2$OH) were achieved by refluxing of TiO$_2$-GPS (1.0 g) in the 100mL of ethanol solution of HCl (1.6M) at 100°C for 2 h. The resulting suspension was centrifuged and rinsed with the distilled water thoroughly until the pH of 7 and dried under vacuum at 40°C for 24 h.

The esterification procedure was the following: 0.1 g of TiO$_2$-CH$_2$OH and 0.2 g of PMMA-COOH were suspended in THF (20 mL) and ultrasonicated for 10 min. Then, a solution of DCC (1.85 g) and DMAP (0.135 g) in THF (10 mL) were added, and the mixture was stirred at room temperature for 3 days. The resulting suspension was centrifuged, washed with acetone and extracted extensively in toluene. Finally, the product was dried in vacuum oven at 40°C for overnight.

2.4 Instrumentation

The changes in the surface chemical bonding of functionalized TiO$_2$ nanoparticles were captured by Fourier Transformed Infrared (FT-IR) spectrometry using a BOMEM Hartman & Braun FT-IR Spectrometer. Thermogravimetric analysis (TGA) was conducted with



Scheme 1. The procedure of grafting PMMA chains onto the TiO_2 NPs via esterification reaction.

Perkin-Elmer Pyris 1 analyzer (USA). Surface composition was investigated using X-ray Photoelectron Spectroscopy (XPS) (Thermo VG Multilab 2000) in ultra high vacuum with Al Kα radiation. The crystallographic state of the nanocomposites was studied by a Philips X'pert-MPD system diffractometer. Transmission Electron Microscopy (TEM) images were recorded using a Joel JEM 2010 instrument (Japan) with an accelerating voltage of 80 kV.

3. Results and Discussion

The schematic processes for modification of the TiO_2 NPs and the synthesis of the PMMA-grafted TiO_2 are described in Scheme 1.

The surface composition of TiO_2 NPs, TiO_2-GPS, and PMMA-*g*-TiO_2 nanocomposites were investigated by XPS analysis. Compared with the XPS spectrum of the pristine TiO_2 NPs (Fig. 1A), which showed the peaks of oxygen (O1s at 529.5 eV), titanium (Ti2p at 457.8 eV) and carbon (C1s at 285.3 eV), the additional peak of silicon (Si2p at 102.4 eV) indicated the immobilization of GPS on the surface of TiO_2 NPs (Fig. 1B). After grafting of PMMA chains onto TiO_2 NPs by the esterification reaction, the XPS scan of PMMA-*g*-TiO_2 (Fig. 1C) showed that the intensity the C1s peak is higher than the peak of TiO_2-GPS (Fig. 1B), indicating that the polymeric chains were directly grafted from the surface of TiO_2 NPs.

Figure 2 shows the typical FT-IR transmittance spectra of TiO_2 NPs, TiO_2-GPS, PMMA-COOH and PMMA-*g*-TiO_2 nanocomposites. The TiO_2 NPs exhibit broad absorption bands at 3422, 1633 and 600 cm^{-1} assignable to the -OH stretching, H-O-H bending and vibrations of Ti-O and Ti-O-Ti framework, respectively (Fig. 2A). By contrast, the FT-IR spectrum of TiO_2-GPS (Fig. 2B) shows -CH bending and stretching vibration at 1483 and 2909 cm^{-1}, respectively. After esterification reaction, the strong absorption peaks

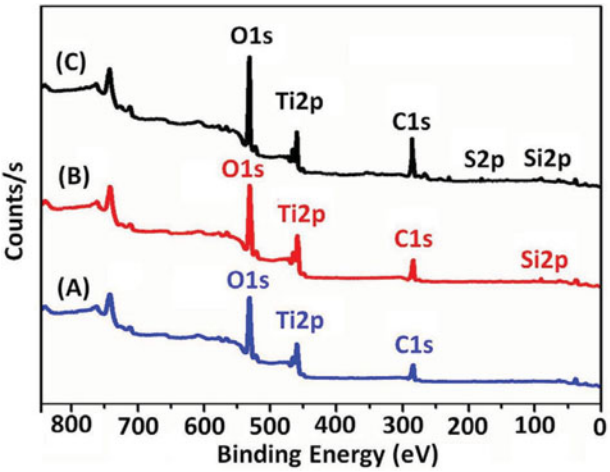


Figure 1. XPS wide-scan spectra of TiO_2 NPs (A), TiO_2-GPS (B), and PMMA-*g*-TiO_2 (C).

were shown at 1727 cm^{-1} and 2800-2950 cm^{-1} which were assigned to C = O stretching vibration and C-H stretching vibration (Fig. 2D) respectively, indicating that PMMA-COOH (Fig. 2C) was anchored onto the TiO_2 NPs surface [15,16]. The FT-IR results confirm that the esterification reaction between TiO_2 NPs and PMMA-COOH took place undoubtedly and PMMA chains have been grafted onto the surface of TiO_2 NPs.

The thermal decomposition behavior of TiO_2 NPs, TiO_2-GPS, PMMA-COOH and PMMA-*g*-TiO_2 were investigated by TGA analysis as shown in Figure 3. The TiO_2 NPs have weight loss of around 2.7% due to the loss of water molecules adsorbed on the surface (Fig. 3A). The GPS modified TiO_2 showed the weight loss of 6.1% between 50-800°C,

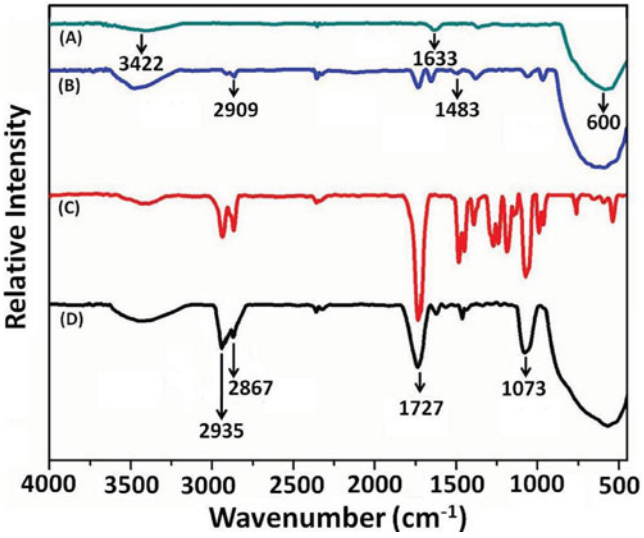


Figure 2. FT-IR spectra of (A) TiO_2 NPs, (B) $TiO\text{-}_2$-GPS, (C) PMMA-COOH and (D) PMMA-*g*-TiO_2

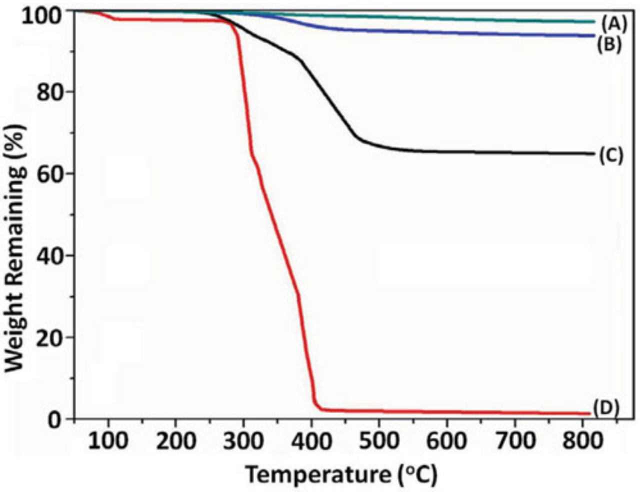


Figure 3. TGA curves of (A) TiO_2 NPs, (B) TiO-$_2$-GPS, (C) PMMA-*g*-TiO_2 and (D) PMMA-COOH.

thus the content of the coupling agent grafted onto the surface of TiO_2 is 3.6 wt%, as estimated from the TGA curve in Figure 3B. The PMMA-*g*-TiO_2 nanocomposites showed thermal decomposition at temperature range from 280 to 490°C, which may be due to the decomposition of the grafted PMMA. The grafted PMMA content on the TiO_2 surface was estimated 35.1% by the weight loss, which corresponds to 30.8 wt% of the nanocomposites, indicating that the amount of the grafted polymer is not too high. In addition, the PMMA-*g*-TiO_2 nanocomposites have showed significantly higher thermal stability than neat PMMA.

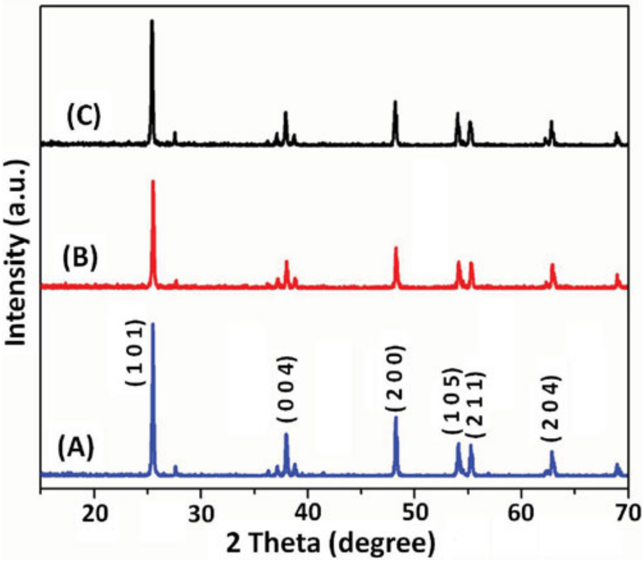


Figure 4. X-ray diffraction patterns of (A) TiO_2 NPs, (B) TiO_2-GPS and (C) PMMA-*g*-TiO_2

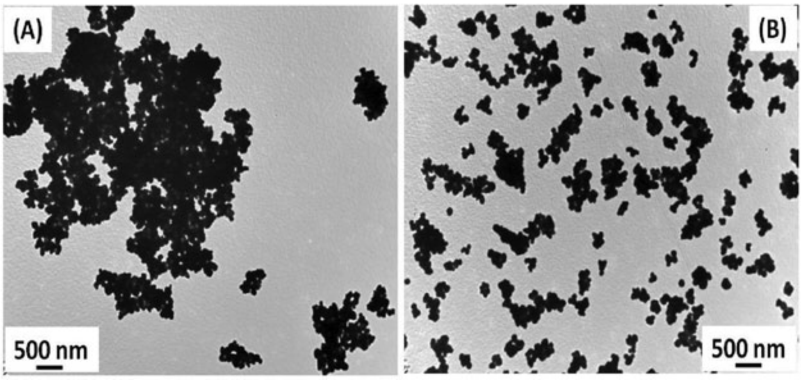


Figure 5. TEM images (A) TiO_2 NPs and (B) PMMA-*g*-TiO_2 from chloroform.

The crystalline phase and physical changes of PMMA grafted TiO_2 nanoparticles were investigated using XRD analysis. The pristine TiO_2 NPs exhibited sharp peaks centered at $2\theta = 25.49$, 37.97, 48.25, 54.11, 55.25 and 62.85 which correspond to the (1 0 1), (0 0 4), (2 0 0), (1 0 5), (2 1 1) and (2 0 4) reflections, respectively (Fig. 4A). The esterification of PMMA on TiO_2 NPs surfaces generated PMMA-*g*-TiO_2 nanocomposites, whose XRD patterns were similar to the main peaks of the pure TiO_2 NPs suggesting that the grafting of the polymer did not alter the crystallinity of TiO_2 nanoparticles (Fig. 4C).

TEM micrographs of TiO_2 NPs and PMMA-*g*-TiO_2 are shown in Figure 5. In the TEM image of TiO_2 NPs, a huge number of agglomerated particles are visualized (Fig. 5A). The reason behind the phenomenon is that the high surface energy of TiO_2 NPs may cause the aggregation of particles. To prevent the agglomeration, the surface of TiO_2 NPs should be well modified to ensure its perfect dispersion. It is clearly observed that the PMMA-*g*-TiO_2 nanocomposites are well dispersed in chloroform (Fig. 5B), which might be because of the reduced surface energy originated from steric hindrance of PMMA between TiO_2 NPs.

4. Conclusions

The PMMA-*g*-TiO_2 nanocomposites were synthesized by the direct esterification reaction under mild conditions. XPS and FT-IR data suggested the presence of PMMA groups grafted on the surface of TiO_2 NPs. The nanocomposites showed good thermal stability compared to pure PMMA, and the grafted polymer content on the TiO_2 NP surface was estimated about 30.8 wt% of the nanocomposites. The grafting of TiO_2 NPs by PMMA dramatically improved the dispersion of TiO_2 NPs in an organic solvent as studied by TEM, which suggests their potential application in diverse areas.

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