Modification of Titanium Dioxide Nanoparticles with 3-(Trimethoxysilyl)propyl Methacrylate Silane Coupling Agent

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This paper presents some characteristics, properties, and morphology of TiO2 nanoparticles (nano-TiO2) modified with various contents of 3-(trimethoxysilyl)propyl methacrylate (TMSPM) coupling agent. The treatment process was carried out in ethanol solvent at 50°C using ammonia as a catalyst for hydrolysis reaction of silane to silanol. Infrared spectroscopy, thermogravimetric analysis, transmission electron microscopy, field emission scanning electron microscopy, dynamic light scattering, ultraviolet-visible spectroscopy, and X-ray diffraction methods were used for determination of the characteristics, properties of nano-TiO2 before and after modification. In addition, the contact angle and grafting efficiency of TMSPM on the surface of TiO2 nanoparticles was also evaluated. The obtained results confirmed that TMSPM was grafted to the TiO2 nanoparticles, the agglomeration of nano-TiO2 was decreased, and surface of TiO2 nanoparticles became hydrophobic after modification by TMSPM.

1. Introduction

Recently, TiO2 nanoparticles (nano-TiO2) have been commonly used in numerous fields (materials science, medicine, pharmacy, agriculture, environmental protection, cosmetics, etc.) thanks to its advantages such as small particle size, large specific surface area, stability, photocatalyst ability, high light reflectivity, high opacity, low light absorption, heat durable, ultraviolet protecting ability, and cheapness [1, 2]. In addition, nano-TiO2 has low toxicity and antimicrobial ability. Thus, it can be used in food industry and drug delivery systems [2, 3]. In polymer and coating processing, nano-TiO2 plays a role of an inorganic additive to improve the thermal, mechanical, long-term durability/weatherability, processability, optical properties (whiteness, opacity, and brightness), self-cleaning, and anticorrosion of the above materials [4–6]. In case, the dispersibility of nano-TiO2 in polymer matrix is a main factor which causes a strong influence on the enhancement ability of properties of the nanocomposites. To increase the dispersibility as well as decrease the agglomeration of TiO2 nanoparticles in polymer matrix, surface modification of nano-TiO2 is a key pathway. Some popular techniques which were applied to functionalize the inorganic nanoparticles are (i) encapsulation
of inorganic nanoparticles through reactions in solutions, (ii) high temperature reactions with organosilanes, and (iii) use of plasma methods. Among these methods, methods (ii) and (iii) are complicated, energy consuming, and time consuming or complex equipment, while method (i) is quite simple and saves time [7]. The modification of TiO$_2$ nanoparticles by silane coupling agents has been widely used due to simple process and no requirement of special equipment [5, 7–22]. The formation of covalent Ti-O-Si linkage between the silane molecules and the nanoparticles in modification reaction process can contribute in functionalization of surface of nano-TiO$_2$. The nature and amount of the organosilanes, the size, and distribution of nano-TiO$_2$ influence on the effectiveness of treatment process and surface characteristics, properties of modified nano-TiO$_2$. Some silanes which have been used for modification of TiO$_2$ particles are 3-methacryloxypropyltrimethoxysilane, 3-triehoxysilyl)propyl isocianate, vinyltrimethoxysilane, (3-aminopropyl)trimethoxysilane, hexadecyltrimethoxysilane, (3-glycidoxypropyl)trimethoxysilane, bis(3-triethoxysilylpropyl)tetrasulfide, octadecyl- trimethoxysilane, and so on [9–15]. As reported in some literature studies, TiO$_2$ was modified with 3-methacryloxypropyltrimethoxysilane, TiO$_2$ particles were in micromet size [9], and treatment solvent was o-xylene [18]. Study on the modification of nano-TiO$_2$ with 3-methacryloxypropyltrimethoxysilane in ethanol solvent in alkali environment has rarely reported. One advantage of nano-TiO$_2$ modification using ethanol solvent is more environmentally friendly than using xylene solvent. In our previous reports, nano-TiO$_2$ was treated with vinyltrimethoxysilane and was used as an additive for polymer composites [23, 24]. The characterization of modified nano-TiO$_2$ has been not presented clearly. Therefore, in this work, TiO$_2$ nanoparticles were modified with 3-(trimethoxysilyl)propyl methacrylate—TMSPM—in ethanol solution using ammonia solution as a catalyst for hydrolysis reaction of the silane coupling agent. The TMSPM with two functional groups (C=O and O=C=O) can work more effectively and interact more strongly with hydroxyl groups on the surface of nano-TiO$_2$ together with functional groups of polymer matrix than vinyltrimethoxysilane with only one functional group (C=C). The characteristics, properties, and morphology of nano-TiO$_2$ before and after modification was investigated and reported. The purpose of this modification is to increase hydrophobicity of nanoparticles as compared to the nonmodified ones, leading to enhancement of dispersion and interaction of modified nanoparticles in resin matrix, resulting in the improvement of properties of the nanocomposites.

2. Experimental

2.1. Materials. Rutile TiO$_2$ (Kronos 2360, 92%, South Korea) has an average particle size of 160 nm and density of 3.9 g/cm$^3$. 3-(Trimethoxysilyl)propyl methacrylate silane (TMSPM, Sigma Aldrich) has a purity of 98%. Ethanol (99.7%) and ammonia solution (25%) are commercial products of Duc Giang Co., Vietnam.

2.2. Modification of Nano-TiO$_2$. The procedure of treatment nano-TiO$_2$ was carried out as follows: firstly, TMSPM silane was hydrolysed in 100 mL of ethanol solvent and 1 mL of ammonia at 50°C for 60 min with the stirring speed of 400 rpm on a magnetic stirrer to obtain A solution containing silanol substances. Next, 5 g of nano-TiO$_2$ was introduced into the A solution, and the mixture was stirred continuously with a speed of 400 rpm for 120 min at 50°C combined with high-speed stirring (15000 rpm) for 30 min. In this process, the silanol groups were condensed onto the surface of nanoparticles, and the bonds between silane and nanoparticles were formed. The residue of TMSPM after surface treatment was taken away from mixture by Soxhlet process for 4 h in water/ethanol solution (1/1 v/v). Then, the precipitate was obtained by centrifuging with a speed of 6000 rpm at room temperature and washing with ethanol to remove the silane residue in the sample. The solid part was dried in a vacuum oven at 80°C for 4 h to get modified TiO$_2$ nanoparticles (abbreviated as m-TiO$_2$). The volume of silane used and signature of samples are shown in Table 1.

2.3. Characterization

2.3.1. Infrared (IR) Spectroscopy. IR spectra of nano-TiO$_2$ before and after modification were taken on a Nicolet iS10 spectrometer (Thermo Scientific, USA) in wavenumbers ranged from 400 cm$^{-1}$ to 4000 cm$^{-1}$, resolution of 8 cm$^{-1}$, and scans of 32 times. Samples in powder were pressed with KBr to form a pellet before taking IR analysis.

2.3.2. Field Emission Scanning Electron Microscopy (FESEM) and Transmission Electron Microscopy (TEM). The FESEM images of nano-TiO$_2$ before and after modification were performed by using a S-4800 FESEM machine (Hitachi, Japan) with the magnification of 1000 to 200,000 times. TEM images of samples were performed on a JEM1010 (JEOL, Japan). The samples were coated with Pt to increase their conductivity.

2.3.3. Dynamic Light Scattering Analysis (DLS). The zeta potential and size distribution of nano-TiO$_2$ before and after modification was determined by the DLS method by using a SZ-100 Zetasizer (Malvern). Before, the samples were dispersed in distilled water.

2.3.4. Thermogravimetric Analysis (TGA). TG diagrams of samples were recorded on a TGA 60H device (Shimadzu, Japan) in nitrogen gas with a heating rate of 10°C/min at temperature from room temperature to 800°C.

2.3.5. X-Ray Diffraction Analysis (XRD). XRD patterns were taken from the samples on a Siemens D5000 powder diffractometer (Germany) with 2θ in the range of 2°~80° and CuKα radiation (45 kV, 40 mA, λ = 1.5407 Å).
Table 1: Composition and signature of modified nano-TiO$_2$.

| Sample | Composition | Signature | $m_{TiO_2}$ (g) | $V_{TMSPM}$ (mL) |
|--------|-------------|-----------|----------------|-----------------|
| 1      | TiO$_2$     | TiO$_2$   | 5              | 0               |
| 2      | TiO$_2$ + 1% TMSPM | TiO$_2$ T1 | 5              | 0.05            |
| 3      | TiO$_2$ + 3% TMSPM | TiO$_2$ T3 | 5              | 0.15            |
| 4      | TiO$_2$ + 5% TMSPM | TiO$_2$ T5 | 5              | 0.25            |
| 5      | TiO$_2$ + 7% TMSPM | TiO$_2$ T7 | 5              | 0.35            |
| 6      | TiO$_2$ + 20% TMSPM | TiO$_2$ T20 | 5             | 1.00            |

2.3.6. Ultraviolet-Visible Spectroscopy (UV-Vis). UV-Vis transmittance spectra of samples in water were determined by using a UV-Vis spectrometer (S80 Libra, Biochrom, UK) in the wavelength of 200–800 nm.

2.3.7. Contact Angle Analysis. Contact angle of samples was carried out by measuring water droplet particle size on the surface of samples by using a Phoenix Phoenix-150 SEO meter.

3. Results and Discussion

3.1. IR Spectra of TiO$_2$ Nanoparticles before and after Modification. The IR spectra of nano-TiO$_2$ before and after modification with different volume of TMSPM are presented in Figure 1.

It can be seen from Figure 1 that some peaks characterized for vibrations of OH groups on the surface of nano-TiO$_2$ at the wavenumber of 3364 cm$^{-1}$ and at 1049 and 600 cm$^{-1}$ were attributed to Ti-O-Ti bond of nano-TiO$_2$ and modified nano-TiO$_2$. As compared the IR spectra of modified nano-TiO$_2$ with that of nano-TiO$_2$, the appearance of some new peaks confirmed that TMSPM was grafted successfully on the surface of nano-TiO$_2$ [9, 18]. For examples, the peak at 2954 cm$^{-1}$ corresponded to C-H stretching vibration in TMSPM; the peaks at 1636 and 1716 cm$^{-1}$ were characterized for C=C and C=O vibrations in the methacrylate group of TMSPM, respectively. In addition, the vibrations at 1451, 1324, and 1298 cm$^{-1}$ were assigned to C-H bending vibration, C-O, and C-C stretching vibrations in TMSPM. Moreover, a weak peak at 955 cm$^{-2}$ was attributed to Ti-O-Si vibration [15, 18]. As increasing the TMSPM volume, the intensity of peaks corresponding to C=O and C=C was increased. These are evidences for the success of the modification reaction of TMSPM to nano-TiO$_2$.

3.2. Thermal Behaviour of TiO$_2$ Nanoparticles before and after Modification. The TG and DTG diagrams of nano-TiO$_2$ before and after modified with different volume of TMSPM are presented in Figures 2 and 3. Observing from Figure 2, the TiO$_2$ nanoparticles were slightly decomposed at 200–300°C corresponding to the vaporization of water in TiO$_2$ nanoparticles, and then it was relatively stable with heat. For modified nano-TiO$_2$, the weight of nano-TiO$_2$ modified with TMSPM was lost continuously from 200 to 650°C. This weight loss was caused by the evaporation of water, the decomposition of OH groups in the silanol groups, and predominantly degradation of organosilane chains grafted on nano-TiO$_2$ [9, 15]. As increasing the TMSPM volume, the weight loss of modified nano-TiO$_2$ was increased (Table 2). This result also proved that TMSPM was grafted succesfully on surface of nano-TiO$_2$ according to the mechanism as suggested in [5, 9, 15] and mentioned in other literature studies.

The thermal decomposition of TMSPM exhibited clearly through sharp maximum degradation peaks on DTG diagrams in Figure 3. The maximum degradation temperatures of modified TiO$_2$ nanoparticles were higher than that of TiO$_2$ nanoparticles (Table 2). The intensity and area of degraded peaks of modified TiO$_2$ nanoparticles were larger than those of TiO$_2$ nanoparticles. This also indicated that the TMSPM grafted on nano-TiO$_2$ was decomposed by heat.

3.3. Grafting Efficiency of TMSPM on Nano-TiO$_2$. Based on the results of TGA analysis, the content of TMSPM grafted on the surface of nano-TiO$_2$ can be estimated [15]. The grafting efficiency (GE) of TMSPM on nano-TiO$_2$ is shown in Table 3. It can be seen that the GE was increased with a rising mass ratio of organosilane to nano-TiO$_2$ from 1 to 3% with a maximum grafting efficiency of 97.7% for the TiO$_2$-T3 sample. This could be caused by the crosslinked framework generated by the TMSPM condensation reaction on the surface of nano-TiO$_2$ [9, 15]. At the ratio of TMSPM/nano-TiO$_2$ of 3%, the silane was formed as a monodentate layer on nano-TiO$_2$. Therefore, GE reached to the maximum value [5]. As increasing the TMSPM content, GE was reduced due to the formation of bidentate and tridentate structures of silane on the surface of nano-TiO$_2$, leading to the steric hindrance, causing the reduction of grafting ability of TMSPM on nano-TiO$_2$ [5, 15]. Moreover, the low concentration of OH groups on the nano-TiO$_2$ surface also caused to the decrease in grafting ability of TMSPM at its high content. From the obtained above results, the TiO$_2$-T3 sample was chosen for further investigation.

3.4. Size Distribution and Zeta Potential of TiO$_2$ Nanoparticles before and after Modification. Figure 4 and Table 4 present the size distribution diagrams of TiO$_2$ nanoparticles before and after modified with 3% TMSPM. As dispersing the nanoparticles in water, the nanoparticles tend to agglomerate together leading to the size of nanoparticles which was much larger than the data provided by the provider (average particle size of 160 nm). However, the result in Figure 4 and Table 4 also confirmed that, after modification, the agglomeration of nano-TiO$_2$ decreased significantly, causing the reduction in the average particle size of the TiO$_2$-T3 sample. This exhibited that the surface of modified nano-TiO$_2$ became more hydrophobic after modification. Therefore, it is difficult for these nanoparticles to interact and agglomerate together. The increase of hydrophobicity for modified nanoparticles is necessary to apply them in polymer nanocomposites. The polydispersity index (PDI) of nano-TiO$_2$ and TiO$_2$-T3 nanoparticles was 0.293 and 0.409 indicating that the samples have different size distribution algorithms (ISO 22412:2008).
Figure 1: IR spectra of nano-TiO$_2$ and nano-TiO$_2$ modified with different volumes of TMSPM.

Figure 2: TG diagrams of nano-TiO$_2$ before and after modified with different volume of TMSPM.

Figure 3: DTG diagrams of nano-TiO$_2$ and nano-TiO$_2$ modified with different volume of TMSPM.
The zeta potential of TiO2 nanoparticles before and after modified with 3% TMSPM is performed in Figure 5. It is clear that the surface charge of nano-TiO2 was changed after modification. A high zeta potential will confer stability behavior of nanoparticles in the solution or dispersion of nanoparticles which will resist aggregation of modified nano-TiO2. As we know, with zeta potential of ±10 to ±30 mV, the behavior of particles is incipient instability, and with zeta potential of ±30 to ±40 mV, the behavior of particles exhibits moderate stability, and with zeta potential of ±40 to ±60 mV, the behavior of particles exhibits good stability, and if zeta potential is higher than 61 mV, the behavior of particles exhibits excellent stability. The zeta potential value of ±30 mV was considered optimum for good stabilization of nanodispersion [25]. In this research, the zeta potential of both nano-TiO2 and modified nano-TiO2 is very high. It indicated that the nanoparticles before and after modification with organosilane can be dispersed well and stably in water, and the modified nanoparticles seem to exhibit more excellent stability.

3.5. XRD Pattern and Nitrogen Sorption Analysis of TiO2 Nanoparticles before and after Modification. Figure 6 presents the XRD patterns of TiO2 nanoparticles before and after modified with 3% of TMSPM. The position of diffraction peaks reflecting rutile crystal structure of TiO2 in the XRD pattern of TiO2 nanoparticles is similar to that in the XRD

| Sample | Weight loss (%) | Maximum degradation temperature (°C) |
|--------|------------------|---------------------------------------|
| TiO2   | 1.87             | 277.82                                |
| TiO2-T1| 2.24             | 325.65                                |
| TiO2-T3| 4.80             | 332.72                                |
| TiO2-T5| 5.75             | 329.09                                |
| TiO2-T7| 5.98             | 331.18                                |
| TiO2-T20| 10.58            | 344.65                                |

| Sample  | Percentage of initial silane (%) | Weight loss obtained from TGA (%) | Percentage of grafted silane (%) | Grafting efficiency (%) |
|---------|---------------------------------|----------------------------------|---------------------------------|-------------------------|
| TiO2    | 0                               | 1.87                             | 0                               | 0                       |
| TiO2-T1 | 1                               | 2.24                             | 0.37                            | 37.0                    |
| TiO2-T3 | 3                               | 4.80                             | 2.93                            | 97.7                    |
| TiO2-T5 | 5                               | 5.75                             | 3.88                            | 77.6                    |
| TiO2-T7 | 7                               | 5.98                             | 4.11                            | 58.7                    |
| TiO2-T20| 20                              | 10.58                            | 8.71                            | 43.6                    |

| Sample | Size distribution range (nm) | Average particle size (nm) |
|--------|------------------------------|----------------------------|
| TiO2   | 712.4–1484                   | 1059 ± 68.15               |
| TiO2-T3| 24.36–955.4                  | 52.01 ± 7.36 (13.2%)       |
|        |                              | 316.3 ± 81.30 (86.8%)      |

Figure 4: Size distribution diagrams of nano-TiO2 (a) and TiO2-T3 (b).
Figure 5: Zeta potential of nano-TiO$_2$ (a) and TiO$_2$-T3 (b).

Figure 6: XRD patterns of nano-TiO$_2$ (1) and TiO$_2$-T3 (2).
pattern of modified nano-TiO$_2$. For instance, the diffraction peaks appeared at $d$-spacing of 3.242, 2.483, 2.184, 1.686, 1.624, and 1.359 Å corresponding to Miller indices (101), (004), (200), (105), (211), and (204) of TiO$_2$ rutile crystal [15]. The modification does not affect on the crystal structure of nano-TiO$_2$.

The specific surface area was determined by using Brunauer–Emmett–Teller (BET) measurement on a TriStar II 3020 Micromeritics (USA) and presented in Table 5. There is not hysteresis loop in N$_2$ sorption isotherms of nano-TiO$_2$ and TiO$_2$-T3. It means that TiO$_2$ nanoparticles have a solid and nonporous structure. The BET surface area of nano-TiO$_2$ was decreased slightly, while the average pore width was increased after modification. The reduction of BET value can be caused by the cover of organosilane on the surface of nano-TiO$_2$.

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3.6. Morphology of Nano-TiO$_2$ before and after Modification. Figures 7 and 8 are FESEM and TEM images at different magnifications of TiO$_2$ nanoparticles before and after modified with 3% TMSPM, respectively. It can be seen that the size of TiO$_2$ nanoparticles ranged from 100 to 200 nm with mainly particles in 160 nm, and they were agglomerated together. The size and shape of modified nano-TiO$_2$ is similar to that of nano-TiO$_2$. This indicates that the silane modification cannot cause the change in size and shape of nano-TiO$_2$.

3.7. UV-Vis Transmittance Spectra of TiO$_2$ Nanoparticles before and after Modification. The UV-Vis transmittance spectra of TiO$_2$ nanoparticles before and after modified with TMSPM in Figure 9 display that the modification process can affect on dispersion stability of the colloidal solution of nano-TiO$_2$ in water. The TiO$_2$ nanoparticles tend to precipitate in water with the transmittance of 0% [15]. As modification with TMSPM, the transmittance of samples was increased, from 58 to 77%. This indicates that modified nano-TiO$_2$ was dispersed well in water. This result is similar to the size distribution result of original nano-TiO$_2$ and modified nano-TiO$_2$.

3.8. Contact Angle of Nano-TiO$_2$ before and after Modification. The contact angle of nano-TiO$_2$ before and after modification with 3% TMSPM expresses that water droplet was quickly and completely absorbed into the surface of nano-TiO$_2$. After modification, the contact angle of TiO$_2$-T3 is

| Sample   | BET surface area (m$^2$·g$^{-1}$) | Pore volume (cm$^3$·g$^{-1}$) | Average pore width (nm) |
|----------|----------------------------------|------------------------------|-------------------------|
| TiO$_2$  | 13.693                           | 0.032                        | 9.782                   |
| TiO$_2$-T3 | 12.420                           | 0.033                        | 10.114                  |

Figure 7: FESEM images of nano-TiO$_2$ (a, b) and TiO$_2$-T3 (c, d) at magnifications of 50 and 100 times.
Figure 8: TEM images of nano-TiO$_2$ (a, b) and TiO$_2$-T$_3$ (c, d).

Figure 9: UV-Vis transmittance spectra of nano-TiO$_2$ before and after modification with TMSPM in water.
111.76° (Figure 10). It confirmed that the modification contributed to the increase in hydrophobic properties of nano-TiO₂. This can enhance the application ability of modified nano-TiO₂ in the polymer nanocomposites.

4. Conclusion

In this work, nano-TiO₂ particles was modified successfully with 3-(trimethoxysilyl)propyl methacrylate silane coupling agent in the alcohol solvent using ammonia as a catalyst for silane hydrolysis reaction. The TMSPM was grafted on the surface of nano-TiO₂ with the maximum grafting efficiency of 97.7% when using 3% TMSPM. The crystal structure and basic particle size of nano-TiO₂ has not been affected after the modification process. The analysis results of IR, TGA, UV-Vis, SEM/TEM, size distribution, zeta potential, and contact angle showed that the agglomeration of modified nano-TiO₂ was decreased; it exhibited excellent stability in water; and its surface became more hydrophobic. The modified TiO₂ nanoparticles with great characteristics and properties are promising for application in polymer nanocomposite processing.

Data Availability

The data used to support the findings of this study are included within the article.

Conflicts of Interest

The authors declare no conflicts of interest.

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Figure 10: Photo of water droplet on the surface of TiO₂-T3.
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