




Research Article

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

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Received 28 July 2020; Revised 10 October 2020; Accepted 14 October 2020; Published 28 October 2020

Academic Editor: Gulaim A. Seisenbaeva

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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 treatment. 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 TiO₂ 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-TiO₂. The nature and amount of the organosilanes, the size, and distribution of nano-TiO₂ influence on the effectiveness of treatment process and surface characteristics, properties of modified nano-TiO₂. Some silanes which have been used for modification of TiO₂ particles are 3-methacryloxypropyltrimethoxysilane, 3-(triethoxysilyl)propyl isocyanate, vinyltrimethoxysilane, (3-aminopropyl)trimethoxysilane, hexadecyltrimethoxysilane, (3-glycidoxypropyl)trimethoxysilane, bis(3-triethoxysilylpropyl)tetrasulfide, octadecyltrimethoxysilane, and so on [9–15]. As reported in some literature studies, TiO₂ was modified with 3-methacryloxypropyltrimethoxysilane, TiO₂ particles were in micromet size [9], and treatment solvent was *o*-xylene [18]. Study on the modification of nano-TiO₂ with 3-methacryloxypropyltrimethoxysilane in ethanol solvent in alkali environment has rarely reported. One advantage of nano-TiO₂ modification using ethanol solvent is more environmentally friendly than using xylene solvent.

In our previous reports, nano-TiO₂ was treated with vinyltrimethoxysilane and was used as an additive for polymer composites [23, 24]. The characterization of modified nano-TiO₂ has been not presented clearly. Therefore, in this work, TiO₂ nanoparticles were modified with 3-(trimethoxysilyl)propyl methacrylate—TMSPM—in ethanol solvent using ammonia solution as a catalyst for hydrolysis reaction of the silane coupling agent. The TMSPM with two functional groups (C=C and O-C=O) can work more effectively and interact more strongly with hydroxyl groups on the surface of nano-TiO₂ together with functional groups of polymer matrix than vinyltrimethoxysilane with only one functional group (C=C). The characteristics, properties, and morphology of nano-TiO₂ 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 TiO₂ (Kronos 2360, 92%, South Korea) has average particle size of 160 nm and density of 3.9 g/cm³. 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-TiO₂. The procedure of treatment nano-TiO₂ 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-TiO₂ 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 TiO₂ nanoparticles (abbreviated as m-TiO₂). 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-TiO₂ before and after modification were taken on a Nicolet iS10 spectrometer (Thermo Scientific, USA) in wavenumbers ranged from 400 cm⁻¹–4000 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-TiO₂ 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-TiO₂ 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-TiO₂.

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 TiO₂ Nanoparticles before and after Modification*. The IR spectra of nano-TiO₂ 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-TiO₂ at the wavenumber of 3364 cm⁻¹ and at 1049 and 600 cm⁻¹ were attributed to Ti-O-Ti bond of nano-TiO₂ and modified nano-TiO₂. As compared the IR spectra of modified nano-TiO₂ with that of nano-TiO₂, the appearance of some new peaks confirmed that TMSPM was grafted successfully on the surface of nano-TiO₂ [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⁻¹ 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-TiO₂.

3.2. *Thermal Behaviour of TiO₂ Nanoparticles before and after Modification*. The TG and DTG diagrams of nano-TiO₂ before and after modified with different volume of TMSPM are presented in Figures 2 and 3. Observing from Figure 2, the TiO₂ nanoparticles were slightly decomposed at 200–300°C corresponding to the vaporization of water in TiO₂ nanoparticles, and then it was relatively stable with heat. For modified nano-TiO₂, the weight of nano-TiO₂ 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-TiO₂ [9, 15]. As increasing the TMSPM volume, the weight loss of modified nano-TiO₂ was increased (Table 2). This result also proved that TMSPM was grafted successfully on surface of nano-TiO₂ 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 TiO₂ nanoparticles were higher than that of TiO₂ nanoparticles (Table 2). The intensity and area of degraded peaks of modified TiO₂ nanoparticles were larger than those of TiO₂ nanoparticles. This also indicated that the TMSPM grafted on nano-TiO₂ was decomposed by heat.

3.3. *Grafting Efficiency of TMSPM on Nano-TiO₂*. Based on the results of TGA analysis, the content of TMSPM grafted on the surface of nano-TiO₂ can be estimated [15]. The grafting efficiency (GE) of TMSPM on nano-TiO₂ is shown in Table 3. It can be seen that the GE was increased with a rising mass ratio of organosilane to nano-TiO₂ from 1 to 3% with a maximum grafting efficiency of 97.7% for the TiO₂-T3 sample. This could be caused by the crosslinked framework generated by the TMSPM condensation reaction on the surface of nano-TiO₂ [9, 15]. At the ratio of TMSPM/nano-TiO₂ of 3%, the silane was formed as a monodentate layer on nano-TiO₂. 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-TiO₂ leading to the steric hindrance, causing the reduction of grafting ability of TMSPM on nano-TiO₂ [5, 15]. Moreover, the low concentration of OH groups on the nano-TiO₂ surface also caused to the decrease in grafting ability of TMSPM at its high content. From the obtained above results, the TiO₂-T3 sample was chosen for further investigation.

3.4. *Size Distribution and Zeta Potential of TiO₂ Nanoparticles before and after Modification*. Figure 4 and Table 4 present the size distribution diagrams of TiO₂ 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-TiO₂ decreased significantly, causing the reduction in the average particle size of the TiO₂-T3 sample. This exhibited that the surface of modified nano-TiO₂ 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-TiO₂ and TiO₂-T3 nanoparticles was 0.293 and 0.409 indicating that the samples have different size distribution algorithms (ISO 22412:2008).

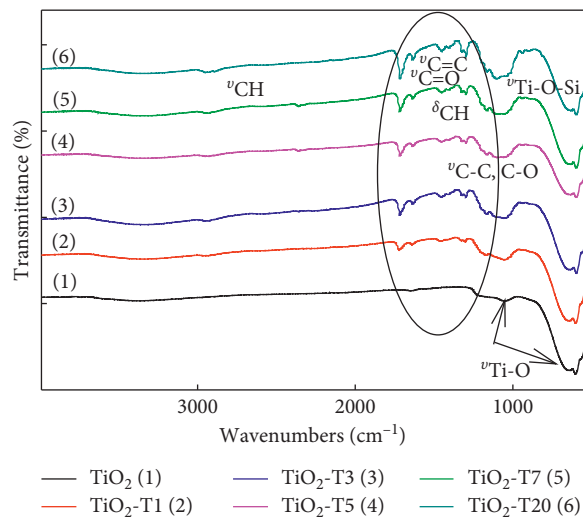


FIGURE 1: IR spectra of nano-TiO₂ and nano-TiO₂ modified with different volumes of TMSPM.

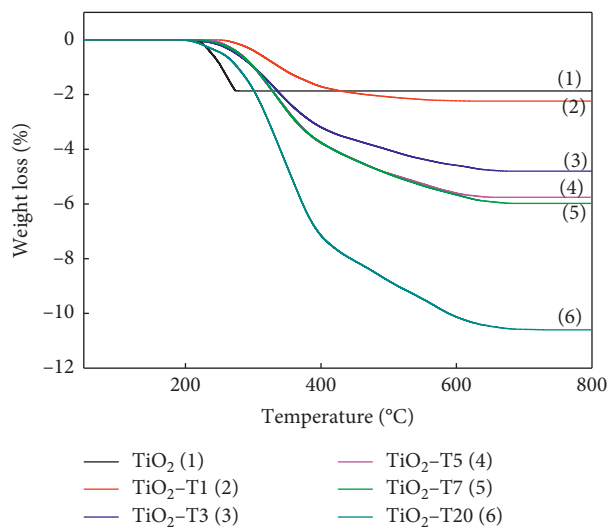


FIGURE 2: TG diagrams of nano-TiO₂ before and after modified with different volume of TMSPM.

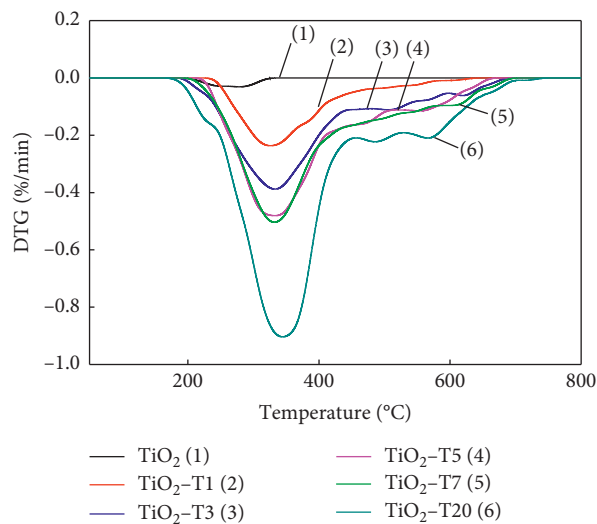


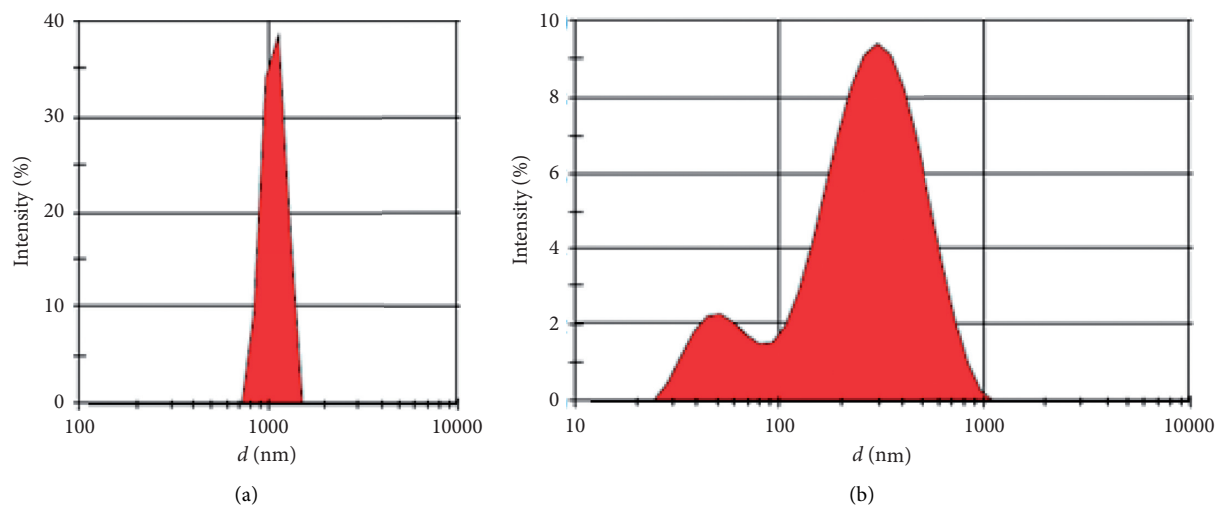
FIGURE 3: DTG diagrams of nano-TiO₂ and nano-TiO₂ modified with different volume of TMSPM.

TABLE 2: Thermal parameters of nano-TiO₂ and nano-TiO₂ modified with TMSPM.

Sample	Weight loss (%)	Maximum degradation temperature (°C)
TiO ₂	1.87	277.82
TiO ₂ -T1	2.24	325.65
TiO ₂ -T3	4.80	332.72
TiO ₂ -T5	5.75	329.09
TiO ₂ -T7	5.98	331.18
TiO ₂ -T20	10.58	344.65

TABLE 3: Grafting efficiency of TMSPM on nano-TiO₂.

Sample	Percentage of initial silane (%)	Weight loss obtained from TGA (%)	Percentage of grafted silane (%)	Grafting efficiency (%)
TiO ₂	0	1.87	0	0
TiO ₂ -T1	1	2.24	0.37	37.0
TiO ₂ -T3	3	4.80	2.93	97.7
TiO ₂ -T5	5	5.75	3.88	77.6
TiO ₂ -T7	7	5.98	4.11	58.7
TiO ₂ -T20	20	10.58	8.71	43.6

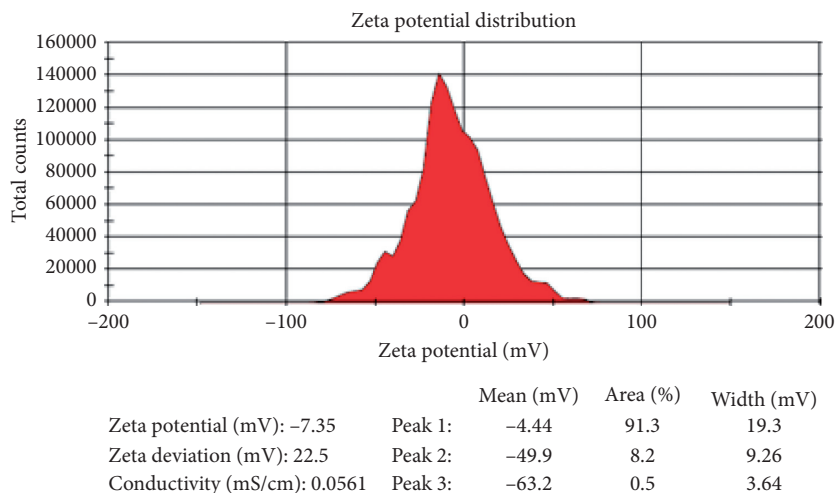
FIGURE 4: Size distribution diagrams of nano-TiO₂ (a) and TiO₂-T3 (b).TABLE 4: Size distribution of nano-TiO₂ and TiO₂-T3 samples.

Sample	Size distribution range (nm)	Average particle size (nm)
TiO ₂	712.4–1484	1059 ± 68.15
TiO ₂ -T3	24.36–955.4	52.01 ± 7.36 (13.2%) 316.3 ± 81.30 (86.8%)

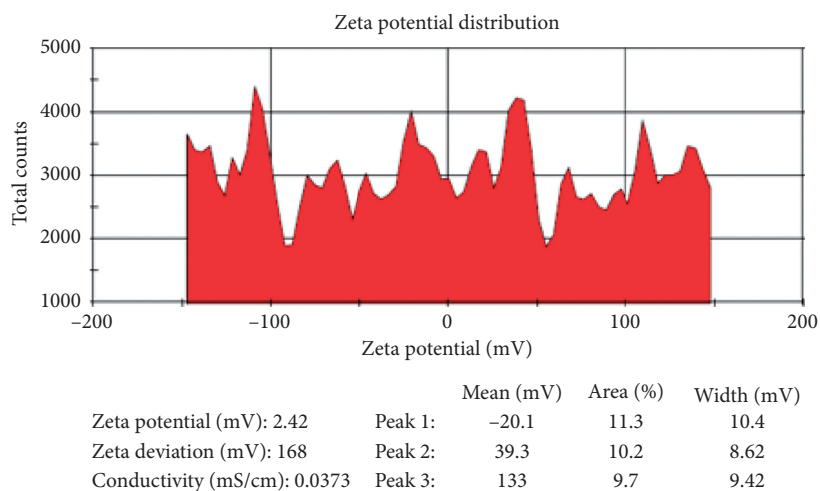
The zeta potential of TiO₂ nanoparticles before and after modified with 3% TMSPM is performed in Figure 5. It is clear that the surface charge of nano-TiO₂ was changed after modification. A high zeta potential will confer stability behavior of nanoparticles in the solution or dispersion of nanoparticles 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



(a)



(b)

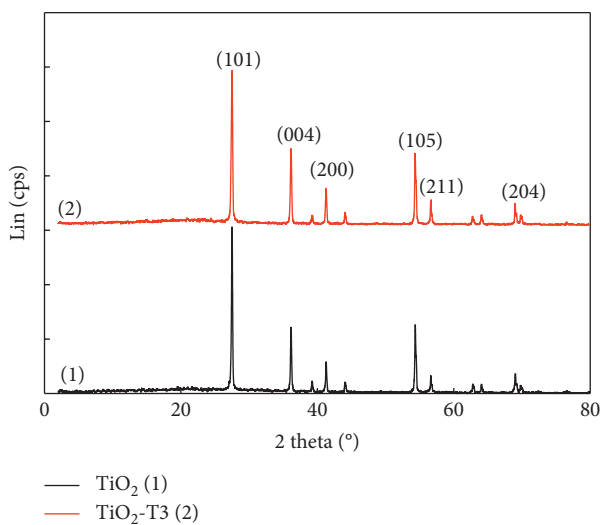
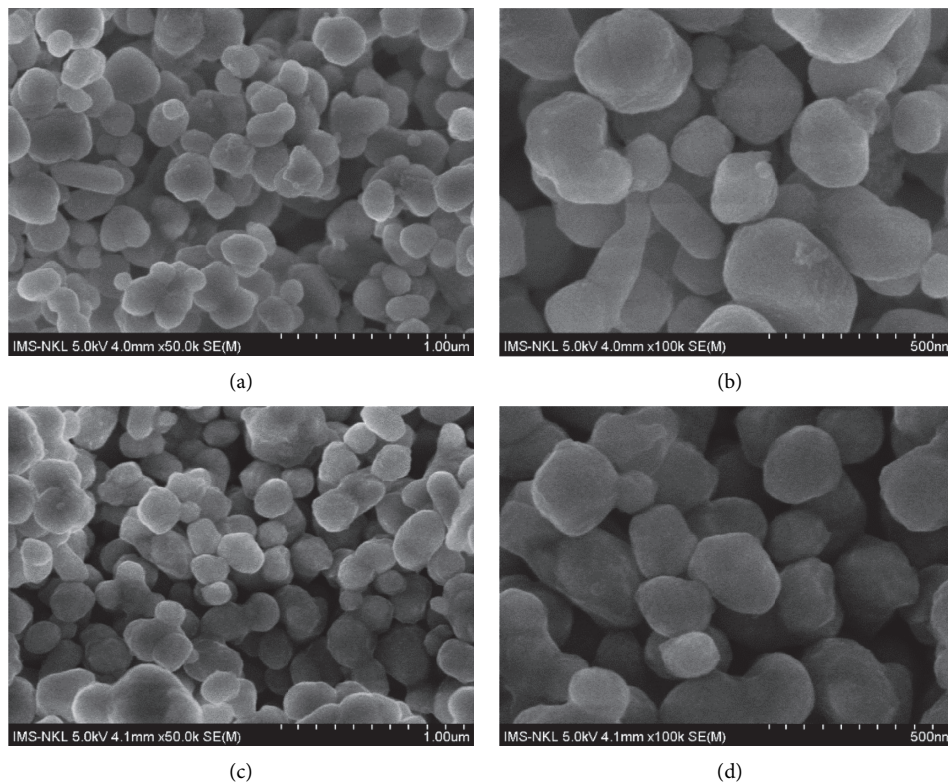
FIGURE 5: Zeta potential of nano-TiO₂ (a) and TiO₂-T3 (b).FIGURE 6: XRD patterns of nano-TiO₂ (1) and TiO₂-T3 (2).

TABLE 5: Specific surface area, pore volume, and pore size of nano-TiO₂ and TiO₂-T3 samples.

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-TiO₂ (a, b) and TiO₂-T3 (c, d) at magnifications of 50 and 100 times.

pattern of modified nano-TiO₂. 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 TiO₂ rutile crystal [15]. The modification does not affect on the crystal structure of nano-TiO₂.

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 N₂ sorption isotherms of nano-TiO₂ and TiO₂-T3. It means that TiO₂ nanoparticles have a solid and nonporous structure. The BET surface area of nano-TiO₂ 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-TiO₂.

3.6. Morphology of Nano-TiO₂ before and after Modification.

Figures 7 and 8 are FESEM and TEM images at different magnifications of TiO₂ nanoparticles before and after modified with 3% TMSPM, respectively. It can be seen that the size of TiO₂ 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-TiO₂ is similar to that of nano-TiO₂. This indicates that the silane modification cannot cause the change in size and shape of nano-TiO₂.

3.7. UV-Vis Transmittance Spectra of TiO₂ Nanoparticles before and after Modification. The UV-Vis transmittance spectra of TiO₂ 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-TiO₂ in water. The TiO₂ 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-TiO₂ was dispersed well in water. This result is similar to the size distribution result of original nano-TiO₂ and modified nano-TiO₂.

3.8. Contact Angle of Nano-TiO₂ before and after Modification.

The contact angle of nano-TiO₂ before and after modification with 3% TMSPM expresses that water droplet was quickly and completely absorbed into the surface of nano-TiO₂. After modification, the contact angle of TiO₂-T3 is

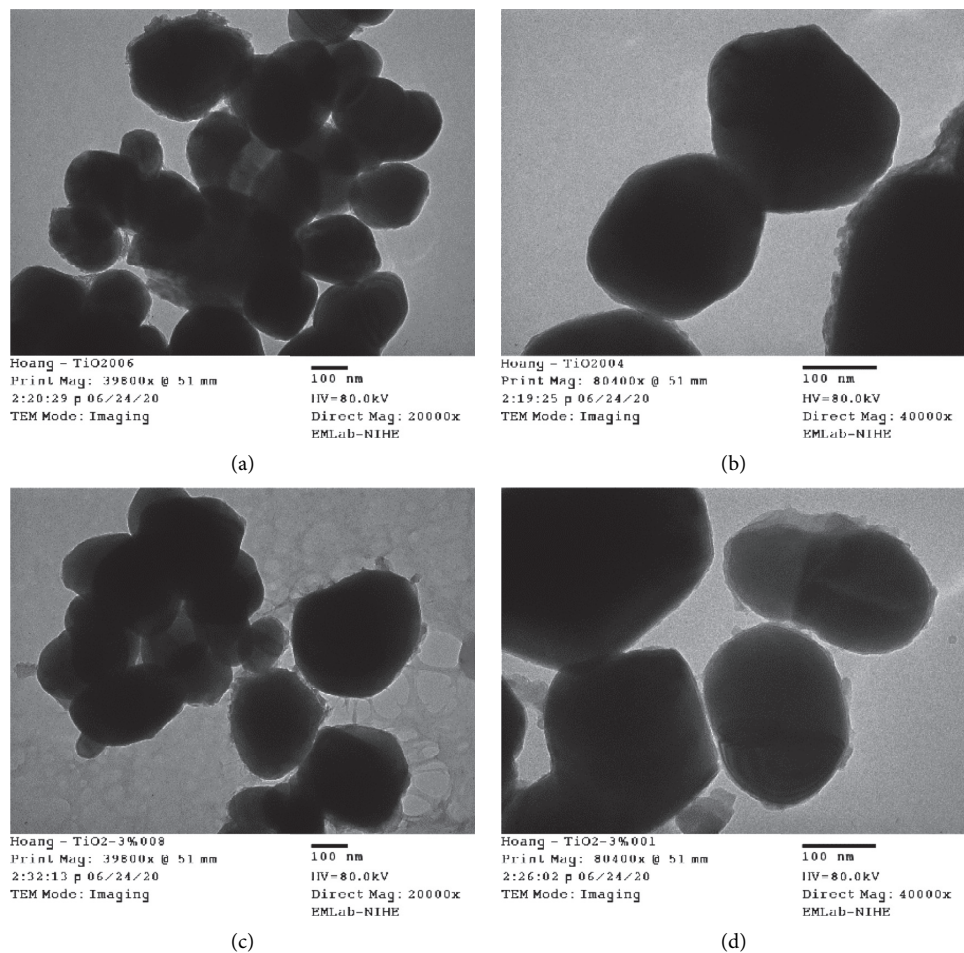


FIGURE 8: TEM images of nano-TiO₂ (a, b) and TiO₂-T3 (c, d).

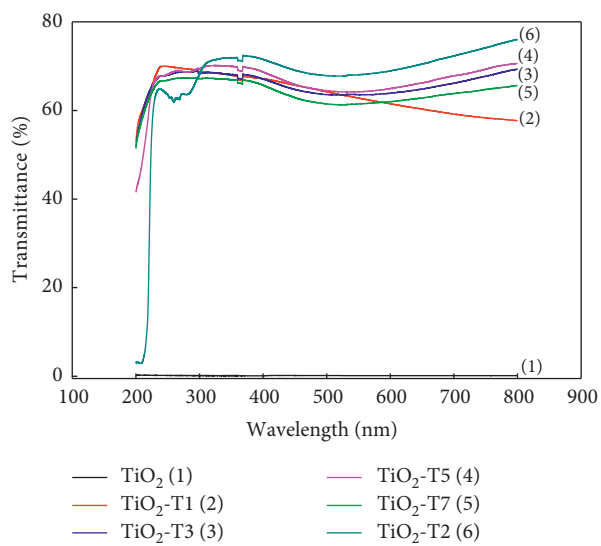


FIGURE 9: UV-Vis transmittance spectra of nano-TiO₂ before and after modification with TMSPM in water.



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

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.

Acknowledgments

This research was funded by Vietnam Academy of Science and Technology under grant number KHCBHH.01/20-22, for a period of 2020–2022.

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