

Research Article

Assessment of Some Characteristics and Properties of Zirconium Dioxide Nanoparticles Modified with 3-(Trimethoxysilyl) Propyl Methacrylate Silane Coupling Agent

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Received 29 March 2021; Revised 4 June 2021; Accepted 15 June 2021; Published 22 June 2021

Academic Editor: Shahid Hussain

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This study presents the results of surface modification of zirconium dioxide (ZrO₂) nanoparticles by 3-(trimethoxysilyl) propyl methacrylate silane coupling agent by assessing some characteristics and properties of modified ZrO₂ nanoparticles by infrared spectroscopy, thermogravimetric analysis, size distribution, zeta potential, and field emission scanning electron microscopy methods. The modified and unmodified ZrO₂ nanoparticles have been used as nanoadditives for organic coatings based on acrylic emulsion resin. The abrasion resistance of acrylic coating was evaluated according to ASTM E968-15. The obtained results show that ZrO₂ nanoparticles were functionalized successfully with 3-(trimethoxysilyl) propyl methacrylate silane. The modified ZrO₂ nanoparticles exhibit a positive effectiveness in the enhancement of the abrasion resistance of acrylic resin coating compared to unmodified ZrO₂ nanoparticles.

1. Introduction

Zirconium dioxide (ZrO₂) or zirconia nanoparticles have been used in many technological fields such as catalysis, sensors, dielectric materials, polymeric nanocomposites, metallic nanocomposites, coating, semiconductor, or optical materials, thanks to their advantages including high strength, good natural color, high transparency and chemical stability, transformation toughness, thermal stability, chemical resistance, anticorrosion, and microbial resistance. There are several available methods for producing zirconia nanoparticles, consisting of hydrolysis, sol/gel,

hydrothermal, pyrolysis, microwave plasma, or thermal treatment [1–4].

Recently, zirconia nanoparticles are interested as an enhancement additive for organic coating to improve the transparency, refractive index, hardness, elastic modulus, tensile strength, and thermal stability of polymer matrixes including poly (urethane-acrylate), poly (N-isopropylacrylamide), poly (methylmethacrylate), polyacrylamide hydrogels, or polypyrrole- (PPy-) derived polymer due to their great physical and chemical properties [5–11]. The properties of the ZrO₂ nanocomposites depend on the size and content of zirconia nanoparticles in the polymer.

There are few studies on surface modification of zirconia nanoparticles to increase the dispersion of zirconia nanoparticles in polymer matrices [12–14]. The ZrO_2 nanoparticles modified with 3-methoxysilyl propyl amine significantly improved the mechanical properties of epoxy resin [12, 13]. Yan et al. modified ZrO_2 nanoparticles using N-(2-aminoethyl)- γ -aminopropylmethyl dimethoxy silane coupling agent and investigated the effect of nanometer ZrO_2 content and silane coupling agent on the friction and wear properties of bismaleimide (BMI) nanocomposites [14]. The presence of ZrO_2 nanoparticles contributed to the decrease in the frictional coefficient and the wear rate of the nanocomposites. The modified ZrO_2 nanoparticles were dispersed in a polymer matrix better than untreated ZrO_2 nanoparticles, leading to the better tribological performance of nanocomposites containing modified ZrO_2 nanoparticles. Xu et al. ex situ synthesized functionalized ZrO_2 nanoparticles from zirconium (IV) isopropoxide isopropanol complex in benzyl alcohol and 3-(trimethoxysilyl) propyl methacrylate and applied them in UV curable poly (urethane-acrylate) (PUA) coating [5]. The coating was completely transparent when using 20 wt.% of ZrO_2 . The mechanical and thermal properties of PUA coating were improved significantly with the presence of functionalized ZrO_2 nanoparticles. Sayilkan et al. modified the surface of ZrO_2 nanoparticles with 2-acetoacetoxyethyl methacrylate for optical purposes [3]. The modified ZrO_2 nanoparticles have a size of 6.22 nm (transmission electron microscope) and 14.7 nm (particle size analysis). The surface modification also increases the stabilization of ZrO_2 nanoparticles [15].

Emulsion acrylic resin is widely used in daily life and industry because it has valuable properties such as high UV resistance, high aesthetics, weather resistance, and working well for various materials. In addition, it is environmentally friendly, low cost, and thus widely used in water-based paints and coatings for interior applications [16–19]. The evaluation of the effect of modified ZrO_2 nanoparticles on the abrasion resistance of emulsion acrylic resin can contribute to developing the paint system based on acrylic and nanoadditives in life sciences and technologies.

It can be recognized that the surface modification of ZrO_2 nanoparticles is necessary to improve their dispersibility in a polymer matrix. However, there are few reports related to the assessment of the efficiency with grafting of silane coupling agent on the surface of ZrO_2 nanoparticles [20]. The purpose of this work is to evaluate some characteristics, properties including grafting efficiency, functional groups, thermal stability, size distribution, and water stability of ZrO_2 nanoparticles modified with 3-(trimethoxysilyl) propyl methacrylate silane. Moreover, the effect of silane content as well as modified ZrO_2 nanoparticle content on abrasion resistance of emulsion acrylic coating has been also tested and discussed.

2. Experimental

2.1. Materials. ZrO_2 nanoparticles (99%) and 3-(trimethoxysilyl) propyl methacrylate silane (MSPMS) were provided by Sigma Aldrich, USA. Emulsion acrylic resin

(Plextol R 4152, solid content of $49 \pm 1\%$, pH = 7.0–8.5, density of 1.05 g/mL at 25°C) was purchased from Synthomer Company. Texanol ester alcohol (2,2,4-trimethyl-1,3-pentanediol, monoisobutyrate, 99%, density of 0.95 g/mL at 25°C), as a film-forming additive, was purchased from Dow Company. Others (ethanol 99.7%, ammonia 25%, and paint additives) are analysis chemicals.

2.2. Modification of ZrO_2 Nanoparticles. The procedure for modification of ZrO_2 nanoparticles by MSPMS was carried out based on different reports [11, 12, 21, 22] as follows: first, MSPMS was hydrolyzed in 100 mL of ethanol solution for 30 minutes at 50°C. Next, 5 g of ZrO_2 nanoparticles was added into above solution and magnetic stirred continuously for 2 hours at 50°C. The solution was then homogenized on a T25 Ultra-Turrax digital high-speed homogenizer (IKA, Germany) for 30 minutes at a speed of 15,000 rpm. After that, the solid part was obtained by centrifuging and washing with ethanol 3–4 times before drying in a vacuum oven at 70°C to obtain modified ZrO_2 nanoparticles (abbreviated by m- ZrO_2). The weight ratio of silane and ZrO_2 nanoparticles and designation of the samples are presented in Table 1.

2.3. Characterization. The functional groups of unmodified and modified ZrO_2 nanoparticles were analyzed by infrared (IR) spectroscopy, which means by a Nicolet iS10 (Thermo Scientific, USA) in 400–4000 cm^{-1} wavenumbers, 8 cm^{-1} resolutions, and 32 scans. The thermogravimetric (TG) analysis of the unmodified and modified ZrO_2 nanoparticles was carried out using a DTG 60H (Shimadzu, Japan) at a heating speed of 10°C/min in air from room temperature to 800°C. Field emission scanning electron microscopy (FESEM) images of unmodified and modified ZrO_2 nanoparticles were taken using S4800 FESEM (Hitachi, Japan). The dynamic light scattering (DLS, Zetasizer SZ-100, Horiba, Japan) was used to determine the size distribution and zeta potential of unmodified and modified ZrO_2 nanoparticles. The samples were dispersed in distilled water, and DLS spectra were recorded at 25°C.

2.4. Preparation of Acrylic Resin Coatings Containing Unmodified and Modified ZrO_2 Nanoparticles and Evaluation of Their Abrasion Resistance. The acrylic resin coatings were prepared according to the following steps: first, the unmodified or modified ZrO_2 nanoparticles were dispersed in distilled water by a TPC-15H ultrasonic tank for 30 minutes at room temperature with the nanoparticles/water ratio of 1/10 w/v (mixture A). Next, Texanol and other paint additives were added into acrylic resin at the additives/resin ratio of 1.5/100 (w/w) on an IKA RW16 stirrer with a speed of 400 rpm for 15 minutes at room temperature (mixture B). The mixture A was mixed with mixture B on an IKA RW16 stirrer with a speed of 600 rpm for 15 minutes at room temperature before ultrasonication in the Branson sonifier 450 device for 5 minutes. The coating samples were made by the Erichsen film applicator thickness wiper (model 360) at wet film thickness of 120 μm on glass.

The abrasion resistance test of the coating samples has been performed using the falling sand abrasion method according to ASTM D968-15. The ElektroPhysik MiniTest 600 machine was used to measure the thickness of coatings. The volume of abrasive sand per unit coating thickness was the abrasion resistance of coating, expressed in L/mil (1 mil = 25 μm) as

$$\text{Abrasion resistance} \left(\frac{L}{\text{mil}} \right) = \frac{V}{d}, \quad (1)$$

where V is the volume of sand (L), and d is the coating thickness (mil).

The dispersion of ZrO_2 nanoparticles in the acrylic resin matrix was evaluated by the field emission scanning electron microscopy (FESEM) method on a S4800 FESEM (Hitachi, Japan).

3. Results and Discussion

3.1. TG Analysis and Grafting Efficiency of Silane on ZrO_2 Nanoparticles. Figures 1 and 2 show the TG and DTG diagrams of unmodified and modified ZrO_2 nanoparticles. The weight loss of unmodified ZrO_2 is zero, confirming that there is no presence of hydroxyl groups on the surface or inside the structure of ZrO_2 nanoparticles [23]. From the TG diagrams, it can be seen that the modified ZrO_2 (m- ZrO_2) nanoparticles lost the weight in the range temperature of 200°C–500°C. There is a broad peak on the DTG diagrams of m- ZrO_2 samples corresponding to the degradation of organosilane grafted on the surface of ZrO_2 nanoparticles [21]. As varying the MSPMS content, the maximum degradation temperatures of m- ZrO_2 samples were changed (Table 2); however, the onset degradation temperatures of all m- ZrO_2 samples are similar.

The grafting efficiency of MSPMS to ZrO_2 nanoparticles was estimated by the TG method [20, 21] and is given in Table 2. Because the surface of ZrO_2 nanoparticles is hydrophobic, the grafting efficiency of MSPMS to ZrO_2 nanoparticles is low, lowest value of 3.4% for m- ZrO_2 -15 and highest value of 13.0% for m- ZrO_2 -3. As increasing the silane content, the grafting efficiency of MSPMS to ZrO_2 nanoparticles was decreased. This exhibits that the organosilane was residue in the modification process. In the investigated MSPMS contents, 3% of MSPMS is the most suitable for modifying ZrO_2 nanoparticles with a high effectiveness.

3.2. IR Spectra of Unmodified and Modified ZrO_2 Nanoparticles. The IR spectra of unmodified and m- ZrO_2 nanoparticles are shown in Figure 3. A strong band can be seen with the peaks at 570 cm^{-1} and 670 cm^{-1} characterized for Zr-O-Zr stretching vibration of ZrO_2 nanocrystals [13, 24–26]. There is no new peaks appeared in IR spectra of m- ZrO_2 nanoparticles, suggesting that the surface modification does not have any influence on the vibration of ZrO_2 nanocrystals. It is difficult to observe the vibration of functional groups in MSPMS on m- ZrO_2 nanoparticles. This may be due to the high hydrophobic

surface of ZrO_2 leading to difficult formation of bonding between organosilane and ZrO_2 nanoparticles. Moreover, the content of silane grafted on the surface of ZrO_2 nanoparticles is quite small causing an effect on the appearance of organic groups in MSPMS on IR spectra of m- ZrO_2 nanoparticles. Therefore, only a small peak at 1120 cm^{-1} which is assigned to the stretching vibration of Si-O-Zr in the IR spectrum of m- ZrO_2 -5 nanoparticles [12, 13] can be seen, as shown in Figure 4.

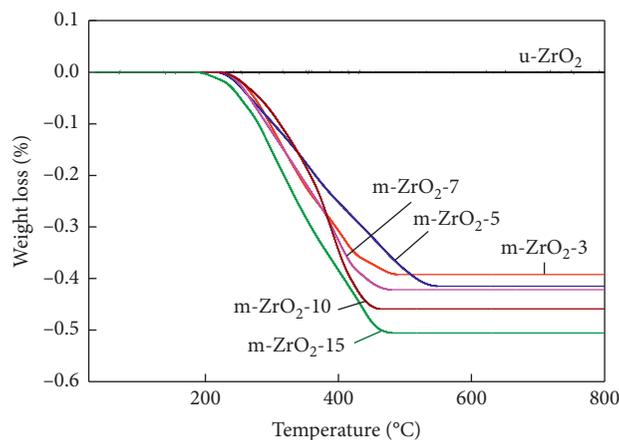
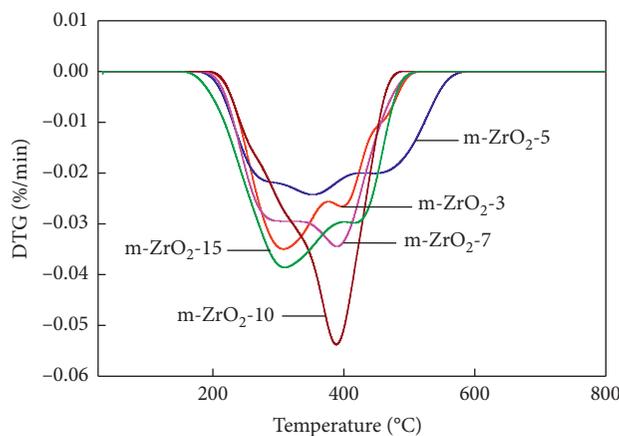
3.3. Morphology of Unmodified and Modified ZrO_2 Nanoparticles. As observation from the FESEM images of unmodified and m- ZrO_2 nanoparticles in Figure 5, the ZrO_2 nanoparticles are in spherical shape and have size in range from 50 nm to 150 nm. The tendency to agglomerate ZrO_2 nanoparticles can be observed due to the affinity of nanoparticles. The modification process has a negligible effect on morphology of ZrO_2 nanoparticles.

3.4. Size Distribution and Zeta Potential of Unmodified and Modified ZrO_2 Nanoparticles. The size distribution of unmodified and m- ZrO_2 nanoparticles is shown in Figure 6. The average particle size of u- ZrO_2 , m- ZrO_2 -3, m- ZrO_2 -5, m- ZrO_2 -7, m- ZrO_2 -10, and m- ZrO_2 -15 nanoparticles is 287.1 \pm 77.5, 283.6 \pm 59.0, 414.6 \pm 99.1, 269.7 \pm 24.6, 457.6 \pm 37.7, and 422.0 \pm 35.7 nm, respectively. The size distribution of m- ZrO_2 nanoparticles at different contents of MSPMS is not systematic. This may be due to agglomeration of m- ZrO_2 nanoparticles occurred when using the high content of MSPMS. Moreover, the modification process of ZrO_2 nanoparticles with MSPMS also increases the hydrophobic of nanoparticles [22, 27], leading to a difficult dispersion of m- ZrO_2 nanoparticles in water. The polydispersity index (PI) of all tested samples is higher than 0.3, corresponding to a broad size distribution of nanoparticles as reported by Danaei et al. [28]. The difference between particle sizes obtained in the FESEM method and DLS method is caused by the different dispersions of unmodified and m- ZrO_2 nanoparticles. For FESEM analysis, the nanoparticles were in solid and taken FESEM images, while for DLS analysis, the ZrO_2 nanoparticles were dispersed in distilled water before taking size distribution. The nature of ZrO_2 nanoparticles is hydrophobic; thus, they were dispersed difficultly in water, leading to the bigger size of the ZrO_2 nanoparticles.

The zeta potential of unmodified ZrO_2 (u- ZrO_2) nanoparticles and m- ZrO_2 -3 nanoparticles shown in Figure 7 demonstrates the u- ZrO_2 nanoparticles have a positive charge surface (21.4 mV) while m- ZrO_2 -3 nanoparticles have a negative charge surface (–12 mV). The modification process that caused the change in the charge on the surface of ZrO_2 nanoparticles from the positive region to the negative region may be due to the conjugation effect of C=C–C=O bond in MSPMS grafted onto the surface of ZrO_2 nanoparticles to form the negative charge on oxygen atom. From the above results, it can be recognized that the ZrO_2 nanoparticles were modified successfully with MSPMS.

TABLE 1: Composition and designation of modified ZrO₂ nanoparticles.

No.	Composition	Designation	Weight	
			m _{ZrO₂} (g)	m _{silan} (mg)
1	ZrO ₂	u-ZrO ₂	5	0
2	ZrO ₂ + 3 wt.% MSPMS	m-ZrO ₂ -3	5	15
3	ZrO ₂ + 5 wt.% MSPMS	m-ZrO ₂ -5	5	25
4	ZrO ₂ + 7 wt.% MSPMS	m-ZrO ₂ -7	5	35
5	ZrO ₂ + 10 wt.% MSPMS	m-ZrO ₂ -10	5	50
6	ZrO ₂ + 15 wt.% MSPMS	m-ZrO ₂ -15	5	75

FIGURE 1: TG diagrams of unmodified and modified ZrO₂ nanoparticles.FIGURE 2: DTG diagrams of modified ZrO₂ nanoparticles.TABLE 2: Maximum degradation temperature and grafting efficiency of MSPMS to ZrO₂ nanoparticles.

Sample	Weight of MSPMS in the sample (%)	Maximum degradation temperature (°C)	Weight loss (%) at 500°C	Δm (%)	Grafting efficiency (%)
u-ZrO ₂	0	0	0	0	0
m-ZrO ₂ -3	3	307.11	0.39	0.39	13.0
m-ZrO ₂ -5	5	354.30	0.42	0.42	8.4
m-ZrO ₂ -7	7	390.13	0.42	0.42	6.0
m-ZrO ₂ -10	10	388.61	0.46	0.46	4.6
m-ZrO ₂ -15	15	309.90	0.51	0.51	3.4

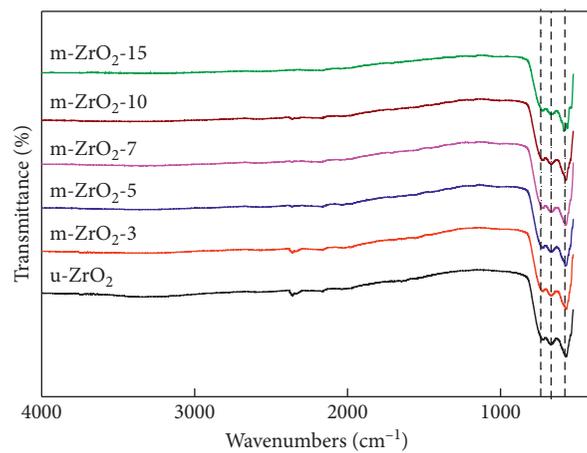
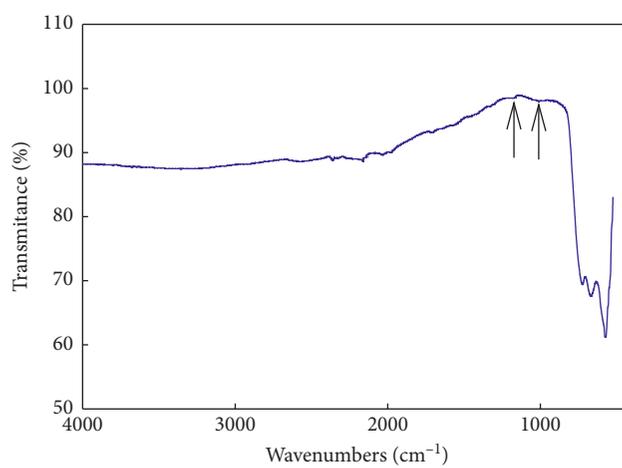
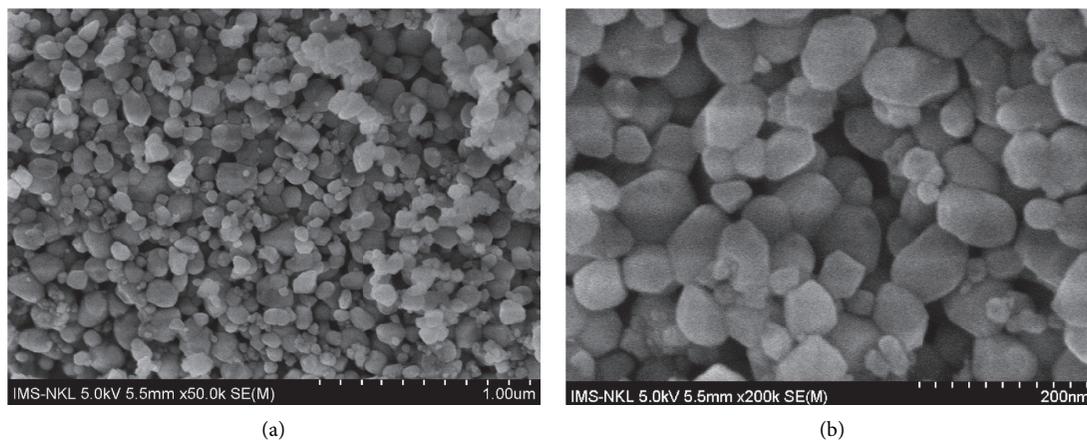
FIGURE 3: IR spectra of unmodified and modified ZrO₂ nanoparticles.FIGURE 4: IR spectrum of m-ZrO₂-5 nanoparticles.

FIGURE 5: Continued.

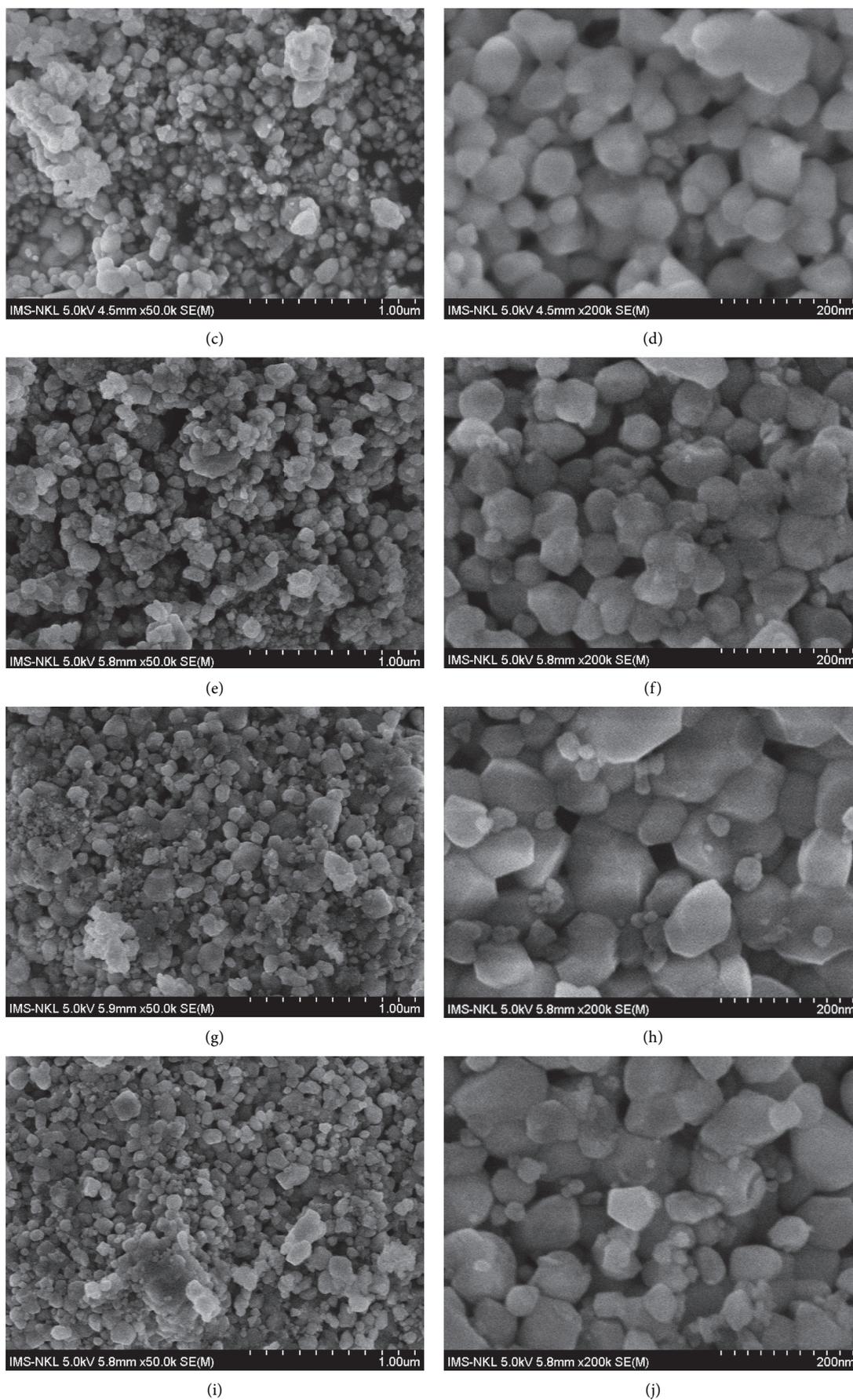


FIGURE 5: Continued.

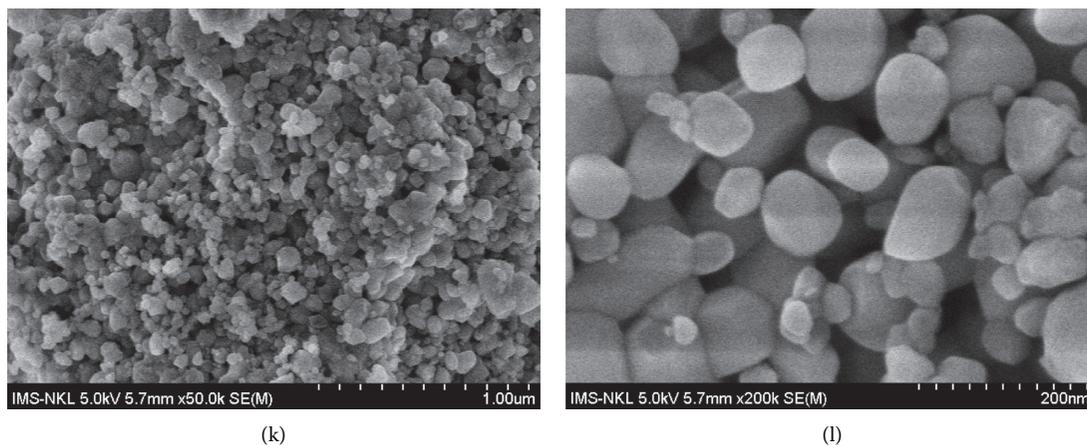


FIGURE 5: FESEM images of unmodified and modified ZrO_2 nanoparticles at magnification of 50,000 times and 200,000 times. u- ZrO_2 (a, b), m- ZrO_2 -3 (c, d), m- ZrO_2 -5 (e, f), m- ZrO_2 -7 (g, h), m- ZrO_2 -10 (i, j), and m- ZrO_2 -15 (k, l).

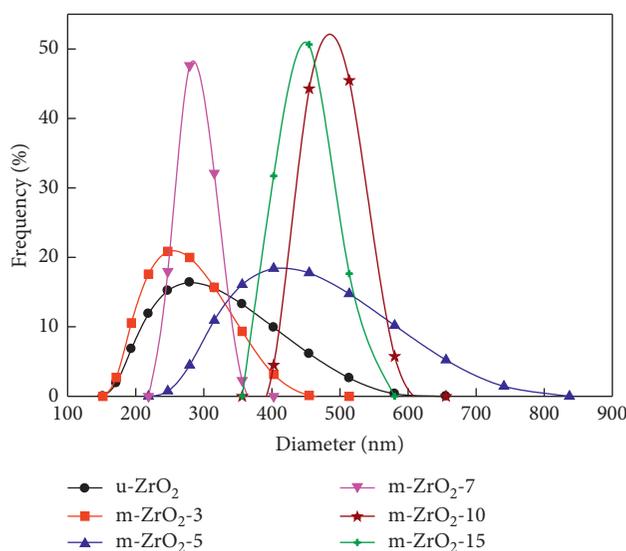


FIGURE 6: Size distribution of unmodified and modified ZrO_2 nanoparticles.

These zeta potential values also suggest that unmodified and modified ZrO_2 nanoparticles are relative stable in water.

3.5. Application of Unmodified and Modified ZrO_2 Nanoparticles for Emulsion Acrylic Resin Coating

3.5.1. Abrasion Resistance. The effect of MSPMS content on the abrasion resistance of acrylic based coating containing 2 wt.% of nanoparticles was evaluated and is given in Table 3. The acrylic resin and acrylic/u- ZrO_2 coating has a low abrasion resistance, 83.60 ± 4.47 L/mil and 77.50 ± 4.08 L/mil, respectively. In this case, u- ZrO_2 nanoparticles are not able to improve the abrasion resistance of acrylic coating due to the less dispersion of u- ZrO_2 nanoparticles in acrylic matrix, leading to the agglomeration of ZrO_2 nanoparticles and the formation of defect in structure of coating, causing the decrease in the abrasion resistance of acrylic coating.

Using m- ZrO_2 nanoparticles makes a remarkable enhancement in abrasion resistance of coating containing because m- ZrO_2 nanoparticles dispersed more regularly in acrylic matrix. The best improvement in abrasion resistance of coating was observed for acrylic/m- ZrO_2 -3 coating, an increase of 62.33% as compared to acrylic resin coating.

To assess the influence of m- ZrO_2 nanoparticle content on the abrasion resistance of acrylic coating, the coatings based on acrylic resin and different contents of m- ZrO_2 -3 nanoparticles were prepared. It can be seen that the abrasion resistance of coating containing m- ZrO_2 -3 nanoparticles was increased as increasing the content of m- ZrO_2 -3 from 0.5 to 2 wt.% and then decreased at the 5 wt.% of m- ZrO_2 -3 nanoparticles. This reduction can be caused by the agglomeration of m- ZrO_2 -3 nanoparticles when using at high content. From obtained results, the suitable content of MSPMS silane for modification is 3 wt.% and of m- ZrO_2 -3 nanoparticles in acrylic resin coating is 2 wt.% (Table 4).

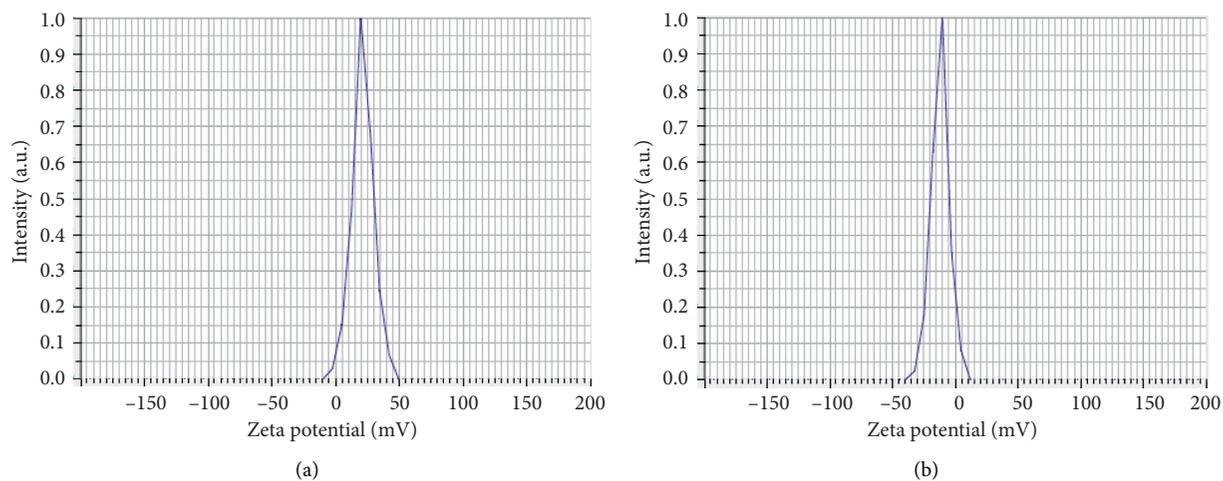


FIGURE 7: Zeta potential of u-ZrO₂ (a) and m-ZrO₂-3 (b) nanoparticles.

TABLE 3: Abrasion resistance of coating based on acrylic resin and 2 wt.% ZrO₂ nanoparticles.

Coating	Abrasion resistance (L/mil)
Acrylic resin	83.60 ± 4.47
Acrylic/u-ZrO ₂	77.50 ± 4.08
Acrylic/m-ZrO ₂ -3	135.71 ± 9.05
Acrylic/m-ZrO ₂ -5	127.50 ± 6.07
Acrylic/m-ZrO ₂ -7	125.71 ± 7.38
Acrylic/m-ZrO ₂ -10	123.57 ± 8.57
Acrylic/m-ZrO ₂ -15	112.50 ± 6.62

TABLE 4: Abrasion resistance of coating based on acrylic resin and different contents of m-ZrO₂-3 nanoparticles.

Coating	Abrasion resistance (L/mil)
Acrylic/0.5 wt.% m-ZrO ₂ -3	116.67 ± 8.97
Acrylic/1 wt.% m-ZrO ₂ -3	120.83 ± 9.29
Acrylic/2 wt.% m-ZrO ₂ -3	135.71 ± 9.05
Acrylic/5 wt.% m-ZrO ₂ -3	120.69 ± 7.79

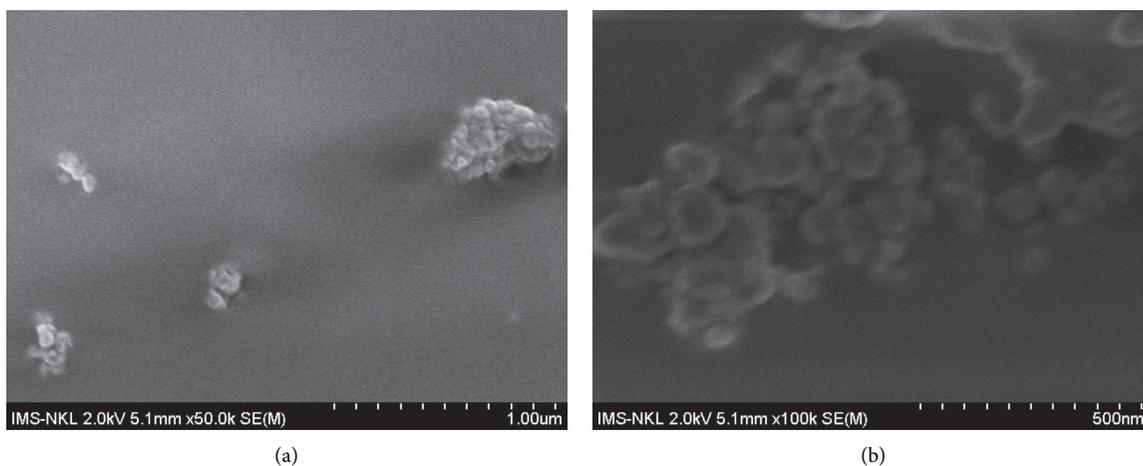


FIGURE 8: Continued.

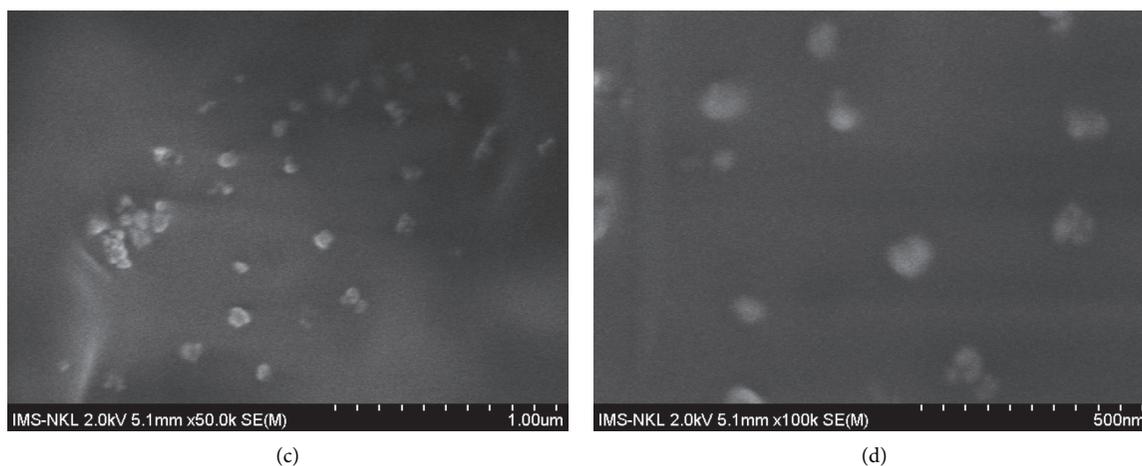


FIGURE 8: FESEM images of acrylic/2 wt.% u-ZrO₂ (a, b) and acrylic/2 wt.% m-ZrO₂-3 (c, d) coatings.

3.5.2. Morphology. The FESEM images of the cross-surface of acrylic coating containing unmodified or modified ZrO₂ nanoparticles are shown in Figure 8. It can be seen that the unmodified ZrO₂ nanoparticles were agglomerated in acrylic resin matrix, while the ZrO₂ nanoparticles modified with 3 wt.% MSPMS were dispersed regularly in acrylic resin. The interaction of carbonyl and vinyl groups in MSPMS on the surface of modified ZrO₂ nanoparticles with carbonyl groups in acrylic resin leading to the MSPMS plays a role of binder for acrylic resin and ZrO₂ nanoparticles [29], resulting in the good dispersion of modified ZrO₂ nanoparticles in acrylic resin. Thanks to the good dispersion of m-ZrO₂-3 nanoparticles in the acrylic resin, the abrasion resistance of the coating was improved as discussed above.

4. Conclusions

In conclusion, ZrO₂ nanoparticles were modified successfully with 3-(trimethoxysilyl) propyl methacrylate silane (MSPMS). The modification process does not affect morphology and functional groups but cause the change in surface charge and thermal behavior of ZrO₂ nanoparticles. The grafting efficiency of silane to ZrO₂ nanoparticles reached 13.0% when using 3 wt.% MSPMS for modification. The content of organosilane and content of modified ZrO₂ nanoparticles have an effect on the abrasion resistance of acrylic resin coating. The modified ZrO₂ nanoparticles improved significantly the abrasion resistance of acrylic resin coating, especially, when using 2 wt.% ZrO₂ nanoparticles modified with 3 wt.% MSPMS. This is the initial result to open up the prospects for the application of modified ZrO₂ nanoparticles in coatings based on emulsion acrylic resin or other polymers.

Data Availability

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

Conflicts of Interest

The authors declare that they have no conflicts of interest.

Acknowledgments

This research was funded by the Vietnam National Foundation for Science and Technology Development (NAFOSTED) (01/2020/TN).

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