

CHARACTERISTICS, PROPERTIES AND MORPHOLOGY OF CALCIUM SILICATE NANOPARTICLES MODIFIED WITH SOME SILANE COUPLING AGENTS

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Abstract. This paper presents the characteristics, properties and morphology of calcium silicate (CS) nanoparticles modified with different silane coupling agents, namely vinyltrimethoxysilane (VTMS) and [3-(methacryloyloxy)propyl]trimethoxysilane (MPTS). The effect of the initial content of silane coupling agents on the properties of the treated CS nanoparticles was investigated. The IR analysis and TGA diagrams of untreated and treated CS suggested that silane coupling agents were successfully grafted onto the surface of CS nanoparticles. The performance and silane coupling agent's content grafting on CS nanoparticles depended on the nature and initial content of silane coupling agents. The highest grafting yield on CS nanoparticles reached 32.8 % for VTMS with an initial content of 5 wt. % and 48.80 % for MPTS with an initial content of 10 wt. % (compared to CS content). Organo-modification reduced the thermo-oxidation stability of the modified CS nanoparticles because of the decomposition of organic moiety in silane coupling agents while the hydrophobicity of the modified CS surface increased. Thus, the agglomeration of modified CS nanoparticles was significantly reduced. The unmodified CS nanoparticles had a size distribution (in distilled water) peak near 500 nm while the size distribution (in distilled water) peak of CS modified with 10 wt.% MPTS was approximately 150 nm.

Keywords: calcium silicate, surface modification, silane coupling agent, grafting yield, hydrolysis method.

Classification numbers: 2.5.3, 2.9.4.

1. INTRODUCTION

In recent years, calcium silicate (CS, CaSiO_3) nanoparticles have been used as an additive for paint and organic coatings. The CS nanoparticles can improve some characteristics, properties of coatings such as thermal stability, mechanical properties, flame resistance, weather durability, etc. [1 - 4]. The properties of the nanocomposite coating depend on the dispersion ability of the CS nanoparticles in the polymer matrix. The CS nanoparticles tend to agglomerate in the polymer matrix due to the interaction between the inorganic phase and the organic polymer matrix. Hence, silane coupling agents have been used as bridges between the inorganic phase and the organic matrix. Rok Sinkovec *et al.* used CS treated with 3-aminopropyltriethoxysilane (commercial product) or CS mixed with 3-glycidyloxypropyltrimethoxysilane or 3-aminopropyltriethoxysilane as additives for epoxy resin [3]. Modified CS could significantly enhance the tensile strength and rheological behavior (i.e. flow curing behavior and spiral flow length) of epoxy resin. The hierarchical calcium silicate-calcium sulfate whiskers (H-CSW), which was formed by the treatment of calcium sulfate whiskers (size of 70 - 100 nm) with a sodium silicate solution, were also used to improve the flexibility and thermal properties of epoxy resin. The increase of flexural strength, flexural modulus, storage modulus and glass transition temperature of epoxy resin was caused by the mechanical interlocking between H-CSW and the epoxy matrix [5]. Some other reports indicated that CS nanoparticles modified with silane coupling agents were effective additives for polymer coating [6 - 8]. The structure of CS nanoparticles modified with n-hexyltriethoxysilane (HTES) was interlayer bilayer arrangement (organic molecules were intercalated inside the CS layers) [6]. The interaction ability between CS and polymers was improved after modifying CS with polydimethylsiloxan by the sol-gel method [9]. In another report, the biocompatibility of CS was also enhanced thanks to modifying CS with alkoxy silane by the sol-gel method [10]. Nevertheless, none of these studies addressed the use of vinyltrimethoxysilane (VTMS) or/and [3-(methacryloyloxy)propyl]trimethoxysilane (MPTS) to modify CS nanoparticles. Therefore, the purpose of this work was to investigate the characteristics, properties and morphology of CS nanoparticles modified with different kinds of silane coupling agents as well as the content of these coupling silane agents, namely VTMS and MPTS. Our study focused on the evaluation of changes in functional groups, size distribution, silane coupling agent grafting yield on the surface of CS nanoparticles, thermal stability, morphology and hydrophobic/hydrophilic properties of CS nanoparticles.

2. EXPERIMENTAL

2.1. Materials

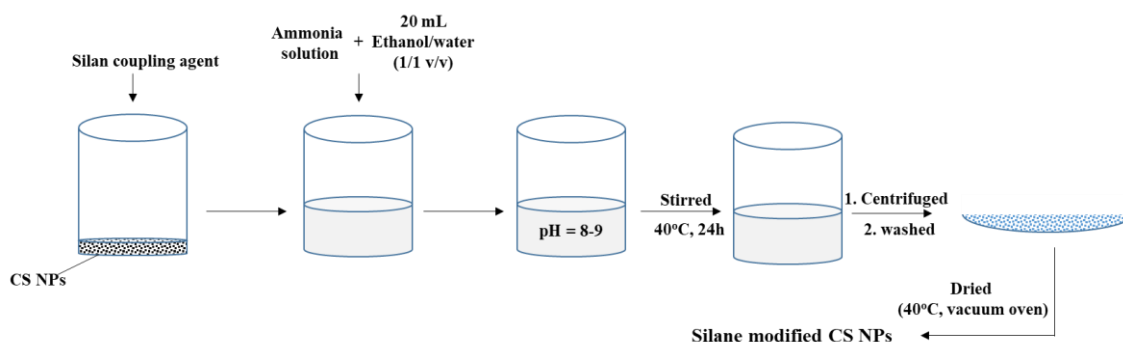
CaSiO_3 nanoparticles (CS) with diameters from 40 to 90 nm, vinyltrimethoxysilane (VTMS) (purity of 98 %), and [3-(methacryloyloxy) propyl] trimethoxysilane (MPTS) (purity of 98 %) were provided by Sigma Aldrich (USA). Ethanol (99.5 %) and acetone (99 %) were analytical chemicals of Chemical Xilong company (China). Ammonia solution (25 %) was purchased from Duc Giang Chemical Company (Viet Nam).

2.2. Modification of CS with silane coupling agents

Surface modification of nanoparticles with silane coupling agents is usually carried out through the hydrolysis method in water or a solution of water and a polar solvent (ethanol, propanol, or acetone) [11] or via condensation mechanism in non-polar organic solvents such as cyclohexane, toluene, and xylene [12]. However, surface modification of nanoparticles through

condensation mechanism is not suitable for scale-up production because of the requirement of a large amount of organic solvents. This means that the modification of nanoparticles through condensation mechanism is costly and has a negative effect on the environment. Therefore, CS nanoparticles were modified with silane coupling agents by the hydrolysis method in this work as the process below (as shown in Scheme 1):

Silane coupling agents (VTMS or MPTS) with weight ratios of 5, 10, and 30 wt. % to the CS weight were dropped directly into CS nanoparticles. 4 mL of ammonia solution and 20 mL of ethanol/distilled water (1/1 v/v) were used to adjust the pH of the mixture to 8-9. The mixture was blended well in a closed vessel and incubated at 40 °C for 24 hours. After incubation, the mixture was centrifuged to remove residual silane coupling agents and washed with acetone until pH of washing water reached 7. Next, the solid part was naturally evaporated before drying in a vacuum oven at 40 °C to constant weight to obtain modified CS.



Scheme 1. Surface modification procedure of calcium silicate nanoparticles.

The abbreviations of the samples prepared by hydrolysis method and the proportions of the components are listed in Table 1.

Table 1. Abbreviations of samples prepared by hydrolysis and proportions of components for modifying CS nanoparticles.

No.	Abbreviation	Precursors		
		CS (g)	VTMS (g)	MPTS (g)
1	CaVS 5	4.75	0.25	-
2	CaVS 10	4.5	0.5	-
3	CaVS 30	3.5	1.5	-
4	CaPM 5	4.75	-	0.25
5	CaPM 10	4.5	-	0.5
6	CaPM30	3.5	-	1.5

2.3. Characterization

The functional groups in the modified CS nanoparticles were determined by infrared (IR) spectroscopy, recorded on a Nicolet iS10 IR spectrometer (USA) using KBr pellets (made from

KBr powder and unmodified/modified CS nanoparticles with a weight ratio of 50/1) of the same thickness. Thermal behavior and silane coupling agent grafting yield on modified CS nanoparticles were determined by thermogravimetric analysis method (TGA) on a TG 209F1 analyzer (Netzsch, Germany). The samples were heated from room temperature to 750 °C at a heating rate of 10 °C/min in air atmosphere. SEM images of the modified CS nanoparticles were taken on a JSM-6510 LV (Japan). The size distribution of modified CS nanoparticles dispersed in distilled water was recorded using an SZ-100Z2 instrument (Horiba, Japan). The hydrophobic/hydrophilic characteristics of modified CS nanoparticles were evaluated by determining the contact angle of the samples on a SEO Phoenix-150 analyzer (USA).

3. RESULTS AND DISCUSSION

3.1. Functional groups in modified CS nanoparticles

The IR spectra of unmodified CS nanoparticles and CS nanoparticles modified with 10 wt.% MPTS or 10 wt.% VTMS are shown in Figure 1.

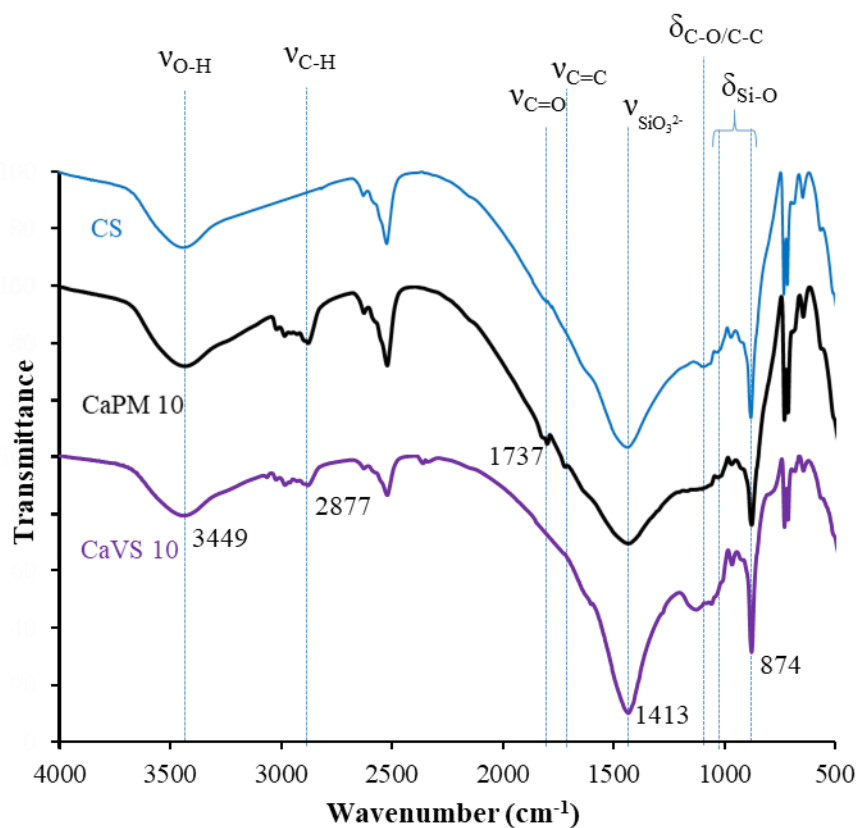


Figure 1. IR spectra of unmodified CS nanoparticles and CS nanoparticles modified with 10 wt.% MPTS and CS modified with 10 wt.% VTMS.

The characteristic wavenumbers at 1063 and 874 cm⁻¹, corresponding to the asymmetric and symmetric stretching vibrations of the Si-O bond in CS nanoparticles, respectively, appeared

in all the spectra in Figure 1. The bending vibration of Si-O-Si bond in SiO₄ tetrahedron was assigned to peaks at 400-600 cm⁻¹. The vibration of SiO₃²⁻ group was placed at 1413 cm⁻¹ [13].

In comparison with IR spectra of unmodified CS nanoparticles, there were some new absorptions appearing in the IR spectra of CS nanoparticles modified with MPTS. For instance, the peaks at 1637 cm⁻¹ and 1737 cm⁻¹ corresponded to the vibrations of C=C and C=O linkages in MPTS, respectively [14]. In addition, the stretching and bending vibrations of C-H linkages were attributed by peaks placed at 2958, 2923, 2854 and 1435 - 1300 cm⁻¹, respectively. The peaks at 3449 cm⁻¹ and 1637 cm⁻¹ were assigned to the stretching and bending vibrations of O-H linkages in water adsorbed in the samples. The absorptions of C-O and C-C linkages appeared at 1119 cm⁻¹ [15]. These were evidences for the successful grafting of silane coupling agents on the surface of CS nanoparticles.

The wavenumbers corresponding to some functional groups in CS modified by silane coupling agents with various ratios are presented in Table 2. The appearance of absorptions of O-H, C-H, C=O, C=C, C-O, C-C linkages in the spectra of modified CS nanoparticles confirmed that VTMS or MPTS grafted successfully onto the surface of the CS nanoparticles. From the data in Table 2, it can be seen that the absorptions which characterized the vibration of SiO₃²⁻ groups in the modified CS nanoparticles were slightly shifted (~ 20 cm⁻¹) compared to that in the unmodified CS nanoparticles. This could be explained by the resonance of the bending vibration of C-H groups (in the silane coupling agent) with the vibration of SiO₃²⁻ groups (in the CS nanoparticles).

Table 2. Wavenumbers of some functional groups in modified CS nanoparticles.

Sample	Wavenumbers (cm ⁻¹)						
	O-H	C-H	C=O	C=C	C-C	Si-O	SiO ₃ ²⁻
CS	3449	-	-	-	-	1063, 874	1413
CaVS5	3449	3020,2985, 2877	-	1637	1126	1061, 876	1432
CaVS10	3449	3020,2985, 2877	-	1637	1126	1061, 876	1432
CaVS30	3449	3020, 2983, 2878	-	1637	1126	1061, 876	1432
CaPM5	3449	3025, 2985, 2865	1737	1637	1128	1062, 877	1433
CaPM10	3449	3025, 2985, 2865	1737	1637	1128	1062, 877	1433
CaPM30	3449	3025, 2985, 2865	1737	1637	1128	1062,876	1433

3.2. Thermal behavior and grafting yield of silane coupling agent onto surface of CS nanoparticles

TGA diagrams of unmodified and modified CS nanoparticles are shown in Figure 2. The unmodified CS nanoparticles had high thermo-oxidation stability. Their weight loss in the temperature range from room temperature to 700 °C was zero. From 700 to 750 °C, the weight of the unmodified CS nanoparticles was slightly lost (0.29 %). Some authors suggested that this weight loss was caused by the decomposition of organic residues [16, 17]. Besides, the cause might be due to the loss of hydroxyl groups on the surface of CS nanoparticles [18]. After modification, the thermo-oxidation stability of CS nanoparticles was reduced due to the

decomposition of organic moiety in the silane coupling agent in the temperature range from 430 to 750 °C [19, 20].

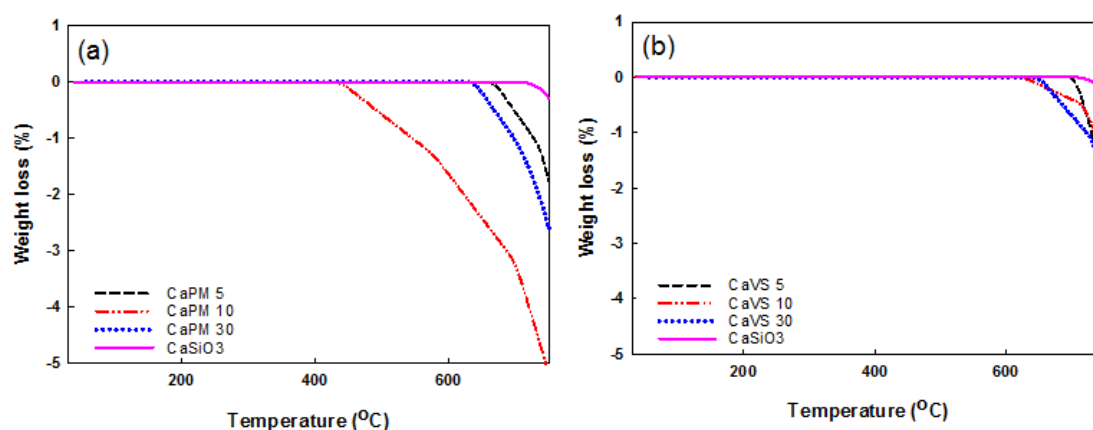


Figure 2. TGA diagrams of unmodified and modified CS nanoparticles, (a) CS nanoparticles modified with MPTS and (b) CS nanoparticles modified with VTMS.

Table 3. Weight loss, grafted silane coupling agent content and grafting yield of modified CS nanoparticles.

No.	Sample	Initial silane coupling agent content (%)	Weight loss at 750 °C (%)	Grafted silane coupling agent content (%)	Silane coupling agent grafting yield (%)
1	CS	0	0.29	0	0
2	CaVS 5	5	1.93	1.64	32.80
3	CaVS 10	10	1.42	1.13	11.30
4	CaVS 30	30	2.11	1.82	6.07
2	CaPM 5	5	1.76	1.47	29.40
3	CaPM 10	10	5.17	4.88	48.80
4	CaPM 30	30	2.61	2.32	7.73

From the TGA data, it could be calculated for the VTMS and MPTS content grafted onto the surface of the CS nanoparticles and the grafting yield of these silane coupling agents according to the following formula: grafting yield = $(W_2 - W_1) \times 100 / W_0$. Where, W_2 and W_1 are the weight loss of the modified and unmodified CS, respectively. $(W_2 - W_1)$ was also the content of silane coupling agents grafted onto the CS nanoparticles. W_0 was the initial weight of silane coupling agents. The grafting content and grafting yield are presented in Table 3. As can be seen from Table 3, the VTMS and MPTS content grafted onto the surface of CS nanoparticles and the grafting yield depended on the initial VTMS and MPTS content. Their grafting yield was the lowest with the initial VTMS and MPTS content of 30 wt.% among the investigated initial contents. This could be explained that at contents lower than 30 wt.%, VTMS or MPTS was grafted onto the surface of the CS nanoparticles and thus covering the surface of the CS nanoparticles. Hence, in spite of increasing the VTMS or MPTS content, they could not attach more onto the surface of the CS nanoparticles. The silane coupling agent residues could be polymerized or remain in the solution [19, 20].

Compared to the grafting yield VTMS, the grafting yield of MPTS onto the surface of the CS nanoparticles was higher. This might be explained that MPTS contained methacrylate while VTMS contained vinyl group. Hence, MPTS could be more active with the ester exchange reaction than VTMS. As a result, MPTS could achieve a high-performance reaction with the hydroxyl groups in the CS nanoparticles, leading to a higher grafting yield onto the surface of the modified CS nanoparticles. The CaPM 10 sample had the highest silane grafting yield, leveling off at 48.80 %.

3.3. Size distribution of modified CS nanoparticles

The size distribution of unmodified and modified CS nanoparticles is shown in Figure 3. The CS nanoparticles were dispersed in distilled water to determine the size distribution.

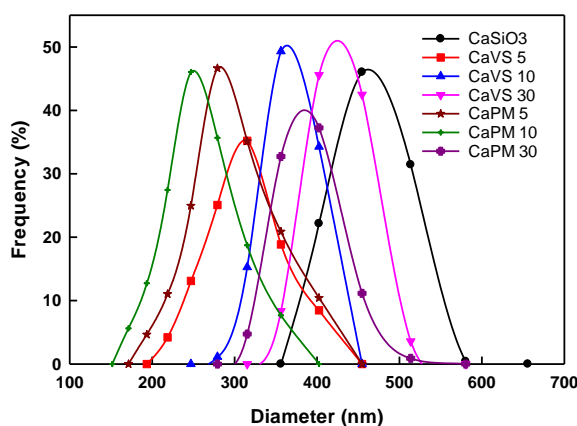


Figure 3. Size distribution diagrams of unmodified and modified CS nanoparticles.

It could be seen that the unmodified CS nanoparticles had the largest mean diameter. It suggested that the dispersion of the modified CS nanoparticles in distilled water was better than that of the unmodified CS nanoparticles. This could be explained by the decrease in the agglomeration of the CS nanoparticles after organo-modification. The CS nanoparticles modified with low silane coupling agent content had lower mean diameter than the CS nanoparticles modified with high silane coupling agent content. The reason could be that silane residues limit the dispersion of the modified CS nanoparticles in distilled water. The mean diameter of the CS nanoparticles modified with MPTS was smaller than that of the CS nanoparticles modified with VTMS at the same initial content. This is because the MPTS molecule has a longer hydrocarbon chain than the VTMS molecule. Consequently, the ability of MPTS to reduce agglomeration of the modified CS nanoparticles as well as improve their dispersion in distilled water was better. The CaPM 10 sample had the lowest mean diameter because of its highest grafting yield.

3.4. Morphology of modified CS nanoparticles

Figure 4 demonstrated FESEM images of the unmodified CS nanoparticles and CS nanoparticles modified with 10 wt.% of MPTS or VTMS at a magnification of 80,000. The unmodified CS nanoparticles had particle sizes in the range of 50 - 100 nm. They agglomerated together in the form of bigger clusters. The nanoparticles usually interact and adhere to each other due to their large charge density and high specific surface area. After modification with

silane coupling agents, the morphology and size of the CS nanoparticles did not change, but the agglomeration of these nanoparticles decreased. This could be explained that silane coupling agents grafted onto the surface of CS nanoparticles contributed to limiting the interaction and adhesion between the CS nanoparticles. As a result, the boundaries of modified CS nanoparticles were observed quite clearly. The distribution of CS nanoparticles modified with VTMS or MPTS was similar.

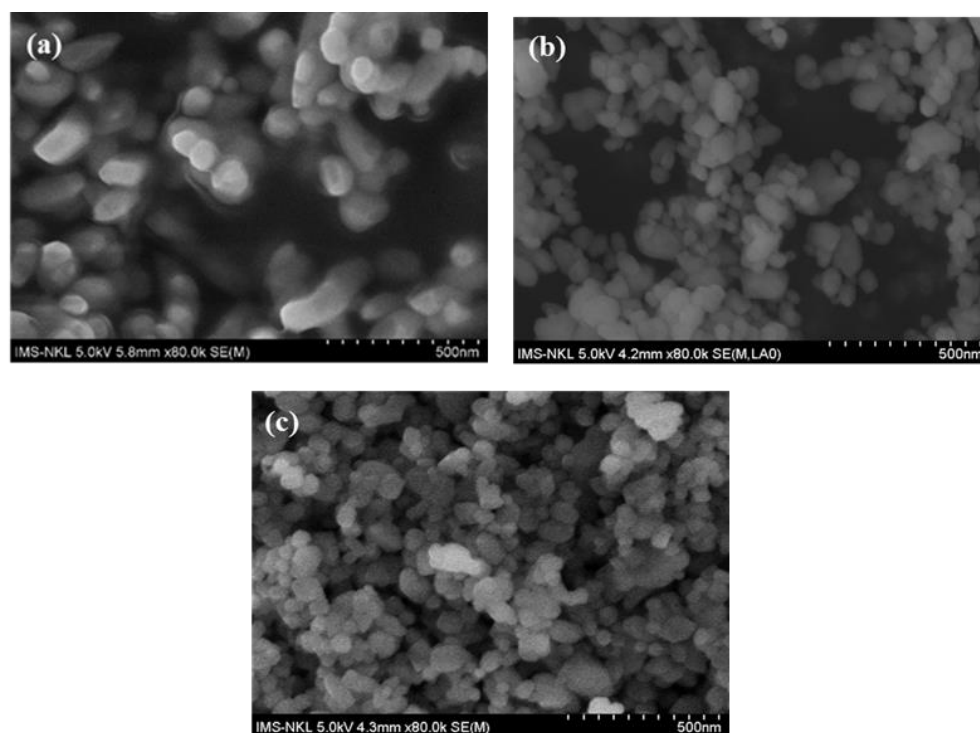


Figure 4. FESEM images of unmodified CS nanoparticles (a), CaPM 10 (b) and CaVS 10 (c).

3.5. Hydrophobic characteristic of modified CS nanoparticles

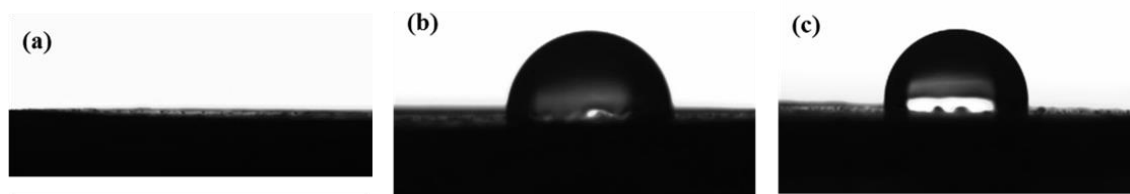


Figure 5. Images of water droplet on pellets' surface of unmodified CS nanoparticles (a), CS nanoparticles modified with 10 wt.% of VTMS (b), and CS nanoparticles modified with 10 wt.% of MPTS (c).

Figure 5 shows the images of water droplets on the pellet surface formed by unmodified and modified CS nanoparticles. It could be seen that the water droplet penetrated immediately onto the unmodified CS surface after dripping while it was kept on the surface of the modified CS nanoparticles. This suggested that the surface of CS nanoparticles became more hydrophobic after modification with MPTS or VTMS. The contact angle values of CaVS 10 and CaPM 10 nanoparticles were 84.81° and 88.58° , respectively. The improvement of hydrophobic

characteristics was an advantage of CS nanoparticles after organo-modification when dispersed into an organic polymer matrix which will be investigated in the near future.

4. CONCLUSIONS

In this study, CaSiO₃(CS) nanoparticles were successfully modified with two silane coupling agents, namely MPTS and VTMS. For instance, the functional groups of silane coupling agents including C-H, C=C, C=O, C-O, C-C groups were found in the IR spectra of treated CS nanoparticles. With the same initial content, MPTS had higher silane grafting yield on CS nanoparticle surface than VTMS. The highest MPTS grafting yield was 48.80 % with an initial content of 10 wt.%. The CS nanoparticles modified with MPTS exhibited better characteristics, i.e. smaller distribution size and slightly higher hydrophobicity, than the CS nanoparticles modified with VTMS. The suitable initial content of MPTS was 10 wt.% (compared to CS content) for modification of the CS nanoparticles. Compared to unmodified CS nanoparticles, modified CS nanoparticles had lower thermo-oxidation stability but better dispersion in distilled water. The modification of CS nanoparticles with the above silane coupling agents could reduce agglomeration of CS nanoparticles and improve hydrophobicity of the CS nanoparticles' surface.

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Credit authorship contribution statement. Nguyen Anh Hiep: setting up scientific content and receiving finance. Nguyen Thuy Chinh: data curation. Mai Duc Huynh: formal analysis. Dao Phi Hung: editing and revisions. Phung Thi Lan: formal analysis. Nguyen Tien Dung: writing original draft. Nguyen Thi Nga: investigation. Thai Hoang: setting up scientific idea, editing and revising the paper. All the authors have read and approved the final version of the manuscript.

Declaration of competing interest. The authors declare that they have no known competing financial interests or personal relationships that could have appeared to influence the work reported in this paper.

REFERENCES

1. Rangavar H., Khosro S. K., Javy M. T. - The effect of nano wollastonite on the fire resistance and the adhesion properties of water based acrylic coating on wood surface, Iranian journal of Wood and Paper Science Research **33** (2) (2018) 178.
2. Tiimob B. J., Rangari V. K., Jeelani S. - Effect of reinforcement of sustainable b-CaSiO₃ nanoparticles in bio-based epoxy resin system, Journal of Applied Polymer Science **131** (2014) 40867.
3. Sinkovec R., Music B. - Effect of organosilane coupling agents on thermal, rheological and mechanical properties of silicate-filled epoxy molding compound, Materials (Basel) **13** (1) (2020) 177.
4. Chen Q., Xiu-Yin Z., Bang-Shang Z., Kai-Li L., Jiang C., Xin-Jing Z. - The effect of CaSiO₃ nano-particles reinforced denture polymethyl methacrylate, Advanced Composites Letters **20** (1) (2011) 5-12.
5. Yu-rong Y., Qing-jie Z., Wei C., Mei-gui Y., LanX. - Formation and application of hierarchical calcium silicate-calcium sulfate whiskers, Materials & Design **146** (2018) 172-179.
6. Minet J., Abramson S., Bresson B., Sanchez C., Montouillot V., Lequeux N. - Newlayered

- calcium organosilicate hybrids with covalently linked organic functionalities, *Chemistry of Materials* **16** (2004) 3955-3962.
7. Minet J., Abramson S., Bresson B., Franceschini A., Van Damme H., Lequeux N. - Organic calcium silicate hydrate hybrids : a new approach to cement based nanocomposites, *Journal of Materials Chemistry* **16** (2006) 1379-1383.
 8. Franceschini A., Abramson S., Mancini V., Bresson B., Chassenieux C., Lequeux N. - New covalent bonded polymer–calcium silicate hydrate composites, *Journal of Materials Chemistry* **17** (2007) 913-922.
 9. Zheyu Z., Zhongping W., Yue Z., Yongqi W., Anming S. - Synthesis and structure of calcium silicate hydrate (C-S-H) modified by hydroxyl-terminated polydimethylsiloxane (PDMS), *Construction and Building Materials* **267** (2021) 18.
 10. Ohtsuki C., Miyazaki T., Kamitakahara M., Tanihara M. - Design of novel bioactive materials through organic modification of calcium silicate, *Journal of the European Ceramic Society* **27** (2007) 1527-1533.
 11. Liu Q., Ding J., Chambers D.E., Debnath S., Wunder S. L., Baran G.R. - Filler-coupling agentmatrix interactions in silica/polymethylmethacrylate composites, *Journal of Biomedical Materials Research* **57** (3) (2001) 384-93.
 12. Posthumus W., Magusin P. C. M. M., Brokken-Zijp J. C. M., Tinnemans A. H. A., Van der Linde R. - Surface modification of oxidic nanoparticles using 3-methacryloxypropyltrimethoxysilane, *Journal of Colloid and Interface Science* **269** (1) (2004) 109-125.
 13. Yu P., Kirkpatrick R. J., Poe B., McMillan P. F., Cong X. - Structure of calcium silicate hydrate (C-S-H): Near-, Mid-, and Far-Infrared spectroscopy, *Journal of the American Ceramic Society* **82** (3) (2004) 742-748.
 14. Lopes I. M. F., Abersfelder K., Oliveira P. W., Mousavi S. H., Junqueira R. M. R. - Flower-like silicon dioxide/polymer composite particles synthesized by dispersion polymerization route, *Journal of Materials Science* **53** (2018) 11367-11377
 15. Lin-Vien D., Colthup N. B., Fateley W. G., Grasselli J. G. - *The Handbook of infrared and raman characteristic frequencies of organic molecules*, Elsevier Inc., 1991 (ISBN 978-0-12-451160-6).
 16. Reddy M. V., Pathak M. - *In vitro* biological evaluations of Zn doped CaSiO₃ synthesized by sol–gel combustion technique -*Journal of Inorganic and Organometallic Polymers and Materials* **28** (2018) 2187-2195.
 17. Zhang Z., Shao H., Lin T., Zhang Y., He J., Wang L. - 3D gel printing of porous calcium silicate scaffold for bone tissue engineering, *Journal of Materials Science* **54** (2019) 10430-10436.
 18. Peng L., Qisui W., Xi L., Chaocan Z. - Investigation of the states of water and OH groups on the surface of silica, *Colloids and Surfaces A: Physicochemical and Engineering Aspects* **334** (2009) 112-115.
 19. Zhijian W., Xiang H., Taehoon K., Myung-Suk C., Kangtaek L. - Surface properties of submicrometer silica spheres modified withaminopropyltriethoxysilane and phenyltriethoxysilane, *Journal of Colloid and Interface Science* **304** (2004) 119-124.
 20. Hui P., Xiao Dong W., Sha Sha X., Lai Gui Y., Zhi Jun Z. - Preparation and characterization of TiO₂ nanoparticles surface-modified by octadecyltrimethoxysilane, *Indian Journal of Engineering and Materials Sciences* **20** (2013) 561-567.