Full Length Article

Thermal treatment to improve the hydrophobicity of ground CaCO$_3$ particles modified with sodium stearate

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ABSTRACT

The surface modification of calcium carbonate (CaCO$_3$) particles, which is used as a filler, significantly affects the properties of the composed materials. The effects of thermal treatment on ground calcium carbonate (GCC) particles subjected to hydrophobic modification using sodium stearate (RCOONa) were studied. The contact angle of the modified GCC particles increased from 24.7° to 118.9° when the amount of RCOONa added was increased from 0% to 5% and then decreased to 97.5° when the RCOONa content was further increased to 10%. When a large amount of RCOONa was added, RCOO$^-$ reacts with Ca^{2+} and generates (RCOO)$_2$Ca nuclei, which are adsorbed on the surface of the GCC particles, forming a discontinuous (RCOO)$_2$Ca modified layer. After thermal treatment under sealed conditions, the contact angle of the GCC particles modified using 1.5% RCOONa/GCC increased from 112.8° to 139.6°. The thermal stability of the (RCOO)$_2$Ca modified layer was increased, with the temperature increase of the mass-loss peak from 358.0 to 463.0 °C. It is confirmed that the spreading of melted (RCOO)$_2$Ca nuclei on the surface of the GCC particles during the thermal treatment increased the continuity of the modified layer, converting the physical adsorption of the (RCOO)$_2$Ca nuclei into chemisorption. The grafting density of RCOO$^-$ on the GCC particle surface after thermal treatment approximates to 5.00/nm^2, which is close to the single-molecular-layer grafting density of RCOO$^-$, indicating that excellent modification was achieved.

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1. Introduction

Calcium carbonate particles are widely used as fillers in materials such as rubbers, plastics, and paints [1–3], and the ground calcium carbonate (GCC) is over 80% of the total consumption. CaCO$_3$ particles are very adhesive and easy to agglomerate, resulting in poor dispersion in organic matrices. The poor affinity of hydrophilic CaCO$_3$ particles in a non-polar organic matrix is detrimental to the properties of the composite materials. Therefore, it is necessary to produce CaCO$_3$ particles with hydrophobic surfaces through modification, in order to improve their affinity and dispersion in the organic matrices. Commonly used modifiers for CaCO$_3$ particles include silane coupling agents [4,5], titanate coupling agents [6], and fatty acids and their salts [7–9]. In particular, stearic acid and its salt are popular modifiers [10,11].

Modification methods include the dry route [12], solvent route [13,14], and aqueous route [15–18]. The dry route involves addition of the modifier during the dry grinding of CaCO$_3$ particles, and addition of the modifier under high-speed stirring [19,20]. In the solvent route, CaCO$_3$ particles are dispersed in a solvent containing a modifier. Methanol, hexane, xylene, and ethyl acetate are typically used as solvents for this process [21,22]. However, the solvent route has disadvantages related to solvent recovery, possible contamination of the product, and environmental pollution, and is thus rarely used in industry. The aqueous method is carried out in an aqueous solution containing a modifier under stirring conditions. Ukrainczyk [23], Tran [24] and Barhoum [25] et al. carbonized Ca(OH)$_2$ in modifier solutions to prepare hydrophobic calcium carbonate. Since the precipitated CaCO$_3$ (PCC) is synthesized in an aqueous solution, the aqueous route is more convenient for PCC modification, but is rarely used for the modification of GCC particles. GCC particles with a smaller size are produced via a wet grinding process and show excellent performance in a variety of applications; thus, the aqueous route for these particles is expected to be effective for their hydrophobic modification.

In the existing modification processes, the contact between the particle surface and the modifier is poor. In the dry route, the nano, submicro, or micro particles usually form large agglomerates, which may contain millions of particles or more. Many particles do not contact the modifier droplets or molecules during the entire modification process. As a result, uniform surface modification of the primary CaCO$_3$ particles is not achieved, resulting in a low den-

sity grafting of the modifier onto the particle surface. In the solvent method, the hydrophilic GCC particles are poorly dispersed in the non-polar organic solvents as primary particles, and the hydrophobic modifier in the solvent is unable to diffuse into the hydrophilic agglomerates, leading to a diffusion control problem. In the aqueous route, the $CaCO_3$ particles are easily dispersed as primary particles and the hydrophilic surface modifier is easily dispersed as single molecules. However, the boiling point of water ($100\,°C$) restricts the reaction temperature. In aqueous solutions, the modifier molecules may undergo homogeneous nucleation reactions, forming nano-nuclei, which are then adsorbed on the $CaCO_3$ particle surface, resulting in poor modification. In our previous research, APTES [26] and SDS [27] were used to modify the SiO_2 surface at a high grafting density by aqueous mixing, spray drying, and thermal treatment. The homogeneous mixing of hydrophilic particles and modifiers in the aqueous route, and the enhanced reaction at a high temperature in the dry route were well combined.

In this study, $CaCO_3$ particles obtained from wet-grinding were modified by aqueous mixing with sodium stearate, and subsequently subjected to thermal treatment after drying. The reaction of GCC particles and sodium stearate in the slurry was studied. The effects of thermal treatment on the hydrophobicity of the modified GCC particles and the behavior of stearic acid salt on the modified GCC particles were investigated.

2. Experimental

2.1. Reagents

Commercial $CaCO_3$ particles produced in a wet-grinding process (GCC, Guangyuan chemical Co. Ltd., Jiangxi, China), with an average particle size of $2.39\,\mu m$ and BET specific surface area of $6.15\,m^2/g$ (measured under N_2 at $77\,K$) were used. The pH of its water suspension was 9.1. Analytical reagent (AR) grade sodium stearate ($C_{17}H_{35}COONa$) was used.

2.2. Modification process

GCC particles ($100\,g$) were added to deionized water ($200\,mL$) in a beaker and mechanically stirred to obtain a uniform dispersion. A set amount of sodium stearate (RCOONa) was added to the deionized water ($100\,mL$) and maintained at $80\,°C$ in a water bath, in order to dissolve the RCOONa. The aqueous solution of RCOONa was added to the GCC slurry under mechanical stirring for 1 h in a thermostatic water bath at $80\,°C$; the pH of the slurry was monitored and recorded. Then, the suspension was filtered and dried at $105\,°C$ for 24 h. Thereafter, GCC particles were added to a sealed tube or crucible and placed in a muffle furnace for thermal treatment at a set temperature for a set time.

2.3. Characterization

The morphology of the GCC particles was examined using a high-resolution scanning electron microscope (SEM, JSM7401, JEOL, Japan). Nitrogen adsorption and desorption isotherms at $77\,K$ were measured for the GCC particles, using an automated gas sorption instrument (Quantachrome AUTOSORB-1, USA). The specific surface area of the GCC particles was calculated according to the BET equation. The amount of $RCOO^-$ grafted on the GCC particles was determined by a thermogravimetric analyzer (TGA/DSC 1, Mettler-Toledo, Switzerland). For the TG analysis, the heating rate was $20\,K/min$ from $30-900\,°C$ under a flow of nitrogen. The TG analysis for mass loss measurement has a precision of 0.01%. Three tablets were prepared by pressing the GCC particles in a model under $12\,MPa$, then the contact angle of water droplet on each tablet was measured once the droplet was dropped on the surface using a contact angle analyzer (HARKE-SPCA, Beijing Harke, China). The average value of the three measurements was taken as the contact angle of the sample.

3. Results and discussion

3.1. Contact angle of modified GCC particles

During aqueous mixing under mechanical stirring, the GCC particles are assumed to be dispersed as primary particles and RCOONa as molecules; thus, the contact between the GCC particles and RCOONa is expected to be in an ideal state in the mixture. In the absence of thermal treatment, the contact angles of the GCC particles modified with different amounts of RCOONa are listed in Table 1. As the amount of RCOONa added increased from 0–5.0%, the contact angle of the modified GCC particles increased from $24.7°$ to $118.9°$. However, as the added amount was further increased to 10%, the contact angle decreased to $97.5°$. Thus, the surface of the GCC particles changed from hydrophilic to hydrophobic in the aqueous mixing process, but the maximum contact angle attained is $118.9°$.

Fluorine, with its small atomic radius and the highest electronegativity among the atoms, is effective for chemically lowering the surface free energy. When the solid surface is modified with a continuous uniform monolayer of n-perfluoroeicosane, the $-CF_3$ groups are expected to achieve the lowest surface free energy of the materials, with the maximum contact angle for a completely flat surface, $119°$ [28]. Considering the rough surface produces higher contact angle of the hydrophobic surface than the flat surface [29,30], the contact angle of the modified rough surface is expected to be higher if the modifier was well-grafted onto the surface. For the GCC particles modified by 1.5% RCOONa/GCC, thermal treatment was carried out at $220\,°C$ for 60 min under sealed conditions with anaerobic environment to restrain the oxidation of $RCOO^-$. The contact angles of the unmodified and modified GCC particles were quite different before and after thermal treatment, as shown in Fig. 1. The contact angle of the unmodified GCC particles is $24.7°$, which increases to $112.8°$ after aqueous mixing, and reaches $139.6°$ after thermal treatment.

Fig. 1 indicates that the contact angle of the modified GCC particles increases significantly after thermal treatment, reaching a high hydrophobicity. In order to design a rational thermal treatment process, the modified GCC particles after aqueous mixing (1.5% RCOONa/GCC) were thermally treated under sealed and open conditions. Under the sealed condition, the sealed tube was fully filled with GCC particles, which was approximated to an anaerobic environment. The open condition was considered as an environment containing sufficient oxygen.

For a fixed thermal treatment time of 30 min, the contact angle of the GCC particles was measured at different temperatures, as shown in Fig. 2. Under sealed conditions, the contact angle of the modified GCC particles was maintained at $\sim130°$ when the thermal treatment temperature was lower than $350\,°C$; above this temperature, the contact angle decreased. Under open conditions, the contact angle of the modified GCC particles remained at $\sim115°$ after thermal treatment at temperatures lower than $250\,°C$; above this temperature, the contact angle dropped sharply. This is because the organic chain of $(RCOO)_2Ca$ decomposes at $380-500\,°C$ under N_2 atmosphere (sealed conditions), and is thermally oxidized at $180-330\,°C$ in air (open conditions) [31]. Thus, the thermal treatment temperature affects the reaction of the modifier on the GCC particle surface and the contact angle of the modified GCC particles significantly. The optimum thermal treatment temperature range for the GCC particles after aqueous mixing is $180-220\,°C$.

Table 1
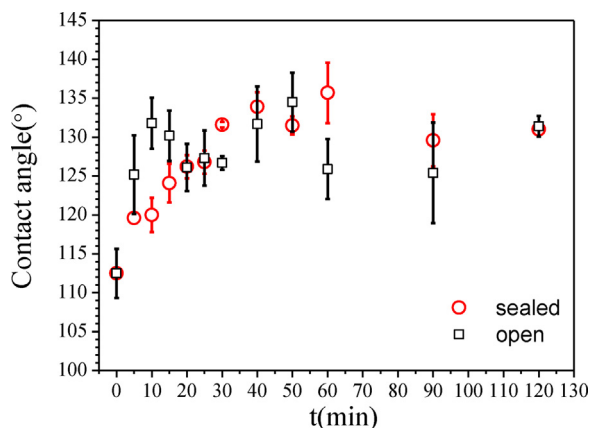Contact angle of the GCC particles after aqueous mixing with different amounts of RCOONa (at 80 °C).

Amount of RCOONa added (%)	0	0.5	1.0	1.5	2.0	5.0	10.0
Contact angle (°)	24.7 ± 1.5	59.0 ± 2.5	95.3 ± 2.3	112.8 ± 1.8	115.8 ± 1.2	118.9 ± 1.0	97.5 ± 2.5

Fig. 1. Contact angle of GCC particles (a) unmodified; (b) after aqueous mixing with RCOONa; (c) with thermal treatment (220 °C, 60 min) after aqueous mixing.
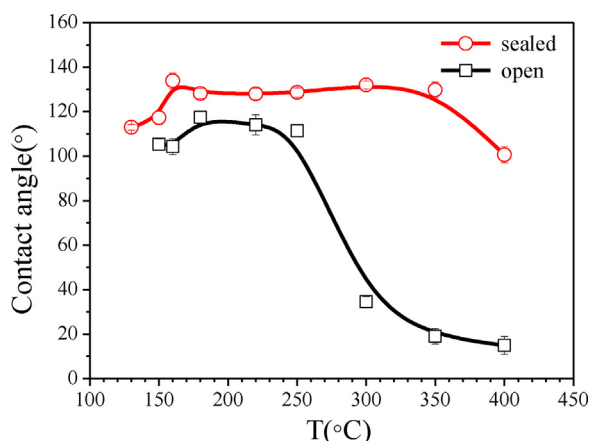
Fig. 2. Contact angle of modified GCC particles vs. thermal treatment temperature under sealed and open conditions (1.5% RCOONa/GCC).

Fig. 3. Contact angle of GCC particles vs. thermal treatment time under sealed and open conditions (1.5% RCOONa/GCC).
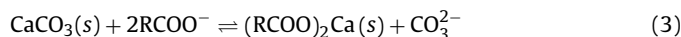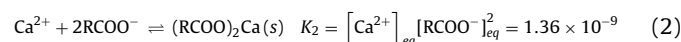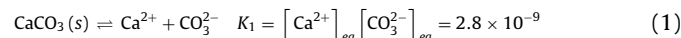
The contact angle of the modified GCC particles changes with the duration of thermal treatment at 220 °C, as shown in Fig. 3. The variation of contact angle with the duration of thermal treatment was found to be similar under sealed and open conditions. In the range 0–50 min, the contact angle of the modified GCC particles increases from 110–135° with the increase of thermal treatment time. In the range 50–120 min, the contact angle no longer increases, but fluctuates between 125° and 135°. This shows that the contact angle of the modified GCC particles increases significantly after thermal treatment for 50 min, reaching excellent hydrophobicity.

3.2. Aqueous mixing of RCOONa and GCC particles

The surface morphology of the modified GCC particles with different added amounts of RCOONa is shown in Fig. 4. The unmodified GCC particles possessed a smooth surface, which was coated with a large number of nanoparticles after modification by aqueous mixing with 2% RCOONa. When the amount of RCOONa added was further increased to 10%, the GCC particle surface was coated with a discontinuous layer. It is inferred that at high saturation, the $(RCOO)_2Ca$ nuclei formed a discontinuous layer of $(RCOO)_2Ca$ on the surface of the GCC particles. Since the contact angle of the pure $(RCOO)_2Ca$ reagent is measured as ~75.2°, it is inferred that the addition of a large amount of RCOONa mainly formed a discontinuous coating layer rather than the monomolecular grafting; as a result, the contact angle of modified GCC particles does not continue to increase.

For further analysis, the aqueous mixing process of RCOONa and the GCC particles was studied. Two solutions of RCOONa (2% and 10%) were prepared in 150 mL of deionized water, and the GCC particles were dispersed in each of them. The initial pH values of the GCC slurry and RCOONa solution were about 9.10 and 9.80, respectively.

In the GCC slurry, a dissolution-precipitation equilibrium of Ca^{2+} was attained as Eq. (1). When the concentration of RCOONa reaches supersaturation, Eqs. (2) and (3) occur in the bulk phase. K_1 and K_2 are the equilibrium constants in Eqs. (1) and (2), respectively. The supersaturation of RCOONa was calculated from K_1 and K_2, using Eq. (4). Considering that CO_3^{2-} is more alkaline than $RCOO^-$, a change in the pH of the slurry indicates whether reaction Eq. (3) occurs or not, along with the degree of the reaction. The pH change in the mixing process of the GCC particles and RCOONa was recorded, as shown in Fig. 5.

$$CaCO_3(s) \rightleftharpoons Ca^{2+} + CO_3^{2-} \quad K_1 = \left[Ca^{2+}\right]_{eq}\left[CO_3^{2-}\right]_{eq} = 2.8 \times 10^{-9} \quad (1)$$

$$Ca^{2+} + 2RCOO^- \rightleftharpoons (RCOO)_2Ca(s) \quad K_2 = \left[Ca^{2+}\right]_{eq}[RCOO^-]_{eq}^2 = 1.36 \times 10^{-9} \quad (2)$$

$$CaCO_3(s) + 2RCOO^- \rightleftharpoons (RCOO)_2Ca(s) + CO_3^{2-} \quad (3)$$

$$S = \frac{\left[Ca^{2+}\right]_{eq}[RCOO^-]^2}{\left[Ca^{2+}\right]_{eq}[RCOO^-]_{eq}^2} = \frac{\left[RCOO^-\right]^2}{\left[RCOO^-\right]_{eq}^2} \quad (4)$$

The supersaturation, S, of RCOONa was 1.06 when 2% RCOONa was added, and the pH of the mixture was 9.73 (at the moment of mixing), which was in the same range as the GCC slurry (9.12) and RCOONa solution (9.80). There was no rapid increase in pH value, indicating that the reaction in Eq. (3) did not occur to a significant extent after mixing. When 10% RCOONa was added, the supersaturation of RCOONa was 26.51 and the mixture pH increased rapidly
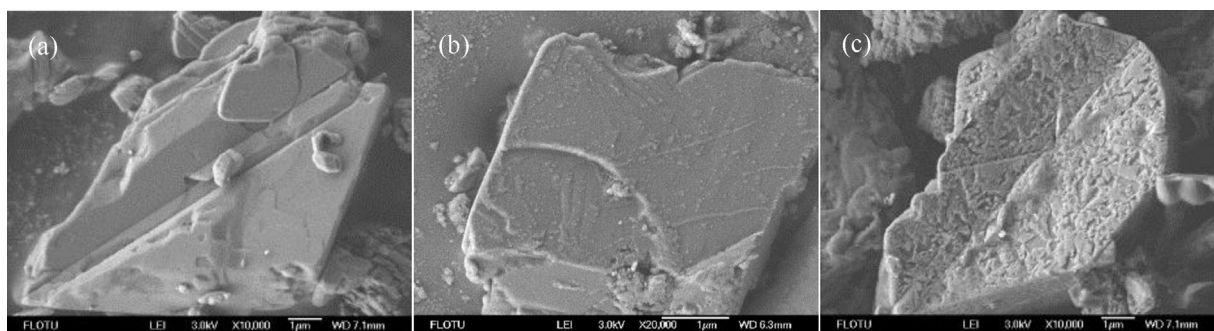
Fig. 4. SEM images of the GCC particles modified with different amounts of RCOONa (a) 0; (b) 2%; (c) 10%.
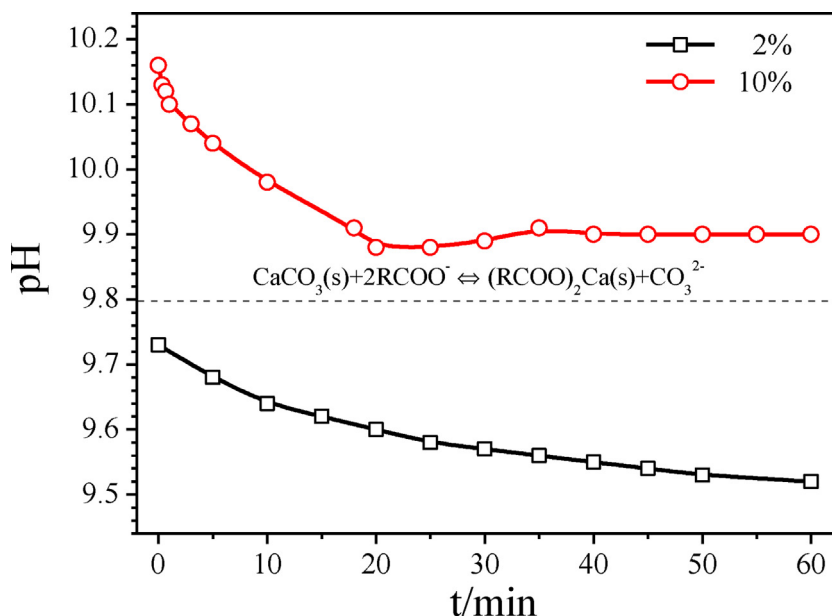

Fig. 5. pH change of the RCOONa and GCC mixture in the aqueous mixing process (at 80 °C).

to 10.16 at the initial moment of mixing, which indicated the formation of CO_3^{2-}; this confirmed the occurrence of Eq. (3) after mixing.

As the mixing occurred, the mixture pH decreased for both 2% and 10% RCOONa. In the case of 2% RCOONa, the unreacted $RCOO^-$ was gradually adsorbed onto the GCC particle surface and its activity decreased, resulting in a decrease in the mixture pH. After mixing for 60 min, the pH became stable, indicating that the adsorption reached equilibrium. In the case of 10% RCOONa, the decrease of $RCOO^-$ activity due to adsorption onto the GCC particle surface also resulted in the left shift of Eq. (2), i.e., the increase of Ca^{2+} concentration and the decrease of CO_3^{2-} concentration, leading to a decrease of the mixture pH. The pH became stable after mixing for 25 min. It is inferred that high concentration of RCOONa results in high reaction rate and short equilibrium time. Furthermore, as Eq. (3) occurred in the case of 10% RCOONa and increased the CO_3^{2-} concentration, the equilibrium pH value of 10% RCOONa was higher than that of 2% RCOONa.

It is summarized that two reactions occur on the GCC particle surface when RCOONa is added: (1) At low supersaturation of $RCOO^-$, the $RCOO^-$ ions move to the vicinity of the GCC particles and react with the Ca^{2+} on the GCC particle surface, producing $Ca(HCO_3)OOCR$ or $\equiv CaOOCR$ [23,24,32], where $\equiv Ca$ is the calcium ion on the surface. (2) At high supersaturation of $RCOO^-$, $RCOO^-$ reacts with Ca^{2+} in the bulk phase to form the insoluble

salt $(RCOO)_2Ca$, which precipitates on the GCC particle surface and forms a discontinuous coating layer, as shown in Fig. 4c.

3.3. Effect of thermal treatment on the hydrophobicity of the modified GCC particles

Our investigations revealed that modulation of the aqueous mixing conditions yields a maximum contact angle of 118.9° for the modified GCC particles, while thermal treatment increased the contact angle to 139.6°. In order to reveal the mechanism of thermal treatment, and its relationship with the contact angle of the modified GCC particles, their characteristics before and after thermal treatment were analyzed.

Since the melting point of calcium stearate nanoparticles is ~150 °C, the $(RCOO)_2Ca$ on the GCC particle surface melts during thermal treatment at higher temperatures. The melted $(RCOO)_2Ca$ spreads again on the GCC particle surface, increasing the continuity of the coating layer. As shown in Fig. 6, after thermal treatment at 220 °C for 30 min, the GCC particle surface displays a partially continuous coating layer. After 60 min of thermal treatment, the GCC particle surface exhibits a completely continuous $(RCOO)_2Ca$ coating layer.

As reported in the literatures [23,32], calcite predominantly consists of rhombohedral {104} planes with a surface density of 5.05 Ca^{2+} ions/nm^2, on which $RCOO^-$ was chemisorbed with a tilt of 7%. $RCOO^-$ reacts with calcite through the formation of site-specific
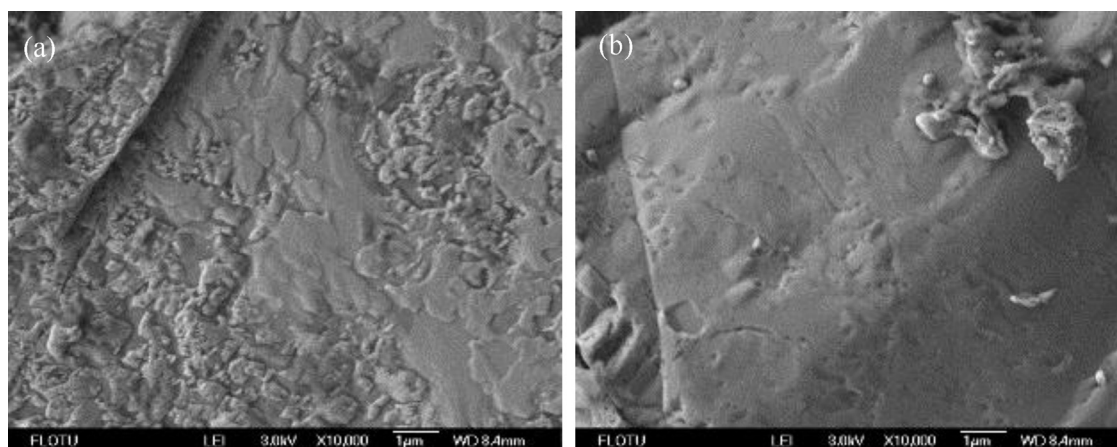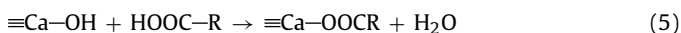
Fig. 6. SEM images of 10% RCOONa modified GCC particles after thermal treatment at 220 °C (a) 30 min; (b) 60 min.

bonds between the surface calcium ions and the oxygen from the carboxyl group, which is described by the reaction,

$$\equiv Ca\!-\!OH + HOOC\!-\!R \rightarrow \ \equiv Ca\!-\!OOCR + H_2O \tag{5}$$

where, $\equiv Ca$ is the calcium ion on the surface, and R is the alkyl chain. Therefore, the theoretical density of a monolayer of RCOO$^-$ on the GCC particle surface is calculated to be 4.70/nm^2. For the GCC particles with the BET specific surface area measured to be 6.15 m^2/g, the modification density of 4.70/nm^2 corresponds to 1.36% in mass.

In order to analyze the effects of thermal treatment on the GCC coating layer further, the modification of GCC particles with 1.5% RCOONa/GCC in mass was conducted under different treatments. The thermogravimetric (TG) analysis of the samples under N$_2$ atmosphere was shown in Fig. 7. At temperatures below 200 °C, the free water and part of the hydroxyl groups on the GCC particle surface were removed in TG analysis [33]; no difference was observed in the derivative thermogravimetry (DTG) curves for the unmodified sample and modified samples, with and without thermal treatment. In the temperature range 200–300 °C, the modified sample without thermal treatment shows a mass-loss peak at ~250 °C, resulted from the entrainment of liquid RCOONa (liquid phase: 150–359.4 °C) spread on the GCC particle surface due to N$_2$ stripping during TG analysis. The modified GCC samples after thermal treatment do not show the mass-loss peak of free RCOONa, which was converted to physically adsorbed or chemically reacted RCOO$^-$ on the GCC particle surface during thermal treatment. In the temperature range 300–400 °C, the modified GCC sample before thermal treatment shows a high mass-loss peak at 358.0 °C, which is assigned to the evaporation of the physically adsorbed RCOONa (boiling point of RCOONa: 359.4 °C) and (RCOO)$_2$Ca nanoparticles formed in the bulk phase. The modified sample after thermal treatment for 5 min has a mass-loss peak at a higher temperature of 382.0 °C and its fraction decreases. In the temperature range 400–550 °C, the mass loss is assigned to the decomposition of RCOO$^-$. The modified sample before thermal treatment alone has a slight mass-loss peak, attributed to the reaction of RCOONa on the GCC particle surface. The modified sample after thermal treatment for 5 min displayed both the temperature peak of the mass loss and the mass fraction increase; after 50 min of thermal treatment, the peak of mass loss increases to a high temperature of 463.0 °C and a very high fraction, which can be assigned to a large amount of chemical grafting. This indicates that thermal treatment produces more RCOONa molecules that are grafted onto the GCC particle surface. In addition, the chemical grafting also increases the stability of the modified GCC particles. When the modified GCC particles are filled in an organic matrix such as PVC, they undergo a high temperature mixing process at ~300 °C. The increase in thermal stability of

Table 2
Mass loss of different modified GCC particles in TG analysis (1.5% RCOONa/GCC).

Samples	Mass loss (%)		
	200–300 °C	300–400 °C	400–550 °C
1$^\#$ (unmodified)	0.30	0.26	0.76
2$^\#$ (modified)	0.47	0.93	0.88
3$^\#$ (thermal treatment for 5 min)	0.23	0.62	0.89
4$^\#$ (thermal treatment for 50 min)	0.05	0.16	1.58

the modified GCC particles can eliminate the foaming phenomenon in GCC-organic matrix composites, which improves the composite performance.

The mass loss in different temperature ranges for modified GCC samples (1.5% RCOONa/GCC) is listed in Table 2. For unmodified particles (sample 1$^\#$), the mass loss in 200–550 °C is resulted from the removal of the free water and the hydroxyl groups on the GCC particle surface in TG analysis. For modified GCC particles before thermal treatment (sample 2$^\#$), compared to the unmodified sample, the increase in mass loss is mainly in the temperature ranges 200–300 °C and 300–400 °C, and a little in temperature range 400–550 °C. It indicates that the hydrophilic terminal of RCOONa reacts partially with Ca^{2+} on the GCC particle surface in the aqueous mixing process, and most of the RCOONa and the (RCOO)$_2$Ca are just mixed with or physically adsorbed on the GCC particle surface. In the mixture, some hydrophilic terminals of RCOONa and (RCOO)$_2$Ca are also outward, so the contact angle does not increase even upon addition of 10% RCOONa.

For the modified GCC particles after thermal treatment for 5 min (sample 3$^\#$), the mass loss in the ranges of 200–300 °C and 300–400 °C decreases and the mass loss in temperature range 400–550 °C increases. It is analyzed that two factors result in the change of the mass loss. One is the gradually removal from the free water and hydroxyl groups on the GCC surface as the thermal treatment time increases. The other is that the high temperature causes the unreacted RCOONa and (RCOO)$_2$Ca nanoparticles to melt, migrate, and get distributed more uniformly on the GCC particle surface, and converts more RCOO$^-$ from physical adsorption (300–400 °C) to chemical grafting (400–550 °C) on the GCC particle surface, resulting in an increase in the mass loss in temperature range 400–550 °C. For modified GCC particles after thermal treatment for 50 min (sample 4$^\#$), the change of the mass loss is more obvious, and the mass loss in temperature range 200–300 °C (0.05%) due to the removal of the hydroxyl groups is only one-sixth of mass loss of the unmodified particles (sample 1$^\#$, 0.30%). For simplifying the analysis, the mass loss of the hydroxyl groups in temperature range 400–550 °C for the sample 4$^\#$ is also assumed to be one-sixth
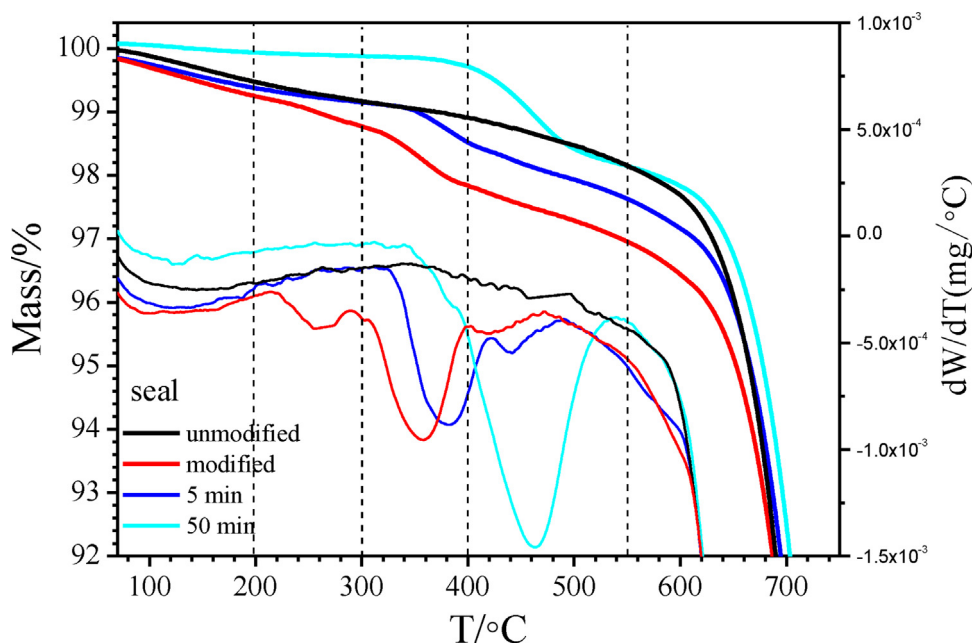
Fig. 7. TG and DTG curves of the GCC particles for different duration of thermal treatment, under sealed conditions (1.5% RCOONa/GCC).
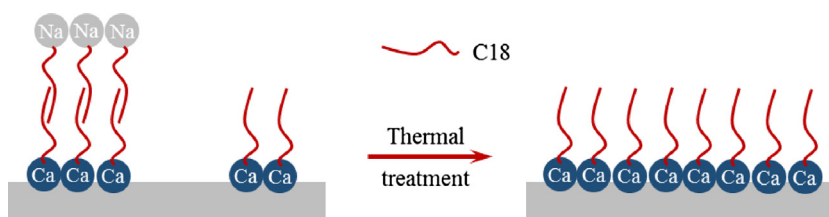

Fig. 8. Effect of thermal treatment on the surface structure of RCOONa modified GCC particles.

of the sample 1# (0.76%), i.e., 0.13%, then the mass loss of chemical grafted RCOO⁻ (400–550 °C) is estimated to be 1.45%. From the molecular weight of RCOO⁻ (283.5 g/mol) and the specific surface area of GCC particles (6.15m²/g), the grafting density of RCOO⁻ on the modified GCC particle surface is calculated as 5.00/nm². This density is close to the theoretical grafting density of RCOO⁻ in the monomolecular layer (4.70/nm²), and the mass loss of physically adsorbed RCOO⁻ (300–400 °C) is very low. It indicates that more RCOO⁻ on the GCC particle surface is grafted in a monomolecular layer as the thermal treatment time increases.

As can be seen from Fig. 7 and Table 2, before thermal treatment, the physical adsorption and chemical grafting RCOO⁻ coexists on the GCC particle surface, and there exist three states, i.e., multilayer, monolayer, and bare. After thermal treatment, the amount of physically adsorbed RCOO⁻ (300–400 °C) decreases and chemical grafting RCOO⁻ (400–550 °C) increase as the thermal treatment time increases. The thermal treatment causes the hydrophobic RCOO⁻ layer on the GCC particle surface to become uniform and the hydrophobic C long chain is uniformly outward, thus enhancing the hydrophobicity of the modified GCC particles, as shown in Fig. 8.

4. Conclusions

GCC particles were modified with RCOONa and reached a high hydrophobicity via aqueous mixing and subsequent thermal treatment. When the amount of RCOONa added was increased from 0 to 5%, the contact angle of the modified GCC particles before thermal treatment increased from 24.7° to 118.9°. As the added amount of

RCOONa increased to 10%, the contact angle no longer increased but decreased to 97.5°. Subsequent thermal treatment enhanced the reaction of RCOONa on the GCC particle surface, increasing the hydrophobicity of the modified GCC particles significantly. The contact angle of the GCC particles modified with 1.5% RCOONa/GCC increased from 112.8° to 139.6° after thermal treatment at 220 °C for 60 min.

In aqueous mixing, when RCOO⁻ is supersaturated, RCOO⁻ reacts with Ca²⁺ ions and produces the insoluble salt, (RCOO)₂Ca, which precipitates on the GCC particle surface and forms a discontinuous coating layer; this limits the contact angle of the modified GCC particles at ∼118°. Thermal treatment causes the (RCOO)₂Ca to melt and spread out on the GCC particle surface, increasing the uniformity of the coating layer. The grafting density of RCOO⁻ on GCC particle surface after thermal treatment for 50 min approximates to 5.00/nm², close to the reported theoretical monomolecular layer grafting density of RCOO⁻. As the thermal treatment time increases, more RCOO⁻ on the GCC particle surface is grafted in a monomolecular layer. Moreover, the thermal treatment also increases the thermal stability of the modified layer, with the temperature increase of the mass-loss peak from 358.0 to 463.0 °C.

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