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## Encapsulation Method for CaCO<sub>3</sub> Nanoparticles

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**Abstract:** In this study, a simple wet encapsulation method was used to coat the nano calcium carbonate particles at the temperature of 80°C. Stearic acid was used as the coating agent at 3, 6 and 9 wt%. Analysis of SEM images indicates that agglomeration can be reduced significantly by using 3wt% amount of SA. TGA analysis proved that the coated nanoparticles has the same stability with uncoated particles at temperature below 230°C. XRD peaks show that coating has no effect on crystallization and there was no phase change after coating. Lowest surface area of 22.9 m<sup>2</sup>/g was obtained from BET analysis when coating was done at 3wt % SA. The DRIFT analysis also showed that it can be successfully used to investigate the change of molecules structure after coating. XPS data showed that the carbon surface element increased significantly with increasing amount of SA used for coating.

**Key words:** Nanoparticles, calcium carbonate, stearic acid, agglomeration, surface area

### INTRODUCTION

In many industrial processes, CaCO<sub>3</sub> are very commonly used as filler material and in plastic processing to enhance mechanical and physical properties of finished products. Micron size particles are used for this purpose but attention is not being focused on nano CaCO<sub>3</sub> particles with particle size less than 100nm. Studies have proven that use CaCO<sub>3</sub> nano particles increase the mechanical properties of products (Jiang *et al.*, 2005; Chan *et al.*, 2002). Some studies also suggest that coated nano CaCO<sub>3</sub> particles improves the mechanical strength of plastics further due to reduced agglomeration of nano particles introduced during the plastic processing stage. The improvement was also attributed to better dispersion of coated nano particles in the plastic matrix (Di Lorenzo *et al.*, 2002). On the other hand, coating of nano particles poses its own challenges. The parameters that determine the coating success are type of coating agent, coating method, coating material to nano particle ratio and coating temperature (Rothon, 2003).

Coating agent is chosen based on the inertness and ability for the agent to bond itself with the CaCO<sub>3</sub> and stearic acid is one good choice with these characteristics (Parirer *et al.*, 1984; Fekete *et al.*, 1990; Moczo *et al.*, 2004; Pukanszky *et al.*, 1999; Rothon, 1999; Maged and Ulrich, 2002).

However one of the crucial treatments is the amount of coating material used. The optimum amount to be used depends on the type of the interaction, the size of the

treating molecule, its alignment to the surface and other factors. Determination of the optimum amount of coating material is essential for the efficiency of the treatment. Insufficient amount of coating material does not bring about the desired effect, while excessive amounts lead to processing problem.

As for the choice of the temperature, theoretically the coating can be conducted at anywhere in between the melting and vaporization temperature of stearic acid as long as the stability of nano particles are not effected. In this Study 80°C was chosen for practical reason where the melting of stearic acid can be done with a water bath.

The aim of present study was to investigate the optimal coating of stearic acid on nano precipitated calcium carbonate (NPCC). The effect of stearic acid was evaluated by comparing the surface characteristics of NPCC before and after the modification with various weight % of stearic acid.

### MATERIALS AND METHODS

**Materials:** The nano precipitated calcium carbonate (NPCC-111) was obtained from NanoMaterials Technology (Singapore Ltd.). The calcium carbonate particulates are in cubic shape with an average primary particle size of ~40nm. It was delivered in wet cake form (with 50wt% water content). The stearic acid used in this experiment was supplied by Cognis Oleochemicals (M) Sdn. Bhd with 98% purity.

**Table 1: The summary of analysis done on coated particles**

No.	Parameters determined	Equipment/method
1	To investigate the morphology of particles	SEM
2	It is used for identifying the crystalline phases present in solid materials and powders and for analyzing structural properties of the phases	XRD
3	To measure surface area	BET
4	To determine the thermal stability	TGA
5	To examines particle size (higher resolution than SEM).	TEM
6	To study comparative changes in a series of spectra that gives detail structure of molecules and chemical grouping present in molecule. It is surface sensitive and thus provide for assessing how much additive (SA) actually on the CaCO <sub>3</sub> surface	DRIFTS
7	To determine chemical composition of filler surfaces	XPS

**Encapsulation method:** NPCC filter cake and de-ionized water were added into a beaker. The mixture was sheared to form slurry using a mixer agitated at 1500 rpm. An appropriate amount of melted stearic acid was then added drop-wisely in about 5 minutes period to the slurry of NPCC, which was maintained at 80°C and homogenized continuously throughout the addition. Then, the uncoated and coated NPCC was filtered off, washed with water and oven dried at 65°C for 24 h. The oven dried filter cake was then de-agglomerated in a centrifugal ball mill (7 h @ 350 rpm). A white powder was obtained which was the surface coated NPCC with SA. By changing the proportion of SA added to NPCC, a series of samples were prepared

## RESULTS AND DISCUSSION

**SEM images:** Figure 1 shows the SEM images obtained for uncoated particles (a) 0%, (b) 3%, (c) 6 and 9% coated (d) particles. From these images it can be seen that the size of agglomerates are the smallest at 3% coating. Increase in coating material from 3 to 6 and 9% stearic acid does not reduce agglomeration. Therefore the optimal amount of stearic acid needed to cover the surface of NPCC with stearic acid molecule lies between 3 and 6wt% of SA. The images also prove that SEM can be used to study the effect of coating the nanoparticles on agglomeration, which is the primary concern in obtaining the advantageous of nanoparticles for filler application.

**TEM images:** The morphology analysis of CaCO<sub>3</sub> nanoparticles were conducted by using TEM. Figure 2 shows the TEM images of uncoated and coated NPCC. Figure 2 (a) and (c) are TEM images, which are magnified 10,000 times. It was found that the coated NPCC nanoparticles are well dispersed. It can be seen that uncoated nanoparticles overlaps and distinct particles can

hardly be observed. The image shows many aggregates. Figure 2 (b) and (d) are the TEM images, which are magnified 16,300 times. Figure 2 (d) shows that coated NPCC are distinct and individual particles can be distinguished. The reduced degree of agglomeration was observed after surface coating. These results confirm that phenomena of nanoparticles agglomeration where cores are kept apart by surface modification layer and the repulsion between the particles increased (Chan *et al.*, 2002).

**TGA analysis:** Thermogravimetric analysis (TGA) indicates that the coated nanoparticles lose a significant fraction of their weight upon heating. Figure 3 shows the weight loss expressed as weight percent as a function of temperature for different amount weight of stearic acid in comparison to uncoated NPCC. This technique does not require aromaticity or a certain functional group for detection. The TGA curve of uncoated and coated NPCC with temperature 550°C is shown in Fig. 3. There are two weight loss steps in temperature ranges 50-230 and 230-370°C. The weight loss at 50-230°C may be attributed to the loss of moisture whereas at 230-370°C the loss may be attributed to the decomposition of the stearic acid. It is clearly seen that the weight loss during the second step increased markedly which is about 3, 4 and 6% for 3, 6 and 9wt% addition of SA respectively. These results indicate that coated NPCC can be used as filler in many commodity thermoplastics (PVC and polyethylene) processing because most processing temperatures are below 250°C. The general effect of this sort of coating is to improve processing and resistance of the composite to effects of water. TGA analysis for coated NPCC also shows that the NPCC is in its stable form, proofing that the coating agent does not affect the NPCC decomposition.

**Data of DRIFTS:** Diffuse reflection spectroscopy (DRIFT) is the preferred infrared technique for studying organic coatings on inorganic powders (Sutherland *et al.*, 1998). DRIFT spectra for uncoated NPCC and a series of coated samples are shown in Fig. 4. A group of alkyl CH peaks is detected in the coated samples. Coating the surface with stearic acid give rise to new bands at 2800-3000 cm<sup>-1</sup>, which may assigned to C-H vibrations in the alkyl chain of the coated particles.

**XPS results:** In general, surface organic coating is very thin and cannot be detected easily by conventional techniques. X-ray Photoelectron Spectroscopy (XPS), which is known as electron spectroscopy for chemical analysis (ESCA) is probably the most widely used technique in the surface characterization of polymers and

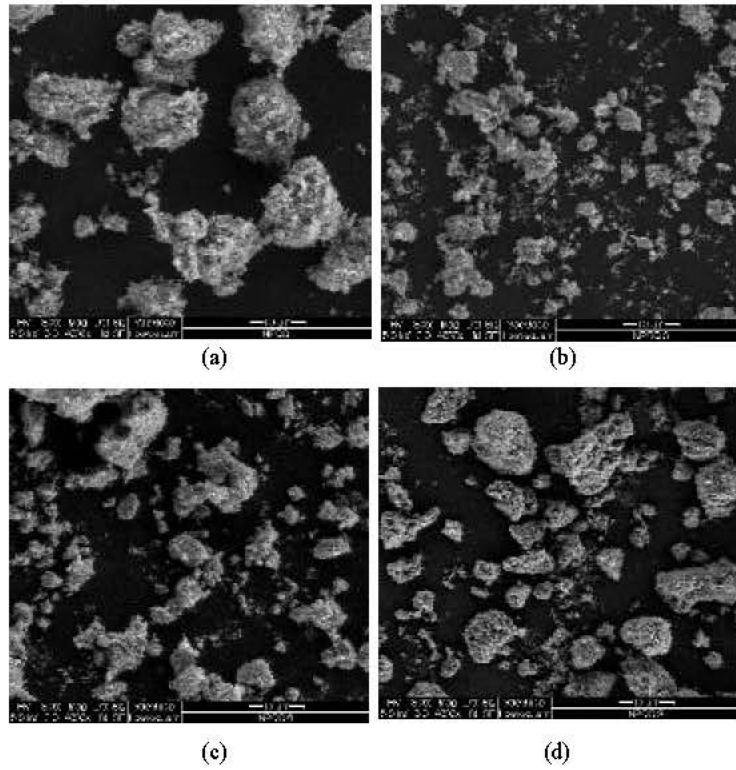


Fig. 1: SEM images of uncoated NPCC nanoparticles (a) and coated NPCC with various amount of SA; (b) 3 , (c) 6 (d) 9 wt% magnified at 4,000x

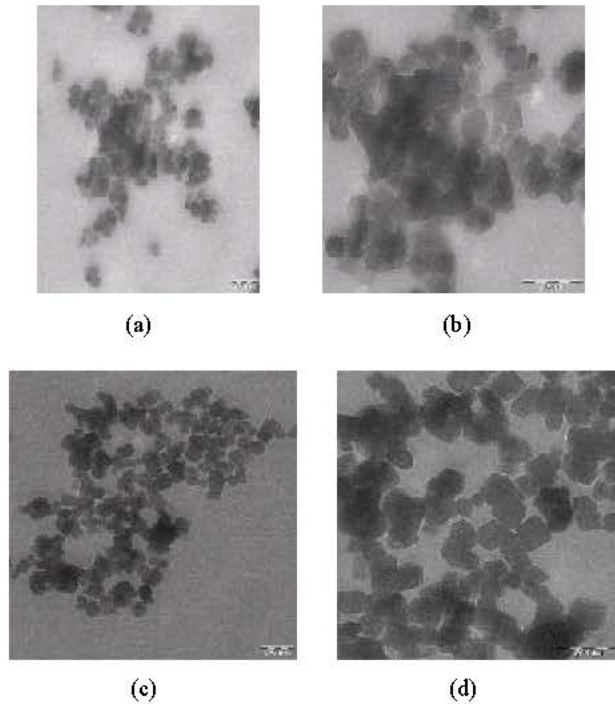


Fig. 2: TEM images of uncoated NPCC (a and b) and coated NPCC (c and d)

Table 2: Surface chemical compositions of uncoated and coated NPCC

Surface materials	Surface chemical compositions (at % atomic)			
	C	O	Ca	C/Ca
Uncoated NPCC	54.57	43.91	1.52	35.90
With 3wt% stearic acid	57.62	40.40	1.98	29.10
With 6wt% stearic acid	58.59	38.40	3.01	19.47
With 9wt% stearic acid	59.61	37.34	3.05	19.54

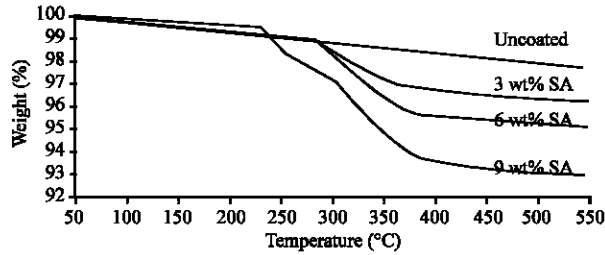


Fig. 3: Thermogravimetric analysis recorded on NPCC coated with various amount of stearic acid at temperature below 550°C. (a) Uncoated NPCC (b) 3 (c) 6 (d) 9wt%

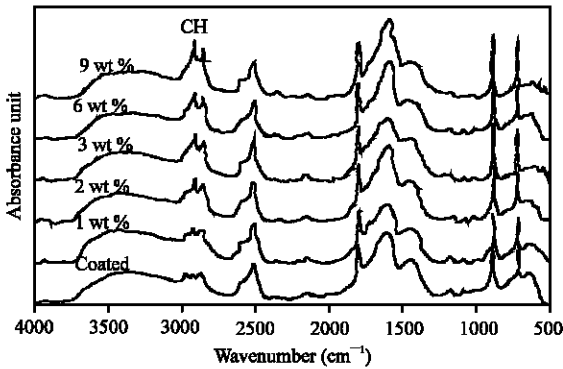


Fig. 4: DRIFT spectra of uncoated and coated NPCC with various amount of stearic acid

other materials (Maged, 2002). Table 2 indicates the XPS spectra of the three major elements on the surface including carbon, oxygen and calcium

For uncoated NPCC surface, the composition value of carbon is the lowest and the oxygen composition is higher. With increasing stearic acid amount, the composition of carbon increases steadily and composition of calcium decreases. This indicates that a hydrophobic surface is associated with higher concentrations of carbon. Similar result were also found by Chan *et al.* (2002), who investigated characteristics of nanoparticles surface modified with organic layer that consists mostly stearic acid.

The substrate signal (atomic ratio Ca) is increased drastically and the ratio C/Ca reflect the total surface carbon is decreased with increasing amount SA. It is deviated from the Gilbert *et al.* (2001) results that

Table 3: Effect of various amount of stearic acid on BET surface area of NPCC

Sample	BET surface area (m <sup>2</sup> /g)
Uncoated	24.5042
With 3wt% SA	22.8989
With 6wt% SA	23.8224
With 9wt% SA	23.3652

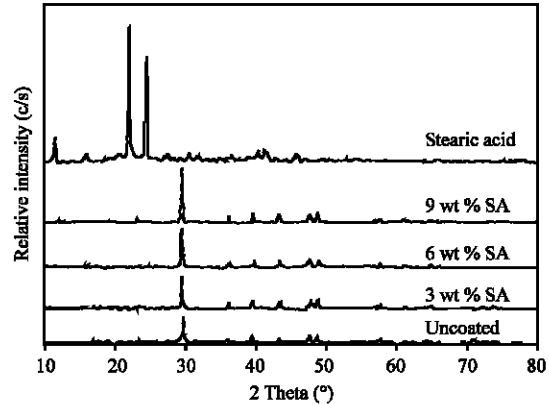


Fig. 5: XRD patterns of pure stearic acid and various amount of stearic acid coated NPCC

according to them Ca and C/Ca are decreased and increased with amount increasing amount of SA respectively. Since XPS only probes the outer few nanometers (1-2 nm) then it is probably indicates composition of the outermost surfaces that could be detected with this infrared radiation.

**XRD results:** Figure 5 shows below XRD patterns corresponding to the uncoated and coated NPCC. The spectra for coated NPCC were similar to the uncoated NPCC. On the surface of coated NPCC, the crystalline peaks were identified at  $2\theta$  of 29.6°. This result also indicates that crystalline structure of NPCC was dominated for all coated samples in comparison with pure stearic acid. It was also confirmed by SEM interpretation that the variation amount of SA obviously no change on particle shape of nanoparticles. Therefore, it can be concluded that stearic acid deposited on the surface of NPCC has no effect on crystallization performance of nanoparticles.

**BET results:** Surface area is frequently used as defining parameter for the filler types encountered in thermoplastics applications. The results of surface area of uncoated and coated NPCC with various amount stearic acid is shown in Table 3. These results indicate that the highest BET surface area belongs to uncoated NPCC, which is about 24m<sup>2</sup>/g. Many aggregates that can be seen from TEM images and the primary particle size is difficult

to be determined due to their aggregate nature of these nanoparticles. It can be seen that 3wt% SA is the lowest surface area with 22m<sup>2</sup>/g, which was due to their weak tendency to agglomerate. Higher surface area may result in more interfacial interaction between nanoparticles and the polymer. The results obtained proved that it can be used for commercial application in polymers based on their ultimate particle size (50-100nm) and specific surface area of 15-25m<sup>2</sup>/g (Rothon, 1999). The surface area of coated NPCC increased again for 6 and 9wt% of SA. Therefore, an optimal coating can be obtained with addition of 3wt% of SA.

### CONCLUSION

Nano calcium carbonate particles with an average diameter of 40nm were successfully synthesized via simple wet coating method at temperature 80°C. The characterizations of uncoated and coated NPCC were carried out by microscopic image (SEM), thermal analysis, BET measurement, DRIFT and XPS analysis. The coating reduced the degree agglomeration as well as surface area in comparison to uncoated nanoparticles as detected by SEM and BET analysis respectively. TGA analysis showed the weight loss of coated nanoparticles below 1wt%. In this Study, 3-6wt% of amount stearic acid was used. It is probably more advantageous to coat the NPCC with optimal amount of stearic acid to cover its surface with stearic acid unless the influence of excessive coating can be exploited in certain application.

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