

Characterization of CaCO₃ Nanoparticles Synthesized by Reverse Microemulsion Technique in Different Concentrations of Surfactants

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ABSTRACT: Calcium carbonate nano-particles were synthesized by a reverse micro-emulsion method at room temperature with Tween[®] 80 and Span[®] 80 as co-surfactants. The nano-particles synthesized were surface modified by stearic acid. An important operating variable in the Span 80-Tween 80/toluene/water reverse micro-emulsion system, the ω -value (water/surfactant molar ratio) was investigated. The material was characterized by SEM, TEM, X-Ray Diffraction (XRD), FT-IR, UV-VIS and TGA/DTA techniques. The size of the nano-particles was determined by TEM as well as XRD data for various concentrations of surfactants. The results showed that the size of the nano-particles was influenced by the concentration of the surfactants in the micro-emulsion system. The XRD analysis at room temperature showed single phase formation of calcite. FT-IR confirmed the formation of calcite with characteristic absorption bands observed at 712, 881 and 1460 cm⁻¹, corresponding to ν_4 , ν_2 , and ν_3 modes of CO₃²⁻ absorption bands of calcite. The results of the UV-VIS spectrophotometric analysis indicated that the calcite (CaCO₃) is an indirect gap material [(5.60 eV (30 wt.% surfactant), 5.40 eV (36 wt.% surfactant) and 5.36 eV (42 wt.% surfactant)] at room temperature.

KEY WORDS: Calcium carbonate, Reverse micro-emulsion technique, Co-surfactant, Optical properties, Particle morphology.

INTRODUCTION

Particles have distinctive properties when their crystalline sizes are reduced to submicron range with respect to corresponding bulk materials, including prominent mechanical/optical properties, high specific surface area and chemical activity, and superior barrier effects especially in polymer matrix. Among the numerous nano-sized materials synthesized during

the past decade, calcium carbonate remains one of the most useful and abundant [1].

Nano-particles of calcium carbonate have received much attention due to its wide applications in the areas of polymers, paints, plastics, rubber etc [2]. Calcium carbonate (CaCO₃) nanoparticles (<100 nm) have shown many unique properties compared to regular CaCO₃

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particles ($>3 \mu\text{m}$) [3]. Thus, fine particles of CaCO_3 with distinct morphology are used for specific applications [4]. *Qui et al.* (2000) studied the application of CaCO_3 nano-particles as additives in lubricating oils and found that they exhibited good load-carrying capacity, antiwear and friction-reducing properties [5]. Due to the wide ranging application of nano/micro-sized calcium carbonate, technique to synthesize calcium carbonate with particle size below $1 \mu\text{m}$ has been an interesting research topic. There are several methods for producing nano/micro-sized calcium carbonate, among which the carbonation process to prepare precipitated calcium carbonate is an economical one [6].

Hence, different methods such as break down and mechanical method [7, 8], sol-gel method [7, 9], colloidal method [10, 11], gas phase synthesis method [12] and chemical vapour condensation [13] have been reported for synthesis of nano-particles in literature. However, among the above methods mentioned, the Water-in Oil (W/O) micro-emulsion method, as a unique class of colloidal systems, has been widely used as an ideal medium to prepare inorganic nanoparticles, which consists of nanometer-scale water droplets surrounded by surfactant that are dispersed in oil [14].

The two-reverse-micro-emulsion technique has been applied to synthesize calcium carbonate nano-particles [1]. For instance, *Chibowski et al.* (2010) produced calcium carbonate nano-particles in water-in-oil micro-emulsion at $20\text{-}30^\circ\text{C}$ temperature. Calcite precipitation experiments were conducted in the presence of PolyEthylene Glycol (PEG). Nano-particles synthesized in this way have a spherical shape and almost uniform size varying from 20 to 30 nm [15]. *Ying et al.* (2010) prepared CaCO_3 nano-particles via micro-emulsion route at room temperature with ethanol and n-hexanol as co-surfactant. This process did not demand any additional energy such as heating or continuous agitation. They reported that diameter and length of nano-particles were 20-30 nm and 100-300 nm respectively [14]. *Alves et al.* (2008) have studied the optical and vibrational properties of some samples of mineral calcite CaCO_3 by the UV-VIS absorption and the Fourier-Transform InfraRed (FT-IR) Spectroscopy. They found that, at room temperature, the calcite, CaCO_3 is an indirect gap material ($E_g = 5.80 \pm 0.01 \text{ eV}$) [16].

In this study, the two-reverse-micro emulsion technique has been used to synthesize nano-sized calcium carbonate. The structural and morphological properties of

synthesized powder were characterized by XRD, SEM and TEM. The optical properties of the sample were investigated by UV-VIS and FT-IR spectrophotometry. The Thermal decomposition behaviour of the powder was studied by TGA/DTA.

EXPERIMENTAL SECTION

Analysis

The crystal structure of CaCO_3 nano-particles was studied using a Rigaku X-ray Powder Diffractometer with Cu anode (Cu $K\alpha$ radiation $\lambda=1.54186 \text{ \AA}$) in the range of $20^\circ \leq 2\theta \leq 80^\circ$ at 30 kV. The particle size was determined from TEM (JEOL JEM-2100F, Japan) results and also calculated from XRD data using Scherer's formula. Samples for TEM examination were prepared by dispersing the nano- CaCO_3 particles in ethanol in an ultrasonic bath for 10 min. FT-IR spectra were recorded on a (Interspec-2020, SPECTROLAB, UK) spectrophotometer using potassium bromide (KBr) pellets. The morphology of the surface of the samples were analyzed using the Scanning Electron Microscope (SEM, Carl Zeiss: EVO40) at 20 kV after the samples were sputter-coated (Sputter Coater: POLARON-SC7640) with a thin platinum layer. Thermogravimetry analysis was carried out using TGA/DTA (Schimadzu: DTG-60 H; C30574300134) up to 800°C in air at the heating rate of $10^\circ\text{C}/\text{min}$ after purging it with N_2 gas. The optical absorbance spectra were measured using a UV-VIS Double Beam Spectrophotometer (Perkin Elmer Precisely: Lambda 35) at room temperature in the wave length range of 200-800 nm.

Materials

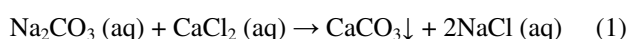
CaCO_3 particles (99.95%) with an average size of $2 \mu\text{m}$, Na_2CO_3 (99.999%), CaCl_2 (99.999%), Span[®]80, Tween[®]80, Toluene (99%), Methanol (99.9%), Stearic acid (97%) were all from Merck Company, Germany. Distilled water was used to prepare all water solutions.

Synthesis of nano- CaCO_3 particles

A reverse micro-emulsion system of Surfactants (Span[®]80 & Tween[®]80)/Toluene/water was selected for this study due to its wide stable-region and a weight ratio of Span[®]-80 (49 g) & Tween[®]-80 (51 g) was used [17]. The first step was to prepare two reverse micro-emulsions of CaCl_2 and Na_2CO_3 solutions by mixing surfactants,

toluene, and certain amount of one molar (1M) aqueous CaCl₂ or Na₂CO₃ solutions in two 250 ml beakers agitated by a magnetic stirrer at room temperature (27°C) [1].

Microemulsion-I was prepared as follows. In a 250 mL beaker, 17.64 g of Span-80 and 18.36 g of Tween-80 were completely mixed followed by addition of 48 g of toluene. The mixture was homogenized by using a magnetic stirrer (1000 rpm) to get the mixture of surfactant and oil. The pH of the homogeneous mixture was recorded through pH meter. Subsequently, 16 g of aqueous solution of calcium chloride was added to the above and was mixed using magnetic stirrer (2500 rpm) at room temperature (27-33°C) for about 12h until microemulsion was formed. Milky colour of the mixture solution and lack of phase separation implies formation of the microemulsion. Microemulsion-II was prepared in the same way and with similar weighted combinations as microemulsion-I except that sodium carbonate solution was used for the water phase. Thus, microemulsion-I contained calcium chloride while microemulsion-II contained sodium carbonate. The two reverse micro-emulsions of CaCl₂ and Na₂CO₃ (I and II) were mixed together in a 500 ml beaker at 27 to 33°C under agitation. After the pH of micro-emulsions mixed got close to the pH of surfactants and oil phase mixed as well as constant colour of the suspension the reaction was stopped [1]. It is pertinent to put on record that the completion of the reaction is normally controlled by monitoring the pH of the solution. In this work, the pH of mixture of toluene and surfactant before addition of water phase was 8.30. It was observed that after mixing the two microemulsions, the pH of the mixture initially dropped rapidly (which may be attributed to the initial fast reaction) and then continued to decrease slowly until a pH of 9.10. After 30 min, because of the constant pH (~8.10), formation of calcium carbonate supposed to be finished. It should be noted that the speed and geometry of stirring in solutions, colour of solutions as well as the quantity of calcium carbonate nanoparticles obtained in temperatures of 27-34°C were in a similar situations. In general, the reaction between sodium carbonate and calcium chloride to form calcium carbonate is given by Eq. (1).



After the completion of the reaction, the calcium carbonate nano-particles were separated by centrifugation

for 30 minutes at 8500 rpm. In the centrifuge tube, the middle portion (the interface between the light and heavy phases) was surrounded by calcium carbonate (and sodium chloride) particles sticking to the walls of the tube. The light and heavy phases were easily separated by decantation. After the decantation process, with most of the impurity removed, the precipitates were re-slurried by an ultrasonic device for 15 min, using a methanol/water (80/20 volume ratio) mixture as washing solvent, to ensure that the particles were suspended completely before next centrifugation. The washing process was repeated twice using methanol and distilled water as solvent. Finally, the collected calcium carbonate particles were re-dispersed in a small amount of methanol to form a suspension, followed by a drying process to obtain calcium carbonate particles. Particles were dried in a vacuum oven at 100°C for 12 h.

The effect of surfactant concentration on the size of the calcium carbonate nano-particles was also investigated. In such experiments, only the ratio of the surfactant (30 and 42 wt.%) and water (22 and 10 wt.%) was changed, other conditions (the organic and the reactant concentrations) remained constant. Thus three concentrations of surfactants (30, 36, and 42 %) were used and calcium carbonate particles synthesized.

Surface modification of CaCO₃ nano-particles

Surface-treatment of CaCO₃ particles is done to improve the fluidity and dispersion of the filler particles in polymer composites. Surface treatment of CaCO₃ reduces the inter particle interaction, enhances the polymer filler compatibility [18]. Pronounced effect of treatment is expected to be obtained by decreasing the filler size. Several methods may be used to surface-treat the CaCO₃ particles. However, stearic acid has been for surface treatment in this study, as it manifested better mechanical properties by improving dispersion of filler [19]. The surface-treatment of synthesized calcium carbonate nanoparticles was carried out as follows:

Nanosized CaCO₃ particles were first dried under vacuum (5 kPa) at 100°C for 12 h to remove probable absorbed humidity. A typical process was as follows: stearic acid (~0.002 mol) was dissolved in 100 mL pure toluene and the solution was placed into a flask equipped with a stirrer. The 5g of CaCO₃ nano-particles were added slowly over a period of 10 min under rapid stirring (2,500 rpm). When all the CaCO₃ particles

were added into the mixing chamber, the materials were further mixed for 1 hour under fixed stirring. Finally, the solvent was removed under vacuum at 60°C. Then the dried mixture was ground to get a fine powder of stearic acid coated calcium carbonate. The introduction of reactive groups onto CaCO₃ surface was achieved and it can be attributed to the fact that the stearic acid coating imparts hydrophobic characteristic on CaCO₃ surface [18]. It is postulated that the stearic acid molecules interact with the calcium carbonate, with the carboxylate ion reacting with the surface and the organic chains sticking out normal from the surface [20].

RESULTS AND DISCUSSION

XRD analysis

Fig. 1 shows typical powder X-Ray Diffraction (XRD) patterns of surface modified nano-CaCO₃ particles obtained in various concentrations of surfactants in the Span and Tween 80/toluene/water reverse micro-emulsion system at room temperature. The analysis of XRD patterns shows that the samples are formed in single phase with calcite crystal symmetry. All peaks are very well matched with the calcite structure and no indication of a secondary phase is found. The lattice parameters calculated from the XRD patterns are $a = 4.813 \text{ \AA}$ and $c = 17.10 \text{ \AA}$ for all samples, which are quite close to the values reported by Roeges in 1994 [21]. The maximum deviation that occurred between the observed and calculated values of interplanar spacing (d) remains below 0.1022 \AA . Diffraction peaks at (012), (104), (110), (113), (202), (018) and (116) came from a typical calcite of CaCO₃ crystal [22]. In order to calculate the crystal size (D) of the samples, Scherer's formula was used [23]. The crystal size of the samples was found $\sim 40 \text{ nm}$ (30 wt.% surfactant), $\sim 33 \text{ nm}$ (36 wt.% surfactant) and $\sim 21 \text{ nm}$ (42 wt.% surfactant), estimated from the line width of the (104) XRD peak.

SEM and TEM characterizations

The morphology of the resulting coated nano-particles was examined using Scanning Electron Microscopy (SEM). The SEM micrographs of the calcite CaCO₃ powders in various (three) surfactant concentrations are shown in Fig. 2. This shows that the materials are formed in single phase and the constituents are spherical in shape.

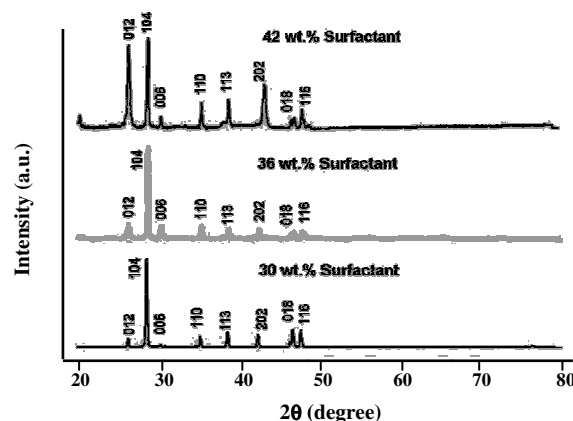


Fig. 1: X-ray diffraction (XRD) patterns of synthesized nanopowders in different concentrations of surfactants (the indexed peaks correspond to calcite phase).

The size and morphology of coated and surface modified nano-CaCO₃ particles analyzed by TEM are presented in Fig. 3. These images reveal that most of the coated CaCO₃ nano-particles are quasi-spherical and have rough surface. Many aggregates can be seen. The nano-particles have a strong tendency to form agglomerates due to their high surface energy which is a result of the small particle size. Because of the aggregate nature of these nano-particles, it is difficult to determine the primary particle size precisely. The primary particles size was determined by measuring the size of randomly chosen particles of 39 nm (30 wt.% surfactant), 33 nm (36 wt.% surfactant) and 19 nm (42 wt.% surfactant). These results are in accordance with the value calculated from the X-ray diffraction.

By examining the XRD and TEM data, it is observed that an increase in the concentration of surfactants results in decreased size of the synthesized nano-particles. This phenomenon can be interpreted as follows: increasing the concentration of surfactants leads to more stable and durable micro-emulsion and at the time it causes to form smaller droplets of water [1, 24]. The particle size is intensively dependent on the size of reverse micelles and consequently when the concentration of surfactants increases, water-surfactant molar ratio (ω) decreases resulting in the formation of smaller particles. In another viewpoint, when ω decreases, the interface of micelles becomes more condensed [25]. This condensation causes less diffusion of micelles in each other and finally the reactant ions present in the micelles react more slowly and therefore the formed or generated particles will have smaller size distribution.

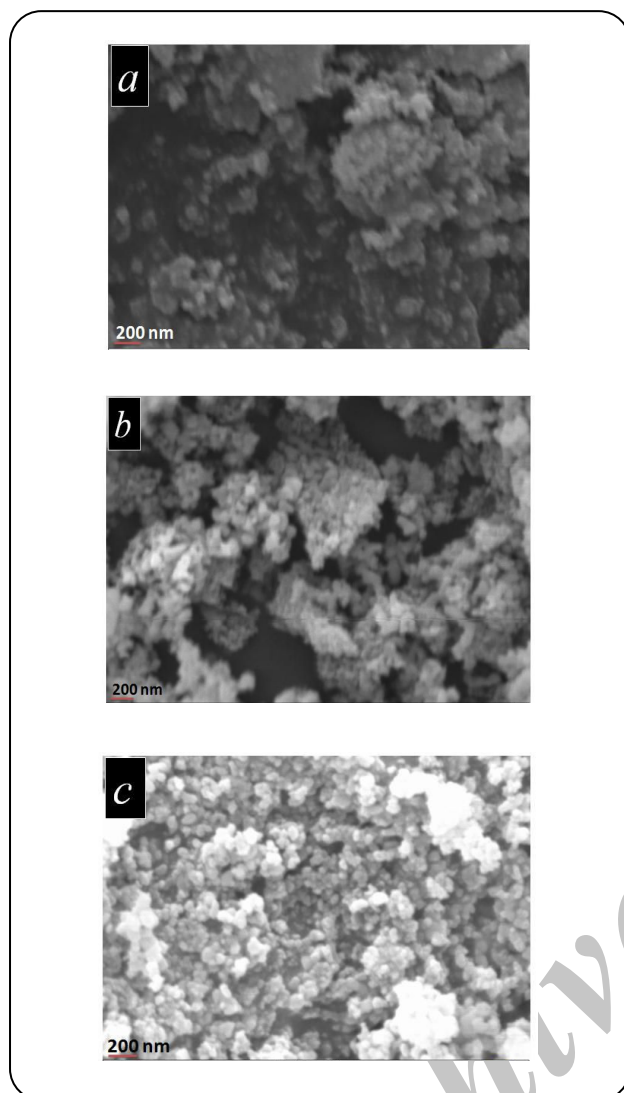


Fig. 2: SEM images of CaCO_3 nano-particles in different concentrations of surfactants: (a) 30 wt.% , (b) 36 wt.% and (c) 42 wt.% surfactants.

FT-IR spectroscopy

FT-IR spectra were recorded in KBr matrix in $400\text{-}4000\text{ cm}^{-1}$. The FT-IR spectrum of surface modified nano-particles indicated the presence of organic compounds such as alkynes, carboxylic acid and alkanes. The strongest peaks were observed at 1464.36 cm^{-1} (30 wt.% surfactant), 1478.87 cm^{-1} (36 wt.% surfactant) and 1480.02 cm^{-1} (42 wt.% surfactant) which belong to the functional group of alkanes and are in good agreement with the results reported earlier by *Blessie et al.* (2007) [26]. FT-IR spectra also confirmed the formation of calcite with characteristic absorption bands observed at 712 , 881 and 1460 cm^{-1} , corresponding to in-plane

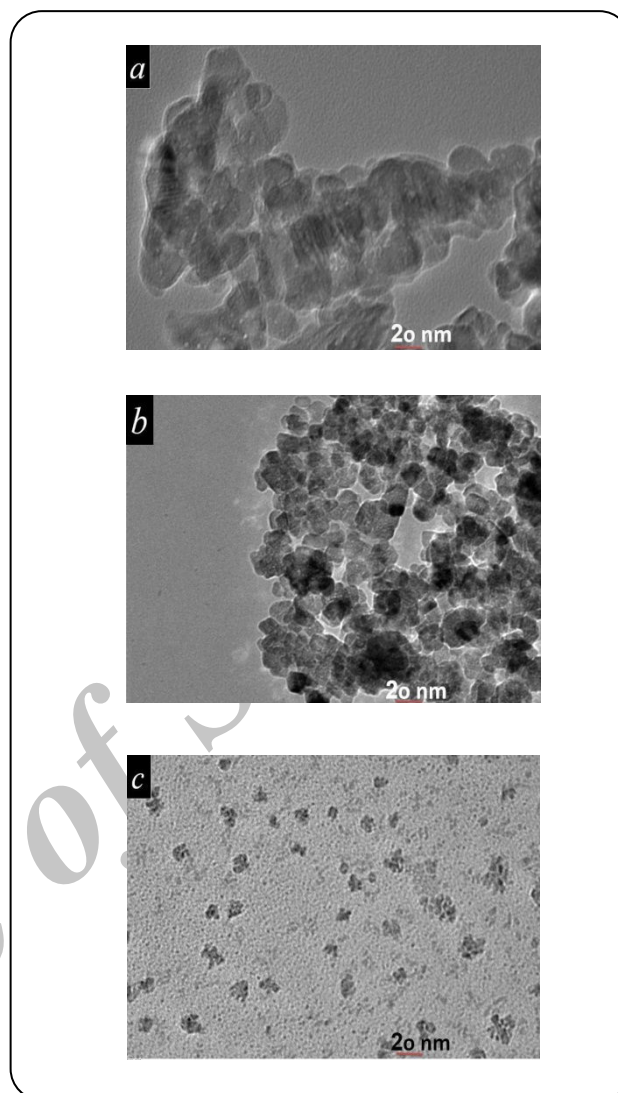


Fig. 3: TEM images of CaCO_3 nano-particles in the different concentrations of surfactants: (a) 30 wt.% , (b) 36 wt.% and (c) 42 wt.% surfactants.

bending (ν_4), out-of-plane bending (ν_2), and asymmetric stretching (ν_3) modes of CO_3^{2-} absorption bands of calcite [27]. Two bands in wavelengths of 2923 and 2856 cm^{-1} (30 wt.% surfactant), 2924 and 2856 cm^{-1} (36 wt.% surfactant) and 2924 e 2857 cm^{-1} (42 wt.% surfactant) can be attributed to $-\text{CH}_2$ groups probably referred to either the surface treatment of the nano-particles [28] or surfactant molecules remained strongly associated with the calcite crystals even after extensive washing [27] which has the main function of avoiding agglomeration of the nano-particles but can also be used to increase polymer/particle compatibility [29].

UV-Vis adsorption spectra

Optical properties of surface modified CaCO_3 nano-particles were characterized using a UV-Vis spectrophotometer. UV absorption spectrums are shown in Fig. 4. The band positions at 205 and 265 nm correspond to CaCO_3 nano-particles. The absorption coefficient α can be calculated from the relation:

$$\alpha = 2.303 \frac{A}{t} \quad (2)$$

where A is the absorbance and t is the thickness of the cuvette. The optical band gap of the nano-powders was determined by applying the Tauc relationship is given by [30]:

$$\alpha h\nu = A(h\nu - E_g)^n \quad (3)$$

Here, h is Planck's constant, ν is the photon frequency, E_g is the optical band gap, A is a constant, and $n = 2$ for indirect band gap insulator.

An extrapolation of the linear region of a plot of $(\alpha h\nu)^{1/2}$ on the Y-axis vs photon energy ($h\nu$) on the X-axis gives the value of the optical band gap (E_g) to be 5.62 eV for bulk CaCO_3 and 5.60 eV (30 wt.% surfactant), 5.40 eV (36 wt.% surfactant) and 5.36 eV (42 wt.% surfactant) for nano-particles as shown in Fig. 5. The calculated band gaps of nano-powders of CaCO_3 were less than the band gap of the bulk CaCO_3 which show blue shift and are in good agreement with the calculated band gap reported earlier by *Alves et al.* [16].

Thermal properties

TGA/DTA measurements were carried out to determine the stability of the stearic acid coated CaCO_3 nano-particles. These results for various concentrations of surfactants (Span80-Tween 80)/toluene/water reverse micro-emulsion system are presented in Figs. 6 (a) and (b).

The TGA curves for crystalline CaCO_3 , which were obtained for different concentrations of surfactants in the micro-emulsion system, are indicated in Fig. 6 (a). It is obvious that a larger weight loss occurs in the temperature range of 230-620°C, which may be attributed to the thermal decomposition of organic substrates in the CaCO_3 powders. It is further observed that the weight loss of the products from the nano-powders obtained with 30, 36 and 42 wt.% surfactants are about 2.3%, 3.8% and 5.8%,

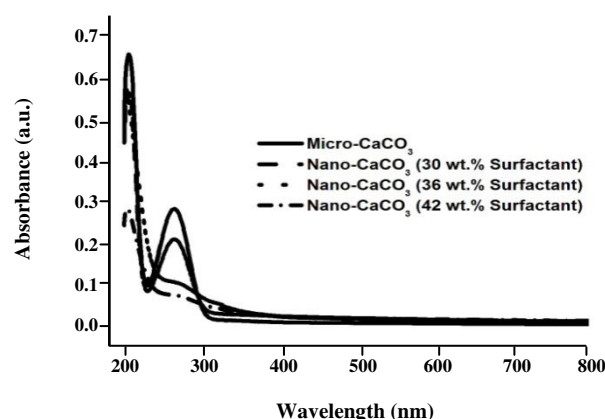


Fig. 4: UV-visible absorption spectrum of nano CaCO_3 powders (calcite phase).

respectively. Another stage is from 620°C to 755°C, where the largest loss of mass was observed. This may be explained by the thermal decomposition of calcite ($\text{CaCO}_3 \rightarrow \text{CaO} + \text{CO}_2 \uparrow$) [31]. At 755°C and above, the horizontal portion represents the stable CaCO_3 . These results suggest that these CaCO_3 nano-particles can be used as fillers for many thermoplastics, because most processing temperatures are below 400°C [32].

The DTA curves show an endothermic peak at 42°C, due to removal of water. Thermal decomposition of the CaCO_3 powders begins at temperatures higher than 220°C in air under atmospheric pressure accompanied by an exothermic peak appearing at 305°C (30 wt.% surfactants), 330°C (36 wt.% surfactants), and 440°C (42 wt. % surfactants) as shown in Fig. 6 (b).

CONCLUSIONS

Three different sizes of surface modified nano- CaCO_3 particles were synthesized using reverse micro-emulsion technique, characterized by TEM and determined as 39, The X-Ray Diffraction (XRD) analysis at room temperature showed single phase formation of calcite. The particle size estimated were found to be ~40 nm (30 wt.% surfactant), ~33 nm (36 wt.% surfactant) and ~21 nm (42 wt.% surfactant), using Scherer's formula. Based on these observations, it may be concluded that by increasing the concentration of surfactants the water-surfactant molar ratio (ω) decreases and resulting in the decrease of the size of the synthesized nano-particles.

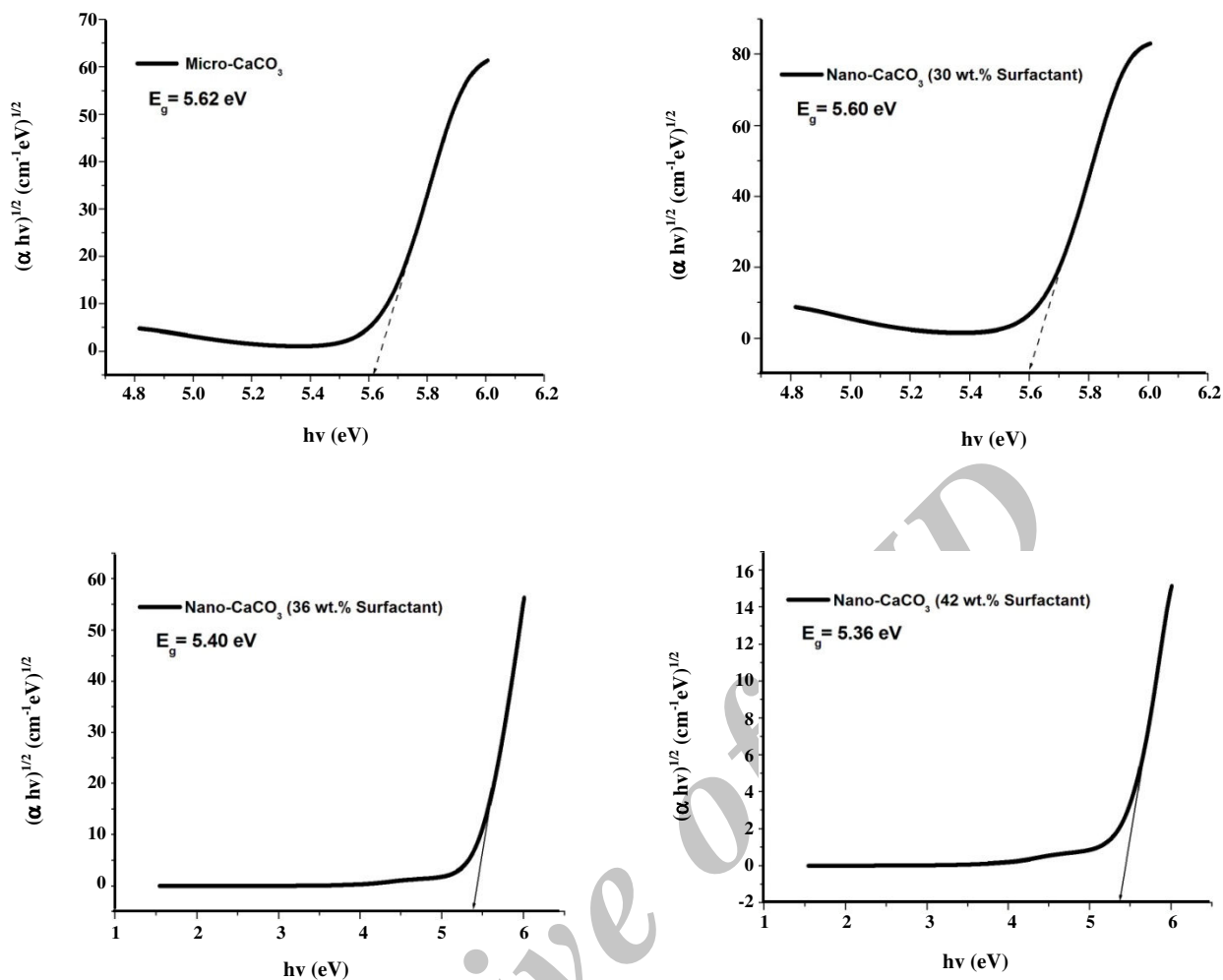


Fig. 5: Plot of $(\alpha hv)^{1/2}$ vs. $h\nu$ for CaCO₃ nanopowders.

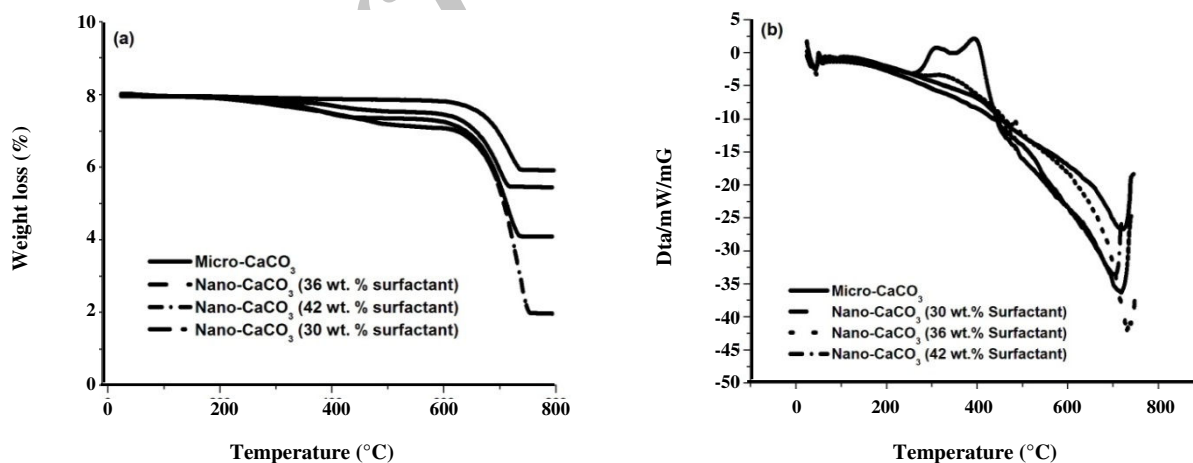


Fig. 6: (a) TGA curves of CaCO₃ nanopowders; (b) DTA curves of CaCO₃ nanopowders.

FT-IR spectra confirmed the formation of calcite with characteristic absorption bands observed at 712, 881 and 1460 cm^{-1} . The value of n in the Tauc's relationship from the fit of the absorption spectra was found to be 2. It means it allowed an indirect transition for these samples. The band gaps calculated from UV-VIS spectrum were found to be 5.60 eV (30 wt.% surfactant), 5.40 eV (36 wt.% surfactant) and 5.36 eV (42 wt.% surfactant) respectively which are slightly lower than the band gap of bulk CaCO_3 (5.62 eV) and show a blue shift. Higher weight loss from decreasing sizes of nano-particles observed through the TGA analyses may be attributed to the thermal decompositions of calcite.

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