Synthesis and Surface Modification of Calcium Carbonate Nanoparticles Using Ultrasound Cavitation Technique

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Abstract Calcium carbonate nanoparticles (nCaCO_3) was synthesized using optimized process of ultrasound assisted precipitation technique. Due to ultra-sonication phenomena, reacting components of reaction mixture gets dispersed uniformly, and at the same time nCaCO_3 particles agglomerate with each other due to strong electrostatic force of attraction developed over their surface. The de-agglomeration and charge nullification were achieved using surface modification of CaCO_3 nanoparticles using triethoxy vinyl silane (TEVS) under ultrasound environment. The surface modification of nCaCO_3 particles was confirmed using Fourier transforms infrared (FTIR) spectroscopy. Size, shape and formation of nCaCO_3 particles at nanoscale were studied using transmission electron microscopy (TEM). The size of unmodified and modified nCaCO_3 was found to be ≈ 50 -80 and 50-90 nm, respectively, with square crystal structure morphology. Due to the surface modification by TEVS, thin layer was formed over the surface of nCaCO_3 particle, which was confirmed by TEM micrograph. The purpose behind carry out this reaction under ultrasound environment is to optimize synthesis procedure of nCaCO_3 particles, to provide effective ultrafine precipitation and give stable & uniform dispersion of inorganic particles with reactants. Moreover, the acoustic waves of ultrasound treatment are an effective controlling parameter to obtain uniform dispersion of inorganic nanoparticles in solution by producing non-linear effects in reaction mixture. In this ultrasound treatment, transient cavitation and acoustic stretching are the most dominant affecting parameters, which give homogeneous dispersion of nCaCO_3 .

Keywords Ultra-sonication, Surface Modified nCaCO_3 , TEM, and FTIR

1. Introduction

Various research group have successfully incorporated inorganic nanofillers in to the polymers like polypropylene (PP) [1-4], epoxy [5-7], polyamide (PA) [8], polyvinyl

chloride (PVC) [9-11], polystyrene (HIPS) [12-13], poly methyl methacrylate (PMMA) [14], and rubber like styrene butadiene rubber (SBR) [3,10,15], silicone rubber [16,17], Ethylene propylene diene monomer rubber (EPDM) [18] and polybutadiene rubber (PBR) [19] for improvement in their thermal, mechanical and rheological. Inorganic nanoparticles have received an acceptance as reinforcing & hydrophobic fillers, because of their ease of fabrication and low cost.

CaCO_3 is one of the most important inorganic filler which can be used in plastics, rubber and paint industries but it's hydrophilic nature creates the problem of dispersion in polymer matrix. The elegant approaches like insitu deposition [1,5,8,10-11], conventional precipitation method [1,20], solution spray process [2,16-17,19], matrix mediated growth technique [3,9,15], solution bubbling & industrial carbonation methods [11], crystallization and sonochemical carbonization [13-14] and ultrasound cavitation [7] have been used for the synthesis of nCaCO_3 particles. Surface modification of CaCO_3 with hydrophobic species can solve this problem, which also lead them for major applications as mineral particles reinforced polymer nanocomposites [1,4,11,16-17,21-22]. The surface modification using various surfactants has been extensively studied e.g. bio and synthetic molecules [23-24], the surfactants containing reactive functional groups such as silane coupling agents [2,4,22], titanate coupling agents, biomacromolecules, designed peptide, double hydrophobic block copolymers, micelles, vesicles, sodium stearate, dihydrogen phosphate and oleic acid [11], stearic acid [6,16-17,20], and sodium oleate [13] which can improve the hydrophobic nature of CaCO_3 . Above all, surfactants have been studied to elucidate their effect on crystallization of CaCO_3 particles. Because of high hydrophobic character, the surfaces can possess interesting characteristics, like low water and snow adhesion, low friction in surface dragging and easy dirt removal [22].

Particle size and morphology of CaCO_3 particles heavily depend on preparation methods. Inorganic nanoparticles have tendency to agglomerate because of their high surface energy, so it is difficult to achieve the homogeneous dispersion of these nanoparticles in polymer matrix [11].

Also, high density of inorganic particles allows them to settle down or to form aggregates. Surface modification of nCaCO_3 by ultrasound cavitation technique is the best way to reduce their surface energy up to some extent and also increase their compatibility with polymer matrix along with homogeneity into the bonding. The surface of the CaCO_3 nanoparticles must be hydrophobic that is required for encapsulation and close interaction with the polymer chains [6-7,13,18-19,23], which also depend on the functional groups of surfactants to be modified over the surface of CaCO_3 nanoparticles. Therefore, the CaCO_3 nanoparticles were treated by a reactive silane coupling agent triethoxy vinyl silane (TEVS) to obtain the functionalized surface of CaCO_3 nanoparticles. The reaction can proceed by reacting each $\text{Si-OC}_2\text{H}_5$ groups with hydroxyl groups on the surface of nanoparticles and as a result surface of CaCO_3 nanoparticles were modified by bonding TEVS molecules.

The main importance of this research work is to synthesize the surface modified CaCO_3 nanoparticle using an ultrasound assisted precipitation technique by considering the need of the industry, which could be a continuous and an elegant approach for production. The present work also focuses the use of ultrasonic irradiations for uniform dispersion of agglomerated materials into the reacting mixture, which can control the effectiveness of overall synthesis and surface modification of CaCO_3 nanoparticles. When ultrasonic waves pass through a liquid medium large numbers of micro bubbles form, grow and collapse in very short period of time, which lead to the cavitation effects on intense turbulence, liquid circulation currents and formation of free motion to the molecular level. In present study, the collapse of cavitation bubbles near the interface of immiscible liquids can cause disruption of the phase required for formation of

very fine nanoparticles. And at the same time growth of electrostatic forces may cause agglomeration, which can be overcome by encapsulation or surface modification of nanoparticles.

2. Experimental

2.1. Materials

Calcium chloride (CaCl_2), ammonium bicarbonate (NH_4HCO_3), sodium dodecyl sulphate (SDS), acetone and TEVS (modifying coupling agent) were procured from S. D. fine chemicals Ltd, Mumbai (India).

2.2 Synthesis of CaCO_3 Nanoparticles

0.5M solution of NH_4HCO_3 was mixed in a beaker containing solution of 250 ml of distilled water and 0.7 g of SDS, which was dissolved properly and this solution was denoted as solution A. Similarly, in another beaker 0.25 M solution of CaCl_2 was dissolved in solution (25ml of distilled water + 0.25 wt% of SDS) which was denoted as solution B. 1.25 g of SDS was dissolved in 500 ml distilled water denoted as solution C. As shown in Figure 1, Ultra sonication probe was inserted in beaker containing solution C and sonication was started. After 5 min of ultrasound treatment, both solution of A and B were added by drop wise at the constant rate using burette, during this mixing ultrasound effect which was kept continue till complete addition of both solutions.

Figure 1. Schematic representation of reaction setup with ultrasonic probe for synthesis of nCaCO_3 particles by ultrasound cavitation technique.

2.3 Surface Modification of CaCO_3 Nanoparticles

The various coupling agent (silane coupling agents e.g. TEVS) can be used effectively for surface modification of CaCO_3 nanoparticles [2,4,11]. 100 g of nCaCO_3 particles was uniformly dispersed in acetone under ultrasound environment for 30 min to form CaCO_3 nanoparticles, this solution was denoted as D, while 5 g of TEVS was also dissolved in acetone and denoted as solution E (Figure 1). The ultrasonic probe was also immersed in solution D to generate sonic waves and at the same time solution E was added drop wise in solution D with constant rate. The effect of ultrasound cavitation provides very efficient mixing and strong dispersion. At the initial period of nCaCO_3 particles preparation, these particles were agglomerated due development of strong electrostatic forces of attraction. This agglomeration was discarded by surface modification as discussed in earlier texts. Figure 2 shows the schematic representation of synthesis of CaCO_3 nanoparticles without surface modification and with surface modification, both under ultrasound environment. Without surface modified CaCO_3 nanoparticles showed clusters or agglomerated forms, while surface modified one showed de-agglomerated CaCO_3 nanoparticles.

Figure 2. Schematic representation of surface modification of nCaCO_3 particles by TEVS.

2.4. Characterizations

FTIR spectrophotometer (model- shimadzu, 8400, Tokyo, Japan) was used to obtain the IR spectra of TEVS, which can confirm the bond formation of TEVS with surface of nCaCO_3 particles. Samples were finely divided and dispersed in a KBr powder for analysis. The scans were taken for each sample recorded for $4000\text{--}400\text{ cm}^{-1}$ at a resolution of 4 cm^{-1} in the transmittance mode. The morphology, exact size and shape of nCaCO_3 particles were investigated by TEM (CM200, Philips Netherlands) were used at a resolution of $2.4\text{ \AA}$. The samples were dispersed in water and deposited on a copper grid before viewing under the microscope.

3. Results and Discussions

3.1. Confirmation of Surface Modification Using FTIR

FTIR absorption spectra of unmodified nCaCO_3 particles and surface modified nCaCO_3 particles are shown in Figure 3 (a-b). In the spectrum of unmodified CaCO_3 nanoparticles denoted as (a) in Figure 3, the broad absorption band was observed at 3435 cm^{-1} which confirm the presence of hydroxyl (OH) group on the surface of nCaCO_3 particles due to presence of moisture [2].

The absorption that occurred around 2900 cm^{-1} and 2850 cm^{-1} was characteristic of H–C–H asymmetric and symmetric stretching vibrations [16-17,22]. TEVS surface modified CaCO_3 nanoparticles showed the sharp peak at 1641 cm^{-1} which indicated unsaturated C=C double bond of ethoxy group (present in TEVS) attached to surface of CaCO_3 nanoparticles [2]. Silicone could be characterized by Si–CH₃ symmetric deformation, stretching vibration observed at 802 cm^{-1} , while Si–O–Si asymmetric stretching vibration was observed in the range $1100\text{--}1090\text{ cm}^{-1}$ [2]. From these spectra, it is clear that silicone was successfully attached to CaCO_3 nanoparticles. The broad absorption bands as shown in (b) spectra of Figure 3 ranging between 1098 and 1082 cm^{-1} were characteristic peaks of Si–O–C group present in TEVS, which indicates the formation of Si–O– CaCO_3 bond on surface modified CaCO_3 nanoparticle [2,22]. Schematic representation of surface modification of CaCO_3 nanoparticles is already shown in Figure 2.

Figure 3. (a) FTIR spectra of surface modified nCaCO_3 particles (b) Schematic representation of mechanism of surface modification of nCaCO_3 .

3.2. Size and Shape of CaCO_3 Nanoparticles

The size of unmodified CaCO_3 nanoparticles was recorded $\sim 50\text{--}80\text{ nm}$ with few agglomerations, and nature of particles was rod shape as shown in Figure 4(a). The size of TEVS modified CaCO_3 nanoparticles was recorded in the range of $\sim 50\text{--}90\text{ nm}$ as shown in Figure 4(b). Particle size of unmodified nCaCO_3 particles was observed having size $< 39\text{ nm}$ and surface morphology of non-uniform ellipse-like nCaCO_3 particles [1,3,8,15,16,19,22].

Figure 4. TEM of (a) unmodified nCaCO₃ particles (b) surface modified nCaCO₃ particles by TEVS

The agglomeration in untreated CaCO₃ nanoparticles is due to electrostatic forces of attraction and therefore the CaCO₃ nanoparticle behaves like a commercial CaCO₃ [16]. The increase in particle size of modified nCaCO₃ particles i.e. ~90 nm was due to its encapsulation by silane group of TEVS. The de-agglomeration of modified CaCO₃ nanoparticles was due to surface modification, which reduces the surface energy along with reduction in electrostatic forces of attraction. A single CaCO₃ nanoparticle can be observed in Figure 4(b) which looks like crystal structure and cubic morphology [11,14] due to ultrasound cavitation effect.

3.3. Characteristic Properties of Modified and Unmodified CaCO₃ Nanoparticles

Nanoparticles of nCaCO₃ particles < 39 nm (prepared by insitu deposition) can absorb 139 j/g of heat [1] and onset decomposition temperature was only 24.7°C [10]. It is reported that there was no change in onset decomposition temperature of TEVS modified nCaCO₃, and percentage weight loss was 1.2% because of decomposition of silane coupling agent and adsorbed water on the particles surface [2]. Maximum weight loss (3-5%) was occurred in the temperature range of 200-620°C due to thermal decomposition of modified nano-CaCO₃ particles using of sodium stearate, dihydrogen phosphate and oleic acid [11]. Unmodified nCaCO₃ particles were reported with highest thermal stability with 3% weight loss during 0-430°C [14], which is also a characteristic property of nCaCO₃ particles.

The effect of the surface modification can be evaluated by the relative contact angle and active ratio [11,22]. The water contact angle was observed at 122.25° for the modified nCaCO₃ in the presence of sodium stearate, dihydrogen phosphate and oleic acid [11]. No stable drop shape was observed, and water was imbibed in the pellet. The water contact angle of on pure CaCO₃ powders was very small (nearly 0) and the unmodified CaCO₃ is hydrophilic. Adding oleic acid to the CaCO₃ processing, the relative

contact angle was increased to 95°, indicated good hydrophobic character. The contact angle of the final modified CaCO₃ using silane coupling agent was 152°, indicated super hydrophobic character [22]. The water contact angles of the pellets after drying at 100°C for 24 h were not changed, which indicated that volatile compounds were absent. The active ratio can reflect the effect of surface modification, which is defined as the weight ratio of the floated product to the overall product mixed with water under vigorous stirring and it can be evaluated by the floating test. It was observed that the amount of surfactant had a dramatic effect on the active ratio of CaCO₃ nanoparticles. As the loading of modifiers or surfactants was increased, the active ratio of hydrophobic CaCO₃ increased gradually and reached almost 99.9% when the loadings of modifiers to CaCO₃ was only 2% and the product changed from hydrophilic to hydrophobic completely. However, when the dosage of modifiers was more than 2%, part of the polar groups was outward owing to the multilayer physical adsorption. Whiteness value of nCaCO₃ particles can be detected by digital displaying whiteness meter. The influence of the different modifiers loading on the value of whiteness showed that value of whiteness was increased as increase in modifier loadings [11].

XRD studies of modified and unmodified of nCaCO₃ particles showed that ion binding, lattice matching and stereo chemical recognition were important factors for oriented nucleation. In the reaction of CaCO₃ synthesis, Ca²⁺ was located at lattice position in (001) layers, alternating with layers of CO₃²⁻. Ca²⁺ can be bonded to the negatively charged surfactants and result in the nucleation of the modified CaCO₃ [11]. In XRD study, there was sharp peak observed at 2.5° for nCaCO₃ which was 2.8° in the case of commercial CaCO₃ [3].

4. Conclusions

Synthesis of CaCO₃ nanoparticles and surface modification by TEVS were done successfully using optimized process of ultrasonic cavitation technique. During

the synthesis and surface modification of nCaCO_3 the major affecting process parameters were (i) lower reaction temperature (ii) faster conversion rate (iii) achieved higher conversion (iv) nanoparticles with well reduced size and (v) de-agglomeration and uniform distribution of nanoparticles. The morphology transformation is observed from growth and shape of the modified nCaCO_3 particles due to the addition of surfactants. Therefore, a conclusion can be drawn that the compatibility with surfactants and the distribution of nCaCO_3 particles are obviously enhanced, which are potential for the industrial process of biomineralization. This mineral inorganic (CaCO_3) nanomaterial can be used as a nanofiller as well as binder in the polymer and in paint industry. Surface modified nCaCO_3 particles can show good dispersion in to the polymer matrix as compared to unmodified and commercially available material. Ultra-sonication technique is less time consuming with high yield and uniform distribution. This method can also be applicable to the surface modification of other mineral nanofillers, which can be synthesized using chemical and/or physical route.

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