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Synthesis and Characterization of Nano-Size $CaCO_3$ via Thermal Treatment and Solid State Method.

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Abstract

$CaCO_3$ nanoparticles have been synthesized via heat-treatment of a new precursor and solid state reaction. Effect of calcinations temperature and quantity of surfactant on particle size has been investigated. The products were characterized by X-ray diffraction (XRD), scanning electron microscopy (SEM), transmission electron microscopy (TEM) and Fourier transform infrared (FT–IR) spectroscopy.

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1. Introduction

The use of inorganic fillers has been a common practice in the plastics industry to improve the mechanical properties of thermoplastics. As an important inorganic filler or pigment, calcium carbonate ($CaCO_3$) is used in many fields [1]. $CaCO_3$ is one of the most commonly used inorganic fillers for thermoplastics, such as poly(vinylchloride) and polypropylene [4]. $CaCO_3$consists of three anhydrous crystalline polymorphs: calcite, aragonite, and vaterite.

Calcite is thermodynamically the most stable phase, whereas vaterite is the least stable phase and it transforms into one of other two forms. Vaterite particles do not show well-defined morphologies, and usually aggregate into spherical particles. Nano-$CaCO_3$ is the cheapest commercially available inorganic particle and although the surface of nano-$CaCO_3$ particles is pretreated with different compounds such as stearic acid [2], phosphonate, and titanate to facilitate dispersion in the polymer matrix, the weak interface interaction and poor compatibility between those compounds and the polymer matrix will also prevent the enhancement of mechanical properties for the polymer/inorganic nanoparticle composites [3].

Thermal treatment method has some advantages such as simple process, low cost and easiness to obtain high purity products.Hence,this method is quite promising and facile route for industrial applications.

Solid-state decomposition is introduced as one type of the thermal decomposition processesin dry condition under air atmosphere. Hydrothermal, solvothermal andthermal decomposition usingorganic solvent or surfactantcarry out undervigorous controlledconditions but the choice ofsuitablemetal precursor and calcination temperature are known as key factors in solid-state decomposition.

In this work thermal treatment and solid state methods were applied to prepare nano-sized $CaCO_3$. First, a new precursor was synthesized using phthalic acid in thermal treatment method and then was transformed to nano-sized $CaCO_3$.

2 Experimental

2.1 Materials and characterization

All chemicals were of reagent grade and were used as received. XRD patterns were recorded by a Rigaku D-max C III, X-ray diffractometer using Ni-filtered Cu Kα radiation. Elemental analysis were obtained from Carlo ERBA Model EA 1108 analyzer. Scanning electron microscopy (SEM) images were obtained on Philips XL-30ESEM equipped with an energy dispersive X-ray spectroscopy. Transmission electron microscopy (TEM) images were obtained on a Philips EM208 transmission electron microscope with an accelerating voltage of 100 kV. Fourier transform infrared (FT-IR) spectra were recorded on Shimadzu Varian 4300 spectrophotometer in KBr pellets

2.2. Thermal treatment method

For synthesis of the precursor, calcium nitrate was dissolved in ethanol and phthalic acid was dissolved in ethanol too. Then dissolved phthalic acid was added to salt by dropping. After that sodium acetate was added to the mixture and then the mixture was refluxed. The complex was characterized by FT-IR. The synthesized complex was placed in furnace at different temperatures (300-700 ^oC). The results of XRD pattern and FT-IR spectroscopy showed that the optimum reaction temperature for the forming of $CaCO_3$ via thermal treatment of precursor had been at 500 ^oC and nano-size $CaCO_3$ without any impurity was formed.

2.3. Solid state method

$Ca(NO_3)_2$ and Phthalic acid were fully mixed by grinding in 1:1, 1:2, 1:3 and 1:4 molar ratio. Then the samples was placed in furnace at different temperature (250-550 ^oC) for 4 h. The results of XRD pattern and FT-IR spectroscopy showed that

the optimum reaction temperature for the forming of $CaCO_3$ had been at 550 ^oC. Also the results showed that the optimum molar ratio for the forming of $CaCO_3$ had been at 1:2.

3. Results and discussion

Fig. 1 show IR spectra of samples were formed via solid state method at 550 ^oC and Fig. 2 show IR spectra of samples were formed via thermal treatment method.

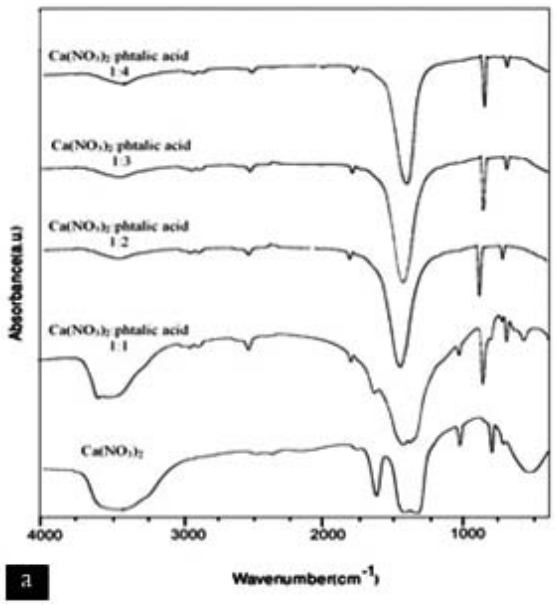

Fig. 1. IR spectra of samples were formed via solid state method at 550 ^oC

In Fig. 1 we can see that $CaCO^3$ was formed at 1:2 molar ratio. Also we can see the formation of $CaCO^3$ at 500 ^oC via thermal treatment method. Fig. 2 at 500 oC show the IR spectrum of $CaCO^3$ which represents the characteristic absorbance of our high purity nanoparticles. Isolated, planar CO_3^{2-} anion has a D_3h symmetry. The absorption bands attributed to the vibrations in CO_3^{2-} anion are located within the 400–1800 cm^{-1} region. The strong board absorption centered at about 1448 cm^{-1} is connected with the asymmetric stretching vibrations, and a strong sharp absorption band at about 694 cm^{-1} and 856 cm^{-1} can be assigned to the bending out of plane vibrations and in plane vibrations, respectively. Also a weak sharp absorption band at about 1058 cm^{-1} owing to the symmetric stretching vibrations is observed [6].

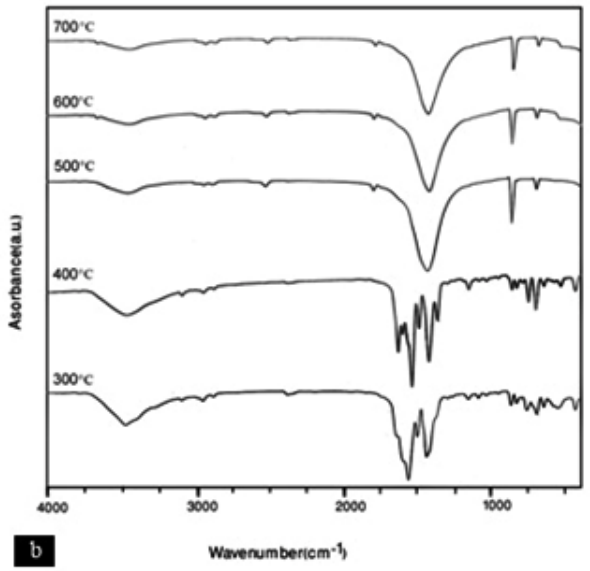

Fig. 2. IR spectra of samples were formed via thermal treatment method

Fig. 3 show XRD pattern of $CaCO_3$ obtained by solid state method. The results indicated that the crystal structure of $CaCO_3$ is rhombohedral (JCPDS card no. 86-2339). The calculated lattice parameters are a =4.9840 nm, b =4.9840 nm, c =17.1210 nm. There are some other peaks in XRD pattern of $CaCO_3$ that indicate the impurity of CaO which shown in Fig. 2a. Nano-size $CaCO_3$ with an average size of 35, 34, 28 nm was estimated by using the Debye-Scherrer formula at 1:2, 1:3, 1:4 molar ratio respectively that indicate the effect of quantity of surfactant on particle size. The results of XRD pattern show that $CaCO_3$ particles decrease with increasing of quantity of surfactant.

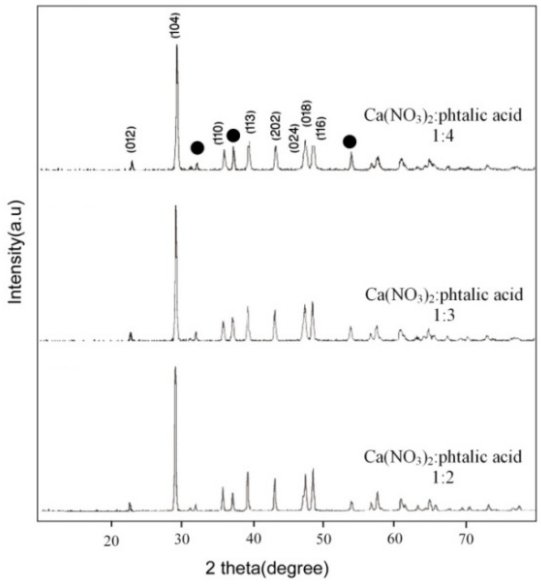

Fig. 3. XRD pattern of $CaCO_3$ Synthesis by solid state

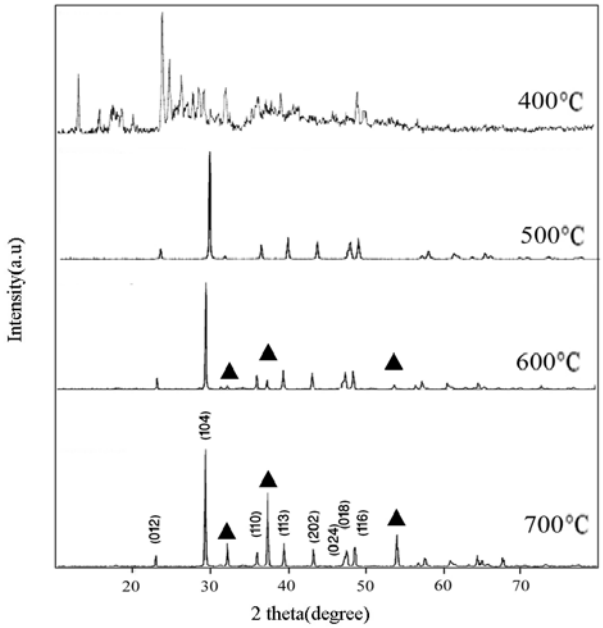

Fig. 4. XRD pattern of $CaCO_3$ synthesis by Thermal Treatment.

Fig. 3 show XRD pattern of $CaCO_3$ obtained by thermal treatment method. The results indicated that the crystal structure of $CaCO_3$ is rhombohedral, similar to solid state method. There are not any impurity in $CaCO_3$ obtained by thermal treatment method at 500 ^oC that shown in Fig. 3. The XRD patterns of $CaCO_3$ at 600 ^oC and 700 □C indicated the impurity of CaO in samples. Nano-size $CaCO_3$ with an average size of 35, 46 nm was estimated by using the Debye-Scherrer formula at 500, 600 ^oC respectively that indicate the effect of temperature on particle size. Debye-Scherrer formula is:.

$$D_c = \frac{K\lambda}{\beta \cos\theta}$$

where K is a constant (ca. 0.9); λ is the X-ray wavelength used in XRD (1.5418 Å); □ the Bragg angle; β is the pure diffraction broadening of a peak at half-height, that is, broadening due to the crystallite dimensions.

Thus optimum reaction temperature for preparing of pure nano-size $CaCO_3$ is 500 ^oC and between of two used methods, the best way to preparing of pure nano-size $CaCO_3$ is thermal treatment method.

The typical SEM images of $CaCO_3$synthesized at different molar ratios via solid state at 550 ^oC are shown in Fig. 5. As shown in Fig. 5, the effects of quantity of surfactant on the morphology of $CaCO_3$ are clearly observed. In 1:1 molar ratio,nano-sized $CaCO_3$ has not formed yet,when the molar ratio is increased to 1:2 we can see the formation of agglomerated structures. At last the smaller particle size was observed in 1:3 and 1:4 molar ratios.

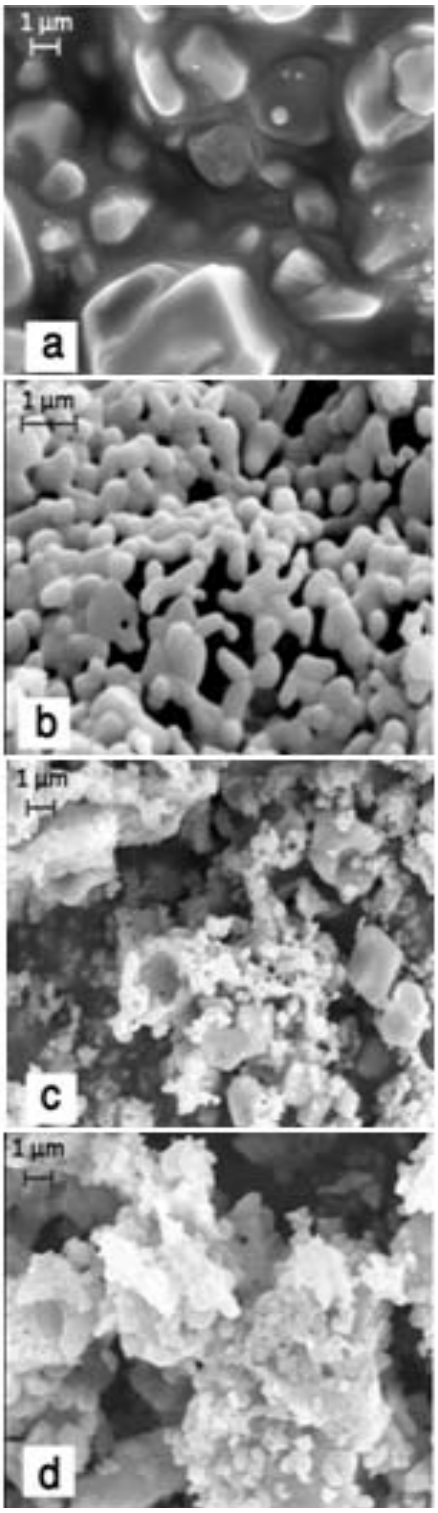

Fig. 5. SEM micrographs of products synthesis by solid state method (a) 1:1. (b) 1:2. (c)1:3. (d) 1:4

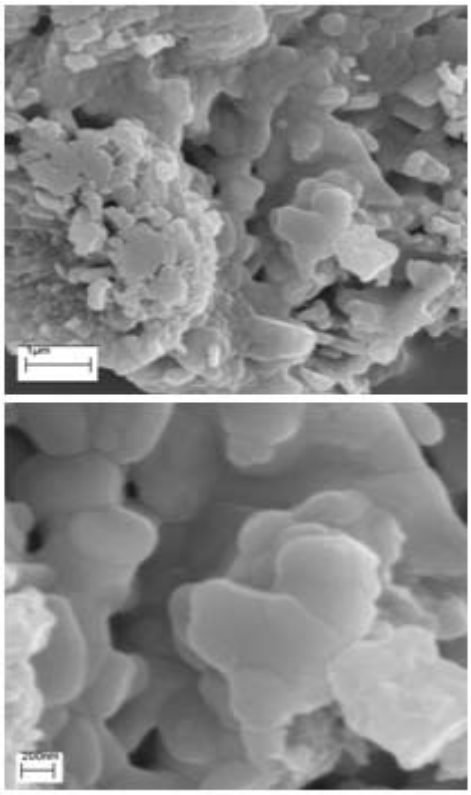

Fig. 6. SEM micrographs of products synthesis by Thermal Treatment at 500 □C.

The typical SEM images of $CaCO_3$ synthesis via thermal treatment at 500 □C are shown in Fig. 6

In order to observe the morphological details of the $CaCO_3$, TEM images of sample at 500 □C were taken. Fig. 7. shows TEM micrograph of $CaCO_3$ prepared at 500 □C via thermal treatment method. The particle size of $CaCO_3$ obtained at 500 ºC observes about 50-70 nm from TEM image. The morphology of $CaCO_3$ obtained at 500 ºC is spherical

Fig. 8. shows TEM micrograph of $CaCO_3$ prepared via solid state with 1:4 molar ratio. The results of TEM images showed that the morphology of samples is cubic liked

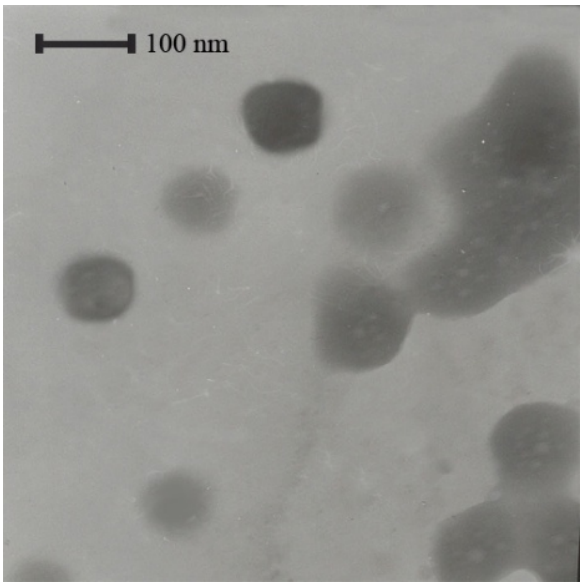

Fig. 7. TEM micrographs of $CaCO_3$ synthesis by solid state method

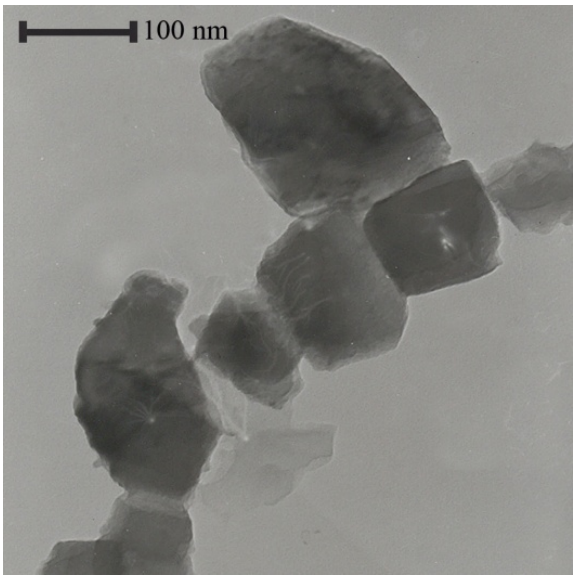

Fig. 8. TEM micrographs of $CaCO_3$ synthesis by solid state method

4. Conclusion

$CaCO_3$ nanospherical have successfully been prepared via a simple thermal treatment of a new precursor. Also nanocubic structure of $CaCO_3$ have been prepared via solid state method. FT-IR, XRD, SEM and TEM techniques have been used for characterization of the structure, morphology, and purity of $CaCO_3$ products. Proposed solvent free and surfactant-free fabricating procedure was simple, cheap, and safe which maybe suitable for industrial production of high purity, nano-sized, pure $CaCO_3$ crystallites.

Acknowledgements

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