

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 processes in dry condition under air atmosphere. Hydrothermal, solvothermal and thermal decomposition using organic solvent or surfactant carry out under vigorous controlled conditions but the choice of suitable metal 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 $\text{Cu K}\alpha$ 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 °C). 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 °C and nano-size CaCO_3 without any impurity was formed.

2.3. Solid state method

$\text{Ca}(\text{NO}_3)_2$ 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 °C) 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°C . 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°C and Fig. 2 show IR spectra of samples were formed via thermal treatment method.

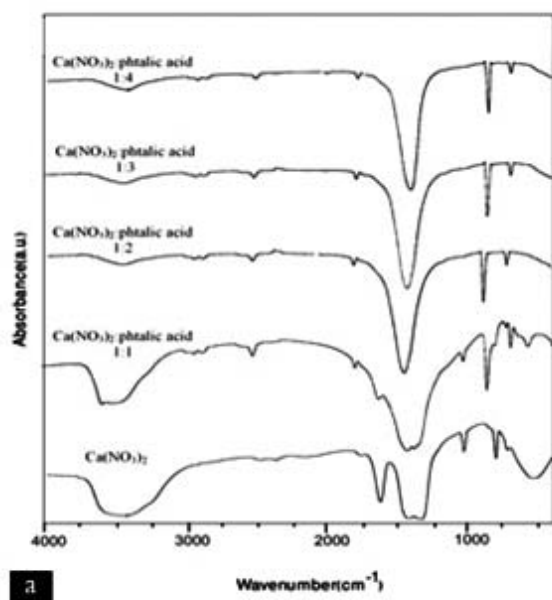


Fig. 1. IR spectra of samples were formed via solid state method at 550°C

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°C via thermal treatment method. Fig. 2 at 500°C 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 $400\text{--}1800\text{ cm}^{-1}$ region. The strong broad 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].

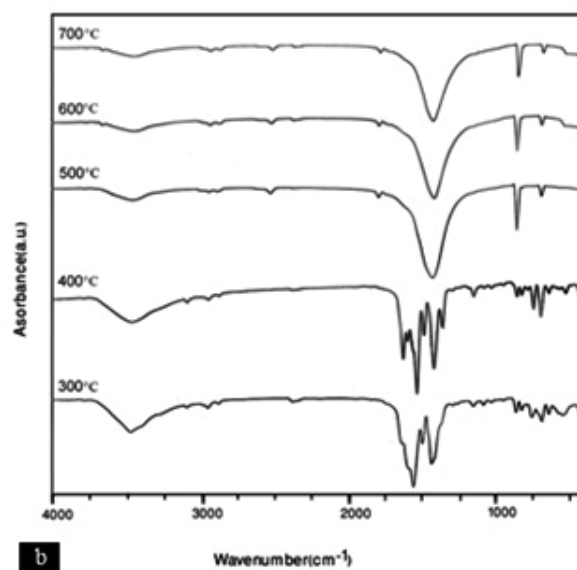


Fig. 2. IR spectra of samples were formed via thermal treatment method

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 $a = 4.9840\text{ nm}$, $b = 4.9840\text{ nm}$, $c = 17.1210\text{ nm}$. 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.

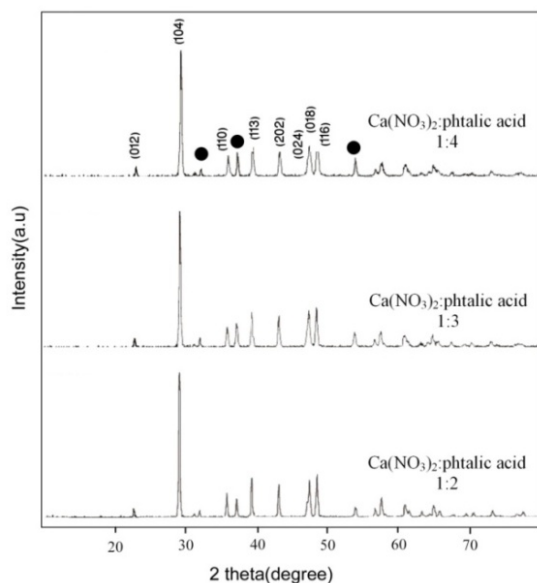


Fig. 3. XRD pattern of CaCO₃ Synthesis by solid state

Fig. 3 show XRD pattern of CaCO₃ obtained by thermal treatment method. The results indicated that the crystal structure of CaCO₃ is rhombohedral, similar to solid state method. There are not any impurity in CaCO₃ obtained by thermal treatment method at 500 °C that shown in Fig. 3. The XRD patterns of CaCO₃ at 600 °C and 700 °C indicated the impurity of CaO in samples. Nano-size CaCO₃ with an average size of 35, 46 nm was estimated by using the Debye-Scherrer formula at 500, 600 °C 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); θ the Bragg angle; β is the pure diffraction broadening of a peak at half-height, that is, broadening due to the crystallite dimensions.

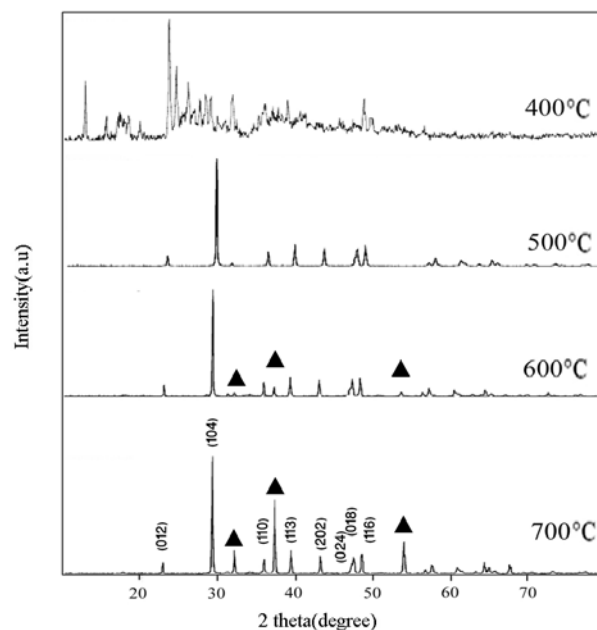


Fig. 4. XRD pattern of CaCO₃ synthesis by Thermal Treatment.

Thus optimum reaction temperature for preparing of pure nano-size CaCO₃ is 500 °C and between of two used methods, the best way to preparing of pure nano-size CaCO₃ is thermal treatment method.

The typical SEM images of CaCO₃ synthesized at different molar ratios via solid state at 550 °C are shown in Fig. 5. As shown in Fig. 5, the effects of quantity of surfactant on the morphology of CaCO₃ are clearly observed. In 1:1 molar ratio, nano-sized CaCO₃ 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.

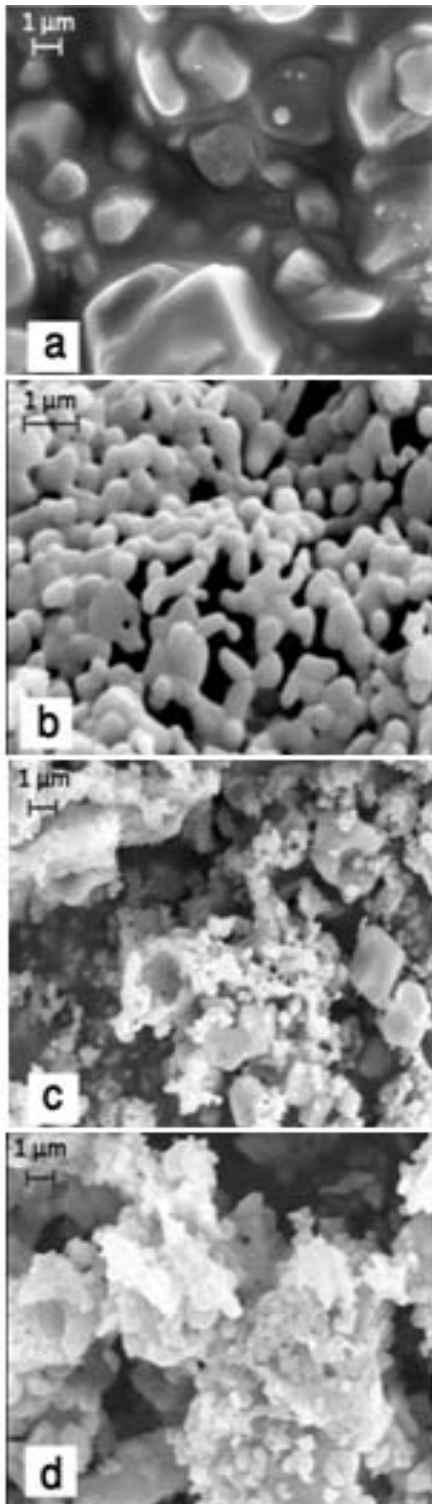


Fig. 5. SEM micrographs of products synthesis by solid state method (a) 1:1. (b) 1:2. (c) 1:3. (d) 1:4

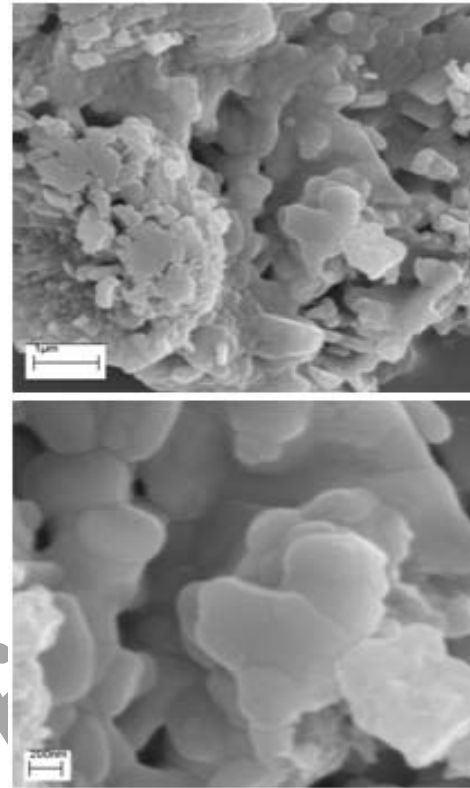


Fig. 6. SEM micrographs of products synthesis by Thermal Treatment at 500 °C.

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 °C observes about 50-70 nm from TEM image. The morphology of CaCO_3 obtained at 500 °C 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

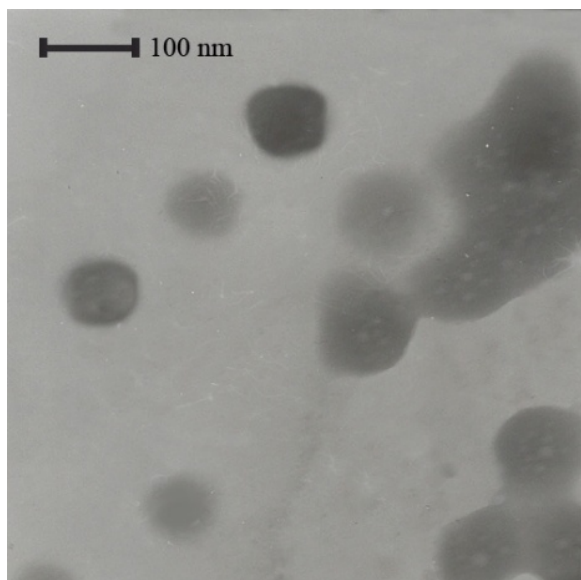


Fig. 7. TEM micrographs of CaCO_3 synthesis by solid state method

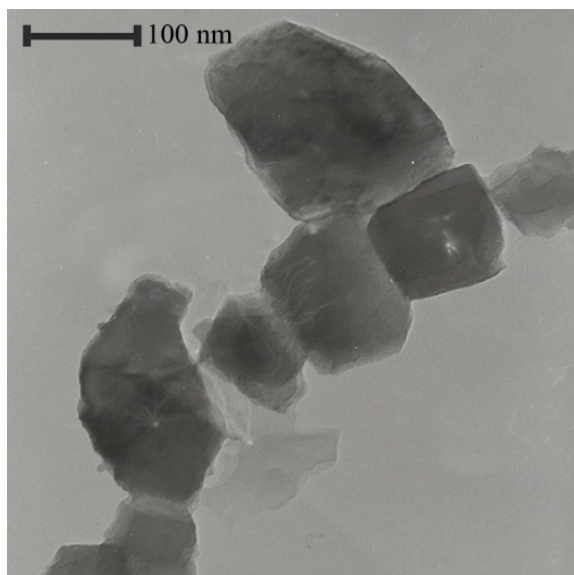


Fig. 8. TEM micrographs of CaCO_3 synthesis by solid state method

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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