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Synthesis of $Baso_4$ Nanoparticles by Precipitation Method Using Polycarboxylate as a Modifier

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Abstract: Problem statement: Barium Sulfate ($BaSO_4$) is suitable for many applications because of its whiteness, inertness and high specific gravity. **Approach:** Nanoparticles of barium sulphate ($BaSO_4$) have been synthesized from barium nitrate by precipitation method in the presence of water soluble organic polycarboxylic polymer as a modifying agent. Transmission electron microscopy, Scanning electron microscopy, Fourier transform infrared spectroscopy and X-ray powder diffractometry were used to characterize the products as well as laser grainmeter. **Results:** The results indicate that spherical $BaSO_4$ nanoparticles are obtained with poor crystalline and diameters ranging from 30-35 nm. **Conclusion:** The organic polycarboxylate shows as good modifier agent. So, this method can be employed to synthesize higher yield of $BaSO_4$ nanoparticles.

Key words: Barium sulphate, precipitation method, barium nitrate, water soluble organic, direct precipitation, crystal growth, micron scale, coupling agents, X-Ray Diffraction (XRD)

INTRODUCTION

Syntheses of inorganic powders with ultrafine size, controlled surface properties and controlled morphology attract increasing interest because of its important use in various fields. Barium Sulfate ($BaSO_4$) is suitable for many diverse applications because of its whiteness, inertness and high specific gravity (Bala *et al*., 2006). Barium sulfate is a kind of important inorganic chemical product as packing and additive in painting, coating, plastics and medicines fibers (Shen *et al*., 2007; Wu *et al*., 2007; Kucher *et al*., 2008). Nanometer barium sulfate has more scientific advantages of size reduction. Crystallization and precipitation processes are widely used in the chemical industry. One of the most well-known crystallization processes is the reaction of barium (Ba^{2+}) and sulphate ($SO^{2-}{}_4$) ions into barium sulphate ($BaSO_4$), as shown in Eq. 1 (Oncul *et al*., 2006; Kieffer *et al*., 2009):

$$Ba^{2+}(aq) + SO^{2-}{}_4(aq) \rightarrow BaSO_4(s)\downarrow \quad (1)$$

Liquid/liquid reaction is the main method of the preparation of nano-$BaSO_4$. This method has some divisions such as direct precipitation, micro emulsion (Adityawarman, 2005) membrane separation (Wu *et al*., 2007), microchannels reactor (Wang *et al*., 2009). Preparation of $BaSO_4$ particles has been widely studied in order to assess the effect of mixing, precipitation models, agitator speed and feed position on particle size distribution, crystal growth and morphology (Judat and Kind, 2004; Bala *et al*., 2005).

Many different approaches have been reported for preparation of $BaSO_4$ nanoparticles including the addition of different additives (Jones *et al*., 2003; Wang *et al*., 2005) induction by Monolayer and microemulsion (Nagaraja *et al*., 2007) The addition of additives and induction by LB monolayer could causea significant change in morphology, but the size was generally in the micron scale rather than nanometer scale. The size and corresponding morphology obtained in W/O microemulsions (Chen *et al*., 2005) or reverse micelle approach could be controlled well by adjusting the molar ratio of water to surfactant. However, the product yield was rather low because of the poor solubility of salts in conventional microemulsions. There were also some reports about preparation of organo-modified $BaSO_4$, but the $BaSO_4$ obtained was in micron scale. Although preparation of organocapped $BaSO_4$ was earlier described, (Sui *et al*., 2004) the condition was not suited to the industry. Preparation of barium sulphate nanoparticles by use of tetradecanoic

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acid, hexadecanoic acid and stearic acid as modifier was studied (Shen *et al*., 2007).

When inorganic fillers with surface functional groups reach the polymer matrix, it can be expected to enhance stiffness and impact properties simultaneously (Li *et al*., 2002; Bala *et al*., 2006). However, the surface of inorganic particles (e.g., $BaSO_4$) is hydrophilic, so it is not easy to disperse these particles in a lipophilic matrix. For this reason, it is very important to conduct surface modification of $BaSO_4$. One of the several ways to achieve a good dispersivity is to modify the hydrophilic particle surface so that it is lipophilic in nature. For this purpose various coupling agents, which are capable of introducing a certain functional group onto the particle surface, have been employed: Titanate coupling agents (He *et al*., 2005), silane coupling agents (Bala *et al*., 2006) and organophosphonic acids (D'Andrea and Fadeev, 2003; Sheng *et al*., 2004). This study aims to synthesize nanoparticles of barium sulphate ($BaSO_4$) from barium nitrate by precipitation method in the presence of water soluble organic polycarboxylic polymer as a modifying agent.

MATERIALS AND METHODS

Chemicals and instruments: The starting materials used in this study were Barium nitrate, ammonium sulphate and polycarboxylates. They were used without further purification. Double distilled water was used in all experiments. The prepared barium sulfate was characterized by using (SEM :JEOL JSM 6360 DLA, Japan), Transmission Electron Microscope ((TEM; Hitachi, H-800), Fourier transform Infrared (FT-IR) spectra were measured using a Perkin Elmer 880 FT IR spectrometer by incorporating samples in KBr (1: 99 mg) disks to confirm the characteristic vibrational bands, with resolution of 4 cm^{-1}, X-ray Diffraction (XRD) pattern of $BaSO_4$ was recorded on (M/S. Shimadzu Instruments, Japan) diffractometer XRD 7000 with Ni filtered Cu Kα as a radiation source at 2θ scan speed of 4° min^{-1} and the particle size distribution was analyzed by L4 submicron particle size analyzer He-Ne Laser beam, Fluoride, USA.

Preparation of the samples:

Direct Precipitation (DP) procedure: 50 mL 0.1 M $Ba(NO_3)_2$ was added to 50 mL 0.1M $(MH_4)_2SO_4$ in the presence of water soluble organic polymers as modifier agent. The solution was added drogpwise into the flask while stirring at room temperature with dispersant at strong mechanical stirring 2000-2500 rpm.

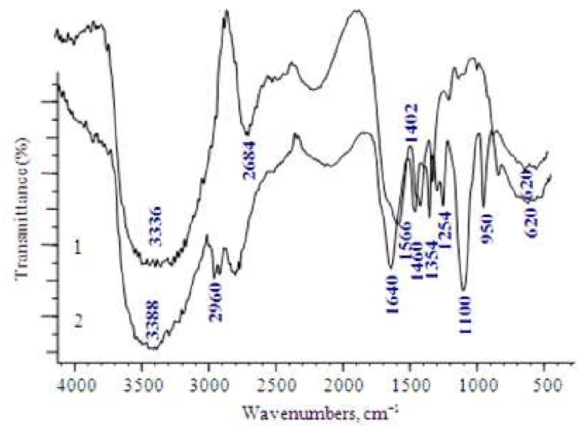


Fig. 1: FT-IR spectra of polycarboxylate

The steady drop rate was 20 drops min^{-1}. Gelatinous white precipitates were formed instantly. The precipitates were separated from the mother liquid by centrifuged at 3000 rpm for 20 min. and then the supernatant solution was discharged and the solid was redispersed in deionized water. This process was repeated three times in order to rinse the particles. After the last centrifugation, sedimented particles were dried in the microwave oven. The products were slightly grinded for analysis (Bala *et al*., 2005; Gupta *et al*., 2010).

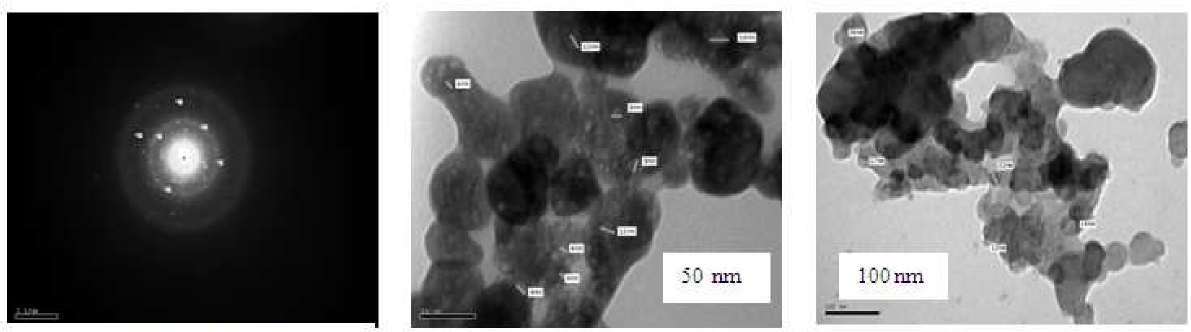
Figure 1 show the IR spectra of polycarboxylates 1 and 2. Note the band around 3400 cm^{-1} for to H_2O. The band at near 3000 cm^{-1} for carboxylic acid O-H stretch also for, in the same region, the C–H stretching bands of both alkyl and aromatic groups. The carbonyl stretch C = O of a carboxylic acid appears as an intense band from 1760-1690 cm^{-1}. The C = C stretch band is at 1640 cm^{-1}. The C-O stretch appears in the region 1320-1210 cm^{-1} and the O–H bend is in the region 1440-1395 cm^{-1} and 950-910 cm^{-1} from C-H bending bands in the same region (Khenifi *et al*., 2007).

RESULTS AND DISCUSSION

TEM micrographs: The TEM micrograph (Fig. 2) shows that the $BaSO_4$ particles are nearly elliptical and have a round shape. The particle size is between 6 and 26 nm, with an average size of 18 nm. In addition, there are some uniform mesopores in the particles and the diameter of the cavities is about 6-8 nm. These regions appear brighter because they have absorbed fewer electrons than their surroundings. The larger particles contain more pores and the number of pores decreases as the diameter of the particles decreases, especially in small particles that only contain one pore. The high dispersibility of the powder in water might be related to the mesopores of the particles. The formation of the mesoporous structure is related both to nucleation and to the growth mechanism of the $BaSO_4$ particles. Judat and Kind (2004) and Nagaraja *et al*. (2007) investigated the particle morphology and internal structure (the cavities contained within the particles) of precipitated $BaSO_4$. They showed that $BaSO_4$ grows according to a combined mechanism involving molecular and aggregative growth. The pore size increases with increasing supersaturation.

SEM Micrographs: The SEM images (Fig. 3-c) shows that the spherical shell types nanoparticles are distributed uniformly. The larger particles contain more pores and the number of pores decreases as the diameter of the particles decreases, especially in small particles that only contain one pore. This reveals that the high dispersibility of the powder in polycarboxylate might be related to the mesopores of the particles and the high rate of adsorption of polycarboxylate onto their surfaces. The formation of the mesoporous structure is related both to nucleation and to the growth mechanism of the $BaSO_4$ particles (Nagaraja *et al*., 2007).

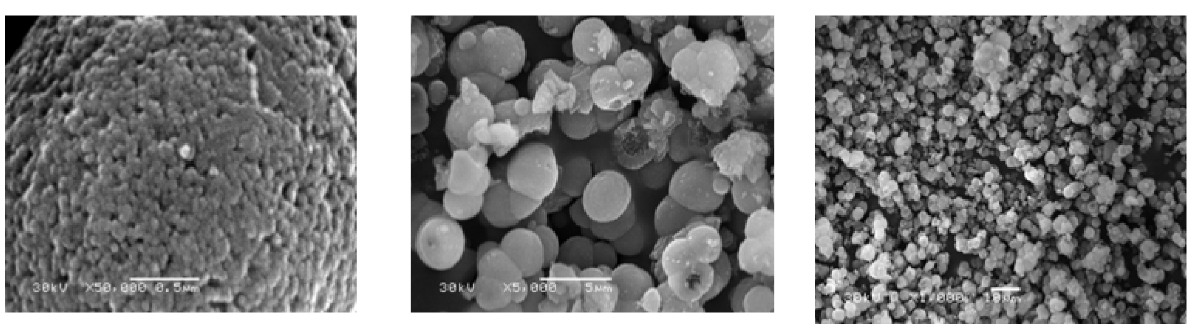
XRD spectra: Figure 4 shows the XRD pattern of nano barium sulfate. It is shown that the nano barium sulfate composed mainly from barite. All of the peaks could be indexed as a typical orthorhombic structure of $BaSO_4$, with crystalline cell constants a = 7.144 Å, b = 8.865 Å, c = 5.445 Å, which were basically in agreement with the reported values (JCPDS No. 80-0512) (Salah *et al*., 2009; Shen *et al*., 2007). The crystallite sizes of the sample are estimated from the line width of the (212) XRD peaks.



Electron diffracton pttem
of the particles

(a) (b) (c)

Fig. 2: TEM images of Nano $BaSO_4$



(a) (b) (c)

Fig. 3: SEM Micrographs of Nano $BaSO_4$

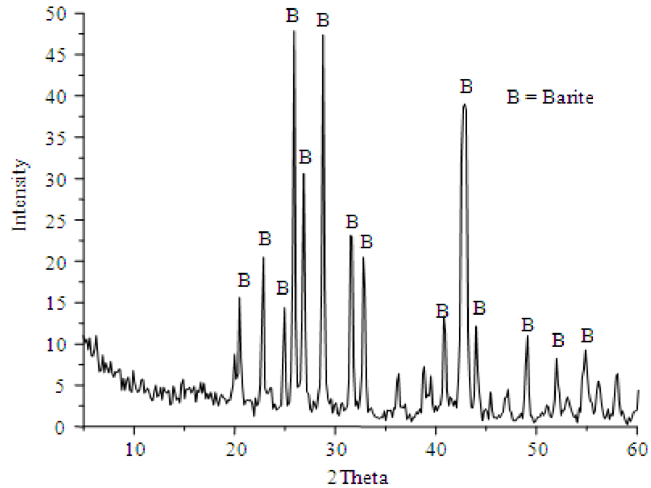


Fig. 4: XRD patterns of Nano $BaSO_4$

Fig. 5: FT-IR spectra of Nano $BaSO_4$

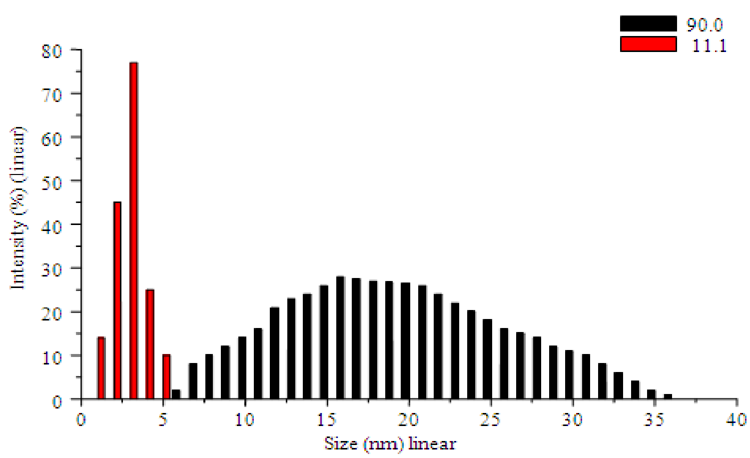


Fig. 6: Size distribution of $BaSO_4$ particles prepared

Table 1: Different Angle SDP Set 1 Intensity Results for Repetition 1, SDP Results Summary

	Parameter			Calculated results			
Angle	SDP range (nm)	Size (nm)	Amt (%) (nm)	Std dev (nm)	Mean Size(nm)	Mean SD(nm)	Dust (%)
11.1	1.0-5000.0	8.7	100.0	1.2	8.7	1.2	0.0
90.0	1.0-5000.0	17.35	100.0	7.5	17.35	7.5	34.5

FTIR spectra: Figure 5 shows the FT-IR spectra of $BaSO_4$ nanoparticles. The bands centered at 1073–1192 cm^{-1} and the shoulder at 982 cm^{-1} were the symmetrical vibration of SO_4^{-2}. The peaks at 610 and 638 cm^{-1} corresponded to the out-of-plane bending vibration of the SO_4^{-2}. The peaks at 2851 and 2920 cm^{-1} could be assigned to the symmetric and asymmetric vibrations of -CH2-and-CH3 groups. The peaks at 1436 and 1402 cm^{-1} were ascribed to the scissoring of -CH2- or the symmetric deformation of the -CH3 group. The FT-IR spectra showed that the particles contained polycarboxylate and there were no corresponding peaks in XRD patterns. This may be because the polycarboxylate was absorbed on the surface of $BaSO_4$ rather than entering the $BaSO_4$ crystal to form composite (Shen *et al*., 2007; Gupta *et al*., 2010).

Partical size distribution: The particle size distributions of the prepared $BaSO_4$ nanoparticles are given in Fig. 6 and also Table 1. It can be found that the average particle size is 17.35 nm.

DISCUSSION

In this study we have exposed nanoparticles of barium sulphate ($BaSO_4$) from barium nitrate by precipitation method in the presence of water soluble polycarboxylate polymer as a modifying agent. The reason that the average diameter of $BaSO_4$ particles in the presence of polycarboxylate polymer was smaller than that obtained without polycarboxylate polymer (Saraya *et al*., 2010) was that when the polycarboxylate polymer was added into the reaction system, the growth of $BaSO_4$ was prevented due to the steric hindrance of polycarboxylate polymer on the surface of $BaSO_4$ particle. But the steric hindrance was so weak that the difference was negligible. The possible reactions were as follows:

$PRCOONH_4 + H2O \rightarrow PRCOO^- + NH^+_4$
$PRCOO^- + Ba^{2+} \rightarrow P(RCOO)_2Ba$ (soluble)
$P(RCOO)_2Ba$ (soluble) $+ SO_4^{2-} \rightarrow BaSO_4 \downarrow$

When polycarboxylate polymer was first added into water the $PRCOO^-$ was fully released. Ba^{2+} was relatively surplus because $SO^{2-}{}_4$ was dropped into Ba^{2+} in the process. Polycarboxylate $P(RCOO^-)$ acted as an inducer to attract Ba^{2+} via electrostatic forces. With the addition of SO_4^{2-}, $BaSO_4$ crystals formed gradually. $PRCOO^-$ still covered the surface of the $BaSO_4$ crystals, resulting in the inhibition of further growth of $BaSO_4$ nanoparticles, which was the reason for smaller size and uniform distribution of particles. During the process, polycarboxylate two roles: inducer and inhibitor. The average diameter of $BaSO_4$ nanoparticles decreased in the order of addition of tetradecanoic acid, hexadecanoic acid and stearic acid, which was possibly related to the chain length of organic acid. The longer the chain length, the greater the steric hindrance (Shen *et al*., 2007).

CONCLUSION

We have synthesized $BaSO_4$ nanoparticles using water soluble organic stabilizing agent, polycarboxylate. Nanoparticles crystallize in the orthorhombic structure. FT-IR and electron microscopy studies confirm that the nanoparticles free from the surfactant and they are in the range of 30-55 nm. This method can be employed to synthesize higher yield of $BaSO_4$ nanoparticles.

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