Green chemistry approach: Synthesis, morphological and thermal studies of nanocomposites of barium carbonate nanoparticles

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In the present study barium carbonate ($BaCO_3$) nanoparticles were synthesized by using barium chloride dihydrate, sodium hydroxide, urea and lemon juice as stabilizing agent. Thereafter, one polymer polymethyl methacrylate and three nanocomposites have been synthesized by using different concentrations (0.025, 0.050, 0.075 mg) of nanoparticles by adopting microwave assisted method. Nanoparticles were characterized by FT-IR, UV-Visible, X-Ray Diffraction, Transmission Electron Microscopic (TEM) and Scanning Electron Microscopic (SEM) studies. X-Ray diffraction peak broadening was used to evaluate the sizes of nanoparticles by using Debye-Scherrer equation. Nanocomposites were characterized by FT-IR, Scanning Electron Microscopic (SEM) studies. The thermal stability of polymer and nanocomposites was determined by TG/DTA. XRD studies and TEM images revealed average particle size of nanoparticles 17.09 nm. Thermal studies revealed that thermal stability of all nanocomposites has increased as compared to polymer.

Keywords: Nanoparticles, microwave assisted synthesis, FT-IR, P-XRD, Transmission Electron Microscope, Scanning Electron Microscope.

Introduction

Polymethyl methacrylate (PMMA) is the most important acrylic polymer. The significance of this polymer can be well understood by its diversified applications. It is used for the manufacturing of artificial glasses[1], dielectric films[2], acrylic paints[3], micro-cell foam[4] etc. The most attractive applications of PMMA based materials are their use in a variety of biomedical applications such as intraocular lenses[5], vertebroplasty[6], good adhesion to teeth[7] and for skin and soft-tissue augmentation[8]. The properties of PMMA polymer may be alter by fabricating of these polymers by mixing nanoparticles i.e. by conversing polymers in to nanocomposites. Researchers have reported that the mechanical[9], electrical[10], thermal[11], optical[12] and electrochemical[12] properties of the nanocomposites vary from that of the component materials.

Barium carbonate ($BaCO_3$) is an important chemical used in the preparation of glass capillary columns[13], as precursor in the synthesis of magnetic ferrites[14], as electrodeposition material for coatings on stainless steel substrates[15]. In recent years, barium carbonate nanoparticles have been reported as potential anticancer agents[16], synergistic catalysts for the oxygen reduction reaction[17] and as a dendritic nanofiller[18]. In addition, $BaCO_3$ nanoparticles embedded sulphonated poly(ether sulfone) (SPS) membranes showed Mg^{2+} retentive and cation selective properties from natural water[19]. Various chemical and physical methods are available for the synthesis of nanoparticles, reversed micelles[20], chemical co-precipitation[21], spray pyrolysis[22], ultrasonic irradiation[23], sol-gel[24], microemulsion-plant mediated solvothermal[25], sonochemical[26], microwave-assisted[27].

Among the aforesaid methods microemulsion-plant mediated and microwave assisted methods have gained much attention of the researches due to pro-active approach to pollution prevention. These methods targets pollution at the design stage, before it even begins. In continuation[28,29] of our previous work the present study was aimed to investigate green synthesis of $BaCO_3$ nanoparticles, one polymer polymethyl methacrylate (PMMA) and their $BaCO_3$/polymethyl methacrylate nanocomposites, characterization and thermal studies with a view to observe their change in properties, morphology and thermal stability.

Results and discussion

Infrared spectral studies:

IR spectra of synthesized $BaCO_3$ nanoparticles exhibited absorption band at 1749.18 cm^{-1} which may be attributed due to stretching vibrations of C=O group. A strong peak at 1439.96 cm^{-1} may be attributed due to asymmetric stretching vibrations of C-O moiety of CO_3^{2-}. Two absorption band at 857.51 cm^{-1} and 693.11 cm^{-1} may be attributed due to the bending in-plane vibrations[30,31] and out-of-plane vibrations of O-C-O of CO_3^{2-}.

IR spectra of nanocomposites of barium carbonate (0.025 mg, 0.050 mg and 0.075 mg) with polymethyl methacrylate exhibited bands peaks in the region 2996.69–2994.91, 2886.28–2846.38, 1731.09–1730.51, 1718.36–1636.95, 1450.67–1449.30, 1387.41–1385.67, 1242.78–1237.00, 1193.33–1148.18, 1064.85–1061.12, 841.36–841.32 and 664.31–607.33 cm^{-1} due to C-H stretching vibrations of CH_3 group, C-H stretching vibrations of CH_2 moiety, symmetric stretching vibrations of C⋯O of CO_3^{2-}, stretching vibrations of C=O, bending vibrations of C-H moiety, asymmetric stretching vibrations of C⋯O bond of CO_3^{2-}, C-O-C stretching vibrations, O-CH_3 stretching vibrations, C-C stretching vibrations[32,33], bending vibrations of O-C-O (in-plane) of CO_3^{2-} and bending vibrations of O-C-O (out-of-plane) of CO_3^{2-} of $BaCO_3$ nanoparticles respectively.

UV-Visible spectral studies:

The UV-Visible spectrum (Fig. 1) of synthesized barium carbonate ($BaCO_3$) nanoparticles exhibited the peaks at 275.00 and 271.00 nm which confirmed the formation of $BaCO_3$ nanoparticles[31].
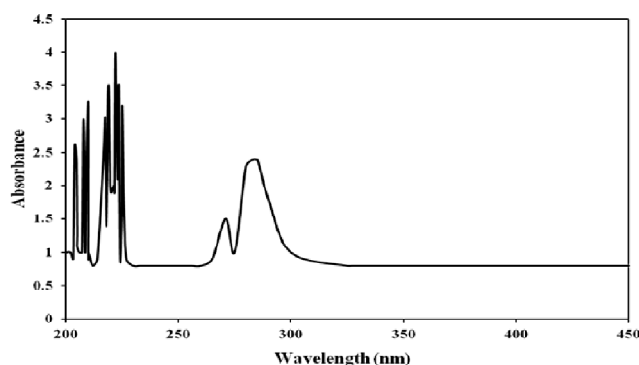

Fig. 1. UV-Visible spectrum of $BaCO_3$ nanoparticles.

P-XRD spectral studies:

The diffraction pattern of synthesized barium carbonate nanoparticles was measured in the range of 3° < 2θ < 80°. The XRD spectra (Fig. 2) of nanoparticles showed that particles were crystalline in nature. Full widths at half maximum values have been used to find the size distribution of particles. It has been observed that the broader is the peak, broader is the size distribution of nanoparticles[34]. The crystalline size of nanoparticles was calculated by the width of X-ray peaks supposing they are free from non-uniform strains using Debye-Scherrer's formula.

$$D = k\lambda/\beta \cos\theta$$

D is the average crystallite domain size perpendicular to the reflecting planes, λ is the X-ray wavelength, β is the full width at half maximum (FWHM) and θ is the diffraction angle.

On applying Debye-Scherrer formula on different peaks of P-XRD graph of barium carbonate nanoparticles it has
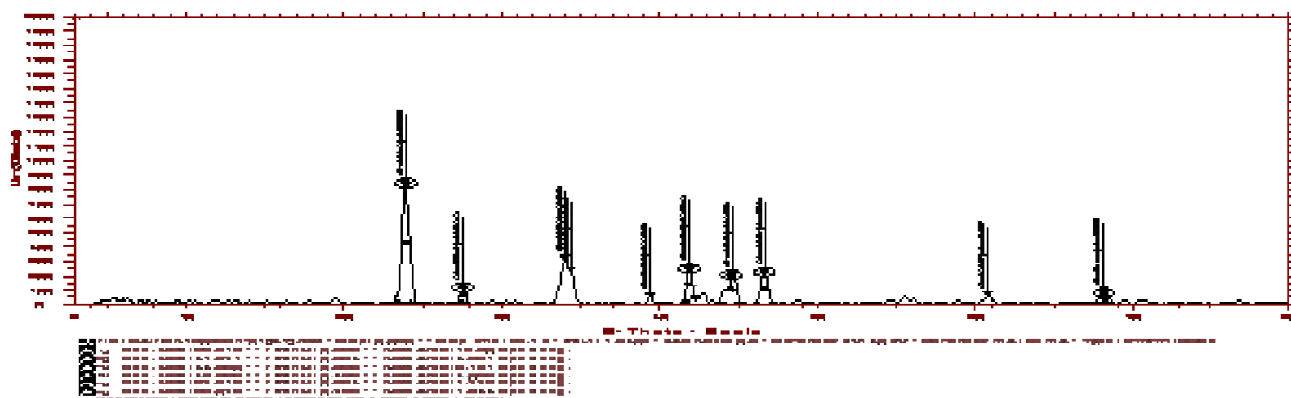

Fig. 2. P-XRD graph of $BaCO_3$ nanoparticles.

been found that the synthesized nanoparticles have different size like 15.78, 21.07, 10.06, 16.87, 21.61 and 13.75 nm. The average particle size of synthesized barium carbonate nanoparticles has been found to be 16.52 nm.

Transmission electron microscopic studies:

The TEM images (Fig. 3) of synthesized nanoparticles indicated that the size of barium carbonate nanoparticles lies in the range of 10.63–21.36 nm. The average particle size was found to be 17.09 nm.
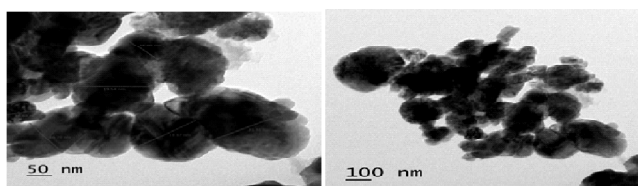

Fig. 3. TEM images of synthesized $BaCO_3$ nanoparticles.

Scanning electron microscopic studies:

SEM images (Fig. 4) of nanoparticles indicated their crystalline morphology with highly agglomerated in nature. Most of the nanoparticles exhibited spherical shape but they exist as agglomerated form. However, some of them were rod shape and irregular in shape.
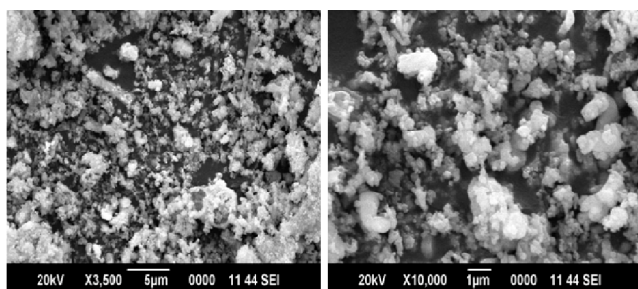

Fig. 4. The SEM images of $BaCO_3$ nanoparticles.

SEM images (Fig. 5) of $BaCO_3$ (0.025 mg)/nanocomposite indicated flaky morphology with some degree of agglomeration and irregular shapes.

SEM images (Fig. 6) of $BaCO_3$ (0.050 mg)/nanocomposite indicated most of the nanoparticles were dispersed on the smooth morphological surface of PMMA. However some of the nanoparticles are dispersed in the agglomerated form on the surface of the polymer.
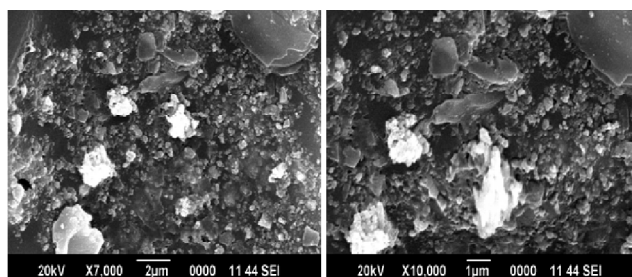

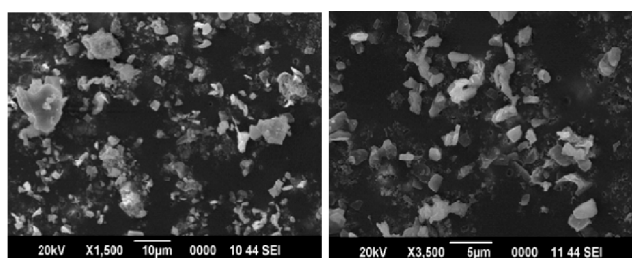**Fig. 5.** The SEM images of $BaCO_3$ (0.025 mg)/polymethyl methacrylate nanocomposite.

Fig. 6. The SEM images of $BaCO_3$ (0.050 mg)/polymethyl methacrylate nanocomposite.

SEM images (Fig. 7) of $BaCO_3$ (0.075 mg)/nanocomposite indicated smooth morphology in which nanoparticles have been dispersed on the surface of PMMA with some agglomeration.
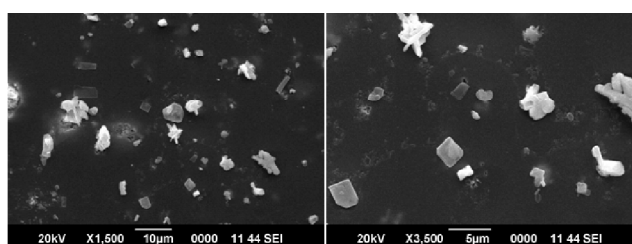

Fig. 7. The SEM images of $BaCO_3$ (0.075 mg)/polymethyl methacrylate nanocomposite.

Thermogravimetric analysis:

TG thermogram of polymethyl methacrylate exhibited degradation in 3 steps. First degradation occurred between 149.98–257.33°C corresponds to weight loss 19.16%, in second step it degraded between 257.33–367.05°C corresponds to weight loss 37.24% and third degradation occurred between 367.05–444.10°C corresponds to weight loss

39.52%. DTA curve indicated that these weight losses take place by endothermic decomposition. TG/DTA thermogram of $BaCO_3$ (0.025/0.050/0.075 mg)/PMMA nanocomposites also indicated three steps thermal degradation. It has been found that final degradation of $BaCO_3$ (0.025 mg)/PMMA nanocomposite was observed between 470.84–680.50°C. This degradation temperature was much higher as compared to 372.17–631.20°C and 363.63–640.81°C corresponding to the $BaCO_3$ (0.050 mg)/PMMA and $BaCO_3$ (0.075 mg)/PMMA nanocomposites respectively. The results of study indicated that final decomposition temperatures of nanocomposites were higher than that of pure PMMA. However, the thermal stability of $BaCO_3$ (0.025 mg)/PMMA nanocomposite has increased much more as compared to $BaCO_3$ (0.050 mg)/PMMA and $BaCO_3$ (0.075 mg)/PMMA nanocomposites. The increased in the thermal stability of this nanocomposite may be due to the incorporation of nanoparticles in polymer matrix which reduces the mobility of polymer chains while heating.

Experimental

Microwave synthesizer Discover Lab Mate with Intellivent Pressure, 240 V/50 Hz has been used to synthesize nanoparticles, polymer and nanocomposite. IR spectra of the synthesized nanoparticles, polymer and nancomposites were recorded by FT-IR spectroscopy in the range 4000–400 cm^{-1} on Bruker spectrophotometer by using KBr pellets. UV-Visible spectra of synthesized nanoparticles were recorded by UV-Visible spectroscopy on lab-India UV-Visible spectrophotometer UV 3000$^+$ in DMSO at room temperature. The P-XRD analysis of nanoparticles were carried out on XPERT-PRO X-ray diffractometer operated at a volume of 45 kV and a current of 40 mA with Cu Kα' radiation in a θ-2θ configuration. The TEM **s**tudies of nanoparticles were carried out by using Jeol/JEM 2100 operated at an accelerating voltage of 200 kV with the resolution-point 0.23 nm and lattice 0.14 nm. The Scanning Electron Microscopic studies of nanoparticles and nanocomposites have been carried out by using JEOL model JSM-6390LV with resolution of 3 nm (Acc V30 kV, WD 8 mm, SEI) and magnification 5X to 300,000 x (both in high and low vacuum modes), operating at a voltage of 1 pA to 1 mA. The Thermogravimetric/Differential Thermogravi-metric analysis of the polymer and nanocomposites were carried

out with model Parkin-Elmer, Diamond TG/DTA and TG measurement range 200 mg and TG sensitivity 0.2 mg.

Synthesisof $BaCO_3$ nanoparticles:

4.85 g barium chloride dihydrate, 2 g sodium hydroxide (NaOH) and 7.2 g [(NH$_2$)$_2$CO] were dissolved in 50 ml deionized water. 10 ml lemon extract was added drop wise to the above solution under constant stirring. The resulting solution was irradiated with microwaves at 110 W for 30 min at 90°C with continuous stirring in the microwave synthesizer. The obtained precipitate was separated by centrifugation and washed with deionised water for four times. Finally, the precipitate was dried in an oven at 120°C for 6 h.

Synthesis of polymethyl methacrylate (PMMA):

5 ml methyl methacrylate, 10 mg benzoyl peroxide and 10 ml toluene were mixed in a 100 ml round bottom flask. The contents were subjected for heating in microwave synthesizer at an emitted power of 100 W for 6 min by maintaining the temperature at 80°C. The precipitation was done by using acidified CH_3OH (1 ml HCl + 5 ml CH_3OH). The obtained viscous liquid was then homogeneously spread on a glass plate. On drying at room temperature a thin film was obtained.

Synthesis of $BaCO_3$/polymethyl methacrylate nanocomposites:

1 g polymethyl methacryalate was dissolved in 50 ml tetrahydrofuran (THF) and stirred by magnetic stirrer for about 30 min to form a homogenous solution. The contents were subjected for heating in microwave synthesizer at an emitted power of 100 W for 10 min by maintaing the temperature 80°C. 0.025/0.050/0.075 mg of $BaCO_3$ nanoparticles suspended in water:HCl (3:1) were added with stirring in the viscous state of polymethyl methacryalate. The obtained viscous liquid was homogeneously spread on a glass plate. A thin film was obtained on drying at room temperature.

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