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Green Chemistry Approach: Synthesis, Characterization and Thermal Studies of Nanocomposites of Lead Oxide Nanoparticles

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ABSTRACT

This paper deals a novel method for the synthesis of PbO nanoparticles by biochemical reaction between lead salt solution and leaf extract of *Coriandrum sativum* and facile, rapid & eco-friendly microwave assisted synthesis of two polymers poly methyl methacrylate & poly butyl methacrylate and two nanocomposites PbO/Poly methyl methacrylate (PbO/PMMA) and PbO/ Poly butyl methacrylate (PbO/PBMA). The synthesized nanoparticles were characterized by FT-IR, UV-visible, X-Ray Diffraction (XRD) and Transmission Electron Microscopic (TEM) studies. Nanocomposites were characterized by FT-IR, Scanning electron microscopy (SEM) and TG/DTA. XRD studies and TEM images revealed average particle size of synthesized nanoparticles 20 nm. Thermal studies revealed that overall thermal stability of PbO/PMMA and PbO/PBMA nanocomposites decreased due to incorporation of PbO nanoparticles in the polymer matrix.

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

INTRODUCTION

Green chemistry provides an approach to synthesize materials without the use of harmful chemicals. It has some aims and objectives to control environmental pollution caused due to the use of hazardous chemicals. The use of plant extract is an efficient way to apply green chemistry approach in the synthesis of nanoparticles, because of low cost, eco-friendly, non-pathogenic, economical protocol and providing a single step technique for the biosynthesis processes [1]. Nanoparticles produced from plant extract are more stable and rate of synthesis is also faster as compared to other synthetic approaches [2].

Nanotechnology field is revolutionary, widespread and interdisciplinary in nature. One of the critical aspects of nanotechnology research is to modify the surface of different nanoparticles to make them compatible with polymer matrices and more useful for different applications.Nanoparticles significantly influence the polymer matrix due to their surface area, leading to new properties which are not present in the pure materials [3]. 'Nanocomposites' are those substances comprising of materials or particles at nanoscale dimension embedded in ceramic, metal or polymer matrix [4]. These are high performance materials which exhibit unusual property of combinations and unique design possibilities [3]. Therefore various properties of nanocomposites are enhanced such as optical property [5, 6], mechanical property [7, 8], thermal stability [7], magnetic [9] and biosensing [10] property. Nanocomposite also exhibited excellent antibacterial activity [11, 12] against gram positive and gram negative bacteria.

Metal oxide nanoparticles are known as heterogeneous catalysts. It has been shown that PbO nanoparticles act as catalysts in various organic reactions (like oxidative coupling reactions). Lead oxide nanoparticles can be used in batteries [13], as photocatalyst in degradation of methyl blue dye [14] and in biomedical applications [15]. These significant applications of PbO nanoparticles prompted us for the synthesis of PbO nanoparticles.

Coriandrum sativum leaves extract was chosen for the synthesis of Lead oxide nanoparticles due to its good bioreductant property. This paper incorporates the green synthesis of PbO nanoparticles, two polymers poly methyl methacrylate (PMMA) & poly butyl methacrylate (PBMA), their nanocomposites, characterization and thermal studies with a view to observe their change in properties, morphology and thermal stability.

EXPERIMENTAL SECTION

All chemicals used were of analytical grade. Aqueous leaf extract of *Coriandrum sativum* was used as reducing agent. Lead acetate trihydrate (E. Merck), Sodium hydroxide (Sisco), Benzoyl peroxide (E. Merck), Methyl methacrylate (E. Merck), Butyl methacrylate (E. Merck), Hydrochloric Acid (E. Merck), Methanol (E. Merck), Toluene (E. Merck), DMSO (Qualigens) were used as received.

Preparation of aqueous leaf extract of *Coriandrum sativum*

25 g fresh leaves of *Coriandrum sativum* was washed thoroughly with double distilled water to remove the dust particles and other contaminants and grinded in a high speed blender. The blended pulp was filtered by using muslin cloth to remove solid particles. The obtained liquid was again filtered by using Whatman filter paper No.1. The filtrate was kept at 4ºC and used within a week for the preparation of nanoparticles.

Preparation of PbO nanoparticles

0.02 M (0.758 g) lead acetate trihydrate was dissolved in 50 ml distilled water under constant stirring and 10 ml aqueous leaf extract of *Coriandrum sativum* was added drop wise during stirring. 0.1 M (0.4 g, 100 ml) NaOH solution was added to adjust pH 12 during stirring within 2 h. The obtained dirty green precipitate was separated, washed with distilled water, dried at 80 ^{o}C and calcined at 300^{o}C for 3 h. The dark beige colored powder of PbO nanoparticles was obtained. The resulting product was dried in a vacuum desiccator over anhydrous $CaCl_2$.

Synthesis of Poly methyl methacrylate (PMMA)

In a 250 ml conical flask 5 ml methyl methacrylate, 10 mg benzoyl peroxide was taken and 10 ml toluene was added to it. The contents were mixed homogenously by stirring and placed in a microwave oven at an emitted power of 150W for 6 min by maintaining the temperature at 60-70ºC. The precipitation was done by using acidified CH_3OH (1ml HCl + 5 ml CH_3OH) and then homogeneously spread on a glass plate. On drying at room temperature a thin film was obtained.

Synthesis of Poly butyl methacrylate (PBMA)

5 ml butyl methacrylate, 10 mg benzoyl peroxide and 10 ml toluene were mixed by stirring. This mixture was placed in the microwave oven at an emitted power of 180W in the temperature range 60-70^{o}C for 4 min. Acidified CH_3OH (1 ml HCl +5 ml CH_3OH) was used for the precipitation of the formed polymer and finally spread on the glass sheet to obtain a thin film.

Synthesis of PbO/ Poly methyl methacrylate nanocomposite (PbO/PMMA)

5 ml methyl methacrylate, 10 mg benzoyl peroxide and 10 ml toluene were mixed by stirring. The contents were subjected for microwave irradiations in an oven at an emitted power of 140W for 20 min with an interval of 5 min by maintaining the temperature of reaction at 60-70 ^{o}C a sticky solution was obtained. To this sticky solution 0.05 mg lead oxide nanoparticles dissolved in 2 ml 1M-HCl was mixed by stirring and further subjected to microwave radiation for 3 min at 160W. The precipitation was done by using acidified CH_3OH (1ml HCl+ 5 ml CH_3OH). Finally, this solution was spread on a glass sheet to get a thin film.

Synthesis of PbO/ Poly butyl methacrylate nanocomposite (PbO/PBMA)

5 ml butyl methacrylate, 10 ml benzoyl peroxide and 10 ml toluene were mixed homogeneously and the contents were subjected for microwave irradiations in a microwave oven at an emitted power of 160W for 10 min at an interval of 2 min. The temperature of reaction was maintained at 60-70ºC, a sticky solution was obtained. To this sticky solution 0.05 mg of lead oxide nanoparticles dissolved in 2 ml 1M-HCl was mixed and the solution was again heated in the microwave oven for 5 min. Finally, the formed PbO/PBMA composite was precipitate out by using acidified CH_3OH (1ml HCl + 5 ml CH_3OH) and spread on the glass sheet homogeneously. On drying it at room temperature a thin film was obtained.

RESULTS AND DISCUSSION

Infrared spectra of the synthesized nanoparticles, polymers and nanocomposites were recorded by ‘Bruker’ spectrophotometer in the range of 4000–400 cm^{-1} by using KBr pellets. UV-Visible spectra of nanoparticles was recorded 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 voltage of 45 kV and a current of 40 mA with Cu Kα radiation in a θ-2θ configuration. The TEM studies of nanoparticles were carried out by using JOEL model JEM 2100, operated at an accelerating voltage of 200kV with the resolutionpoint 0.23 nm and lattice 0.14 nm. The Scanning Electron Microscopic (SEM) studies of nanocomposites have been carried out by using JEOL Model JSM-6390LV operating and resolution of 3 nm (Acc V30 kV, WD 8 mm, SEI) to 8 nm (Acc V 1.0 kV, WD 6 mm, SEI) and magnification 5 x to 300,000 x (both in high and low vacuum modes), operating at a voltage of 1 pA to 1mA.The Thermo gravimetric and Differential Thermogravimetric Analysis of polymers and nanocomposites were carried out with model Perkin Elmer, USAA, Diamond TG/DTA and TG measurement range 200 mg and TG Sensitivity 0.2 mg.

Infrared spectral studies

FT-IR spectra of PbO nanoparticles exhibited peaks at 689.02 cm^{-1} due to stretching vibrations of Pb-O bond [16] and 469.41 cm^{-1} due to Pb-O bending vibrations [17]. Poly methyl methacrylate exhibited the bands at 2997.93 cm^{-1} due to C- H stretching vibrations of CH_3, 2951.12 cm $^{-1}$ due to C- H stretching vibrations of CH_2 group, 1733.80 cm^{-1} due to C=O stretching vibrations, 1449.84 cm^{-1}due to bending vibrations of C-H moiety. The bands at 1193.70 cm^{-1}, 1146.28 cm^{-1} and 1062.42 cm^{-1}may be attributed due to $O\text{-}CH_{3,}$ C–O–C and C-C stretching vibrations respectively. IR spectra of nanocomposite PbO/PMMA exhibited the bands at 2950.23, 2844.18, 1749.00, 1454.25, 1150.65, 1030.41 and 988.68 cm^{-1} which may be due to C-H stretching vibrations of methyl group, C-H stretching vibrations of CH_2 group, C=O stretching vibrations, bending vibrations of C-H moiety, $O\text{-}CH_3$ stretching vibrations, C-O-C stretching vibrations and stretching vibrations of C-C respectively. The bands at 696.75 cm^{-1}, 490.04 cm^{-1}, 479.81 cm^{-1}may due to stretching and deformation vibrations of PbO. Poly butyl methacrylate exhibited the bands at 2957.94 cm^{-1} due to C- H stretching vibrations of CH_3, 2933.48 cm^{-1} due to C- H stretching vibrations of CH_2, 1722.78 cm^{-1} due to C=O stretching vibrations, 1454.54 cm^{-1}due to C- H bending vibrations of CH_2, 1142.21 cm^{-1} due to C–O–C stretching vibrations and 1063.50 cm^{-1}due to stretching vibrations of C-C bonds. In the IR spectra of nanocomposite PbO/PBMA bands at 2856.40, 2738.31, 1730.83,1455.05, 952.75 and844.46 cm^{-1} may be attributed due to C-H stretching vibrations of CH_3 group, C-H stretching vibrations of CH_2 group, C=O stretching vibrations, C-H bending vibrations of CH_2 group, C-O-C stretching vibrations and C-C stretching vibrations respectively. The bands at 702.97, 464.41 and 454.53 cm^{-1} may be attributed due Pb-O stretching and deformation vibrations.

UV-Visible spectral studies

The UV-Visible spectrum of synthesized Lead oxide (PbO) nanoparticles exhibited the peaks at 314.05 and 420.07 nm which clearly indicated the formation of PbO nanoparticles [18, 19].

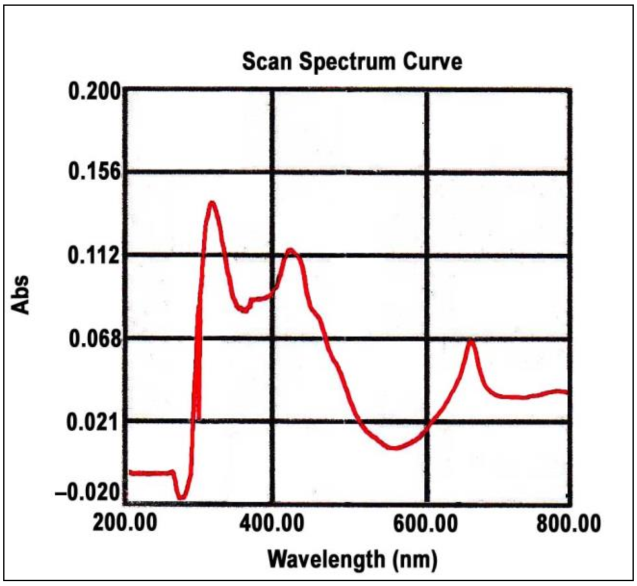


Figure 1: UV-Visible spectrum of PbO nanoparticles

P-XRD studies

The structure and composition of synthesized lead oxide nanoparticles was determined by X-ray diffraction technique. The XRD spectra (Fig.2) of nanoparticles exhibited crystalline nature of PbO nanoparticles. Full width at half maximum has 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. Theoretical model suggested that the full width at half maximum increases with the increase in particle size [20]. The crystalline domain size was calculated by using the width of X-ray peaks, assuming that they are free from non- uniform strains, using Debye-Scherrer formula:

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

Where 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 equation on different peaks of P-XRD graph it has been found that the synthesized nanoparticles have different sizes such as 20.70, 62.13, 15.53, 10.35, 20.70, 15.53, 10.35, 7.27 nm. The average particle size has been found to be 20.32 nm.

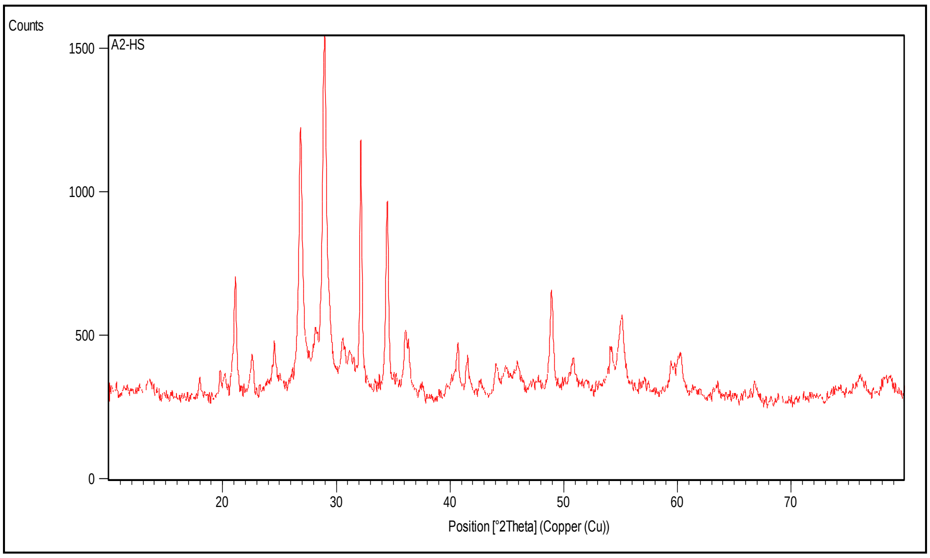


Figure 2: P-XRD graph of PbO nanoparticles

Transmission electron microscopy studies

The TEM images (Figure 3) indicated that the particle size of synthesized lead oxide nanoparticles lies in the range 4.69- 62.13 nm. The average particle size was found 20.14 nm.The results were very close to the values obtained from P-XRD analysis.

Scanning electron microscopic studies

The SEM images of PbO/PMMA nanocomposite indicated that the particles have core shell structure [21] and their surface is covered with PMMA film. It is also observed that PMMA has irregularly shaped PbO nanoparticles dispersed in its composites.

The SEM images of PbO/PBMA nanocomposite showed homogeneous polymer surface with high stress zone [22]. The high stress zone is depicted by fracture surface which indicate the increased reinforcement and good dispersion of PbO nanoparticles in PBMA matrix.

The SEM images of PbO/PMMA and PbO/PBMA nanocomposites have been shown in Figure 4 and Figure 5.

Thermogravimetric analysis

TG/DTA thermograms (Figure 6) of poly methyl methacrylate exhibited degradation in 3 steps. First degradation occurred between 128.52-276.44^{o}C corresponds to weight loss 9.070 %, in second step it degraded between 276.44-422.37^{o}C corresponds to weight loss 37.400 % and third degradation occurred between 422.37-726.2^{o}C corresponds to weight loss 19.520 %. Final degradation occurred at 726.2^{o}C. DTA curve of PMMA polymer indicated that these weight losses take place by endothermic decomposition.

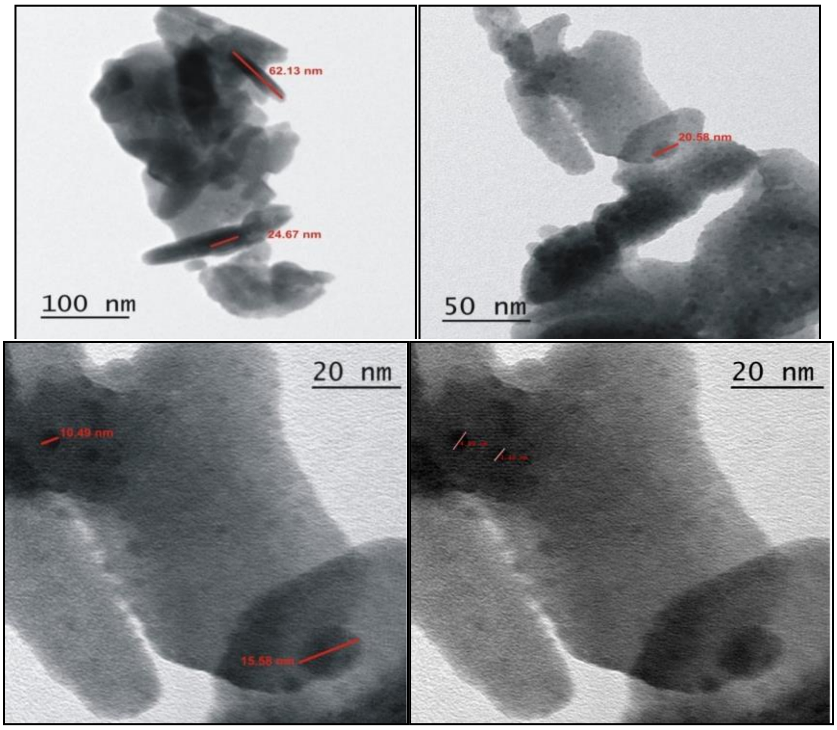


Figure 3: TEM images of synthesized PbO nanoparticles

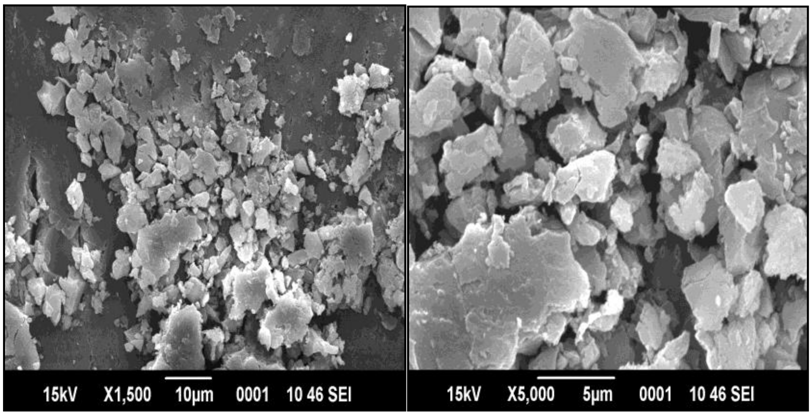


Figure 4: The SEM images of PbO/Poly methyl methacrylate nanocomposite

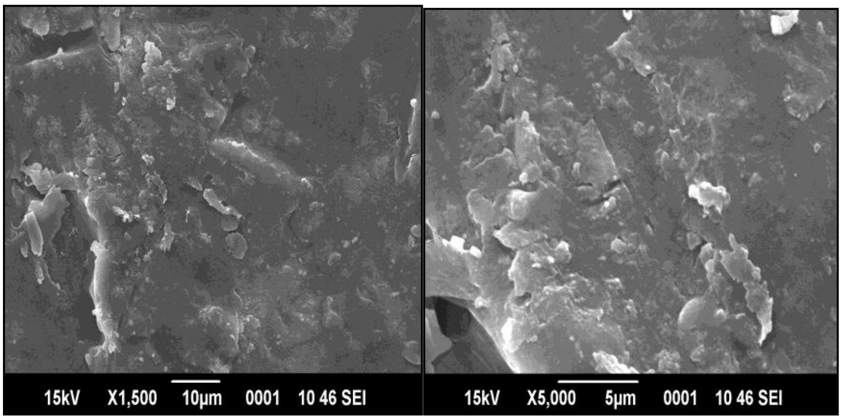


Figure 5: The SEM images of PbO/Poly butyl methacrylate nanocomposite

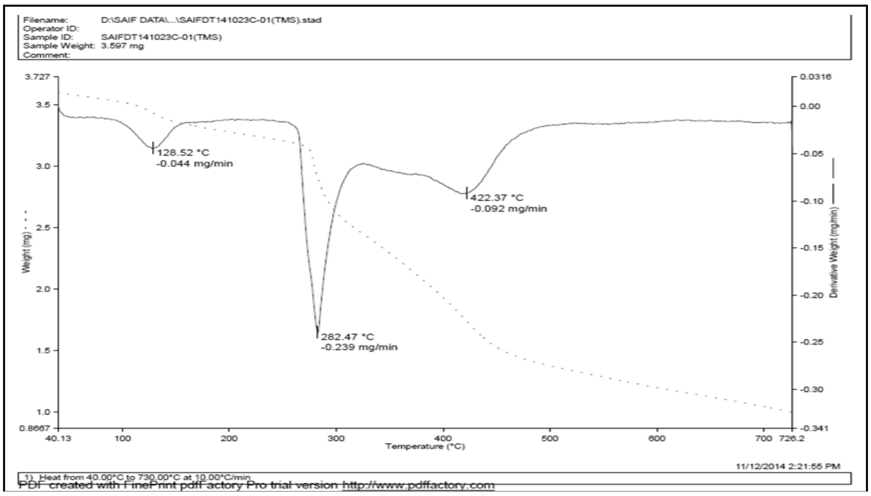


Figure 6: TG/DTA thermogram of PMMA nanocomposite

TG/DTA thermograms (Figure 7 a & b) of PbO/PMMA indicated three steps thermal degradation. The first step degradation occurred between 30-228ºC corresponding to weight loss of 14.152%. In the second step degradation occurred between 228-315ºC which corresponds to weight loss of 39.679%. Final degradation occurred between 315-426ºC which corresponds to weight loss of 46.215%. DTA curve indicated that first two weight losses occur by endothermic decomposition and third weight loss occur by exothermic decomposition. The overall thermal stability of PbO/PMMA nanocomposite decreased as nanocomposite finally degraded at 426ºC and PMMA degraded at 726.2ºC.

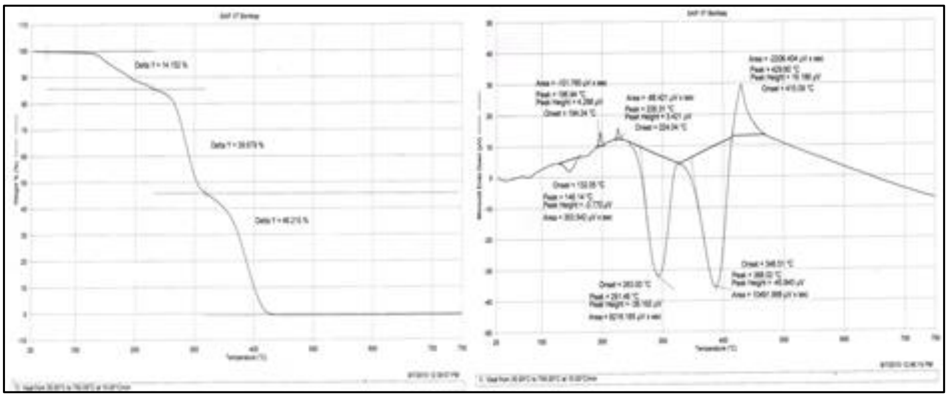
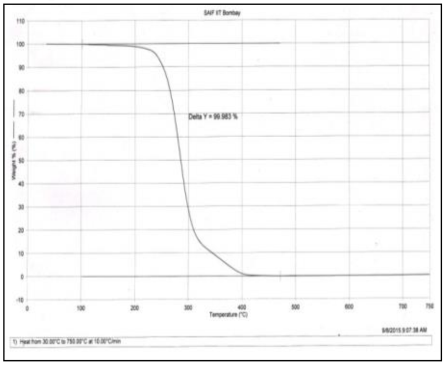


Figure 7a: TG thermogram of PbO/PMMA Fig.7b: DTA thermogram of PbO/PMMA

TG/DTA thermograms (Figure 8a &b) of the PBMA sample indicated single step thermal degradation. This single step degradation occurred between 106.68- 462.10ºC corresponds to weight loss of 99.983% with endothermic decomposition.



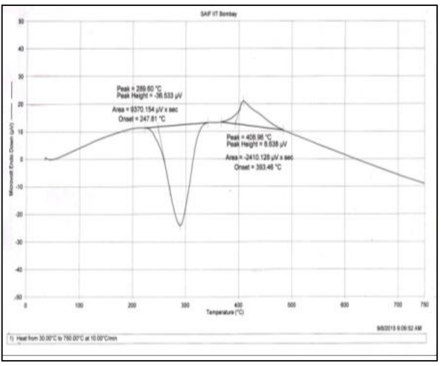
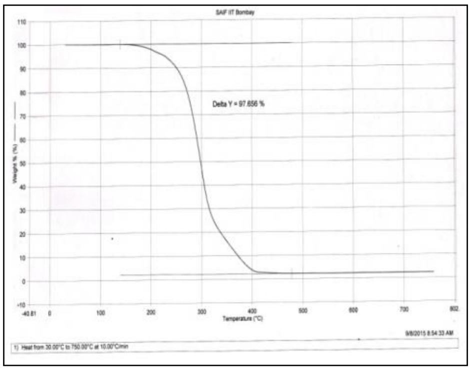


Figure 8a: TG thermogram PBMA Figure 8b: DTA thermogram of PBMA

TG/DTA curves (Figure 9a & b) of the PbO/PBMA sample indicated single step thermal degradation. This single step degradation occurred between 30-453ºC corresponding to weight loss of 97.656% with endothermic decomposition as indicated by DTA curve. However, the overall thermal stability of PbO/PBMA nanocomposite decreased as it finally degraded at 453ºC and PBMA degraded at 434ºC.



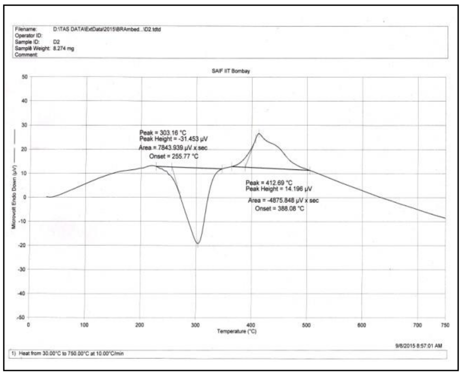


Figure 9a: TG thermogram of PbO/PBMA Figure 9b: DTA thermogram of PbO/PBMA

CONCLUSIONS

In this study PbO NPs and PbO/PMMA & PbO/PBMA nanocomposites were synthesis and characterized. PbO NPs were synthesized by using aqueous extracts of *Coriandrum sativum* leaf extract and lead acetate. PbO/PMMA and PbO/PBMA nanocomposites were prepared by using microwave heating method in a typical experimental set up and in a short time. P-XRD studies and TEM images revealed average particle size of synthesized nanoparticles 20 nm approx. Thermal studies revealed that overall thermal stability of PbO/PMMA and PbO/PBMA nanocomposites decreased due to incorporation of PbO nanoparticles in the polymer matrix.

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