



Thermal and Electrical behaviour of CaSO₄ nanoparticles mixed with Polymethylmethacrylate and Polystyrene Polymer matrix

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Abstract

Polymethyl methacrylate/CaSO₄ (PMMA/CaSO₄) and Polystyrene/CaSO₄ (PS/CaSO₄) nanocomposites were synthesized by deposition technique. Chemical structure and morphology of synthesized PMMA/CaSO₄ and PS/CaSO₄ nanocomposites were investigated using Fourier Transform Infrared (FTIR) and scanning electron microscope (SEM). SEM indicated that nano-CaSO₄ particles present in nanosphere and have been homogeneously encapsulated in the PS matrix with irregular size. The FTIR shows characterized peaks in the region where from 400-700cm⁻¹ which shows the probability of existence of bonding between CaSO₄ nanoparticles and the polymer network in their respective polymer/CaSO₄ nanocomposites. Thermal gravimetric analysis (TGA) shows that both PMMA/ CaSO₄ and PS/CaSO₄ nanocomposites have higher decomposition temperature in comparison with the purified polystyrene. Electrical conductivity measurement shows that PMMA/ CaSO₄ and PS/CaSO₄ nanocomposites show semiconducting in nature with conductivity lies between 10⁻⁷ to 10⁻⁵ S/cm.

Keywords: polymethylmethacrylate, polystyrene, CaSO₄ nanoparticles, SEM, TGA

Introduction

The general class of nanocomposites organic/inorganic materials is a fast growing area of research. Significant efforts are focused on the ability to obtain control of the nanoscale structures via innovative synthetic approaches. The properties of nanocomposites materials depend not only on the properties of their individual's parents but also on their morphology and interfacial characteristics.

Nanocomposites also offer the possibility to combine diverse properties which are impossible within a single material, e.g., flexible mechanical properties and superconducting properties. Properties which have been shown to undergo substantial improvement such as mechanical properties (strength, modulus and dimensional stability), decreased permeability to gases, water and hydrocarbons, thermal stability and heat distortion temperature, flame retardancy and

reduced smoke emissions, chemical resistance, surface appearance, electrical conductivity, optical clarity in comparison to conventionally filled polymers etc.

Nanoparticles have been extensively studied as drug carriers [1, 2] in the pharmaceutical and medical field. They may possess controllable and sustainable release properties sub cellular size and biocompatibility with tissue and cells. It has been demonstrated that a significant improvement in drug specificity of action can be reached upon its incorporation into nanoparticles, this effect being mainly attributed to changes in tissue distribution and pharmacokinetics [3, 4]. In comparison with microparticles, number distinct advantages are offered by nanoparticles, including relatively higher intracellular uptake simplicity in biological fluids.

PMMA acrylic glass is used for construction residential and commercial aquariums, lenses of exterior lights of automobiles, helmet visors etc. Polystyrene produced with conventional methods are used world wide on a large scale for copolymerization submarine periscope, rubber, fiberglass, pipes, food container etc.

In the present we reported synthesis of PMMA/CaSO₄ and PS/CaSO₄ nanocomposites by deposition technique to improve polymer properties like thermal resistance, electrical conductivity etc. The chemical structure and morphology were investigated by FTIR and SEM respectively. The thermal behavior of nanocomposites studied by thermal gravimetric analysis (TGA). Electrical conductivity of nanocomposites was also measured.

Materials and Methods

Chemicals

Monomer (methyl methacrylate and styrene) was procured from Alfa Aesar. Monomers were washed by 1% NaOH solution before they were used and were kept in cool and dry place. Polyethylene glycol (PEG) and ammonium sulfate were obtained from Merck and kept in dark and dry place. Calcium chloride procured from Sisco India and used after purification and dried by standard methods [5]. Benzoyl peroxide (CDH, Laboratory reagent) was used as an initiator.

Common organic solvents were procured either from Qualigens, E- Merck or Alfa Aesar. Solvents such as methyl alcohol, ethyl alcohol, butyl alcohol, benzene, toluene, THF, acetone, carbon tetrachloride, DMF etc. were used after purification and kept in dry and cool place.

Synthesis of Polymethyl methacrylate (PMMA) and Polystyrene (PS)

A procedure to prepare polymer of methyl methacrylate (MMA) and styrene was followed, which involve placing 20ml of monomer into 0.15g (0.75%) of benzoyl per oxide (BPO), which was used as initiator. Solution of monomers was placed in 100 ml round bottom flask and the solution was stirred for 2hrs at 70°C to complete the polymerization of MMA and styrene. Then solution was precipitated with 5% acidified methanol and finally dried at 110°C for 2hrs under oven to yield polymer material.

Synthesis of Nanoparticles of CaSO₄

Step I

Firstly take 11.1 gm (0.1 mol) of CaCl₂ which was dissolved in minimum quantity of water. Then 24.8 gm (0.1mol) polyethylene glycol (PEG) which was used as surfactant was mixed in the minimum quantity of water. PEG solution were added drop by drop with continue shaking

in to CaCl₂ solution in ratios (PEG: CaCl₂) 4:1 for 15 min and stirred 4 hrs. Then solution was kept for 12 hrs.

Step II

13.2 gm (0.1 mol) (NH₄)₂SO₄ solution were added drop by drop with continuous stirring in step 1 solution with in 15 min and stirred. Finally the solution was kept for overnight and filtered it with Whatmann filter paper No.1. The nanoparticles collected on the filter paper were dried in oven at 110°C for 12 hrs.

Preparation of PMMA/CaSO₄ and PS/CaSO₄ Nanocomposites

The preparation of nanocomposites was carried out by dissolving 500mg of purified polystyrene in 10ml toluene while PMMA in acetone. The solution was vigorously stirred with predissolved 50mg CaSO₄ nanoparticles. The mixture was stirred for 2 hrs. The homogeneously mixture obtained were poured in Petri dish and dried in oven for 12 hrs. at 110°C.

The various nanocomposites were prepared by varying the concentration of CaSO₄ nanoparticles with respect to polymer followed by above methods.

Characterization

FTIR (Perkin Elmer spectrophotometer RX1) spectra of nanocomposites sample with toluene solvent, in the range 450-4000 cm⁻¹ using resolution of 4cm⁻¹ on a computer interfaced Perkin-Elmer. Morphology was studied using scanning electron microscope (Hitachi FM-SEM S 4700) and the samples were gold coated prior to measurement. Thermo gravimetric analysis (Perkin – Elmer Pyris – 1 TGA) was performed on Perkin-Elmer in presence of nitrogen and samples were heated to 450°C at a rate of 20.00°C. Conductivity was measured with LCR meter.

Results and Discussion

SEM

Figure 1 illustrated the micrograph of the obtained composites revealing that their production was successfully achieved yielding materials with particles well dispersed with in the polymer matrix. From micrograph it is clear that the distribution of nanoparticles is homogeneously and the particles size in the range of 150-200 nm. This illustrated that the nanoparticles are intercalated into the structure of polymer.

FTIR

Figure 3 shows the FTIR spectra of PMMA/CaSO₄ nanocomposites show C-H stretching of methyl group at 3004cm⁻¹. The absorption peak at 1460, 1440, 1426, 1408 and 1365 cm⁻¹ associated to the C-H symmetric and asymmetric mode. A peak at 1212cm⁻¹ assigns the torsion of CH₂ group. A absorption peak at 1712 cm⁻¹ show C=O stretching vibration. PS/CaSO₄ nanocomposites shows the band at 3060, 3027, 2920, 1604, 1460, 728 and 694cm⁻¹ were all characteristic absorbance band of polystyrene which are well in accord with that reported by literature [6], in which the characteristic peak of the polystyrene including the C-H aromatic stretching vibration at 3027cm⁻¹, the C-H stretching vibration at 2920 cm⁻¹ and phenyl ring stretching vibration at 1604 cm⁻¹, 1495 cm⁻¹, 728 cm⁻¹ and 694 cm⁻¹ clearly observed [Figure 4]. The IR spectra of CaSO₄ nanoparticles show absorption at 450-1400 cm⁻¹ [7]. In PS/CaSO₄ nanocomposites there is a peak at 464cm⁻¹ which shows the probability of existence of bonding between CaSO₄ particles and polymer network, where typical band at 529 cm⁻¹ show incorporation of CaSO₄ nanoparticles on PMMA matrix.

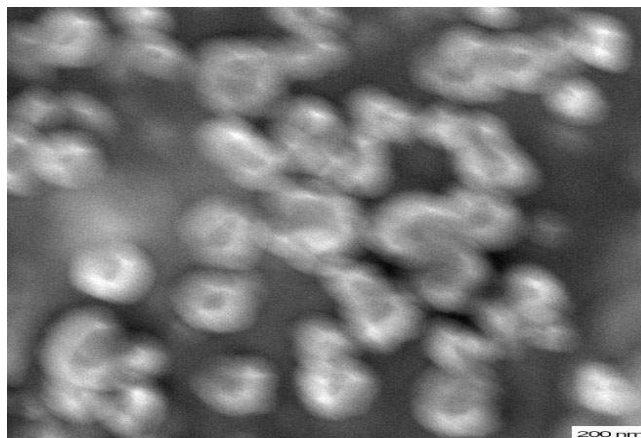


Fig 1. SEM image of PS/CaSO₄ nanocomposites

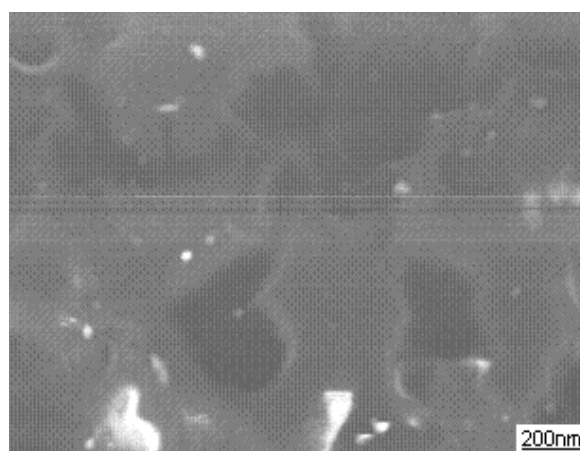


Fig 2. SEM image of PMMA/CaSO₄ nanocomposites

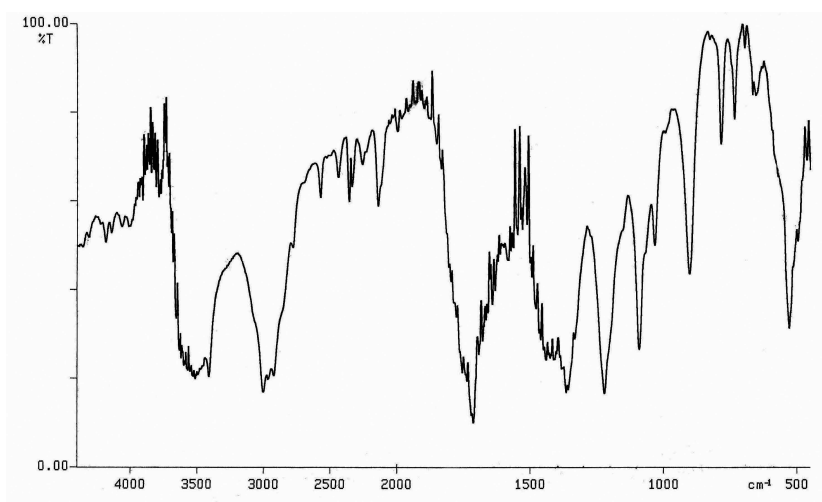


Fig 3. FTIR spectra of PMMA/CaSO₄

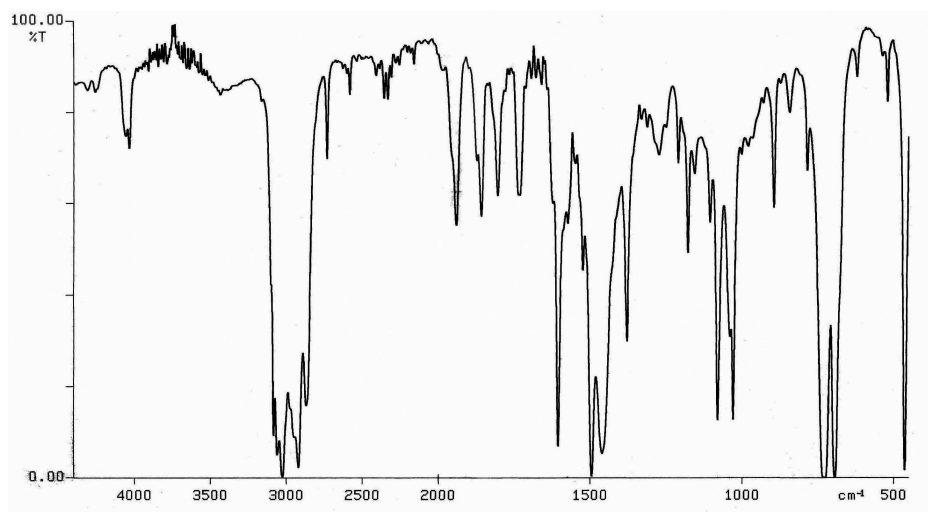


Fig 4. FTIR spectra of PS/CaSO₄ nanocomposites nanocomposites

TGA

Figure 5 shows thermo gravimetric analysis plots of PMMA/CaSO₄ nanocomposites. The degradation exhibits mainly three steps. The first and second steps degradation is due to scission of head-to-head and unsaturated chain end of the polymer respectively. The first region which is least important can be seen between 0°C to 300°C. This region shows nearly 30% weight loss. The second region is most important and easily identify from curve which is between 30-400°C and comprise nearly 55-60% weight loss of nanocomposites. The third region can be seen above 400°C.

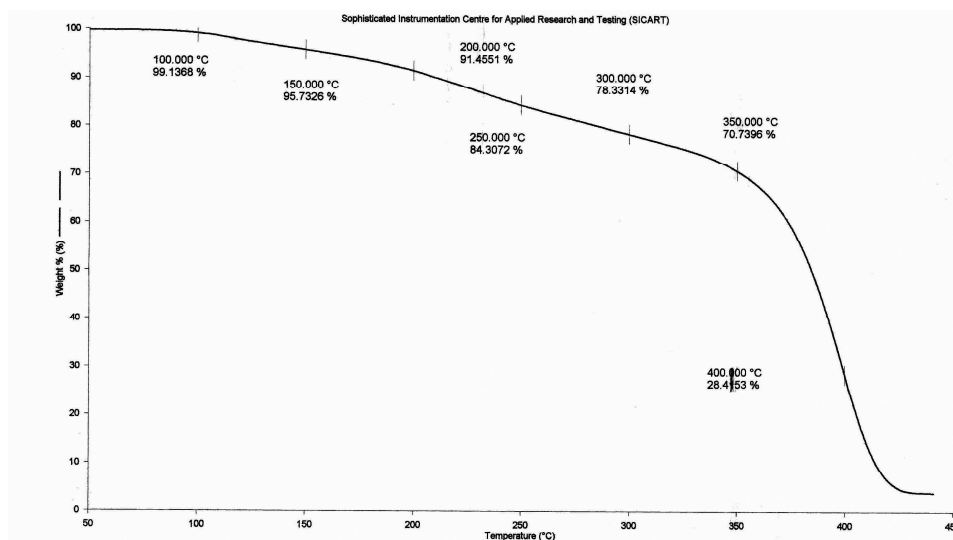


Fig 5. TGA Graph of PS/CaSO₄ Nanocomposites

The PMMA/ CaSO₄ nanocomposites decompose at higher temperature, which is consistent with the degradation of pure PMMA [8]. The degradation of the PS/CaSO₄ nanocomposites start at higher temperature (350-420°C) and the weight loss is slower, which is consistent with the degradation of pure polystyrene [9], in other word the degradation of PS/CaSO₄ nanocomposites can be effectively retarded by CaSO₄ nanoparticles. The loss of weight at

temperatures lower than 200°C is attributed to low molecule weight polystyrene and small molecules such as water and styrene. The mass loss at temperature is higher than 200°C is attributed to higher molecular weight polystyrene and CaSO₄ nanoparticles. The mass remains constant at temperature higher than 430°C assigned to CaSO₄ nanoparticles [10].

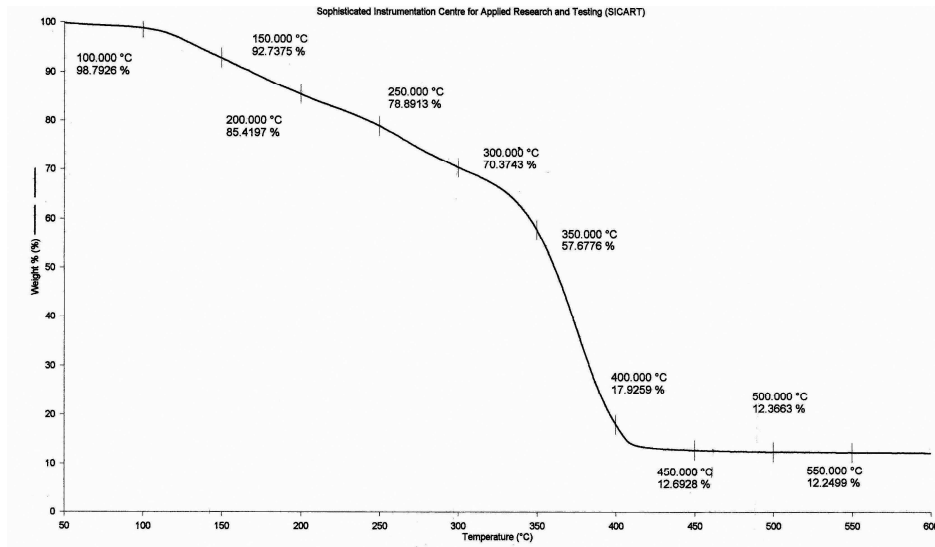


Fig 6. Electrical Conductivity of PS/ CaSO₄ Nanocomposites

Electrical Conductivity

The electrical conductivity of the nanocomposites was determined by Impedance analyzer, where resistivity was measured by varying the frequency. The conductivity was evaluated from the above equation. The observation show that nanocomposites is conducting in nature with the conductivity values lies between 10⁻⁵ to 10⁻⁷ S/cm for all the nanocomposites and the conductivity increases with the increase in frequency.

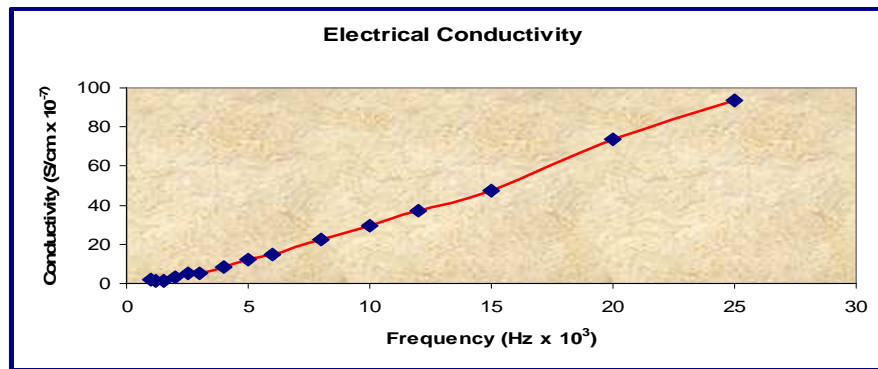


Fig 6. Electrical conductivity graph of PMMA/CaSO₄ Nanocomposites

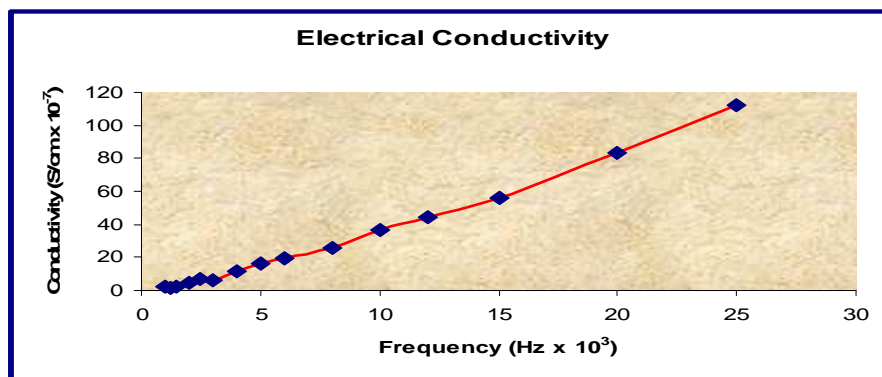


Fig 7. Electrical conductivity graph of PS/CaSO₄ nanocomposites

Conclusion

Nano-CaSO₄/PS nanocomposites latex microspheres were synthesized through the deposition technique and nano-CaSO₄ was encapsulated in the PS phase. In SEM micrographs, CaSO₄ nanoparticles display approximately spherical morphology and homogeneous dispersion of nanoparticles. FTIR shows a characteristic peak in the region 400-700 cm⁻¹ which shows the probability of the existence of bonding between CaSO₄ particles and the polymer network. TGA confirms unambiguously that the enhancements in the thermal properties largely deepened on the CaSO₄ nanoparticles and also demonstrate improvement of the thermal stability of both PMMA/CaSO₄ and PS/CaSO₄ nanocomposites.

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