

Properties of Core-Shell Silica Nanoparticles with Reinforced Transparent Polymers

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Abstract- The hybrid organic-inorganic nanocomposite of silica nanoparticles with transparent polymer poly (methyl methacrylate) (PMMA) were synthesized by Wet chemical method. To start with, the silica nanoparticles were created by utilizing tetraethoxysilane (TEOS) and ethanol as starting materials. The surface of nanoparticles was modified by surface modifier Cetyltrimethylammonium Bromide (CTAB). In situ polymerization of MMA (methyl methacrylate) was done with the synthesized nanoparticles to form core shell structured organic-inorganic hybrid composites. The thin films of hybrid nanoparticles of Silica-PMMA were prepared by spin coater method on the substrate of glass. These composite particles were investigated by UV-Vis spectrophotometer and Fourier Transform Infrared Spectroscopy (FTIR). The structural and morphological investigations were also done with X ray diffraction (XRD) and High Resolution Transmission electron microscopy (HRTEM) respectively.

Keywords - Silica Nanoparticles, PMMA

I. INTRODUCTION

Numerous works reported on the exaggeration of nanoparticles by introducing the inorganic particles in the polymeric matrix [1-10]. The new formed hybrid particles correspond to a different class of polymeric materials which combine the individual properties of both of the inorganic particles with the organic polymer matrix. Among all, the synthesis of core-shell nanoparticles has attained a particular space due to the extra-ordinary applications [11-13]. There are many procedures used for synthesis of core shell nano particles, with the polymerization techniques used more extensively with inorganic particles. To date, the most important path to organic/inorganic core-shell nanocomposite polymer shell and inorganic core is by means of heterophase polymerization or more exclusively by the structure control and morphology, and by emulsion polymerization in different ways [14-22].

The core-shell structure can be subdivided into organic-inorganic, inorganic-organic, inorganic-inorganic and organic-organic. Among the inorganic substances, nano-silica (SiO_2) is for the most representative materials for its application potential in various fields including paints, catalysis, drug delivery systems, composite materials and so on [23-26]. Among the organic substances, poly (methyl methacrylate) (PMMA) plays an imperative part in the family of polyacrylic and meth acrylic esters due to their good different properties such as exceptional optical clarity, good weather ability, high strength, excellent dimensional stability, reduced gas permeability, improved physical performance and increased heat resistance.

The Surface modification of the nanoparticles is necessary to improve the steadiness of nanoparticles in the polymer matrix. Surface modification can be performed by introducing coupling agents or reactive functional groups on the nanoparticles surface [27]. For example, Silane-modified silica sol and silica based hybrid films were prepared by Bokobza et al. [28]. The silica nanoparticles integrated in the matrix of polymer can improvise the strength, resistance towards the abrasion and the aging-resistance of the polymeric materials. Ma et al. prepared polyacrylate-based silica nanocomposite by sol-gel process and in situ emulsion polymerization [29]. Yu et al. produced surface modified particles of silica and further copolymerized the modified particles with MMA monomers [30]. Various polymerization techniques with surface-modified inorganic nanoparticles as dispersion, suspension and emulsion process can be used to form hybrid nanocomposites [31-33].

In this paper, the surface-modified nanoparticles of silica were prepared by wet chemical process and integrated directly into the polymer matrix for polymerization to produce a well dispersed organic–inorganic nanocomposite.

II. EXPERIMENTAL

2.1 Experimental Synthesis of SiO₂ nanoparticles

The TEOS (Tetraethoxy Silane) and CTAB were used to synthesize the SiO₂ nanoparticles. In this process, First 1ml TEOS is 1ml distilled water and stirred for 30 min. CTAB is dissolved in basic solution and stirred to make the solution clear and transparent. Now add TEOS (dissolved in water) and CTAB (basic solution) in 1:2 ratio and continuously stirred for 1 hour at 100°C until precipitates not formed. After 6 hours, the synthesized product is filtered and washed with double distilled water and methanol for three or five time. For phase formation, the calcination of the filtered powder is done at 700 °C for five hours.

2.2 Synthesis of Silica-PMMA nanoparticles:

The nanoparticles particles of silica with PMMA were prepared by performing polymerization of methylmethacrylate monomer and mixing of silica nano Particles simultaneously. In this process, first we mix silica nanoparticles in methylmethacrylate monomer in the presence of toluene as reaction medium. Then 1% Benzoyl Peroxide was added to the solution to initiate the polymerization. The solution was continuously stirred for 30 mins at 80°C. The optimized viscous solution is used for the spin coating technique to deposit thin films on glass substrate.

2.3 Characterization

The powdered X-ray diffractometer (Panalytical Xpert Pro) was used to obtain a thin-film X-ray diffraction (XRD) using CuK α radiation ($k = 0.1542$ nm) operating at 40 kV and 40 mA. Transmission electron microscopy (TEM), the microscope of FEI tencai G² 20-win microscopes equipped with a LaB₆ filament operating at an accelerated voltage of 200 kV was used for the morphological characterization of the samples. TEM grids are used to prepare samples by depositing solutions of precursors in lattices. Fourier transform infrared spectroscopy (FTIR) is an analytical technique used to identify organic (and in some inorganic) materials. This technique measures the absorption of infrared radiation from the sample material as a function of wavelength. The infrared absorption bands identify the molecular components and the structure. To obtain the UV-Vis absorption spectra of the silica-PMMA nanoparticles, a double-beam UV spectrophotometer (UV 704SS) was used.

III. RESULTS AND DISCUSSIONS

The thin film of silica nanoparticles with polymer PMMA were characterized by X-Ray Diffractometer (XRD) using CuK α ($\lambda = 1.54$ Å) as a source of radiation. Fig. 1 demonstrates the diffractograms of silica, pure PMMA and particles of SiO₂-PMMA combination in the 2θ range between 20° and 80°, which are approximate similar and not showing any sharp diffraction peaks confirming their non-crystalline nature.

The interlayer spacing of the composite system was found by the diffraction peaks in the X-ray diffractogram, using the Bragg equation

$$\lambda = 2d\sin\theta \dots\dots\dots (1)$$

Where d is the interlayer spacing between diffraction lattice planes, θ the diffraction position whereas λ is the wavelength of the X-ray (1.5405 Å). PMMA is recognized as an amorphous polymer and the composite illustrates three broad peaks at 2θ values of 14°, 29° and 41° with their intensity decreasing steadily. The shape of the first most intense peak reflects the ordered packing of polymer chains while the second peak denotes the ordering inside the main chains. The addition of SiO₂ does not induce any crystallinity in these polymers. This also explains the homogeneous nature of these samples.

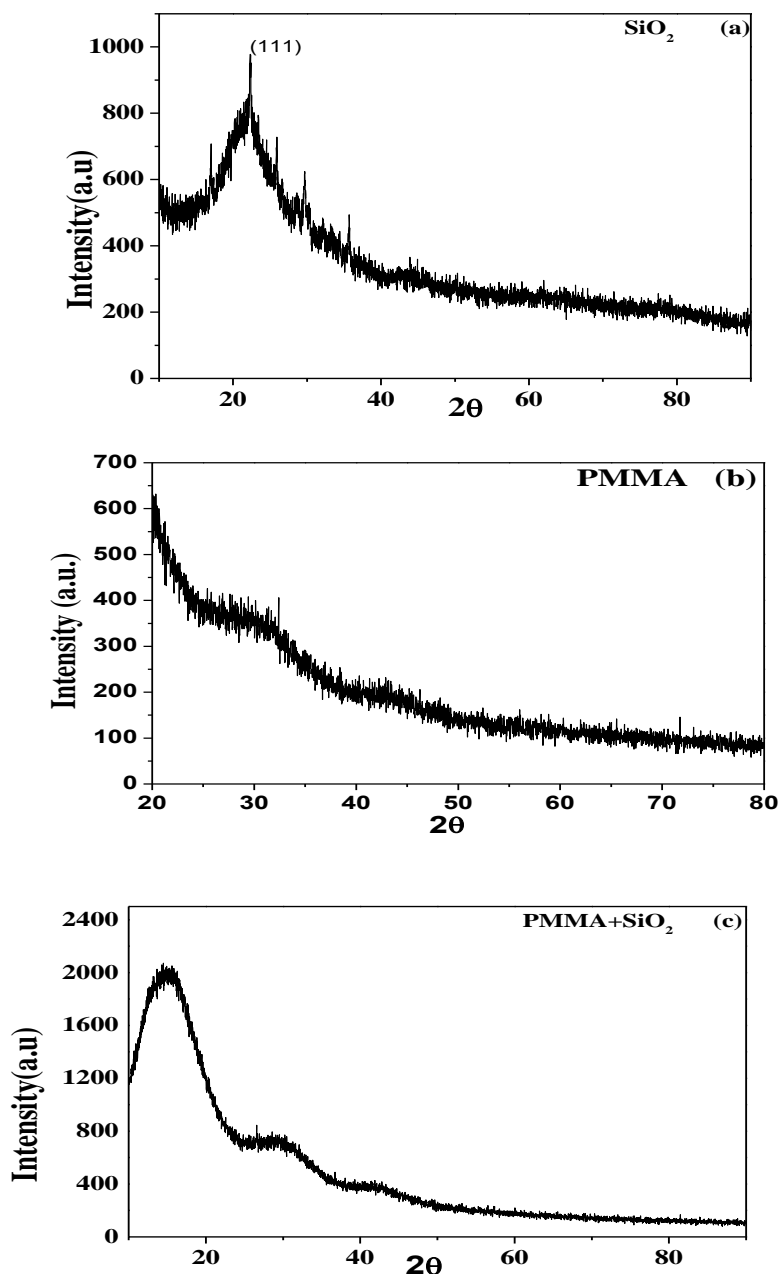
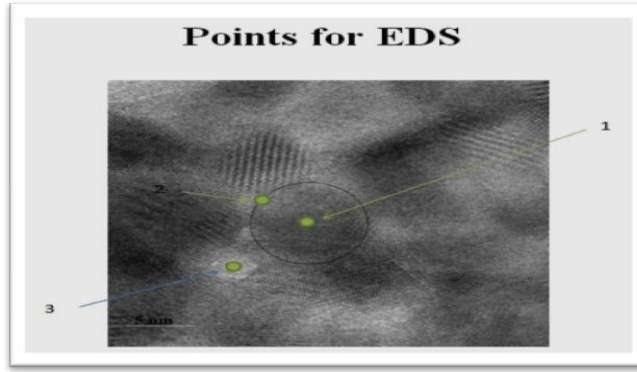


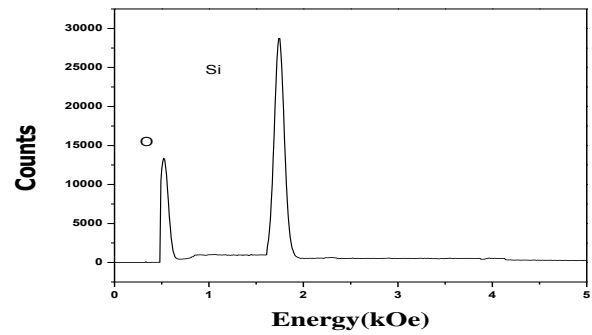
Fig.1: XRD Pattern of (a) Pure Silica nanoparticles (b) Pure PMMA (c) Silica-PMMA nanoparticles

The HRTEM images of the SiO₂-PMMA nanoparticles are shown in Fig. 2. The image clearly indicates the core shell like structure of the nanoparticles. To prove the above structure, the Energy Dispersive X-ray spectroscopy (EDS) was performed at different positions 1, 2 and 3 in which position 1 represents location of the oxide nanoparticles. The position 2 indicates the boundary of nanoparticle and polymer (PMMA) whereas position 3 represents the location on polymer. It is clearly noted the centre part of this nanoparticles contains only Si and O elements however outside this surface, EDS shows only carbon (C) which represent the polymer. In nutshell, core shell like structure is evident from this study.



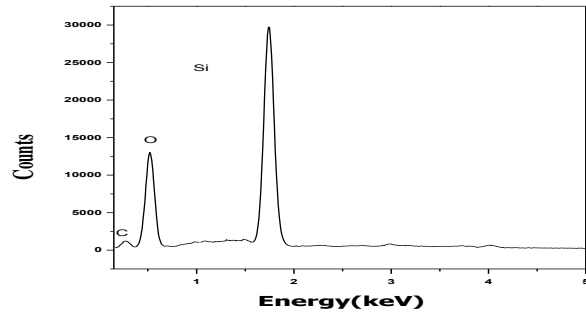
EDS at Point 1

Element	Weight%	Atomic%
OK	62.97	74.90
Si K	37.03	25.10
Totals	100.00	



EDS at Point 2

Element	Weight%	Atomic%
CK	16.36	23.30
OK	55.97	59.84
SiK	27.67	16.85
Totals	100.00	



EDS at Point 3

Element	Weight%	Atomic%
CK	100.00	100.00
Totals	100.00	

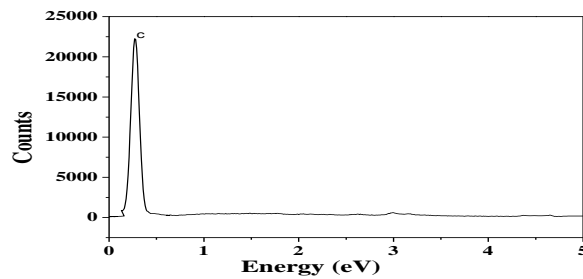


Fig.2: EDS Pattern of HRTEM image of SiO₂-PMMA nanoparticles thin film with three different points

The FTIR spectrum of the SiO₂-PMMA nano composite has been performed. The various bands are shown in the Fig.3. All the bands represent the vibrational activity of the bonds of the PMMA. The mode corresponds to 805 cm⁻¹ represents the Si-O-Si stretching and deformation vibration. The bands and there vibrations are given in the table below.

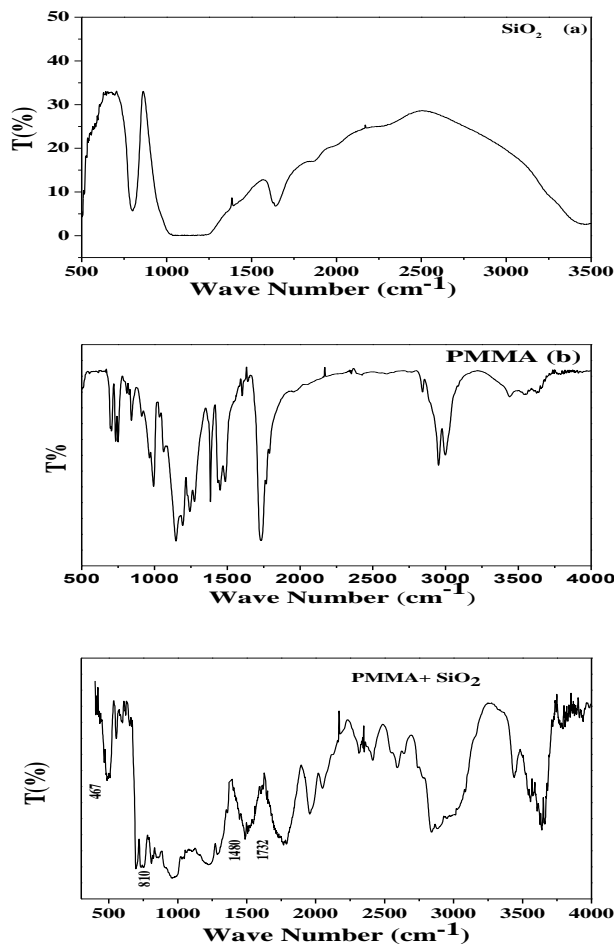


Fig.3: FTIR Spectra of (a) Pure SiO₂ nanoparticles, (b) Pure Poly Methyl methacrylate (PMMA) and (c) Nanocomposite of Poly Methyl methacrylate and SiO₂ nanoparticles.

Table 1: The Bands Observed in FTIR Investigations and Corresponding Vibrations

805	Due to vibration stretching of Si-O-Si
1480	CH ₂ Stretching
1732	Due to free Carbonyl C=O Stretching
2845.59-2960.26	Due to Asymmetric and symmetric vibration of methylene group of CH ₂ of aliphatic carbon chain
Above 3400	OH Stretching vibration either from water or hydroxyl terminated compounds, Silicates or N-H stretching vibration either from urea or amino group

The UV-Vis spectra of PMMA and PMMA-silica composites film were analyzed by Tau'c plot (fig. 4) with the intention to acquire optical band gap, Eg. The equation used for Tau'c plot was given by

$$\alpha = A (h\nu - E_g)^x / h\nu \dots\dots\dots(2)$$

where, α is absorption coefficient of the film, E_g is optical gap of the film, x is parameter that gives type of transition and A is transition probability taken to be constant for the optical frequency range.

In the Fig.4, Tauc's plots of $[(\alpha h\nu)^{1/2}$ vs. $h\nu]$ of pure Silica nanoparticles, pure PMMA thin films and Silica-PMMA nanoparticles thin films are shown. It is clear from the figure that Silica has a clear absorption edge and the energy band gap of Silica nanoparticles is found to be 5.36 eV. As pure PMMA has absorption bands representing different functional groups in the UV-Visible region, its integration with Silica nanoparticles totally modifies the energy band gap absorption of Silica to get an absorption profile of UV-visible radiations spread over the entire range. The Silica-PMMA nanoparticles totally changed the optical properties of Silica nanoparticles. The observed band gap of silica -PMMA is about 3.40 eV.

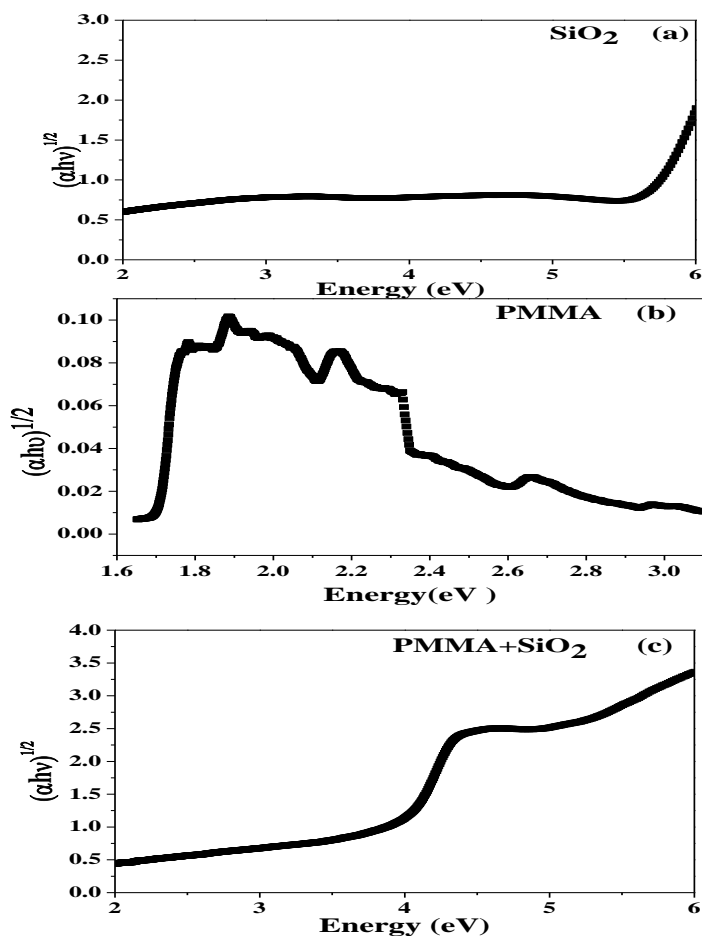


Fig. 4 : UV-VIS Spectra of (a) Pure SiO_2 nanoparticles, (b) Pure Poly Methyl methacrylate (PMMA) and (c) Nanocomposite of Poly Methyl Methacrylate and SiO_2 nanoparticles.

IV. CONCLUSION

The core-shell SiO_2 -PMMA nanoparticles were prepared by a novel technique by in situ polymerization of MMA monomer. The influence of polymer matrix on the silica oxide nanoparticles was studied. The XRD results revealed that the SiO_2 -PMMA nanoparticles presented simultaneously the amorphous nature of polymethylmethacrylate and SiO_2 . The SiO_2 -PMMA nanoparticles are of Core-shell structured, depicted by HRTEM. The FTIR and UV results clearly show that the thin films produced have a good amount of transparency to visible radiation and low band gap of SiO_2 -PMMA makes them suitable for optical applications.

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