chapter 4

summary, conclusions and scope of the future work

4.1 Introduction

Nanocomposites comprising of nanoparticles dispersed in polymeric matrices have captured the interest of many researchers and academicians as advanced technological materials because of their unique optical [1], electrical [2], mechanical [3] and thermal properties [4] as a result their usage has increased tremendously in various applications such as optoelectronic devices, data storage systems, sensors, waveguides, photovoltaic cells, aerospace applications etc [5-7]. These extraordinary properties are accredited to the combined features of the polymeric host (light weight, processability, flexibility etc.) and novel properties of embedded nanoparticles (size dependent electrical and optical properties, high catalytic activity, high surface to volume ratio etc.) [8-10]. The intrinsic properties of nanocomposite materials are determined by the size, shape, composition and structure of the nanoparticles as well as the polymer matrix itself [11].

The present research endeavour is an effort to understand and optimize various parameters for synthesis of SiC-PVA and Ag-PVA nanocomposites and to study remarkable changes produced in the optical properties: optical energy gap, refractive index and dielectric constant, mechanical properties: microhardness, thermal properties and electrical conductivity behaviour of the synthesized nanocomposites.
4.2 Summary

In the present research work, SiC-PVA and Ag-PVA nanocomposite films have been synthesized by solution casting technique. The effect of varying concentration of SiC and Ag nanoparticles on structural, optical energy gap, Urbach’s energy, refractive index, dielectric constant, electrical conductivity, thermal stability and surface hardness behavior of PVA has been studied. These studies have been carried out using X-ray diffraction (XRD), transmission electron microscopy (TEM), scanning electron microscopy (SEM), fourier transform infrared spectroscopy (FTIR), raman spectroscopy, UV-Visible Spectroscopy, four probe I-V measurements, thermogravimetric analysis (TGA) and knoop microhardness testing.

In the present research work, all chemicals used were of analytical reagent grade. Poly (vinyl alcohol) (PVA) (molecular weight = 1,25,000 g/mol) was obtained in powder form from Ranbaxy, India and it was used as received. For the preparation of surface treated SiC-PVA nanocomposites, nitric acid and ammonium nitrate were obtained from Rankem, India and were used as received. For the preparation of PVA grafted SiC-PVA nanocomposites, ethylene glycol was procured from Rankem, India. For the preparation of Ag-PVA nanocomposites, salt of AgNO₃ (molecular weight = 169.87 g mol⁻¹) was purchased from Rankem and salt of NaBH₄ (molecular weight = 37.83 g mol⁻¹) was purchased from Merck. Double distilled water used for the preparation of reactant solutions was prepared in our own department.

SiC nanoparticles were synthesized using nanoporous carbon black (Vulcan® XC-72) as the carbon source which result in particle size of 25 - 35 nm ascertained using Scherer formula. The carbon black was reacted with SiO vapors which were generated in situ by heating a uniform 1:1 molar mixture of silicon and silica powder at 1450°C. The carbon black was placed next (downstreams) to this mixture in the alumina crucible. The furnace was heated to a temperature of 1450°C for 12-15 hr in an argon flow of 250-300 ml/min [12]. The second reaction utilized for the formation of SiC nanoparticles is the solid phase reaction of carbon with molten silicon which result in particle size in the ranges of 50–150 nm obtained using Scherer formula. The silicon powder with the crystal sizes in the range 200 nm – 5
μm was uniformly mixed with carbon black in a 1:1 molar ratio with the help of a pestle and mortar. The mixture was transferred into an alumina crucible and heated to a temperature of 1525°C ± 25°C in a tubular furnace for 6 hr in an argon flow of 250-300 ml/min. The furnace was heated and cooled at the rate of 5°C/min [12].

SiC-PVA nanocomposites were synthesized using three different approaches. In the first approach, SiC-PVA nanocomposites were prepared by dissolving appropriate amount of PVA in distilled water. The solution was stirred until the polymer completely dissolved and formed a clear viscous solution. Varying concentrations of SiC nanoparticles were dissolved in distilled water in separate beakers under high ultrasonication for 30 min. These solutions were slowly added to the viscous polymer solution to obtain SiC-PVA nanocomposites having 1 wt%, 2 wt% and 3 wt% SiC nanoparticles. For uniform dispersion of nanoparticles into PVA matrix ultrasonication was carried out for another 30 min. This procedure was carried out at room temperature and under ambient pressure. The resulting solutions so obtained were poured in petri dishes and left for a period of 7 days for solidification. The resulting nanocomposite films of ~15 μm thickness were then peeled off for further characterization. For comparison purpose, thin film of PVA was also prepared in the same manner.

In second approach, surface treatment of SiC nanoparticles was performed by mixing SiC nanoparticles with concentrated nitric acid. 500 mg SiC nanoparticles were taken in a flask and mixed with an acidic solution of 8.0 M HNO₃ and distilled water (8 ml). This solution containing the acid and SiC nanoparticles was sonicated for 10 min to ensure the dispersion of the SiC nanoparticles. After the sonication, the solution was transferred to a spherically bottomed flask immersed in a silicone oil bath. After the surface treatment, the SiC nanoparticles were transferred to a beaker and separated from the acids by suspension and then filtered using electric pump. After filtration, new suspensions were prepared by ultrasonication of the SiC nanoparticles in deionized water. pH of the suspension was adjusted to 10 by adding NH₃·H₂O. The suspensions were subjected to filtration to remove the solvent with repeated addition of distilled water. The filtered SiC nanoparticles were then dried in oven [13]. For the synthesis of nanocomposite, 5 g PVA was dissolved in 100 ml distilled water at room temperature. A known amount of surface treated SiC (t-SiC) nanoparticles were dissolved in the distilled water at room temperature. For
homogenous dissolution of t-SiC nanoparticles, the solution was sonicated for 1 hr. Solutions having 0.01 wt%, 0.015 wt% and 0.023 wt% t-SiC nanoparticles were mixed with solution of PVA using a magnetic stirrer followed by sonication. These solutions were casted in petri dishes, and then dried in air at room temperature for about 7 days until the solvent was completely evaporated. The resulting nanocomposite films of ~15 μm thickness were then peeled off for further characterization.

In the third approach, PVA was grafted onto the surface of SiC nanoparticles. 500 mg of SiC nanoparticles were suspended in 100 ml mixture of concentrated sulfuric acid and concentrated nitric acid (1:1) for 6 hr with the ultrasonicator. Subsequently SiC nanoparticles were separated by centrifugation and washed with deionized water several times till pH reaches in the range of 5–7. Later they were dried at 50°C in oven for 4 hr. For grafting procedure, 1 g PVA was mixed with 80 ml ethylene glycol in a beaker and heated to 140°C while stirring vigorously on a magnetic stirrer. A transparent and viscous solution was obtained after stirring the solution for 4 hr. Temperature was then adjusted to 90°C and oxidized SiC nanoparticles were added to the resulting PVA solution. The resulting solution was homogenized by stirring followed by ultrasonication for 3-4 hr and resulted in a black solution. The precipitates were allowed to settle down, washed several times with deionized water to neutralize the pH. Finally the PVA grafted SiC (PVA-g-SiC) nanoparticles were dried in the oven at 50°C [14]. For the synthesis of nanocomposite, 1g of PVA was dissolved in 20ml distilled water at room temperature. A known amount of PVA-g-SiC nanoparticles were dissolved in distilled water at room temperature. The solution was sonicated for 1 hr for homogenous dissolution of PVA-g-SiC nanoparticles. Solution having 0.015wt% PVA-g-SiC nanoparticles and PVA were mixed together using a magnetic stirrer followed by sonication. The resulting solution was casted in petri dish, and then dried in air at room temperature for about 7 days until the solvent was completely evaporated. The resulting nanocomposite film of ~15 μm thickness was then peeled off for further characterization.

Ag nanoparticles were prepared by the reduction of aqueous silver nitrate (AgNO₃) solution using aqueous sodium borohydride (NaBH₄) solution which was used in excess in order to reduce the ionic silver as well as to stabilize the Ag nanoparticles. 100 ml aqueous AgNO₃ solution (0.017 g, 0.1 mmol) was added drop wise to an ice-cooled 300
ml aqueous NaBH₄ solution (0.02 g, 0.52 mmol) under continuous magnetic stirring over a period of 30 min. The resulting solution first turned light yellow which continued to brighten and finally bright (golden) yellow after complete addition in 30 min. The solution so obtained was used for the formation of nanocomposites. For the synthesis of nanocomposite, the Ag colloid having 0.02 wt%, 0.04 wt%, 0.048 wt%, 0.056 wt% and 0.062 wt% was combined in an appropriate ratio with aqueous solution of PVA. These solutions were stirred magnetically for 1 hr for homogenous dissolution of nanoparticles. To make films, the prepared solutions were casted in petri-dishes. Finally, after evaporation of the solvent at room temperature in about 7 days in the absence of light, yellow transparent Ag-PVA nanocomposite films of ~15 μm thickness were obtained. The samples were stored in a dark medium to avoid direct exposure to light.

In the present work, XRD measurements were carried out on a Mini Flex II Rigaku diffractometer using CuKα radiation (λ = 0.154 nm) in the wide angle region from 20° to 80° available at the Department of Physics, National institute of Technology, Kurukshetra. TEM measurements were performed using a Hitachi “H-7500” transmission electron microscope available at Sophisticated Analytical Instrumentation Facility (SAIF), Punjab University, Chandigarh operated at an accelerating voltage of 80 kV with a resolution of ~ 3 Å. For TEM measurements, a small amount of nanocomposite film was dispersed in distilled water followed by ultrasonication for 30 min. Few drops of the suspension of nanocomposite film was put on a carbon-coated copper grid and after drying the grid, TEM analysis was carried out. Surface morphology of the synthesized nanocomposites was carried out using LEO 435 VP scanning electron microscope available at the Department of Physics and Chemistry, University of Southern Denmark, Denmark. For SEM measurements, nanocomposite films were coated with a very thin layer of gold by sputtering technique. The coated sample was then used to obtain SEM images. FTIR spectroscopy in the range from 4000 to 400 cm⁻¹ was done using ABB Horizon (mb 3000) FTIR spectrometer available at the Department of Chemistry, Kurukshetra University, Kurukshetra. The fundamental vibrations of the nanocomposite films were obtained by a Dilor Raman spectrometer, using 532 nm wavelength laser with a resolution of 3-5 nm available at the Department of Physics and Chemistry, University of Southern Denmark, Denmark.
The UV-Visible absorption and reflection spectroscopy measurements of all the samples were carried out using Shimadzu Double Beam Double Monochromator UV-Visible Spectrophotometer (UV-2550) equipped with an Integrating Sphere Assembly ISR-240A in the wavelength range of 190 nm to 900 nm with a resolution of 0.5 nm available at Department of Physics, Kurukshetra University, Kurukshetra. I-V behaviour of the synthesized nanocomposite films was studied using four probe Keithley (6517A) electrometer at room temperature available at Department of Physics, Kurukshetra University, Kurukshetra. For I-V measurements samples were laid between the Keithley 8009 resistivity text fixture and a testing voltage of 100 V was applied. Nanocomposite films were thermally characterized using Perkin Elmer Diamond TGA analyzer at a heating rate of 10ºC/min, from room temperature up to 700ºC, in air atmosphere at a flow of 20 ml/min available at Department of Chemistry, Kurukshetra University, Kurukshetra. Surface microhardness of the nanocomposite films were carried out using Knoop microhardness technique with a UHL microhardness tester available at Department of Physics, Kurukshetra University, Kurukshetra.

The major outcomes of the present work are based on the results obtained from various experimental techniques used to characterize SiC-PVA and Ag-PVA nanocomposites.

The main conclusions drawn from the present studies are as follows:

[1] XRD pattern of all the SiC-PVA nanocomposite films reveal peaks around 20 value of ~ 35.2º, 41.03º, 59.7º and 71.6º which corresponds to (111), (200), (220) and (311) planes of SiC nanoparticles [15]. XRD pattern of t-SiC nanoparticles and PVA-g-SiC nanoparticles revealed that the crystalline geometry of SiC nanoparticles had not changed after the surface treatment/grafting of PVA on its surface. The XRD pattern of Ag-PVA nanocomposite films revealed peaks at 20 values of about 38.1º, 44.3º, 64.5º and 77.6º representing the (111), (200), (220) and (311) planes of silver, indicating the presence of Ag nanoparticles in the nanocomposite [16].

[2] In the FTIR spectra, the assignments of the various peaks of PVA matrix are in reasonable agreement with those reported in the literature [17]. The addition of SiC nanoparticles in PVA matrix resulted in diminished intensity and
displacement of the peaks suggesting changes in molecular structure of PVA. These changes might be attributed to the formation of bonding between SiC and PVA. The vibrational peak at ~785 cm$^{-1}$ characteristic of Si–C stretching vibrations [18] was present in all SiC-PVA nanocomposites films however, characteristics of PVA as well as SiC nanoparticles was more pronounced in FTIR spectra of PVA-g-SiC/PVA nanocomposites as compared to t-SiC-PVA nanocomposites. FTIR spectra of Ag-PVA nanocomposite film show the presence of interaction between Ag nanoparticle and O-H group of PVA matrix.

Surface plasmon resonance (SPR) peak characteristic of Ag nanoparticle formation was observed at around 395 nm for Ag nanoparticle colloids and around 405 nm for Ag-PVA nanocomposite films [11, 19]. SiC-PVA nanocomposites did not show such resonance in the visible region.

Addition of t-SiC and PVA-g-SiC nanoparticles in PVA matrix has led to the decrease in the optical energy gap. For the t-SiC-PVA nanocomposite, it decreased from 4.1 eV for PVA to 3.4 eV for 0.015 wt% t-SiC-PVA nanocomposite film and to 3.0 eV for 0.023 wt% t-SiC-PVA nanocomposite film. For PVA-g-SiC/PVA nanocomposite film, it decreased from 4.1 eV for PVA to 3.4 eV for 0.015 wt% PVA-g-SiC/PVA nanocomposite film. The decrease in the optical energy gap has been attributed to the formation of charge transfer complexes as localized electronic states within the highest occupied molecular orbital-lowest unoccupied molecular orbital (HOMO-LUMO) gap of PVA, which makes the lower energy transitions feasible [20].

Sharp increase in the value of Urbach’s energy for t-SiC-PVA and PVA-g-SiC/PVA nanocomposite films had been observed. For t-SiC-PVA nanocomposite, it increased from 0.55 eV for PVA to 0.92 eV for 0.015 wt% t-SiC-PVA nanocomposite film and to 1.16 eV for 0.023 wt% nanocomposite film. For PVA-g-SiC/PVA nanocomposite film, it increased from 0.55 eV for PVA to 1.01 eV 0.015 wt% PVA-g-SiC/PVA nanocomposite film. Urbach’s energy is a measure of disorder hence it can be inferred that disorder in the form of localized states within the HOMO-LUMO gap has increased due to the increasing concentration of nanoparticles [21].
Enhancement in the refractive indices had been observed for all the nanocomposite films. Refractive index of PVA was found to be increased from 1.7 to 2 for 0.015 wt% t-SiC-PVA nanocomposite film and to 2.2 for 0.023 wt% t-SiC-PVA nanocomposite film at 550 nm wavelength. For PVA-g-SiC/PVA nanocomposite film, it increased from 1.7 for PVA to 2 for 0.015 wt% PVA-g-SiC/PVA nanocomposite film. For Ag-PVA nanocomposite films, refractive index increased from 1.5 for PVA to 1.96 for 0.062 wt% Ag-PVA nanocomposite film at 550 nm wavelength. High value of refractive index is an indication of high density of films [22]. High value of refractive index of t-SiC-PVA and PVA-g-SiC/PVA nanocomposite films as compared to Ag-PVA nanocomposite films at similar concentration suggest that the density of SiC-PVA nanocomposites films is high.

Electrical conductivity of all the SiC-PVA nanocomposite films was enhanced with respect to PVA. The electrical conductivity of t-SiC-PVA and PVA-g-SiC/PVA nanocomposite films is more as compared to as received SiC-PVA nanocomposite films. This enhancement in conductivity properties of PVA after addition of t-SiC and PVA-g-SiC nanoparticles is perceived to be due to homogenous distribution of nanoparticles in the PVA matrix. Detailed analysis of I-V data indicates that the conduction mechanism responsible for increase in conductivity of all the nanocomposite films was voltage dependent and Schottky mechanism is the dominant conduction mechanism at high voltage regions and Poole Frenkel mechanism at low voltage regions. For Ag-PVA nanocomposites, analysis of I-V data predicts that when the concentration of Ag nanoparticles in PVA matrix was low, insulating properties of PVA were enhanced. This enhancing of insulating properties of PVA matrix can be explained on the basis of Coulomb blockade effect [23]. When the concentration of Ag nanoparticles in PVA matrix was further increased the conductivity had increased as the nanoparticles begins to aggregate and provides the conductive paths across the nanocomposites films. It was perceived from I-V studies that the increase in conductivity was due to Poole Frenkel mechanism.

TGA studies had revealed that at low temperature (< 400°C) addition of 3 wt % as received SiC nanoparticles in PVA and 0.062 wt% Ag nanoparticles decreased the stability of PVA by shifting the onset of thermal decomposition temperature to lower values. Addition of 0.023 wt % t-SiC nanoparticles did not show any
substantial effect on onset of thermal decomposition temperature however, addition of 0.015 wt% PVA-g-SiC nanoparticles improved the thermal decomposition temperature by slightly shifting it to higher temperature. The enhancement in thermal stability of PVA-g-SiC/PVA nanocomposites films is attributed to the improved interfacial interaction of PVA-g-SiC nanoparticles with PVA.

[9] Knoop microhardness values increased from 2.4 Kgf/mm$^2$ for PVA to 4.1 Kgf/mm$^2$ for 0.015 wt% t-SiC-PVA nanocomposite film and to 4.6 Kgf/mm$^2$ for 0.023 wt% t-SiC-PVA nanocomposite film at 9.8 mN load. For PVA-g-SiC/PVA nanocomposite film containing 0.015 wt% PVA-g-SiC nanoparticles it increased from 2.4 Kgf/mm$^2$ to ~5 Kgf/mm$^2$. For Ag-PVA nanocomposites it increased from 2.4 Kgf/mm$^2$ for PVA to 2.9 Kgf/mm$^2$ for 0.02 wt% Ag-PVA nanocomposite film and to 12.1 Kgf/mm$^2$ for 0.062 wt% Ag-PVA nanocomposite film. The enhancement in microhardness is more in case of PVA-g-SiC/PVA nanocomposites as compared to t-SiC-PVA and Ag-PVA nanocomposites, hence it can be inferred that PVA-g-SiC nanoparticles had better interfacial interaction with PVA matrix.

[10] Distribution of t-SiC nanoparticles and PVA-g-SiC nanoparticles is homogenous inside PVA matrix as compared to as received SiC nanoparticles. The extent of improvement in thermal stability and surface hardening had been found to be more in case of PVA-g-SiC/PVA nanocomposite as compared to t-SiC-PVA nanocomposites as well as Ag-PVA nanocomposites at similar concentrations.

4.3 Future Projections

The results of the experiment reported in this thesis lead to the possibilities of further work that will be conducted in future.

- To study the photoluminescence properties of the synthesized nanocomposites.
- Detailed and systematic approach to study tensile properties of the nanocomposites discussed in the present work.
- To study systematically the dielectric behaviour of these nanocomposites. Those studies may provide an opportunity to utilize these nanocomposites in diverse range of applications.
To synthesize SiC based nanocomposites with other polymer matrices such as polystyrene, polymethylmethacrylate etc.

Analysis of gas barrier properties of the synthesized nanocomposites.

Formation of SiC-Ag nanoparticles hybrid nanocomposites to study their various properties.
Chapter 4 Summary, Conclusions and Scope of the Future Work

References


15) X-ray powder diffraction file JCPDS-ICDD (Joint committee on powder diffraction standard- international centre for diffraction data, 1999) File no 29-1129.

16) X-ray powder diffraction file JCPDS-ICDD (Joint committee on powder diffraction standard- international centre for diffraction data, 1999) File no. 04-0783.


LIST OF PUBLICATIONS


International/National Schools/Workshops attended

1) One week short term course on “Advanced materials and Characterization” organized by Department of Physics, NIT, Kurukshetra from 8th to 12th June, 2015.

2) “PhD School on nanobeams” organized by CRP-Lippmann, Luxembourg, Europe from 12th to 21st November 2014.

3) Two days National Workshop on “Ion Beam Induced Growth and Engineering of Materials” organized by Department of Physics, Kurukshetra University, Kurukshetra from 11th to 12th March, 2014.

4) “IUAC School on thin films” organised by Inter-University Accelerator Centre, New Delhi from 11th to 13th December 2012.

5) National workshop on “Advanced Characterization and simulation techniques” organized by Department of Physics, Kurukshetra University, Kurukshetra from 12th to 17th March, 2012.
Research Papers in International/National Conferences


