INVESTIGATION ON STRUCTURAL, MORPHOLOGICAL, THERMAL AND OPTICAL PROPERTIES OF BLEND PPY- PVA THIN FILMS DOPED WITH NANO TiO$_2$ PARTICLES

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ABSTRACT

Poly Vinyl Alcohol (PVA), Poly Pyrrole (PPY), and PPY-PVA blend thin films loaded with varying concentrations of nano TiO$_2$ particles were prepared by using the in-situ chemical oxidative polymerization technique. Prepared films have undergone several characterization techniques i.e., XRD, UV- Spectroscopy, SEM, and DSC to study their structural, morphological, optical, and thermal properties. SEM images revealed that the surface morphology of PPY has been significantly modified upon the addition of PVA and nano TiO$_2$ particles and observed the presence of pores on the surface. XRD spectra disclose that the amorphous nature of PPY whereas semi-crystalline nature of PVA and the amorphous nature of PPY-PVA blend thin film, also revealed that the concentration of dopant imparts the crystallinity to the nanocomposite thin films. The DSC thermographs confirmed that the shifting of melting temperature towards the higher temperature side in PPY-PVA blend thin film compared to pure PPY and PVA and the addition of dopant has changed melting points towards slightly lower temperature side. Direct band gap values of prepared thin films have been calculated by plotting UV graphs, and these were diminished as rising in the concentration of dopant which supports the conductivity level of thin films.

Keywords: Pyrrole, PPY, PVA, PPY-PVA Blends, Nano TiO$_2$, Thin Films.

INTRODUCTION

For the past two decades, conducting polymers has established cumulative attention in the field of research i.e., engineering, industrial, electronic and scientific applications purpose. Especially, conducting polymers and their doped nanocomposites show huge surface area, and provide a short pathway for ion transportation, for the exhibition of high electrical conductivity. Conducting polymers have been used in various applications like Sensors, Batteries, Opto-electronic devices, Supercapacitors, FET, etc. due to their exclusive properties like lightweight, admirable chemical stability, high conductivity, and flexibility. The Poly pyrrole exhibits high conductivity, Sensitivity, and Biocompatibility, which made it possible as a gas detection device. In this present work, the Author focused on improving the mechanical properties of Poly pyrrole since the mechanical properties of Poly pyrrole limit its applications.

In order to improve mechanical properties Poly Pyrrole is blended with Poly Vinyl Alcohol. Polyvinyl alcohol polymer (PVA) dissolved in water which exposes to light (transcalent), biodegradable, biocompatible, can be used in the food industries as a coating agent. PVA adds supplementary mechanical strength to Poly pyrrole in consequences, it produces an excellent free-standing PPY-PVA blended films with an enhanced mechanical and conductivity properties. Providing better conducting and sensing properties, the PPY-PVA blend thin films have been doped with nano TiO$_2$ particles, which may promote the adsorption and desorption of huge gasses, due to the huge surface area to volume ratio of nano Titanium dioxide particles. Hence thin films were prepared and have undergone for different characterization techniques to obtain desired properties.

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EXPERIMENTAL

Pyrrole monomer (99.9% pure) was purchased from Sigma Aldrich Laboratory, and pure Poly Vinyl Alcohol powder, Acetone, and FeCl$_3$ were bought from Research lab Fine Chem Industries, Mumbai, India. In-situ chemical oxidative polymerization technique has been adopted to prepare Poly Pyrrole, PVA, PPY-PVA blend thin films doped with varying weights of nano TiO$_2$ particles. Pyrrole monomer of 0.85 ml was dissolved in 25 ml of distilled water under constant stirring for 2 hrs. About 2 gr of FeCl$_3$ aqueous solution was prepared and then added dropwise to the Pyrrole solution. A black color Poly Pyrrole solution was obtained and washed thoroughly then filtered. Pyrrole monomer of 0.85 ml dissolved in 25 ml of double distilled water under stirring process for 2 hours. Then Pyrrole aqueous solution and 20 ml of PVA solution (already prepared 4% of Poly Vinyl Alcohol aqueous solution) were mixed carefully under stirring. In another beaker, 2 grams of FeCl$_3$ dissolved with 20 ml distilled water further these solution drops were added to the above mixture which underwent a stirring process for 4 hours, and a black color uniform solution was obtained further same transferred into a Petri dish for evaporation of the solvent, hence finally a PPY-PVA black color thin film of was formed. TiO$_2$ nanoparticles of the quantity of about 10 mg were mixed with already prepared aqueous Pyrrole solution thoroughly followed by adding PVA solution of 20 mL under continuous stirring. Recently prepared FeCl$_3$ solution was added slowly to the above reaction mixture under stirring. A black color PPY-PVA-TiO$_2$ thin film was obtained by removing excess water content. A set of PPY-PVA-TiO$_2$ composite thin films were synthesized using a similar process by varying weights of nano TiO$_2$ particles (20 mg, 30 mg, and 40 mg). Further, the prepared thin films have been examined by XRD, SEM, UV-Visible, and DSC characterization techniques, and attained results were discussed here.

RESULTS AND DISCUSSION

Structural Studies

XRD is an efficient method that discloses materials’ structural properties like size, lattice constant, interplanar spacing, miller indices, nature of crystal, etc. XRD results were carried out for prepared thin films in the range of 10$^\circ$-50$^\circ$ Bragg’s angle shown in Fig.-1. Pure Poly Pyrrole thin film showed broad peaks at angles of $\theta=21^\circ$ and $\theta=25^\circ$ (Fig.-1(a)) which were evident for the presence of amorphous nature, on the other hand, pure Poly Vinyl Alcohol showed a single high intense peak at $\theta=19.6^\circ$ (Fig.-1 (b)), confirmed that presence of semicrystalline nature. It was observed that the peaks were broadened and peaks intensity was decreased in XRD spectra of PPY-PVA blend thin film, revealing that the presence of more amorphous content in the blend thin film may enhance better applications in the sensor field. It was noticed that the structure (atomic arrangement) of polymer thin films has been modified significantly, which might be due to the distribution of TiO$_2$ nanoparticles in the blend PPY-PVA polymer network. As the concentration of TiO$_2$ dopant increased in blend thin film, peak intensity also increased and became narrower which could be due to the crystal-like structure of polymer composite thin films. It was also noticed that shifting of peaks towards a higher angle of diffraction in PPY-PVA-TiO$_2$ blend composite thin films at a higher concentration of nano TiO$_2$ dopant.

![Fig.-1: XRD Spectra of (a) PPY (b) PVA (c) PPY-PVA (d) TiO$_2$(10 mg)-PPY-PVA (e) TiO$_2$(20 mg)-PPY-PVA (f) TiO$_2$(30 mg)-PPY-PVA (g) TiO$_2$(40 mg)-PPY-PVA](image-url)
Morphological Studies

Scanning Electron Microscope is an important tool that gives a high-resolution image of the sample which reveals the surface morphology of materials. The surface of pure Poly Pyrrole showed almost smooth and the presence of globular particles on the surface which establishes the presence of amorphous nature also confirmed with XRD results and also observed that particles were agglomerated and had large size interstices. Pure PVA thin film SEM image appeared nearly rough, indicating that semicrystalline in nature. It was observed that the surface of blended thin film PPY-PVA was smooth and mixed both polymers uniformly which was confirmed by the SEM image (Fig.-2(c)). Pyrrole monomer was spread homogeneously in Poly Vinyl Alcohol polymer network, and PVA is only responsible for amended order and decrease in accumulation of Poly Pyrrole which dynamically influences geomorphology of blend thin film of PPY-PVA. PPY-PVA-TiO₂ thin films SEM images (Fig.-2 (d-g)) revealed that the morphology of blend PPY-PVA film has been changed significantly upon the addition of TiO₂ nano powder. The spherical nano TiO₂ particles can be seen on the surface of doped composite thin films and were incorporated into the PPY-PVA matrix their distribution on the surface of prepared thin films was not uniform and as the dopant changes the morphology changed significantly. There was a clear lineation in the SEM image of composite thin films further indicated granular structure, and porous surface morphology of thin films which might support the permeability of the thin films to gases. The films may suitable for detecting leakage of various gasses.

Fig.-2: SEM Images of (a) PPY (b) PVA (c) PPY-PVA (d) TiO₂ (10 mg)-PPY-PVA (e) TiO₂ (20 mg)-PPY-PVA (f) TiO₂ (30 mg)-PPY-PVA (g) TiO₂ (40 mg)-PPY-PVA
Thermal Studies
DSC is a unique technique that helps to determine glass transition, melting, and freezing temperatures and helps to analyze the thermal stability of a sample. Obtained glass transition and melting temperatures \((T_g, T_m)\) on the DSC curves of pure Poly Pyrrole, pure PVA, PPY-PVA blend, and nano TiO\(_2\) particles doped PPY-PVA thin films depicted in Fig.-3. The melting temperature of PPY was observed at 41°C but the disappearance of glass transition temperature was noticed above room temperature, on the other hand, it was noticed that glass transition and melting temperatures of PVA thin film at 123°C and 198°C respectively. The glass transition and melting temperatures on the curve of PPY-PVA blend thin film have been shifted \((T_g=138^\circ C\text{ and } T_m=245^\circ C)\) towards a higher temperature side compared to pure PPY and PVA thin films\(^{25}\), which revealed that blend thin film may offer higher thermal stability. The addition of dopant (TiO\(_2\) nanoparticles) significantly changes the physical properties like stiffness, rigidity, and brittleness and it was observed that there were almost sharp melting points obtained with an increase of dopant content which supports the crystalline nature of polymer composite thin films (Fig.-3 (e-g)). It was also noticed that, the shifting of melting points towards the lower temperature side at a higher concentration of dopant.

Optical Studies
Electronic spectroscopy is a promising spectroscopic technique that helps to calculate optical constants such as transmission coefficient, coefficient of reflection and absorbance coefficient, etc. of sample materials. The values of Direct optical band gap \((E_g)\) of pure Poly Pyrrole, pure Poly Vinyl Alcohol and blend PPY-PVA films filled with variable weights of TiO\(_2\) nanoparticles were obtained by drawing \((\alpha h\nu)^2\) vs \((h\nu)\) graphs which are depicted in Fig.-4 and reported in Table-1.

Obtained energy band gap values of prepared thin films of pure PPY, pure PVA, blend PPY-PVA, TiO\(_2\) (10 mg)-PPY-PVA, TiO\(_2\) (20 mg)-PPY-PVA, TiO\(_2\) (30 mg)-PPY-PVA, and TiO\(_2\) (40 mg)-PPY-PVA are 2.920 eV, 5.40 eV, 2.922 eV, 2.01 eV, 1.72 eV, 1.65 eV, and 1.61 eV respectively. The energy gap value of blend film (PPY-PVA) is the same as pure PPY which indicated the presence of amorphous nature but the addition of PVA and PPY may enhance the mechanical strength of the film. It was understood that values of direct optical energy band gaps were diminished gradually with rising in weights of nano TiO\(_2\) dopant which might be due to offering polarons and bipolarons state of Poly Pyrrole. The composite thin films exhibit high intense absorbance peaks and the ability of higher absorption which could be due to a greater number of conjugated bonds\(^{26-27}\). Addition of TiO\(_2\) nanoparticles with varying concentrations (the interaction amongst PPY-PVA and TiO\(_2\) nanoparticles) leads to generating polarons and bipolarons sub-energy levels within the gap. Thin films of PPY-PVA loaded with varying quantities of nano TiO\(_2\) particles may offer improved conductivity which could be due to decreasing values of optical energy band gaps with rising in weights of nano TiO\(_2\) dopant.
**Fig.-4: UV plots-Direct Optical Band Gaps**

**Table-1: Values of Direct Band Gap (optical)**

| Name of the sample       | TiO$_2$ Concentration (mg) | Values of Direct optical band gap (eV) |
|--------------------------|----------------------------|---------------------------------------|
| Poly Pyrrole             | 0                          | 2.920                                 |
| PVA                      | 0                          | 5.40                                  |
| PPY-PVA                  | 0                          | 2.922                                 |
| TiO$_2$-PPY-PVA          | 10                         | 2.01                                  |
| TiO$_2$-PPY-PVA          | 20                         | 1.72                                  |
| TiO$_2$-PPY-PVA          | 30                         | 1.65                                  |
| TiO$_2$-PPY-PVA          | 40                         | 1.61                                  |
CONCLUSION
The author adopted In-situ chemical oxidative polymerization technique to prepare PPY, PVA, blend PPY-PVA, and PPY-PVA-TiO$_2$ composite thin films, further synthesized composite thin films were examined by various characterization tools like XRD, SEM, DSC, and UV-Visible spectroscopy. The addition of TiO$_2$ dopant has modified the morphology of composite thin films which was established by SEM in addition to this, pores can be seen on the surface of prepared polymer thin films. The films with pores-like structures may support detecting some kind of gasses. Shifting of glass transition and melting temperatures were noticed with the help of DSC thermographs which suggests that, the composite thin films may offer enhanced mechanical properties and thermal stability. The direct optical band gap values of pure Poly Pyrrole, pure PVA, and their blend nanocomposite thin films were determined by UV plots. As the concentration of TiO$_2$ dopant increases, the values of direct optical band gaps were decreased gradually which might suggest the combining of electronic energy states in prepared composite polymer films. Nano TiO$_2$-doped PPY-PVA composite thin films may offer higher conductivity levels than pure PPY-PVA blend thin films. Therefore, PPY-PVA nanocomposite thin films may be used in various gas sensing devices.

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