

Synthesis and Characterization of TiO₂ nanoparticles in PVA Polymer Matrix

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Abstract

Polyvinyl alcohol (PVA) is one of the soluble polymers in water. It is used in ceramics, pharmacy and electronic industry. Titanium oxide (TiO₂) is a chemically stable, active with its high surface area in the form of nanoparticles. PVA doped with TiO₂ nanoparticles increases its amorphous phase and ionic conductivity. In this article TiO₂ nanoparticles at different weight percentages (0.5, 1.0, 1.5, 2.0) are doped in 3 g of PVA using the casting technique. Its properties are characterized by XRD, FTIR, UV-Vis and DSC techniques. The XRD studies showed the nano size of TiO₂ particles and amorphous nature of PVA increased with rising the TiO₂ quantity. In FTIR studies the presence of dopant with PVA are examined. The UV-Vis showed the irregular changes of absorption, transmittance, reflection and optical constants. With increasing TiO₂ content, optical band gap decreased and refractive index increased. DSC characteristics showed the T_g and T_m values.

Key words: PVA, TiO₂, XRD, FTIR, UV-Vis and DSC

Date of Submission: 28-09-2021

Date of Acceptance: 12-10-2021

I. Introduction

Nowadays addition of nanomaterial improves the performance of polymers due to their small size, large surface area, quantum confinement effects and strong interfacial interactions [1]. They are important for both industrial and academic applications. PVA is a good film forming polymer, water soluble, nontoxic, biocompatible, semicrystalline nature with good physical properties and chemically stable polymer. When such polymer is doped with suitable dopant it may interact with either amorphous or crystalline fraction of the polymer which changes different properties.

In this article TiO₂ nanoparticles at different compositions (0.5, 1.0, 1.5 and 2.0 wt%) are doped with 3g of PVA. Magnetic stirrer is used in the preparation of better dispersion and films are obtained. Its properties are characterized by XRD, FTIR, UV-Vis and DSC techniques.

II. Materials

TiCl₄, HCl for the preparation of TiO₂ and PVA for base matrix.

III. Experimental

Synthesis of TiO₂: 500ml beaker containing ¾ volume ice is taken. Ice is formed by placing the beaker in the refrigerator. Another 100ml beaker containing ½ volume distilled water is placed in the ice bath beaker. TiCl₄ liquid in a bottle taken. Its mouth gets solid by TiCl₄ with light green. When the solid is pierced with a pin white fumes come out as TiCl₄ evaporates. Gently the liquid is poured into the 100ml beaker containing water. The water becomes white liquid as TiCl₄ dissolves in water and the liquid solidifies instantly in white colour. The aqueous TiCl₄ solution is mixed dilute HCl and magnetically stirred well at 80 °C. Initially the white solution is dissolved with clear transparent solution, as time passes water evaporates and white layer of TiO₂ is formed. The prepared amorphous TiO₂ clusters are placed in an oven at high temperature (569 °C) and slowly cooled to get TiO₂ crystals.

Pure PVA film: A 100ml beaker containing 80ml of distilled water is taken and 3g of PVA was transferred into the beaker. The mixture was magnetically stirred well until the solution becomes a homogenous viscous gel. The gel is poured in to petri dishes and dried at room temperature for about one month. A film of thickness about 50µm is formed.

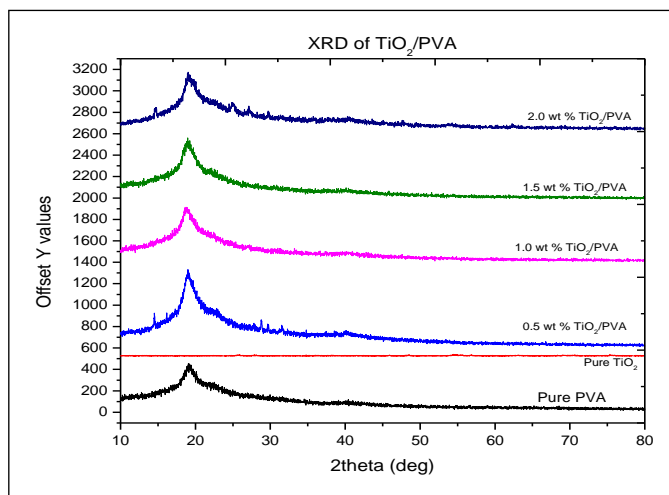
TiO₂/PVA nanocomposite: 3g of PVA solution is formed in the same method as discussed above. Now 0.5 weight percent ($0.5\%wt = \frac{0.5}{100} \times 3.000g = 0.015g$) of TiO₂ nanoparticles were dissolved in water and poured into the PVA solution. The mixture is magnetically stirred well for about 4 hours to get a good dispersion without agglomeration. So, formed TiO₂/PVA gel was cast in to a glass petri dishes. Air bubbles were removed by shaking and blowing air. It was left for one month or until dry to form a film of thickness about 50µm. This

process was repeated for different weight percentages, 1.0%, 1.5% and 2.0% of TiO₂/PVA composites to get a series of films.

IV. Measuring Techniques

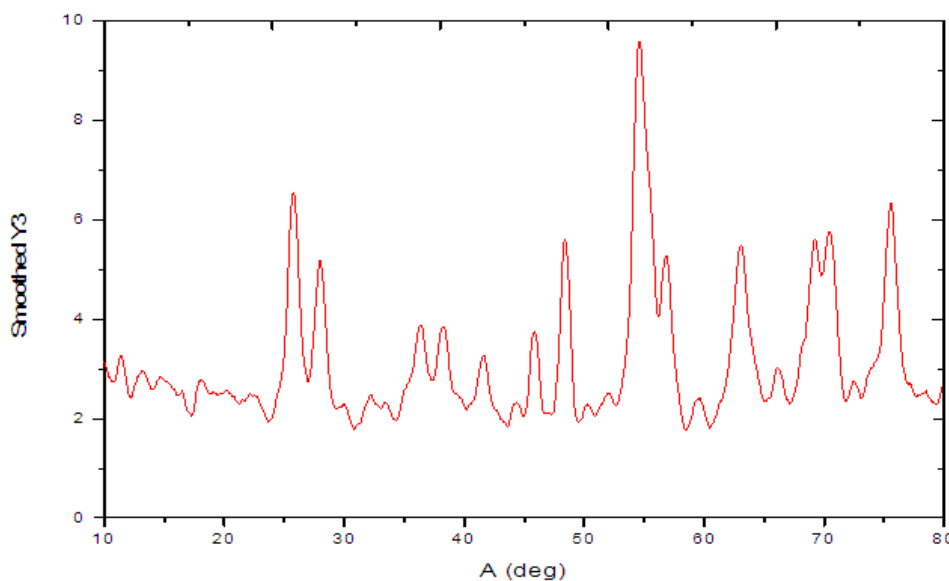
a) X-ray diffraction (XRD):

Measurement Condition: X-ray tube target used is Cu at voltage of 40.0 kV and current 30.0 mA. The X-ray diffraction measurement has been done to investigate the nanostructure and crystallinity of pure and TiO₂/PVA



nanocomposite. In order to find grain size of the TiO₂ using its XRD curve, it is smoothed first for the clear visible of peaks. Full Width of Half Maximum (FWHM) is to be found for the identified peaks. Using Debye-Scherrer formula the grain size is calculated. It is $d = \frac{k\lambda}{\beta \cos \theta}$, where k is the shape factor usually of the value 0.9, λ is the wavelength of monochromatic light used in the X-ray machine, here wavelength used is $\lambda = 0.15406nm$, β is the full width half maximum (FWHM) found for the identified, clearly visible peaks in radians and θ is half the central value of those each peak. From the XRD graph of TiO₂ 13 peaks were identified by smoothing the graph and grain size is

found to each of them using the Debye-Scherrer formula. The average grain size from all those peaks is calculated as **8.4983 nm**.



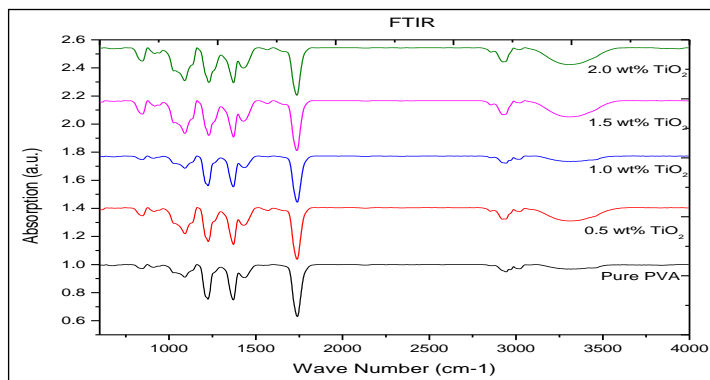
| Peak No | Peak Position 2θ | θ in rad | FWHM (deg) | FWHM (rad) | Crystallite size (nm) |
|---------|------------------|-------------|------------|-------------|-----------------------|
| 1 | 25.77887 | 0.224963079 | 1.07805 | 0.018815522 | 7.559613063 |
| 2 | 27.98634 | 0.244226889 | 0.99658 | 0.017393602 | 8.215345736 |
| 3 | 36.33988 | 0.317125278 | 1.19718 | 0.020894733 | 6.984091278 |
| 4 | 38.23814 | 0.333690721 | 0.99712 | 0.017403027 | 8.43236428 |
| 5 | 41.5832 | 0.362881877 | 0.73148 | 0.012766734 | 11.61710102 |
| 6 | 45.86782 | 0.40027224 | 0.63457 | 0.011075336 | 13.59368227 |
| 7 | 48.42943 | 0.422626504 | 0.78518 | 0.013703976 | 11.09389157 |
| 8 | 54.76887 | 0.477948555 | 1.57349 | 0.027462581 | 5.68600512 |
| 9 | 56.81647 | 0.495817235 | 1.13353 | 0.019783831 | 7.967949457 |

| | | | | | |
|-----------------------------|----------|-------------|---------|-------------|--------------------|
| 10 | 63.10545 | 0.550698939 | 1.46515 | 0.025571692 | 6.362859262 |
| 11 | 69.26828 | 0.604479777 | 1.62844 | 0.02842164 | 5.929118294 |
| 12 | 70.62439 | 0.616314069 | 1.00133 | 0.017476505 | 9.722543383 |
| 13 | 75.5633 | 0.659414189 | 1.37432 | 0.023986409 | 7.31386627 |
| Avg. Grain size (nm) | | | | | 8.498340847 |

b) FTIR Spectroscopy:

The investigation of polymer composites structures can be done using FTIR Spectroscopy. It gives the occurrence of interaction between the various molecular functional groups according to the induced charges in the vibration modes and band positions.

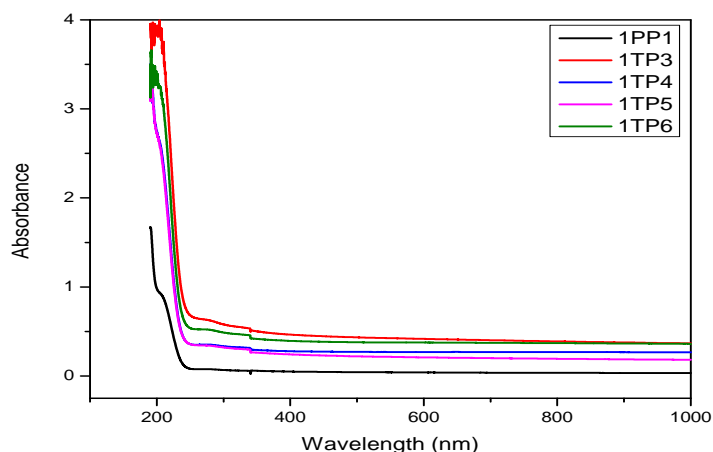
The figure shows FTIR spectra of TiO₂/PVA composite films with different weightage percentages. The spectrum shows peak at 846 cm⁻¹ is the presence of Ti-O vibrations, C-O bond at 1089 cm⁻¹, OH stretching at 3312 cm⁻¹ appears in the band range 3043 cm⁻¹ to 3639 cm⁻¹. It can be observed clearly that CH₂ symmetric appears at 2939 cm⁻¹ and symmetric bending of CH₂ appears at 1439 cm⁻¹. This confirms the possibility of interaction between TiO₂ and PVA.



c) UV-Visible Spectroscopy:

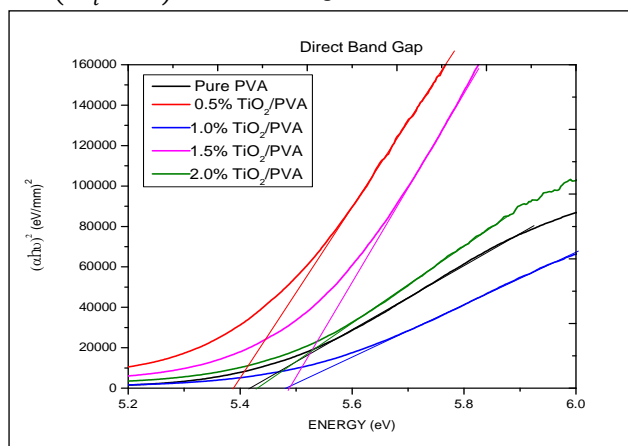
UV-Visible Spectroscopy is an important tool to investigate the electronic structure of the material through the optical band constants. The figure shows the electronic absorption

UV-Visible spectra of pure PVA and TiO₂/PVA composites.



Direct band gap energy: The below graph shows the direct band gap calculated using Tauc plot relation

$$\left(\frac{2.303 A}{l} hv\right)^2 = k(hv - E_g)$$



The direct band gap can be obtained from the X-intercept, from the graph its values for the composites are.

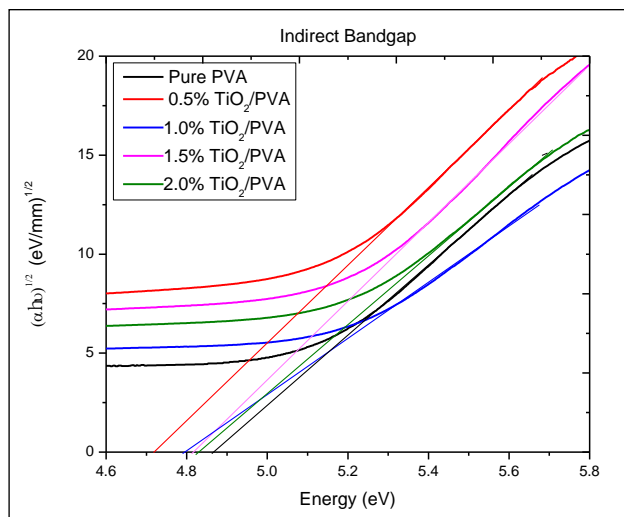
- Pure PVA $E_g = 5.42$ eV
- 0.5% TiO₂/PVA $E_g = 5.39$ eV
- 1.0% TiO₂/PVA $E_g = 5.48$ eV
- 1.5% TiO₂/PVA $E_g = 5.49$ eV
- 2.0% TiO₂/PVA $E_g = 5.43$ eV

Indirect band gap energy: The next graph shows the indirect band gap calculated using Tauc plot relation

$$\left(\frac{2.303 A}{l} h\nu\right)^{1/2} = k(h\nu - E_g)$$

The indirect band gap can be obtained from the X-intercept, from the graph its values for the composites are.

- Pure PVA $E_g = 4.837$ eV
- 0.5% TiO₂/PVA $E_g = 4.720$ eV
- 1.0% TiO₂/PVA $E_g = 4.792$ eV
- 1.5% TiO₂/PVA $E_g = 4.812$ eV
- 2.0% TiO₂/PVA $E_g = 4.829$ eV

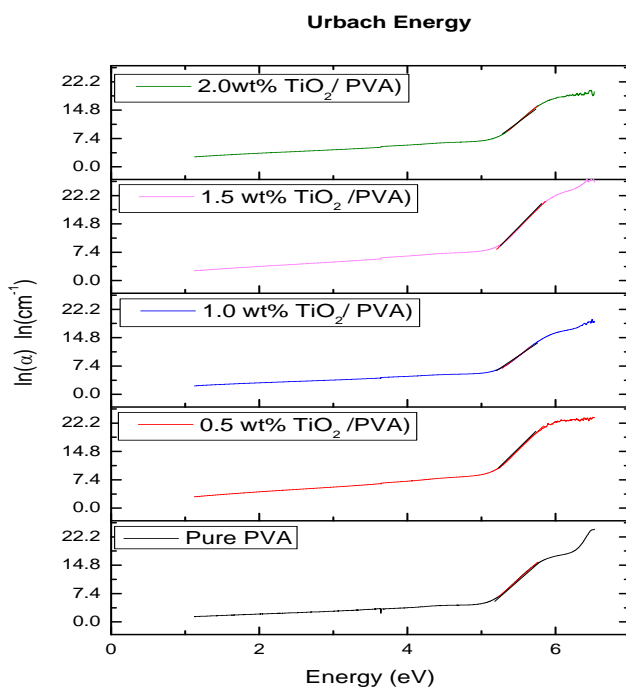


Urbach energy: The defect states in optical band gap region are represented by an optical parameter known as Urbach energy. These localized defect states in the band gap region is responsible for the formation of absorption spectra and it can be calculated using following relation.

$$\alpha = \alpha_0 \exp\left(\frac{E}{E_u}\right)$$

Where α is the absorption coefficient, α_0 is constant, E is incident photon energy which is equal to $h\nu$ and E_u is the Urbach Energy. The Urbach energy is estimated from $\ln(\alpha)$ versus photon energy plot. The reciprocal of the slope obtained by fitting linear part of the curve gives the value of the Urbach energy E_u .

From the graph slope is calculated. The reciprocal of slope gives the Urbach energy. $\left(E_u = \frac{1}{\text{slope}}\right)$

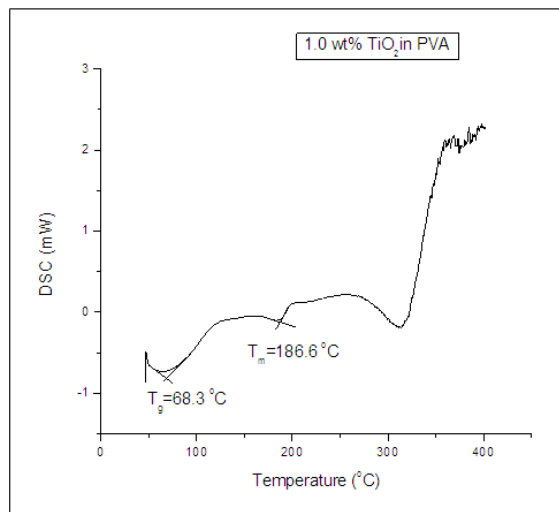
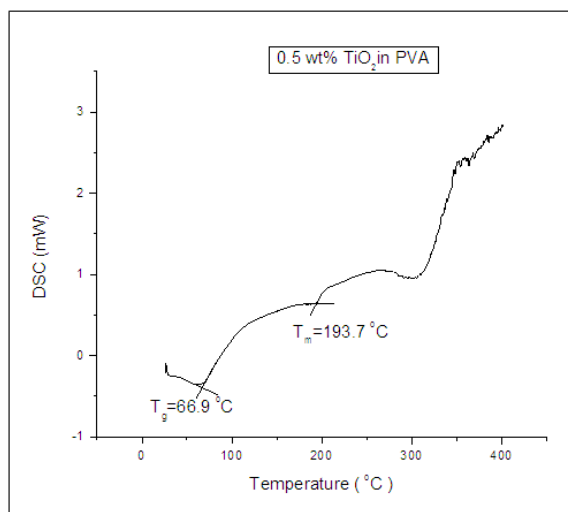
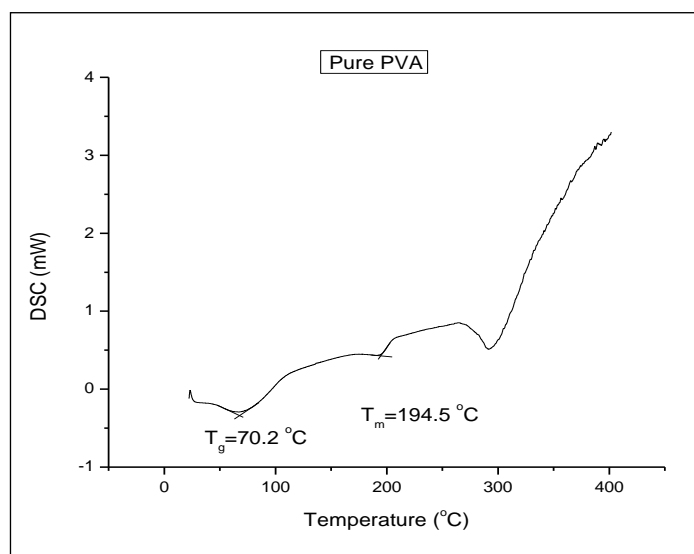


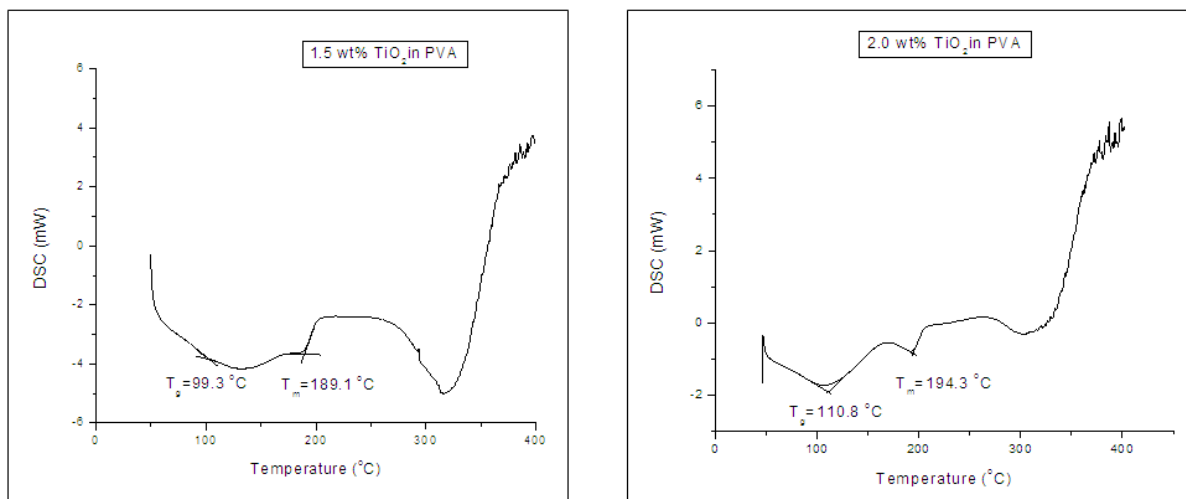
- For pure PVA $E_u = \frac{1}{17.215} = 0.058$
- 0.5%wt TiO₂/PVA $E_u = \frac{1}{18.329} = 0.055$
- 1.0%wt TiO₂/PVA $E_u = \frac{1}{14.593} = 0.068$
- 1.5%wt TiO₂/PVA $E_u = \frac{1}{19.081} = 0.052$
- 2.0%wt TiO₂/PVA $E_u = \frac{1}{16.471} = 0.06$

d) **DSC Thermal Analysis:**

Thermal studies of PVA and TiO_2 /PVA nanocomposites were carried out by Differential Scanning Calorimetry (DSC). In DSC technique, a graph is plotted for heat flow of material with respect to time or temperature. This heat flow may be into material or out from it. If the heat flows into the material, then endothermic peaks appear downwards and if the heat flows out from the material, then exothermic peaks appear upwards.

The DSC curves for pure PVA and TiO_2 /PVA nanocomposites (0.5 wt%, 1.0 wt%, 1.5 wt% and 2.0 wt%) are shown in figure. TiO_2 doped PVA nanocomposite DSC graphs contains both exothermic and endothermic reactions. Endothermic peaks correspond to glass transition region (T_g), and melting point region (T_m). For pure PVA, glass transition temperature and melting point temperature were observed at 70.2 °C and 194.5 °C respectively. The glass transition temperatures obtained for TiO_2 /PVA nanocomposites with 0.5 wt%, 1.0 wt%, 1.5 wt%, and 2.0 wt% were at 66.9 °C, 68.3 °C, 99.3 °C, 110.8 °C respectively. The melting point temperatures obtained for TiO_2 /PVA nanocomposites with 0.5 wt%, 1.0 wt%, 1.5 wt%, and 2.0 wt% were at 193.7 °C, 186.6 °C, 189.1 °C and 194.3 °C respectively.





V. Conclusion

TiO₂ nanoparticles at different compositions (0.5, 1.0, 1.5 and 2.0 wt%) are doped with 3g of PVA solution by solvent casting technique. Magnetic stirrer is used in the preparation of better dispersion and films are obtained. Its properties are characterized by XRD Technique, FTIR Spectroscopy, UV-Vis Spectroscopy and DSC thermal analysis Technique.

From the XRD graph of TiO₂ 13 peaks were identified and grain size is found to each of them using the Debye-Scherrer formula. The average grain size from all those peaks is calculated as **8.4983** nm. The FTIR spectra confirms the possibility of interaction between TiO₂ and PVA of TiO₂/PVA composite films with different weightage percentages. The peak at 846 cm⁻¹ is the presence of Ti-O vibrations, C-O bond at 1089 cm⁻¹, OH stretching at 3312 cm⁻¹ appears in the band range 3043 cm⁻¹ to 3639 cm⁻¹. It can be observed clearly that CH₂ symmetric appears at 2939 cm⁻¹ and symmetric bending of CH₂ appears at 1439 cm⁻¹. Using UV-Visible Spectroscopy direct and indirect band gaps were determined and they were increased with increasing wt% of TiO₂ nanoparticles in TiO₂/PVA nanocomposite. DSC results showed that thermal stability of TiO₂/PVA nanocomposite films was improved by doping of TiO₂ nanoparticles. It is observed that with increasing wt% of TiO₂ doping T_g and T_m values were increased. Thus, TiO₂ nanoparticles have modified the electronic structure and thermal stability of PVA so that it can be used as UV mask and anti-reflection coating material for different applications.

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J.Satheesh Goud, et. al. "Synthesis and Characterization of TiO₂ nanoparticles in PVA Polymer Matrix." *IOSR Journal of Applied Physics (IOSR-JAP)*, 13(5), 2021, pp. 50-55.