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Effect of Pomegranate Plant Dye on Some of Structural Properties of (Polyvinyl Alcohol + Dioxide Titanium) Thin Films

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ABSTRACT

Four thin films of PVA+TiO_2 were prepared with different concentration of natural pomegranate dye. The results of the optical microscope showed the formation of a network of TiO2 nanoparticles inside the polymer that increased the movement of electrons. FT-IR spectroscope recorded 3325.28, 2908.94, 1423.46 and 1056.99/cm corresponding to O-H, C-H, C-C and C-O functional groups, respectively. The structure of natural dye (anthocyanin) had a benzene skeleton, a conjugated double bond, a C-H carbonyl group and an OH bond, according to the IR spectrum. The results revealed that when the quantity of pomegranate dye increased, so did the absorption, and the absorption coefficient increased when the wavelength of the sample was increased. The results demonstrated that as the dye concentration increased, the optical energy gap of the (PVA/TiO_2/pomegranate dye) film reduced (3.65-3.59 eV).

Key words: Pomegranate natural dye, TiO_2 nanoparticles, (PVA/TiO2/pomegranate dye) thin films, FTIR spectroscopy, optical spectroscopy

INTRODUCTION

The pomegranate fruit came from a deciduous shrub. Its botanical name is *Punica granatum.* Pomegranate came under the classification of berries and had flower-shaped stem. Pomegranate dye absorption was discovered in the visible area at the 555 nm peak. So, it will act as a light sensitizer (Kawhena *et al.*, 2022). PVA (polyvinyl alcohol) is a water-soluble transparent polymer that is widely used in industry due to its outstanding chemical and physical qualities, as well as its non-toxicity and chemical resilience. It has a carbon chain backbone with methane carbons connected to hydroxyl groups. These OH groups act as a source of hydrogen bonding, which helps to build polymer blends (Byrne, 2021). Nanoparticles employed in liquids, particularly water, had sparked renewed attention, mostly for technical and medicinal purposes (Bahaa *et al.*, 2020). Therefore TiO_2 nanoparticles had a wide range in industrial and commercial applications and widely utilized in gas sensing and solar cells (Reghunath *et al.*, 2021). Other materials, such as graphene, have been employed as gas sensors (Salah and Ameen, 2020). In this study focus was on (PVA/TiO_2/pomegranate plant dye) thin films to examine its use for optical microscopy and FTIR spectroscopy.

MATERIALS AND METHODS

Titanium dioxide was obtained as powder from (Nano shel USA) company with grain size (20 nm) and high purity (99.9%); density of 4.23 g/cm^3 as white hue. PVA was a white granular type of polyvinyl alcohol with a molecular weight of (26,300-30,000) g/mol from Shanghai Kaidu Industrial Development Co. Ltd., China. The active part of pomegranate was the seed of the pomegranate, which was carefully removed from the peels and put over a low heat. The pomegranate dye was extracted by filtering it which was concentrated by boiling at 75°C and eliminating 20% of the water to preserve its perfume. Thus, the dehydration was completed in a dryer (oven) at 75°C for 10 h, resulting in a dry paste that was crushed to generate the dye powder. In a glass beaker, one gram of polyvinyl alcohol was fully dissolved in 20 ml of water over one hour at 90°C with steady stirring. After the pure sample was dissolved, a little amount of titanium dioxide nanoparticles (0.30 wt%) was added, and the glass beaker was placed in an ultrasonic device to disperse the titanium dioxide and mixing with different ratios (1, 2, 3 and 4) ml of pomegranate dye per 20 ml (PVA+TiO_2) and forming diverse samples. A vacuum spin coater was then utilized to generated films with a thickness of 774±3 nm on glass substrates using droplets of each thin film that had been made. Glass slides having a surface area of 2.57.5 cm^2 and a thickness of 0.1 cm served as the substrates.

Absorption, polarization and any other quality involving the interaction of electromagnetic radiation or light with matter were examples of optical properties of materials. The study of polymer optical properties added to our knowledge of the type of polymer internal structure and the nature of the bonds, as well as the range of polymer applications that were available. The absorption and transmittance spectrum of a polymer was used to detect a number of optical properties over a wide range of wavelengths (Jawad *et al.*, 2021).

Absorbance was the ratio of the material's absorbed light intensity (I_A) to the incoming light intensity (I_o) following Soliman *et al.* (2020):

$$A = I_A/I_O$$

The absorption coefficient (α) was well-defined as material's capacity to absorb light of a specific wavelength (Jawad *et al.* (2021):

$$\alpha = 2.303A/t$$

The absorbance was A, and the sample thickness was t. The energy band gap was calculated following Soliman *et al.* (2020).

$$\alpha h\upsilon = B(h\upsilon - Eg)\ x$$

Where, Eg was the optical energy band gap, h was photon energy, B was a constant and x was constant, and took the values (1/2, 3/2) for permitted and prohibited direct transitions, and (2, 3) for allowed and forbidden indirect transitions, respectively.

RESULTS AND DISCUSSION

In the PVA/TiO2/pomegranate dye thin films at 10x magnification for samples of various concentrations of pomegranate dye observed black dots representing concentration of titanium dioxide nanoparticles within the polymer (Fig. 1 A). A network was formed inside the polymer that helped electrons to pass through it (Reddy, 2020). The dyes did not show any change in the various images because the light passed from the films and only TiO_2 particles appeared in the image, and no colour appeared due to the low concentration of the dye. Further, TiO_2 with pomegranate dye was employed as solar cells (Thenmozhi *et al.*, 2022). The O-H group at wave number 3325.28/cm, strain C-H at wave number 2908.94/cm, the C-C strain at wave number 1423.46/cm, and the C-O group at wave number 1056.99/cm were the four unique functional groups detected (Figs. 2 and 3). The structure of natural dye (anthocyanin) had a benzene skeleton, a conjugated double bond, a C-H carbonyl group, and an O-H bond, according to the IR spectrum. FT-IR increased with increasing concentration of pomegranate dye (Nnorom and Onuegbu, 2019).

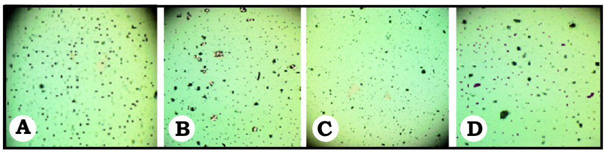

Fig. 1.Photomicrographs at 10x for PVA/TiO_2 thin films at 1, 2, 3 and 4 ml pomegranate dye.

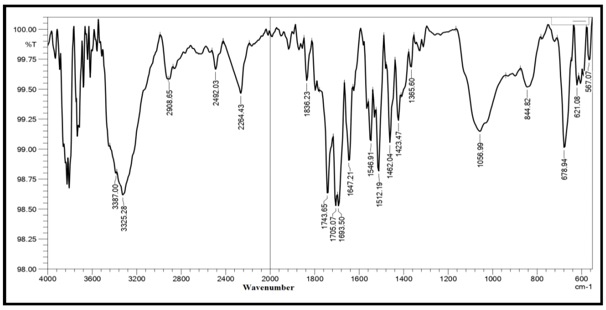

Fig. 2. FT-IR of (PVA/TiO_2/1 ml pomegranate dye).

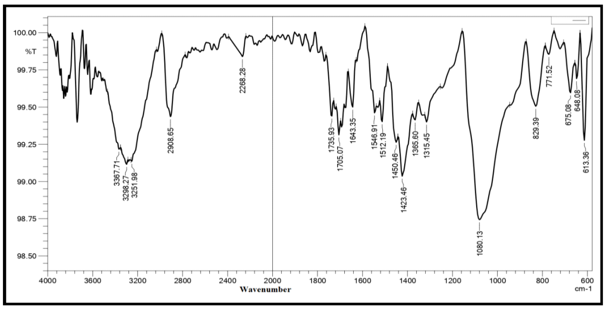

Fig. 3. FT-IR of (PVA/TiO_2/4 ml pomegranate dye).

Fig. 4 demonstrates that the film was very absorbent in the lower wavelengths (ultraviolet area) for all samples, and gradually diminished with increasing wavelength (VIS and IR regions). The results revealed that when the quantity of pomegranate dye increased, so did the absorption. The presence of PVA and carbonyl groups associated with ethylene unsaturation in such materials resulted in a

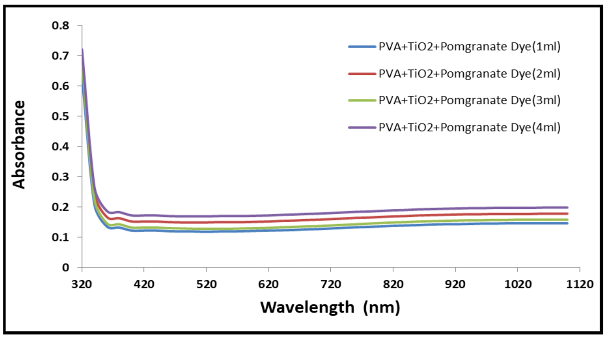

Fig. 4. Absorbance spectra as a function of wavelength of (PVA+TiO2) and different concentration of pomegranate dye.

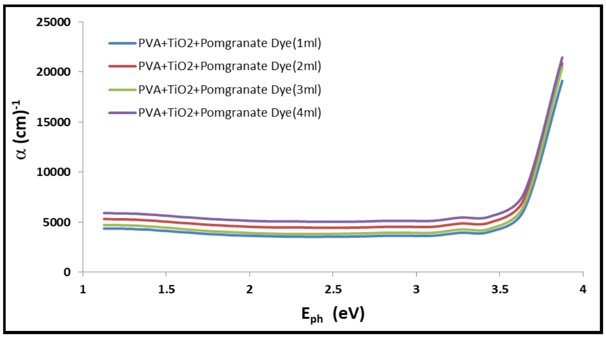

Fig. 5. The absorption coefficient and photon energy (hυ) for (PVA+TiO2) and different concentration of pomegranate dye.

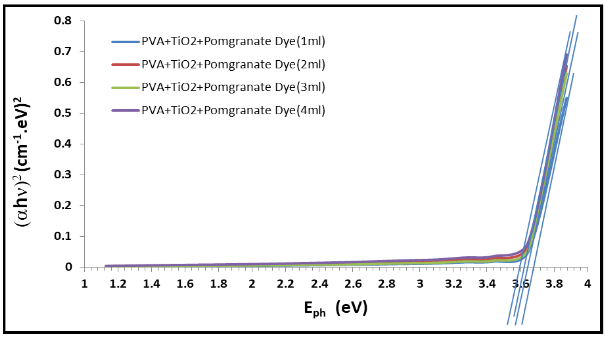

Fig. 6. Graphically relation for the allowed direct transition between $(\alpha h\upsilon)^2$ and photon energy (hυ) of (PVA+TiO2) and different concentration of berry dye.

bottom at 400 nm in all film samples (Alsulami and Rajeh, 2022). The absorption coefficient was used to determine the nature of electronic transitions. The absorption coefficient increased when the wavelength of the sample increased (Pashameah *et al.*, 2022). A rise in pomegranate dye concentration and electronic transit between the bonding and non-bonding molecular orbits may explain it (Fig. 5).

Fig. 6 shows the direct energy gap vs. photon energy for all samples, as well as the slope tangent findings for all samples. The results demonstrated that as the dye concentration increased, the optical energy gap of the (PVA/TiO_2/pomegranate dye) film reduced (3.65-3.59eV; Prabavathy *et al.*, 2017).

CONCLUSION

FTIR measurements were used to determine the effect of pomegranate plant colour on morphological features. Some polymer chains were broken and others were produced once the concentration of natural pomegranate colour was increased. Increased concentration resulted in the formation of new bonds in this range. The two (3387 and 1080.13)/cm peaks represented the distinguishing feature of this thin films corresponding stretching (O-H) and C-O bond, respectively. The (O-H) stretching band was by far the most characteristic feature of alcohols; it appeared in range (3000-3500)/cm. The results demonstrated that as the dye concentration increased, the optical energy gap of the (PVA/TiO_2/pomegranate dye) film reduced (3.65-3.59 eV).

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