



### RESEARCH ARTICLE

## STUDYING THE EFFECT OF ADDING LIGNOSULFONATE STABILIZERS ON THE STRUCTURAL, THERMAL AND OPTICAL PROPERTIES OF POLYMERS POLYVINYL ALCOHOL

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### Abstract

Composite films made from blends of Polyvinyl Alcohol (PVA) and Lignosulfonate (LS) were prepared using the casting technique in this study. The aim was to investigate the impact of LS concentrations at (0, 0.01, 0.05, and 0.1 wt. %) on the optical, thermal, and structural properties of PVA. The composite films were examined using X-ray diffraction (XRD) and UV-VIS spectroscopy. Results showed that adding LS led to a more compact structural arrangement, increasing the refractive index and amorphous phase due to the composites' disorder, which reduced the optical energy gap. The Absorbance of the PVA/LS composite film increased as LS concentration increased, indicating a strong intermolecular interaction between LS and PVA. This interaction suggested a strong hydrogen bond formation between the hydroxy group in PVA chains and the outer site groups of LS. These findings suggest that LS can effectively modulate the optical properties of PVA, making it useful in various fields such as optics and photonics.

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### Introduction:-

Recently, blending polymers has garnered significant attention from both scientists and industries due to their ease of process and ability to create unique polymeric materials with distinct physical properties compared to their parent polymers [1]. Polymers such as PVA and their blends have various applications such as packaging [2], cosmetics [3], and emulsifiers and adhesives [4], among others in the field of the usage of polymeric thermoplastics which has increased remarkably. PVA is a suitable base polymer for additives because of its distinguished characteristics including high chemical stability, mechanical properties, dielectric power, and high-quality membrane modification capacity during casting procedures [5]. Furthermore, Blending PVA with other organic polymers creates a novel invented polymeric material with significant characteristics [6-7]. Also, the blending of these polymers prevents the collapse of the holes within PVA through annealing. This enhances the balance of water content and can maintain a compressive pressure up to many mega pascals which allows the application in medical equipment and increases the use of the resulting materials in industrial applications [8]. However, despite its usefulness, PVA still requires improvement due to structural imperfections that may occur during polymerization [9]. Therefore, stabilizing the polymer with various additives is necessary. Previous studies have demonstrated that strong interfacial interaction is effective in achieving excellent reinforcement effects [10-15]. Also, as environmental awareness continues to rise and oil reserves decline, the demand for bio-based materials is on the rise. Thus, Lignin industrial polymers have demonstrated great potential as functional additives in various materials and emerged as a highly sought-after renewable resource. Thanks to their ready availability, cost-effectiveness, and versatility across a range of applications, including coatings, optical films, packaging materials, and nanofibers, which have shown great

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potential as a functional additive in various materials. [16]. LS in particular, is a water-soluble anionic polyelectrolyte with a broad range of molecular mass and significant technical and economic importance that has been shown to enhance specific material properties when blending with other polymers or natural resources, such as PVA polymers used in our study [17]. This research involves the preparation and fabrication of PVA blends by casting technique in an attempt to obtain cast films with good physical properties. Furthermore, the effect of adding the LS additive on PVA nanocomposite blends was studied with varying concentrations. The study investigated the thermal behavior and kinetic of thermal degradation through a thermal analysis, and the changes in morphology of the crystal structure and for the prepared blends. The analysis revealed that changes in crystallinity are related to structural changes, as observed using X-ray diffraction. Additionally, the optical properties of the nanocomposite were examined to understand better how PVA/LS interactions affect important properties of PVA polymers. The results of this study provide valuable insights that can help advance the industrial application of these polymers as materials with reduced cost.

## Experimental

### Materials:-

Eucalyptus lignosulfonate Sodium (LS, ~99%) was purchased from Sigma-Aldrich (St Louis, MO), PVA (degree of hydrolysis = 99%, Molecular Weight= 27,000 g/ mol) was supplied by Sigma-Aldrich in granule form. Both homopolymers were used for the preparation of the films.

### Preparation of Pure PVA and PVA /LS Blends

The films for PVA blends were prepared using the solution cast method. To prepare a composite film using PVA and LS, predefined weights of PVA and LS were dissolved in 100ml of distilled water and stirred for three hours at a temperature of 80°C. The PVA/LS solution was then cast into Petri dishes and dried in an oven at 70°C. Subsequently, PVA/LS films were obtained with varying compositions of LS to PVA (0, 0.01, 0.05, and 0.1 wt.%). The PVA and PVA/LS composite films were subjected to a hot plate at 35°C for three days to eliminate residual solvent. The resulting composite films were then sectioned into 2 x 2 cm<sup>2</sup> squares of 0.2 mm thickness for further measurements and testing. Films as visually observed were obtained for the blends shown in Table 1, which have LS concentrations up to 0.1wt%.

**Table 1:-** Films prepared at different ratios of (LS) concentrations.

Samples	(LS) concentrations
Pure PVA (control)	0%
PVA/LS 1	0.01 wt.% Ls
PVA/LS 2	0.05 wt.% Ls
PVA/LS 3	0.1 wt.% Ls

### Characterization techniques

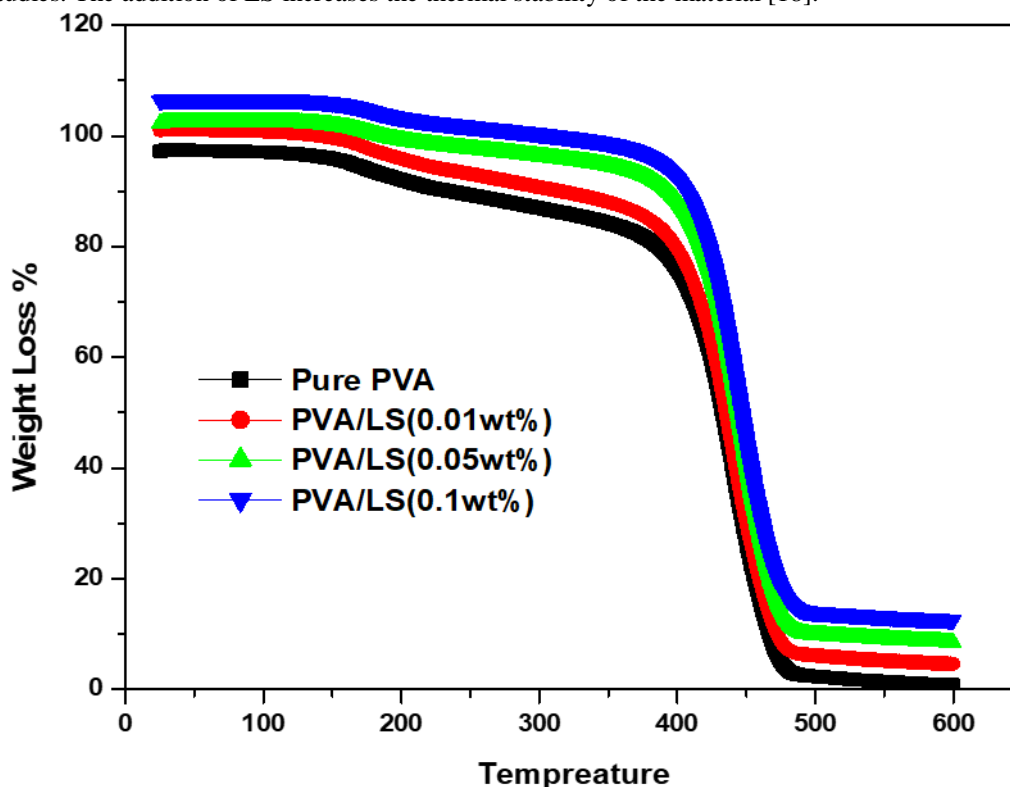
X-ray diffraction measurements were conducted using a Shimadzu 6000 X-ray diffractometer with Cu- $\alpha$  radiation of wavelength at  $\lambda = 1.5406 \text{ \AA}$ . Optical absorption spectra were recorded at room temperature using a UV-VIS-NIR spectrophotometer type JASCO V670 double beam spectrophotometer, which covered a wavelength range of 190–2700 nm. Thermal behavior and the kinetics of thermal degradation were analyzed using a thermogravimetric analyzer (TGA) (Shimadzu), which is a common technique for thermal analysis. The reflectance spectrum was measured at a 6-degree angle from the normal direction of the sample surface. Fourier transform infrared (FTIR) spectra measurements of these films were recorded using (Shimadzu UV-2600) IR spectrometer with a resolution of 4 cm<sup>-1</sup>. The measurements were taken over the wave number range 500–4000 cm<sup>-1</sup>. From these data, the optical constants such as band edge, optical band gap (both direct and indirect), and refractive index were determined.

## Results and Discussions:-

### Thermal Behavior

Figure 1 shows the thermogram for PVA/LS and pure PVA samples. The TGA graph shows weight loss versus temperature, from which the conversion and decomposition stages can be determined. The analysis shows a decrease in mass due to heating, as the sample is heated from room temperature until it undergoes exhaustive decomposition. The weight loss of the material during the heating process is monitored and recorded. It can be observed that the remaining mass at the end of the test for the PVA/LS sample is about 9.11% higher than that of the pure PVA. The

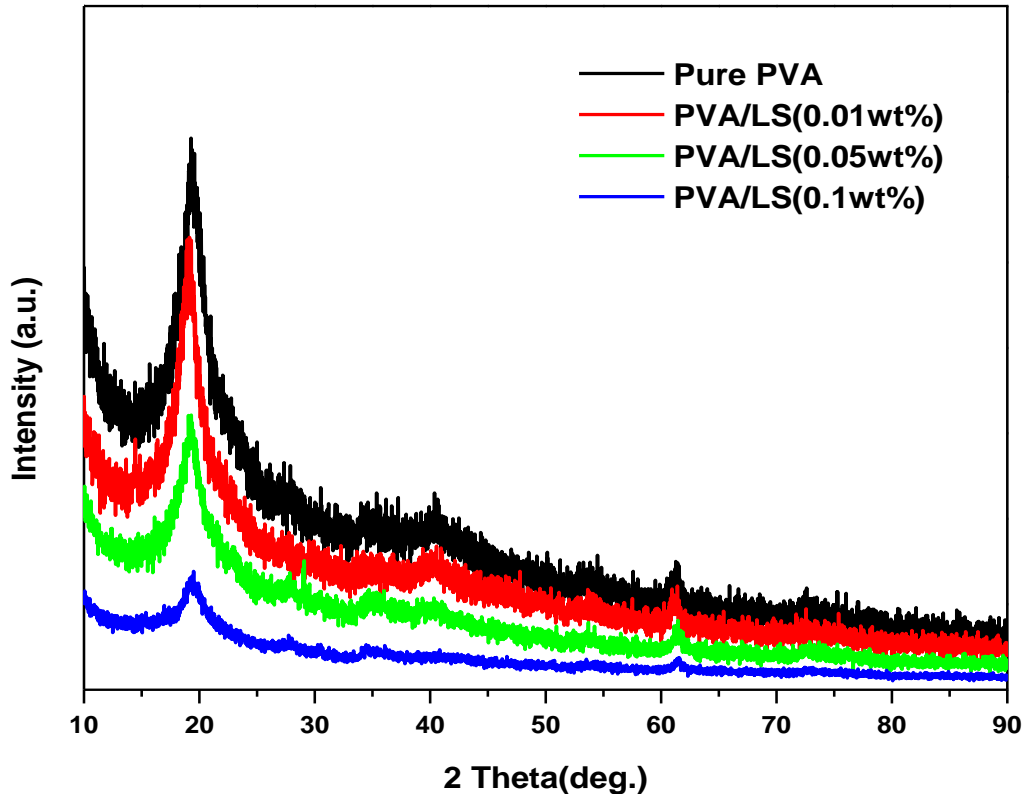
percentage of remaining mass at the end of the test for PVA/LS and pure PVA was 15.01% and 5.9%, respectively. Bioplastics that contain lignin have better thermal stability than those containing only PVA, which is consistent with previous studies. The addition of LS increases the thermal stability of the material [18].



**Figure 1:-** Thermogravimetric curve of Pure PVA and PVA/LS (0.01 wt.%), PVA/LS (0.05 wt.%), and PVA/LS (0.1 wt.%).

### X-Ray Diffraction

In Figure 2, X-ray diffraction patterns representing pure polyvinyl alcohol (PVA) and PVA/LS composites at varying concentrations (0.01 wt%, 0.05 wt%, 0.1 wt%) are displayed. The PVA/LS samples demonstrate a shift in their optical behavior with increasing LS content, possibly due to induced structural modifications. The X-ray diffraction pattern in Figure 1 of the pure PVA sample denotes a sharp and narrow diffraction peak at  $2\theta = 19.88^\circ$ , along with two weaker peaks at  $2\theta = 41.73^\circ$  and  $2\theta = 63.37^\circ$ . The diffraction peaks at  $2\theta = 19.88^\circ$  and  $2\theta = 41.37^\circ$  signify the oriented structure of PVA, indicating the semi-crystalline nature of PVA. This structure relies on the sequence of molecular chain arrangement that corresponds to (101) and (100) crystal phase diffraction planes, respectively [19]. The third peak at  $2\theta = 63.37^\circ$  corresponds to the oriented structure of PVA that aligns with the (210) crystal phase plane. The analysis of the other samples in Figure 1 demonstrates that the diffraction peak intensity and integrated intensity (area under the main diffraction peak) of the (1 0 1) profile of PVA/LS crystal decrease with increasing LS content from 0.01 wt% to 0.1 wt%, consistent with prior reports [20]. Additionally, the diffraction peak width of the samples at the (1 0 1) profile of PVA crystal increases after adding LS compared to the pure PVA samples. Furthermore, the diffraction peaks at  $2\theta = 40.8^\circ$  and  $2\theta = 63.37^\circ$ , which were previously observed in pure PVA, decrease in the latter samples. The decreasing integrated intensity indicates an increase in the disordered character of the composite samples, which suggests that the arrangement order of the PVA main chain at the crystalline region is disrupted by the incorporation of LS. However, it is worth mentioning that the bonds between PVA and LS may modify the crystallinity of PVA/LS and the interplanar spacing due to the specific interactions between PVA and LS hydroxyl groups, which suggests that strong hydrogen bonds are formed between them [21]. Finally, after a close inspection of the XRD patterns, it was revealed that the peak broadening is almost similar, and the full width at half-maxima intensity indicates that the thickness of the lamella layer is not affected by increasing the LS concentration.



**Figure 2:-** XRD pattern of Pure PVA and PVA/LS (0.01wt.%), PVA/LS (0.05wt.%), and PVA/LS (0.1wt.%).

Based on Figure 3, it can be observed that the Full Width at Half Maximum (FWHM) gradually increases to a maximum value when the LS ratio reaches 0.1 w%. As the LS ratio increases, the integrated intensity decreases significantly, suggesting that PVA/LS samples have an ordered structure. This increased orderliness is due to LS doping, which leads to degradation and a reduction in entanglements per molecule, resulting in an increase in chain mobility. Conversely, the decrease in integral intensity indicates damage to the crystalline structure due to cross-linking, resulting in a reduction of ordered phases present within the samples. Moreover, the data also shows that increasing LS ratios increase FWHM, suggesting an increase in the amorphous nature of the samples. The increase in FWHM indicates a reduction in crystal size for samples with ratios of 0.01, 0.05, and 0.1, as depicted in Figure 3. However, for the 0.1 ratio, there is an alerted increase in FWHM and a decrease in crystal size, indicating a slight decrease in the thickness of the lamella.

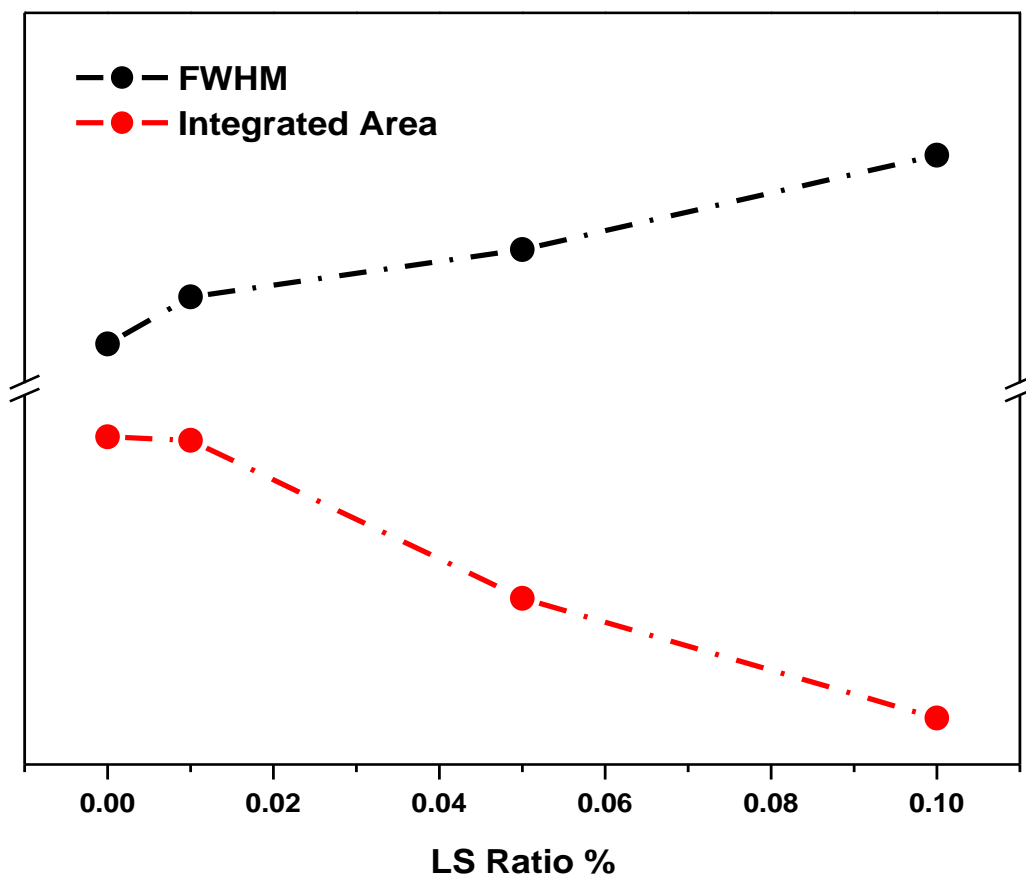


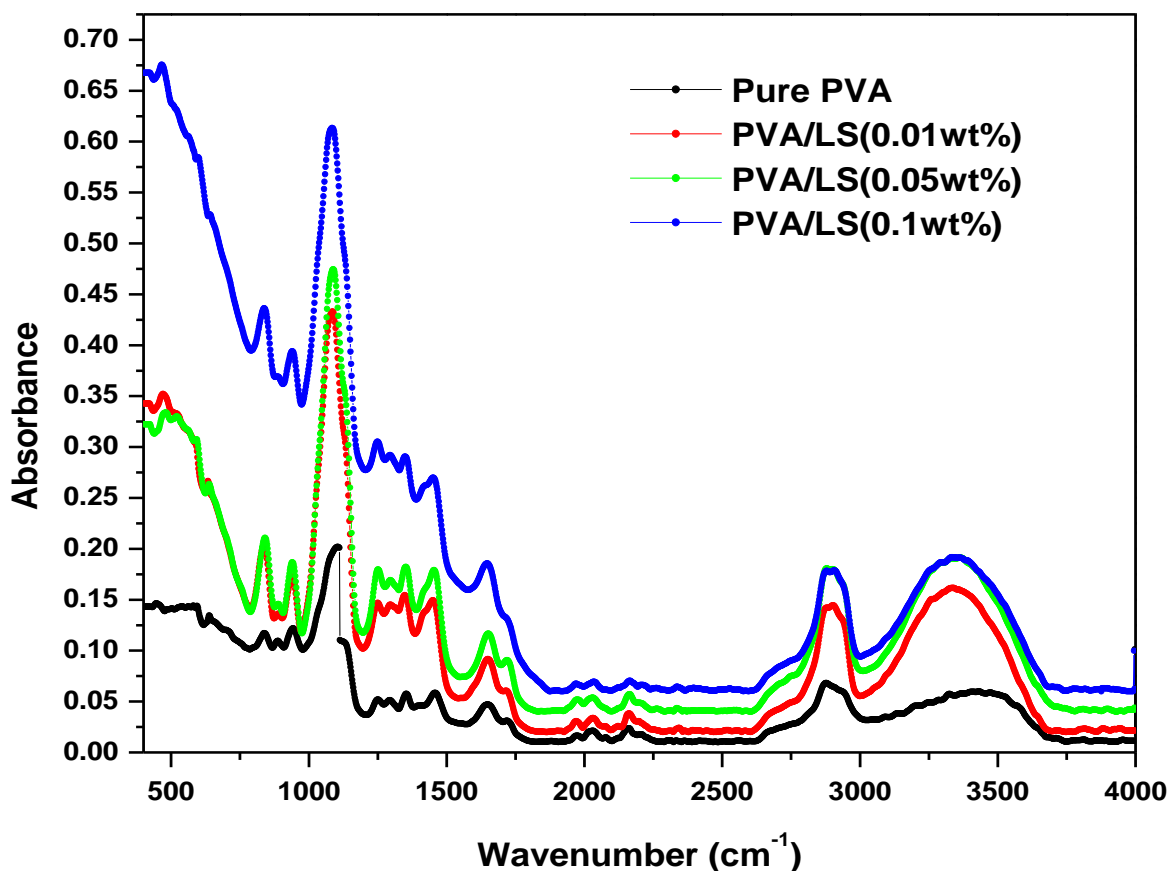
Figure 3:- The effect of LS ratio on the a) FWHM and b) the Integrated intensity.

#### FTIR Analysis

Optical analysis was performed to examine the structural changes in the PVA matrix caused by the addition of LS at different ratios. The degree of these changes was estimated by comparing the intensity of the peaks associated with the functional groups present in the polymers. Figure 3 displays the infrared absorption spectra (FTIR) of the control and doped samples at various ratios of LS (0.01, 0.05, and 0.1 wt.%). The change in the absorbance measured at characteristic wavenumbers with varying LS ratios showed that the PVA/LS sample characteristic absorption peaks were observed at 1330, 1421, 1100, 3300, and 851  $\text{cm}^{-1}$ , corresponding to the C–O–C, C<sub>6</sub>H<sub>6</sub>, C–C, –OH, and C–H bonds, respectively. The results show that the intensity of the C–O–C ether bond increased up to 2% LS. The FT-IR spectrum indicated that the position of OH stretching absorption maximum for the blend films is marginally shifted to lower wavenumbers at 3250  $\text{cm}^{-1}$ . The strong absorption peak at 1630  $\text{cm}^{-1}$  of the transmission spectra of PVA could be attributed to the hybridization of the carbon holding the hydrogen, which occurs at 2800–3000  $\text{cm}^{-1}$  for tetrahedral carbon and at 3000–3100  $\text{cm}^{-1}$  (alkenes) for trigonal carbon. Additionally, the C=O stretching vibration occurs at 1600  $\text{cm}^{-1}$  of LS, but the position of the C=O stretching vibration of blend films shifts to higher wavenumbers at 1730  $\text{cm}^{-1}$ . This could be evidence of intermolecular hydrogen bonding between the phenolic hydroxyl or carbonyl group of LS and the hydroxyl groups or carbon-hydrogen stretching vibration of PVA.

#### UV Spectroscopy

Optical absorption analysis of absorbance spectra offers a valuable understanding of the configuration and energy gap of polymeric materials. To investigate the structural modifications and the impact of different LS ratios in PVA blends, optical absorption measurements were performed. Figure 5 shows the absorption spectra of pure PVA and PVA/LS blends in the UV-vis range from (190–900 nm). The represented spectra exhibit a maximum absorption band (shoulder) at approximately 195 nm for PVA/LS, originating from the aromatic ring of LS molecules. The position of this band is slightly blue-shifted as the LS ratio increased in the blends, reaching 205 nm for PVA/LS (0.1 wt.%). These observed shoulders are caused by the absorption of simple carbonyl groups along the PVA chain. Therefore, this broadband can be attributed to the interaction between the LS molecules and PVA.

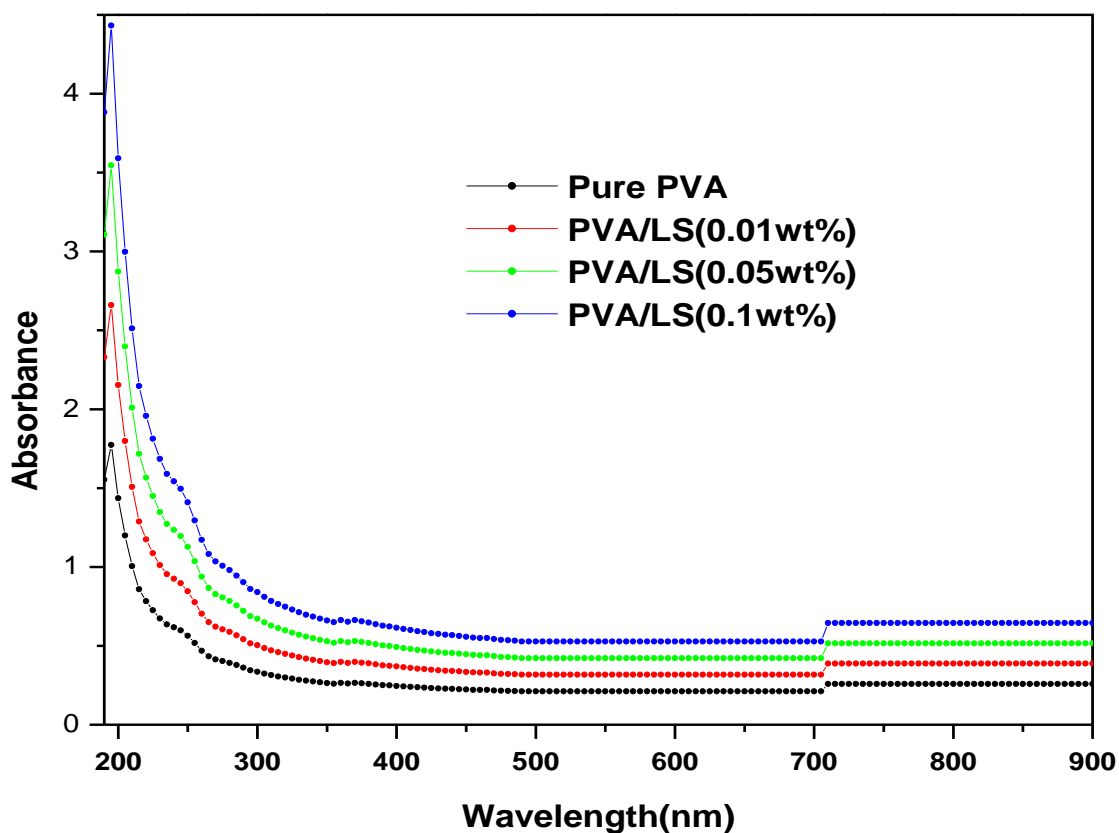


**Figure 4:-** FTIR spectra (Absorbance vs. wavenumbers) of the blend samples a) PVA, b) PVA/LS(0.01wt%), c)PVA/LS(0.05wt%), and d) PVA/LS(0.1wt%).

The relation of Tauc's was applied to extract the optical energy gap for pure PVA and PVA /LS samples, which were expressed as follows:

$$\alpha = \beta h\nu (h\nu - E_g)^x \quad (1)$$

where  $\beta$  is the electronic transition probabilities constant,  $h\nu$  is the photon energy,  $E_g$  is the optical forbidden gap, and  $x$  is an exponent factor. The exponent values determine the type of electronic transitions that occur during the process of photon absorption. For forbidden and allowed direct transition,  $x = 3/2$  and  $1/2$ , while for indirect  $x = 2$  and  $3$ , respectively. Regarding to equation (1), the optical energy gap is calculated by plotting  $(\alpha h\nu)^{1/2}$  as a function of  $h\nu$ , taking into account the linear portion of the fundamental absorption edge of the UV-visible absorption spectra as shown in Figure 5. Extrapolating the linear portion to the  $h\nu$  axis yields the corresponding indirect band gap. The obtained values are plotted as a function of LS concentration in Figure 6. A decrease in the values of the optical energy gap with increasing LS concentration has been observed from 2.90 eV for the control sample to 1.73 eV for samples with LS concentration of 0.1wt% as presented in Table 2.

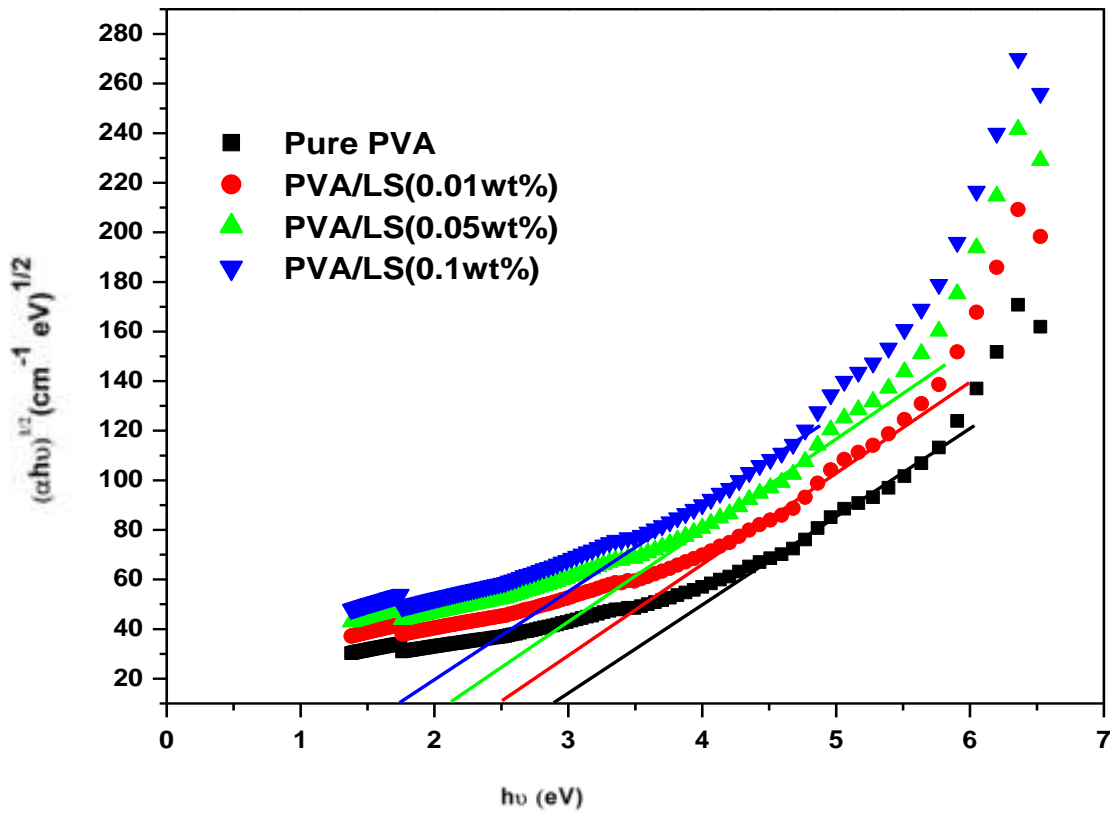


**Figure 5:-** UV–VIS absorption spectra of the blend samples a) pure PVA, b)PVA/LS(0.01wt%), c) PVA/LS(0.05wt%), and d) PVA/LS(0.1wt%).

The practical decrease in the optical band gap indicates that the LS induces changes in the morphology of the PVA matrix and increases the disorder in the PVA/LS composite samples. The present study reports on the values of the absorption coefficient of pure PVA/LS composites. The obtained results reveal that the value for the absorption coefficients is less than  $10^4 \text{ cm}^{-1}$ , which implies an indirect electronic transition. These findings shed light on the electronic properties of PVA and PVA/LS composites and have potential implications for their use in various applications. Further research exploring these properties is warranted to fully elucidate the underlying mechanisms and optimize their utility.

**Table 2:-** The values of the energy gap for indirect ( $E_g$  eV) for the prepared samples at different ratios of (LS) concentrations.

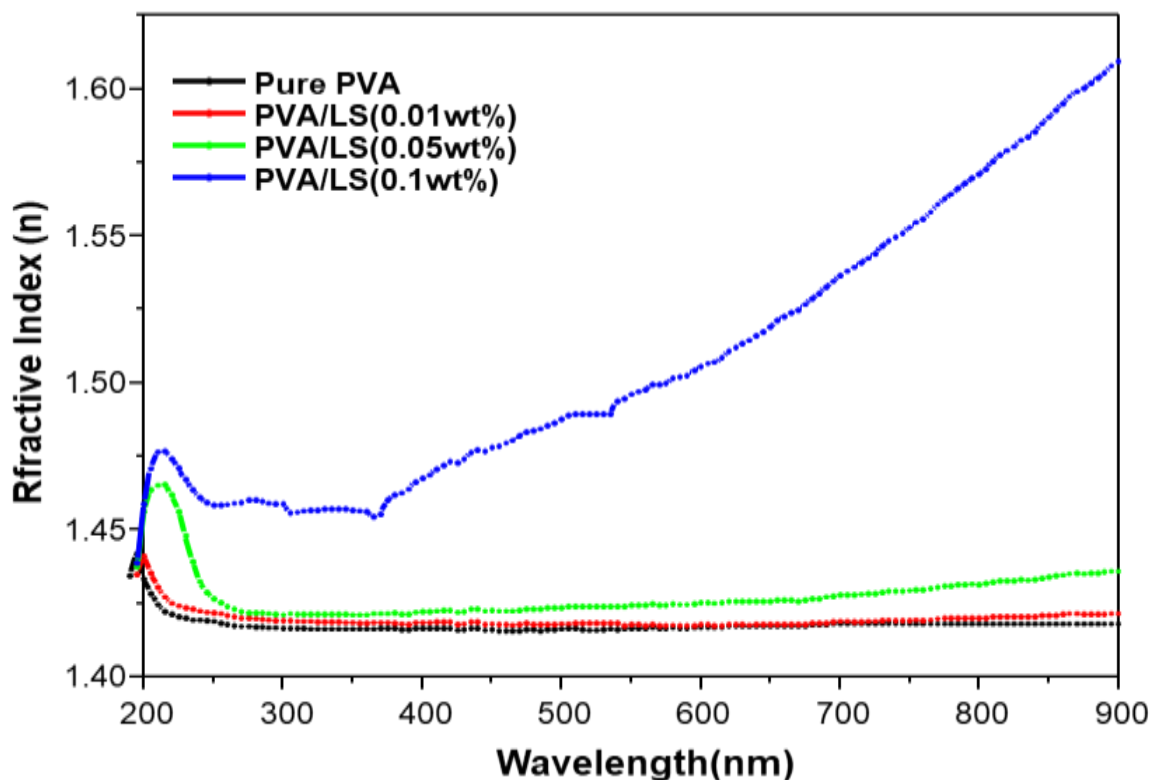
Samples	$E_g$ (eV)
Pure PVA (control)	2.90 eV
PVA/LS 0.01 wt. %	2.48 eV
PVA/LS 0.05 wt. %	2.12 eV
PVA/LS 0.1 wt. %	1.73 eV



**Figure 6:-** The variation of  $(\alpha h\nu)^{1/2}$  against the energy of the photon ( $h\nu$ ) of the blend samples a) PVA, b) PVA/LS(0.01wt%), c) PVA/LS(0.05wt%), and d) PVA/LS(0.1wt%).

Figure 7 demonstrates the variation of the refractive index of PVA and PVA/LS blends at different ratios. The figure describes that the refractive index reduced with an increase in magnitude until it reached a minimum value. This reduction can be expressed by the terms of degradation and crosslinking persuaded by LS into the polymer matrix. The molecules of LS are chemically dynamic, allowing the formation of covalent bonds between different chains (cross-linking). This results in the formation of free radicals that distribute through the main polymer chain, causing a decrease in the refractive index. However, the refractive index increases with an increase in LS concentration up to 0.1wt%. This increase may be ascribed to the formation of intermolecular hydrogen bonding between LS and PVA, signifying the integration of LS into the PVA polymeric chains, replacing the labile atoms, and annihilating the structural defects.





**Figure 7:-** The variation of the refractive index versus the wavelength of the blend samples a) pure PVA, b) PVA/LS(0.01wt%), c) PVA/LS(0.05wt%), and d) PVA/LS(0.1wt%).

### Conclusion:-

The study aimed to investigate the effects of doping LS into the PVA polymer on the thermal, optical, and structural properties at variable ratios. The PVA matrix exhibited significant enhancement when the LS was incorporated. The degree of these changes was estimated by the results of the TGA, UV-Vis, and XRD studies, as the increment of the LS concentrations caused a reduction in the composite and a decline in the ordering character. These results suggested the creation of new defect states in the energy band gap, along with an increase in the structural disorder of the PVA/LS. Even more, the results of the refractive index confirmed that the addition of the LS up to 0.1wt% dispersed the LS molecules all over the main polymer chain, suggesting a new main chain scission that resulted in a refractive index decline.

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