

RESEARCH ARTICLE

STUDYING THE PHYSICAL PROPERTIES OF PVA-PEG LOADED WITH DIFFERENT CONCENTRATIONS OF LIGNOSULFONATE

Aiyeshah Alhodaib and Najah Alharbi

.....

Department of Physics, College of Science, Qassim University, Buraydah 51452, Saudi Arabia.

Manuscript Info

Abstract

Manuscript History Received: 25 January 2024 Final Accepted: 27 February 2024 Published: March 2024

Key words:-Polyvinyl Alcohol/Polyethylene Glycol, Blends, Lignosulphonate, Optical Energy Gap Polyvinyl Alcohol (PVA) and Polyethylene Glycol (PEG) blend composite films were prepared using the casting technique. The study aims to investigate the effect of the addition of various Lignosulfonate (LS) concentrations at (0.01, 0.02, and 0.04 wt %) on the optical and structural properties of the PVA/PEG using UV-VIS spectroscopy and X-ray diffraction (XRD). The results showed that the addition of LS led to a more compact structure of PVA/PEG, which increased its refractive index and amorphous phase. This resulted in a reduction in the optical energy gap that could be attributed to the increase in the disordered structure of the composites. Additionally, the Absorbance of PVA/PEG/LS composite film increased as the LS doping concentration increased in the matrix. These results reflect the proper dispersion of LS into the PVA/PEGmatrix, causing a strong intermolecular interaction between LS and PVA/PEG blends, suggesting strong hydrogen bond formation between the hydroxyl group in PVA chains and the outer site groups of LS. This study has yielded significant insights that may aid in the advancement of polymer applications in industries by reducing costs. Theseresults could be instrumental in enhancing production processes and making the use of polymers a more viable and costeffective option for industrial operations.

.....

Copy Right, IJAR, 2024,. All rights reserved.

Introduction:-

In recent years, blending polymers considered one of the most attractive subjects that received great attention from both scientists and contemporary industries, due to the easy process and the ability to fabricate novel polymeric materials with unique physical properties as compared to that of the parent polymers[1]. Polymers such as PVA and PEG 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, PEG has high mobility, deficiency of toxicity, and flexibility [6]. Blending PVA withPEG creates a novel invented polymeric material with significant characteristics [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 serves to increase the use of the resulting materials in industrial applications [8]. However, despite its usefulness, PVA-PEG still requires improvement due to structural imperfections that may occur during

Corresponding Author:- Aiyeshah Alhodaib Address:- Department of Physics, College of Science, Qassim University, Buraydah 51452, Saudi Arabia. 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 havedemonstrated great potential as functional additives in various materialsand emerged as a highly sought-after renewable resource. Thanks to their ready availability, costeffectiveness, and versatility across a range of applications, including coatings, optical films, packaging materials, and nanofibers, which have shown great 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-PEG polymers used in our study [17]. This research involves the preparation and fabrication of PVA/PEG blendsby casting technique in an attempt to obtain cast films with good physical properties. Furthermore, the effect of adding the LS additiveon PVA/PEG nanocomposite blends wasstudied with varying concentrations. Also, the study investigated the changes in the crystal structure and morphology of PVA/PEG/LSblends. 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/PEG/LS interactions affect important properties of PVA/PEG 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) and PEG (powder, Molecular Weight = 4000 g/mol) were supplied Sigma-Aldrich in granule form. Both homopolymers were used for the preparation of PVA/PEG.

Preparation of Pure PVA/PEG Blends

The films for PEG/PVA blends were prepared using the solution cast method. After conducting multiple experimental trials, the results have shown that acceptable films with good transparency were obtained for PVA/PEG blendsonlyat PEG loadings with5, 10, 15, and 20 wt.%. This reveals that the prepared blends with polyethylene glycol (PEG) above the specified loading range tend tolose transparency and phase separation. These findings suggest that the incorporation of PEG beyond the recommended limit may result in unfavorable consequences for the blend's characteristics. It is, therefore, recommended that the loading range of PEG in blends be cautiously monitored to prevent the occurrence of phase separation and loss of transparency, which can negatively impact the quality and stability of the final films. Films with acceptable transparency (as visually observed) were obtained for the blends shown in Table 1, which have a PEG loading of 15 wt%.

To prepare pure PEG/PVA blends, separate amounts of PEG and PVA were dissolved in deionized water. In all PVA/PEG blends, a fixed amount of 23g of PVA and 0.04L of PEG were used. The polymer mixtures were dissolved by magnetic stirring at 400 rpm and 80°C for 2 hours to ensure complete dissolution and mixing. The entire mixture was then degassed in the oven for 10 minutes. After that, the solution was poured into a petri dish and left to dry at room temperature for 6 days. Finally, the film obtained was peeled off from the petri dish and stored in a desiccator filled with silica gel to avoid moisture uptake [18]. The film was obtained, preserved, and used as a pure control sample for further characterization.

(LS) concentrations
0%
0.01 wt.% Ls
0.02 wt.% Ls
0.04 wt.% Ls

Table 1:- Films with acceptable transparency at different ratios of (LS) concentrations.

Preparation of Pure PVA/PEG/LS Blends

To prepare a composite film of PVA, PEG, and LS, predetermined weights of each component are dissolved in 50ml of distilled water. The LS is added in variable weights of 0.01, 0.02, and 0.04 Wt.%. The mixture is then stirred at 400 rpm for 3 hours at 90°C to ensure complete dissolution and mixing. After that, the solution is poured into a petri

dish and left to be dry at room temperature for around 6 days. The resulting composite films of PVA/PEG/LS have different ratios of LS to PVA-PEG which are as follows (0.01, 0.02, and 0.04 W%). To remove any residual solvents, the composite films are placed on a hot plate at 35° C for three hours. Finally, the composite films are cut into square pieces measuring $2x2cm^2$ with a thickness of 0.05mm for characterization and testing.

Characterization techniques

X-ray diffraction measurementswere conducted using a Shimadzu 6000 X-ray diffractometer with Cu-k α radiation of wavelength at $\lambda = 1.5406$ Å.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.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⁻¹. The measurements were taken over the wave number range 500–4000 cm⁻¹. 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:-

X-Ray Diffraction

Figure 1 shows the X-ray diffraction patterns for the PVA/PEG and PVA/PEG/LS composites at different concentrations (0.01 wt%, 0.02 wt%, 0.04wt%) correspondingly. The variation of the LS content in PVA/PEG/LS samples results in changing theoptical behavior, which may be associated with the induced structural changes. It can be observed from the X-ray diffraction patternin Figure 1(a) for the pure PVA/PEG sample that there are three sharp and narrowdiffraction peaks at $2\theta = 19.88^{\circ}$, $2\theta = 23.73^{\circ}$ and $2\theta = 41.37^{\circ}$. According to the reference [19], the diffraction peak at $2\theta = 19.88^{\circ}$ and $2\theta = 41.37^{\circ}$ can be attributed to the oriented structure of PVA which indicates the semi-crystalline nature of PVAthatdepends on the sequence of molecular chain arrangement corresponding to(101) and (100) crystal phase diffraction planerespectively. Moreover, the shoulder peak at $2\theta = 23.73^{\circ}$ can be assigned to the oriented structure of PEGcorresponding to the (210) crystal phase plane. Following a thorough analysis observed in Figure 1(b), (c), and (d), it has been found that the diffraction peak intensity and the integrated intensity (area under the main diffraction peak)of the (1 0 1) profile of PVA/PEG crystal has decreased with increasing the LS content from 0.01 wt% to 0.04 wt%, consistent with prior reports [20]. Furthermore, the diffraction peak width of the samples at (1 0 1) profile of PVA/PEG crystal has increased after adding the LS compared to the pure PVA/PEG samples. In addition, the diffraction peak at $2\theta = 40.8^{\circ}$ formerly observed in the Pure PVA/PEG has disappeared in the latter samples. This behavior of the decreasing in the integrated intensity indicates an increase in the disordered character of the composite samples, which means that the arrangement orderinthe PVA/PEG main chain at the crystalline region is disturbed by the incorporation of LS. However, here it should be pointed out that the bonds between PVA/PEG and LS can also change the crystallinity of PVA/PEG and the interplanar spacing due to the specific interactions between PVA and LS hydroxyl groups suggesting strong hydrogen bondsformed between them [21]. Also, a close inspection of XRD patterns shows almost similar peak broadening where the full width at halfmaximaintensity, indicating that the thickness of the lamella layer is not affected by increasing the LS concentration.



Figure 1:- XRD pattern of PVA/PEG and PVA/PEG/LS:a)pure PVA/PEG, b)PVA/PEG/ Ls (0.01Wt.%), c) PVA/PEG/ Ls (0.02Wt.%),d) 4 PVA/PEG/ Ls (0.04Wt.%).

Figure 2 demonstrates that the integrated intensity increases gradually to a maximum value at LS ratio of 0.02 w%. However, as the LS ratio increases, the integrated intensity decreases. The observed uptick in integrated intensity provides evidence of the ordering character of the PVA/PEG samples. This enhanced orderliness is attributed to the degradation caused by LS doping, which results in a reduction of entanglements per molecule and a consequential increase in chain mobility. Conversely, the decrease in integral intensity signals a reduction in the quantity of ordered phases present within the samples. This decrease is indicative of damage to the crystalline structure due to cross-linking.On the other hand, the data also indicates that an increase in LS ratios leads to an increase in the full width at half maximum (FWHM), which suggests an increase in amorphous nature. This increase in FWHM demonstrates that samples with ratios of 0.01, 0.02, and 0.04 have a reduction in crystal size, as depicted in Figure 2. However, in the case of the 0.04 ratio, there is a slight increase in FWHM and a decrease in crystal size, indicating a slight decrease in the thickness of the lamella.



Figure 2:- The effect of LS ratio on thea) FWHM and b) theIntegrated intensity.

FTIR Analysis

FTIR spectral analysis was conducted to investigate the structural modifications in the PVA/PEG co-polymer due to doping of LS at different ratios. The extent of these changes was estimated from the relative increase or decrease in the intensity of the peaks associated with the functional groups present in the polymers. Figure 3 showsthe infrared absorption spectra of the control and doped samples at different ratios of LS (0.01, 0.02, and 0.04 wt.%).The variation of the absorbance measured at these characteristic wavenumbers with the varying LS ratio showedthat thePVA/PEG sample characteristic absorption peaks were observed at 1330, 1421, 1100, 3300, and 851 cm⁻¹, corresponding to the C–O–C, C6H6, C–C, –OH, and C–H bonds, respectively. From the figure, it is evident that the intensity of the ether bond C–O–C 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 3250cm⁻¹. The strong absorption peak at 1630cm⁻¹ of the transmission spectra of PVA can be attributed to the hybridization of the carbon holding the hydrogen: at 2800-3000cm⁻¹ for tetrahedral carbon and at 3000-3100cm⁻¹ (alkenes) for trigonal carbon. In addition, the C=O stretching vibration occurs at 1600cm⁻¹ of LS, but the position of the C=O stretching vibration of intermolecular hydrogen bonds between the phenolic hydroxyl or carbonyl group of LS and the hydroxyl groups or carbon-hydrogen stretching vibration of PVA.



Figure 3:- FTIR spectra (Absorbance vs. wavenumbers) of the blend samples a) PVA/PEG, b) PVA/PEG/LS(0.01wt%), c)PVA/PEG/LS(0.02wt%), and d) PVA/PEG/LS(0.04wt%).

UV Spectroscopy

The analysis of optical absorption spectra offers valuable insights into the composition and energy gap of polymeric materials. To investigate the impact of different LS ratios in PVA/PEG blends, optical absorption measurements were conducted. Figure 3 displays the absorption spectra of all PVA/PEG blends in the UV-vis range (190-900 nm). The recorded spectra exhibit a maximum absorption band (shoulder) at approximately 195 nm for PVA/PEG, 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/PEG/LS (0.04 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/PEG.



Figure 4:- UV–VIS absorption spectra of the blend samples a) PVA/PEG, b)PVA/PEG/LS(0.01wt%), c) PVA/PEG/LS(0.02wt%), and d) PVA/PEG/LS(0.04wt%).

Tauc's relation was utilized to determine the optical energy gap of both PVA/PEG and PVA/PEG/LS samples, which can be expressed as follows:

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

where β is the constant associated with electronic transition probabilities, hu is the photonenergy, Eg is the optical forbidden gap, and x is an exponent factor where the exponent values determine the type of electronic transitions that could occurduring the process of photonabsorption. For forbidden and allowed direct transition, x = 3/2 and $\frac{1}{2}$, while for indirect x = 2 and 3, respectively. According to Tauc's equation, the optical energy gap is determined by plotting $(\alpha hv)^{1/2}$ as a function of hv, 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 hv axis yields the corresponding indirect band gap. The obtained values are plotted as a function of LS concentration in Figure 5. A decrease in the values of the optical energy gap with increasing LS concentration has been observed from 3.56 eV for the control sample to 1.33eV for samples with LS concentration of 0.04wt% as presented in Table 2. The observed reduction in the optical band gap indicates that the LS induces changes in the morphology of the PVA/PEG matrix and increases the disorder in the PVA/PEG/LS composite samples. The present study reports on the values of the absorption coefficient of pure PVA/PEG and PVA/PEG/LS composites. The obtained results reveal that the value for the absorption coefficients is less than 10^4 cm⁻¹, which implies an indirect electronic transition. These finding sheds light on the electronic properties of PVA/PEG and PVA/PEG/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	$E_{g}(eV)$
PVA/PEG (control)	3.56 eV
PVA/PEG/LS 0.01 wt.%	3.20 eV
PVA/PEG/LS 0.02 wt.%2	2.91 eV

PVA/PEG/LS 0.04 wt.%

1.33 eV



Figure. 5:- The variation of $(\alpha hv)^{1/2}$ against the energy of the photon (hv) of the blend samples a) PVA/PEG, b) PVA/PEG/LS(0.01wt%), c) PVA/PEG/LS(0.02wt%), and d) PVA/PEG/LS(0.04wt%).

Figure 6 illustrates the variation of the refractive index of PVA/PEG and PVA/PEG/LS blends at different concentrations. The figure depicts that the refractive index almost decreased with an increase in magnitude until it reached a minimum value. This behaviour can be explained by degradation and crosslinking induced by LS ratios. The LS molecules are chemically active, 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 0.04w%. This rise may be attributed to the formation of intermolecular hydrogen bonding between LS and PVA/PEG, suggesting the incorporation of LS into the PVA and PEG polymeric chains, replacing the labile atoms and annihilating the structural defects.



Figure. 6:- The variation of the refractive indexversus the wavelengthof the blend samples a) PVA/PEG, b) PVA/PEG/LS(0.01wt%), c) PVA/PEG/LS(0.02wt%), and d) PVA/PEG/LS(0.04wt%).

Conclusion:-

The optical and structural properties of the PVA/PEG matrix underwent significant changes when the LS was incorporated. According to UV-Vis and XRD studies, the addition of LS led to a reduction in the composite and decreased the ordering character. These results could be attributed to the formation of a new trapped level in the forbidden band gap, as a point defect, along with an increase in the structural disorder of the PVA/PEG/LS composite samples. Furthermore, refractive index measurements confirmed that the inclusion of LS up to 0.04 w% distributed LS molecules throughout the primary polymer chain, implying a main chain scission that resulted in a refractive index decline.

References:-

[1] Nouh, S. A., Alhazime, A. A., Benthami, K., Mahrous, E. M., & Barakat, M. M. (2023). Structural and optical studies of gamma-irradiated polyvinyl alcohol, polyethylene glycol, and lignosulfonate thin film. Radiation Effects and Defects in Solids, 178(1-2), 5-19.

[2] Verma, R. (2018). Design, fabrication and characterization of PVA/Nanocarbon composite fibers (Doctoral dissertation, Arizona State University).

[3] Sharma, J. P., Kumar, P., Sharma, K., Kumar, M., Arora, A., & Singh, P. K. (2021). Optical and structural properties of drop-cast PVA/PEG polyblends. Materials Today: Proceedings, 34, 705-709.

[4] Andrade Chapal, J. C. (2021). Biodegradable materials based on poly (vinyl alcohol)(PVA) and poly (lactic acid)(PLA) with antioxidant and antimicrobial activity for food packaging applications (Doctoral dissertation, UniversitatPolitècnica de València).

[5] Alhazime, A. A., Barakat, M. M. M., Benthami, K., & Nouh, S. A. (2021). Gamma irradiation-induced modifications in the structural, thermal, and optical properties of polyvinyl alcohol-polyethylene glycol/cobalt oxide nanocomposite films. Journal of Vinyl and Additive Technology, 27(2), 347-355.

[6] Musa, B. H., & Hameed, N. J. (2021, March). Effect of crosslinking agent (glutaraldehyde) on the mechanical properties of (PVA/Starch) blend and (PVA/PEG) binary blend films. In Journal of Physics: Conference Series (Vol. 1795, No. 1, p. 012064). IOP Publishing.

[7] Sajjan, A. M., Naik, M. L., Kulkarni, A. S., Rudgi, U. F. E. H., Ashwini, M., Shirnalli, G. G., ... & Kalahal, P. B. (2020). Preparation and characterization of PVA-Ge/PEG-400 biodegradable plastic blend films for packaging applications. Chemical Data Collections, 26, 100338.

[8] Falqi, F. H., Bin-Dahman, O. A., Hussain, M., & Al-Harthi, M. A. (2018). Preparation of miscible PVA/PEG blends and effect of graphene concentration on thermal, crystallization, morphological, and mechanical properties of PVA/PEG (10 wt%) blend. International Journal of Polymer Science, 2018.]

[9] Nouh, S. A., Benthami, K., & Abutalib, M. M. (2016). Modification of structural and optical properties of polyvinyl alcohol/polyethylene glycol thin film by laser irradiation. Radiation Effects and Defects in Solids, 171(1-2), 87-95.

[10]. Liu, P., Chen, W., Liu, C., Tian, M., & Liu, P. (2019). A novel poly (vinyl alcohol)/poly (ethylene glycol) scaffold for tissue engineering with a unique bimodal open-celled structure fabricated using supercritical fluid foaming. Scientific reports, 9(1), 9534.

[11] Heiba, Z. K., Mohamed, M. B., & Ahmed, S. I. (2022). Exploring the physical properties of PVA/PEG polymeric material upon doping with nano gadolinium oxide. Alexandria Engineering Journal, 61(5), 3375-3383.

[12] Alibwaini, Y. A., Hemeda, O. M., El-Shater, R., Sharshar, T., Ashour, A. H., Ajlouni, A. W., ... &Henaish, A. M. A. (2021). Synthesis, characterizations, optical and photoluminescence properties of polymer blend PVA/PEG films doped eosin Y (EY) dye. Optical Materials, 111, 110600.

[13] Alhazime, A. A., Barakat, M. M. M., Benthami, K., & Nouh, S. A. (2021). Gamma irradiation-induced modifications in the structural, thermal, and optical properties of polyvinyl alcohol-polyethylene glycol/cobalt oxide nanocomposite films. Journal of Vinyl and Additive Technology, 27(2), 347-355.

[14] Li, Y., Zhang, A., Lu, H., Zhang, X., Zheng, W., & Li, M. (2018). Effect of polar polymers of PEG and PVA on the enhanced microwave-absorbing properties of MWNTs. The Journal of Physical Chemistry C, 122(29), 16956-16963.

[15] Rani, P., Ahamed, M. B., & Deshmukh, K. (2020). Dielectric and electromagnetic interference shielding properties of carbon black nanoparticles reinforced PVA/PEG blend nanocomposite films. Materials Research Express, 7(6), 064008.

[16] Sadiq, M., Khan, M. A., Hasan Raza, M. M., Aalam, S. M., Zulfequar, M., & Ali, J. (2022). Enhancement of electrochemical stability window and electrical properties of CNT-based PVA–PEG polymer blend composites. ACS omega, 7(44), 40116-40131.

[17] Feng, Z., Hu, F., Lv, L., Gao, L., & Lu, H. (2021). Preparation of ultra-high mechanical strength wear-resistant carbon fiber textiles with a PVA/PEG coating. RSC advances, 11(41), 25530-25541.

[18] Deshmukh, K., Ahamed, M. B., Sadasivuni, K. K., Ponnamma, D., Deshmukh, R. R., Pasha, S. K., ... & Chidambaram, K. (2016). Graphene oxide reinforced polyvinyl alcohol/polyethylene glycol blend composites as high-performance dielectric material. Journal of Polymer Research, 23, 1-13.

[19] Sharma, M., Beniwal, P., & Toor, A. P. (2022). The effect of rice straw derived microfibrillated cellulose as a reinforcing agent in starch/polyvinyl alcohol/polyethylene glycol biocompatible films. Materials Chemistry and Physics, 291, 126652.

[20] Nandy, S., Goswami, S., Marques, A., Gaspar, D., Grey, P., Cunha, I., ... & Martins, R. (2021). Cellulose: a contribution for the zero e-waste challenge. Advanced Materials Technologies, 6(7), 2000994.

[21] Nikolaidis, P. (2020). Analysis of green methods to synthesize nanomaterials. Green synthesis of nanomaterials for bioenergy applications, 125-144.