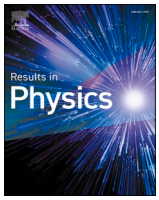
Results in Physics 58 (2024) 107456

Contents lists available at ScienceDirect

Results in Physics

journal homepage: www.elsevier.com/locate/rinp



Linear and nonlinear optical investigations of polyvinyl chloride modified La_2O_3 nanocomposite films

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ARTICLE INFO

Keywords:
PVC
La_2O_3
Band gap
Refractive index
Dispersion energy

ABSTRACT

In the present work, we report the effect and improvement of PVC polymer blend nanocomposites performance with addition of lanthanum oxide (La_2O_3) nanofiller. The structural properties of the samples were studied using different characterization techniques such as XRD, FTIR, Ramman and SEM. The X-ray diffraction peaks of La_2O_3 are with agreement with the pure hexagonal phase. The La_2O_3 sample was found to have crystallites size with an average about 15 nm. XRD, FTIR and SEM analysis confirmed the interaction of PVC/La_2O_3 polymer nanocomposites. The obtained band gaps of PVC/La_2O_3 polymer nanocomposites decreased (5.72 – 5.0 eV) upon increasing the nanofiller content. The obtained values of single oscillator energy (E_0) showed a decrease (5.88 – 3.28 eV) while dispersion energy (E_d) increases (5.64 – 7.20 eV) upon increasing the concentration of La_2O_3. The estimated values of static refractive index (n_0) showed an increase (1.40 – 1.79) upon increasing the percentage of La_2O_3. Moreover, the nonlinear refractive index (n_2) value was changed from 1.56 10^{-13} to 33.56 x 10^{-13} esu. Finally, the addition of La_2O_3 nanofillers increase the polarizability of the polymer molecules and hence the nonlinear refractive index.

Introduction

Polymer nanocomposites are a new class of materials that have attracted significant interest from both researchers and industrial scientists. This interest stems from the promising properties that these composites offer, such as enhanced mechanical, thermal, and electrical properties [1–3]. Indeed, the employment of regular and highly bright light in conjunction with polymer composites has resulted in the creation of numerous practical applications in the field of optoelectronics. These applications include sensors, devices that limit optical power, and saturable absorbers, all of which have demonstrated their significance [4,5]. Instead of resorting to costly and time-consuming procedures to identify novel monomers, it has become a standard practice to combine existing polymers to synthesis new materials which have unique properties. The ease of processing and low production cost has significantly expedited research efforts to explore new types of blends for diverse purposes. Therefore, to integrate the cost-effectiveness of organic materials with the high performance of inorganic materials, researchers have focused on developing hybrid materials, such as polymer-based nanocomposites. Polymer matrices strengthened with nanoscale fillers are referred to as polymer nanocomposites, which represent a novel class of hybrid materials.

One of the well-known polymers is polyvinyl chloride (PVC). It is a synthetic polymer that is widely used in the manufacturing of various industrial and consumer products due to its excellent physical, chemical, and mechanical properties [6]. PVC is a type of thermoplastic polymer that is produced through the polymerization of vinyl chloride (VC) monomers. It has a high tensile strength, good chemical corrosion resistance, excellent electrical insulation properties, and is easy to process into a wide range of shapes and sizes [7–9]. PVC can also be used as a matrix in the development of polymer nanocomposites by incorporating nanofillers such as clays [10], carbon nanotubes [11], and metal oxides [12]. The resulting nanocomposites often exhibit enhanced mechanical, thermal, and optical properties compared to pure PVC or traditional PVC composites, making them valuable materials for variety of applications. However, the dispersion of nanofillers in the PVC matrix can be a challenge due to the strong interactions between the polymer and the filler, which can affect their properties and performance.

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https://doi.org/10.1016/j.rinp.2024.107456
Received 19 September 2023; Received in revised form 17 December 2023; Accepted 5 February 2024
Available online 7 February 2024

Therefore, various processing techniques have been developed to achieve improved dispersion and to optimize the properties of PVC-based nanocomposites. Furthermore, several methods including solution casting, spin coating, and dip coating which can be employed for the preparation of polymer blends. Among these methods, solvent casting stands out as the simplest and fastest for producing polymer nanocomposites. Solution casting is the most widely accessible method and does not necessitate a film processing device [13]. The structure of the resulting cast film layers is affected by the concentration of the solution. Furthermore, the thickness of the films generated by solution casting can be easily controlled by varying the amount of solution added dropwise to the Petri dishes. Recently, a study investigated by Hasan et al. [14], anatase TiO_2/PVC nanocomposites were prepared using the solution casting technique at 5 wt% and 10 wt% loading of TiO_2. The results of the study indicate a successful incorporation of TiO_2 with PVC polymer, as well as a significant enhancement in the mechanical properties of the nanocomposite when the TiO_2 loading was increased to 10 wt%, in comparison with unfilled PVC. More Recently, Gholami et al. [15] developed a composite membrane for the removal of lead heavy metals from waste waters using a casting procedure approach based on PVC-blend cellulose acetate/Fe_2O_3 NPs. Incorporating inorganic metal oxide NPs seems to be a successful method of improving PVC performance. Rare earth elements, due to their unique electron configuration, have been found to have wide-ranging applications in materials. Rare earth polymers refer to polymers that incorporate rare earth elements through physical or chemical bonding. Many functional rare earth polymers have been produced, with much of the study concentrating on luminescence, fluorescence, laser protection, optical, and magnetic properties. [16–18].

Lanthanide oxide (La_2O_3) is recognized as a cost-effective alternative in comparison to other rare earth oxides such as (Y_2O_3) and gadolinium oxide (Gd_2O_3). The incorporation of La_2O_3 nanoparticle-based nanocomposite materials has been investigated to enhance and modify the properties and performance of polymers [19,20]. Moreover, it has been found that La_2O_3 can significantly improve the abrasion resistance, while small amounts of La_2O_3 can increase thermal stability [21]. Recently. Polyvinylidene fluoride (PVDF) polymer was loaded with La_2O_3 to investigate the effect of nanofiller on the structure and crystallization of PVDF. Their studies demonstrated that the XRD analysis indicated that the addition of La_2O_3 did not modify the PVDF structure but reduced the size of its crystal structure. The Avrami equation was also used in their study to analyse isothermal crystallization, which revealed that La_2O_3 did not change the nucleation mechanism of PVDF but drastically reduced the crystallization rate [21]. Another study conducted PVC with rare earth elements like lithium triflate ($LiCF_3SO_3$) salt using FTIR measurement. Their results revealed that there were some overlapping and shifting of peaks in the spectra of the samples, confirming the interaction between ($LiCF_3SO_3$) and PVC [22]. Moreover, the synthesis of nanocomposites involved the utilization of hydrothermal and chemical methods to combine Polyaniline (PANI) nanofibers and La_2O_3 nanoparticles. To form thin films, the pure PANI and PANI/ La_2O_3 nanocomposites were deposited on n-Si and glass substrates through the spin-coating technique. Analysis of their findings indicated that the XRD pattern confirmed the crystalline properties of PANI nanofiber films and the cubic structure of PANI/ La_2O_3 films. The pure PANI films displayed a structure resembling nanofibers, while PANI/ La_2O_3 nanocomposite films showed PANI nanofibers coating La_2O_3 nanoparticles. Furthermore, their studies demonstrated that the UV–Vis spectrum of pure PANI exhibited absorption peaks at 340 and 651 nm (B and Q bands), whereas PANI/ La_2O_3 films exhibited a shift in the positions of these peaks to 320 and 620 nm. This shift indicated the occurrence of charge transfer between the PANI nanofibers and La_2O_3 nanoparticles. The optical band gap of PANI/ La_2O_3 hybrid nanocomposite films decreased as the La_2O_3 content increased from 1 to 4 vol % in the PANI nanofibers, with the B-band decreasing from 2.97 to 2.81 eV and the Q-band decreasing from 1.49 to 1.43 eV. These results led to the conclusion that the inclusion of La_2O_3 significantly enhanced the photodetector performance of the system [23]. Additionally, S. Khound et al. conducted a study on La_2O_3 modified with polyvinyl phenol (cPVP). The key finding of this study was that a bilayer dielectric film consisting of cross-linked cPVP modified La_2O_3 improved the electrical performance of pentacene thin film transistors (TFT). Moreover, the surface properties of the La_2O_3 layer were found to enhance the growth of pentacene organic semiconductors. As a result, the on–off ratio and sub-threshold slope were significantly improved. Furthermore, the field-effect mobility of the La_2O_3/cPVP pentacene TFT was higher than that of the single-layer La_2O_3 device. This study also demonstrated the potential of integrating the rare earth oxide La_2O_3 with cPVP as a promising dielectric system for developing transistors with hybrid polymer gate dielectrics [24].

In this study, we report the impact and enhancement of PVC polymer blend nanocomposites performance through the introduction of La_2O_3 at varying concentrations (e.g., 0.3, 0.6 and 1.0 wt%). In the current investigation, the solution casting method was used to create the blend nanocomposites made of PVC-La_2O_3. The structural properties of the samples were studied using different characterization techniques such as XRD, FTIR, Ramman and SEM. The optical properties of prepared nanocomposites were also investigated.

Experimental

Analar grade PVC (MERK, Germany), tetrahydrofuran (THF) solvent supplied by CARLO ERBA and La_2O_3 nanopowder (Nanografi, Ankara, Turky) were used to prepare PVC/La_2O_3 nanocomposite films.

The solution casting method was used to prepare the investigated samples. The first step in the preparation process is to dissolve 1.0 g of polyvinyl chloride in 30 ml of tetrahydrofuran (THF) using magnetic stirring over a room temperature period of 1.0 h. La_2O_3 was added to the PVC clear solution in increments of 0.003, 0.006, and 0.01 g, and the mixture was stirred regularly for 1.0 h. After being transferred to a glass Petri dish, the PVC/La_2O_3 combination completed room-temperature air drying. The polymer sheets, which had a thickness of around 200 mm, had been peeled off the glass plates.

For analysing the polymer films, a Shimadzu X-ray diffraction spectrometer of the model 7000 was employed, featuring $CuK_{\alpha 1}$ radiation with a wavelength of 1.5406 Å. To conduct an ATR analysis on the polymer films, a Shimadzu FTIR-Tracer 100 was employed. The analysis revealed vibrational absorption bands corresponding to wavelengths ranging from 2000 to 399 cm^{-1}. A 785 nm Hound Unchained Labs Raman spectrometer was used for collecting the Raman signals at an exposure time of 5 s. The Thermo Fisher Quattro ESEM, an advanced environmental scanning electron microscope, is an exceptional and highly effective tool for analysing the morphology and microstructure of polymer films. Typically, before introducing the sample into the electron microscope, it is common practice to sputter a thin gold film onto the surface of the polymer film. This gold film helps enhance the conductivity and improves the quality of the imaging during the electron microscopy process. The UV–Vis optical absorption spectra of the PVC/La_2O_3 films were recorded using the highly capable Agilent Cary 60 UV–Vis spectrophotometer.

Results and discussion

The XRD analysis was conducted to investigate the effect of La_2O_3 on PVC. The X-ray diffraction spectra of the La_2O_3, pure PVC and the PVC/La_2O_3 polymer blend nanocomposites are shown in Fig. 1. Pure PVC exhibits peaks at $2\theta \approx 18^\circ$ and 24.6°, which correspond to PVC, indicating amorphous nature (low crystallinity). After addition of La_2O_3 to polymer blend, the crystallinity of the polymer blends increased (e.g., 0.6 and 1.0 wt%), as indicated by the XRD pattern of PVC/La_2O_3 blend nanocomposites. As the loading percentage of La_2O_3 increased up to 1.0 wt%, the intensity and sharpness of peaks at 18° and 24.6° also

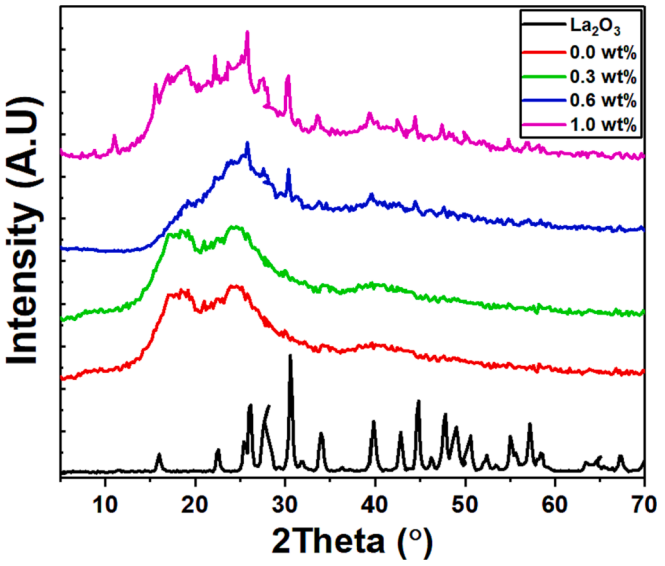

Fig. 1. XRD patterns of pure PVC, La_2O_3, and PVC-La_2O_3 nanocomposites with different concentration.

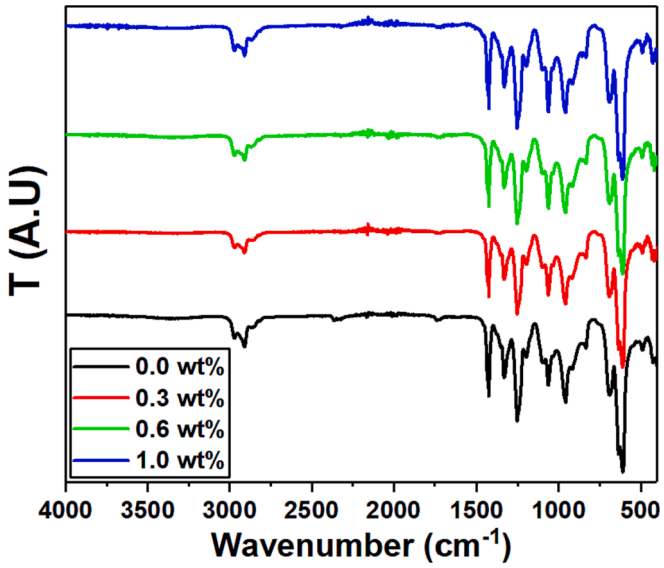

Fig. 2. FTIR spectra of pure PVC and PVC-La_2O_3 nanocomposites with different concentration.

increased, suggesting an expansion in the crystalline region. As established by Hodge [25] there is a direct correlation between the degree of crystallinity and peak intensity. La_2O_3 nanoparticles can interact with the surface of the PVC chains through various forces, such as hydrogen bonding or electrostatic interactions. These interactions can restrict the mobility of the polymer chains, making it more difficult for them to crystallize. This can also contribute to a decrease in peak intensity. The observed increase in peak intensity therefore suggests an increase in the crystalline portion of PVC composites. This change can have a direct impact on the mechanical properties of PVC. The X-ray diffraction peaks of La_2O_3 are with agreement with cards (JCPDS 00–101-0278). All the peaks can be indexed to the pure hexagonal phase. The pure La_2O_3 exhibits diffraction peaks at $2\theta = 16°$, 26.1°, 30.6°, 39.8°, 44.7°, 46.2°, 49°, 52.4°, 55°, 63.5°, and 67.3°, these peaks are corresponded to (*hkl*) with (0 0 1), (1 0 0), (1 0 –1), (1 0 –2), (0 0 3), (2 –1 0), (2 –1 1), (1 0 –3), (2 –1 2), (1 0 –4), and (2 0 –2), respectively. It is noticeable, some peaks in the samples of 6 and 10 wt% of La_2O_3 are left shifted toward lower 2θ which are may due to the increase in d spacing. It is important to notice that the presence of the peak at $2\theta = 11°$ in the sample of PVC/1 wt% La_2O_3 is due to the (0 0 2) plane of $La_2O_3CO_3$ according to the JCPDS 00-022-0642.

The Scherrer formula was employed to determine the crystallite size diameter (D) for La_2O_3 nanocomposites all samples [26,27];

$$D = \frac{k\lambda}{\beta cos\ddot{I}} \quad (1)$$

In the above equation, β-FWHM (full-width at half-maximum or half-width) is expressed in radians, while λ represents the X-ray wavelength of $Cu_{k\alpha 1}$ (1.5406 Å). The variable θ denotes the position of the diffraction peak at its maximum, and k represents the shape factor, typically assumed to be 0.9. Upon analysis, it was determined that the La_2O_3 sample exhibited crystallite sizes with an average of approximately 15 nm.

The FTIR spectrum of pure PVC and PVC-La_2O_3 nanocomposite films in the range of 400 to 4000 cm^{-1} is shown in Fig. 2. In the pure PVC, the FTIR bands peaks observed at 609 cm^{-1}, 833 cm^{-1}, 956 cm^{-1}, 1062 cm^{-1}, 1254 cm^{-1}, 1332 cm^{-1} and 1425 cm^{-1}. The FTIR peak of PVC polymer film at 609 cm^{-1} is assigned to the C-Cl stretching vibration [28]. This is a strong and characteristic peak for PVC, and it is due to the presence of chlorine atoms in the PVC molecule. The chlorine atoms are attached to the carbon atoms in the backbone of the PVC chain, and they give rise to a strong dipole moment. The rocking motion of CH_2 groups gives rise to the peak at 956 cm^{-1}. The peak at 1026 cm^{-1} corresponds to C–C stretching, which peak indicates the vibration of the carbon atoms along the polymer backbone. The other peak at 1254 cm^{-1} arises from the in-plane bending vibration of the hydrogen atoms in the CH_2 groups. While the peak at 1332 cm^{-1} corresponds to the in-plane bending vibration of the hydrogen atoms in the C–H groups. Moreover, the peak located at 1425 cm^{-1} indicates the symmetric stretching vibration of the two hydrogen atoms in the CH2 groups [29]. Also, bands peaks observed at high wavenumber 2912 cm^{-1} to 2970 cm^{-1}, these peaks assigned to the C–H stretching mode [30]. After the inclusion of La_2O_3 nanoparticles, the strong peak at 609 cm^{-1} was shifted to 611 cm^{-1}. The La_2O_3 nanoparticles interact with the chlorine atoms in the PVC chain through electrostatic forces or weak chemical bonding. This interaction slightly alters the vibrational energy of the C-Cl bond, causing the peak to shift to a higher wavenumber (611 cm^{-1}).

A new absorption band at 856 cm^{-1} appeared in samples containing 2 and 3 wt% La_2O_3 which is assigned to C–O bending vibrations. In addition, there is another new absorption band at around 417 cm^{-1} presented in all samples containing different weights of La_2O_3 due to La-O bending [31]. Final observation the absorption band at 1064 cm^{-1} increased with increasing the content of the La_2O_3 into the PVC films. These outcomes illustrated the interaction between La_2O_3 and PVC in the form of polymer nanocomposites film. La_2O_3 form weak chemical bonds with the carbon atoms in the PVC chain, altering the vibrational energy of the C-C bond and leading to a stronger absorption signal.

It is observed that the nanocomposite films exhibit a small shift in peak position towards higher wave numbers with an increase in La_2O_3 content (0.3–1.0 wt%). However, the FTIR spectra do not show any absorption band associated with La_2O_3, and the positions of all peaks change slightly due to the low content of La_2O_3 nanoparticles. Analysis using complementary techniques such as X-ray diffraction (Fig. 1) or scanning electron microscopy (SEM) could provide additional insights into the structure and incorporation of the nanocomposite materials with PVC matrix. Therefore, these outcomes from FTIR and in combination with the XRD results, indicate the interaction between PVC and La_2O_3 in the polymer nanocomposite films.

Raman Spectroscopy is a practical and efficient method to characterize the structure of nanocomposites materials. The Raman spectra of pure PVC and PVC-La_2O_3 with different content are shown in Fig. 3. The Raman spectra analysis of pure PVC exhibited characteristic bands attributed to specific vibrational modes. The spectral region between

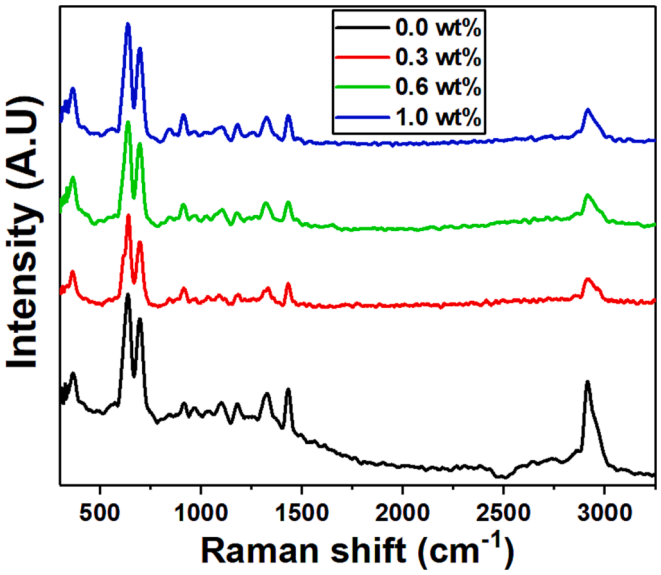

Fig. 3. Raman spectra of pure PVC and PVC-La_2O_3 nanocomposites with different concentration.

630 and 690 cm^{-1} was assigned to the (C–Cl) stretching vibrations [32], whereas the band observed in the range of 1328 to 1432 cm^{-1} was associated with the CH_2 scissors vibration. Additionally, the Raman band at 2914 cm^{-1} corresponds to the (C–H) stretching mode in the pure PVC sample [33,34]. The results showed that the intensity signals of PVC-La_2O_3 blend had decreased in comparison to that of the pure PVC spectra. This can be attributed to the complexing of nanoparticles into the polymer matrix, resulting in a decrease in the regularity of PVC upon the incorporation of La_2O_3. The La_2O_3 particles might be interacting with the PVC chains, restricting their vibrational freedom, and leading to a weaker (C-H) stretching signal. This provides strong evidence of the successful loading of La_2O_3 metal oxides on the PVC surface.

The SEM surface morphology of polymer films was studied using an environmental scanning electron microscope (ESEM). The SEM micrographs for PVC/La_2O_3 nanocomposite films are given in Fig. 4a-d. All the polymer films showed a smooth surface morphology. Moreover, the scans of polymer films revealed homogeneous distribution of La_2O_3 nanofillers.

Optical absorption spectra of polymer films provide several benefits for studying their properties. Firstly, they allow for the investigation of the optical properties of the films, such as absorption and transmission spectra, absorption coefficient, and energy gap [35]. These properties provide insights into the electronic structure and energy levels of the polymers, which are important for understanding their behaviour in various applications [36]. Additionally, optical absorption spectra can be used to determine the dielectric constant of the films, which is crucial for characterizing their electrical properties [37]. Fig. 5a,b show the results of absorbance and transmittance for the PVC/La_2O_3 films in the spectral region of 200–1000 nm. A band of absorption at 280 nm was visible in the spectra of PVC film that is produced by the $\pi \rightarrow \pi^*$ transitions of unsaturated C=O and C=C [28].

Increasing the content of La_2O_3 in the PVC polymer film led to a red shift in the absorption edge. the red shift indicates interactions between the nanofiller and the polymer matrix, leading to the formation of charge transfer and improved crystallinity of the hybrid polymer nanocomposites [38]. The addition of La_2O_3 nanoparticles to polymer films leads to a decrease in transmittance at specific wavelengths, resulting in enhanced optical properties. This decrease in transmittance can be advantageous for applications that require controlled light transmission, such as optical devices [39]. The decrease in optical transmittance of polymer films with increasing content of nanofiller can be attributed to increased light scattering within the film because of

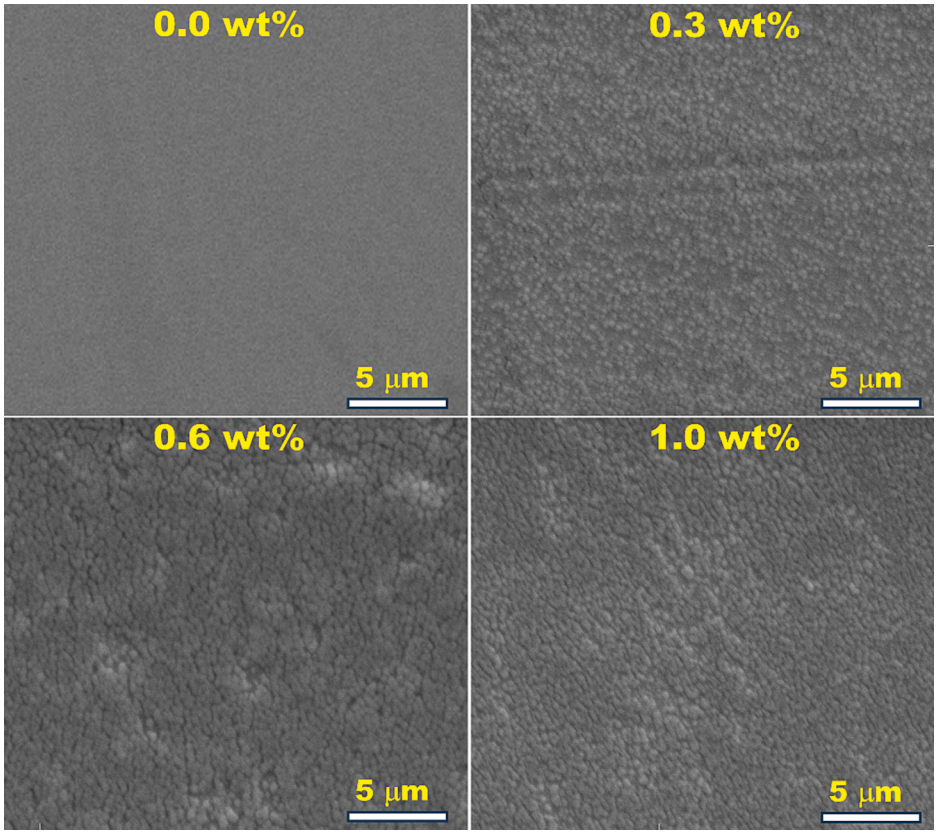

Fig. 4. ESEM micrographs for the PVC/La_2O_3 films.

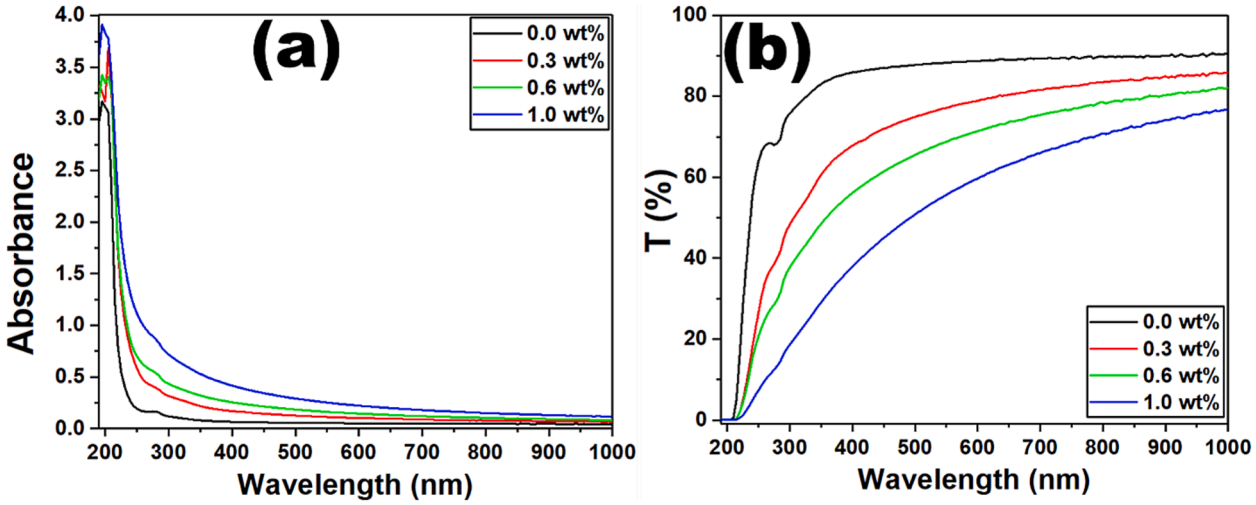

Fig. 5. Plots of (a) absorbance and (b) transmittance for the PVC/La_2O_3 films.

development of molecular complexes between the polymer and the filler [40].

The band gap values of manufactured polymer composites may be changed by varying the amount and type of nanofiller. The Tauc equation is commonly used for determining the optical band gap and electronic transitions within the band gap of polymer film materials. Therefore, Tauc analysis is used to calculate the optical band gap by extrapolating the linear section of the Tauc's plot. [41,42];

$$\alpha h\upsilon = B(h\upsilon - E_g)^n \tag{2}$$

where α represents the absorption coefficient, hν stands for the energy of the incident photons, and B represents a constant. The values of n determine the type of optical transitions, where n = 0.5 for direct allowed transitions. However, n = 2 for indirect allowed transitions. As illustrated in Fig. 6a,b, these values are obtained by extrapolating the linear portion close to the beginning of the absorption edge to cross the energy axis.

The obtained band gaps ($E_{g(ind)}$ and $E_{g(dir)}$) are listed in Table 1. The presence of La_2O_3 nanofillers leads to the development of molecular complexes between the polymer matrix and the filler, as indicated by FTIR analysis. This interaction results in modifications in the electronic structure of the polymer, leading to a decrease in the energy gap [38]. The presence of La_2O_3 nanofillers in PVC polymer matrix leads to the formation of localized electronic states, acting as trapping and recombination centres, resulting in a change in the optical band gap. This change can also be attributed to an increase in disorder caused by alterations in the polymer structure [43].

Table 1
Optical parameters of PVC/La_2O_3 polymer films.

La_2O_3 (wt%)	$E_{g(ind)}$ (eV)	$E_{g(dir)}$ (eV)	E_0 (eV)	E_d (eV)	n_0
0.0	5.46	5.72	5.88	5.64	1.40
0.3	5.33	5.54	3.92	5.13	1.52
0.6	5.23	5.46	3.69	6.22	1.64
1.0	5.0	5.37	3.28	7.20	1.79

Studying the refractive index of polymer films offers several benefits. The optical and electrical performance of high refractive index polymer films has been the subject of investigation in optoelectronic applications. The refractive index of a polymer film is influenced by factors such as molecular structure, dopants, film thickness, and stretching [44]. Reflectance is a measure of the amount of light that is reflected from a surface. We have estimated the reflectance through the equation ($R = 1 - \sqrt{Te^A}$). The variation of reflectance versus wavelength at different content of La_2O_3 is displayed in Fig. 7a. The relation between reflectance (R) and refractive index (n) can be determined using the following equation [45,46];

$$n = \left(\frac{1+R}{1-R}\right) + \sqrt{\frac{4R}{(1-R)^2} - k^2} \tag{3}$$

where ($k = \alpha\lambda/4\pi$) stands for the extinction coefficient. The refractive index rises in direct proportion to the increase in La_2O_3 content, as seen in Fig. 7b. This densification of nanocomposite films results from the

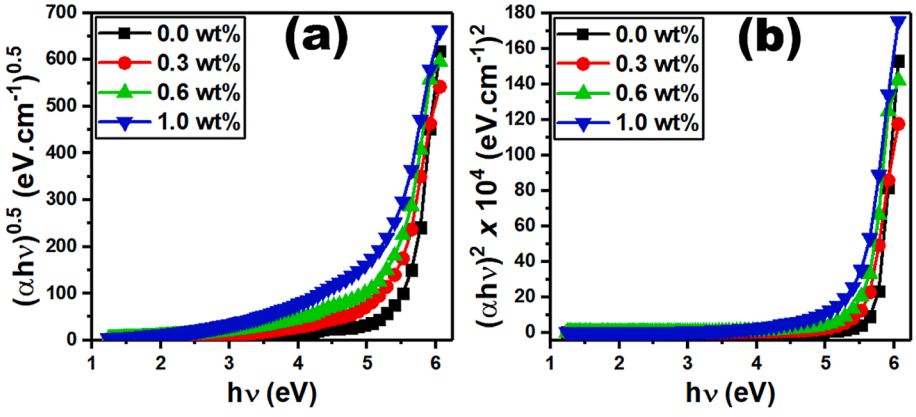

Fig. 6. Variations of (a) $(\propto h\upsilon)^{0.5}$ and (b) $(\propto h\upsilon)^2$ vs. $h\upsilon$ for the PVC/La_2O_3 films.

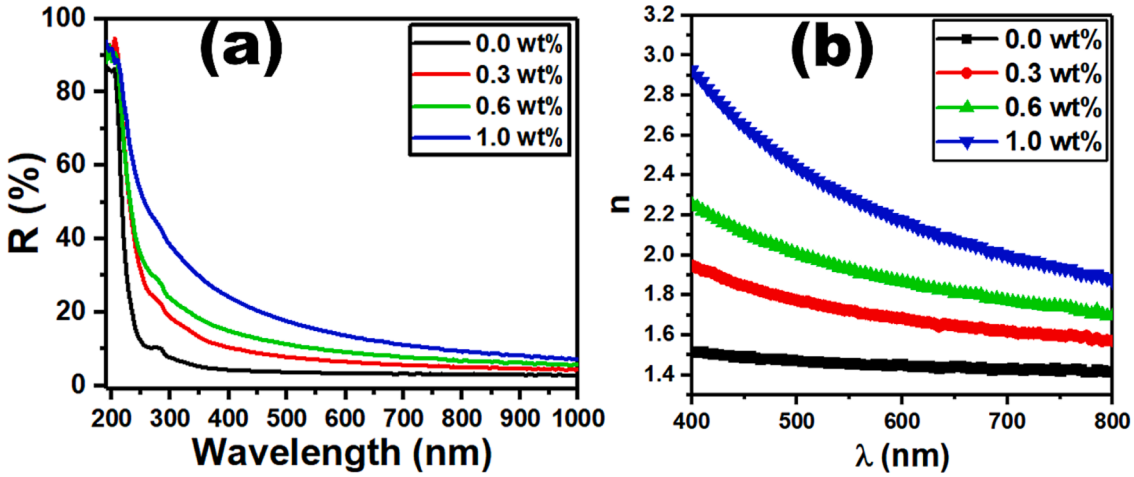

Fig. 7. Variation of (a) reflectance (R) and (b) refractive index vs. wavelength for the PVC/La_2O_3 films.

combination of small La_2O_3 nanoparticles into a large cluster [47]. The possible applications of a high-refractive-index polymer film include optical coatings, anti-reflection coatings, and optical devices. The refractive index enhancement of polymers can be used in applications such as reflectors and nanophotonic systems [48].

The single oscillator model proposed by Wemple and DiDomenico estimates the dispersion parameters of the material, such as oscillator energy, dispersion energy, and transition moments, which are essential for calculating the refractive index [49]. The refractive dispersion includes the single-oscillator energy (E_0) and dispersion energy (E_d) which are calculated from the single oscillator model which proposed by Wemple and DiDomenico [50];

$$\left(n^2-1\right)^{-1}=\frac{E_0}{E_d}-\frac{1}{E_0E_d}(h\upsilon)^2 \tag{4}$$

The slope and intercept of the $(n^2\text{-}1)^{-1}$ versus $(h\upsilon)^2$ plots located in Fig. 8a were used to determine the values of E_0 and E_d. The obtained values of E_0 showed a decrease (5.88 – 3.28 eV) while E_d increases (5.64 – 7.20 eV) upon increasing the concentration of La_2O_3 nanofiller (see Table 1). The increase in dispersion energy in a polymer film is attributed to increased polymer chain packing during orientation, leading to enhanced intermolecular interactions [51]. Moreover, the long-range van der Waals or dispersion force can amplify thermal fluctuations in thin polymer films, leading to an increase in dispersion energy [52].

The static refractive index (n_0) of a polymer can be determined using the single oscillator model proposed by Wemple and DiDomenico at zero photon energy ($h\upsilon = 0$) as follows [53];

$$n_0{}^2=\left(1+\frac{E_d}{E_0}\right) \tag{5}$$

The estimated values of n_0 showed an increase (1.40 – 1.79) upon increasing the percentage of La_2O_3 nanofiller. High refractive index polymers offer promise for usage in a variety of optoelectronic devices. These applications include complex display devices, where they can be employed to improve performance, as well as light-emitting diode encapsulants. They can also be used in the fabrication of plastic lenses for eyeglasses [54]. Therefore, the addition of La_2O_3 nanofiller improved the refractive index of polymer films and thus allows for better performance in optical applications such as micro lenses, image sensors, and organic light-emitting diodes [55].

The recommended optical transitions are determined via the real band gap (E_r) that can be obtained by extrapolating the linear part near the onset of the absorption edge to the intersection of the optical dielectric loss ($\varepsilon_2 = 2nk$ [56]). The plots of ε_2 versus $h\upsilon$ for the PVC/La_2O_3 films are displayed in Fig. 8b. The calculations revealed the values recorded in Table 2 which is close to the $E_{g(dir)}$. Therefore, the major optical transitions occur in the PVC/La_2O_3 films are the direct transitions.

The oscillator strength (f) of a polymer film can be affected by several factors, including the chemical structure of the polymer, the molecular

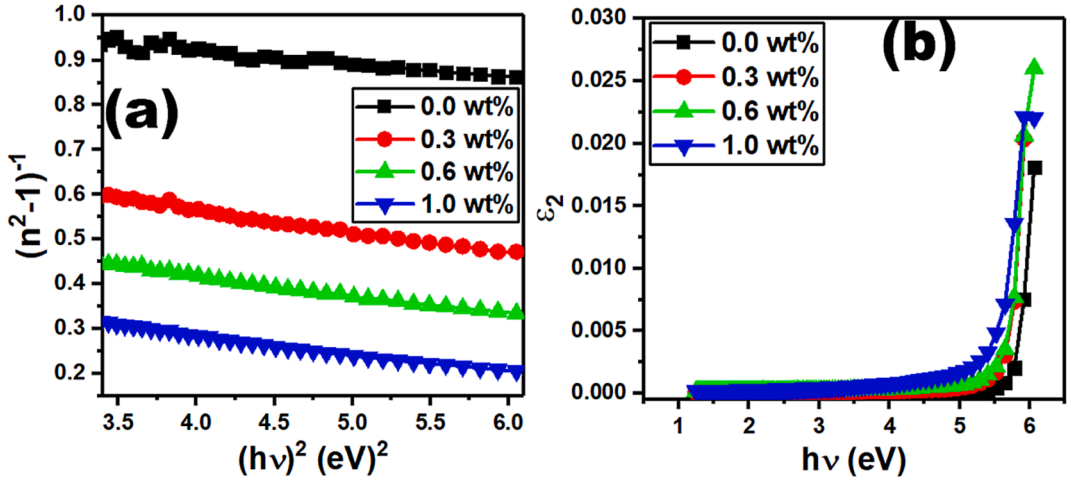

Fig. 8. Variation of (a) $(n^2-1)^{-1}$ vs. $(h\upsilon)^2$, and (b) ε_2 vs. h υ for the PVC/La_2O_3 films.

Table 2
Dispersion parameters PVC/La_2O_3 polymer films.

La_2O_3 (wt %)	f (eV^2)	$\chi^{(1)}$ (esu)	$\chi^{(3)} x 10^{-15}$ (esu)	$n_2 x 10^{-13}$ (esu)	E_r (eV)
0.0	33.21	0.08	5.77	1.56	5.77
0.3	20.15	0.10	19.97	4.96	5.70
0.6	22.91	0.13	55.20	12.70	5.66
1.0	23.58	0.17	159.22	33.56	5.54

weight of the polymer, the film thickness, and the aggregation of the polymer molecules. The oscillator strength of a polymer film is an important parameter for several applications, such as organic solar cells, light-emitting diodes, and lasers. By understanding the factors that affect the oscillator strength, it is possible to design polymers with the desired optical properties for these applications. The oscillator strength can be calculated using the following equation [57]:

$$f = E_d E_0 \tag{6}$$

The data of oscillator strength are given in Table 2. The addition of La_2O_3 nanofillers decreased the oscillator strength of a polymer film.

The electronic structure of molecules in polymer films is intricately linked to their underlying chemical structure, thereby influencing the linear and nonlinear optical susceptibilities. These susceptibilities play a pivotal role in various applications, including optical data storage, optical switching, and the development of nonlinear optical devices. Hence, understanding and characterizing the linear and nonlinear optical susceptibilities of polymer films become essential for leveraging their potential in these technological domains [58]. The linear optical susceptibility ($\chi^{(1)}$) and third-order nonlinear optical susceptibility ($\chi^{(3)}$) of polymer films can be calculated using the following equations [59]:

$$\chi^{(1)} = \frac{E_d/E_0}{4\pi}, x^{(3)} = 6.82 \times 10^{-15}(E_d/E_0)^4 \tag{8}$$

The estimated values of ($\chi^{(1)}$) and ($\chi^{(3)}$) are listed in Table 2 for PVC/La_2O_3 polymer films. The nanofillers can enhance the local electric field at the polymer-nanofiller interface, which can increase the third-order nonlinear optical susceptibility. Moreover, the nanofillers can interact with the polymer molecules and form new energy levels, which can also increase the third-order nonlinear optical susceptibility [60]. The nonlinear refractive index (n_2) of a polymer film can be affected by the chemical structure of the polymer molecules that determines the polarizability of the molecules, which in turn affects the nonlinear refractive index [61]. The nonlinear refractive index of polymer films is an important parameter for a variety of applications, such as optical limiters, optical switches, and optical data storage [62]. The following equation is used for the calculation of nonlinear refractive index (n_2) [63];

$$n_2 = \frac{12\pi x^{(3)}}{n_0} \tag{9}$$

The data estimated for n_2 were recorded in Table 2. The addition of La_2O_3 nanofillers increase the polarizability of the polymer molecules and hence the nonlinear refractive index. This enhancement is attributed to the strong interfacial interactions between the nanofiller particles and the polymer matrix, which cause a distortion of the electron cloud around the polymer molecules. This distortion, in turn, increases the susceptibility of the polymer to electric fields, leading to an increase in the nonlinear optical properties of the material [64]. The improvement of the nonlinear refractive index of polymer films is a promising area of application. By improving the nonlinear refractive index, it is possible to develop polymer films with even better optical properties for a variety of applications.

Conclusions

In-depth analysis and discussion have been conducted on the impact of La_2O_3 inclusion on the structural, physical, linear, and non-linear optical characteristics of PVC polymer films. The crystal structure of La_2O_3 was confirmed as hexagonal phase from XRD analysis. The La_2O_3 nanostructure was found to have crystallites size with an average about 15 nm. The obtained band gaps of PVC/La_2O_3 polymer nanocomposites decreased upon increasing the nanofiller content. The obtained values of E_0 showed a decrease (5.88 – 3.28 eV) while E_d increases (5.64 – 7.20 eV) upon increasing the concentration of La_2O_3. The estimated values of n_0 showed an increase (1.40 – 1.79) upon increasing the percentage of La_2O_3. Finally, the addition of La_2O_3 nanofillers increase the polarizability of the polymer molecules and hence the nonlinear refractive index.

Compliance with ethical standards

Yes, this paper complies with the journal's ethical guidelines.

Research data policy and Data Availability statements

On reasonable request, the author will make the datasets created during and/or analyzed during the current investigation.

Authors contributions

All the authors have contributed equally.

Funding

The authors extend their appreciation to the Deputyship for Research & Innovation, Ministry of Education in Saudi Arabia for funding this research work through the project number 223202.

CRediT authorship contribution statement

Sultan Alhassan: Writing – review & editing, Writing – original draft, Investigation. **Khulaif Alshammari:** Writing – review & editing, Investigation, Formal analysis. **Majed Alshammari:** Writing – review & editing, Visualization. **Turki Alotaibi:** Writing – original draft, Conceptualization. **Alhulw H. Alshammari:** Writing – review & editing, Methodology, Conceptualization. **Ali Alhamazani:** Investigation, Conceptualization. **Mohamed Henini:** Writing – review & editing, Supervision. **Taha Abdel Mohaymen Taha:** .

Declaration of competing interest

The authors declare that they have no known competing financial interests or personal relationships that could have appeared to influence the work reported in this paper.

Data availability

Data will be made available on request.

Acknowledgments

The authors gratefully acknowledge the central lab at Jouf University for providing the advance experiments methods used in this manuscript.

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