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Photophysical and electronic properties of Congo red dye embedded in polyvinyl alcohol as an efficient laser optical limiter: Enhancement the electrical conductivity and dielectric properties

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Abstract

High-quality polymeric composite films containing Congo red dye and PVA were prepared using the casting technique. The proposed Cr-doped PVA composites were examined using XRD, UV–visible optical, dielectric, and optical limiting effect techniques. The XRD patterns of CR-doped PVA composite films display diffraction peaks, which belong to CR organic dye. There was a broadening and reduction of the initial peak intensity in polymer composite films at higher doping concentrations. The band edge of CR: PVA composites reduced with a massive shift from 4.63 eV to 1.86 e, where Congo red controls the energy bandgap of the PVA polymer. Dielectric permittivity diminishes with increasing the frequency and achieves constant values at higher frequencies through the relation between the electric dipole and the electric field differences. Increasing the percentage ratio of the CR doping enhances the

electrical conductivity and dielectric permittivities due to the large size of the CR molecules. The strong optical limiting of the CR-doped PVA composites is determined using different laser sources of 632.8 and 532 nm wavelengths. The amazing obtained results imply that CR: PVA composite films are very significant for applying large-scale CUT-OFF laser filters for medical optical and electronic device systems.

Keywords: Congo red-doped PVA, Polymeric composites films, XRD, Optical properties, Dielectric properties, Optical limiting, Laser filters, and Medical optics.

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1. Introduction

Optical filters are devices transmitting or blocking specific wavelengths of the incident light. Synthetic glass or plastic materials dyed in bulk or coated interference films can control the transmitted or blocked light [1]. The optical properties of the filters were adequately designed to adjust the spectral response of the input electromagnetic signal to the filter [2]. Filters can generally be divided into two categories of absorptive filters and dichroic (interference filters) [3]. The vision of the filter is based on the absorption of specific wavelengths of the incident light and the transfer of the remaining residues [4]. The optical filters are divided into two categories: low pass filters (SP) and long-range (LP) [5]. As of late optical glass has been replaced with optical polymer since it is cheap, light, and easy to manufacture, for example, polyvinyl alcohol (PVA), polymethylmethacrylate (PMMA), and polycarbonate (PC) [6,7].

PVA is one of the most widely used polymers. It has distinctive features such as high mechanical strength, chemical stability, water solubility, and outstanding transparency because it contains significant hydroxyl group numbers [8]. It also has a low conductivity limit and a lower refractive index. PVA has several applications due to its advantages: low cost, non-toxicity, biocompatibility, high durability, and chemical stability [9-11].

Congo red dye (CR) is an organic compound (azo dye) that is water-soluble and yields a red colloidal solution, where its solubility is more excellent in organic solvents. CR dye is more commonly used in histology, biochemistry, paper printing, and textile dyeing. CR-doped polymeric composites were examined as optical amplifiers, optical storage media, solid-state lasers, and optical waveguides [12–13]. The suggested procedures show that the aromatic rings of the dye molecules have hydrophobic interactions leading to the pi-pi stacking phenomenon. CR: PVA composites have a powerful optical limiting effect [14,15]. CR-doped PVA composite films can absorb wavelengths of less than 600 nm that are more effective than the elevated wavelengths [16–18].

In this current research, PVA doping with different concentrations of Congo red dye composite films was prepared for optoelectronic applications using a simple casting method. X-ray diffraction (XRD), optical, dielectric studies, and optical

limiting effects were used to support the advantages of Cr-doped PVA composites for large-scale laser CUT- OFF filters. All the required parameters were calculated and discussed in detail to stand up the properties for the applications in the optical laser's limiters.

2. Experimental Techniques.

2.1. Synthesis of CR: PVA Polymeric Composite Films.

PVA and Congo red (CR; C.I. 22120) were provided from LOBA Chemicals (India) and Sigma-Aldrich (St Louis, MO). The chemical structure of the Congo red dye is presented in Fig 1. A solution casting method was developed to prepare CR-doped PVA composite films at various concentrations of Congo red. In 1 L of distilled water, nearly 22.5 g of PVA was dissolved for 24 hours with a magnetic stirrer at a temperature of 50 °C. Different contents of CR dye from 0.11 wt% to 27.27 wt% were doped with PVA polymeric films. All CR: PVA nanostructured samples were operated at room temperature using a magnetic stirrer at 700 rpm. The CR-doped PVA composites were solubilized in 30 ml distilled water, and then they were dehydrated at 35 °C for five days. After that, the proposed CR: PVA composite films were removed and cut into suitable dimensions for further structural and optical investigations.

2.2. Devices and Measurements.

Shimadzu Lab XRD-6000 diffractometer with CuK_{α} ($= 1.5406 \text{ \AA}$) radiation at 30 kV voltage, 30 mA of the current was used to measure X-ray diffraction pattern. A double beam spectrophotometer of wavelength 190 to 2500 nm (JASCO, model V-570 UV-vis-NIR) at room temperature was applied for the optical characterizations of the examined CR: PVA composites. The CR-doped PVA composites' electrical conductivity and dielectric properties were performed using a programmable automatic LCR meter (Model FLUKE-PM6306). The impedance Z , capacitance C , and loss tangent ($\tan\delta$) were determined at room temperature over a broad frequency area scale from 100 Hz to 1 MHz.

The optical limiting effects were investigated using two sources of laser beam: He-Ne with 632.8 nm, diode laser with 532 nm wavelengths, to get the normalized power of the CR: PVA composites. The 10 cm focal lens was mounted on an optical

base, where the holder of the CR: PVA sample was then detached at the lens focus. An optical measuring instrument was linked to the photodetector (Newport 1916-R) to estimate the input/output powers.

3. Results and Discussion.

3.1. Structural Analysis of CR: PVA Polymeric Composite Films.

XRD histograms of CR: PVA composite films are exhibited in Fig.2. The XRD diffraction patterns of pure CR dye exhibited firm diffraction peaks at $2\theta = 27.25^\circ$, 32.18° , 37.84° , 44.91° , and 45.33° that were matching to (101), (111), (117), (124), and (134) planes, respectively [19,20]. The XRD pattern of pure PVA polymer reveals the semi-crystalline character with a peak at $2\theta = 19.32^\circ$ [21,22], which results from the hydrogen bonding between PVA chains and leads to partial polymer chains ordering. Besides, intramolecular and intermolecular hydrogen bonds are generated between the PVA matrix and CR dye. These hydrogen bonds were obtained between the external site of CR dye (amino groups or sulfonate groups) or will be in the inner CR site (the azo group) with the OH group in the PVA chain [23–24]. The obtained diffraction peak for pure PVA nanostructure was well-matched with the PVA published XRD bands of sodium iodide doped poly (vinyl alcohol) polymer by Balaji Bhargav et al. [25].

No diffraction peaks in CR-doped PVA composite films have belonged to Congo red at lower dye contents, but the central peak of the PVA polymer has been broadened. This relates to CR dye being dispersed and well absorbed within the PVA structure. Suppose the solution casting method is employed to prepare CR: PVA composite membranes. In that case, the dopant can react with the polymer through weak bonds or distribute as an isolated phase by creating a weak bond through the functional PVA polymer group (hydroxyl group) [26]. Thus, if the CR dye molecules were inserted into the PVA matrix, they can be restricted or distributed within free volumes such as interstitial sites or voids between the PVA matrix chains. At the higher dye concentration, more crystalline peaks appeared that belonged to the CR dye, and the degree of crystallinity was reduced due to the increased PVA chain disorder [27]. R.M. Hodge et al. identified a linear dependency between the PVA crystallinity level and the intensity of the diffraction peaks. A decrease in the intensity was indicated with the increase of the amorphous structure [28].

3.2. Optical Analysis of CR: PVA Polymeric Composite Films.

Optical transmittance spectra for CR-doped PVA composite films are represented in Fig. 3(a,b). High transmission over 91 % is noticed for pure PVA due to the lack of a free electron. In CR: PVA composite films containing 1.11 wt% of CR dye or less, there are two broad absorption bands at 290 nm and 410 nm, distinguishing CR dye molecules and referring to the interaction between dye molecules and PVA polymer [12]. As seen in Fig. 3, all prepared CR: PVA thin films have high transmittance after 566 nm wavelength. As the dye content increased in the studied Cr: PVA composites, transmittance values reduced in the wavelength range (190 - 585 nm) due to greater CR absorption. If the concentration of CR dye in the proposed composites is greater than 1.11 wt%, in the region from 190 to 585 nm, the incident light is completely blocked, and the transmittance reaches zero ($T = 0$). These CR: PVA composites can be used as laser CUT-OFF filters (laser blocking filters) and multiple optoelectronic applications [29–31]. They are taking advantage of the attained linear optical results; F.A. Mustafa stated that the material transmission decreased as the doping concentrations increased in the region of short wavelengths [32], which excellently agreed with the recorded data in this current study CR dye-doped PVA films.

Fig. 4 depicts the absorbance spectra for CR dye-doped PVA composite films, where the absorption of pure PVA is less than CR: PVA composites. For composites containing (0.11 wt%, 0.85 wt%, and 1.1 wt%) CR dye, Congo red's characteristic absorption peaks were distinguished due to several electronic transitions within the Cr: PVA composite polymeric films. The first characteristic absorption peak was located at around 290 nm can be attributed to the $n-\pi^*$ transition of the benzene ring in the CR molecule. The second peak, which was about 410 nm, was due to the transition of $n-\pi^*$ to the chromophore $-N=N-$ along the axis of the CR molecule [33]. The absorption intensity increases at higher concentrations (5.5 wt%, 11.11 wt%, and 27.27 wt%) of CR dye in the proposed composites. Also, the absorption peaks disappeared in the region between 190 and 585 nm due to an increase in the number of molecules (or complexes) absorbed, increasing the interaction between the CR dye molecules in the PVA matrix.

The variation in the PVA bandgap was estimated when using CR dye to study their interaction. The optical energy bandgaps (E_g) for CR: PVA composite films were acquired according to Mott and Devi's equation [34].

$$\alpha h\nu = B(h\nu - E_g)^r, \quad (1)$$

where B is a constant, $\alpha(\nu)$ is the absorption coefficient that is calculated from Beer's law $= 2.303 \frac{Abs}{d}$, *Abs* and *d* are the absorbances and the thickness of the examined film, and *r* is an exponent that takes the values of 1/2 and 2 relying on the kind of electronic transitions for allowed indirect and direct transition. Figs. 5 (a,b) depicts the relation between $(ah\nu)^{1/2}$ and $(ah\nu)^2$ with photon energy ($h\nu$) for the proposed CR-doped PVA materials. From the extrapolation of the straight-line portion to the x-axis at $(ah\nu)^{1/2}$ and $(ah\nu)^2 = 0$, the bandgap values (indirect and direct) are obtained and listed in Table. 1. The diagrams show that both direct and indirect optical band gaps decrease due to an increase in CR dopants into a PVA matrix. Both $E_g(ind)$ and $E_g(dir)$ values of the neat PVA are 4.63 and 5.24 eV, respectively, but their 27.27 wt% PVA-doped CR composite film values are 1.77 and 1.87 eV, indicating bandgap engineering for the added CR dye effects in the PVA matrix. In this present study, the calculated optical bandgaps were in excellent agreement with the reported data for TiO₂-PVA nanocomposites via S. Sugumaran and C. S. Bellan [35]. Moreover, S. Mahendia et al. utilized the sol-gel method to prepare Ag: PVA nanostructured films, where the PVA optical bandgap was calculated to be 4.92 eV, and that value decreased to reach 3.93 eV [36], which were greatly compatible with the estimated bandgaps in this recent research.

CR dye generates multi absorption bands in ultraviolet-visible optical zones. Captivated CR to PVA matrix generates a new trapped level as a point defect inside the HOMO-LOMO gap. The composition of the Congo red dye contains groups with high electronegativity (oxygen and nitrogen atoms) [37]. Consequently, the hydrogen bond was formed between CR dye (amino- and the sulfonate-groups) and hydroxyl group in the PVA matrix. The inclusion of CR in the elevated content into the PVA matrix produces additional molecular dipoles. It, therefore, changes the performance of PVA from dielectric material into a semi-conductive material with a small bandgap [38,39]. This confirms the enhanced interaction among CR-doped PVA composites by raising the concentration of the dye. Similar findings are consistent with those

reported in prior research [12,40]. T. H. AlAbdulaal et al. investigated the structural and optical properties of Nd₂O₃: PVA polymeric composites that were prepared using the solution casting method. They concluded that the optical energy bandgaps of the PVA polymer decreased as increasing the dopant concentrations [40].

To determine the extinction coefficient, the following equation can be applied through the absorption coefficient as follows [41,42]:

$$k = \frac{\alpha\lambda}{4\pi}, \quad (2)$$

Fig. 6 represents the extinction coefficient (k) as a function of the wavelength of CR: PVA composites of different concentrations of the CR dye. Increasing the concentrations of the CR dye in the PVA matrix leads to an increase in the absorption coefficient. CR: doped PVA films showed multi-absorption bands at the lower wavelength due to the CR presence in the PVA matrix. Optically, O. G. Abdullah concluded that the extinction coefficient of the PVA polymeric film increased as increasing the doping concentrations [43], which are in a great match with the finding current results. With increasing the dye-doping ratio, the absorption and denser of the films increased and hence the lower light velocity propagation. Then, the CR: PVA material becomes opaquer to the incident lights; thus, the speed of light decreases, and the absorption coefficient increases [44]. This result indicates that the CR dopant will modify the structure of the PVA host polymer [45].

3.3. Dielectric behavior and AC electrical conductivity of CR/PVA polymeric composite films.

The research of the dielectric properties of polymeric materials is essential in estimating appropriate applications of polymeric materials [46]. The dielectric constant ε^* can be given using the following equation:

$$\varepsilon^* = \varepsilon' - i\varepsilon'', \quad (3)$$

where ε' is the dielectric constant and ε'' is the dielectric loss. Dielectric constant (ε') can be evaluated from the following formula [47]:

$$\varepsilon' = Cd / \varepsilon_0 A, \quad (4)$$

where C is the capacitance, and ε_0 is the vacuum permittivity. The dielectric loss (ε'') can be estimated from the values of ε' and loss tangent ($\tan\delta$), as follows [48]:

$$\varepsilon'' = \varepsilon' \tan\delta, \quad (5)$$

All measured dielectric parameters were examined at room temperature in the frequency range of 100 Hz – 1 MHz. Figs. (7,8) represent the dielectric constant (ε') and dielectric loss (ε'') spectra for the investigated CR: doped PVA polymeric films. For all composite films, ε' and ε'' values decline as the frequency increases to nearly 3 kHz owing to the interfacial effects at the electrode–electrolytes interfaces [49]. In a polar matter, the initial values of ε' and ε'' are regarded to be high, but the dielectric value begins to decline by increasing the frequency. This is because the dipole is unable to change in frequency. The periodic reversal of the electrical field occurs rapidly at higher applied frequencies so that there is no over propagation of ions towards the relevant field. ε' and ε'' values were increased with the increase wt% of CR dye, but the increase in ε'' is very low.

The total AC electrical conductivity $\sigma_{Total.AC}(\omega)$, the AC electrical conductivity $\sigma_{AC}(\omega)$ and DC electrical conductivity $\sigma_{DC}(\omega = 0)$ can be calculated by using the following Jonscher's equations [50-52]:

$$\sigma_{Total.AC}(\omega) = \frac{t}{ZA}, \quad (6)$$

$$\sigma_{Total.AC}(\omega) = \sigma_{AC}(\omega) + \sigma_{DC}(\omega = 0), \quad (7)$$

$$\sigma_{AC}(\omega) = \sigma_{Total.AC}(\omega) - \sigma_{DC}(\omega = 0), \quad (8)$$

where Z is the measured impedance, t is the thickness of the film, ω is the angular applied frequency, and A is the cross-section area. The frequency-dependent of AC conductivity for CR-doped PVA composites obtained at room temperature is presented in Fig. 9. It is noted that the values of σ_{AC} increase by increasing the applied frequency and the level of CR-doping in the polymeric composite films. Increased values of σ_{AC} The increased applied frequency has been caused by an increase in the oscillation field and the enhanced used frequency, which will raise the polarization of the composites [50-52].

The frequency dependence of σ_{AC} can be analyzed Jonscher's power law to determine the conduction mechanism as follows [50-52]:

$$\sigma_{AC}(\omega) = A \omega^{(s)}, \quad (9)$$

where A is a constant, and (s) is exponential power, in which the s value is the slope of the straight-line segment of the relationship among $\log\sigma_{AC}$ Fig. 10 shows that (s) dependence on wt% of CR-content for all studied composites. And $\log\omega$. Pure PVA polymer has a value close to unity (one), where on the other hand, the (s) values are slightly reduced by increasing the CR concentrations in the PVA matrix. The (s) behavior assumes the most favorable conduction mechanism is the correlated barrier hopping (CBH) model [50,53]. In conclusion, the optical conductivity of the undoped PVA polymer increased where the CR doping ratios increased, which are outstanding consistent with the published optical data of NaI-doped PVA nanostructured films by F.A. Mustafa [32].

3.4. Optical limiting study of CR- doped PVA polymeric composite films.

The optical limiting effect of CR: PVA composite films is studied using two different laser beams (He-Ne laser of 632.2 nm and green laser diode of 532 nm). The conventional Z-scan experimental technique was used in which the sample is constant. Fig.12 reveals the relationship between the normalized power curves (Normalized power = output power/input power) against the weight percent of CR-content. Pure PVA has a small optical limiting effect on the power intensity of the two laser sources. The normalized power is decreased by increasing the weight of CR dye in the film composites, attaining about (11 and 13) % of its initial value for 11.11 wt% CR/PVA composite film for the two laser beams. Concentration is known to play an essential role in the optical limiting effect. The added CR-content reinforces it due to the increase in the number of molecules per unit volume that contributes to the interaction of the added CR material during nonlinear absorption processes. Thus, the optical limit for low CR samples is much weaker than that recognized for elevated concentration samples [54-56].

From Fig. 11, the samples have a higher optical limiting effect for the laser beam of 532 nm than 632.8 nm. Because of the distinctive red-Congo two broad bands that appear in CR: PVA films at 290 nm and 410 nm, composites that contain less than 1.1 wt% of CR content are presented in Fig. 3. After 1.11 wt%, CR/PVA

composite films exhibited UV-Vis blocking, enabling these composites as laser blocking filters (laser cut-off filters). Therefore, these composite films, which contain 11.11 wt% and 27.27 wt% CR, can be used extensively in optoelectronic applications and are appropriate for various types of laser wavelengths in the range 190 - 566 nm, like gas, chemical, dye, metal vapor, semiconductor, and solid-state lasers [12].

Many research groups have used various materials as fillers with PVA to enhance the optical limiting and use them as laser blocking filters (laser CUT-OFF filters). We have, therefore, compared the normalized power of present composites with that of other PVA composites with different dye content (see Table. 2). From this Table, one can notice that CR/PVA composite films improve the optical limiting effects characteristics compared to most composites doping with other colors, as shown in the Table. 2.

4. Conclusion

Congo Red/PVA composite films were prepared using a simple solution casting technique. XRD was used to reveal the changes in the sample structures. Due to the intermolecular hydrogen bond between the hydroxyl group in PVA chains and amino and sulfonate groups in the CR dye, the transmission values of CR/PVA composites increase with reducing CR-content. Also, the composites of a higher concentration of CR (11.11 and 27.27 wt.%) are suitable for a wide-scale cut-off filter varying from 190 to 566 nm. ϵ' and ϵ'' values were reduced as the frequency increased, as shown by the dielectric analysis. Congo red dye in PVA matrix changed in a good way the electrical conductivity and the dielectric properties of highly insulator PVA matrix. The correlated barrier hopping (CBH) model is the primary model. Laser beams at 632.8 nm and 532 nm wavelengths were used to stand up the optical limiting behavior of CR/PVA composites. The best optical behavior is determined at the higher dye content. CR/PVA composite films can be used in large-scale CUT-OFF laser filters for medical optical devices and other electronic systems.

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-Ethical Approval

Dr. Ibrahim Yahia has approved the ethics of this study.

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-Competing Interests

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 manuscript.

-Authors Contributions

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-Consent to Participate (Ethics)

The authors participate to complete this paper from the beginning until sending it to the journal.

-Consent to Publish (Ethics)

All authors are agreed to publish this work in the journal of Optical and Quantum Electronics.

-Availability of data and materials

In this current research, the datasets obtained and analyzed are available with the corresponding author “**Dr. Ibrahim Yahia**”

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Table. 1

The optical band gap (indirect and direct) of CR- doped PVA composite films.

Bandgap/ polymer composites	$E_{g1(ind)}$, (eV)	$E_{g2(ind)}$, (eV)	$E_{g3(ind)}$, (eV)	$E_{g1(d)}$, (eV)	$E_{g2(d)}$, (eV)	$E_{g3(d)}$, (eV)
Pure PVA	4.63	----	----	5.24	----	----
0.11 wt% CR: PVA	4.49	2.34	2.04	5.03	----	----
0.55 wt% CR: PVA	3.46	2.25	1.98	4.83	----	1.98
1.1 wt% CR: PVA	2.4	2.14	1.94	3.73	2.75	1.95
5.5 wt% CR: PVA	----	----	1.92	----	----	1.94
11.11 wt% CR: PVA	----	----	1.79	----	----	1.91
27.27 wt% CR: PVA	----	----	1.77	----	----	1.87

Table. 2

Comparative analysis of optical limiting parameters of CR-doped PVA composite films.

Composites of PVA with different dyes	concentrations	Normalized power = output power/input power		References
		He-Ne laser at 632.8 nm	Diode laser at 532 nm	
CR	0.11wt %	0.85	0.84	Present work
	27.27 wt %	0.23	0.1	
MEO dye	0.5 wt %	0.35	---	[51]
	3.2 wt %	0.1		
Rose Bengal (RB) dye	0.04 wt %	0.3	----	[7]
	20 wt %	0.06		
chicago sky blue 6B	1wt %	0.075	0.04	[57]
Light Green (LG) dye	2.02x10 ⁻⁴ M	0.25	---	[58]
Fluorescein sodium salt (FSS)	0.37 wt %	0.9	----	[40]
	37 wt %	0.45		

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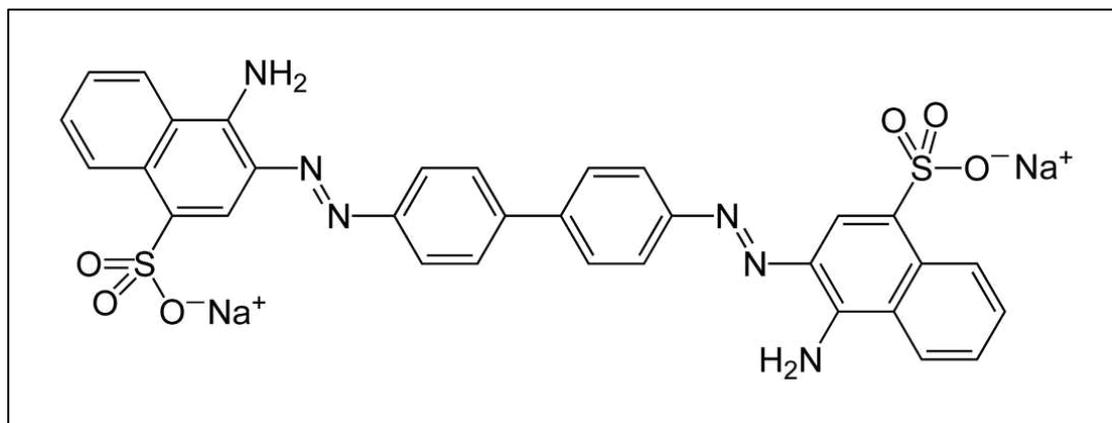


Fig. 1: Molecular structure of Congo red (CR) dye.

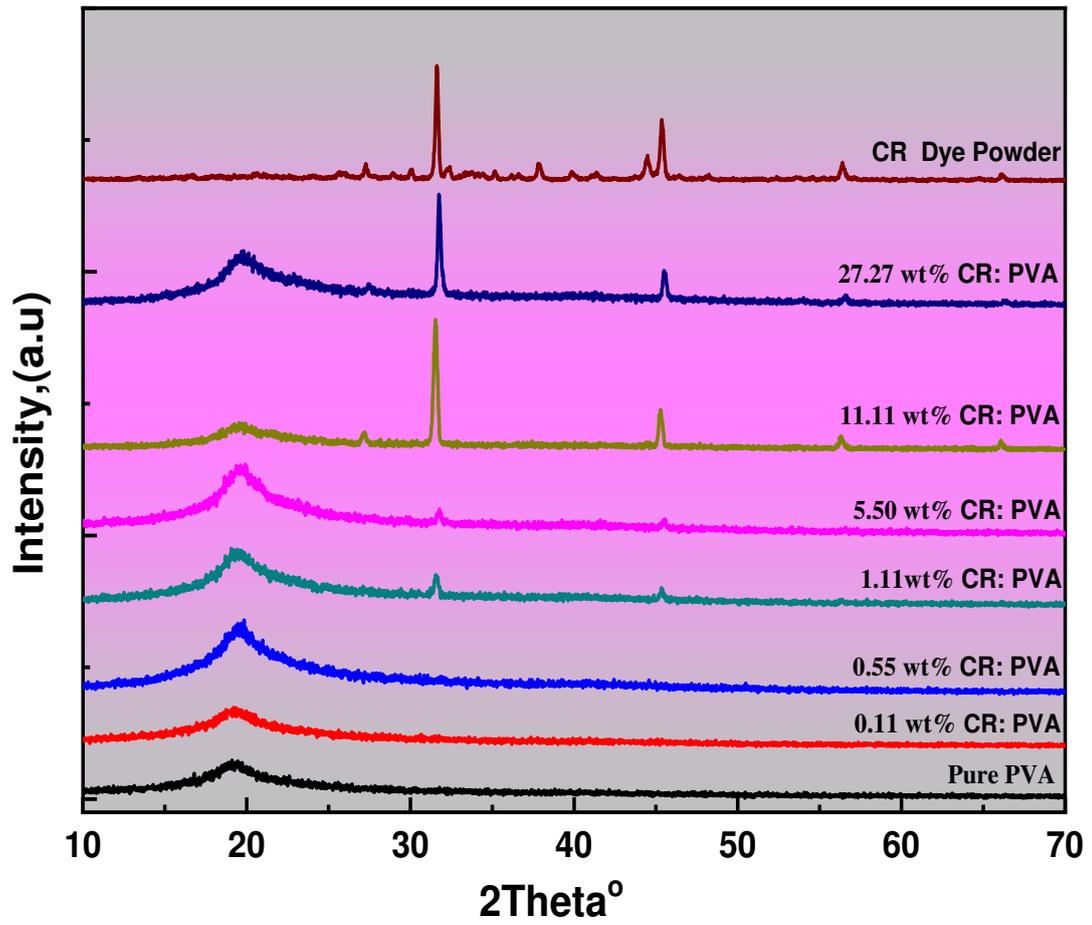
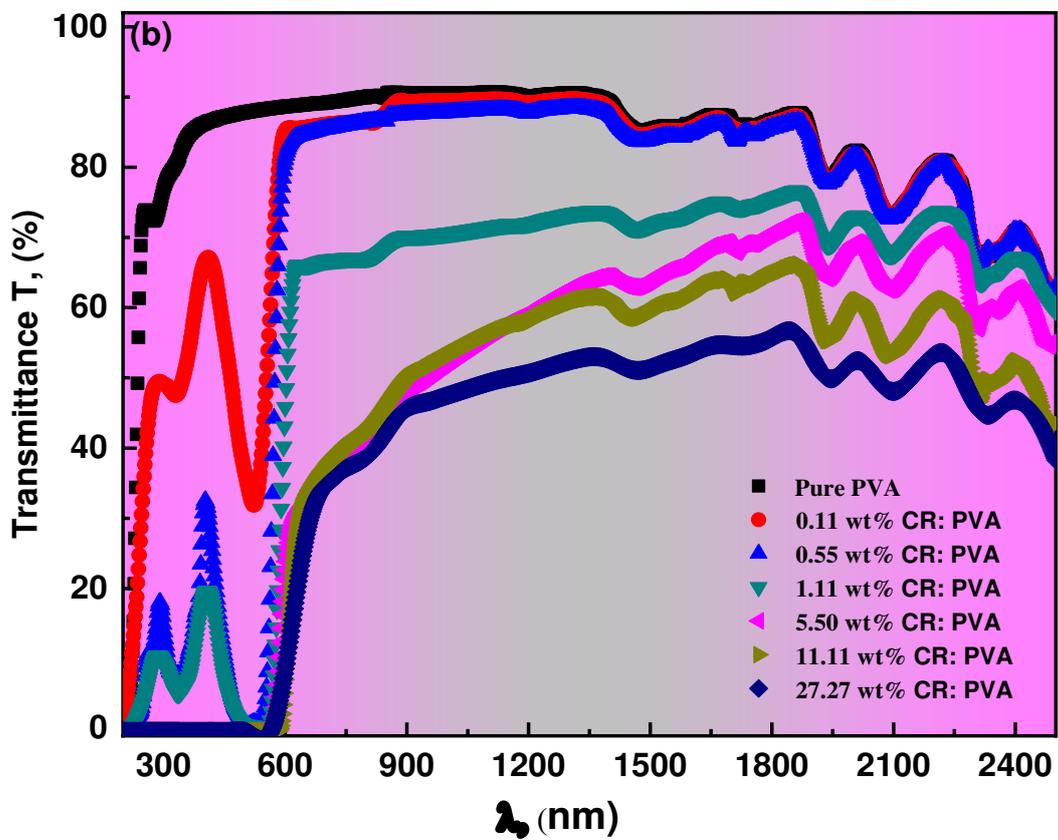
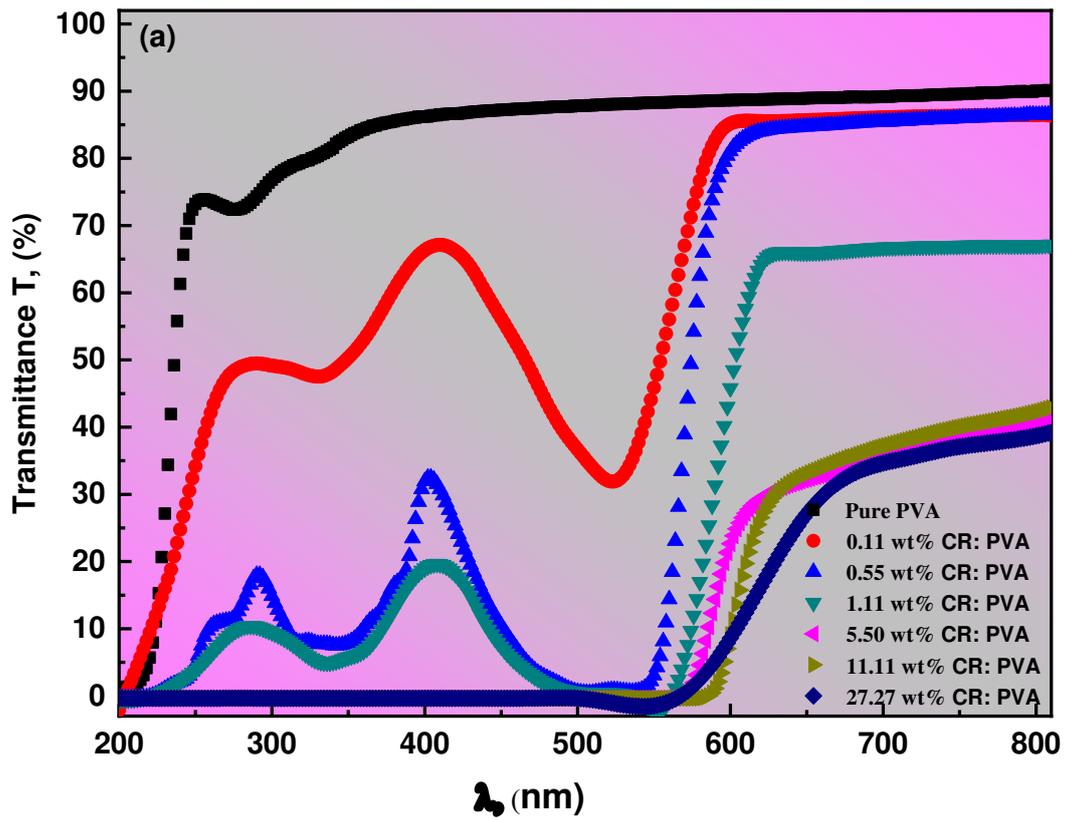


Fig. 2: XRD pattern for pure Congo Red dye and CR-doped PVA composite films.



Figs. 3: UV-Vis-NIR transmittance curves of CR-doped PVA composite films, (a) in the wavelength region of 200–900 nm, (b) in the wavelength region of 200–2500 nm.

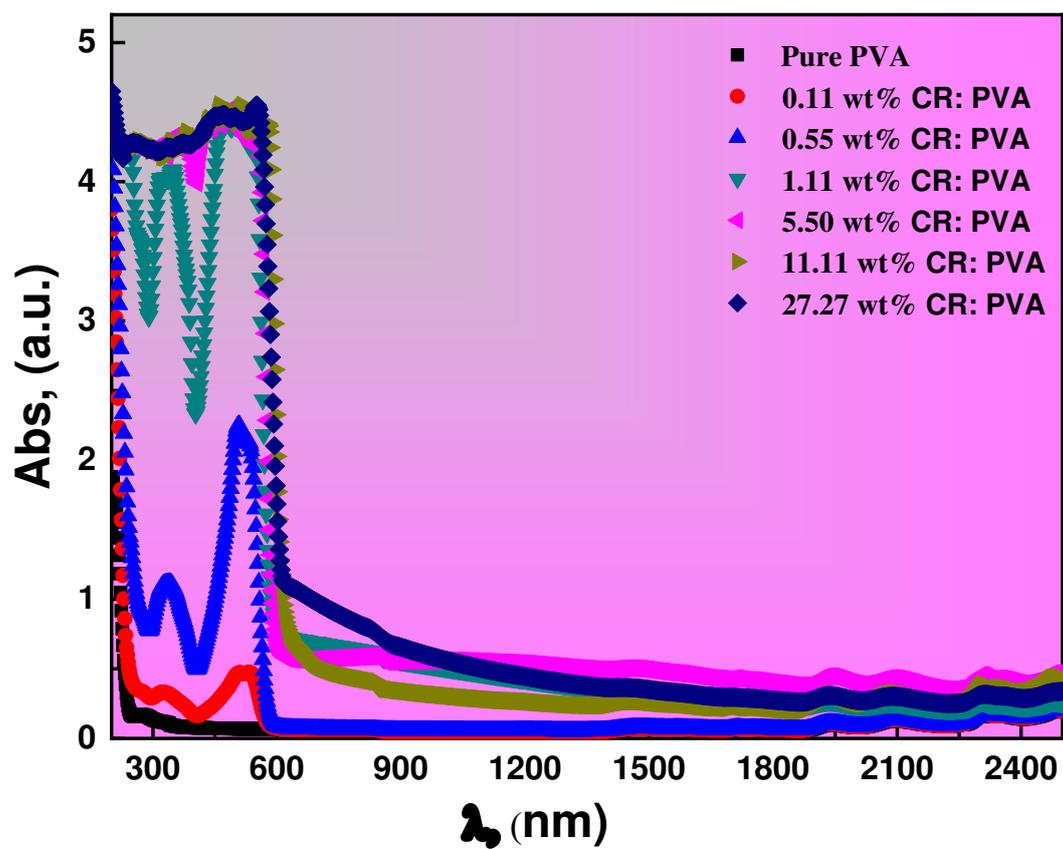


Fig. 4: Absorbance curves of CR-doped PVA composite films.

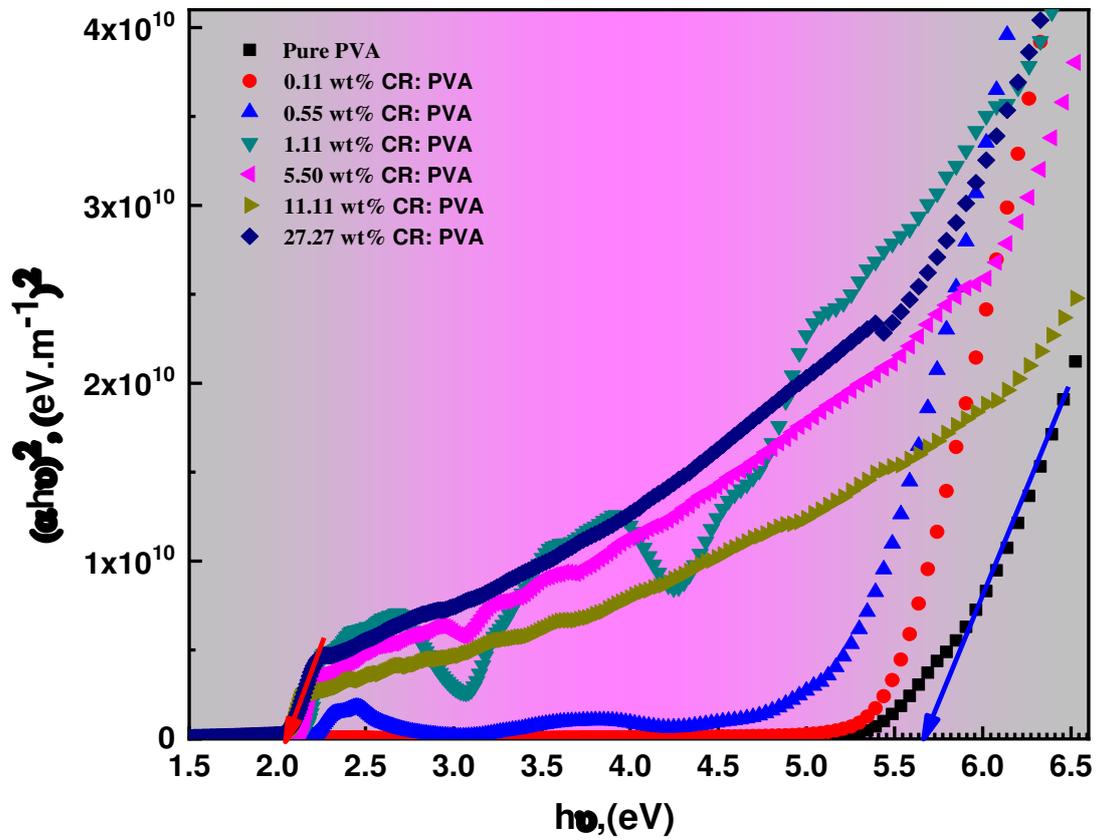
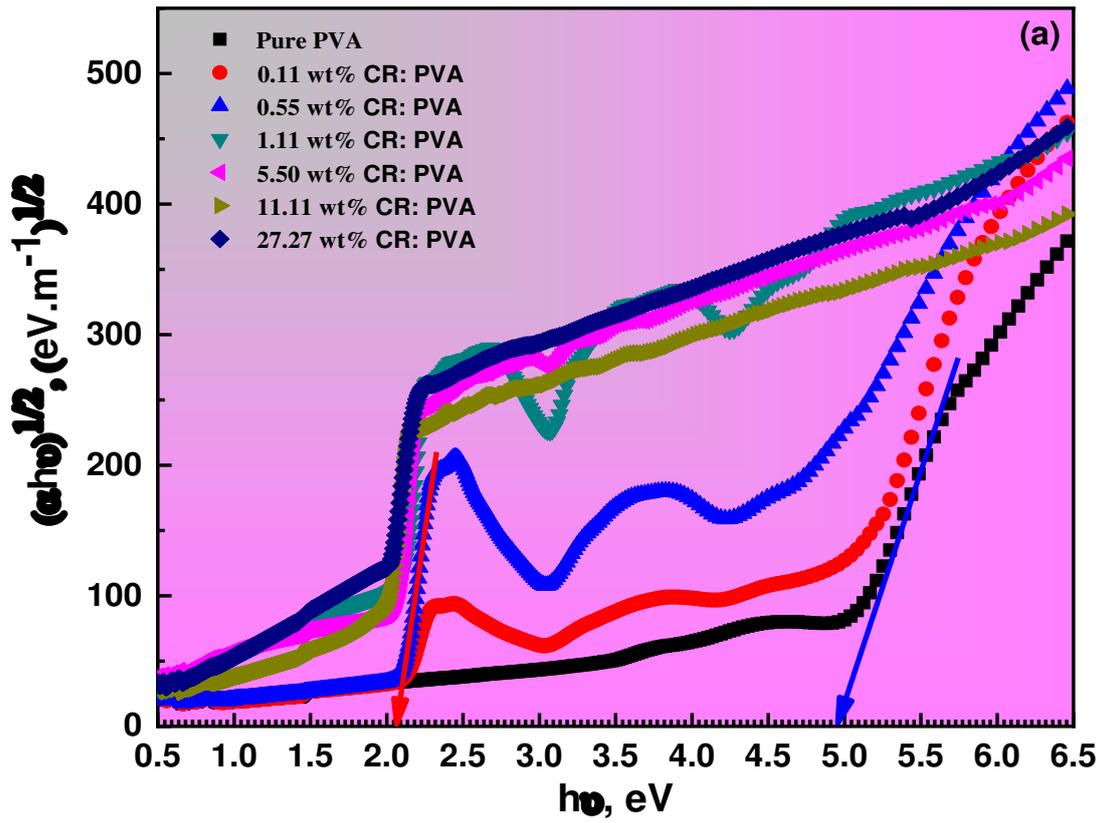


Fig. 5: Plotting of (a) $(\alpha h\nu)^{1/2}$, (b) $(\alpha h\nu)^2$ versus $h\nu$ for CR- doped PVA composites.

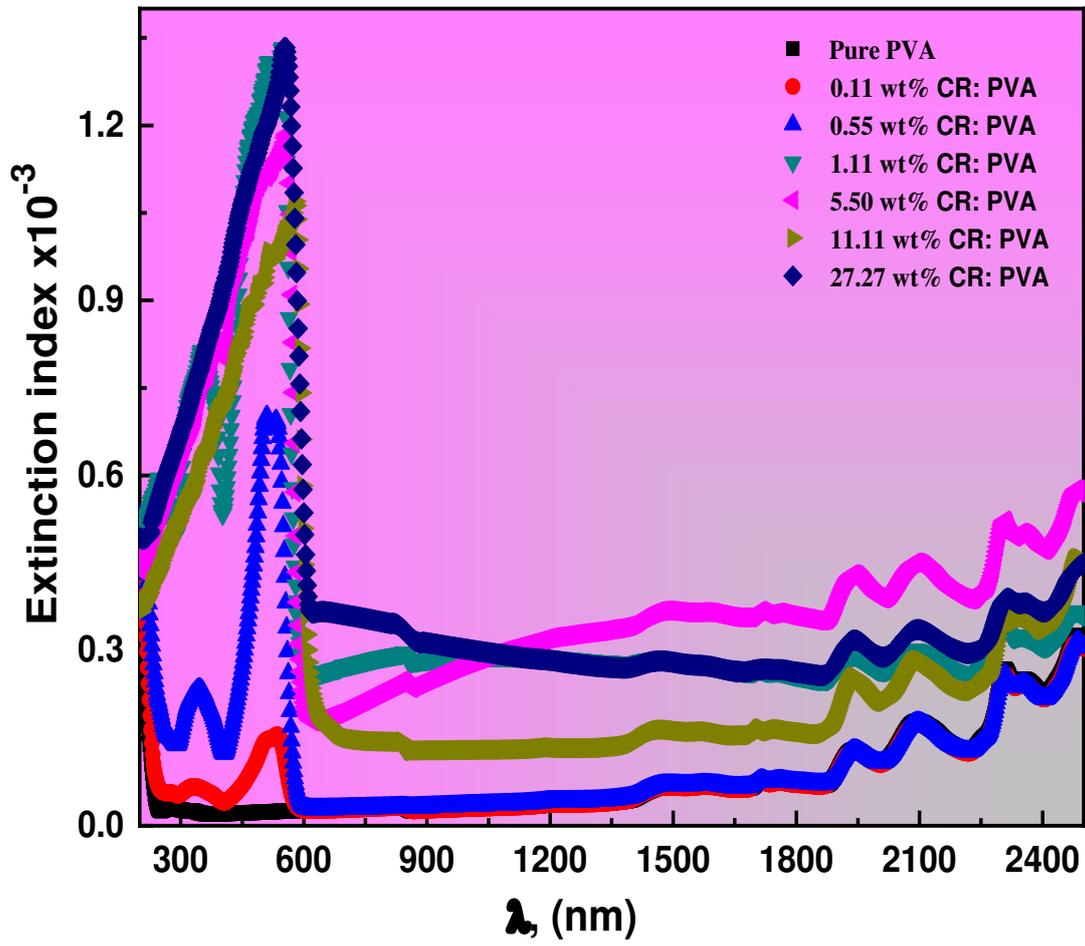


Fig. 6: Extinction index spectra of CR-doped PVA composite films.

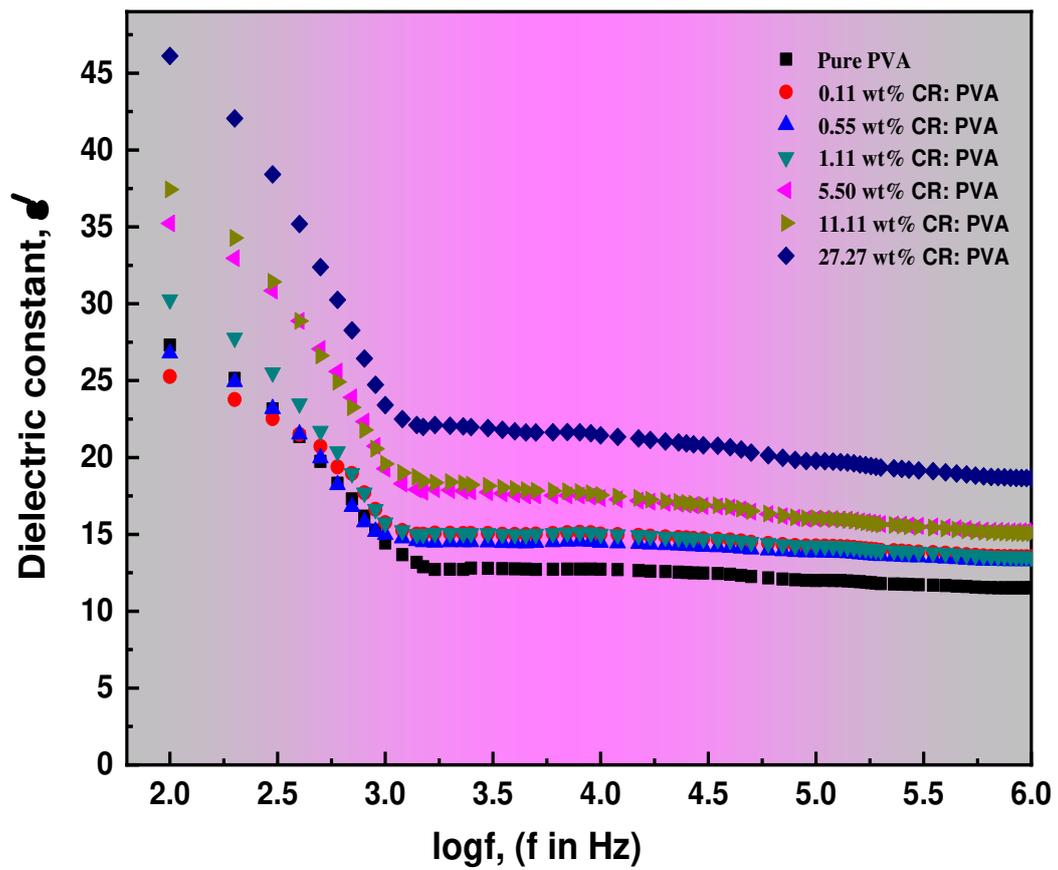


Fig. 7: The frequency dependence of dielectric constant, ϵ' for CR-doped PVA at room temperature.

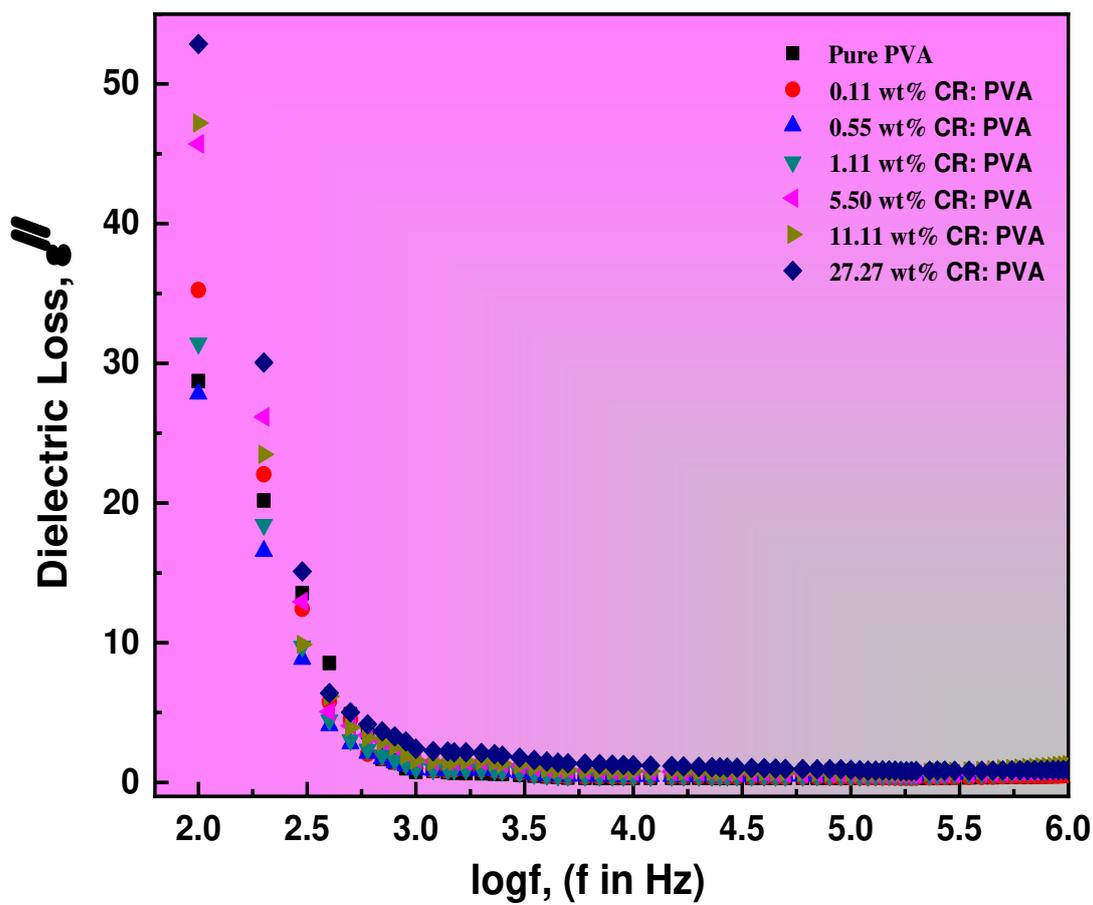


Fig. 8: The applied frequency dependence of dielectric loss, ϵ'' for CR-doped PVA films at room temperature.

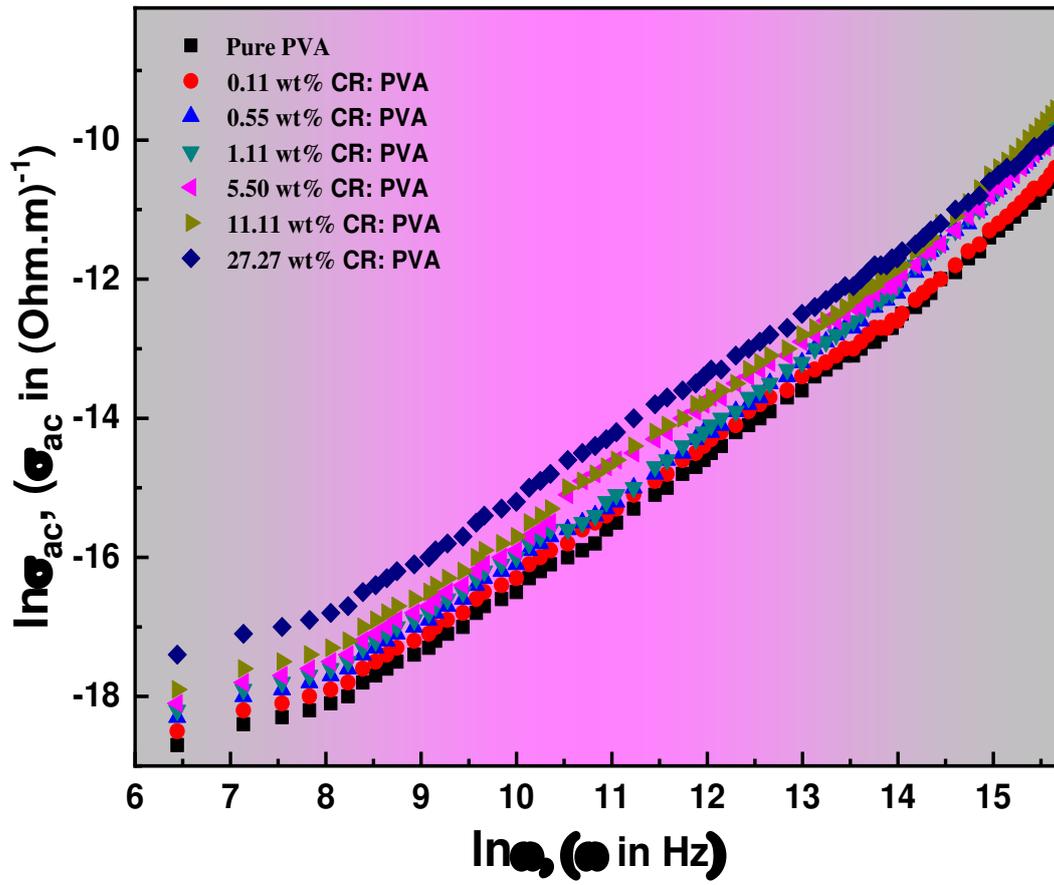


Fig. 9: AC electrical conductivity for CR-doped PVA composite films at room temperature.

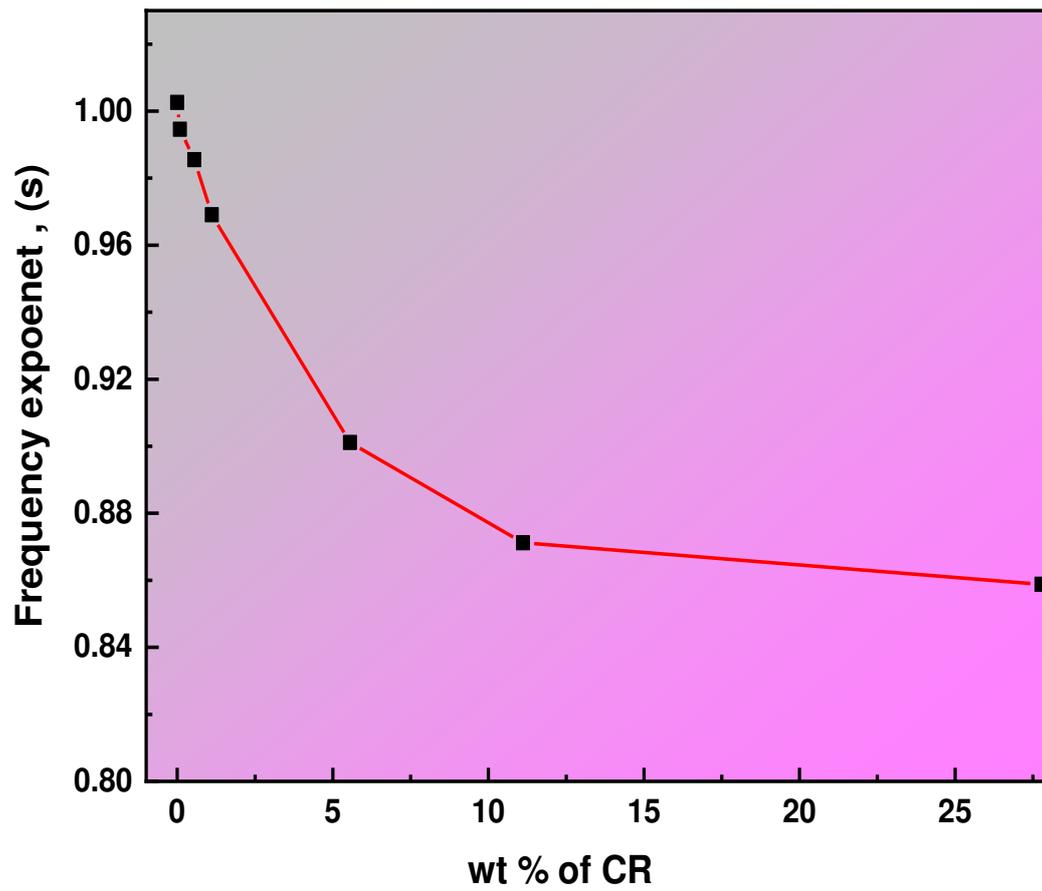


Fig. 10: The reliance of s for CR-doped PVA composite films.

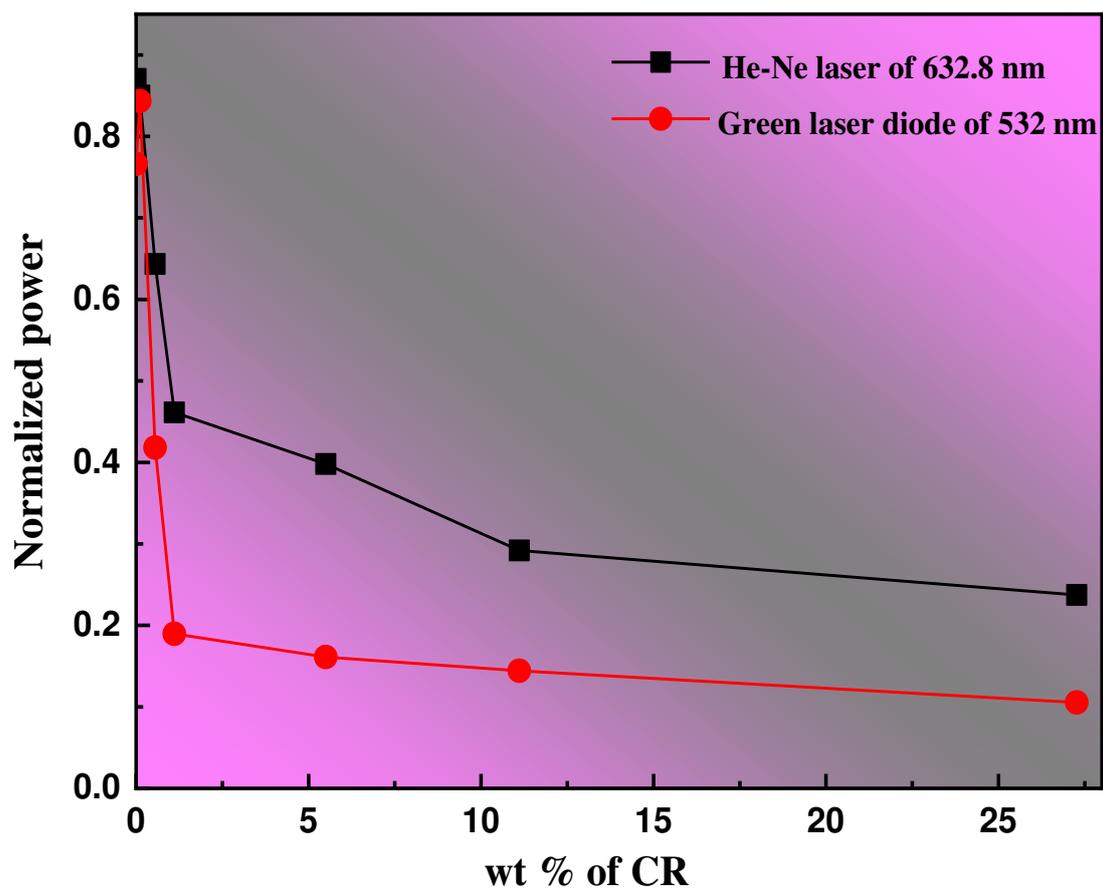


Fig. 11: The normalized power for CR-doped PVA composite films by using a He-Ne laser of 632.8 nm and a green diode laser of 532nm.