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RESEARCH PAPER

Enhancing Structural and Optical Properties of PVA: CMC Blend by NiO Nanoparticle

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ABSTRACT

In this study, nickel nitrate and ammonium hydroxide are utilized in an aqueous solution as initial substances, along with a chemical precipitation technique to create NiO nanoparticles, avoiding the need for complex machinery or harmful and costly solvents. Research was conducted to study the characteristics of films made of NiO nanoparticles doped with CMC/PVA, focusing on both structural and optical characteristics. The CMC/PVA polymer blend films were infused with varying amounts of NiO nanoparticles (3%, 5%, 7%, and 8%) through the solvent casting method, resulting in films with a thickness of 30±1 µm. The results showed that the NiO doping content influenced the optical transmittance (%) in the 190-1200 nm wavelength range, resulting in reduced transmittance for all samples. The doping ratio affected the optical parameters of the films.

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INTRODUCTION

The past few years have seen a notable emphasis on studying and creating polymer blends to enhance the properties of polymeric materials [1-3]. Combining various polymers improves mechanical, thermal, and optical characteristics in comparison to utilizing solely pure polymers or traditional composites. More specifically, blends of polymers with nanoscale fillers, like nanocomposites based on metal oxides, have shown significant advantages in strength, stability, and barrier characteristics. These nanocomposites have opened up new possibilities for high-quality materials that can be utilized in various ways [4, 5]. One area where polymer blend techniques have been successful is in enhancing the amorphous phases of semi-crystalline polymers [6]. Multiple polymers have been used to produce solid mixtures of polymers that exhibit improved electrical and dielectric characteristics relative with the origin states. The instances include PEO/carboxyl-methyl cellulose [7], PVA/sodium alginate (SA) [4], PEO/methylcellulose (MC) [6], PEO/poly-vinyl pyrrolidone (PVP) [8], and CA/PVA blends [9]. These mixtures display improved electrical and dielectric characteristics, making them appealing for various applications, PVA, a polymer with hydroxyl groups linked to a carbon atom, and carboxymethyl cellulose (CMC), a cellulose derivative, both have superior film-forming qualities that result in

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transparent coatings [5, 10]. Adding nanoparticles to synthetic and polymer films has been shown to be an effective method for enhancing their characteristics. NiO nanoparticles have caught the interest of scientists because of their affordable cost, stability, and optoelectronic characteristics. NiO is a semiconductor with a broad indirect band gap energy between 3.4 and 4 eV and a cubic crystal structure, as indicated by references [11, 12-15].Various methods like solvothermal [16], co-precipitation [17], PLD for pulsed laser deposition [18], (sol-gel) [19], and thermal method have been used to prepare NiONPS nanoparticles [20].

This research shows the enhancement of polymeric blends' structural, optical, and electrical properties by incorporating nanoparticles. It emphasizes the importance of modifying processing conditions to get specific applications of characteristics. In this research, the blend preparation of equal parts of PVA and CMC, with NiO nanoparticles added to the polymer blend at concentrations of 3%, 5%, 7%, and 9%. Adding nanoparticles has been demonstrated to improve the characteristics of nanocomposite films.

MATERIALS AND METHODS

Materials

NiO NPs (particle size < 40 nm) Carboxymethyl cellulose (CMC) type (CAS. NO .9004- 32- 4), SINOCMC and a Chinas company manufacture the product and polyvinyl alcohol (PVA) Central Drug House (P) Ltd. and Now Delhi and INDIA manufacture it. It has a molecular weight rang of (13 000 -23000).

Synthesis of (CMC/PVA: NiO) Nanocomposites

0.5 g of CMC and 0.5 g of PVA were individually dissolved in 100 milliliters of deionized water at 50 and 80 degrees Celsius, and subsequently combined and swirled for two hours after complete dissolution. Then, (3, 5, 7 and 9) % wt. of NiONPS were added to mixes and agitated for another one hour. Ultimately, the mixed solutions were casting into flat diameter of plastic Petri dishes equal 90 mm and dried at room temperature for two days. Then the dried and homogeneous membranes are easily removed using tweezers. Similar films were made to guarantee that the dried samples would not bubble or suffer from heat damage. The prepared films' thickness, as determined by a digital micrometer, was around 30 µm. The characterization of materials CMC: PVA and CMC: PVA-NiO the Shimadzu FTIR-8400S Fourier Transform Infrared Spectrophotometer was used for the study. A twin beam UV/VIS spectrometer, the Shimadzu Japan UV-160 A, was used to analyze transmittance and absorbance.

RESULTS AND DISCUSSION

Fig. 1a-c present scanning electron microscope (SEM) images of pure cellulose carboxymethyl/ polyvinyl alcohol (CMC/PVA) film before and after reinforcement with nano-sized nickel oxide (NiO) powder at ratios of 3% and 9% at calcined 800°C temperatures. The images reveal that the pure polymeric film (CMC/PVA) has a rough and irregular surface composed of aggregated and closely packed particles [21]. However, when NiO powder particles are added, as shown in Fig. 1, the images demonstrate good dispersion of the NiO powder particles within the blend. Compared to the movie before reinforcement, the reinforced polymeric films exhibit relatively smoother and more regular surfaces with reduced roughness and low surface porosity [22]. In Fig. 1b, the polymeric films are spherical and semi-regular, while in Figure 1c, it is a honeycomb structure with walls of homogeneous thickness shape, hexagonal and regular [23]. These results indicate that the nano-sized particles tend to form well-organized aggregates within the nano-composite films.

FTIR analysis of the CMC/PVA composite with varying amounts of NiO NPs are shows in Fig. 2, The pure mix spectra exhibit the distinctive absorption bands of CMC/PVA at the intensity of the peaks attributed to the polymer indicates the presence of nanoparticles and polymer mixture interacting with each other, leading to improved polymer properties. The polymer blend samples exhibited broad ranges around (3535, 3270) cm-^{1}, This is explained by the existence of (O-H) groups [24]. Peaks at (2925) cm^{-1}, which correspond to stretching vibrations, show the presence of (C-H) bonds. The (C=C) bond's stretching vibration occurs at 1591cm-1, which is ascribed to the absorption of the bond by FTIR [25-26]. At 1421.1 cm-^{1}, the (-CH2) group experiences asymmetric bending vibrations [27]. The stretching vibrations of (C-O) can be noticed at (1054) cm^{-1}. A new peak at 695cm-^{1}, as shown in the study [28], indicates the presence of (Ni-O) bonds in the polymer blend.

The results obtained indicate that the inclusion of nano-sized nickel oxide (NiO) powder resulted in distinct peaks centered at around (600) cm^{-}

^{1}, as illustrated in Fig. 2. The presence of these peaks signifies the oscillations of the (Ni-O) chemical bonds. Additionally, the peaks exhibit greater prominence and clarity when nano-sized NiO particles are present, indicating a robust interaction between the (NPs) nanoparticles and the active functional groups of the polymeric blend. This indicates the effective incorporation of the nano-sized particles within the base material [29, 30].

Transmittance and reflectance spectrum analysis is an effective method for comprehending and growing the polymer's composition and (E_g) energy gap. Fig. 3 shows the spectrum of transmittance and reflectance for the pure blend of (CMC/PVA) and their composites reinforced

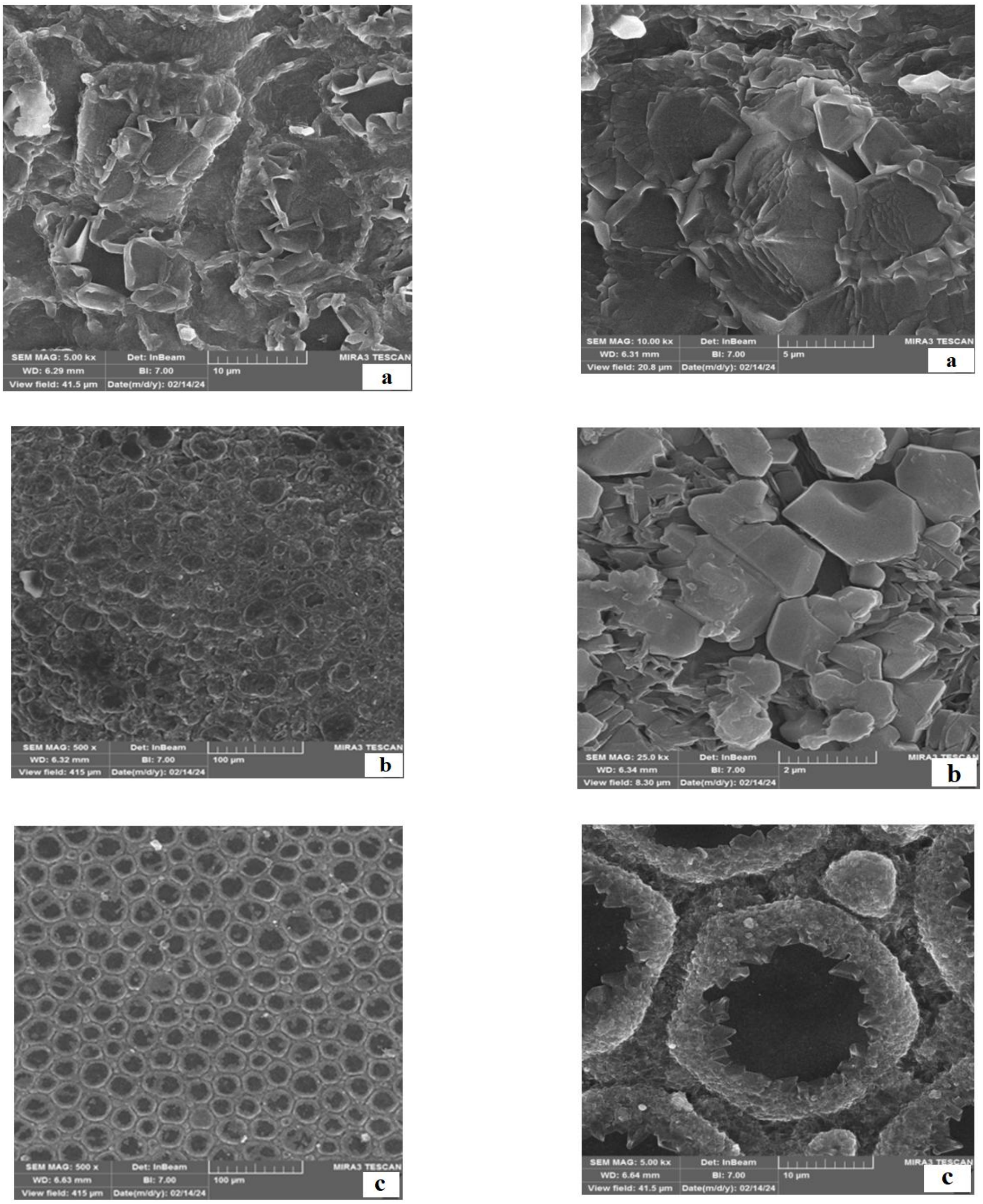

Fig. 1. FE-SEM images of CMC: PVA-9%NiO.

with various weight ratios of calcined nickel oxide nanoparticles (NiO_{NPs}) at a temperature of 800 °C.

Fig. 3, shows that the inclusion of nickel oxide NPs (NiO_{NPs}) resulted for a decrease in the transmittance of the blend CMC/PVA that was created. The reduction in transmittance became more pronounced as the ratios of NiO_{NPs} nanoparticles increased. The transmittance of the prepared models increases with increasing wavelength until it almost stabilizes at wavelengths above (650 nm). This is because an increased weight ratio of nanoparticles results in higher nanoparticle density, leading to increased scattering and reduced transmittance, which is consistent with reference [31].

On the other hand, the reflectivity and

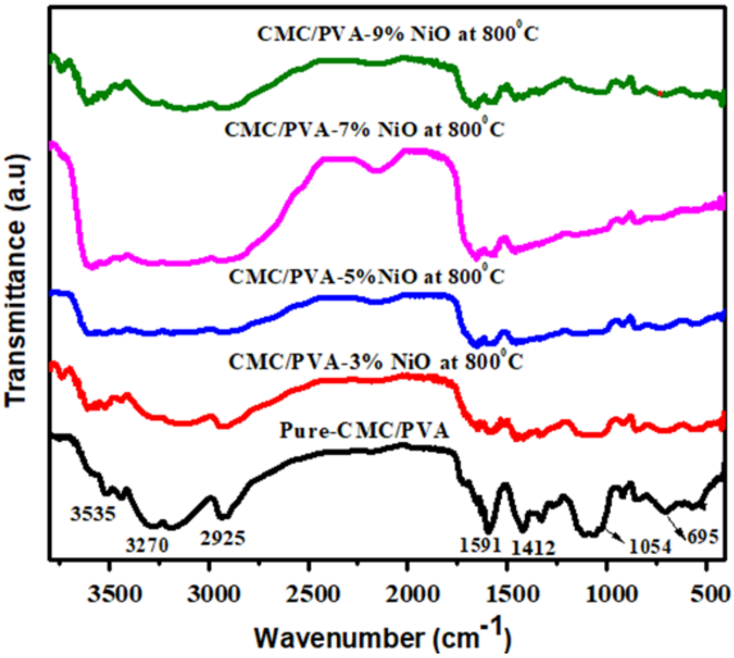

Fig. 2. FTIR for CMC: PVA- NiO Nanocomposite.

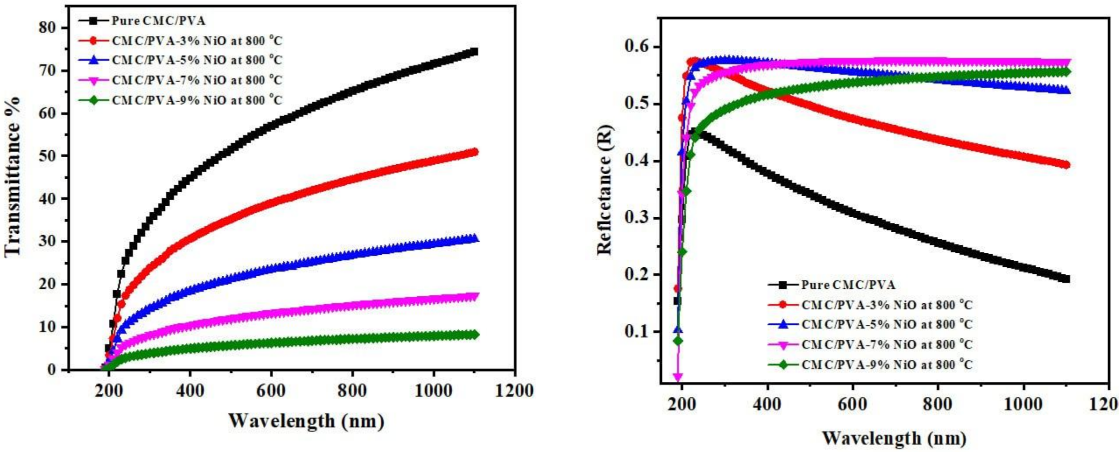

Fig. 3. (T %) & (R) for CMC: PVA-NiO Nanocomposite.

transmittance of the CMC/PVA blend increased accompanied by the addition of NiO_{NPs}. Additionally, the reflectivity decreased significantly with increasing wavelength of the incident light, stabilizing at a wavelength higher than 650 nm. This can be attributed to the absorption and scattering of the incident light by the nickel oxide nanoparticles within the CMC/PVA blend, which absorb part of the incident light and disperse the rest [32, 33].

Fig. 4, shows that the prepared Films' absorption coefficient is higher at higher photon energies and decreases as the photon energy decreases. The absorption coefficient increases with an increase in the ratio of nickel oxide NiO_{NPs}. This can be attributed to increased charge carriers, resulting in higher absorption and absorption coefficient for the nanocomposite Films. [34, 35] Additionally, the energy band gap value for the pure CMC/PVA Films is measured at 4.99 eV. In contrast, the energy band gap values for the reinforced Films decrease with an increase in the content of nickel oxide nanoparticles. At a temperature of 800 °C, the values become (4.88, 4.54, 4.43, and 3.99) eV for reinforcement ratios of 3%, 5%, 7%, and 9%, respectively [36,37].

The reduction in (Eg) the energy gap value is ascribed to film flaws, which occur because of the increasing concentration of NiONPs. These flaws generate localized states inside the energy

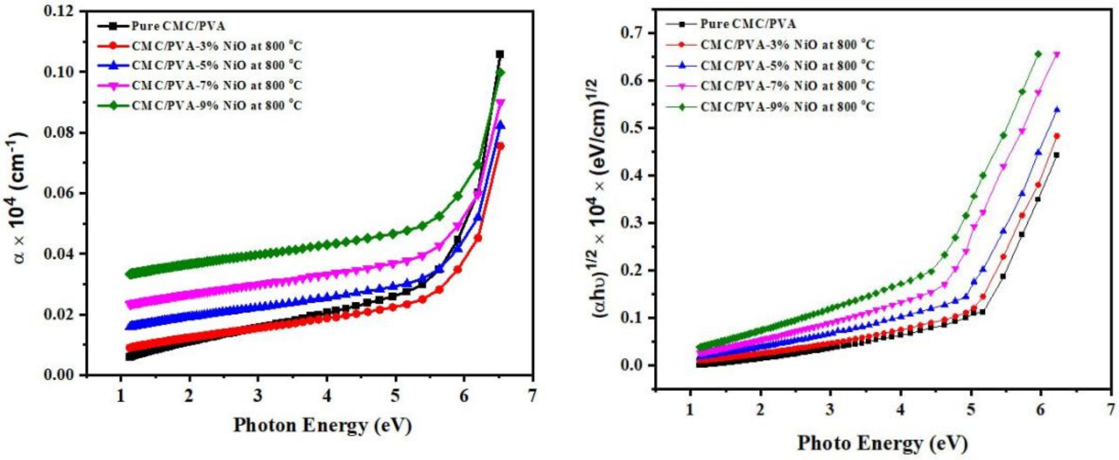

Fig. 4. (α) & (Eg) for PVA: CMC-NiO Nanocomposite.

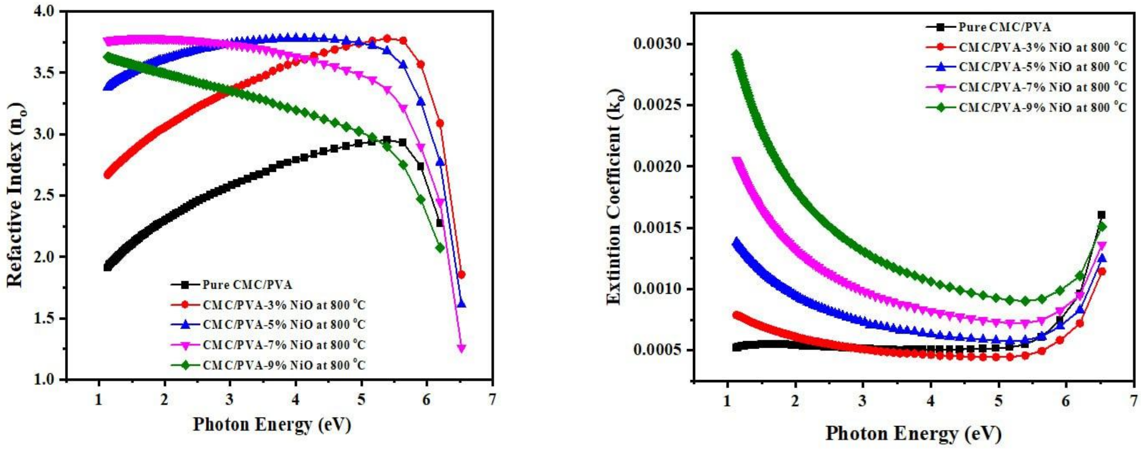

Fig. 5. (n_o) & (k_o) for CMC: PVA-NiO Nanocomposite.

gap, thereby causing a reduction in the energy gap values. Furthermore, the nanoparticles' surface defects and imperfections may cause additional electronic states, which in turn cause changes in the optical characteristics of the final material [38]. This relationship is illustrated by the equation provided [39].

$$\alpha h\upsilon = A\left(h\upsilon - E_g\right) \quad (1)$$

Fig. 5 shows that as the concentration of NiONPs increases, Additionally, rising are the refractive index and the extinction coefficient. The greater density of the nanoparticles causes the incident photon to scatter, raising the refractive index. On the other hand, the rise in the extinction coefficient is cause to the higher absorption coefficient, as the extinction coefficient is closely related to the absorption coefficient [40, 41-43]. The refractive index (n_0) and the extinction coefficient (k_0) can be determined by applying the following formulae [44, 45]:

$$n_o = \left[\left(\frac{1+R}{1-R}\right)^2 - \left(k_o^2+1\right)\right]^{1/2} + \frac{1+R}{1-R} \quad (2)$$

$$k_\circ = \alpha\lambda/4\pi \quad (3)$$

Fig. 6 shows the changes in both the real and the imaginary parts of the dielectric constant between pure and reinforced CMC/PVA composites with varying weight ratios of nickel oxide nanoparticles (NiO_{NPs}), according to the photon energy, the findings show that the real and imaginary components of the dielectric constant an increase when adding calcined nickel oxide nanoparticles (NiO_{NPs}) are introduced at a temperature of 800°C. This increase is attributed to the higher concentration of nanoparticles, which leads to enhanced absorption and scattering of incident light. These results are presented in Table 1 and are supported by references [46-48].

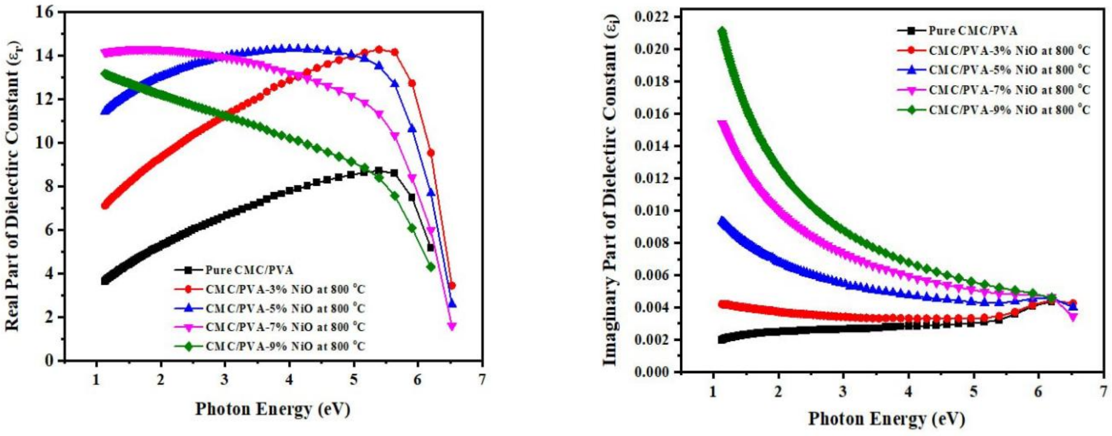

Fig. 6. (E_r) and (E_i) for CMC: PVA-NiO Nanocomposite.

Table 1. Optical Properties of CMC/PVA Films with varying ratios of (NiONPs) at a temperature of 800 °C.

Sample	Energy Gap (eV)	($\alpha*10^4 cm^{-1}$) Maximum	(n_o) Maximum	(k_o) Maximum
CMC-PVA	4.99	0.1058	2.9539	0.0016
CMC-PVA: NiO_{NPs} (3%)	4.88	0.0756	3.78006	0.00114
CMC-PVA: NiO_{NPs} (5%)	4.54	0.08239	3.7822	0.00138
CMC-PVA: NiO_{NPs} (7%)	4.43	0.09	3.78226	0.00205
CMC-PVA: NiO_{NPs} (9%)	3.99	0.09985	3.62872	0.00291

CONCLUSION

The process of solution casting was employed to prepare (CMC / PVA) films supported by different proportions of NiONPs (3%, 5%, 7%, 9%) wt. The spectroscopy of FE-SEM, FTIR and optical properties were used to verify the samples prepared. The electronic microscope SEM reveals that nanoparticles make up regular aggregates and conglomerates and are published in films (CMC / PVA: NiO). The optical characteristics of nano-composites (CMC / PVA: NiO) were assessed within the wavelength range of (190 – 1200) nm. The optical outcomes are demonstrated that the concentration of nanomaterial had a direct impact on several properties. Specifically, raising the concentration led to higher values of reflectance, absorption coefficient, refractive index, extinction coefficient, and both the real and the imaginary electrical insulation constant. However, when the concentration increased, the energy gap and transmittance decreased.

CONFLICT OF INTEREST

The authors declare that there is no conflict of interests regarding the publication of this manuscript.

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