Flexible Methyl Cellulose/Polyaniline/Silver composite films with Enhanced Linear and Nonlinear Optical Properties

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Abstract

In order to potentiate implementations in optical energy applications, flexible polymer composite films comprising methyl cellulose (MC), polyaniline (PANI) and silver nanoparticles (AgNPs) were successfully fabricated through a solution cast preparation method. The composite structure of the fabricated film was confirmed by X-ray diffraction and infrared spectroscopy, indicating a successful incorporation of AgNPs into the MC/PANI blend. The optical parameters such as band gap (Eg), absorption edge (Ea), number of carbon cluster (N), and Urbach energy (Eu) of pure MC polymer, MC/PANI blend and MC/PANI/Ag film were determined by using the UV optical absorbance in the wavelength range 200 to 110 nm. The influence of AgNPs and PANI on linear optical (LO) and nonlinear optical (NLO) parameters such as reflection extinction coefficient, refractive index, dielectric constant, nonlinear refractive index and nonlinear susceptibility of MC polymer were also investigated. The results showed a decrease in the band gap of MC/PANI/AgNPs compared to the pure MC film. Meanwhile, the estimated carbon cluster number enhanced with the incorporation of the AgNPs. The addition of AgNPs and PANI also improved the optical parameters of MC polymer, a trait that makes the current composite a convenient material for optical energy applications.

Keywords: Methyl Cellulose; Polyaniline; Silver nanoparticles; Optical properties
1. Introduction:

Flexible composite materials are receiving a great deal of attention in optical energy applications due to their remarkable electrical, thermal, mechanical, dielectric and optical properties versus the other traditional materials [1-2]. Currently, polymer composites are of high interest in different energy applications because of their pliable characteristics and their easy to use. [3]. Huge attention has been given to reveal the optical properties of polymers, and to potentiate their implementations in optical energy applications [4].

Among the various polymers used in optical energy applications, is the polyaniline (PANI). PANI has been widely studied as a nonlinear optical (NLO) material because of its UV radiation resistance, ultrafast response, steady electrical conductivity, flexibility and easy relative processing [5]. However, PANI has limited mechanical properties, fusibility, and solubility. Thus, it has to be modified with other materials to improve these limitations and to enhance its uses, especially in energy applications. On the other hand, MC polymer is a semi-crystalline structure water soluble polymer carries high mechanical properties, a unique chemical stability, and a perfect optical behavior [6-7]. Hence, the composite of MC and PANI is envisioned to provide a material with remarkable optical properties.

The incorporation of inorganic fillers into the polymer matrix is of much interest, because such inorganic-polymer composites have paved the road to modify the polymer composite properties, providing additional and remarkable optical features [8-9]. Conducting-fillers such as AgNPs have showed many advantages in various applications (e.g. conductive inks, photonics and electronic chips, sensors, batteries and solar cells) because it can decrease the optical band gap [10-11]. Thus, the incorporation of AgNPs into the MC/PANI polymer matrix is a topic of interest.

In the current study, we aim to prepare a flexible composite of AgNPs and MC/PANI polymer matrix, studying the possibility of enhancing the optical properties of MC e.g. optical band gap (E_g), band tail (E_e), absorption edge (E_d), refractive index (n), extinction coefficient (K), dielectric constant and optical conductivity. The linear/nonlinear optical parameters (extinction coefficient, refractive index, reflectance, first order linear optical susceptibility, real and imaginary dielectric constant, and third order nonlinear optical
susceptibility) of MC/PANI/AgNPs composite films will be determined by using the UV–Vis spectroscopy.

2. Materials and methods

2.1 Materials

Methyl cellulose (MC; MW 658.7 g/mol) was purchased from Sigma-Aldrich, Hydrochloric acid (35%), and Ammonium peroxidisulfate (grade, 99%), were purchased from Merck Darmstadt Germany, aniline monomer (C₆H₅NH₂) was purchased from Oxford Lab Chemistry, and AgNO₃ was purchased from Nice Chemicals PVT.

2.2 Preparation of MC/PANI/AgNPs composite film

PANI has been prepared by an oxidation polymerization process of aniline in hydrochloric acid using ammonium peroxide-sulfate as an oxidative agent [12]. For the synthesis of MC/PANI blend, 1.0 g of MC was dissolved in 50 mL distilled water at room temperature. Then, 1.0 wt% and 3.0wt% of PANI were added separately to MC solution. The resultant mixture was stirred by an ultrasonic probe at room temperature till a homogenous solution was obtained.

Regarding the preparation of MC/PANI/AgNPs composite films, AgNO₃ powder was added with different concentrations (0.5 wt% and 1.0 wt%) over a period of 30 min under continuous stirring to the MC/PANI composite. Then, the reducing agent NaBH₄ was added dropwise to the composite mixture over a period of 60 min. Subsequently, the obtained mixture was added on a petri dish to cast a film.

2.3 Characterization techniques

The structural properties of the pristine MC film, MC/PANI blend and the MC/PANI/Ag composite films were investigated by using a X-ray powder diffraction (Shimadzu XRD-6000). The chemical bonds and functional groups of prepared films are identified using FTIR spectroscopy (ATI Mattson, Genesis series, Unicam, England). The
optical properties of the prepared films were investigated by a UV–vis spectrometer (Jasco V-670 UV-VIS spectrophotometer) in the wavelength range 200 nm to 1100 nm.

3. Results and Discussion

3.1 Structural investigation of the synthesized films

The XRD spectrum of pristine MC, PANI/MC blend, and Ag/PANI/MC composite films are shown in Fig.1. The spectrum of MC has indicated two diffraction peaks at 8.1° and 20.7° characteristic for MC with a partial crystalline structure. The area under the peak 8.1° of MC was 1104. The XRD pattern for MC/3%PANI film has become more amorphous with almost disappearance of the MC diffraction peak at 20.7°. The area under the peak 8.1° of MC has changed from 1104 to 4066, confirming the amorphous structure of MC obtained after the addition of PANI. This reduction of the MC crystallinity suggested a good interaction between the chains of MC and PANI polymer [13]. The XRD of MC/3%PANI/0.5%Ag has showed a new peak at 38.6° which is attributed to the (111) diffraction peak of the face-concentrated-cubic AgNPs. The expansion of full width half maximum (FWHM) of MC characteristic peak at 8.1° has proved a good diffusability of the AgNPs into the MC/PANI blend. The average crystallite size (D) of AgNPs determined from Scherrer equation [14] was 13.5 nm.
Fig. 1: XRD patterns of pristine MC, MC/3%PANI and MC/3%PANI/0.5Ag films

Furthermore, the IR data displayed in Fig. 2 confirmed the structure of synthesized films. Specifically, the black IR spectrum of Fig. 2 has showed the characteristic absorption bands C-O-C stretching vibration, C-H stretching vibration, and O-H stretching vibration of MC at 1110 cm⁻¹, 2900 cm⁻¹ and 3400 cm⁻¹, respectively [15]. After the addition of PANI (yellow and red spectrum), the intensity of the absorption bands of MC has lowered especially the OH stretching vibration band. This lowering of the peaks intensity suggested a breakage of the hydrogen bonding network of MC and the penetration of PANI between the chains of MC. In addition, the characteristic absorption bands of PANI, in particular, the C–N and C=N stretching vibrations have newly emerged at 1250 cm⁻¹ and 1550 cm⁻¹, respectively [16]. The addition of AgNPs (green and blue spectra) has showed no change in the spectra of MC/PANI blends. Only, new bands characteristic for the metal particles have been observed at 750 and 820 cm⁻¹ in the spectrum of the MC/PANI/AgNPs composite [17].
Fig 2: IR spectra of pristine MC, MC/1%PANI, MC/3%PANI, MC/3%PANI/0.5%Ag and MC/3%PANI/0.5Ag films

3.2. Optical properties of the synthesized films.

The UV–vis optical absorption of pristine MC, MC/PANI and MC/PANI/Ag films are shown in Fig.3. As observed, the MC absorption peak has increased with the addition of PANI. The two peaks of MC and PANI has also overlapped as a result of the blending process [18]. After the addition of AgNPs, a new adsorption peak characteristic for the surface plasmon resonance (SPR) of the electrons of AgNPs is observed [19]. From the FWHM ($\Delta E_{1/2}$) of SPR band, the radius ($r$) of AgNPs has been estimated assuming free particles behaviour of conduction electrons, using equation (1) [20]:

$$ r = \frac{h v_f}{\Delta E_{1/2}} $$ (1)
Where \( v_f = 1.39 \times 10^6 \text{ m/s} \) related to Fermi velocity of electrons in silver bulk and \( h \) is Planck’s constant. The calculated average particle size of AgNPs was found to be 10 nm, which is close to the value calculated from XRD.

**Fig.3:** UV-Vis Absorption spectra of pristine MC, MC/1%PANI, MC/3%PANI, MC/3%PANI/0.5%Ag and MC/3%PANI/1%Ag films.

The absorption coefficient \( \alpha(\nu) \) is estimated using equation (2) [21].

\[
\alpha(\nu) = \frac{2.303 A}{d}
\]

Where, \( A \) indicates the optical absorbance and \( d \) is the film thickness. The absorption optical coefficients with photon energy of pristine MC, MC/1%PANI, MC/3%PANI, MC/3%PANI/0.5AgNPs, and MC/3%PANI/1AgNPs films are shown in Fig.4. The absorption edge (\( E_d \)) value was determined from extrapolating the linear part of \( \alpha \) against applied \( h\nu \) curves at absorption zero value [22]. As shown, the absorption edge \( E_d \) decreased by the addition of AgNPs and PANI to MC polymer (see the details of Table 1). The \( E_d \) decreased from 5.42 eV for pristine MC to 3.14 eV for MC/3%PANI and reduced to 1.93 eV for MC/3%PANI/1%AgNPs. This reduction in \( E_d \) was related to the changes in the hole and
the electron numbers in the conduction and the valence bands [23]. Another factor for shifting absorption edge was the structural changes in MC polymer matrix, which has been confirmed by the XRD results and the molecular interactions of MC polymer chains and the AgNPs. In other words, the shift in the optical absorption edge has reflected the electronic conjugation between the AgNPs and the PANI beside the increase in the degree of disorder for those composite films [24].

Fig.4: Absorption coefficients $\alpha$ as a function of wavelength for pristine MC, MC/1%PANI, MC/3%PANI, MC/3%PANI/0.5%Ag and MC/3%PANI/1%Ag films

The energy band gap ($E_g$) of all films have been determined from the intercept of the additional plotted linear portion $(\alpha h\nu)^3$ versus $h\nu$ as shown in Fig. 5, which pursues Tauc method (equation 3)[25]:

$$\alpha h\nu = B(h\nu - E_g)^n$$  \hspace{1cm} (3)

where $B$ represents the absorption edge width parameter, $h\nu$ is the incident photon energy calculated from $h\nu=1240/\lambda$, and $n$ is factor takes 3/2 or 1/2 for direct transitions and 2 or 3 for indirect transitions depending on forbidden or allowed transition respectively. The
determined values of direct $E_g$ are listed in Table 1. As observed, $E_g$ has decreased from 5.76 eV for pristine MC, to 5.01eV for MC/3%PANI, and reduced to reach 4.27eV for MC/3%PANI/1%AgNPs. The reduction in MC optical gap was due to the variations of polymer disorder [26]. In addition, the defects induced by the localized states in the band gap, was the main reason for reducing energy band of the polymer. Furthermore, the reduction in optical band gap was related to the charge transfer complexes (CTCs) formation due to the trap levels between LUMO and HOMO bands of MC polymer [27], which enhanced the lower transitions energy. This successfully implies the miscibility of AgNPs and MC/PANI blend chains and strongly supports the XRD results.

![Graph](image)

**Fig.5:** The relation between $(\alpha h\nu)^2$ against photon energy $(h\nu)$ for pristine MC, MC/1%PANI, MC/3%PANI, MC/3%PANI/0.5%Ag and MC/3%PANI/1%Ag films.

For determining the band tail that refers to the width of localized states, the absorption coefficient $\alpha (\nu)$ near band edge as exponential dependence of photon energy $(h\nu)$ has been determined from the Urbach relationship (equation 4) [28]:

$$\alpha (\nu) = \alpha_o e^{\left(\frac{h\nu}{E_u}\right)}$$  \hspace{1cm} (4)


The Urbach tail $E_e$ value recorded in Table 1, has been determined by the reciprocal of the slope of the linear portion of the curves shown in Fig.6. As observed, $E_e$ enhanced from 0.51 eV for pristine MC to 1.52 eV for MC/3%PANI and increased to reach 2.02 eV for MC/3% PANI/1%AgNPs. The band tail $E_e$ values has inversely changed with band gap $E_g$ values. This was a result of the disorder induced in the MC polymer chain after the incorporation of the AgNPs that induced interaction changes in MC/PANI polymer blend [29]. In other words, the changes of Urbach tail $E_e$ was a result of the defects in the MC chains after the addition of PANI and AgNPs. Specifically, the AgNPs and PANI has led to the redistribution from the band states, permitting additional tail to tail transitions [30].

![Graph showing absorption coefficient versus photon energy for pristine MC, MC/1%PANI, MC/3%PANI, MC/3%PANI/0.5%Ag and MC/3%PANI/1%Ag films](image)

**Fig.6:** Absorption coefficient versus photon energy for pristine MC, MC/1%PANI, MC/3%PANI, MC/3%PANI/0.5%Ag and MC/3%PANI/1%Ag films

The carbon cluster number (N) has been estimated from optical gap $E_g$ using equation (5) [31]:

$$E_g = 34.4/\sqrt{N} \quad (5)$$
The estimated N value (see Table 1) of pristine MC was 36. After the addition of PANI, it has increased to be 47, and has increased to reach 65 for MC/3%PANI/1%AgNPs film. This enhancement of N number was a result of the conjugation of monomer units in MC polymer matrix after the addition of PANI and AgNPs in the MC polymer. The enhancement of the N values has been attributed to the amounts of the conducting PANI and the AgNPs, where the higher their content in the host MC matrix, the more defects are introduced causing additional low energy states, and hence a decrease in the band gap is observed leading to an improvement in the N value.

Table 1. Values of absorption edge $E_d$, band gap $E_g$, Urbach energy $E_u$, and carbon cluster number $N$ of pristine MC, MC/1%PANI, MC/3%PANI, MC/3%PANI/0.5%Ag, and MC/3%PANI/1%Ag films

| The samples          | Absorption edge $E_d$ (eV) | Optical band gap $E_g$ (eV) | Urbach energy $E_u$ (eV) | Carbon cluster number (N) |
|----------------------|----------------------------|-----------------------------|--------------------------|---------------------------|
| Pure MC              | 5.42                       | 5.76                        | 0.51                     | 36                        |
| MC/1%PANI           | 3.70                       | 5.06                        | 1.38                     | 45                        |
| MC/3%PANI           | 3.14                       | 5.01                        | 1.52                     | 47                        |
| MC/3%PANI/0.5%Ag    | 2.38                       | 4.41                        | 1.92                     | 61                        |
| MC/3%PANI/1%Ag      | 1.93                       | 4.27                        | 2.02                     | 65                        |

The extinction coefficient ($K$), which is an indication of the debility of absorption alterations when the electromagnetic wave spreads across the material, has been calculated using equation (6) [32].

$$K = \frac{\alpha \lambda}{4\pi} \quad (6)$$

The extinction coefficient $k$ is plotted as a function of wavelength as shown in Fig. 7. As seen, $k$ has displayed high values at the longest wavelengths. This behavior is ascribed to the high absorption coefficient in this region. On other hand, the extinction coefficient $k$ has enhanced by addition of PANI and AgNPs to the MC polymer chain. This is because; PANI and AgNPs have induced modification on polymer structure. Another reason for the enhanced extinction coefficient $k$ was a result of the surface SPR of drugged AgNPs in MC polymer. Additionally, the extinction coefficient $K$ of MC/3%PANI/0.5%AgNPs observed at $\lambda$ of 490 nm has shifted to $\lambda$ of 520 nm for MC/3%PANI/1%AgNPs film. This shift in
wavelength with increasing AgNPs was a result of the new levels in the optical band gap that has led to more crossing of electrons from valence to conduction band [33].

Furthermore, the higher value of the extinction coefficient of MC/PANI/1%AgNPs has showed more scattering of light compared to MC/PANI/0.5%AgNPs. This increase of the extinction coefficient of MC/PANI/1%AgNPs was a result of the enhanced interactions of AgNPs and PANI [34].

![Fig. 7: The extinction coefficient k versus wavelength $\lambda$ for pristine MC, MC/1%PANI, MC/3%PANI, MC/3%PANI/0.5%Ag and MC/3%PANI/1%Ag films.](image)

Fig. 7: The extinction coefficient k versus wavelength $\lambda$ for pristine MC, MC/1%PANI, MC/3%PANI, MC/3%PANI/0.5%Ag and MC/3%PANI/1%Ag films.

Fig. 8 shows the relation of the reflectance (R) versus the wavelength (λ) for pristine MC, MC/PANI and MC/PANI/AgNPs films. As noticed, the reflectance R value has enhanced by the addition of PANI and AgNPs. This increase of reflectance R is attributed to reduction of incident light scattering, which reflects the changes of the disorder degree of the polymer chain [35]. This propagation of light through MC/PANI/AgNPs composite based materials has depended on the functional groups of PANI as well as the nature of AgNPs. Furthermore, the behavior change of the reflectance R with PANI and AgNPs, is attributed to the increasing of the packing density of PANI and the AgNPs content in the composite. In other words, the changes of R value have reflected the effects of both PANI and AgNPs for modifying the electronic structure of the MC polymer chain [36].
The refractive index \( n \), which indicates the electronic polarizability of the ions and the home field into the material is considered as essential one of material characterization properties. Accordingly and in order to deduce the effects of the AgNPs interaction with MC polymer matrix, optical dielectric properties and refractive index are investigated. Fig. 9 shows the changes of \( n \) as a function of wavelength \( \lambda \) for pristine MC, MC/1\%PANI, MC/3\%PANI, MC/3\%PANI/0.5\%Ag and MC/3\%PANI/1\%Ag films. The refractive index \( n \) is thus calculated from equation (7) [37]:

\[
n = \frac{(1+R)}{(1-R)} + \frac{4R}{(1-R)^2} - K^2
\]  

(7)

As can been seen, the \( n \) is first decreased by wavelength increase for all the films as shown in Fig.9. Next, a steady is observed at the higher wavelengths, demonstrating the normal light dispersion. Furthermore, the refractive index \( n \) has enhanced by the addition of PANI and AgNPs the the MC polymer chains. This is because localized hesitance of charged particles in the conducting materials. Moreover, the addition of AgNPs and PANI to the MC polymer has improved the film density to make it compact and hard [38]. In other words, the increase the refractive index was a result of the addition of both PANI and AgNPs and their
interaction with the chains of MC which has led to an enhancement in the density of the composite films.

Fig. 9. The refractive index $n$ versus wavelength $\lambda$ of pristine MC, MC/1\%PANI, MC/3\%PANI, MC/3\%PANI/0.5\%Ag and MC/3\%PANI/1\%Ag films.

In order to highlight the optical properties of the newly fabricated MC/PANI/AgNPs composite films, the characteristic dielectric properties have been measured. The dielectric properties are envisioned to give an idea about the polarization behavior of the MC/PANI/AgNPs composite films in the optical devices. In particular we measure the imaginary $\varepsilon_i$ and real $\varepsilon_r$ dielectric parts which are the most basic material properties that demonstrate the light dispersion of the films. $\varepsilon_i$ and $\varepsilon_r$ have been determined from equation (8) [39]:

$$\varepsilon = \varepsilon_r + i\varepsilon_i \quad (8)$$

The importance of dielectric constants comes from their roles in presenting valuable information about the energy density states of the prepared materials. The real part $\varepsilon_r$ has been estimated from of the refractive index $n$ and extinction coefficient $k$ data using the formula [39]:

$$\varepsilon_r = n^2 - K^2 \quad (9)$$
The variation of real dielectric constant $\varepsilon_r$ versus the wavelength $\lambda$ for pristine MC, MC/1%PANI, MC/3%PANI, MC/3%PANI/0.5%AgNPs and MC/3%PANI/1%AgNPs films are shown in Fig.10. As can be seen, the real dielectric constant $\varepsilon_r$ part has enhanced with increasing both the AgNPs and PANI contents, indicating a good dispersion of PANI and AgNPs into MC polymer chain, because the induced structure changes of Ag and PANI in polymer matrix. By increasing the silver content from 0.5% to 1% into the MC/3%PANI blend, the motion of charge carriers and localized charged particles fluctuations has induced modifications in the optical dielectric dispersion properties, indicating flexible films for optical energy applications.

![Variation of real dielectric constant $\varepsilon_r$ as a function of wavelength $\lambda$ of pristine MC, MC/1%PANI, MC/3%PANI, MC/3%PANI/0.5%Ag and MC/3%PANI/1%Ag films.](image)

**Fig.10:** Variation of real dielectric constant $\varepsilon_r$, as a function of wavelength $\lambda$ of pristine MC, MC/1%PANI, MC/3%PANI, MC/3%PANI/0.5%Ag and MC/3%PANI/1%Ag films.

The imaginary part $\varepsilon_i$, which demonstrate the absorbed energy of electric field as results of dipole moment motion, is given by following equation (equation 10) [39]:

$$\varepsilon_i = 2 n k$$

(10)

The variation of the imaginary dielectric constant ($\varepsilon_i$) as a function of photon energy (hv) of pristine MC, MC/1%PANI, MC/3%PANI, MC/3%PANI/0.5%AgNPs andMC/3%PANI/1%AgNPs films is shown in Fig.11. As noticed, the behavior of $\varepsilon_i$ is similar to the behavior of extinction coefficient k. Probably, this is because the refractive index is very tiny. Furthermore, the imaginary part of the dielectric constant mainly depends on the
(k) values which are related to the variation of the absorption coefficients. The imaginary dielectric constant has enhanced by the addition of PANI and AgNPs into the MC polymer and the MC/PANI blend. This is because the formed defects has induced charge transfer reactions between the MC polymer chains and the AgNPs dopant [40].

**Fig.11:** Imaginary dielectric constant ($\varepsilon_i$), as a function of photon energy ($h\nu$) for pristine MC, MC/1%PANI, MC/3%PANI, MC/3%PANI/0.5%Ag and MC/3%PANI/1%Ag films.

The refractive index values can be modeled according to the single oscillator paradigm, which suggested by Wemple and DiDomenico as indicated in equation (11) [41]:

$$\frac{1}{n^2-1} = \frac{E_o}{E_d} - \frac{1}{E_o E_d} (h\nu)^2$$  \hspace{1cm} (11)

Where, $E_o$ represents the single oscillator energy, and $E_d$ refers to the dispersion energy, which measures the intensity of inter-band transitions and the variations correlating with the structural arrangement of the material. Therefore, by plotting the relation between $(n^2-1)^{-1}$ and $(h\nu)^2$ of the pristine MC, MC/PANI, and MC/PANI/Ag films as shown in Fig. 12, we can deduce the values of the parameters $E_o$ and $E_d$ through the intercept of y-axe and the slope of the linear fit part, respectively. Additionally, the static refractive index values ($n_o$) of the pristine MC, MC/PANI, and MC/PANI/Ag films can be computed via extrapolating upright portion of each curve with ordinate $(h\nu)^2 = 0$ as [42]:
\[ n_0 = (1 + \frac{E_d}{E_o})^{1/2} \quad (12) \]

The zero frequency of dielectric constants \((\varepsilon_\infty)\) of the films has been determined by employing the relation \(\varepsilon_\infty = (n_0)^2\). The parameters \(E_o\), \(E_d\), and \(\varepsilon_\infty\) for the pristine MC, MC/PANI, and MC/PANI/Ag films, have been estimated and recorded in Table 2. As noticed the enhancement of dispersion energy from 0.43 for pure MC to 0.87 for MC/3\%PANI and to 0.90 for MC/3\%PANI/1\%Ag implied that the electronic structure of MC molecules has suffered from both the modifications of PANI and AgNPs added to MC, and the defects developed in MC matrix.

Fig. 12: The relation between \((n^2-1)^{-1}\) and \((h\nu)^2\) for pristine MC, MC/1\%PANI, MC/3\%PANI, MC/3\%PANI/0.5\%Ag and MC/3\%PANI/1\%Ag films.

Besides, other parameters such as the lattice dielectric constant \((\varepsilon_l)\) and the ratio concentration of free carrier and its effective mass \((N/m^*)\) can be deduced using another relation of the real part of dielectric constant in Spitzer–Fan model (equation 13) [43]:

\[ \varepsilon_r = \varepsilon_l - \left( \frac{e^2}{4\pi^2\varepsilon_\infty c^2} \frac{N}{m^*} \right) \lambda^2 \quad (13) \]

Where, \(c\) represents the light speed, \(e\) defines the charge of an electron and \(\varepsilon_\infty\) demonstrates the free space dielectric. Therefore, by plotting the relevance among the real part dielectric
constant and $\lambda^2$ for the pristine MC, MC/PANI, and MC/PANI/Ag films as shown in Fig.13. The values of $\varepsilon_l$ and $N/m^*$ are determined from the intercept of $x$-axe and the slope of the straight portions, respectively. Furthermore, the plasma resonance frequency values ($W_p$) for each valence electron involved in the optical transitions is estimated by employing the following equation (equation 14) [44]:

$$W_p = \frac{e^2}{\varepsilon_0} \frac{N}{m^*} \quad (14)$$

As noticed from the data of Table 2, the values of $\varepsilon_l$, $N/m^*$ and $W_p$ have increased with increasing the contents of both PANI and AgNPs. These increases have been attributed to the variation in bond length with the addition of PANI and AgNPs. In particular, $\varepsilon_\infty$ and $(N/m^*)$ values have been reduced with increasing the AgNPs content due to the reduction in the number of dipoles which contributes to the polarization.

Fig.13: Variation of real dielectric constant ($\varepsilon_r$), as a function of wavelength ($\lambda^2$) for pristine MC, MC/1%PANI, MC/3%PANI, MC/3%PANI/0.5%Ag and MC/3%PANI/1%Ag films.
Table. 2. Values of the optical parameters $E_o$, $E_d$, $\varepsilon_{\infty}$, $\varepsilon_i$, $N/m^*\times10^{38}$ and $W_p\times10^{12}$ of the pristine MC, MC/1%PANI, MC/3%PANI, MC/3%PANI/0.5Ag and MC/3%PANI/1Ag films.

| The samples                  | $E_o$ (eV) | $E_d$ (eV) | $\varepsilon_{\infty}$ | $\varepsilon_i$ | $N/m^*\times10^{38}$ Kg/m$^3$ | $W_p\times10^{12}$ (Sec$^{-1}$) |
|-----------------------------|------------|------------|------------------------|-----------------|-------------------------------|---------------------------------|
| Pure MC                     | 4.1        | 0.43       | 1.10                   | 1.11            | 0.40                          | 0.116                           |
| MC/1%PANI                   | 5.12       | 0.74       | 1.12                   | 1.14            | 0.25                          | 0.072                           |
| MC/3%PANI                   | 4.80       | 0.87       | 1.18                   | 1.18            | 0.20                          | 0.058                           |
| MC/3%PANI/0.5%Ag            | 3.87       | 0.90       | 1.23                   | 1.25            | 0.60                          | 0.171                           |
| MC/3%PANI/1%Ag              | 4.40       | 0.90       | 1.19                   | 1.28            | 0.50                          | 0.150                           |

The long wavelength refractive index ($n_{\infty}$) and medium oscillator wave longitude ($\lambda_o$) of the pristine MC, MC/1%PANI, MC/3%PANI, MC/3%PANI/0.5%AgNPs and MC/3%PANI/1%AgNPs films are determined by analyzing the data of the refractive index utilizing the Sellmeier oscillator equation (equation 15) [45]:

$$\frac{(n_{\infty}^2 - 1)}{(n^2 - 1)} = 1 - \left(\frac{\lambda_o}{\lambda}\right)^2$$

By studying the relation between ($n^2-1$)$^{-1}$ and $\lambda^{-2}$ at longer wavelength as shown in Fig. 14, the values of $n_{\infty}$ and $\lambda_o$ can be obtained from the intercept of the x-axe and the slope of the linear part of the detour, respectively. It is clear from the data of Table 3, that the value of $n_{\infty}$ and $\lambda$ increases with increasing contents of both PANI and AgNPs. The $\lambda_o$ has increased from 477 nm to 500 nm, while the $n_o$ has increased from 1.11 to 1.26 by increasing silver content from 0.5% to 1%. On the other hand, by hiring the single Sellmeier oscillator at depressed energy ($n_o^2/n^2$)$^{-1} =1-(\lambda_o/\lambda)^2$, it was possible to compute the value of oscillator length intensity ($S_o$) through the following equation (equation 16) [46]:

$$S_o = \frac{(n_{\infty}^2 - 1)}{(\lambda_o)^2}$$

In the Drude model, the imaginary part of dielectric constant $\varepsilon_i$ relies on the energy of incident photon and associated with the incident photon wavelength using equation (17)[47]:

$$\varepsilon_i = \frac{1}{4\pi^2\varepsilon_0}\left(\frac{e^2N}{c^3m^*\tau}\right)\lambda^3$$

Therefore, the relaxation time values ($\tau$) of all the fabricated films can be determined through the plotting of the $\varepsilon_i$ and $\lambda^3$ as shown in Fig.15, and listed in Table 3. As can be seen, the time relaxation values gradually decreased with increasing both the PANI and AgNPs. It reduced from $8.8 \times 10^{14}$ sec for pure MC to $5.7 \times 10^{14}$ sec for MC/3%PANI and to $1.1 \times 10^{14}$ sec.
for MC/3%PANI/1%Ag NPs. These results confirmed that the formed films have become more convenient to high rapid optoelectronic devices.

Fig.14: The relation between $(\frac{n^2-1}{\lambda^2})^{\frac{1}{2}}$ and $(\frac{1}{\lambda^2})^{\frac{1}{2}}$ for pristine MC, MC/1%PANI, MC/3%PANI, MC/3%PANI/0.5%Ag and MC/3%PANI/1%Ag films.

Fig.15. Relation between imaginary dielectric constant $\varepsilon_i$ and $\lambda^3$ for pristine MC, MC/1%PANI, MC/3%PANI, MC/3%PANI/0.5%Ag and MC/3%PANI/1%Ag films.
The optical conductivity ($\sigma_{\text{opt}}$) which demonstrates the electrical conductivity that produced as a result of the charge carrier’s transfer due to the variation in the electric field of the fallen electromagnetic waves has been determined from absorption coefficient ($\alpha$) using equation (18) [48]:

$$\sigma_{\text{opt}} = \frac{\alpha n c}{4\pi}$$  \hspace{1cm} (18)

Where $n$ refers to the refractive index and $c$ represents the speed of light. The variation of optical conductivity with photon energy is shown in Fig.16. At high photon energy, we can witness the increase of the optical conductivity of films because the high absorbance value in that region has led to increases of the charge transfer excitations. On the other hand, the optical conductivity has increased with increasing both the PANI and AgNPs, due to the increases of the localized stage densities in the band structure. That has led to an increase in the absorption coefficient. This result supports a good miscibility between AgNPs and MC chains as showed by XRD analysis. Furthermore, the enhancement of the optical conductivity ($\sigma_{\text{opt}}$) and the decrease of the band gap $E_g$ with increasing both the AgNPs and PANI content inside MC has revealed that both the dielectric and the optical measurements are in approval with each other. The optical dielectric properties and the optical conductivity data have reflected the importance the MC/PANI/Ag composite films for optical energy devices.

![Fig.16: Variation of optical conductivity with photon energy for pristine MC, MC/1%PANI, MC/3%PANI, MC/3%PANI/0.5AgNPs and MC/3%PANI/1AgNPs films.](image-url)
Table 3. Values of the optical parameters $W_p$, $n_\infty$, $\lambda_o$, $S_o$, and $\tau$ of the pristine MC, MC/1%PANI, MC/3%PANI, MC/3%PANI/0.5Ag and MC/3%PANI/1Ag films.

| The films               | $n_o$ | $\lambda_o$ (nm) | $S_o \times 10^{12}$ (m$^2$) | $\tau \times 10^{-14}$ (sec) |
|------------------------|-------|-------------------|-------------------------------|-------------------------------|
| Pure MC                | 1.05  | 412               | 0.58                          | 8.8                           |
| MC/1%PANI              | 1.07  | 244               | 2.38                          | 6.6                           |
| MC/3%PANI              | 1.18  | 346               | 3.20                          | 5.7                           |
| MC/3%PANI/0.5%Ag       | 1.11  | 477               | 1.02                          | 1.4                           |
| MC/3%PANI/1%Ag         | 1.26  | 500               | 2.35                          | 1.1                           |

When light waves passes inside the polymer material, it interacts with charge particle of that material and produces a dipole movement. This dipole movement gives the non-linear electron polarizability ($P$). Accordingly, the composite films has possessed an optical nonlinearity (NLO) and rapid response time. In this study, the NLO of the fabricated films can be featured by equation (19) [49]:

$$P = X^{(1)}E + X^{(2)}E^2 + X^{(3)}E^3$$  (19)

where $P$ defines polarization of the material, $X^{(1)}$ represents the linear susceptibility, $X^{(2)}$ related to the second order NLO susceptibility which corresponding to a second harmonic generation, and $X^{(3)}$ refer to the third order NLO susceptibility. Thus, it was possible to calculate the values of $X^{(1)}$ and $X^{(3)}$ by using the following relations (equations 20 and 21) [50]:

$$X^{(1)} = \frac{(n^2-1)}{4\pi}$$  (20)

$$X^{(3)} = A(X^{(1)})^4$$  (21)

The refractive index can thus be written in the following form [50].

$$n(\lambda) = n_o(\lambda) + n_2(E^2)$$  (22)

$n_o$ refer to a linear refractive index, $n_2$ represents NLO refractive index. The values of NLO refractive index from the NLO susceptibility and refractive index ($n$) can be extracted from the following relation [50]:

22
\[ n_2 = \frac{12\pi X^{(3)}}{n_o} \]  \hspace{1cm} (23)

Where, \( n_o = n \), because \( n_o \gg n_2 \). The change of \( X^{(1)} \) and \( X^{(3)} \) versus wavelength (\( \lambda \)) are depicted in Figs. 17a and 17b, respectively of pristine MC, MC/1\%PANI, MC/3\%PANI, MC/3\%PANI/0.5AgNPs and MC/3\%PANI/1\%AgNPs films. Notably, the values of \( X^{(1)} \) and \( X^{(3)} \) have increased with increasing both the PANI and AgNPs contents.

**Fig. 17.** (a). Linear optical susceptibility \( X^{(1)} \) and (b) Non-linear optical susceptibility \( X^{(3)} \) as a function of wavelength (\( \lambda \)) of pristine MC, MC/1\%PANI, MC/3\%PANI, MC/3\%PANI/0.5\%Ag and MC/3\%PANI/1\%Ag films.
This increase was due to the creation of defect centers, which has led to a boost local polarizability. Moreover, the increase of $\chi^{(1)}$ and $\chi^{(3)}$ with increasing PANI and Ag contents has been attributed to the increase in the interaction of AgNPs with PANI/MC blend that resulted in an enhanced $\pi-\pi^*$ and $n-\pi^*$ transitions [51]. This result showed the advantages of fabrication composite films composed of PANI and AgNPs, which envisioned to enhance the absorption for the optical devices.

In addition, Fig. 18 has depicted the change of non-linear refractive index against wavelength of the pristine MC, MC/1%PANI, MC/3%PANI, MC/3%PANI/0.5AgNPs and MC/3%PANI/1AgNPs films. Notably, the values of $n_2$ have the same trend of the valued of $\chi^{(3)}$, as it gradually increased with increasing both the PANI and AgNPs content. These results clearly showed the importance of adding the conducting PANI and AgNPs to MC where the resultant films have indicted an improvement in the nonlinear optical parameters which is favoured for the of the optoelectronic device applications [52].

![Fig: 18. Non-linear refractive index ($n_2$) as a function of wavelength ($\lambda$) of pristine MC, MC/1%PANI, MC/3%PANI, MC/3%PANI/0.5%Ag and MC/3%PANI/1%Ag films.](image)
4. Conclusion:

MC/PANI blends and MC/PANI/AgNPs composite films were successfully synthesized using the casting reduction method. The linear/nonlinear optical parameters (extinction coefficient, refractive index, reflectance, first order linear optical susceptibility, real and imaginary dielectric constant, and third order nonlinear optical susceptibility) of MC/PANI/AgNPs composite films have been determined using the UV–Vis spectroscopy. The XRD results showed successful fabrications of MC/PANI/AgNPs composite films, with AgNPs crystallite size of 13 nm. The optical energy band gap and the absorption edge of the MC film decreased by the addition of both the PANI and AgNPs. In the meantime, the band tail and the number of carbon clusters of the samples increased with the PANI and AgNPs contents. Moreover, the refractive index and optical dielectric constants changed by increasing both the PANI and AgNPs. On the other hand, the optical conductivity of the prepared films increased by doping the MC polymer by the PANI and AgNPs due to the increased localized stage density in the band structure. The refractive index and the related dispersion parameters of MC, MC/PANI blends and MC/PANI/AgNPs composite films have been calculated and elucidated by using the Wemple-DiDomenico model. By increasing silver content from 0.5% to 1%, the motion of charge carriers and localized charged particles fluctuations produced modifications in the optical dielectric dispersion properties. The results indicate that the prepared films can be considered as promising flexible materials for optical energy applications.

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