Spectroscopic Evaluation of Optical Parameters of a Transition Metal Salt Filled Polymer Material

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ABSTRACT

Transition metal salt, manganese chloride was incorporated into polyvinyl alcohol (PVA) to prepare metal salt filled polymer material (M-PVA) and their optical properties were evaluated. XRD, UV-vis, and FTIR analyses reveal that there is strong interaction between PVA and the manganese chloride salt. From XRD analysis, the inter-chain separation in pristine PVA and M-PVA was found to be 5.62 Å and 4.70 Å, respectively; thus indicating that the packing of polymer chains is more compact under the influence of manganese chloride. Optical band gap of PVA was found as 5.06 eV but such band gap was reduced on incorporation of manganese chloride into the PVA matrix system with corresponding increase in optical conductivity. Spectral evaluation indicates that refractive index of M-PVA decreases faster than that of PVA in the visible range. Abbe Number was found to have decreased on incorporation of manganese chloride into the PVA matrix system indicating increase in optical dispersion in conformity with the trend of increase in dispersion energy ($E_d$). The average interband oscillator wavelength was found close to the respective values of absorption edges.

Keywords: Polymer; Metal salt; Optical material

1. INTRODUCTION

For centuries, almost every civilisation has used light in some form or other for communication purpose. In early 1900’s the British Army developed a signaling device called the Mance Heliograph which allowed instantaneous light communication. Heliographs were used by the British and Australian armies up to the 1960’s in the backdrop of the historical emergence of DRDO in 1958. In 1880, Alexander Graham Bell invented a more scientific light communicating device called a photophone which eventually led to the innovation of fibre optics.

Uses of fiber optics are going to grow in all computer and telecommunication network systems. Military copter, aircraft, tanks are all being tried hard to switch over from metal cables to polymer based fiber-optics technology because fiber-optic cables are lightweight, inexpensive, endowed with high-capacity, and extremely secure to connect military systems and installations.

Optical fibre particularly can afford to maintain high level of reliability and secrecy to handle precious data during economic and financial transactions which is especially relevant in the contemporary context of digital initiatives of various agencies. Fiber-optics technology has widen the scope to even in the areas of community antenna television, cable TV and video services. Its scope is further getting widened with the innovation of multimode and thicker fibre technologies for gastroscoped in medical field.

Polymer is a versatile material for the innovation of devices like micro-lense optical waveguide, optical fiber and allied items. Modern optical fiber (OF) comprises several layers of components viz. core, cladding, polymer coating buffer and a jacket. The design guidelines for one fiber optic system is often unsuitable for other systems where polymer material can play great role to influence the design of optical fibre. Each system may require a particular set of optical parameter with a given range of optical properties. Refractive index and dispersion are two important optical parameters which are intimately associated with the development of optical fibre technology.

Polymers are often doped with dopants to change the refractive index of optical fiber. Recently there is report about the research on the graded-index thermoplastic polymer optical fibre (POF) and of a step-index thermosetting polymer optical fibre where both were doped with rhodamine 6G additive.

In this backdrop, evaluation of optical properties is an important curriculum to generate new design data for optical polymer material system. In this investigation, optical properties of polymer composite material system based on the combination of transition metal salt, manganese chloride and polyvinyl alcohol have been evaluated to enrich the knowledge data base for optical material system.

2. EXPERIMENTAL DETAILS

2.1 Samples Preparation

PVA of Molecular weight of 72000 of Emerck, Germany;
Transition metal salt manganese chloride MnCl₂.4H₂O were received from Merck (India). Pristine PVA as well as MnCl₂ filled PVA samples containing 35 per cent of salt was made by solution casting method⁵-⁷ and were characterised by using analytical tools such as XRD (Bruker D8 Adv. X-ray with Cu Ka, 1.54 Å), FTIR (Vertex 70, Bruker), and UV-Vis spectrophotometers (Shimadzu 2450) and the evaluated optical properties are reported.

3. RESULTS AND DISCUSSION
3.1 Structural Studies
3.1.1 XRD Studies

XRD pattern of pristine manganese chloride showed very sharp peaks (Fig. 1) of its crystalline planes whereas pristine PVA film displayed only one prominent peak at 2θ = 19.81° (Fig. 2(a)) but no such sharp or prominent peaks were noticed in M-PVA (Fig. 2(b)) sample implicating manganese chloride interacted strongly with PVA. Interestingly, in the present study when manganese chloride was incorporated into PVA, this peak at 2θ = 19.81° changed to a broadened peak. This is because of the strong interaction between PVA and manganese chloride. Such strong interaction between PVA and MnCl₂ was also evident from the value of interchain separation (R) estimated from the XRD analysis using Eqn (1)

$$R = \frac{5\lambda}{8\sin\theta}$$

R value for PVA and that for M-PVA was found to be 5.62 Å and 4.70 Å, respectively, thus clearly showing the packing of polymer chains is more compact in the MnCl₂ doped polymer, material M-PVA.

3.1.2 FTIR Studies

The FTIR spectra of pristine PVA and M-PVA samples are shown in Fig. 3. >C=O group is present in PVA as small remnant constituent in the industrial product derived from the hydrolysis of polyvinyl acetate⁵-⁷. Even though the number of >C=O groups in the PVA is less than that of OH groups but even such low amount of >C=O groups could bring about remarkable change in the FTIR spectra in the presence of manganese chloride.

![Figure 2. XRD pattern of (a) PVA and (b) M-PVA.](image)

![Figure 3. FTIR of (a) PVA and (b) M-PVA. >CO absorptions is shown in the box.](image)

Resonating Structure of >CO gr. present in polyvinyl alcohol (PVA).

FTIR spectrum shows the presence of triplet of absorptions (1708 cm⁻¹, 1651 cm⁻¹, and 1593 cm⁻¹) in the pristine PVA sample corresponding to the resonating structure of CO (Structure-I, Structure-II and Structure-III). On incorporation of manganese chloride, the Mn²⁺ seems to have interacted preferentially strongly with Structure-II and Structure-III bearing negative charges on oxygen (δ⁻) such that Structure-I disappeared almost totally as clearly evident from absence of peak at 1708 cm⁻¹ but presence of doublet of absorptions visible at 1646 cm⁻¹ and 1564 cm⁻¹ in the M-PVA sample.

Because of the presence of different OH pattern, the peak in the region beyond 3100 cm⁻¹ is broad. It can be seen that on doping, OH stretching is red shifted. The broadness of such
peak for hydroxyl group is due to the presence of multiple types of OH groups at different conformational positions of the polymer chain.

3.2 Optical studies

3.2.1 UV-visible Spectral Analysis

UV-visible spectra of pure PVA and M-PVA material are shown in Fig. 4. PVA contains single bonds in the main chain and double bond in sporadic short branches caused absorption in the 190 nm - 350 nm region. No structure is observed in the visible region and such absorption is seen very low in this region; this is consistent with transparent nature of the PVA sample in the visible light. Clearly, the absorption bands at 280 nm and 330 nm in PVA was not got visible in M-PVA sample. Absence of bands indicates formation of strong bonding of Mn²⁺ with PVA. In M-PVA, no band is seen in the visible region. The absorption bands at around 280 nm and 330 nm can be attributed to π → π* and n → π* transition of resonating >C=O structures. The edge position for PVA sample is found to be at 222 nm which is red shifted on incorporation of dopant to develop M-PVA.

3.2.2 Optical Energy Band Gap

Optical fibres can guide light in the core by the photonic bandgap mechanism. Inherent material property may have role to influence the engineering property of the derived optical fibre.

Energy gap of materials represent fundamental physical aspect to assign their optical and electronic properties. Optical absorption spectrum can be an important tool for determination of such band gap (Eg). Absorption caused by transitions between valence and conduction band states positioned near the respective mobility edges. And this region is useful for determining the optical bandgap. Mott and Devis developed an equation shown below which relates the absorption coefficient as a function of band gap and photon energy:

\[ (\alpha h\nu) = B (h\nu - E_g)^m \]  \hspace{1cm} (2)

In Eqn (2) B is a constant within the optical frequency range whereas m is used to specify the type of electronic transition and is related to the distribution of density of states. m is an index describing the type of optical transition. Here, α is absorption coefficient of the material, hν is the photon energy and E_g is the band gap energy, m = 2 for indirect allowed transitions and m=1/2 for direct allowed transitions. Thus, (αhν)½ was plotted against independent variable photon energy (hν) to obtain indirect band gap. The plots of (αhν)½ vs. hν are shown in Fig. 5 for (a) pure PVA and (b) for the M-PVA sample respectively to obtain indirect band gap energy. Extrapolation of the linear portion of the curve (shown in Fig. 5) to a point where (αhν)½ = 0 gives the indirect optical energy band gap E_g. Such band gap for pure PVA is found as 5.07 eV and that for M-PVA is 4.96 eV. This provides useful information that addition of MnCl₂ into PVA matrix can bring down the optical band gap energy.

![Figure 5. Plot of (αhν)½ vs Energy for (a) PVA and (b) M-PVA.](image)

3.2.3 Refractive Index

Refractive index (RI) of materials is a fundamental physical parameter to assign the optical and electronic properties of the material system. Materials for optical and optoelectronic items are very much controlled by the nature and magnitude of these basic physical properties. These properties also aid in the performance assessment of band gap engineered structures for continuous and optimal absorption of broad band spectral sources. High RI optical transparent materials are needed in various fields including optical waveguides, ophthalmic lenses, LED encapsulation materials, anti-reflection films and adhesives for optical components. In optical fibre technology, Mode-field diameter (MFD) determines losses due to bending and slicing. And MFD is a function of wavelength, core diameter and the RI difference between the core and the cladding of the optical fibre. Thus, evaluation of RI is quite germane to understand the optical material.

In case of pure organic polymers, the refractive index (RI) value is generally remains in between 1.3 to 1.7, while organic polymer doped with different additives may tailor the refractive index of the polymer matrix. Thus, in this section, we investigated the effect of addition of manganese chloride on the refractive index of the doped PVA sample. The refractive indices (n) for the samples were determined by the following equation:

\[ R = \frac{(n-1)^2 + K^2}{(n+1)^2 + K^2} \] \hspace{1cm} (3)
where $R$ is reflectance and $K$ is the extinction coefficient ($K=\alpha\lambda/4\pi$).

Reflectance data are evaluated from the absorbance and transmittance properties of the material and it obeyed the following relation\textsuperscript{19}.

$$T \ast \exp (A) = (1-R)^2 \quad (4)$$

Refractive index ($n$) and extinction coefficient ($K$) are shown in Fig. 6. RI is closely related to the electronic polarization and the local field inside materials. The behaviour of refractive index and extinction coefficient ($K$) follow the same pattern where both were found to decrease with increase in the wavelength. The electronic polarization increases with frequency\textsuperscript{17,23} therefore, the index of refraction also increases with frequency. The value of the refractive index at 600 nm wavelength for the pristine PVA and M-PVA sample is found to be 1.62 and 1.67 respectively. Such increase in refractive index seems to be due to the increase in density of the film as a result of increase in interatomic packing because of strong interaction between manganese chloride and PVA as observed in the XRD and FTIR analyses discussed in the foregoing Sections 3.1.1 and 3.1.2.

Radial distribution of refractive index is the index profile which determines proper operation within a range of wavelengths. Here the difference between the refractive indices of PVA and M-PVA sample decrease with the increase in wave length of the light till the wave length reaches 720 nm. The difference in refractive indices is zero at 720 nm whereas it appears highest at 400 nm in the visible range of our work. And beyond 720 nm PVA has higher compared to M-PVA (Fig. 6). Thus, the refractive index can be tailored as per the need.

When light travelling with different wave lengths, it bends at different angles and produce dispersion. It causes spreading of light pulse during their travel through the optical fibre. Polymer optical fibre is drawing attention in modern technology as it permits transmission of photonic light over longer distances and at higher data rate than other forms of communication and it plays an important role to ensure high level of security. yet an optical fibre still is not ideal for all situations as it is influenced by different parameters such as dispersion and nonlinearity in lightwave communication technology.

Dispersion is an important parameter by which it controls the widening of the pulse; and it influences the properties of signal while transmitted through a fiber. Different types of optical fibres have different dispersions\textsuperscript{17,18,22-24} and accordingly optical fibres are classified, thus when one considers an optical fibre, the first parameter of interest is through the evaluation of dispersion. It is an important parameter to control the crosstalk during transmission in optical fibre. And it limits the information carrying capacity of a fibre.

The variation of refractive index is nothing but a property called dispersion which can influence the functional role of optical fibre. In this backdrop the dimensionless quantity namely the Abbe number ($AN$) as defined by Eqn (5) is an interesting parameter to apprehend the materials’ optical dispersion property and understand the variation of refractive index with reference to wavelength. A high value of Abbe number indicates low dispersion whereas a low Abbe number signifies high dispersion\textsuperscript{21}. Thus, evaluation of Abbe number is useful step while designing optics items.

$$AN = \frac{(n_d - 1)}{(n_f - n_l)} \quad (5)$$

where $n_r$, $n_o$, and $n_l$ are the refractive indices of the material at the wavelengths of the Fraunhofer F-, D-, and C- spectral lines (486.1 nm, 589.2 nm, and 656.3 nm, respectively).

Here the evaluated $AN$-value for pristine PVA and M-PVA is found to be 12.74 and 5.42 respectively. Thus, the optical dispersion of M-PVA should be higher than that of pristine PVA sample.

Evaluation of Abbe Number is much easier method to have first hand knowledge to apprehend the dispersion characteristics and allied optical properties while intended for designing optical elements. With this background knowledge of Abbe Number analysis, optical dispersion energy parameters, the optical oscillator energy were evaluated and discussed below.

Dispersion of refractive index of the samples with maximum transparency region of wavelength could be described as single oscillator model and can be expressed by Wemple-DiDonneco (W-DD) model through Eqn (6).

$$\frac{1}{n^2 - 1} = \frac{E_0}{E_d} - \frac{1}{E_0 E_d} (hv)^2 \quad (6)$$

where $n$ is the refractive index, $E_0$ is the average excitation energy or oscillator energy gap for electronic transitions, and $E_d$ is dispersion energy\textsuperscript{17,24}.

The values of $E_d$ and $E_0$ can be calculated from the intercept and the slope of the lines by plotting $(n^2-1)^{-1}$ against $(hv)^2$ (Fig. 7).

Interestingly, the value of the oscillator energy gap ($E_0$) follows the same trend as with the optical energy band gap ($E_g$) obtained from Eqn. (2). However, it may be noted that the calculated $E_0$ energy gaps from the W-DD model (Eqn. 6) is found to be higher than that obtained ($E_g$) from Eqn. (2).

Values of different evaluated parameters are summarised in Table 1. It shows that the change in the value of different parameters such as $E_f$, $E_g$, RI, $\lambda$, $\sigma$ follow the same trend even though evaluated from different relationships.

\begin{figure}[h]
\centering
\includegraphics[width=\textwidth]{figure6.png}
\caption{Variation of RI (n) and Extinction coeff. (K) with change of wave length for (a) PVA and (b) M-PVA.}
\end{figure}
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Table 1. Optical parameters of PVA and Manganese chloride filled polymer, M-PVA

<table>
<thead>
<tr>
<th>Parameters</th>
<th>PVA</th>
<th>M-PVA</th>
</tr>
</thead>
<tbody>
<tr>
<td>RI at 600 nm, n_{600}</td>
<td>1.62</td>
<td>1.67</td>
</tr>
<tr>
<td>RI at 720 nm, n_{720}</td>
<td>1.59</td>
<td>1.59</td>
</tr>
<tr>
<td>RI at 800 nm, n_{800}</td>
<td>1.60</td>
<td>1.56</td>
</tr>
<tr>
<td>E_o , eV</td>
<td>5.60</td>
<td>5.38</td>
</tr>
<tr>
<td>E_d , eV</td>
<td>7.86</td>
<td>8.87</td>
</tr>
<tr>
<td>S_o (10^{11}/m^2)</td>
<td>2.86</td>
<td>3.12</td>
</tr>
<tr>
<td>\lambda_o (nm)</td>
<td>220.15</td>
<td>229.21</td>
</tr>
<tr>
<td>Optical conductivity (sec^{-1}) at 600 nm</td>
<td>5.01*10^{10}</td>
<td>12.30*10^{10}</td>
</tr>
</tbody>
</table>

Thus from either of the equations (Eqn 2 or Eqn 6), it reveals that the optical band gap decreases with the addition of manganese chloride in the PVA film. It was reported that the dispersion energy (E_d), is related with the average strength of interband optical transitions.

From the dependence of the refractive index on the wavelength (\lambda), the long wavelength refractive index (n_\infty), average interband oscillator wavelength (\lambda_o) and the average oscillator strength (S_o) for all the films were obtained from the relation using the single term Sellmeir oscillator as follows\textsuperscript{25,26}.

\[
\frac{1}{n^2 - 1} = \frac{1}{S_o \lambda_o^2} - \frac{1}{S_o (\lambda_o^2)}
\]  

(7)

S_o and \lambda_o was obtained by plotting 1/(n^2-1) vs. \lambda^{-2} as shown in Figure 8; from the intercept and slope of the plot, it gives rise to \lambda_o and S_o respectively. It is worthy to note that average \lambda_o values presented Table 1 are close to the respective values of absorption edges as seen in Fig. 4.

3.3 Optical Conductivity

Optical conductivity (\sigma) is one of the powerful tools for studying the electronic states in materials. It explains the optical response and is related to the basic energy band structure of the materials; mathematically it is related to absorption coefficient (\alpha) and refractive index, (\sigma = \alpha n c/4\pi; c is the velocity of light)\textsuperscript{24}. Optical conductivity as a function of wavelength is shown in Fig. 9 where it has dimension of frequency. Here the optical conductivity was found to decrease with increase in wavelength in the visible range. The value of the optical conductivity at 600 nm (600 nm is the average of the visible range (400 nm to 800 nm)), is obtained as 5.01*10^{10} s^{-1} and 12.30*10^{10} s^{-1} for the pure PVA and MPVA respectively. Thus optical conductivity has increased by more than 2.5 times than that of pristine PVA on incorporation of manganese chloride salt in PVA matrix.

The other interesting properties related with refractive index are dielectric constant (\epsilon_r) and dielectric loss (\epsilon_i). And they are determined from Eqns (8) and (9) given below\textsuperscript{27}. Figure 10 shows the variation of dielectric properties with the change in wave length of light where the dielectric properties practically remain constant in the visible range of the spectrum;

\[
\epsilon_r = n^2 - K^2
\]  

(8)

\[
\epsilon_i = 2 n K
\]  

(9)

The real part of the dielectric constant (\epsilon_r) is related to the dispersion and the imaginary part (\epsilon_i) shows dissipative rate of the wave in the films\textsuperscript{27}. Real part and imaginary part of the dielectric constant define loss factor tan \delta. Interestingly, the dielectric properties are very stable in the visible range and near IR region.
4. CONCLUSIONS

PVA and MnCl₂ doped PVA (M-PVA) material can be developed. Spectroscopic analysis reveals that transition metal salt interacts strongly with PVA. The optical studies indicate that the band gap of PVA can be decreased by doping of transition metal salt like MnCl₂ into the PVA polymer. Refractive index value depends on the wavelength of light. Evaluation of Abbe number has provided useful information about dispersion. Decrease in Abbe number implicated increase in dispersion. Such increase in dispersion is actually observed also from the spectral analytical information. These are interesting results that may help develop a better Defence knowledge data base for optical material system.

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REFERENCES


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Contributed in the preparation of samples, conduction of experiments with the help of analytical instruments like XRD, FTIR, UV-Vis spectrophotometer and calculations.

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Contributed in planning, spectroscopic experiments, analysis, interpretive enrichment and also helped in writing of the manuscript.

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