

Optical properties of solution grown PVDF-ZnO nanocomposite thin films

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Abstract The optical properties have been investigated using EDX, UV–Visible spectroscopy and Raman spectroscopy. The nanocomposite formation was confirmed using EDX as well as UV-Visible absorption spectroscopy. Raman study confirms the β phase of PVDF. The UV–Vis spectroscopy accounts for a significant continuous decline in optical band gap and optical activation energy, while increase in refractive index with ZnO nanoparticles incorporation. The results imply that the effectiveness in shielding of UV radiation is due to absorption capacity of ZnO nanoparticles incorporated in PVDF. The increase of absorption in the UV-region of the spectrum is due to the excitations of donor level electrons to the conduction band at these energies. This decrease of band gap may be attributed by presence of unstructured bulk defects. The optical properties of nanocomposite thin films were shown to depend on ZnO content and possessed the most optimal optical properties.

Keywords Thin films · Raman spectroscopy · Optical properties · Nanocomposites · Polymers

Introduction

Novel properties of nanocomposites can be obtained by successfully joined characteristics of parent constituents in a single material. These materials are different as both materials like inorganic nanoparticles and pure organic

polymers with some optical, electronic and optoelectronic properties and extensively used in optical applications like lenses, optical waveguides, optical switches, light emitting diodes and nonlinear optical devices [1, 2].

Nanocomposites materials have drawn much attention because of their interesting optical properties which are different from the individual polymers [3]. Combining inorganic nanoparticles and organic polymer together exhibit unexpected properties and enhances the optical properties of nanocomposites, which greatly differ from that of conventional materials [4, 5]. In the last decades, the study of optical properties of nanocomposites has been stimulated by promising applications. Significant changes in optical properties [6] can be observed in properties of such materials even for very small fraction of the nanoparticles. However, as attractive such nanocomposites may be the process of dispersing nanoparticles in a polymer matrix.

Some of the reports showed that the incorporation of ZnO into organic polymer can enhance the optical and electrical properties of polymers due to an interfacial interaction between the organic polymer and the inorganic nanoparticles [7–9]. Apart from that, ZnO is an engineered nonlinear optical nanomaterial and possessing hexagonal wurtzite structure with exciting optoelectronic technological device applications as sensors, light-emitting diodes (LEDs) and solar cells [10–12]. Thus PVDF-ZnO nanocomposites can be used as a UV-shielding material because of their excellent absorption capability. Lee et al. [13] prepared polyvinyl alcohol–ZnO composite films for enhanced optical properties, and Abdullah and Okuyama [14] developed ZnO–polymer composites by insitu growth of ZnO nanoparticles in a polyethylene glycol (PEG) matrix with enhanced properties.

The optical properties such as refractive index, optical bandgap and optical activation energy could be studied. The structural properties of PVDF-ZnO nanocomposites are investigated by Raman spectroscopy.

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The objective of present work is to investigate the effect of ZnO content on the optical properties of PVDF pristine and PVDF-ZnO nanocomposites with varying concentration of ZnO. The present work is mainly focused on the absorption spectrum, optical band gap, and the optical activation energy of PVDF filled with different filling levels.

Experimental

Materials

PVDF (granular) supplied by Redox (India) and ZnO nanoparticles of size less than 100 nm purchased from Sigma Aldrich, New Delhi (India) have been used in present study. The N, N – dimethylformamide (DMF) (received from Merck India ltd) was used as solvent to prepare the PVDF pristine and PVDF-ZnO nanocomposite thin film samples with different ZnO contents (1–9 wt.%) through incorporation of ZnO nanoparticles as filler into PVDF matrix via solution grown technique. Triethoxyvinylsilane (98 % pure sigma Aldrich) has been used as a coupling agent (binder) for the nanocomposite preparation to avoid the phase separation.

Preparation of PVDF-ZnO nanocomposites

The PVDF of 5 g was dissolved in 100 ml of N, N – dimethylformamide (DMF) and then the solution was kept on magnetic stirrer at 60°C for 6 h. The ZnO nanoparticles according to weight ratio (i.e., 1–9 % (w/w)) was dissolved in 20 ml of DMF and mixed drop by drop in solution of PVDF for preparation of PVDF-ZnO nanocomposite thin film samples. Further, PVDF-ZnO solution was kept on magnetic stirrer for 12 h to become homogeneous then 2 μ l of triethoxyvinylsilane binder is added drop by drop and again stirred for 0.5 h. Now the final solution was kept in sonicator at frequency of 20 kHz for 10 min for better dispersion of ZnO nanoparticles. The prepared solution was poured onto glass plate. The solvent was then allowed to evaporate inside an oven at room temperature for 24 h to yield the nanocomposite thin films. The nanocomposites thin films were easily peeled off from glass plates. The dried films were placed in vacuum of 10^{-5} Torr at room temperature for 48 h to remove the residual solvent. The detail of preparation is reported in our earlier publication [15].

Nanocomposites characterization

EDX (Model EVO-40, ZEISS, AIRF-JNU, New Delhi, India) spectra were recorded to justify the PVDF pristine and formation of PVDF-ZnO nanocomposites. The composition of the prepared films was determined using energy dispersive X-ray analysis (EDX). The EDX scans results

coincide with theoretical percentage values of ZnO in nanocomposites thin films. UV-Vis absorption and transmission studies were carried out using Hitachi U-2800 double beam spectrophotometer in the wavelength range of 200–800 nm with a resolution of 0.5 nm.

The chemical and structural changes as a result of incorporation of ZnO were recorded utilizing FT-Raman spectrometer (Model Varian FT-Raman) in the wave-number range of 400–4000 cm^{-1} available at AIRF-JNU, New Delhi, India.

Results and discussion

Energy dispersive X-ray (EDX) analysis

To determine the chemical composition of PVDF pristine and PVDF-ZnO nanocomposites, the energy dispersive X-ray (EDX) spectra was recorded. Figure 1 (a) & (b) show the EDX spectra of pristine PVDF and 9 wt.% ZnO nanofillers dispersed in PVDF matrix respectively. EDX spectrum confirms the presence of ZnO nanoparticles and the observed atomic percentage (%) is close to the nominal value of ZnO nanoparticles in PVDF. The atomic percentages (%) of the elements present in the pristine and nanocomposite samples are shown in Table 1(a) & (b).

The EDX is showing the presence of zinc, oxygen, gold, carbon, potassium, fluorine and chlorine. The elements were identified as carbon and fluorine originating from the PVDF structure and zinc (Zn) and oxide (O) originating from the ZnO. The presence of chlorine is considered as an impurity during sample preparation. The gold is used as coating material for samples. The presence of Zn and O in EDX spectra as shown in Fig. 1(b) is a direct evidence for formation of PVDF-ZnO nanocomposites.

UV-Vis absorption and transmission spectroscopy

The UV-Visible absorption spectroscopy is a powerful tool for the investigation of optical properties of material. Optical absorption spectra were recorded by UV-Vis double beam spectrometer over the range of 200–800 nm as shown in Fig. 2.

The absorption edge was around 204 nm for PVDF and this sharp absorption edge for PVDF indicates the semi crystalline nature [16]. The PVDF film has very limited UV absorbance, and it is enhanced with the addition of ZnO due to its high-energy gap.

After incorporation of ZnO, the intensity of sharp absorption edges increases and its position gets slightly shifted towards higher wavelength/lower frequency (i.e., Fig. 2). The UV-Visible absorption spectra show the hyper chromic shift and red shift or bath chromic shift in nanocomposite samples.

Fig. 1 **a** EDX spectra of PVDF pristine samples. **b** EDX spectra of PVDF+9wt.%ZnO nanocomposites

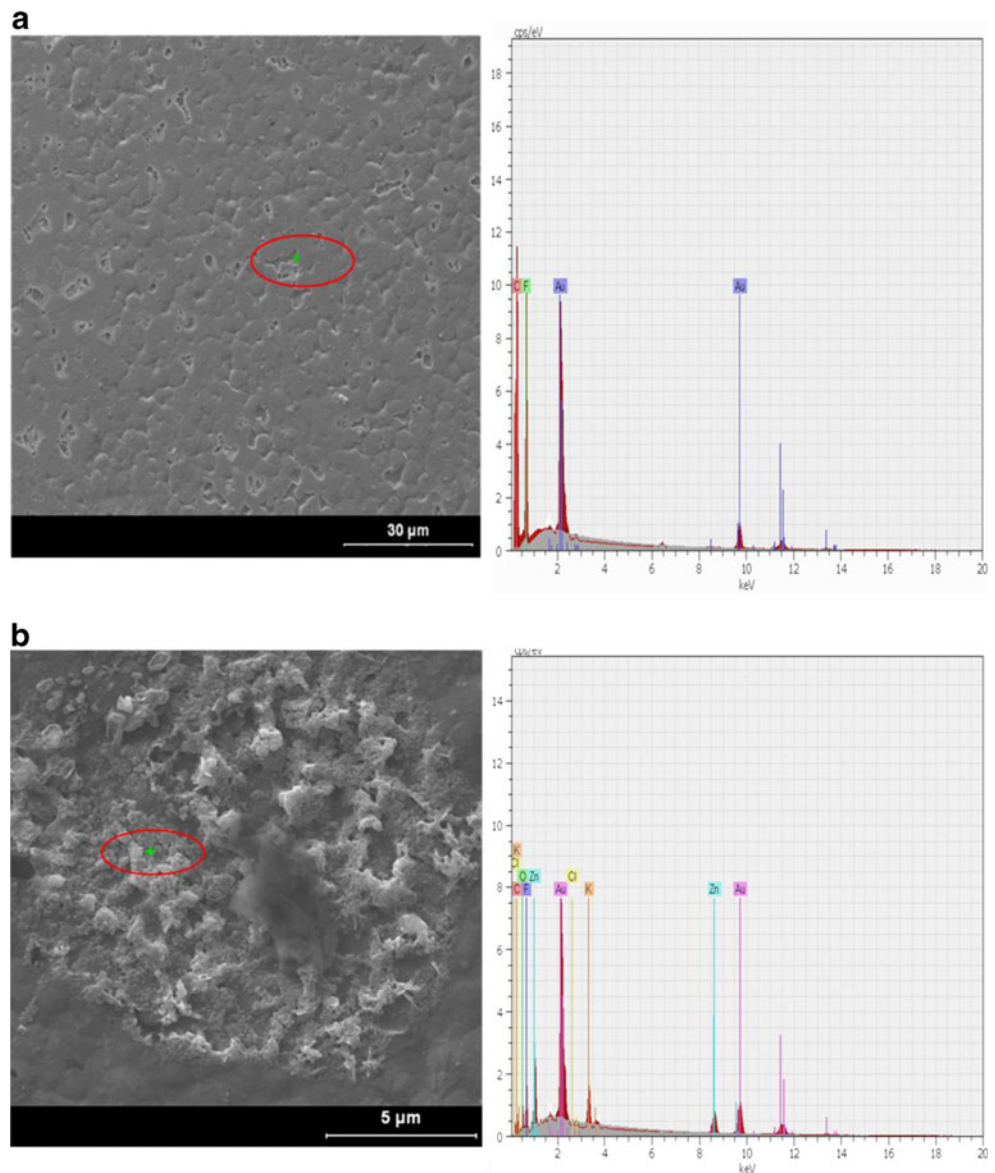


Table 1 **a** The atomic percentage calculated for PVDF pristine. **b** The atomic percentage calculated for PVDF-ZnO nanocomposites

Element	Series	unn. C [wt.-%]	norm. C [wt.-%]	Atom.C [at.-%]	Error [%]
(a) The atomic percentage calculated for PVDF pristine					
Carbon	K-series	27.43	27.43	42.48	8.8
Fluorine	K-series	57.28	57.28	56.07	17.8
Gold	M-series	15.29	15.29	1.44	0.6
(b) The atomic percentage calculated for PVDF-ZnO nanocomposites					
Carbon	K-series	2.64	3.76	9.27	0.4
Fluorine	K-series	25.75	36.71	57.23	3.1
Zinc	K-series	9.10	12.97	5.88	0.3
Gold	M-series	22.78	32.48	4.89	0.9
Chlorine	K-series	0.00	0.00	0.00	0.0
Potassium	K-series	2.14	3.06	2.32	0.1
Oxygen	K-series	7.73	11.03	20.42	1.0

In nanocomposite samples, the optical absorption peak occurs at 376 nm, which is a characteristic UV peak of ZnO nanoparticle [17]. Sharp absorption edges and well-developed excitonic peaks further indicate that incorporated ZnO nanoparticles are rather monodispersed.

The range of UV wavelengths is often subdivided into UV-A (400–315 nm), UV-B (315–290 nm), and UV-C (290–200 nm). ZnO nanoparticles incorporated in PVDF matrix increases the absorption of UV light over the entire characteristics. Higher values of UV-absorbance were obtained in the region between 300–400 nm when ZnO content is increased up to 9 wt.%.

Thus ZnO filled PVDF nanocomposites can be applied to block the UV-A radiation. The results imply that the effectiveness in shielding of UV radiation is due to the UV absorption capacity of ZnO nanoparticles present in the bulk of PVDF. The increase of absorption in the UV-region of the spectrum is due to the excitations of donor level electrons to the conduction band at these energies.

The UV–Vis transmittance spectra of PVDF pristine and PVDF-ZnO nanocomposites are shown in Fig. 3. The transmittance of ultraviolet light was decreased with increasing ZnO contents in nanocomposite films. Lower transmittance observed is due to increase of surface roughness. A significant decrease in transmittance observed for nanocomposite sample is due to Rayleigh scattering caused by ZnO nanoparticles.

For polymer nanocomposites, nanoparticles dispersion, particle size, polymer–interface, surface roughness and refractive index significantly affects the transmittance.

Optical band gap

The common and perhaps most direct method for probing the band structure of the polymer film is to measure its absorption spectra. The absorption coefficient in this region was calculated using the following expression [18]:

$$\alpha(\nu) = 2.303 \left(\frac{A}{t} \right) \quad (1)$$

where A is the optical absorbance and t is the thickness of polymer nanocomposite thin film.

The optical band gap for pristine and PVDF-ZnO nanocomposite films can be obtained by taking into account the linear portion of the UV-Visible spectra at the absorption edge. It is evident from Fig. 2 that all samples exhibit absorption edges which are red shifted with ZnO nanoparticles. The optical absorption edge can be analyzed by the following equation [19]:

$$\alpha h\nu = A(h\nu - E_g)^m \quad (2)$$

where A is a constant and the exponent $m=2$ for allowed

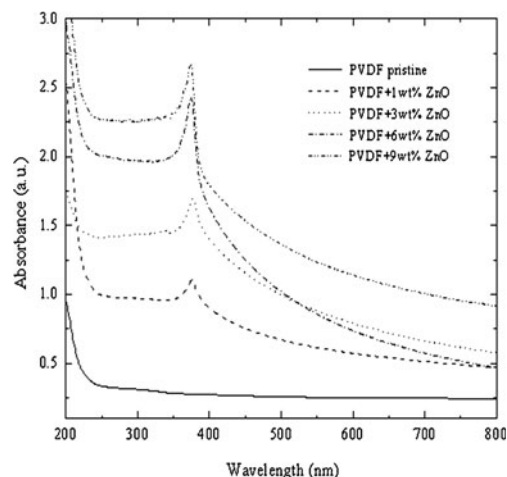


Fig. 2 UV-Visible absorption spectra of PVDF pristine and PVDF-ZnO nanocomposites

direct transition, while $m=1/2$ for allowed indirect transition. Thus, indirect band gaps of the PVDF-ZnO nanocomposite films were determined by Tauc plots:

$$f(h\nu) = (\alpha h\nu)^{1/2} \quad (3)$$

The shift in the absorption edge is correlated with optical band gap, E_g by Tauc's relation. The Tauc plots for PVDF-ZnO nanocomposite films are shown in Fig. 4. E_g is optical band gap energy and A is a constant related to the extent of the band tailing. Plotting $(\alpha h\nu)^{1/2}$ against photon energy ($h\nu$) gives a straight line with intercept equal to the optical band gap for indirect transitions. It has been observed from Table 2 that the optical indirect band gap decreases with increasing the ZnO content, which contributes to states near the band edges, lowering the Fermi level and consequently affecting the energy gap.

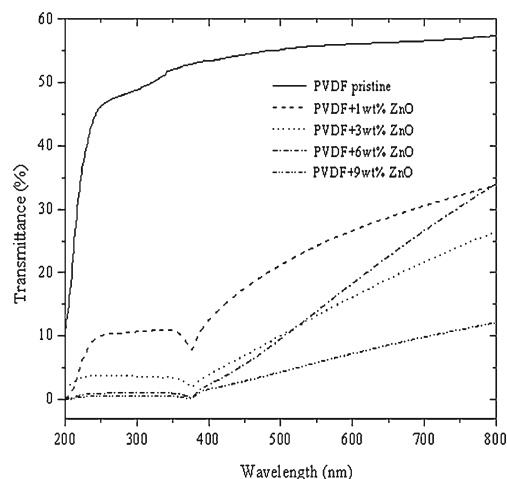


Fig. 3 UV-Visible transmittance spectra of PVDF pristine and PVDF-ZnO nanocomposites

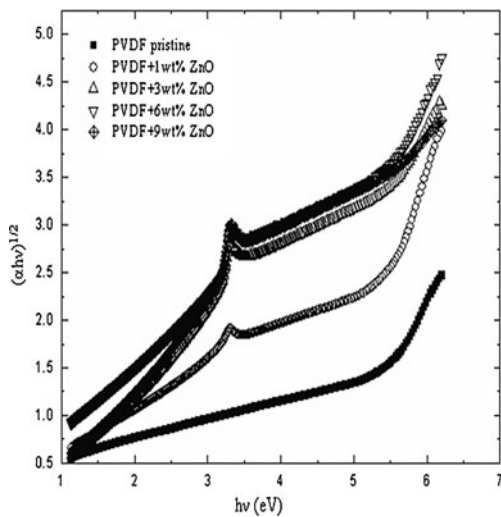


Fig. 4 Tauc plots (indirect band gap) for PVDF pristine and PVDF-ZnO nanocomposites

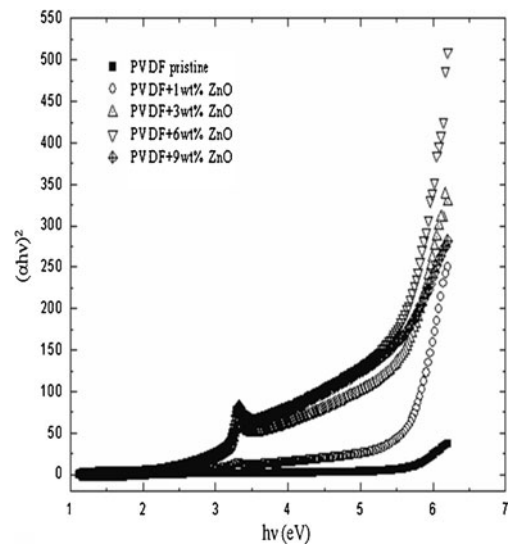


Fig. 5 Plots (direct band gap) for PVDF pristine and PVDF-ZnO nanocomposites

The variation of $(\alpha hv)^2$ with photon energy hv for the PVDF-ZnO nanocomposite film is presented in Fig. 5. Since experimental data do not show perfect linearity, however, we determined best fit line of $(\alpha hv)^2$ as a function of photon energy (hv). The intercepts (extrapolations) of the best fit line on energy axis give the value of direct optical energy band gap. The optical energy band gaps for direct and indirect transitions for this system both decrease as the ZnO content increases, as shown in Table 2. This behavior may be associated with the structural changes occurring after addition of ZnO. Hence the optical band gap (direct and indirect) is found to be compositional dependence. This change which indicates a lowering in energy band gap leads to an increase in the electrical conductivity of the polymer nanocomposite thin film. This decrease in the optical energy values is due to formation of defects and consequently influences the optical properties of materials. The values of the direct band gap are larger than the corresponding values of the indirect band gap (i.e., Table 2). It is observed from Table 2 that optical band gap decreases with increasing

ZnO content. In the studied range of wavelength, the absorption bands are associated with $\pi-\pi^*$ electronic transition. The excitation of π electron requires smaller energy and hence transition occurred in longer wavelength. In the high absorption region where absorption is associated with inter band transition. This decrease of band gap may be attributed to the presence of unstructured defects, which increase the density of localized states in the band gap and subsequently increase in grain size of the film [20].

From the transmission and reflection spectra of the pristine and nanocomposite samples, the refractive index ‘ n ’ of

Table 2 The variation of optical band gap, refractive index and optical activation energy for PVDF pristine and PVDF-ZnO nanocomposites

Concentration (wt% ZnO)	Direct band gap (eV)	Indirect band gap (eV)	Refractive index	Optical activation energy (eV)
0	5.66	4.96	1.51	1.16
1	5.57	4.76	1.56	0.78
3	5.37	4.23	1.62	0.75
6	5.24	3.84	1.69	0.30
9	4.95	3.35	1.71	0.24

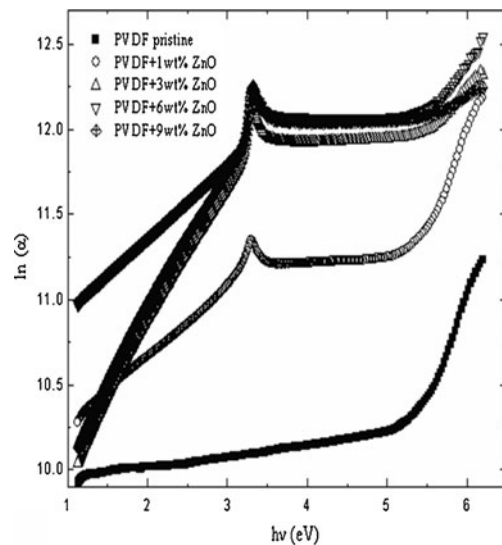


Fig. 6 The logarithmic variation of absorption coefficient ($\ln(\alpha)$) versus photon energy (hv) for PVDF pristine and PVDF-ZnO nanocomposites

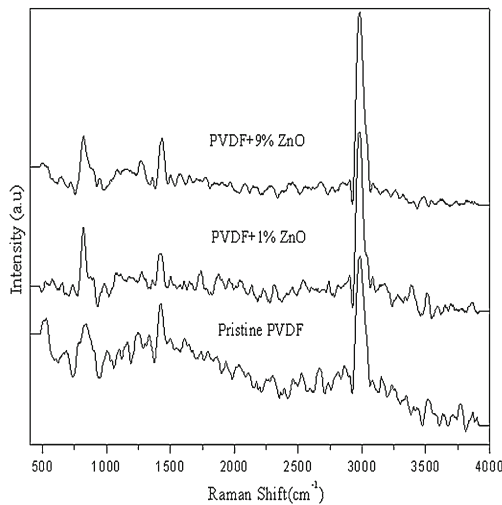


Fig. 7 Raman spectra of PVDF pristine and PVDF-ZnO nanocomposites

these samples was calculated using the following relation [21, 22] and presented in Table 2.

$$R = \frac{(n-1)^2 + k^2}{(n+1)^2 + k^2} \quad (4)$$

where R is the reflectance and k the extinction coefficient, given by the relation,

$$K = \frac{\alpha\lambda}{4\pi} \quad (5)$$

Optical activation energy

The absorption coefficient near the band edge shows an exponential dependence on photon energy and this dependence is given as Urbach rule. The optical activation energy for PVDF-ZnO nanocomposites was determined using Urbach rule [23]:

$$\alpha = B \exp\left(\frac{h\nu}{E_a}\right) \quad (6)$$

Where B is a constant and (E_a), the activation energy. The values of the optical activation energy (E_a) give more detail

about the optical behavior of the pristine and nanocomposites. Figure 6 shows the variation of $\ln(\alpha)$ with the photon energy ($h\nu$) at different content of ZnO for PVDF-ZnO nanocomposites.

The values of the optical activation energy were determined from the slope of the straight lines of these curves. The optical activation energy (E_a) for different compositions are presented in Table 2 and demonstrated in Fig. 6. It was found that the activation energy of nanocomposites decrease with increasing ZnO content. This decrease in activation energy is attributed to the increase in the defects. This defects lead to the formation of lower energy states resulting in the increase in the number of charge carries in the conduction band [24]. The defects are contributed by incorporation of crystalline ZnO nanoparticles in PVDF matrix. The gradual decrease of activation energy with increase in ZnO content confirms the previously obtained decrease in the optical energy gap values.

The optical absorption coefficient just below the absorption edge shows exponential variation with photon energy. It can be seen that the addition of ZnO reduces optical activation energy of PVDF. The decrease of optical activation energy may be due to increase in the crystalline nature of the polymer nanocomposites. It is well known that the shape of the fundamental absorption edge in the exponential region can yield information on the disorder effects [25]. The increase in absorption coefficient is followed with an exponential decay of density of states of the localized states into the gap [26].

Raman analysis

Raman spectra were recorded for the PVDF pristine and PVDF-ZnO nanocomposites thin films with different content of ZnO nanoparticles as shown in Fig. 7. Raman spectroscopy provides more information about the conjugated structure and the chain skeleton of polymers. Raman spectroscopy also yields bands of lower wave number as readily as bands of higher wave number [27].

Thus Raman data provide more spectroscopic information which can not be provided by IR analysis alone. Peak

Table 3 Raman band assignments for PVDF pristine and PVDF-ZnO nanocomposites

PVDF pristine (cm ⁻¹)	PVDF+1wt.%ZnO (cm ⁻¹)	PVDF+9wt.%ZnO (cm ⁻¹)	Assignments
528.49	524.63	505.34	CF ₂ deformation mode
840.96	821.67	821.67	Mixtures of CF ₂ stretching, CC stretching and CH ₂ rocking
1103.28	1087.84	1083.99	CF ₃ symmetric stretching
1249.86	1276.87	1273.01	CF ₂ asymmetric stretching
1423.46	1423.46	1435.03	CH ₂ deformation
2981.94	2981.94	2981.94	CH ₂ Asymmetric stretching

intensity became strong and the full-width at half maximum (FWHM) decreased with increasing ZnO content, which is attributed to the improvement in crystalline nature of PVDF. From Fig. 7, it is clear that there are gradual changes in the intensity of Raman spectra when the ZnO content increases. Employing FT-Raman and near infrared laser excitation avoids most of the fluorescence problems that were seen with conventional Raman. The spectra of the PVDF and PVDF-ZnO nanocomposites have shown much greater fluorescence than other compounds, because PVDF and ZnO are fluorescent material. This is consistent with the tendency shown in the EDX spectra (i.e., Table 1 (a) & (b)). The PVDF film spectra were acquired with short integration times to assess the viability of acquiring Raman images, and thus the Raman signals are smaller in the PVDF and PVDF-ZnO nanocomposite spectra.

The Raman bands at 840.96 cm^{-1} shows the presence of β phase in PVDF film. The intensity of this band increases with increase of ZnO content.

From the Table 3, it is evident that CH_2 asymmetric stretching and CH_2 deformation are mainly from pure modes and they are assigned to the very strong bands at 2981.94 cm^{-1} and strong band at 1423.46 cm^{-1} respectively in PVDF pristine, while in PVDF+9%ZnO nanocomposites a band shifted towards higher wavenumber (i.e., $1423.46\text{--}1435.03$). The CF_2 stretching motions have large change in dipole moment and small change in polarizability [28]. The medium Raman bands at $1297, 840\text{ cm}^{-1}$ are mixtures of CF_2 stretching, CC stretching and CH_2 rocking. The intense Raman lines are due to the symmetric stretching of CC bond [29]. The medium band appears at 528.49 cm^{-1} is mainly composed of the CF_2 deformation mode. The strong Raman band at 1435.03 cm^{-1} in PVDF-ZnO nanocomposites is assigned to the bending vibration of the CH_2 group.

Conclusions

The dependence of the optical properties of the nanocomposites on ZnO content was investigated. The results showed that the nanocomposites would have the most optimal optical properties, viz. high-visible light transparency and high-UV light shielding efficiency. Nanocomposite formation was confirmed by EDX as well as UV-Vis absorption spectra. The composition of ZnO nanoparticles in PVDF increases UV light absorbance, consequently the effectiveness in shielding UV radiation is due to the UV absorption capacity of ZnO nanoparticles incorporated in PVDF. The increase of absorption in the ultraviolet region of the spectrum is due to the excitations of donor level electrons to the conduction band at these energies. The optical band gap for direct and indirect transitions for this system decreases as the ZnO content increases. This

behaviour may be associated with the structural changes occurring after addition of ZnO nanoparticles. The decrease of optical activation energy of nanocomposites is obtained due to addition of ZnO nanoparticles. The decrease in the optical gap could be correlated with decrease of disorder in the network, indicated by optical activation energy. The Raman spectra show the formation of PVDF-ZnO network in nanocomposite thin films.

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