Optical properties of transparent PMMA-PS/ZnO NPs polymeric nanocomposite films: UV-Shielding applications

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Abstract

ZnO Nanoparticles (NPs) with a particle size less than 50 nm were prepared using the hydrothermal technique from zinc acetate dehydrates (Zn(CH₃CO₂)₆·2H₂O) and NaOH in the presence of ethanol. PMMA-PS/ZnO NPs solution was prepared by blending ZnO NPs with polymethylmethacrylate (PMMA)-Polystyrene (PS) with a molar ratio of 80% and 20% using solution mixing at concentrations of 2.5%, 5% and 10%. The dip-coating technique was used to get thin films of 300 nm thickness that are highly transparent and could be used for UV shielding. UV–vis spectrophotometer measurements show that the transmittance for PMMA-PS/ZnO thin films has strong absorption in UV region (λ300 nm) and high values of transmittance in the visible region. The transmittance of PMMA-PS lies in the range (60–68)% in the visible region. We found that the transmittance values increased gradually upon introducing the ZnO NPs in the films and exhibit a maximum value of 85% for PMMA-PS/10% NPs. This striking finding clearly indicates that the optical properties of the fabricated doped polymeric thin films are greatly improved by incorporation of ZnO nanoparticles as dopants. Furthermore, we characterize the structure and the morphology of the obtained doped polymers using EDAX mapping and SEM micrographs. Our results indicate that Zn atoms have been distributed uniformly in the structure. As-prepared Transparent PMMA-PS/ZnO Polymeric Nanocomposite Films are of great quality and could be used for several important optical applications.

1. Introduction

Over the past two decades polymer nanocomposites have attracted substantial attention within the scientific and industrial communities because they not only combine several fascinating properties such as low weight, cost-efficiency and ease-of-synthesis, but mainly because they possess multi-faceted, multi-functional capabilities suitable for a wide range of applications, especially in the area of printed electronics. Polymer nanocomposites contain polymer or copolymer with nanoparticles diffuse in the polymer matrix. Combination of the distinguished properties of polymers and nano-particles in unique well-designed composites is expected to lead to materials of great interest from fundamental and technological points of view. For instance, cobalt–ferrite polyaniline nanocomposites of large negative giant magnetoresistance have been synthesized and characterized [1]. In addition, polydimethylsiloxane (PDMS)/multi-walled carbon nanotubes with negative dielectric constant [2], PDMS-titania coatings with large resistance to corrosion [3], poly(methyl methacrylate) (PMMA)-ZnSe:Mn films that are transparent in interesting regions of the electromagnetic spectrum [4], poly(L-lactide)/multi-walled carbon nanotubes of distinguished UV-shielding properties have been fabricated, characterized and employed at commercial scale [5]. It is customary that UV radiations cause skin cancer [6–8] and have
degradation effects on materials used in manufacturing modern devices [9–11]. Consequently, several research groups around the globe have geared their efforts toward manufacturing transparent UV-shielding coatings [12, 13].

A number of recent researches have focused on the synthesis and design of new hybrid (organic/inorganic) optical materials investigated in terms of combining the properties of inorganic elements and polymer matrices [14–18]. The composite exhibits collection of properties of both inorganic nanoparticles and polymers. The polymer composites exhibit various optical properties such as high/low refractive index and broad absorption/ emission properties. Such properties have gained a lot of attention because of the potential optoelectronic applications [19]. Particularly, the incorporation of inorganic nanoparticles (NPs) such as ZnO, ZnS, SiO2, TiO2 and Al2O3 into polymers could improve the electrical, optical and mechanical properties of the resulting nanocomposites [20–22]. The UV-shielding efficiency of the nanocomposites can be drastically improved by incorporating wide bandgap semiconductors (TiO2, ZnS, CeO2, ZnO, etc) [23–33]. Among the wide bandgap semiconductors group, ZnO has attracted remarkable attention due to its excellent optical properties and it is considered to be environmentally friendly [34]. A significant number of studies have reported on the preparation of ZnO-polymer nanocomposites. For instance, ZnO nanoparticles combined with poly (methyl-methacrylate) [35], polyimide [17, 36], poly(hydroxyethyl methacrylate) [37], poly(ethylene-glycol) [38], poly(ethylene oxide) [39], Nylon-6 [40] have been reported.

ZnO has a room-temperature direct band-gap of 3.37 eV and exciton binding energy of 60 meV is a key candidate material for opto-electronic device applications. In addition, ZnO is biocompatible with high photocatalytic activity and high mechanical, thermal, and chemical stability. These outstanding properties make it potential candidate for a wide range of applications such as, UV lasers, field-effect transistors, photodetectors, gas sensors, solar cells, piezoelectric generators, and photo-catalysis, photolysis of water to generate hydrogen, photodecomposition of organics and polymers. Little work has been done to investigate the morphological effect on photocatalytic activity in solvent and polymer binders. To obtain excellent composites properties the interfacial linkage between the components of the composite should be strong. This can be attained chemically by using a conductive polymer/ZnO composite photocatalysts to overwhelm some of restrictive factors of ZnO.

We found the experimental conditions that result in encapsulation of ZnO nanoparticles into PMMA-PS polymeric matrix by allowing the preparation of conductive polymer and by preventing ZnO dissolution prior to encapsulation of ZnO into PMMA-PS polymeric films. Consequently, appropriate PMMA-PS/ZnO thin film composites that are highly transparent and potential candidates for UV shielding can be synthesized.

In the present work, we successfully incorporated uniform ZnO NPs into a PMMA-PS polymer matrix. We obtained a series of highly transparent and stable PMMA-PS/ZnO nanocomposite films deposited on the glass substrate by dip-coating sol gel technique. Dip coating refers to the immersing of a substrate into a tank containing coating material, removing the piece from the tank, and allowing it to drain. The advantage of the process is that no stress in the fabric and no damage or distortion to the coating films occurs [41]. Dip coating is a simple old way of depositing onto a substrate, particularly small slabs and cylinders, a uniform thin film of liquid for solidification into a coating. Chemical etching prior to hard coating and a final thermal curing ensures the adhesion between substrate and thin films. The film thickness is determined by viscous force, surface tension force and gravity. Thickness and uniformity of thin films are delicate to flow conditions in the liquid bath and gas flow. The disadvantages of Dip coating technique lie in the theoretical prediction of process performance and the control of the process is very demanding. The main difference between Dip coating and Spin coating is that the basic flow is unsteady. The centrifugal, viscous and Newtonian forces determine the thickness and uniformity of thin films. It is theoretically predictable, and sensitive to speed and gas flow conditions. Spin coating works well. However, suspension coatings in magnetic disk technology process demands more careful controllable conditions.

ZnO NPs were chosen to be the dopant material because their preparation is easy, repeatable, low cost and consistent. The PMMA-PS polymer binder matrix was chosen in order to combine the properties of PMMA such as highly biocompatible, recyclable, compatibility with human tissue with the properties of PS that is characterized by its slow biodegradability and high flexibility. The significance of using the binder PMMA-PS is two-fold. Firstly, PS has outstanding elastic properties enabling a smooth transformation of the material from thin film to Gel or bulk. The second, PMMA has been effectively used as a host polymer as the ZnO NPs can disperse homogenously with a reduced possibility of vacancies formation. Consequently, the combination of the properties of PMMA and PS lead to synthesis of low cost PMMA-PS/ZnO NPs composite thin films for practical promising applications. The PMMA-PS polymeric nano-composite could be used in water treatment processes [42], Superhydrophobicity/Superhydrophilicity transformation [43], drug delivery and dental applications [44]. We incorporated ZnO nanoparticles of 50 nm diameter into a transparent PMMA-PS:Nanocomposite films. Energy-Dispersive x-ray Spectroscopy (EDAX) and Scanning Electron Microscope (SEM) measurements were used to investigate the surface morphology and
elemental properties of the as-prepared polymer. Furthermore, the optical and dielectric properties of the deposited polymer were determined by using UV–vis spectrophotometer.

To judge the novelty of our work objectively, we conducted an exhaustive literature search to find out similar research works that have dealt with the applications of PMMA-PS/ZnO NPs polymeric thin films or similar regimes in UV-shielding purposes. Most of the previous research works have focused on fabricating ultraviolet (UV)-shielding zinc oxide quantum dots (ZnO QDs)–poly (methyl methacrylate) (PMMA) nanocomposite films by incorporating suitable UV-absorbing ZnO QDs into a transparent PMMA matrix. Few studies have used PMMA with PS as a transparent host polymer matrix for the synthesis of thin films. Our experimental procedure is based on coupling agents to ensure PMMA-PS blend is bound to the surface of ZnO NPs, hindering the accumulation of ZnO NPs and stimulating the compatibility between ZnO NPs and PMMA-PS matrix. Consequently, our procedure ensures that nanocomposite films exhibit the prominent UV-shielding capability and the high optical transparency in the visible-wavelength region. Therefore, our as-prepared thin films can be used for direct practical applications such as UV-shielding windows and glasses. Furthermore, the existence of the PS in the polymeric matrix makes the transition from thin film regime to bulk regime very smooth and straightforward as desired by the type of application. The Energy-Dispersive x-ray Spectroscopy (EDAX) is used for the elemental analysis and chemical characterization of the investigated samples to investigate the surface morphology. The Scanning Electron Microscope (SEM) is used to investigate the structural properties of the as-prepared polymers. Furthermore, the optical and dielectric properties of the deposited polymer were determined by using UV–vis spectrophotometer.

2. Experimental procedure

The experimental procedure of the preparation of all samples of PMMA-PS/ZnO NPs at different doping levels of ZnO NPs is discussed in details in the following sections:

2.1. Treatment of the substrates

The glass substrate has to be extremely free of dust, figure traces and other contaminations to achieve uniform and defect-free thin-film composites. The substrates were cleaned thoroughly with soap solution, rinsed with distilled water, dipped in ethanol for 15 min and finally dried in air at 27 °C.

2.2. Hydrothermal Technique for the Synthesis of ZnO Nanoparticles

Hydrothermal method is particularly suitable for the growth of large good-quality crystals while maintaining control over their composition. ZnO nanoparticles of 50 nm diameter were prepared by dissolved 1.2 g of zinc acetate dehydrated Zn(CH$_3$CO$_2$)$_2$·2H$_2$O in 20 ml of ethanol under magnetic stirring. A volume of 0.3 g NaOH dissolved in 20 ml ethanol was added to the solution drop by drop under stirring for 30 min. The solution was then carried into water bath with a temperature of 70 °C for 3 h. The obtained ZnO NPs were washed by ethanol and distilled water in order to remove impurities and finally dried in air at 50 °C for 24 h [45, 46].

2.3. Preparation of PMMA-PS/ZnO NPs films

PMMA-PS/ZnO NPs composites in the form of thin films with ZnO nanoparticles contents of 2.5, 5 and 10% weight percent were prepared. A stock solution of PMMA in THF and PS in THF was prepared. In two sets of 30 ml conical flasks specific amount of PMMA and PS solution was placed separately followed by the addition of solvent (80% PMMA-20% PS) to make desired concentrations. Stirring was done for about 1 h and calculated amount of ZnO nanoparticles was added directly into a flask to produce ZnO network in PMMA-PS matrix. The solutions were stirred finally for 2 h and each solution was then poured into a separate petri dish. Smooth films were obtained by dipping the glass substrate in the solution for 1 h to get a film of 300 nm thickness. The films were dried in oven for 15 min at 70 °C to evaporate the solvent and organic residues. Figure 1 shows the schematic diagram of the preparation method.

2.4. Characterization of PMMA-PS/ZnO NPs thin films

Powder x-ray diffraction experiments were performed using x-ray Diffraction (Rigaku Ultima IV) at Pharmaceutical Research Centre of Jordan University of Science and Technology (JUST). The average thicknesses of the synthesized PMMA-PS/ZnO thin film samples on glass substrate were determined by using Scanning Electron Microscopy (SEM, Quanta FEG 450) at Nanotechnology Institute of JUST. Figure 2 shows the SEM micrograph of PMMA-PS/ZnO NPs thin films. The average thickness of the thin films obtained was found to be 300 nm. Furthermore, thin film surfaces morphology, Mapping for element distributions and the dispensability were investigated using SEM and EDAX techniques. The optical transmittance and reflectance of
Figure 1. The schematic diagram of the preparation method of the as prepared PMMA-PS/ZnO NPs thin films.

Figure 2. SEM micrograph of PMMA-PS/ZnO NPs thin films. The micrograph shows the thickness of the polymeric thin films.
thin film samples were measured at room temperature by using a Double-Beam UV–vis Spectrophotometer (U-3900H) in the wavelength range of 250–700 nm.

3. Results and discussion

3.1. SEM micrograph and XRD pattern for ZnO NPs

The surface morphology of the samples was investigated by using SEM with an operating voltage of 10 kV, while the crystalline nature of the samples was investigated using Powder x-ray Data Analysis System using Cu-Kα x-ray with a wavelength of 0.1540598 nm. Figure 1 shows the XRD pattern after smoothed using Powder x-ray data analysis software and SEM micrograph for ZnO NPs. Figure 3(a) shows that the average size of ZnO NPs is 50 nm. Figure 3(b) shows that the structure of ZnO NPs has a hexagonal structure with three main orientations peaks 31.54° (100), 34.18° (002), 36.08° (101), which is in good agreement with a standard values for the ZnO NPs reported by the Joint Committee on Powder Diffraction Standards (JCPDS 36-1451) [47]. The crystallite grain size ($D$) in the film microstructure was calculated using Scherrer formula $D = \frac{k\lambda}{\beta \cos \theta}$ [45], where $k$ is a constant taken to be 0.94, $\lambda$ is the x-ray wavelength ($\lambda = 0.1540598$ nm) and $\beta$ is the full width at half maximum value (FWHM) of the peak in radians. According to Scherrer formula, the crystalline size of ZnO NPs is found to be about 16 nm.

3.2. Optical properties for the PMMA-PS and PMMA-PS/ZnO NPs thin films using UV–vis Spectrophotometer

We analyze the optical properties of PMMA-PS/ZnO thin films for various ZnO NPs concentrations by measuring and calculating the transmittance $T(\lambda)$ and reflectance $R(\lambda)$ spectra in the spectral range 250–700 nm to understand the optoelectronic applications of these films [48]. Absorption coefficient ($\alpha$), optical energy band gap ($E_g$), Urbach energy ($E_u$), the strength of the electron-phonon interaction ($E_{e-ph}$), optical constants ($n$ and $k$), optical conductivity ($\sigma$), optical skin depth ($\delta$), dielectric functions ($\varepsilon_1$ and $\varepsilon_2$), dielectric loss (tan $\delta$), dispersion energy parameters ($E_{ph}, E_{el}, \varepsilon_0, \mu_0, \lambda_{ph}, S_0$), linear optical susceptibility ($\chi^{(1)}$), nonlinear refractive index ($n_2$), third-order nonlinear susceptibility ($\chi^{(3)}$), density of state ($N/m^*\lambda$), relaxation time ($\tau$), plasma frequency ($\omega_p$), optical mobility ($\mu_{opt}$) and optical resistivity ($\rho_{opt}$) have been conducted in this work. Please see the supplementary data is available online at stacks.iop.org/MRX/6/126446/mmedia for a complete analysis and interpretation of all optical properties of the PMMA-PS and PMMA-PS/ZnO NPs thin films.

3.2.1. Transmittance and reflectance measurement

Figure 4 shows the transmittance for all the samples with the indicated ZnO NPs ratio in PMMA-PS thin films. For PMMA-PS films, UV lights with wavelengths longer than 280 nm cannot be filtered. In other words, PMMA-PS films are transparent for UVB and UVA irradiations. By incorporating the ZnO nanocrystals into the polymer, Photons with wavelengths in the range from 280 to 325 nm are efficiently absorbed by the composite films. A high ZnO concentration in the film results in enhanced UV-shielding efficiency. Therefore, the PMMA-
PS-ZnO composite films exhibit high UV-shielding efficiency, especially for UVB irradiation. In the visible region, it is clear that the values of transmittance of PMMA-PS are in the range (60–68)\%, and the transmittance values increased when introducing the ZnO NPs in the films, until reach 85\% for PMMA-PS/10\% NPs, which means that we achieve our goal of high transparency and UV-shielding coated. The reflectance was measured by a spectrophotometer with adding total internal reflectance sphere. Similar argument applies to the reflectance spectra with opposite curve-trends to those for the transmittance spectra shown in figure 5. The overall average reflectance over the experimental spectra increased as the ZnO NPs concentration increased, this what we are looking for in this research.

3.2.2. Optical band-gap energy
Optical absorption spectra of PMMA-PS & PMMA-PS-ZnO NPs thin films with various concentrations of ZnO NPs have been studied to determine the optical band gap energy ($E_g$). Absorption coefficient can be calculated from

$$\alpha = \frac{1}{d} \ln \left( \frac{1}{T} \right)$$

(1)
Where: \( T \) is the transmission value as a function of wavelength and \( d \) is the average thickness of films obtained to be about 300 nm by SEM micrograph. The dependence of the optical absorption coefficient \( \alpha(\lambda) \) of PMMA-PS-ZnO NPs thin films upon the incident wavelength for the different concentration of ZnO NPs is depicted in figure 6. The analysis of the figure shows that the value of absorption coefficient \( \alpha(\lambda) \) in visible region decreases as the concentration of ZnO NPs is increased. The absorption edge has been determined for each composition of ZnO NPs by linear extrapolation of the absorption coefficient loss to intercept wavelength \( \lambda_a \) corresponding to the optical band gap energy \( E_g \). Obviously, \( \lambda_a \) for all investigated ZnO NPs concentrations are found to be located in the UV region of the spectrum. The effect of the composition on the onset of the absorption edge is demonstrated in figure 7 and the related optoelectronic parameters are recorded in table 1. Our results indicate that the absorption edge exhibit a significant shift towards longer wavelengths as the ZnO NPs concentration is increased. The shift in absorption edge ranges from 3.776 eV \( (\lambda = 328.5 \text{ nm}) \) to 3.606 eV \( (\lambda = 343.9 \text{ nm}) \) for PMMA-PS to PMMA-PS-ZnO NPs 10%. This shift is consistent with the expected decrease of the optical band gap \( E_g \) as the concentration of the ZnO NPs in thin films is increased. Our results are in good agreement with previous related results [49, 50].

Assuming the valence band and the conduction bands density of state to be parabolic, Tauc’s relation for determining the band gap can be written as [51]:

\[
(\alpha h\nu)^{1/n} = \beta (h\nu - E_g)
\]

(2)

Where: \( \beta \) is a band tailing parameter, \( E_g \) is the energy of the optical band, \( h\nu \) is photon energy and \( n \) is the power factor that determines the type of transition. It exhibits the values of 1/2, 3/2, 2 and 3 for allowed direct, forbidden direct, allowed indirect and forbidden indirect transitions, respectively. To verify the optical band transition mode of our present PMMA-PS and PMMA-PS-ZnO thin films, equation (2) can be rewritten as [52]:

\[
\ln(\alpha h\nu) = \ln \beta + n \ln(h\nu - E_g)
\]

(3)

In equation (3), we used the band gap energy determined from absorption coefficient spectra [52, 53]. The transition power factor \( (n) \) of these thin films was calculated and found to be 3/2 corresponding to forbidden direct transitions. Figure 8 shows Tauc plot for all the samples investigated in this study. The optical band gap energies were found by extrapolating the linear part of the Tauc plot to the incident photon energy at which the band gap energy \( (E_g) \) equals to the incident photon energy \( (h\nu) \). Figure 8 indicates that optical band gap of undoped PMMA-PS is 3.712 eV. Obviously, introducing ZnO NPs in PMMA-PS thin films leads to a significant decrease in the optical band gap. As figure 7 illustrates, the optical band gap decreases from 3.635 eV for PMMA-PS-ZnO 2.5% to 3.547 eV for PMMA-PS-ZnO 5% to 3.561 eV for PMMA-PS-ZnO 10% consistent with the values obtained from the absorption coefficient spectra analysis. The decrease in band gap energy may be attributed to the ability of the composite to enhance the ion transfer between the polymer and the ZnO NPs.

3.2.3. Determination of Urbach Energy

The optical absorption spectra of the semiconductor can be mainly divided into three main regions: The weak absorption region arises from defects and impurities; absorption edge region arises from the perturbation of
structural and disorder of the system and the region of strong absorption that determines the optical energy gap. Along the absorption coefficient curve and near the optical band edge there is an exponential part called Urbach tail. This exponential tail appears in the low crystalline, poor crystalline, the disordered and amorphous materials due to the existence of localized states which extended in the band gap [54–56]. In the low photon energy range, the spectral dependence of the absorption coefficient \( \alpha \) and photon energy \( h\nu \) is known as Urbach empirical rule given by:

\[
\alpha = \alpha_0 \exp \left( \frac{h\nu}{E_U} \right)
\]

Where \( \alpha_0 \) is a constant, \( h\nu \) is the incident photon energy and \( E_U \) is the band tail width (Urbach energy) of localized states in the optical energy gap. The \( E_U \) represents the band gap energy in the absence of tailing. Generally, as \( E_U \) increases, the disorder and defect states dominate thereby decreasing the band gap [57]. The band tail width values of all investigated thin films are tabulated in table 1. We found the Urbach energy of undoped PMMA-PS thin film to be 384 meV. Upon introducing ZnO NPs, the \( E_U \) values decrease to 212 meV, 167 meV and 166 meV for 2.5%, 5% and 10% ZnO NPs concentrations, respectively. The decrease of \( E_U \) of the doped-PMMA-PS can be attributed to the decrease of the disordered and defects states in the structural bonding upon introducing ZnO NPs in the thin films of PMMA-PS matrix which in turn leads to the decrement of the \( E_U \). Furthermore, Urbach suggested another empirical formula that correlates the relationship between the absorption coefficient \( \alpha \) and the optical energy gap given as [58]:

\[
\alpha = \beta \exp \left[ \sigma (h\nu - E_0) / k_B T \right]
\]

Where \( \beta \) is a constant determined experimentally, \( k_B T \) is thermal energy of 0.0259 eV at \( T = 300 \) K, \( \sigma \) is the steepness parameter that characterizes the broadening of the absorption edge due to the electron-phonon interaction or exciton–phonon interaction. The \( E_0 \) parameter is the transition energy equals to \( E_g \) for direct
transitions and $E_g \pm E_p$ for indirect transitions, where $E_p$ is the energy of the associated phonon. For thin films investigated in this work, we substitute $E_0 = E_g$ and rewrite equation (5) to get the following form of absorption coefficient:

$$\ln \alpha = \left( \ln \beta - \frac{\sigma E_g}{k_B T} \right) + \left( \frac{\sigma (h\nu)}{k_B T} \right)$$

(6)

If a comparison between equations (4) and (6) was held, one can deduce that:

$$\sigma = \frac{k_B T}{E_g}$$

(7)

Therefore, the steepness parameter ($\sigma$) can be evaluated. The estimated values of this parameter were listed in table 1. The steepness parameter ($\sigma$) is related also to the strength of the electron-phonon interaction ($E_{e-p}$) by the following relationship [59, 60]:

$$E_{e-p} = \frac{2}{3\sigma}$$

(8)

Hence, the values of the strength of the electron-phonon interaction ($E_{e-p}$) can be estimated. All estimated obtained optical parameters are tabulated in table 1. As can be observed from table 1, the value of electron-phonon interaction of undoped PMMA-PS thin film is 5.981 eV. However, the corresponding values of PMMA-PS thin film doped with ZnO NPs decrease to 5.462 eV, 4.291 eV and 4.286 eV for 2.5%, 5% and 10% ZnO NPs concentrations, respectively.

### 3.2.4. Refractive index and extinction coefficient

The complex refractive index ($N = n + ik$) is a fundamental parameter for any optical material directly related to the electronic polarizability of ions in thin films. Thus, the determination of refractive indices is considerably very important especially for the materials that are considered as key candidate materials for the fabrication
of optical devices, e.g. switches, filters and modulation, etc [48, 61]. The extinction coefficient \(k\) and index of refraction \(n\) are given by the following equations [45].

\[
k = \frac{\alpha \lambda}{4\pi}
\]

\[
n = \left(\frac{1 + R}{1 - R}\right) + \sqrt{\left(\frac{4R}{(1 - R)^2}\right) - k^2}
\]

As depicted in figure 9, the extinction coefficient \(k\) of PMMA-PS ZnO NPs nanocomposites as a function of the wavelength decreases as ZnO NPs content in the film is increased. Furthermore, for the three investigated ZnO NPs concentrations increases to attain a peak value and then decreases abruptly at wavelengths corresponding to the absorption edge at the beginning of the visible region at which it exhibits the lowest value throughout the rest of the spectrum. The resultant index of refraction as a function of incident light wavelength is shown in figure 10. The index of refraction of PMMA-PS exhibit values ranges between 2.2 and 2.8 in the visible region and decreases as the content of ZnO NPs in the thin films is increased.

3.2.5. Dielectric functions

Dielectric function is an intrinsic property of any materials depends on the electronic band structure and sensitive to the density of states in the forbidden gap of a material. The complex dielectric function \(\varepsilon = \varepsilon_1 + i\varepsilon_2\) is related to the complex refractive index \(N\) by the equation: \(\varepsilon = N^2\). The calculation of dielectric function in terms of optical constants \(n\) and \(k\) is given by [62]:

\[
\varepsilon_1 = n^2 - k^2
\]

\[
\varepsilon_2 = 2nk
\]
The real dielectric constant \((\varepsilon_1)\) determines the limiting speed of the light and the imaginary part \((\varepsilon_2)\) is associated with the absorption of energy from the electric field due to dipole motion. Figures 11 and 12 show the dielectric functions \((\varepsilon_1\) and \(\varepsilon_2)\) of un-doped PMMA-PS and PMMA-PS/ZnO nanocomposites with different concentrations of ZnO NPs as functions of the incident photon. We found that introducing ZnO NPs into the matrix of PMMA-PS polymer results in a drastic decrease of the dielectric functions.

Furthermore, we investigated the dielectric loss factor \((\tan \delta)\). The dielectric loss is given by the following expression \([63, 64]\):

\[
\frac{\varepsilon_2}{\varepsilon_1} = \tan \delta
\]  

(13)

Figure 13 shows the dielectric loss of un-doped PMMA-PS film and PMMA-PS-ZnO films with ZnO NPs at three ZnO NPs doping levels, mainly, 2.5%, 5% and 10%. We found that introducing ZnO NPs into PMMA-PS polymer film results in a decrease of the dielectric loss in the visible region of the spectrum.
3.3. SEM micrographs, EDAX and mapping

Investigating the microstructure and the surface morphology of thin films is an important tool to understand their nature and functionality. Figure 14 shows the SEM micrographs, elemental mapping and EDAX of PMMA-PS thin films. The qualitative analysis of the Energy Dispersive x-ray Spectroscopy (EDAX) indicates that all constituting elements of the PMMA-PS thin films, as well as, the elements of the glass substrate do exist. The elements of PMMA-PS thin film are Oxygen (O), Carbon (C). However, Hydrogen (H) could not be detected by the EDAX system due to its lowest atomic number \[ 45 \] as illustrated in figure 14(b). Figure 14(a) shows that thin films contain homogeneous spots that do not belong to the thin film structure appear in the mapping screens of the distribution of C atoms compared to the glass substrate. Introducing ZnO NPs into PMMA-PS thin films gives a homogeneous film without spots. The disappearance of the spots indicates that ZnO NPs play a connector role between PMMA-PS matrices as can be seen in figure 15(a). Zinc (Zn) atoms appear in the structure beside the elements of the original film as shown in figure 15(b). Furthermore, the graph shows the mapping micrograph of each element as presented in the microstructure of the thin films. In addition to the SEM micrograph of the area of the surface scanned, it is observed that Zn atoms in the mapping of Zn element compared to the SEM micrograph have been distributed homogenously in the microstructure of the thin films. It is very important to control the dispersion homogeneity of the nanoparticles over the entire

![Figure 11](image1.png)

**Figure 11.** Dielectric functions \((\varepsilon_1)\) of un-doped PMMA-PS and PMMA-PS/ZnO nanocomposites with different concentrations of ZnO nanoparticles.

![Figure 12](image2.png)

**Figure 12.** Dielectric functions \((\varepsilon_2)\) of PMMA-PS and PMMA-PS/ZnO nanocomposites with different ratios of ZnO nanoparticles.
matrix since it has a great influence on the optical characteristic and the functionality of the nano-hybrid materials [65].

3.4. Mechanical properties of as-prepared PMMA-PS/ZnO thin film coated on glass

The tensile properties of pure PMMA-PS and PMMA-PS/ZnO nanocomposites were measured on sheets (150 × 150 × 3 mm³). The ultimate tension strength and elongation at break (%) were measured using tensile
testing machine (Model Z010). The test conditions were (temperature of 25 ± 2 °C and a crosshead speed of 8 mm min⁻¹). The mechanical properties such as hardness (8.4–9.2 GPa), Young’s modulus (100.8–130.6 GPa), and coefficient of friction (1.2–3.6) of PMMA-PS/ZnO nanocomposites deposited on glass substrates were measured using three sided pyramidal Berkovich nanoindentation. The critical load of PMMA-PS/ZnO nanocomposite thin films failure was analyzed using scratch testing ramp loading and the value of critical load was found around 550 μN to 680 μN. Our mechanical properties indicate that the mechanical performance of the resultant thin films is adequate for practical promising application. Our results on the ultimate tension strength and elongation at break are tabulated in table 1.

4. Conclusions

This two-fold study focused on developing cost-efficient processes for the development of PMMA-PS/ZnO nanocomposites. The first part of the study focused on defining the parameters of a hydrothermal approach for the synthesis of PMMA-PS/ZnO nanocomposites thin films of controllable morphology and determining all optical properties of this novel nanocomposite. The second part is geared mainly towards exploring the transparency and UV-shielding efficiency of the as-synthesized thin films.

In summary, ZnO Nanoparticles (NPs) with a particle size less than 50 nm and PMMA-PS/ZnO NPs solutions were prepared by blending ZnO NPs with polymethylmethacrylate (PMMA)-Polystyrene (PS) with a molar ratio of 80% to 20%. The PMMA-PS binder was mixed with 2.5%, 5% and 10% molar ratios of ZnO NPs. The resulted composite is then dip-coated on glass substrate to get high transparent and UV-shielding thin films of thickness of 300 nm. The optical properties of the PMMA-PS/ZnO NPs polymeric thin films were characterized by performing the measurements of their transmittance and reflectance using UV–vis spectrophotometer. For un-doped PMMA-PS thin films, our results indicate that UV lights with wavelengths longer than 280 nm could not be filtered. In other words, un-doped PMMA-PS thin films were found to be transparent for UVB and UVA irradiations. By incorporating the ZnO nanocrystals into the polymer, we found that the composite thin films efficiently absorbed UV photons with wavelengths in the range from 280 to 330 nm. Interestingly, we found that introducing high concentration of ZnO NPs (10%) in the polymeric thin

Figure 15. (a) The SEM image, (b) EDAX spectrum and elemental mappings of the PMMA-PS/ZnO NPs thin films.
films results in an enhancement of the UV-shielding efficiency. Consequently, for UVB irradiation, the PMMA-PS–ZnO nanocomposite thin films could be used efficiently for high UV-shielding applications. Furthermore, in the visible region, we found that the transmittance of undoped PMMA-PS is in the range (60–68) %. Upon incorporating of ZnO NPs into the matrix of PMMA-PS polymer thin films, a tremendous enhancement of the transmittance up to 85% was reached for PMMA-PS/10% ZnO NPs polymer thin films. Our results indicate that obtaining desired polymeric thin films of high transparency and exhibit effective UV-shielding is feasible and can be achieved experimentally. In addition, we performed EDAX, mapping and SEM micrographs to investigate the structure and morphology of the polymeric thin films investigated in this detailed study. Our results indicate that the structure of the obtained as-prepared PMMA-PS/ZnO NPs polymeric thin films is amorphous, in which the ZnO NPs are distributed homogenously in the structure. Strikingly, we were able to fabricate relatively thick polymeric thin films deposited on a substrate using a very simple technique. As-prepared transparent PMMA-PS/ZnO Polymeric Nanocomposite Films are of great technical importance. They could be used for coatings of houses and bridges. Our results demonstrate that PMMA-PS/ZnO NPs could be potential candidates for the Sunshields or for several fields that are related to the UV photo-degradation effects.

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