Near IR reflectance characteristics of PMMA/ZnO nanocomposites for solar thermal control interface films

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Abstract

NIR reflectance efficiency of poly(methyl methacrylate) (PMMA) polymer matrix composites reinforced with morphologically varied nano ZnO has been studied and reported. Nanocrystalline ZnO was prepared via reflux and microwave heating methods involving polyethylene glycol (PEG 300), polyvinylpyrrolidone (PVP) and cetyltrimethylammonium bromide (CTAB) capping agents. The techniques produced different ZnO morphologies like 1D nanosheets, flakes, rice shaped grains, unidirectionally grown nanoneedles and spherical nano clusters depending upon the usage of capping agents. 0.1 wt% of nano ZnO was dispersed in PMMA matrix to fabricate PMMA/ZnO nanocomposite films of thickness 0.04 mm through solution-casting technique. NIR reflectance was measured and correlated with ZnO morphology and its particle size. Neat PMMA was highly transparent to NIR waves with only 2% reflectance. When ZnO was introduced, the NIR reflectivity increased to ~55% at a wavelength of 1100 nm. PMMA/ZnO nanocomposite sheet lost transparency to visible light with nano ZnO which became >90% transparent when polyurethane (PU) resin was introduced as a ‘co-filler’. This PU modified PMMA/ZnO nanocomposite exhibited 55% NIR reflectivity at a wavelength of 810 nm. This study confirms that in addition to the ZnO particle size, the morphology also plays significant role to obtain high NIR reflectivity property. In this work, ZnO nanosheets morphology obtained with PEG 300 capping in microwave technique was found to have better NIR reflectance compared to other morphologies. This study is very useful in designing PMMA based multifunctional, UV/NIR shielding solar thermal control inter layers for any glass and polymer based sandwich structures.

1. Introduction

Reinforcement of nanodimensional TiO2, SiO2, Al2O3, ZrO2, CNT, graphene, etc., in industrial polymer matrices has been steadily increasing for developing functional composites and interface structures [1–3]. Such nanocomposites offer attractive properties like resistance against UV radiation, thermal insulation, EMI shielding, antiglare and also scratch resistant. Energy saving, eco-friendly building design and constructions demand these kinds of advanced functional materials to cut the cost towards maintenance and electricity usages. Optically transparent, interphase films and multilayer coatings that can control the heat and light are particularly important in recent years because of drastic rise in overall atmospheric air temperature due to CO2 emissions [4]. Near IR rays in solar radiation (NIR, wavelengths 700–2500 cm−1) are generally termed as ‘heat rays’ because they carry heat energy to generates radiant heat in buildings when it is transferred through conventional glass windows and transparent polymer roofing structures. Polyurethane, polypropylene and polycarbonate polymer sheets are used as roofs and partition walls in buildings. Unfortunately, normal glass and most of these polymers have very poor NIR reflectance quality. Against this back drop, the development of an interface capable of superior NIR shielding for heat control is highly demanding [5]. Semiconducting metal oxides preferably tin oxide, indium tin oxide (ITO), antimony tin oxide (ATO), aluminium oxide (Al2O3), zinc oxide (ZnO), titanium dioxide (TiO2), or a mixture thereof is earlier reported in the literature for obtaining NIR reflecting transparent coatings [6–8]. Such nanosized metal oxides have a regular structure whose equal intermolecular spaces block a large portion of light in the infrared region due to the presence of metal bonds. Composite structures made out of a material with high solar reflectance (ability to reflect sunlight) and high thermal emittance (ability to radiate heat) stay cool in the sun, which in turn reduces the demand for usage of air-conditioners and thereby lower the emission of CO2 and the use of electrical energy. Polymethyl methacrylate (PMMA), a versatile glassy polymer, possesses excellent toughness, stiffness and transparency to visible
light. PMMA polymer has very low thermal conductivity (−0.0012 cal/(s cm K)), which makes it a candidate for thermal-control interface material [9]. As one of the most versatile II–VI semiconductors, ‘zinc white’ [ZnO] is a promising candidate for solar reflectance [10]. It is nontoxic, low cost, and chemically stable towards air and moisture and is less expensive. ZnO has been well known for its multifunctional properties like antibacterial/antifungal and hydrophobic functional properties [11]. Incorporation of NIR shielding nano ZnO in PMMA polymer matrix produces functional nanocomposites which can be a better way to make effective solar thermal control interface structures. ZnO/PMMA exhibits an ensemble of properties of its constituents, and ultimately offers themerothermically stable, UV–NIR shielding multifunctional hybrid materials. Such UV/NIR shielding nanocomposite films and layers find applications in fabricating sandwich glass panels, glazed roofs and active functional-fillers in high performance paints.

In the present work, bulk nano ZnO was synthesized first by reflux and microwave methods using polyethylene glycol 300 (PEG 300), polyvinylpyrrolidone (PVP), N-cetyl-N,N,N-trimethylammonium bromide (CTAB) capping agents. The end products were characterized for phase purity, particle size, morphology and UV/NIR optical properties. Morphologically varied nano ZnO was subsequently employed for fabricating ZnO/PMMA and ZnO/PMMA/polyurethane (PU) nanocomposite films. The NIR reflectance properties of these films were studied and correlated with ZnO morphological features.

2. Experimental

2.1. Materials and methods

Zinc acetate dihydrate ([Zn(CH3COO)2]·2H2O, Merck, India, 99%) and sodium hydroxide (NaOH, Merck, India, 99%) were used as chemicals. Polyvinylpyrrolidone (PVP, SD fine chem.), polyethylene glycol 300 (PEG 300, Merck), N-cetyl-N,N,N-trimethylammonium bromide (CTAB, Analytical Rasayan) were selected as capping agents. Poly(methyl methacrylate) (PMMA, Sigma-Aldrich, India) and polyurethane (PU, commercial paint Sleek) were employed as polymers. Dichloromethane (DCM, Analytical Rasayan) and ethanol were utilized as solvents. All chemicals were used without any further purification. Double distilled water was used as a medium for particle synthesis.

Zinc oxide nanostructures were synthesized by two different methods: reflux and microwave-assisted nucleation and growth processes. The typical procedures followed in these are described below.

2.2. ZnO nanoparticles via conventional reflux method

In reflux method, 0.1 M zinc acetate dihydrate ([Zn(CH3COO)2]·2H2O) solution was prepared in 200 mL distilled water. To this solution, 15 mL of PEG 300 was added drop wise under constant stirring. The reactant mixture was stirred well until it became chemically homogeneous solution. It was then refluxed at 80 °C for 2 h. After 2 h the reaction flask was cooled to ice cold temperature. About 1 M NaOH solution was then added drop wise under vigorous stirring until a milky white precipitate was formed (pH ~ 10). The molar ratio of Zn(CH3COO)2·2H2O to NaOH was fixed as 1:10. The final white product was separated by centrifugation, subsequently washed several times with distilled water and finally with ethanol, and then dried at 60 °C in electrical oven for 24 h. By changing PEG 300 with PVP and CTAB, the nano ZnO was prepared under the same experimental conditions. In PVP and CTAB capping, 20 mL and 2 g were added respectively to the 0.1 M Zn2+ precursor solutions.

2.3. ZnO nanoparticles via microwave method

The preparative conditions were maintained similar to reflux technique. Instead of reflux, in microwave method 0.1 M zinc acetate dihydrate ([Zn(CH3COO)2]·2H2O) solution containing 15 mL PEG was subjected to microwave energy at a power level of 300 W for 30 min. Once the microwave irradiation was complete, the Zn(OH)2 precipitate was cooled to ice cold temperature in an ice bath. White product thus obtained was separated by centrifugation, washed with distilled water and ethanol, finally dried at 60 °C in an oven to collect ZnO nanoparticles. The experiment was repeated with 20 mL PVP and 2 g CTAB to obtain ZnO particles with different morphologies. The possible chemical reactions involved in the nucleation and growth of nano ZnO particles in reflux and microwave heating is represented as follows:

\[
\text{ZnOAc}_2 + 2\text{NaOH} = \text{Zn(OH)}_2 + 2\text{NaOAc}
\]

\[
\text{Zn(OH)}_2 + 2\text{OH}^- \rightarrow \text{Zn(OH)}_4^{2-} \quad \text{(intermediate step)}
\]

\[
\text{Zn(OH)}_2 \rightarrow \text{ZnO} + \text{H}_2\text{O} \quad \text{(reflux or microwave)}
\]

The ZnO prepared under microwave and reflux techniques using PEG, PVP and CTAB capping agents were designated as MW_Uncapped, MW_PVP, MW_PEG and MW_CTAB and Ref_Uncapped, Ref_PVP, Ref_PEG and Ref_CTAB respectively.

2.4. Fabrication of ZnO/PMMA nanocomposite films

Nano ZnO/PMMA composite films were prepared by the solution-casting technique [12]. About 10% PMMA solution was prepared in dichloromethane as solvent. About 0.1 wt% nano ZnO was also separately dispersed in dichloromethane. Both solutions were mechanically at room temperature until a viscous and a homogenous ZnO/PMMA solution was formed. The solution was transferred to glass mould and allowed to dry in normal room temperature. After a particular period of time, a free standing ZnO/PMMA sheets were formed. Finally they were removed from the glass mould and used for further characterizations. Using polyurethane, one set of ZnO/PMMA/PU films was also prepared for any comparison.

2.5. Characterizations

As-prepared nano ZnO particles were structurally characterized by X-ray diffractometer using X’Pert Pro, Philips X-ray diffractometer equipped with CuKα radiation (λ = 1.5406 Å) in the 2θ range 10–80° with 0.02° scan increment. The FTIR spectra were recorded with a Nicolet Magna 560 spectrophotometer in the wavelengths range 4000–400 cm−1 using the KBr pellet technique. The particle size distribution was measured using the DLS technique, a Zetasizer 3000 H (Malvern Instruments, Worcestershire, UK). ZnO particulate colloids were prepared in aqueous media by dispersing 0.01 wt% ZnO and subsequently de-agglomerated through ultrasonication for 15 min before the size measurements. The morphology of the ZnO samples was examined using a scanning electron microscope (model: SEM-JEOL 5600 SL). Further, the transmission electron microscopy (TEM) images of the ZnO samples were also recorded using a JEOL, 100 CX apparatus. A drop of capped colloidal ZnO particles obtained from the microwave as well as reflux methods were dispersed ultrasonically in acetone medium. It was carefully deposited by drop-casting on the TEM grid. After evaporation of the solvent, the surface was examined using TEM. The optical properties of the ZnO samples were monitored by a UV/vis recording spectrophotometer, Shimadzu (UV 240 IPC), at a wavelength ranging from 200 to 800 nm. The near-infrared reflectance of the ZnO reinforced PMMA and also PMMA/PU/ZnO
nanocomposite films were measured by a UV–vis–NIR spectro-photometer (Shimadzu, UV-3600 with an integrating sphere attachment) using poly(tetrafluoroethylene) (PTFE) as reference. The typical experimental procedure as described in Ref. [13] was followed for the diffuse reflectance measurements in UV–vis–NIR regions. Firstly, a set of powder sample holders filled with PTFE was mounted on both the sample and reference sides of the exits port of the integrating sphere to set the baseline measurements. Secondly, the sample holder was filled with nano ZnO prepared in this work and the optical measurements were performed in the 700 nm to 2500 nm range for determining the reflectance property.

3. Results and discussion

In Fig. 1 the powder X-ray diffraction results for different nano ZnO are given. In both reflux and microwave heating techniques, the ZnO samples show excellent crystallinity. All the diffraction peaks are very sharp indicating the high degree of crystallinity. The diffraction lines are consistent with the standard values reported for the polycrystalline ZnO [JCPDS card no.: 36–1451] providing clear evidence on the presence of hexagonal wurtzite-type ZnO with a space group of $P6_3/mmc$ [14]. The X-ray diffraction pattern shows that all the standard ZnO peaks correspond to (100), (002), (101), (102), (110) and (103) crystal planes. No diffraction peaks for any un-reactive ZnAc$_2$·2H$_2$O, Zn(OH)$_2$ and any other vibrations. But in PVP capped ZnO, the C=O and O–H stretching vibrations of the capping molecules adsorbed on the ZnO surface. In the case of pure PVP [18], the strong peak at 1654 cm$^{-1}$ is assigned to the stretching vibration of carbonyl group and the peak at 1292 cm$^{-1}$ is attributed to C–N vibrations. But in PVP capped ZnO, the C=O stretching is shifted to $\sim$1675 cm$^{-1}$ confirming the capping effect. The alkyl C–H stretching vibration of PVP is seen at 2914–2919 cm$^{-1}$ whereas the pyrrolidine ring related bands exist at $\sim$1426 cm$^{-1}$. The characteristic stretching mode of Zn–O vibration bands normally seen at low absorption peaks in the range 415–448 cm$^{-1}$ [19]. In this study, the IR vibrational bands show significant differences in the peak values with respect to the given processing conditions of capping, microwave and reflux synthesis. The characteristic stretching bands of ZnO appear at 415, 437, 472, and 479 cm$^{-1}$ depending upon the synthesis and capping agents. It provided further insight that even though a highly crystalline ZnO was formed at all the given synthesis conditions; they may have crystallographically different growth patterns and orientations leading to morphologically tuned ZnO particles with various surface features [20]. This had been further verified with SEM

The particle size distribution for the ZnO prepared via microwave and reflux methods is shown in Fig. 2. The microwave technique resulted in a very wide size distribution for various capping agents compared to its counterpart, reflux method. The cluster size varied between 50 and 400 nm. The peak maximum represents the mean particle diameter of nano ZnO. The capping effect was distinctly noticed in microwave synthesis. ZnO prepared without capping produced particles with an average size 250 nm, whereas the particles obtained with PVP and PEG capping agents had shown size less than 180 nm. Although the PEG capping showed size controlled ZnO particles, the size distribution was not very narrow. However, in these cases better control over crystal growth was seen compared to CTAB. In conventional heating, heat transport by conduction was the driving force that controls the mass transfer and deciding the ZnO crystal growth. In microwave, the bulk electric heating caused by the reversible dipole movements that happen at molecular level act as a driving force [16]. Water is a highly polar medium and microwaves readily interact with water molecules. As a result of kinetically strong reversible dipole interactions, the molecular heating takes place. The rate of thermal gradient in the reaction vessel depends on the microwave power. The thermal gradients occurred due to dipolar interactions vary with dielectric nature of the capping molecules. It strongly influenced the particle growth and the extent of ZnO clustering, finally resulting in wide size variations. In microwave synthesis, the samples MW_PVP and MW_PEG showed less particle size because of their stable complexation with Zn-precursor, and differential rate of nucleation [17]. In the reflux method, a narrow size distribution was successfully obtained. In this case, only a mild reflux temperature condition was employed. However, the reflux time given for the complete conversion of Zn-precursor to ZnO was longer. Unlike microwave heating, the mild heating highly controls the abnormal ZnO growth. However, as a result of prolonged time, the crystals had grown excessively to the size between 200 and 250 nm for various capping agents.

The uncapped and capped ZnO nanoparticles synthesized using microwave and reflux methods were validated by the vibrational spectroscopy for understanding the nature of the chemical bonding in the metal oxide. The FTIR spectra of the PEG 300, PVP and CTAB capped nano ZnO and uncapped counterpart are shown in Fig. 3 for the microwave and reflux methods. In FTIR, the broad vibrational bands in the range 3342–3389 cm$^{-1}$ represent the O–H stretching which was expected because of aqueous synthesis and mild drying conditions. In PVP and PEG capped samples, the O–H stretching was more prominent because of their more hydrophilic nature. The peaks at $\sim$1400–1600 cm$^{-1}$ indicate the C=O and O–H stretching vibrations of the capping molecules adsorbed on the ZnO surface. In the case of pure PVP [18], the strong peak at 1654 cm$^{-1}$ is assigned to the stretching vibration of carbonyl group and the peak at 1292 cm$^{-1}$ is attributed to C–N vibrations. But in PVP capped ZnO, the C=O stretching is shifted to $\sim$1675 cm$^{-1}$ confirming the capping effect. The alkyl C–H stretching vibration of PVP is seen at 2914–2919 cm$^{-1}$ whereas the pyrrolidine ring related bands exist at $\sim$1426 cm$^{-1}$. The characteristic stretching mode of Zn–O vibration bands normally seen at low absorption peaks in the range 415–448 cm$^{-1}$ [19]. In this study, the IR vibrational bands show significant differences in the peak values with respect to the given processing conditions of capping, microwave and reflux synthesis. The characteristic stretching bands of ZnO appear at 415, 437, 472, and 479 cm$^{-1}$ depending upon the synthesis and capping agents. It provided further insight that even though a highly crystalline ZnO was formed at all the given synthesis conditions; they may have crystallographically different growth patterns and orientations leading to morphologically tuned ZnO particles with various surface features [20]. This had been further verified with SEM

\[ \text{Crystalline size} < D > = 0.89 \lambda / \beta \cos \theta \] (2)
microstructures. The SEM morphologies correspond to various ZnO products are shown in Figs. 4 and 5. The morphology changed entirely with reflux and microwave techniques for the same capping agents. In general, the different crystal growth can be attributed to the change in the surface tension of the reactants solution, length of the molecular chains in the polymeric capping agents, and the strong nature of the complex formation. The uncapped ZnO nanoparticles in the reflux method have weakly agglomerated ZnO whiskers morphology and the same in the microwave method were spherical clusters. The capping agents completely altered the directional growth of the ZnO crystals and their orientations. Capping with PVP observed semi-spherical shaped ZnO nanoparticles in the reflux method and nano-flake structures in microwave technique. The capping agent PEG 300 resulted in rice shaped ZnO in the reflux method and the same attained nano-sheet like structure in microwave. ZnO morphology was quite different when CTAB was used. In this case, ZnO nanoneedles and nanoplatelets were obtained in reflux and microwave methods respectively. The effect of capping agents on the growth of ZnO nanocrystals has been examined by numerous researchers [21,22]. The dispersed Zn$^{2+}$ ions in water quickly reacted with the OH$^-$ ions to form the insoluble Zn(OH)$_2$, which tends to be a cloudy milky solution. It reacted with capping molecules to form respective primary parent oxy-hydroxide [ZnO-Zn(OH)$_2$] complex species. The size and shape of the complex moiety determine the crystal growth directions and orientations and hence the final shapes formed. With PVP addition, the viscosity of water in the solution increased and in result caused a slow diffusion of ions and hence the rate of reaction of Zn$^{2+}$ ion with the hydroxide ion decreased [23], which resulted in the suppressed growth of the ZnO nuclei resulting in semi-spherical and flaky particles.

The role of PEG in controlling the shape and size of nano ZnO was also studied and reported earlier [24]. Water soluble PEG 300 with molecular structure HO–(CH$_2$–CH$_2$–O)$_n$–H is mostly preferred for capping. The –OH group is at the chain ends, and the chain is formed by the repetition of the ethylene oxide group. Such types of capping molecules will bind to the growth units of ZnO nuclei. In the presence of PEG 300, the Zn$^{2+}$ ion is easily adsorbed on the oxygen site of the C–O–C chain. When Zn$^{2+}$ interacts with PEG 300 polymer matrix, the polymer chains containing Zn$^{2+}$ neutralize with hydroxide ions to produce the PEG–Zn(OH)$_2$ complex [25]. Upon microwave irradiation and reflux heating, the PEG–Zn(OH)$_2$ complex dehydrates to form ZnO nuclei and the C–O–C chains decide the growth directions. Although both PEG 300 and PVP are non-ionic capping agents, they would be partially
charged. Especially oxygen in PVP is more partially charged than oxygen in PEG because of positively charged nitrogen in PVP [26]. Therefore, PVP would electrostatically adhere to the surface of ZnO nuclei stronger than PEG 300 resulting in different shapes. Using CTAB as a cationic capping agent, nanoneedle and nanoplatelets shaped ZnO were obtained in reflux and microwave methods. Since CTAB is a kind of strong-acid–weak-base salt, it can accelerate the ionization of $[\text{Zn(OH)}_4]^{2-}$ [27]. The $[\text{Zn(OH)}_4]^{2-}$ anion

Fig. 4. SEM images of ZnO nanoparticles by the MW method: (a) uncapped (b) PEG 300 (c) PVP and (d) CTAB.

Fig. 5. SEM images of ZnO nanoparticles by the reflux method: (a) uncapped (b) PEG 300 (c) PVP and (d) CTAB.
agents which get adsorbed on the environs of the ZnO nuclei. As a result of this, the surface tension of the reactants as well as the surface energy of ZnO nuclei is decreased. At these favorable conditions, ZnO nuclei transform to ZnO crystals at lower saturation temperatures resulting in the formation of long and uniform ZnO nanoneedles and nanoplatelets [28].

The TEM analysis further revealed clearly the extent of the crystallinity, actual size, shape and growth patterns of the ZnO particles at nano-regime with high degree of accuracy. Fig. 6 shows respective TEM images for the uncapped, PEG 300, PVP and CTAB capped ZnO particles obtained through microwave and reflux methods. In microwave technique; spherical, sheet, flake and platelets shaped morphologies were confirmed, whereas in reflux technique; whiskers, rice-like grains, semi-spherical and nanoneedles morphologies obtained. The TEM images confirm structurally uniform, nano dimensional ZnO particles having size ranges 50–100 nm. The SAED patterns taken on the representative ZnO samples revealed the single crystalline nature.

The UV–vis absorption properties of all the nano ZnO products prepared via microwave and reflux techniques with different capping agents are shown in Fig. 7. The as-prepared nanoparticles were ultrasonically dispersed in water medium and the colloids were examined for the UV-absorption using water as the reference. The absorption was corrected for the solvent distribution. The excitonic absorption spectrum of ZnO nanoparticles showed well-defined excitation band between 334 and 364 nm depending upon the size and shape of ZnO crystals formed with various capping agents in both microwave and reflux methods. This absorption curves showed blue-shift by the quantum confinement effect compared to the bulk ZnO excitation absorption at 380 nm (band gap energy $E_g = 3.26\text{ eV}$). In both cases, the UV absorption was very sharp, which indicated the monodispersed nature of the ZnO nanoparticles [29]. This is in fact supportive to the TEM images where a high degree of monodispersity of nanoparticle distribution was seen. The size of the ZnO nanoparticles and its concentration in the solution were also calculated from the absorption studies. L.E. Brus proposed the relationship between the band gap of nanoparticle $E$ and particle radius $r$ which is given by

$$E \approx E_{\text{bulk}} + \frac{\hbar^2 \pi^2}{2\epsilon_0 \varepsilon_\infty} \left( \frac{1}{m_e m_h} + \frac{1}{m_h m_e} \right) - \frac{1.8 e^{-4 \varepsilon_\infty r}}{4 \varepsilon_\infty r^4}$$ (3)

where $E_{\text{bulk}}$ is the bulk band gap, $\hbar$ is Planck’s constant divided by $2\pi$, $e$ is the elementary electric charge, $m_e$ is the electron effective mass, $m_h$ is the hole effective mass, $m_0$ is the electron mass, $\varepsilon$ is the relative permittivity, and $\varepsilon_\infty$ is the permittivity of vacuum. (The following equation was used to calculate the particle size (radius) \[30,31]\):

$$r(\text{nm}) = -0.3049 + \sqrt{(-26.23012 + 10240.72/\lambda_p)/(-6.3829 + 2483.2/\lambda_p)}$$ (4)

The above equation is derived using the effective mass model which described the particle size ($r$, radius) as a function of peak absorbance wavelength ($\lambda_p$) in nm for ZnO nanoparticles. The data extracted from the UV–vis absorbance spectra was used to calculate the average size ($D$) of ZnO nanoparticles according to the expression proposed by Meulenkamp [32] as follows:

$$1240/\lambda_{1/2} = 3.301 + 294.07/D^2 + 1.09/D$$ (5)

where $\lambda_{1/2}$ (nm) is the wavelength corresponding to the absorption profile at the half-height of the intensity and $D$ is the particle diameter (nm) \[33\]. The inset of the Fig. 7 showed its photon energy in terms of electron volt which was used to find out the band gap energy with respect to absorption measurement. The wurtzite ZnO structure possessed a direct band gap and the absorption edge for a direct interband transition is given by
Serpone et al. [34]

\[(\alpha h\nu)^2 = E_0 (h\nu - E_g)\]  

where \(\alpha\) is the optical absorption coefficient, \(h\) is Planck's constant, \(\nu\) is the frequency of incident photon, \(E_0\) is a constant and \(E_g\) is the direct band gap energy. In this study, the absorption coefficient \(\alpha\) could be evaluated by the following equation [35]:

\[\alpha = \frac{A}{d_s}\]  

where \(A\) is the measured absorbance and \(d_s\) is the thickness of the sample in UV–vis cell (0.4 cm).

The plot between \((\alpha h\nu)^2\) versus photon energy \((h\nu)\) for the morphologically varied ZnO nanoparticles was obtained in both microwave and reflux syntheses. The linear dependence of \((\alpha h\nu)^2\) on \(h\nu\) at higher photon energies indicated that the capped ZnO nanoparticles are essentially a direct transition type semiconductor. The linear portion of the curve when extrapolated to zero gave the value of the direct band gap \((E_g)\) corresponding to the morphologically varied ZnO nanoparticles depending upon the capping molecules. According to the results from this figure, the \(E_g\) values of the uncapped ZnO nanoparticles are about 3.22 and 3.40 eV for microwave and reflux methods respectively. The \(E_g\) values of the MW_PEG, MW_PVP and MW_CTAB obtained are 3.71, 3.32 and 3.45 eV respectively. Similarly, the \(E_g\) value of the Ref_PEG, Ref_PVP and Ref_CTAB resulted as 3.46, 3.41 and 3.48 eV respectively. The blue-shift behavior or broadening in the band gap is mainly due to the Moss–Burstein band filling effect [36]. Based on the Moss–Burstein theory, for the samples MW_PEG, MW_PVP, the donor electrons occupied states at the bottom of the conduction band. The average crystalline size of nanosized ZnO powders can be figured out by using the following equation [37]:

\[S_{BET} = 6000/\rho d_{BET}\]  

where \(S_{BET}\) is the BET specific surface area (in m\(^2\)/g), \(\rho\) is the density of nanosized ZnO powder (in g/cm\(^3\)) and \(d_{BET}\) is the crystalline size (in nm). In this study, \(S_{BET}\) was obtained by using the 5.605 g/cm\(^3\) power density. The agglomeration coefficient can be calculated using the following formula:

\[C_f = d_{BET} / <D>\]  

Here, \(C_f\) is the agglomeration coefficient and \(<D>\) is the crystallite size from the XRD Scherrer formula. From the aforementioned mathematical equations, the particle diameter \((2r)\), agglomeration coefficient \((C_f)\), and surface area \((S_{BET})\) were determined for the different ZnO samples and summarized in Table 1.

### Table 1

<table>
<thead>
<tr>
<th>ZnO samples</th>
<th>Morphology</th>
<th>DLS 2r (nm)</th>
<th>&lt;D&gt; (nm)</th>
<th>2r from Eq. (4) (nm)</th>
<th>(C_f)</th>
<th>(S_{BET}) (m(^2)/g)</th>
<th>UV (\lambda) (nm)</th>
<th>(E_g) (eV)</th>
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<tr>
<td>Ref_Uncap</td>
<td>Weekly agglomerated whiskers</td>
<td>222.64</td>
<td>21.29</td>
<td>4.8958</td>
<td>0.11499</td>
<td>219</td>
<td>364</td>
<td>3.40</td>
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<tr>
<td>Ref_PEG</td>
<td>Rice grain</td>
<td>218.20</td>
<td>24.41</td>
<td>4.4679</td>
<td>0.18300</td>
<td>240</td>
<td>358</td>
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<tr>
<td>Ref_PVP</td>
<td>Semi-spherical</td>
<td>205.79</td>
<td>28.39</td>
<td>4.8165</td>
<td>0.16968</td>
<td>222</td>
<td>363</td>
<td>3.41</td>
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<tr>
<td>Ref_CTAB</td>
<td>Nanoneedles</td>
<td>177.59</td>
<td>20.98</td>
<td>4.3828</td>
<td>0.21370</td>
<td>250</td>
<td>355</td>
<td>3.48</td>
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<tr>
<td>MW_Uncap</td>
<td>Spherical clusters</td>
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<td>34.23</td>
<td>4.7357</td>
<td>0.13835</td>
<td>226</td>
<td>362</td>
<td>3.22</td>
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<td>MW_PEG</td>
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<td>4.1816</td>
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<td>353</td>
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<td>MW_PVP</td>
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<td>177.59</td>
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3.1. Near infrared reflectance [NIR] and UV–vis spectra analysis of ZnO/PMMA nano composites

A comparison in the NIR reflectance properties between PMMA and PMMA/PU nanocomposite sheets dispersed with ZnO
nanoparticles prepared with various capping agents is given in Fig. 8. In general, 100% incident light = total reflectance (%) + absorbance (%)+ total transmittance (%), where total reflectance (%) = diffuse reflectance (%) + specular reflectance (%), and total transmittance (%) = diffuse transmittance (%) + specular transmittance (%).

The diffuse reflectance data, without including the specular reflectance, given by the instrument SHIMADZU UV–vis–NIR spectrophotometer [UV-3600] in the wavelength region 800–2500 nm is directly plotted for the PMMA films which were prepared with only 0.1 wt% ZnO particles. Fig. 8(a) depicts NIR reflectance of neat PMMA and PMMA having Polyurethane additive. In both these cases, the NIR reflectance is very poor, and only <10% is observed. Upon 0.1 wt% dispersion of ZnO [sample prepared with CTAB surfactant under microwave], the PMMA/PU films attain NIR reflectivity above 40%. The physical appearance of ZnO/PMMA and ZnO/PU/PMMA was also given for showing the optical transparency [Fig. 8(b)]. Fig. 8(c and d) is only the comparison of PMMA films dispersed with various ZnO particles obtained via microwave and reflux techniques. The microwave derived ZnO shows better NIR reflectivity than the reflux counterpart. In the NIR reflectance spectra, low reflectance means high absorption in that wavelength region. In general we have noticed very strong absorptions in the wavelength regions 1300–2500 nm. These strong absorptions arise from the combination and overtones of fundamental processes that occur in the mid-IR region (λ > 2500 nm) [38]. The composites prepared with microwave derived ZnO showed better NIR reflectance compared to its reflux counterpart at NIR wavelengths 810 and 1100 nm. PMMA film prepared without any ZnO was optically transparent but it showed only 2% reflectivity in the entire NIR region indicating the highest absorption of NIR by the PMMA matrix. Similarly in case of PU/PMMA polymer composites, the control sample prepared without any ZnO, provided only below 10% NIR reflectance. When the PMMA and PMMA/PU films were prepared with only 0.1 wt% nano

**Table 2**

The (%) NIR reflectance of ZnO/polymer sheets at 810 and 1100 nm NIR wavelengths.

<table>
<thead>
<tr>
<th>ZnO/polymer nanocomposite</th>
<th>(%) NIR reflectance at 1100 nm</th>
<th>(%) NIR reflectance at 810 nm</th>
</tr>
</thead>
<tbody>
<tr>
<td>Neat PMMA</td>
<td>2</td>
<td>2</td>
</tr>
<tr>
<td>MW_PEG/PMMA</td>
<td>53</td>
<td>55</td>
</tr>
<tr>
<td>MW_PVP/PMMA</td>
<td>46</td>
<td>48</td>
</tr>
<tr>
<td>MW_CTAB/PMMA</td>
<td>37</td>
<td>38</td>
</tr>
<tr>
<td>MW_Uncapped/PMMA</td>
<td>37</td>
<td>38</td>
</tr>
<tr>
<td>Ref_PEG/PMMA</td>
<td>32</td>
<td>35</td>
</tr>
<tr>
<td>Ref_CTAB/PMMA</td>
<td>31</td>
<td>35</td>
</tr>
<tr>
<td>Ref_Uncapped/PMMA</td>
<td>32</td>
<td>38</td>
</tr>
<tr>
<td>PU/PMMA</td>
<td>11</td>
<td>11</td>
</tr>
<tr>
<td>MW_CTAB/PU/PMMA</td>
<td>45</td>
<td>11</td>
</tr>
</tbody>
</table>

Fig. 8. NIR reflectance of (a) neat PMMA, PU/PMMA and ZnO/PMMA/PU sheets, (b) photographic images of ZnO/PMMA and ZnO/PU/PMMA sheets, (c) microwave method synthesis of ZnO/PMMA sheets with and without different capping agents and (d) the reflux method synthesis of ZnO/ PMMA sheets with and without different capping agents.
ZnO, a high degree of NIR reflectivity was observed. The PMMA/ZnO nanocomposites showed the bulk NIR reflectivity in the range 40–60% depending upon the ZnO size and shape. The same was increased to 45% in PU/PMMA/ZnO nanocomposites. The % NIR reflectance was taken directly at the wavelengths 810 and 1100 nm on the 0.04 mm thick PMMA films and is summarized in Table 2 for various ZnO. The extent of NIR reflectivity strongly varied with the given processing and capping conditions. For example, the PMMA nanocomposite films have highest reflectivity to NIR when it was reinforced with PEG 300 capped ZnO. In microwave technique, it is determined as 55%. It is known that the NIR reflectance property highly depends upon the color of the inorganic fillers, their refractive index and crystalline qualities [39]. TiO2 and ZnO are the most preferred NIR reflecting pigments due to their attractive bright white and the wide optical refractive index values. The refractive index values for TiO2 and ZnO were reported in the range 2.02–2.6. Depending upon the refractive index values, the light beam is refracted, reflected and scattered leading to diffuse reflection of NIR light. For an effective reflection of NIR-radiation, particle size was reported as essential parameter. For highest reflectivity, the particle size should be more than half the wavelength of the light to be reflected. Thus for reflecting infrared light of 700–1100 nm wavelength, particle size should be at least 0.35–0.55 μm [40]. In this study, we obtained ZnO particles with varying physical dimensions and crystalline morphologies ranging from spherical to flake and sheet. The overall physical size of the ZnO particles was found to be within 150–400 nm and 200–250 nm for microwave and reflux techniques respectively. Fig. 9(a) shows the % NIR reflectance of PMMA/ZnO nanocomposites with respect to the ZnO particle size. The NIR reflectance at the wavelength 810 nm was taken for the comparison. From the figure, it is clear that the NIR reflectance increased with decreasing particle size. The ZnO samples prepared with PEG and PVP capping have mean size of 177 and 153 nm respectively in microwaves. These samples have shown high reflectance compared to other ZnO particles where the particle size was above 200 nm.

We have seen that such particle size range, say 150–170 nm, was favorable for effectively reflecting the NIR rays. However, it appeared that, in addition to the particle size, a fine control of morphology is also important to shift the reflectance to a maximum value with minimum amounts of ZnO dispersion. The plot in Fig. 9(a) confirms that among the obtained ZnO morphologies, nanosheets and flakes have better IR reflectance. The NIR reflectance at 810 nm and 1100 nm were plotted against the ZnO morphologies and shown in Fig. 9(b). All the morphologies showed high NIR reflectivity at 810 nm compared to the wavelength of 1100 nm. The ZnO nanosheets obtained for MW_PEG show 55% reflectance at 810 nm and about 53% at 1100 nm. Similarly, the nanoflake structure derived for the sample MW_PVP shows 48% reflectivity at 810 nm and 46% at 1100 nm. The NIR reflectivity was comparatively high for the nano ZnO having relatively large surface features. In sheet, flake and plates, the surface area was high compared to its thickness which was only a few nanometers. The active surface available for the IR to interact with other ZnO morphologies such as semispherical, rice grain and whisker was comparatively less and therefore they exhibit poor reflectivity. Nanosheets showed the highest NIR reflectance followed by nanoflakes, nanoplatelets, spherical, rice grains, whiskers and nanoneedles. Moreover, these kinds of particle morphologies also vary in their degree of agglomeration. It also significantly influences the NIR reflectivity. In this work, the (%) NIR reflectance at the wavelengths 810 nm and 1100 nm was also plotted against the agglomeration coefficient of the various ZnO and is shown in Fig. 9(c). Since the morphologies nanosheets and flakes had less tendency for agglomeration and clustering, these samples had higher NIR reflectance at both 810 nm and 1100 nm wavelengths. As evident from the SEM, the other ZnO morphologies like nanoneedles and semispherical particles have higher agglomeration and exhibit poor NIR reflectance.
The UV absorption properties of nano ZnO cover both UVB and UVA ranges. For this reason, the prepared PMMA/ZnO nanocomposites were also tested for the UV-shielding efficiency. Fig. 10 shows the effect of ZnO addition in PMMA polymer film on the UV absorbance. The absorption range of pure PMMA was seen at the wavelength of 300 nm which was close to the window glass and also commercially available and purchased bulk ZnO (Sigma-Aldrich, India), denoted as Ald_ZnO; dispersed in PMMA at 380 nm. When as-prepared, using microwave method, ZnO nanoparticles were dispersed well and the absorption shifts to wavelengths in ranges 350 nm, 375 nm and 379 nm for the PEG 300, PVP and CTAB as capping agents, respectively. The absorption ranges 350–380 nm indicate the UV shielding efficiency of microwave and reflux reaction of thin ZnO particles in both UVA and UVB ranges [41]. In PMMA nano composite fabricated with PEG capped ZnO nanoparticle, a slight blue-shifting was seen in the absorption that was due to relatively small size of the ZnO particles. In this work, fabrication of thin film PMMA sheets with thickness 0.04 mm is engineered with capped nano ZnO and polyurethane additive for normal solar light transmittance but capability to shield NIR and UV transmission.

4. Conclusions

In summary, we report the NIR reflectance property of ZnO dispersed PMMA polymer nanocomposite films. The UV/NIR shielding property of PMMA polymer was correlated with various ZnO morphologies that differ in the average physical size and surface features. Highly crystalline, hexagonal wurtzite ZnO particles were successfully prepared via microwave and reflux techniques with various capping agents. These techniques produced ZnO with mean particle size in the range 150–400 nm. Morphologically varied nano ZnO having physical shapes such as spherical clusters, rice grains, needle and whiskers as well as one-dimensional nanoneedles and sheets were obtained. This study revealed that in addition to the particle size of ZnO, the morphology and the crystalline quality also played equally an important role in obtaining better NIR/UV shielding quality. The microwave technique resulted in nano-thick one-dimensional sheet shape ZnO morphologies. Such nano-thick sheet like particles had high surface sites that help to reflect the NIR effectively. The PMMA sheet without any ZnO had only 2% NIR reflectivity whereas the same was increased to 55% where 0.1 wt% ZnO was dispersed in the PMMA matrix. The high particle size of ZnO affected the optical transmittance strongly and resulted in highly opaque PMMA/ZnO nanocomposite sheets. The additions of small amount of polyurethane produced visibly clear PMMA/PU/ZnO sheets compared to PMMA/ZnO sheet. The NIR reflectance followed the order nano-sheet > nanoflake > nanoplatelets > spherical > rice grain > whiskers > nanoneedles morphologies. The PEG 300 capped ZnO reinforced PMMA polymer sheet showed comparatively higher reflectance to NIR wavelength than the other capping agents. On comparing the results, the PMMA/ZnO and PU/PMMA/ZnO nanocomposites showed better UV/NIR shielding properties that can be explored as interface layers/films and membranes in glass and polymer type sandwich panels for the effective solar thermal controlled indoors of buildings.

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References


