DIELECTRIC AND UV ABSORPTION STUDIES OF ZnO NANOPARTICLES REINFORCED POLY (3-HYDROXYBUTYRATE) BIO COMPOSITES FOR UV FREE LEDs

J. V. CHANDAR[*], S. SHANMUGAN, D. MUTHARASU, A.A. AZIZ
School of Physics, Universiti Sains Malaysia (USM), 11800, Minden, Pulau Pinang, Malaysia

Biopolymer nanocomposite is a class of material which exhibits superior properties compared to pure biopolymer and conventional composites. Addition of nanofillers to the pure biopolymers which results in nanocomposites improves the dielectric, UV absorption, conductivity and other mechanical properties. In this work, ZnO nano particles (NPs) reinforced (5% to 10%) poly (3-hydroxybutyrate) [P (3HB)] films were synthesized and the effect of ZnO NPs on the dielectric and UV absorption properties were studied. Compared to virgin polymer, ZnO NPs reinforced P (3HB) composites showed significant improvement in the relative permittivity with loss tangent (*tan δ*) < 0.02, especially 10% ZnO NPs reinforced P (3HB) composite film has permittivity value of (ε') ~ 4.03 which is nearly equal to that of FR4 (ε' - 4.8). UV-Vis spectroscopy study revealed the absorbance behaviour of ZnO NPs reinforced P (3HB) composites and observed high values in the UV region (UV-B and UV-C) which is suitable for LED encapsulation. Moreover, the increased transmittance was noticed in the visible region. From the above observations, it is suggested to use ZnO NPs reinforced P (3HB) composites with suitable resin for LED encapsulation applications and also as a UV-blocker for future UV free LEDs.

1. Introduction

The usage of non-degradable and non disposable petrochemical plastic materials such as polypropylene (PP), polystyrene (PS) and polyethylene (PE), polyethylene terephthalate (PET) and polyvinylchloride (PVC) has drastically increased leading to the contamination of ecology across the globe. It is widely used in most of the manufacturing industries related to consumer products, automobiles, lighting and packaging industry due to its easy modification of structure and properties [1-7]. Espescialy the growth of LED technology has drastically increased over the past decades. Much of our daily activities involve interactions with items containing LEDs such as computers, televisions, iPods, mobile phones, camera, other important areas such as aviation lighting, automotive lightings, general lightings, advertising, traffic lights, etc. With these wonderful devices, our lifestyle has been greatly improved. However the main drawbacks in LEDs are thermal and UV radiation emission. There is a growing interest among the governments, societies and researchers to minimize the exhausion of petroleum resources and material responsible for this environmental threat and to develop a biodegradable polymers [5,8,9]. The usage of biodegradable polymers such as polyhydroxyalkanoates (PHA), polylactic acid (PLA) and polycaprolactones (PCL) developed from renewable sources is one of the best strageties to reduce the ecological contamination [10]. PHA is the only 100% biodegradable polymer [2,11] produced from renewable sources [12] (i.e. synthesized by bacterial in form of carbon and oxygen reserves) which exhibits properties similar to polypropylene [13]. Polyhydroxybutyrate (PHB) is a linear polyester, fully biodegradable, bicompatible and is the most widely studied and used polymer from the PHA family [14,15]. However the properties such as brittleness, high production cost, low resistance to thermal degradation and high melting point making them undesirable for

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[*]Corresponding author: vishnuchandar.j@gmail.com

commercial usage. Biopolymer nanocomposites are a class of materials that has already gained a big attention due to their exceptional properties, which are superior to those of the pure polymers and of the conventional composites. New approaches like blending PHB with other polymers and nanofillers such as multiwalled carbon nanotubes (MWCNTs) [16], hydroxyapatite [17], organically modified montmorillonite [18] is reported to overcome these drawbacks and to extend its range of applications. Noble metal oxide nanoparticles like ZnO has drawn great attention among researchers due to its low cost, UV absorption, good thermal conductivity and high antibacterial properties compared to other metal oxides like CaO, TiO_2 and MgO [19].

ZnO nanoparticles was reinforced with PHB [20], poly (3-hydroxybutyrate-co-3-hydroxyvalerate) PHBV [21], polyethylene terephthalate (PET) [22] and its crystallinity properties were studied by some other researchers. In this study, P (3HB) was reinforced with three different ZnO NPs concentrations (0% i.e. virgin polymer, 5% and 10%) using solution casting method and their dielectric and UV absorption properties were analyzed in an attempt to overcome the UV emission problem in LEDs.

2. Experimental details

2.1 Biosynthesis of poly (3-hydroxybutyrate) polymer

Two loopfuls of recombinant cupravidas necator Re2058/pCB113 cells cultured in NR plates for 24 hours were transferred into NR broth and incubated at 30 °C for 8 hours. These cultures were inoculated into 100 mL minimal medium prepared in shake flasks containing 7 gL^{-1} of fructose and 0.54 gL^{-1} of urea. The grown culture was used as inoculum for the fermenter. The fermenter is equipped with control systems for pH, temperature and dissolved oxygen [INFORS HT (Labfors 3), Switzerland]. Through controlled addition of 3M sodium hydroxide and 3 M phosphoric acid, the pH of the culture medium was maintained at 7.0 ± 0.1. The temperature of the culture was kept at 30 °C. Stirring was provided continuously by 3 sic blade Rushton impellor at a speed of 200-900 rpm. Dissolved oxygen concentration was maintained at above 40% and air was supplied through filter cartridges (Sartorius stedim, Germany) at 1 VVM. Autoclave (HV110, Hiryama, Japan) was used to sterilize the fermenter together with the culture medium by autoclaving at 121 °C for 30 minutes.

2.2 Preparation of virgin and ZnO NPs reinforced poly (3-hydroxybutyrate) [P (3HB)] composite films

Freeze-dried cells were mixed with chloroform in the ratio of 1 g: 100 mL for 5 days at room temperature with continuous stirring inorder to extract the polymer. The cell debris was removed from the resultant solution and then the filtered solution was concentrated by using a rotary evaporator. The solution was added drop-wise into vigorously stirred chilled methanol for 1 h to precipitate and purify the polymer. The precipitated and purified polymer was used for the experiments. ZnO NPs was dispersed into chloroform solvent by using mechanical stirrer and ultrasonication for 30 min. Extracted and purified poly (3-hydroxybutyrate) [P (3HB)] polymer was then, put into the ZnO NPs mixed chloroform solution (2 different concentration of ZnO NPs from 5% to 10%) and the stirring was continued until a homogeneous colloidal solution was obtained. Then the films were casted in petri dish (55 mm diameter) and kept at room temperature for 48 hrs. The film thickness and its diameter was measured using ABS digimatic caliper. The observed film thickness and diameter were about 0.3 mm and 50 mm respectively.

2.3 Characterization of virgin P (3HB) polymer and ZnO NPs reinforced P (3HB) composite film

2.3.1 UV-Vis Spectrophotometer

In order to study the UV-absorption properties of virgin P (3HB) and its composites, UV-Vis spectrophotometer (Shimadzu UV-Vis 1800) was used to record the absorbance and transmission spectra for the wavelength ranging from 200 to 1500 nm.

2.3.2 Dielectric Analyzer

RF Impedance / Material Analyzer (4291B - HP) was used to determine the permittivtty and loss tangent of virgin P (3HB) and ZnO NPs reinforced P (3HB) composites in the frequency range of 1MHz to 1GHz at room temperature.

3. Results & Discussions

3.1 Optical analysis – Absorption spectra

The absorption spectra was obtained and plotted as shown in fig. 1 and it clearly shows the effect of ZnO NPs reinforcement on the UV absorption properties of P (3HB) polymer. Figure 1 clearly shows that both composites (5% and 10%) exhibit very good UV absorbtion with intensity value around 10 a.u. at 204 nm (UV-C) and 211 nm (UV-C) respectively. P (3HB) with 10% ZnO NPs composites exhibit two more peaks around 215nm and 349nm (UV-A) with intensity around 10 a.u.. The peak at 349nm for both composites are attributed to the typical excitation absorption peak (355nm) of ZnO NPs at room temperature [23]. It is clearly evident from the fig. 1 that there is a sudden decrease in the intensity (5 a.u.) around 381nm and then gradually decreases till 1500nm (1.32 a.u.) which was observed for P (3HB)/5% ZnO NPs composites. Virgin P (3HB) exhibit slight UV absorption with intensity around 5 a.u. in UV-C region and then gradually decreases till 1500 nm with no excitation peak around 350nm.
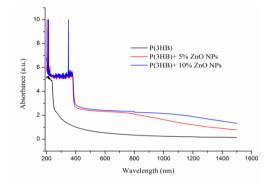

Fig. 1 Absorbance spectra of virgin P (3HB) and ZnO NPs reinforced P (3HB) composites

3.2 Optical analysis – Transmittance spectra

The recorded transmittance spectra of virgin P (3HB) and its composites are plotted as shown in fig. 2. It is clearly evident from the fig. 2 that the transmittance percentage is almost zero for the composites (5% and 10% ZnO NPs) in the wavelength ranging from 200nm to 400nm and then slightly increases to 0.5% for P (3HB)/ZnO NPs composites in 800nm and gradually increases with the increase in wavelength with transmittance reached upto 4% and 16% on 1500nm respectively.
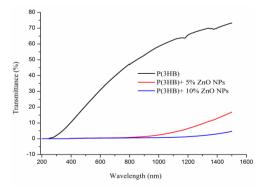

Fig. 2 Transmittance spectra of virgin P (3HB) and ZnO NPs reinforced P (3HB) composites

Virgin P (3HB) exhibit zero percentage transmittance in UV-C region i.e. 200nm to 240nm. Afterwards, the percentage of tranmittance is drastically increased from 0% to 47% in UV-B and UV-A region and 47% to 73% in visible region. UV absorption varies with respect to band gap energy and particle size of ZnO. Generally ZnO is an extremely high-UV-shielding material with low-refractive index and acts as a physical blocker for UV rays [24,25]. According to literature [26], the reinforcement of ZnO NPs in the poly(styrene butylacrylate) latex increased the UV-absorption properties of the nanocomposites and increasing the ZnO NPs content also enhanced the UV shielding properties of the polymer composites. Similarly in this study, the reinforcement of ZnO NPs in the P (3HB) biopolymer resulted in the increase of UV absorption proeperties of the composites.

3.3 Optical analysis – conclusion and future scope

The results obtained from the absorption and transmittance spectra confirmed that the addition of ZnO NPs increases the UV absorption of P (3HB) polymer. It is known that UV-B radiation (290 – 315 nm) is responsible for most of the photochemical degradtion in plastics, suntan and sunburn etc. The newly developed degradable composites shows very good absorption in all UV regions (UV-A, UV-B, UV-C) making it as a desirable material to reduce the above mentioned problems.

In addition to that, LED Technology – the speed of this technology has increased drastically over the past half century. The main problems associated with LED technology are thermal and UV radiation emission. Some industries claims that LEDs donot produce UV radiation. But LEDs do produce and emits small amount of UV radiation outside and are not 100% UV free [27]. The developed material may be reinforced with suitable resin and can be used as encapsulation material for developing future UV free LEDs.

3.4 Dielectric Analysis – Permittivity and Loss tangent spectra

In order to analyze the dielectric nature, the permittivity (ε') and loss tangent (*tan δ*) of virgin P (3HB) and its composites are obtained and the resultant data are plotted as shown in fig. 3 and fig. 4 respectively.
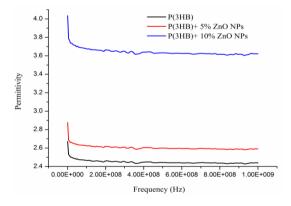

*Fig. 3 Change in Permittivity (ε') of virgin P (3HB) and ZnO NPs reinforced P (3HB)
composites for various frequency*

It is clear from the fig. 3 that the permittivity (ε') of both virgin P (3HB) and its composites decreases with increase in frequency and it remains almost constant as the frequency shift to higher one. Similarly according to literature [28], the dielectric permittivity (ε' - 30 @ 100Hz) of ZnO/Polyvinylidine fluoride (PVDF) nanocomposite is high in lower frequency (10^2 Hz) and viceversa. Virgin P (3HB) exhibit permittivity (ε') value around 2.66, 2.44, 2.43 at 1 MHz, 500 MHz, and 1 GHz respectively. The permittivity (ε') value increases with increase in ZnO NPs concentration with very high value (4.03 at 1 MHz) observed for 10% ZnO NPs reinforced composite sample. Figure 4 shows the effect of addition of ZnO NPs on the loss tangent values of P (3HB) polymer. The *tan δ of* virgin P (3HB) is 0.02 @ 1 MHz, 0.01 @ 500 MHz and

almost zero i.e. 0.009 @ 1 GHz respectively. For 5% ZnO NPs reinforced P (3HB) composites, *tan δ* decreases to 0.01 @ 1 MHz whereas it increases to 0.02 @ 1 MHz for 10% ZnO NPs reinforced composites. Overall the loss tangent (*tan δ*) values of both virgin polymer and composites exhibit a similar trend like permittivity i.e. the loss tangent values decreases with increase in frequency. The obtained permittivity is greater than the commercially available poly tetra fluoro ethylene (2.1) [29], polypropylene (2.2), polycarbonate (2.8) [30] and nearly equivalent to permittivity of FR4 (4.5) [31].
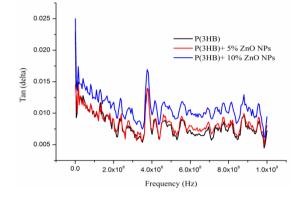

Fig. 4 variation in Loss tangent of virgin P(3HB) and ZnO NPs reinforced P(3HB) composites for various frequency

4. Conclusions

This study investigates the effect of ZnO NPs on dielectric and UV absorption properties of poly (3-hydroxybutyrate) [P (3HB)] films. Dielectric studies revealed that the addition of ZnO nanoparticles increased the permittivity of P (3HB) polymer with very high value obtained for 10% ZnO. UV-Vis results was also showed that the addition of ZnO NPs increased the absorption in UV region (UV-A, UV-B, UV-C). Overall the prepared composites can be reinforced with proper resin and may be used as a encapsulation material for future UV free LEDs. However, indepth analysis is still needed to replace the existing commercial technology.

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