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High refractive index and absorbance insights of poly-acrylates doped with Zinc oxide nanoparticles for molecular switches application

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Abstract

Two types of zinc oxide nanocomposites were synthesized using poly(ethyl hexyl methacrylate (EHM) and poly(butyl methacrylate (BMA) to be applied in manufacturing the molecular switches and the optical memories. The molar ratio of 10/90 was selected for each nanocomposite of ZnO/ PEHM and ZnO/ PBMA to be investigated. The optical characteristics and Raman spectra were conducted at room temperature. Most of the optical studies were sensitively affected by the polymer's chemical nature, composition and the method of interaction. All the prepared nanocomposites were produced, using in-situ chemical oxidative method and deposited using casting solution method. ZnO nanoparticles were combined with PEHM and PBMA as the polymer matrix physically without using of surfactants.

Keywords: Absorbance; Molecular switches; Poly butyl methacrylate; Refractive index; Raman spectra

1. Introduction

There are numerous uses for the thermoplastic poly-butyl methacrylate (PBMA) in numerous productive and technological aspects. PBMA has a remarkable sound due to its special mix of outstanding optical qualities, including transparency over a large wavelength range (near ultraviolet to near infrared) [1].A molecule that has the ability to be reversibly switched between two or more stable states is called a molecular switch. Low-cost polymer poly(ethyl hexyl methacrylate (EHMS) has potential properties such as mechanical resistance, electrical insulation, transparency, and thermal stability [2]. Generally, polyacrylates generated a lot of attention for utilization as optical components and in optoelectronics devices because of its low cost and high output [3]. Zinc oxide's distinct electrical and optical properties make it one of the most appealing oxide semiconductors. In addition to its other noteworthy qualities, which include low cost, non-toxicity, long-term environmental stability, and biocompatibility [4].ZnO is an effective UV absorber due to its large band gap (3.37 eV) in addition to its substantial exciting binding energy (60 meV), which is significantly greater than the thermal energy at ambient temperature (26 meV). Zinc oxide nanoparticles become an attractive material for short-wavelength optoelectronic devices, particularly UV laser diodes and light-emitting diodes.The combined structure of polyacrylates and semiconductor material such as zinc oxide can create successful optical structures that self-assemble to create lightweight photonic devices [5]. Numerous innovative applications, such as colorimetric sensors, active parts of basic display systems, electrically controlled tunable optically pumped lasers, photonic switches, and multiband filters, are released from this system. Polyacrylates have been optically explored due to its high Young's modulus of approximately 3 MPa, which makes them thermoplastic with excellent scratch resistance, strong heat stability, and intriguing optical features [6-9]. Spotting the scope of the high refractive index, Raman spectra and absorbance of the poly(ethyl hexyl methacrylate (EHM) and poly(butyl methacrylate (BMA) after the intercalation with zinc oxide nanoparticles is the main objective of this study where revealing the change after the hybrid formation has been prepared to design new synthetic molecular switches. This advanced application which has currently great attention in the field of the nanotechnology. It could be applied for using in responsive medication delivery systems or molecular computers. Molecular switches have a crucial role in biology as well as they are essential for numerous biological processes, including vision and allosteric control. They are also among the most basic kinds of molecular machinery.In this work, we describe the effects of zinc oxide nanoparticles addition on the optical characteristics of poly(ethyl hexyl methacrylate) (PEHM) and poly(butyl methacrylate) (PBMA) using 10% loading of zinc oxide nanoparticles as a simple model of molecular switch.

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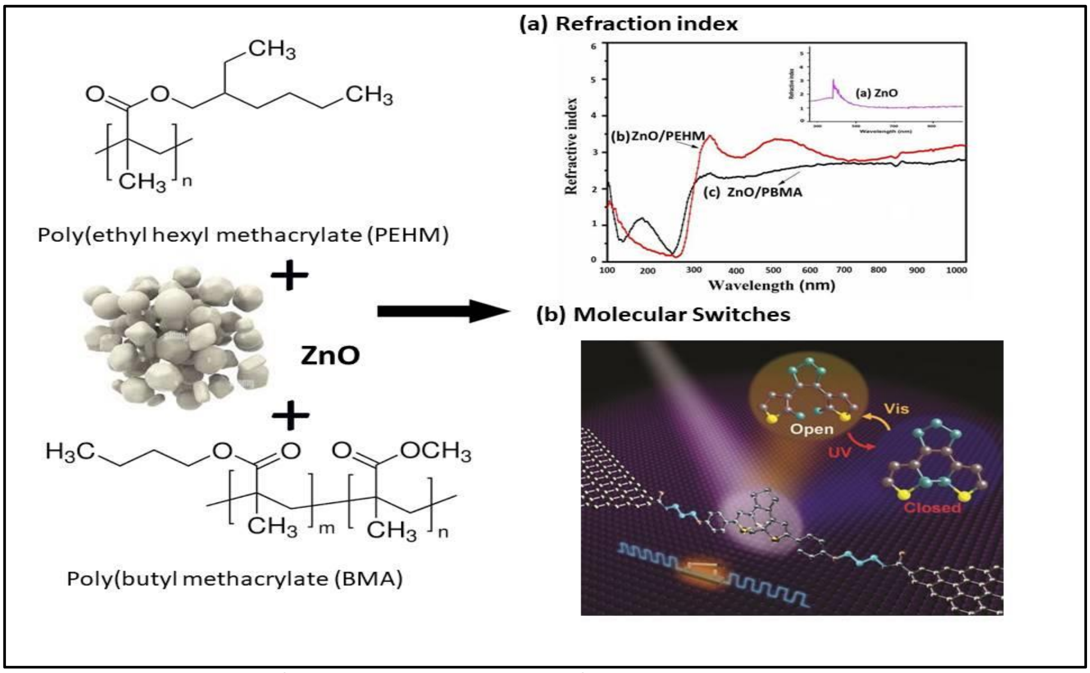

Scheme 1. Illustration for the preparation procedure of ZnO/PEHM and ZnO/PBMA nanocomposite

2. Materials and Methods

2.1. Materials

Zinc oxide nanoparticles (99%), with average particles size of less than 40 nm, with weight percentages of 20 wt% in H_2O was provided from Sigma Aldrich. Toluene from Merck, Germany, Poly(2-ethylhexyl methacrylate) (PEHM) and poly-butyl methacrylate (PBMA) used in this study were provided by (Aldrich Chemical, CO, USA). The Molecular Weight (Mw) of PBMA is ~180,000 and average Mw of PEHM is ~123000 Dalton.

2.2. Preparation of ZnO/Polymers composites

A homogenous solution, 0.5 % of ZnO nanoparticles were suspended in 100 milliliters of DI water and left to disperse in an ultrasonic water bath for half an hour. The stock solutions of PEHM and PBMA were prepared with concentration of 2% by dissolving in Toluene under continuous stirring for five hours at 40 degrees Celsius. ZnO nanoparticles solution was added gradually to the reaction mixture under stirring then the mixture was sonicated for another 1 h to get well dispersion.The mixture was poured in petri-dish and transferred into oven at about 60 ^{o}Ctill complete drying. The preparation of the nanocomposites and their applications was illustrated in scheme 1.

2.3. Characterizations:

Japanese-made JASCO FT-IR 6100 was used to record FT-IR spectra using KBr. The samples were grounded to the dry particles and compressed the resulting mixture to form disks. In order to prevent the disks from absorbing moisture, they were kept in a desiccator. SenterraBruker fitted with Si(Li) detector laser source 532 nm (Germany) with high wave number accuracy and permanent calibration was recorded the features of Raman spectroscopy and the physical spectroscopy characteristics.The technique of surface morphology investigation was employed, utilizing scanning electron microscope (FEG-SEM Quanta 200). Absorbance spectra were acquired utilizing a Jasco model V-570 UV/VIS/NIR spectrophotometer. The wavelength range used for the measurements was 300–800 nm.

3. Results and Discussion

FTIR spectra

Figure (1) shows the FTIR spectra of (a) ZnO/PBMA and (b) ZnO/ PEHM. The zinc oxide sample's FT-IR spectra reveal a prominent ZnO absorption band between 400 and 435 cm^{-1}, which is indicative of the metal's transverse optical stretching modesas shown in Figure (1a). The stretching vibrations of the -OH group on the surface of ZnO nanoparticles are responsible for the large peak at 3461 cm^{-1} [21]. The bands at 1045 cm^{-1} attributed to the Zn–O stretching vibrations and 755 cm^{-1}

assigned to the Zn–O– Zn confirms the interaction of the acrylate polymers physically to ZnO nanoparticles(NPs)as displayed in Figure (1a&b)[10-14]. The C–H stretching vibrations at 2931 cm^{-1}correlated the presence of the attached butyl group. The peak at 1508 cm^{-1} shows the existence of methylene groups, and the peak at 1645 cm^{-1} is assigned to the stretching vibration of the C- O group. Additionally, we note the emergence of a peak at 3442 cm^{-1}, which is the peak of OH absorption. In addition, a peak at 1734 cm^{-1} shows C=O stretching vibration which exists in PEHM and PBMA polymers [21].

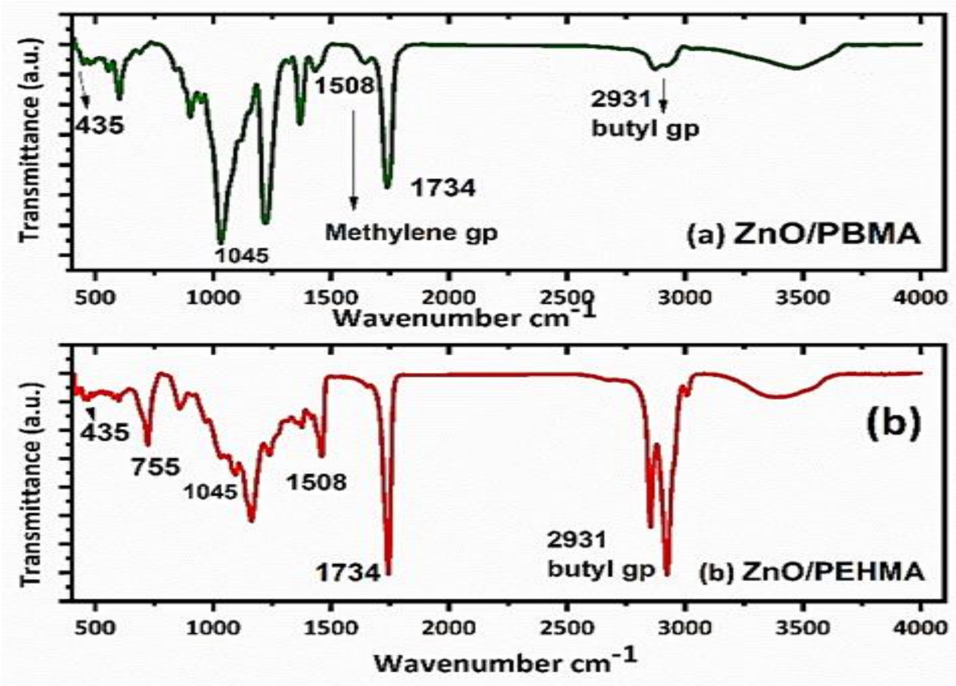

Fig. 1. FTIR spectra of (a) ZnO/ PBMA and (b) ZnO/ PEHM

SEM micrographs

The SEM pictures of ZnO/ PEHM nanocomposite are displayed in Figure (2). These images demonstrate the dispersion ofZnO nanoparticles within and on surface ofthe expanded polymer. The morphology of ZnO nanoparticles has a slight tendency for certain particles to agglomerate. The obtained composite was heterogeneous in nature as the nanoparticles clearly appeared as visible white particles that adhered to the polymer surface [15-17]. The images of the SEM confirmed that ZnO/ PEHM nanocomposites are well-prepared.

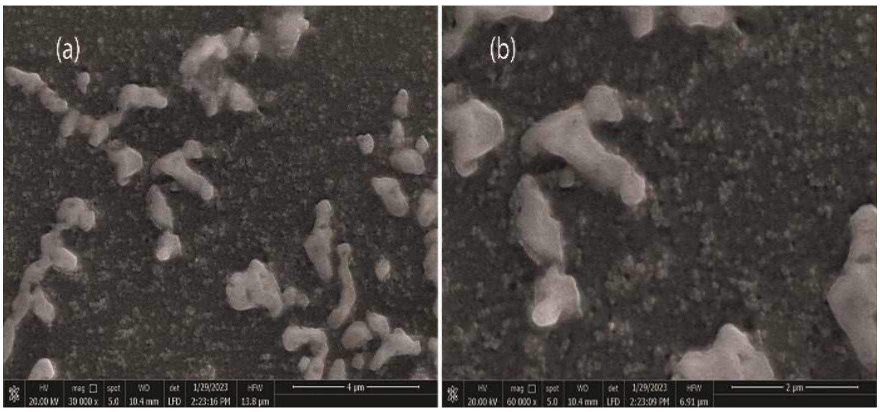

Fig. 2. SEM images of ZnO/ PEHM nanocomposite at different magnifications (a) x 30.000 and (b) x 60.000

UV absorption band

The room temperature absorption spectra for the ZnO/PEHM and ZnO/PBMA nanostructures are displayed in Figure (3). PEHM and PBMA's π-π^* absorption band is characterized by a prominent band located in the UV region around 330 nm [21]. The conjugated ZnO/PEHM and ZnO/PBMA nanocomposites' electronic transition to the first excited singlet state (S1) is confirmed by the occurrence of a peak at about 330 nm [8-9]. This illustrates how Beer's law states that the number of absorbing species has increased. The intensity of the peak of ZnO around 330 nm was increased for ZnO/PBMA and largely increased for ZnO/PEHM composite. The photochemical deformation of ZnO/PEHM and ZnO/PBMA nanostructures is explained by the red shift and rise in peak height at 330 nm.

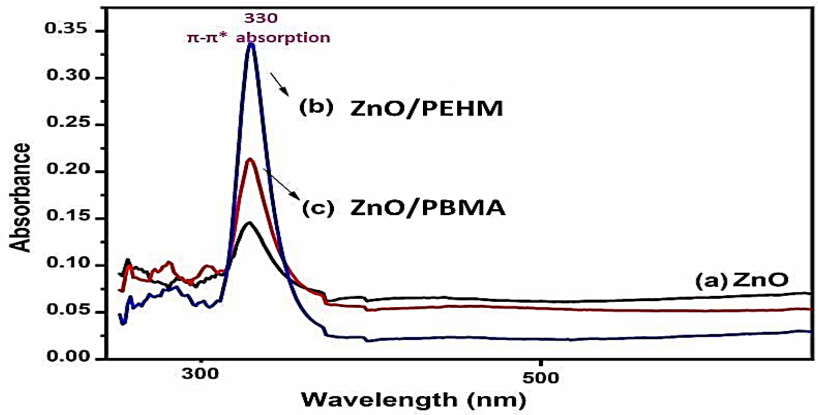

Fig. 3. Absorption spectra of (a) ZnO, (b) ZnO/ PEHM and (c) ZnO/ PBMA at room temperature.

Refraction index

Figure (4) describes the change in refraction index for ZnO/PEHM and ZnO/PBMA compared to ZnO as a function of wavelength that has occurred red due to changing in (n) values with increasing the doping percentage. Since acrylates are amorphous polymeric materials with low density that remarkably affect the refraction index values of the nanostructures at the lowest and greatest wavelengths.

This is basically due to the high transmissions values of the longest wavelength and vice versa. The refractive index of the composites increased with incorporation of ZnO nanoparticles enabling control over light propagation that can achieve advanced optical properties with potential applications in photonics, sensors, and optoelectronic devices.

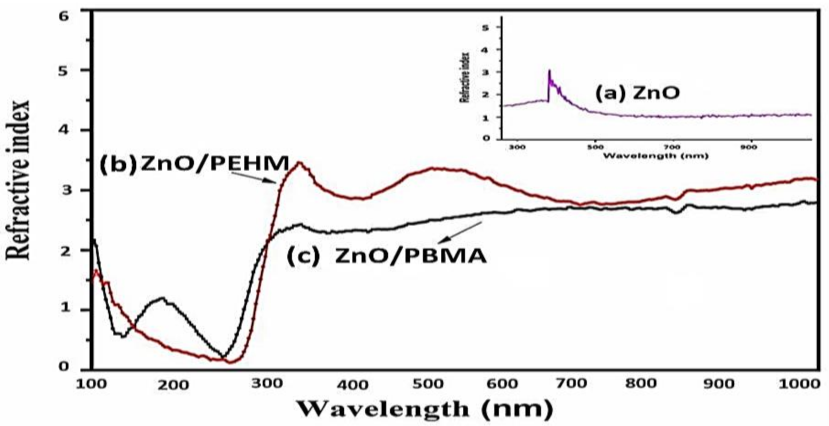

Fig. 4. Refractive index (n) for (a) ZnO, (b) ZnO/PEHM and (c) ZnO/PBMA measured at room temperature

Raman spectra

Raman spectra displayed in Figure (5) and confirmed the characteristic peaks of ZnO/PEHM at 435 and 285 cm^{-1}which were possibly due to the interaction of ZnO's oxygen atom with carbonyl or ethoxy group in acrylates structure [18-20]. The intensity changes of the Raman peaks between 900 and 1800 cm^{-1} where an exponential increase in the intensity was noted for the bands at 1353 and 1531 cm^{-1} reaching 500 ppm [21-25].

Raman spectroscopyis based upon the interaction of light with the chemical bondswhich provides detailed information about chemical structure.

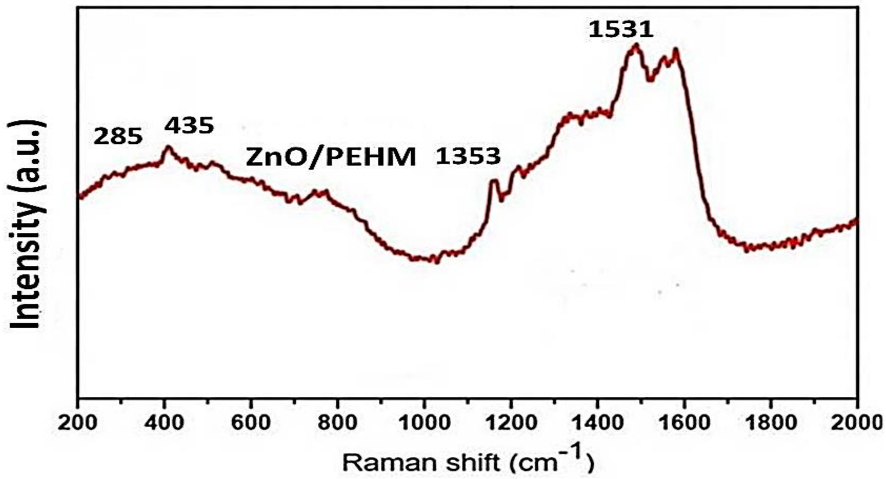

Fig. 5. RAMAN spectra of ZnO/ PEHM nanocomposite

4. Conclusions

Zinc oxide/poly(butyl methacrylate) and poly(ethyl hexyl methacrylate) nanocomposites were prepared using casting evaporation method. The optical molecular switches are recommended as the potential application of this work. The optical molecular switch molecules made up of the different materials affect greatly on the absorption wavelength. The absorbance, Raman spectra and refraction index of the ZnO/ PEHM and ZnO/ PBMA showed a significant performance after the incorporation of ZnO nanoparticles. PEHM and PBMA's π-π* absorption band showed a prominent band located in the UV region around 330 nm. This is in a good match to the electronic transition of ZnO/PEHM and ZnO/PBMA nanocomposites to the first excited singlet state (S1) at a peak about 330 nm.

Conflicts of interest

The authors confirm that there are no conflicts of interest

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