



PMMA/ZnO NANOCOMPOSITE SYNTHESIS BY MICROWAVE RADIATION

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ABSTRACT

The paper reveals the simple, quick, cost effective synthesis technique of polymer based nanocomposite which provides enhanced properties than individual. In the present work, we improve a solution based method to synthesize PMMA/ZnO nanocomposite via a solution mixing method in which various ZnO nanostructures were used as a reinforcement particles in the PMMA matrix in addition to DMAc, the resulting solution is extracted as a thin films by spin coating and are subjected to Microwave radiation. The XRD, FTIR, UV, PSA, SEM, AFM revealed the structural, morphological and optical properties of the polymer nanocomposite PMMA/ZnO.

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INTRODUCTION

Nanocomposites comprises nanosized inorganic particles dispersed in a polymer matrix are suggested as promising materials for various applications in areas like catalysis, organic batteries, electronics and optoelectronics [1]. The existence of nanoparticles in the polymer frequently changes the material properties of the matrix material properties have been reported[2-3]. Nanometer sized particles have been made from different organic inorganic particles and impart composite materials improved properties [4]. Nanoscale materials have a large surface area for a given volume [5]. Since many important chemical and physical interactions are led by surfaces and surface properties, a nanostructured material can have substantially divergent properties from a larger dimensional material of the same composition[6-7]. Depending on the nature of the components used and the method of preparation, significant differences in composite properties may be obtained [8].

Without proper dispersion, the nano material will not offer improved mechanical properties over that of traditional composites, in fact, a poorly distributed nano material may degrade the mechanical properties [9]. Besides, optimizing the interfacial bond between the particle and the matrix, one can tailor the properties of the overall composite.

For instance, good adhesion at the interface will improve properties such as interlaminar shear strength, delamination resistance, fatigue, and corrosion resistance. Finally, it is imperative to identify that nanocomposites research is extremely broad, encompassing areas such as electronics and computing, data storage, communications, aerospace and sporting materials, health and medicine, *harvesting energy (nanogenerator)*, environmental, transportation, and national defense applications [10].

ZnO nanoparticles are often selected as reinforcement particles because of their high transparency, relative low cost and used due to their high hardness, corrosion resistance and strength [11], in polymer nanocomposites, and has shown high potential because of its distinctive optical and electrical properties [16-18]. Nanoscale zinc oxide has a wide band gap of 3.37 eV in the UV region, due to which it is an efficient UV absorber [19, 20]. Polymer nanocomposites employing ZnO, the nanocomposite with poly-methylmethacrylate (PMMA) have been widely investigated for their applicability in UV protecting film and plates, antireflective coating, protective layers or transport barrier and enhanced thermal stability [24-26].

Polymer nanoparticle interface

The large specific surface area of the filler causes the formation of an interfacial polymer layer (shell) attached to the particle core [40]. The physical properties of the polymer localized in the shell are diverse from the bulk polymer due to immobilization. If there are attractive forces between the interfacial polymer and the filler, the mobility of the polymer chains is reduced and the glass transition temperature

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increases. If there are repelling forces between the particle and the interfacial layer, the polymer chain mobility is increased yielding in a plasticizing effect with glass transition temperature depression. Especially precise dynamic mechanical analysis (DMA) and differential scanning calorimetry (DSC) measurements can be used for a measurement of the glass transition temperature change with nano filler load [40]. There is strong evidence that the interaction of the interfacial layer with the particle and the free bulk polymer is responsible for the changes in thermo mechanical and electrical properties.

Nanoparticles and their Stability in Solutions

Nanoparticles in solutions present basic colloidal systems consisting of a continuous phase which is a dispersed medium (solvent) and a dispersed phase (nanoparticle). Each nanoparticle appears to be an aggregate of atoms or more or less simple molecules. A system turns out to be stable when its dispersed phase can exist as separate individual particles for a long time. We may describe the stability of colloidal solutions in two ways:

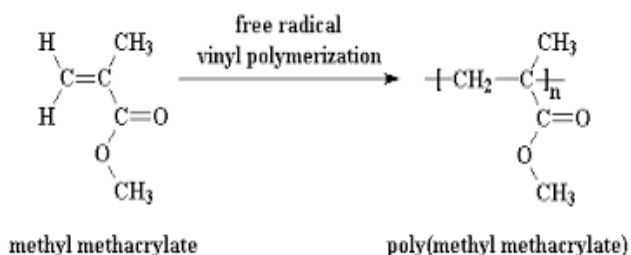
Important factors that describe *kinetic stability* of colloids are Brownian motion, viscosity of the medium and dispersion etc. Kinetically stable systems are where the velocity of dispersed particle precipitation under the action of gravity forces is so slow that it can be neglected [51].

The *Aggregation stability* is the ability of the system to preserve the degree of particle dispersity. This type of stability is attributed to the ability of nanoparticles to create large aggregates to adsorb low molecular ions on their surface from the solution leading to formation of an adsorption layer. This layer consists of potential determining ions and counter ions and a diffusion layer containing residual counter ions.

PMMA: Poly Methyl Methacrylate

Poly (methyl methacrylate) or poly (methyl 2-methylpropanoate) is the polymer of methyl methacrylate, with chemical formula $(C_5H_8O_2)_n$. It has favorable processing conditions, and a wide range of additives have been shown to further improve its properties [51] and its applications in various technological and productive fields take benefits of the unique combination of excellent optical properties (clarity, transparency from the near ultraviolet to the near infrared), with chemical inertness, good mechanical properties, thermal stability, electrical properties, weather resistance[52].

PMMA is produced by free radical polymerization of Methyl methacrylate in mass (when it is in sheet form) or suspension polymerization



PMMA has high mechanical capacity, high Young's modulus and low elongation at break. It is one of the hardest thermoplastics and is also highly scratch resistant. It exposes

low moisture and water absorbing capacity, due to which products made have good dimensional stability. The thermal stability of standard PMMA is only 65°C. Heat stabilized types can resist temperatures of up to 100°C. PMMA can withstand temperatures as low as -70°C.

DMAc

Typically N, N-Dimethylacetamide Structural formula is $CH_3-CO-N(CH_3)_2$ which is constructed from dimethylamine and acetic acid in closed system. Most DMAc is generally used for polymer dissolution in man made fibre production industry. The procedure uses the best recovery technology (>99%), so that DMAc production is only related to replace the solvent losses because of the acid hydrolysis during the recovery and to the environmental releases during the whole processing [55].

Experimentation

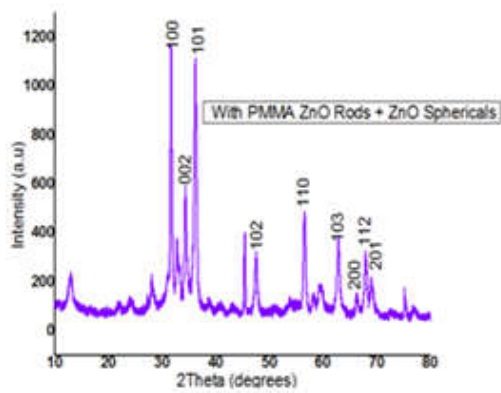
ZnO Nanoparticles of spherical structures are synthesized as reported in[24] and further the same technique is employed with change in temperature, growth time led to the formation of mixture of ZnO Nanorods and Nanowires as reported in [25] were used as a reinforcement particles for the processing of PNC's.

PMMA/ZnO nanocomposite was prepared through an easy solution mixing method. DMAc was taken as the solvent for mixing of ZnO nanostructures into PMMA, as PMMA and ZnO nanostructures are well dispersed in this solvent. In a general synthesis, 1gram PMMA was dissolved in 30 ml of DMAc under continuous stirring at 80°C. In other beaker, different ZnO nano structured contents (Nanoparticles, Nanorods) were dissolved in 20 ml of DMAc and the output solution was subjected to ultrasonic vibration for 30 min to break apart the agglomerates. The resultant ZnO nanostructures solution was added to the above solution. The mixture was consequently heated to 80°C and stirred for 3hours. The output was again sonicated for 30 min. After sonication, nanocomposite films with a thickness of 2 - 4 μm were spin coated onto copper electrodes and placed in microwave oven at 60°C and dried for 1 day. Mixing of solution is a cost effective way to accomplish nanocomposite thin films and provides more benefits than other traditional methods including better scattering of nanoparticles in the polymer matrix and reactions performed at a less temperature[57].

RESULTS AND DISCUSSIONS

XRD Analysis

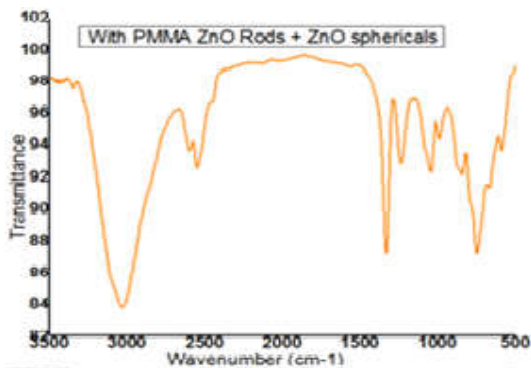
The XRD patterns show a broad non crystalline peak (10-30⁰) of PMMA and nanocrystalline diffraction peaks (30-80⁰) of ZnO. The peaks between 30-80⁰ increase in their intensity with the increase of the ZnO content. All the diffraction peaks corresponding to (100), (002), (101), (102), (110), (103), (112) and (201) planes are in accordance with the typical wurtzite structure of bulk ZnO. The incorporation of ZnO nanostructures produces neither a new peak nor a peak shift with respect to PMMA indicating that ZnO filled PMMA/ZnO Nanocomposite consists of two phase structures.



XRD Spectra of PMMA/ZnO Nanocomposite

FTIR Analysis

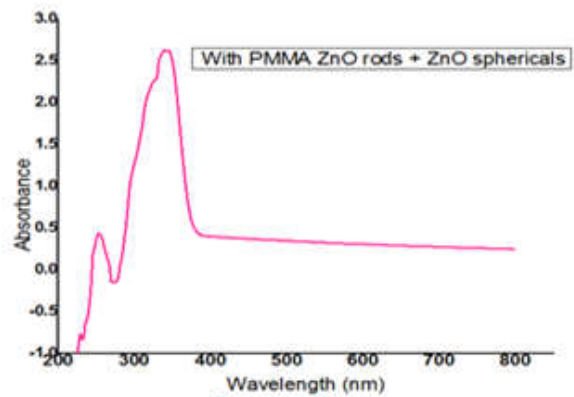
The spectra of the Nanocomposite films are analogous except for the absorption peaks at 3410 cm^{-1} , which are assigned to Acrylate carboxyl group on the ZnO surface. It is found that the absorption peaks at 3410 cm^{-1} gradually increase in intensity with increasing ZnO nanoparticle content, which indicates that an increasing content of ZnO is blended with the polymer matrix. All the composite films exhibit the characteristic strong absorption peaks of 1742 and 1150 cm^{-1} , which are caused by CAOAC stretching of the PMMA linkages. The absorption peak at near 1447 cm^{-1} is attributable to represent the bending, stretching of CH_2 and CH_3 group in PMMA. The incorporation of ZnO nanostructures in PMMA matrix is confirmed by appearance of characteristic Zn-O vibration band at 459 cm^{-1} .



FTIR Spectra of PMMA/ZnO Nanocomposite

UV Analysis

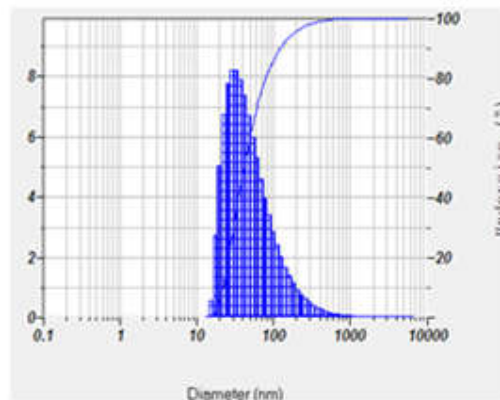
UV-Vis absorption of PMMA/ZnO nanocomposite were measured on UV-Vis spectrometer in the spectral range between 220 nm and 385 nm . The absorption peak is seen at 372 nm corresponding to the exciton state in the ZnO nanostructures. PMMA/ZnO nanocomposite those are prepared by the polymerization have enhanced visible transparency while UV absorption is still close to 100% of the incident UV light. The PMMA/ZnO nanocomposite films containing ZnO nanoparticles of different average sizes together are capable of absorbing UV light in the range from 395 to 190 nm .



UV-Vis Spectra of PMMA/ZnO Nanocomposite

PSA Analysis

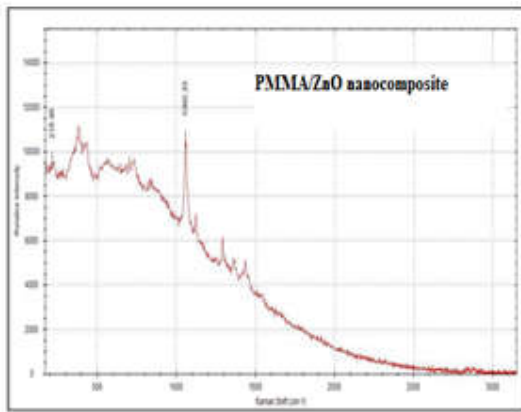
The results of size distribution measurements of PMMA coated on ZnO nanostructures and PMMA/ZnO nanocomposites are shown in Figure 8.29. It could be inferred that cumulated diameters of nanostructures in effect is due to intense micro mixing by sonication. The average size of the nanostructures in PMMA are within the range of 56 nm a slight variation from the size of individual nanostructures i.e 42 nm . A possible reason for increase in particle size distribution could be aggregation of ZnO structures.



PSA of PMMA/ZnO Nanocomposite

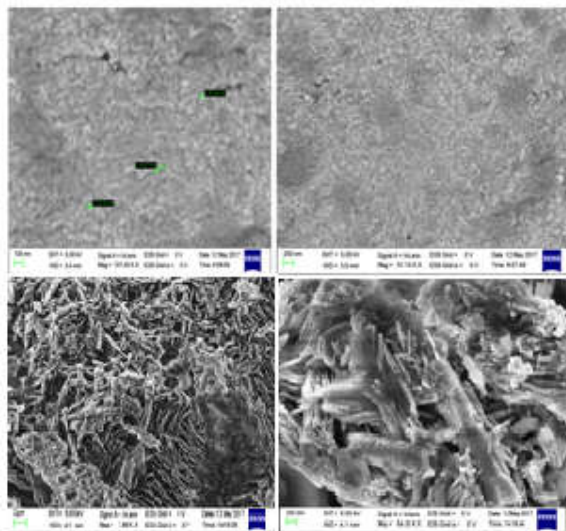
RAMAN Analysis

The Raman Spectra for PMMA/ZnO nanocomposite films are shown in the Figure 8.30. Here it is observed that the maximum intensity occurs at around 1060.33 cm^{-1} for ZnO/PMMA nanocomposite with a slight variation in intensity. The results revealed that the weaker Raman peaks in between 1000 cm^{-1} to 1500 cm^{-1} are due to the interactions of zone-boundary phonons arising due to stretching vibrations of both C-H and Zn-O nanostructures in the composite.



RAMAN Spectra of PMMA/ZnO Nanocomposite

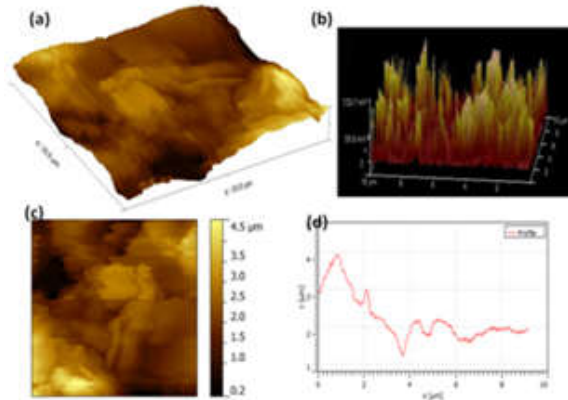
SEM Analysis



SEM Images of PMMA/ZnO Nanocomposite

SEM images of the PMMA/ZnO nanocomposites clearly shows a nearly uniform distribution of the ZnO nanoparticles in the polymer matrix. The ZnO nanoparticle, with average particle size of 10-24 nm, uniformly dispersed in a largely amorphous phase of PMMA matrix. This uniform dispersion is due to the strong interaction of ZnO nanoparticle with the polar solvent DMAc that is used as the common solvent for mixing of ZnO into the polymer matrix, which plays a vital role in breaking the agglomerates. However, distinct local aggregation can also be found as the concentration of ZnO nanoparticle increases in the polymer matrix. These local aggregates were probably found because of high surface energy of ZnO nanoparticles.

Atomic Force Microscope Analysis



AFM Images of PMMA/ZnO Nanocomposite

Figure (a) shows the topography of PMMA/ZnO composite film sample which reveals that the surface has less roughness. Here, the contact area (morphology) plays an important role for enhancing the electrical output performance of the Nanocomposite. Figure 8.3(b) shows the three dimensional current image of the PMMA/ZnO composite film which shows piezoelectric potentials of ZnO. The AFM tip is used as the applied external force on the ZnO nanostructures and the flow of charges come in account and a Schottky barrier is developed between the ZnO nanostructures and the electrode.

CONCLUSIONS

The development of PNC nanocomposites proves to be robust to atmosphere and achieve corrosion resistance, 100% UV absorption. Synthesis technique. of PNC's nanocomposite with analogous dispersion of ZnO nanostructures by the help of Microwave radiation has been a low cost approach is achieved. As thickness of deposition increases porosity automatically decreases. We can get confirmation from the SEM analysis the existence of deposited material is in the nano phase. The AFM studies revealed the surface morphology and led a way to the future development of Nanogenerator.

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