Fabrication of PET/PU/ZnO NPs based Polymer Nanocomposite for Uniform Dispersion of ZnO Nanoparticles by Bar Spreading and Chemical Bath Deposition Method

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Abstract. Currently, nanomaterials are one of the materials being used commercially almost in all domains to improve the quality of products due to its physical, chemical, optical, antimicrobial and catalytic properties. In present paper, one of its roles in polymer chemistry has been explored, in this regards, the fabrication method developed for uniform coating of PET films with ZnO nanoparticles. In this direction, ZnO nanomaterials are very important as they are biocompatible, non-cytotoxic, cheap and easy to produce. The ZnO nanoparticles were obtained by facile hydrothermal route using zinc acetate and urea as precursors in water. The surface coating of nanomaterials on PET/PU films were achieved by bar spreader and chemical bath deposition method. Further, the structural and morphological analysis reveals uniform coating of ZnO nanostructures on to the PET/PU films.

1. Introduction
The barrier properties of existing polymers like polypropylene (PP), low-density polyethylene (LDPE), Polystyrene (PS), polyethylene (PE), polyethylene terephthalate (PET), polyvinyl chloride (PVC) and ethylene vinyl alcohols (EVOH) can improve by incorporation of nanomaterials into existing polymers. These polymer-nanofiller interactions tend to change with size of nanomaterials, which subsequently affect performance of resulting nanocomposites. Initially corrugated materials, paperboard cartons, glass bottles and paraffin wax paper container were developed for packaging of various industrial products [1]. The wax and petroleum based material were used for making packets of dry cereals and biscuits during World War II [2]. This eventually replaced metal, glass and paperboard packaging materials, which helped industries and consumers to protect their goods from extreme conditions [3], [4]. Introduction of polymers as packaging materials revolutionized the packaging industry, as they are light weight, transparent and economical. Although all these packaging
materials raised the standard of packaging, they suffered from major drawbacks like innate permeability to gases and other small molecules. In this regard migration and permeability are the important issues found in existing polymers because no known polymeric material is totally impermeable to atmospheric gases and moisture [5], [6], [4].

Despite the numerous advantages offered by polymers, the present scenario of industries demands the path breaking approach where polymers not only perform the passive role of food packaging, but also they must actively participate in controlling microbial growth, migration of gases and moisture into packets. Therefore, the development of active polymers by incorporation of nanomaterials is need of the day. In this context, nanofillers may improve thermal, mechanical and barrier properties [7, 8]. Additionally, nanomaterials like metal and metal oxide nanoparticles are found to have antimicrobial property which may give extra functionalities to the polymer films to be used in food and medicine packaging [9, 10, 11, 12, 13]. However, the dispersion of nanomaterials onto the matrix is not uniform, which may create problems of agglomeration and leads to affect the overall performance of polymer. In this regards, the PET/PU films and ZnO NPs in different proportion were used to develop polymer nanocomposite (PNC) by bar spreading and chemical bath deposition method to achieve uniform distribution of nanofillers on to the matrix.

2. Materials and Methods

A. Chemicals

All the bulk chemicals, solvents used in the study were of analytical reagent (AR) grade and procured from suppliers including SD fine-chemicals, Loba Chemie, Sisco Research Laboratories and Qualigenes, India.

B. Synthesis and characterization of ZnO nanomaterials

Synthesis of ZnO nanomaterials were carried out by hydro-thermal route. All the analytical grade chemicals were used without any further purification. In typical experimental procedure, 0.1M zinc acetate Zn (O₂ CCH₃ )₂ (H₂ O)₂ was dissolved in 50 mL DI water. 0.6M urea [CO(NH₂ )₂ ] solution was prepared in 50 mL DI water. Both solutions were mixed under constant stirring for 120 minutes at 60 °C then allowed to cool down at room temperature. The resultant settled precipitate was washed by repeated and alternative centrifugation of resultant product at 5000 rpm for 15 minutes each with DI water. The final product was dried in hot air oven at 60 °C for 4 hours to obtain white colored powder of ZnO nanomaterials.

The structural and morphological features of resultant ZnO were characterized by UV-Vis spectroscopy, XRD and Stereoscope for identifying various crystalline phases present in the powder as well as their morphological and optical information.

C. Development PET/PU/ZnONPs active polymer nanocomposite films

The PET/PU/ZnONPs PNC films were obtained by coating MONs (125 μg/mL) dispersed in absolute ethanol, which was then mixed with PU. A one side polyurethane coating on PET films was achieved by dispersing MONs in mixture of PU and isophorone diisocyanate (IPDI) as a hardener component in 4:1 proportion and then resultant mixture were applied on to PET films using bar applicator. The coated films were allowed to cure completely for two hours at room temperature. The same film made out of cured PET/PU films and dispersed MONs (1000 μg/mL) in DI water by chemical bath deposition (CBD) under constant stirring at 60 °C for 2 hours.

3. Results and discussion

A. Characterization of ZnO nanomaterials

The X-ray diffractogram of the hydro-thermally synthesized powder is shown in figure 1 (a). The peak broadening indicates the formation of nanoscale structures and noise indicates the impurities in powder which demands further purification before fabrication of nanocomposites. The powder sample shows the peaks corresponding to (100), (002), (101), (102), (110), (103), (112) and (207) planes.
which indicates formation of hexagonal crystal structure of ZnO. The similar structure observed for ZnO nanomaterial synthesized by semi-solvo thermal method [9]. The absorption spectrum of ZnO powder disperses in ethanol is shown in figure 1 (b). The absorption edge is found to be shifted to the lower wavelength which can be due to size quantization effect. The changed peak intensities have reported with increased reaction time due to the size quantization effect [14].

B. Fabrication of PET/PU/ZnONPs films
The developed PET/PU/ZnONPs films were studied under stereoscope at 400X magnification for understanding surface morphology. Georgopoulos et al., reported the use of stereoscopic optical microscope for study the thermoplastic polymers reinforced with fibrous agricultural residues [15]. Figure 2 reveals the surface of polymer coated with ZnO NPs by bar spreader and CBD method. The more uniform coating of nanomaterials was achieved by CBD method but found to be weakly attached to the matrix of polymer, whereas bar spreading method found to be more effective with respect to surface adherence. The average composition of PET, PU and ZnO NPs in PNC is 40, 30 and 30 % respectively for film coated by bar spreading method and 45, 25 and 30 %, respectively for film coated by CBD method. Further, it discloses that the coating on films by CBD was not 100 % successful as it was removed by friction while, also did not form uniform coating. Therefore, PET/PU films coated with ZnO NPs by bar spreading was found to have complete adhesion and uniform distribution of ZnO NPs throughout the matrix.

Figure 1: (a) XRD graph, (b) UV-Vis Spectrophotometry of ZnO nanomaterials
Figure 2: Surface morphology of PET/PU/ZnONPs under stereoscope at 400X (a) Blank PET; (b) PET/ZnONPs (CB); (c) Blank PET/PU (BS); (d) PET/PU/MONs in water (125 μg/mL) (BS); (e) PET/PU/MONs in ethanol (125 μg/mL) (BS); (f) PET/MONs (CBD) (1mg/mL)

Note: BS- bar spreading method; CBD- chemical bath deposition

4. Conclusion

The X-ray diffractogram of the hydro- thermally synthesized powder was studied. The peak broadening indicates the formation of nanoscale structures and noise indicates the impurities in powder which demands further purification before fabrication of nanocomposites. The absorption edge is found to be shifted to the lower wavelength which can be due to size quantization effect. The synthesized ZnO nanomaterials found to be adhere more in proportion on the matrix of PET/PU films by bar spreading than the CBD method. Therefore, in future such films can be used for packaging of various goods in industries, which demands active properties like antimicrobial activity, improved barrier potential for gases and moisture, improved sensing of factors like humidity and moistures, improved mechanical properties etc.

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