Characterization of Zinc Oxide Nanoparticle from Waste Cooking Oil for Surface Coating

Nurul Hidayah Harun,1 Rosiah Rohani,1,2* and Nur Syafiqah Farhanah Dzulkharnien1

1Department of Chemical & Process Engineering, Faculty of Engineering and Built Environment, Universiti Kebangsaan Malaysia (UKM), Bangi, Selangor 43600, Malaysia.
2Research Centre for Sustainable Process Technology (CESPRO), Faculty of Engineering and Built Environment, Universiti Kebangsaan Malaysia (UKM), Bangi, Selangor 43600, Malaysia.

*Corresponding author:
Associate Prof. Ts. Dr. Rosiah Rohani,
Department of Chemical & Process Engineering,
Faculty of Engineering and Built Environment,
Universiti Kebangsaan Malaysia, 43600 Bangi,
Selangor, Malaysia.
Email: rosiah@ukm.edu.my

ABSTRACT
The use of nanoparticles (nps) for surface coating has increased the researcher's interest in it due to its inherent properties, especially from metal oxide such as zinc oxide (ZnO). It is ideal for combining the coating solution because of its low cost and smaller pigments. Bio-organic materials are used for synthesis of ZnO to produce green or eco-friendly products as well as to replace polymers derived from traditional petroleum. This study aimed to incorporate ZnO into the surface coating with its potential properties to be used as an effective surface coating material. This study was focused on the synthesis of ZnO from waste cooking oil (WCO) via encapsulation of ZnO with APO obtained from WCO, followed by characterization and testing for its suitability in surface coating application. The characteristics of ZnO nps were studied by using the infrared spectroscopy of Fourier transformation (FTIR), x-ray diffraction (XRD), UV spectrum (UV-Vis) and scanning electron microscope (SEM). FTIR analysis is unable to confirm the existence of ZnO nps because it does not show maximum absorption at wavelength of 421 cm⁻¹. X-ray (XRD) shows the particles are in high amorphous conditions. ZnO nps exhibits UV-VIS absorption at a wavelength 330 nm that provides anti-UV property. Analysis from SEM showed Zn element is absent in the dispersion of ZnO-APO paint morphology. In addition, the effectiveness of the antibacterial properties of the ZnO nps for surface coating does not show any inhibition of the bacteria, methicillin-resistant Staphylococcus aureus (MRSA) and Klebsiella pneumoniae (K. pneumoniae). Therefore, better methods of production need to be examined to help in the encapsulation of ZnO nps. The suitability of the organic or inorganic surface coating material is also needed to be explored in by further characterizing the materials based on its composition, strength and effectiveness.
INTRODUCTION

Large infrastructures such as buildings, monuments, and ship hulls to smaller structures such as furniture, house appliances, and most material surfaces around us require protections for long-term use. Surface coatings being deposited on surfaces are expected to provide protective property such as from harmful microorganisms, moisture, and UV radiation depending on the type of materials and their applications. The coatings may consist of polymeric materials and additives to achieve this purpose. There are commercial paints available on the market that kill 99.9% of Staphylococcus aureus (S. aureus), Escherichia coli (E. coli), MRSA, vancomycin-resistant Enterococcus faecalis (VRE) and Enterobacter aerogenes (E. aerogenes) on painted surfaces [1].

In the food industry, packaging films is one of the common methods used to maintain the quality of food. This includes active packaging in which the film is expected to have antimicrobial activity in preserving the food from food-borne bacteria [2]. Eco-friendly products are mostly welcomed in these applications since they can reduce the toxic risks to the environment. An example of the concerning situation is the usage of petroleum-based polymers which leave non-degradable waste [3]. Hence, natural-based polymeric materials from plants and biological materials are introduced. Nanocomposites are currently in trend as it is shown to improve the films and surface coatings properties. One of the famous nanoparticles used is ZnO nps. ZnO nps are widely used due to their abundance in nature and low cost of almost one-fourth of other nps for instance, TiO$_2$ or Al$_2$O$_3$ nps [4]. Other than being easy to get, ZnO nps possess more benefits as it is low cost, UV protective, and antimicrobial. ZnO nps were also chosen in many research that can kill incorporations of nps into films and surface coatings because it is less in terms of its colour [5]. In research where clear coating and films are required, ZnO can give transparent coating as it has fewer pigments [6]. The ZnO is also verified as safe by Food and Drug Administration (FDA). With that, it is suitable for the food packaging industry and promoting eco-friendlier products [7].

ZnO nps are commonly applied in sunscreens for its UV absorption capacity and in antibacterial drugs for its antibacterial ability [8]. ZnO nps can also reduce hydrogen bonding interaction in polymer matrix as it is well dispersed giving less penetration of water into surface [9]. This contributes to the hydrophobic and less water solubility of the surface coatings and films. Small ZnO nps have better performance as antimicrobial agents because it has higher interfacial area which increases its ability to penetrate the cell [10]. This can be due to smaller nanoparticles had bactericidal activity while the larger nanoparticles had bacteriostatic activity against common bacteria such as S. aureus and E. coli. The biocompatibility of ZnO nps can be related to the fact that it has been extensively used as fertilizers and it did support seedling growth and germination [11]. This also shows that ZnO nps are possible to be integrated into organic based material whilst itself being inorganic.

The efficiency of ZnO in surface coatings and films is still uncertain based on the ZnO nps abilities in maintaining their efficiency even after being mixed with polymeric materials. The endurance of ZnO nps toward external conditions such as exposing them to ultraviolet (UV) irradiation is still doubtful. In addition, the sourcing of ZnO nps from green materials for surface coatings application might lead to certain issues in utilizing it. Thus, this work is aimed to depict the current state of ZnO nps incorporation in surface coating solutions with its reported available methods on different types of surfaces. It is also aimed to show the interaction between ZnO nps and the formed matrix to complete each other in protecting surface and films instead of the ZnO nps being in its original form.

Meanwhile, in the support of the chemistry going green race, possible green materials for ZnO nps synthesis and biopolymers suitable for surface coating is discussed as an effort to promote eco-friendly materials. Since certain green materials lack in certain requirements as surface coatings such as low mechanical properties, both synthetic and green materials are discussed to open more rooms for future research by seeing the possible synthetic polymer that can be merged with green polymers and ZnO nps. This study focused on blending ZnO nps with APO synthesized based waste cooking oil followed by characterizing its properties, such as resistant to UV, bacteria, fungi, and rust. Encapsulation of ZnO nps with the synthetic waste started with the production of epoxidized palm olein (EPO) and APO by in-situ process. Then, it was characterized by using FTIR, UV-Vis, XRD and SEM. Lastly, the performance of the ZnO nps was tested for surface coating. ZnO nps were expected to possess properties such as antibacterial, anti-UV and anti-corrosion.

MATERIALS AND METHODS

Materials

Cooking oil from Continental Resources Sdn Bhd was used as the synthetic waste in the production of palm olein (PO). Glacial acetic acid, sodium chloride, formic acid and sodium hydroxide were purchased from System Chemicals. Hydrogen peroxide and acrylic acid were purchased from Chemiz Malaysia. Vinyl acetate copolymer emulsion and thickener were purchased from Chuan Plus Industries Sdn Bhd. Zinc oxide nanoparticles from Sigma Aldrich, sulphuric acid from R&M, sodium bicarbonate from Meriah, triethylamine from F&S while 4-methoxyphenol from Solarbio. The bacterial strain used in this study were MRSA and K. pneumonia. They were obtained from ATCC, USA.

Palm Olein (PO)

Based on all the fractions of palm oil, only PO are suitable to use as cooking oils. PO has a maximum cloud point of 10°C that allows it to be used as cooking oil in Malaysia and hot tropical countries [12]. This shows cooking oil that are sold in the market is PO. Therefore, this study obtained cooking oil from Continental Resources Sdn Bhd as PO and considered the PO as waste cooking oil. The use of PO in the market replaced the waste cooking oil by considering that the waste oil has almost the same characteristics as fresh oil in the market, that went through the purification treatment process.

Preparation of Epoxidized Palm Olein (EPO)

EPO was produced by using the in-situ method. Per-acid solution containing (4 mol of glacial acetic acid, 8.24 mol of hydrogen peroxide and 1% sulfuric acid) was prepared [13]. Then, 1.62 mol PO was put into a per-acid solution at 60-65°C for 2.5 hours. After complete epoxidation reaction, EPO was washed with 11 g of sodium bicarbonate, 10.8 g of sodium chloride and distilled water. However, the use of per-acid solution was changed to 0.5 mol of formic acid and 0.38 mol of hydrogen peroxide [14]. This is because, the per-acid solution that are initially used produced an EPO that has too high acid value from the previous study.

Preparation of Acrylated Palm Olein (APO)

0.06 moles of EPO are stirred in room temperature at 500 rpm. 2% of triethylamine that acts as a catalyst and 1% 4-methoxyphenol as an inhibitor, then it was stirred for 15 minutes. After that, 0.02 moles of acrylic acid are added in the solution
and stirred for 30 minutes. The resulting APO was purified by washing with distilled water three times.

**Encapsulating of Zinc Oxide Nanoparticles with APO**

0.2 g of ZnO nps was dissolved in 1% acetic acid and stirred for 10 minutes. 1.5 g of APO was added before being sonicated for 15 minutes. 0.1 M of sodium hydroxide was added slowly until the solution reaches pH 6. Then, this solution was left overnight at a temperature of 60°C. The solution of ZnO nps was put in centrifuge at 10,000 rpm for 30 minutes before the precipitate was collected. Finally, the sample was dried in the oven at 70°C for 24 hours.

**Zinc Oxide – APO Paint Preparation**

45 mg of ZnO-APO was put in 50 ml of vinyl acetate copolymer emulsion and stirred for 30 minutes. 21 ml of the solution was mixed with 5 ml thickener and 3 ml hardener. After that, 3 ml of acetone was added to the solution and stirred for 15 minutes.

During the coating process, this biopolymer material was applied on the glass plate at a thickness of 40μm by using the automatic film applicator. Then, this solution was dried at room temperature for 24 hours. After 24 hours, the sample was dredged from the glass plate.

**Characterization of Zinc Oxide Nanoparticles**

Some characterization techniques involving the detection of the presence of ZnO nps were used to detect the absorbance of ZnO nps, identify the characteristics functional group, crystalline properties, crystalline size, and its morphology. UV-vis was used to check the optical properties of the synthesized ZnO nanomaterials. It determines the presence of ZnO nps. This test is important for investigating the effects of biopolymer-ZnO that are synthesized on the surface of the material solution made. The ZnO-APO paint sample was mixed with an ethanol solution before being sonicated for 15 minutes at a temperature of 30°C. After the sonication process was completed, ZnO nps absorption was obtained by using UV-vis DR 3900 model from the Hach brand.

FTIR model that was used in this study is 400 FT-IR/NIR from Perkin Elmer brand, this analysis is important as the results reveal the interactions between material as well as the functional groups present in the synthesized material. D8 Advance model from Bruker brand was used for XRD test, it shows the crystallinity and purity of the sample. The sample was scanned at 0-80°C with scanning rate of 30/min. SEM was used to analyze the morphology and particle size distribution of micro and nanostructures by using MERLIN model from Zeiss brand. It can also show the type of nanoparticles formed (nanorods, nanosheets or nanospheres), show if there is any agglomeration occurring and any hollow cavity present in the structure.

**Antibacterial Activity**

Bacteria used in this test are methicillin-resistant *Staphylococcus aureus* (MRSA) and *Klebsiella pneumoniae* (*K. pneumoniae*). These bacteria are chosen because there are studies that show gram-positive bacteria such as MRSA and gram-negatives such as *K. Pneumoniae* can live on a dry surface for several months. Disc diffusion method was used to study antibacterial properties. This test was performed to compare discs containing the synthesized coating with a blank disc. The bacterial inoculum was put in a cultured broth for 24 hours on solid nutrient agar that are prepared in sterile petri plates. A disk with 6 cm in diameter was made by using a puncher before the coating solution was put into it. Then, this agar was incubated for 24 hours at 37°C.

**RESULTS AND DISCUSSION**

**Physicochemical Properties**

One of the physicochemical properties that was obtained in this study was the acid value of PO, EPO and APO (refer Fig. 1). Acid value for PO in this study was 0.53%, and the value has increased to 44.1%, when it turns into EPO. Acid value of EPO produced was too high compared to the previous study, 8.09% [13]. High acid value indicates that the content of free fatty acids in PO was still high and not completely converted into the oxirane ring that should be present in the EPO. Thus, type and quantity of per-acid solution was changed to 0.5 moles of formic acid and 0.38 moles of hydrogen peroxide. The results show the acid value of EPO is 6.95%.

Next, acid value of APO was 7.07%, which very close to the acid value of EPO. It shows that almost all the residues of unreacted acrylic acid in the APO synthesis are successfully removed from the reaction mixture [16]. The number of acid value for APO was slightly higher than EPO due to the existence of unreacted particles of acrylic acid that were miscible with ethanol during the sodium hydroxide titration acid number. The trend for the acid value from PO, EPO and APO decreased because of limiting free acid content in the mixture that developed high of acid functionality group [17].

**Characterization of Zinc Oxide Nanoparticles**

**Fourier Transform Infrared Spectroscopy (FTIR) Analysis**

FTIR spectroscopy helps to identify the expected functional group in its synthesis and distribution. A comparison of FTIR analysis for PO and EPO is shown in Fig. 2. The PO spectrum shows the peak of the stretch vibration =CH found at wavelength 3001 cm⁻¹ and the HC=CH (cis) saturation peak at wavelength 1679 cm⁻¹. The EPO spectrum indicates that PO saturation peak has disappeared. Peak that shows the presence of the oxirane ring was detected at wavelength 863 cm⁻¹. Theoretically, the peak of the stretch vibration =CH can be detected around 3000 to 3050 cm⁻¹ and the oxirane ring can be detected around 750 – 880 cm⁻¹ [14]. The presence of this oxirane ring indicates that EPO was successfully synthesized through the in-situ epoxide method based on palm oil [13].

**Fig. 1. Acid value (%) against oil.**

**Acid value (%) against oil.**

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<th>Oil</th>
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<td>PO</td>
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can be used is dip-coating method. The optical properties of the film in this method can be compared before and after UV exposure.

**X-ray Diffraction (XRD) Studies**

XRD pattern of commercial ZnO nps is shown in Fig. 6(a). The diffraction peaks of commercial ZnO nps were found at 32.0°, 34.6°, 36.2°, 47.8°, 56.8°, 63.0°, 68.1°, 69.2°, 77.0°, 81.8°, 89.8°, 93.0°, 94.5° and 99.8°. XRD result in Fig. 6(c) shows amorphous coating when ZnO-APO was blended in the paint. It was resulted in amorphous state due to the state of the paint used was amorphous as shown in Fig. 6(b). Previous study shows the amorphous coating has good corrosion properties and wear resistance [23]. However, Fig. 6(c) shows no characteristics peaks for ZnO nps crystalline were observed. Sharp and clean peak of ZnO nps in the paint produced cannot be detected. This may happen due to ZnO nps was masked by other big particles in the paint used which indicates blending ZnO-APO in the paint has no effect.

**SEM Analysis**

The morphology of commercial ZnO nps is shows in Fig. 7(a). From the SEM image, there are two or more rods are stacked together which resulted in a formation of large rods. The length of these nps probably was around 100 to 200 nm [24]. On the other hand, SEM image for the paint used shows the particles appear to be round with a smooth surface as shown in the Fig. 7. (b). Good dispersion of ZnO-APO in the matrix of the polymer should result in rugged surfaces on the polymer [25]. However, Fig. 7(c) shows the SEM image for ZnO-APO paint shows the morphology was not remained as round shape and particles were started to aggregate. This has happened due to size particles of the paint used is too big compared to the size of ZnO nps, so nps of ZnO were masked by the big particles of the paint.

**Antibacterial Activity**

The antibacterial properties of ZnO-APO paint have been tested against MRSA and *K. pneumoniae*. Two concentrations of ZnO-APO paint (100 and 200 ppm) were tested. Observations on the Fig. 9(a) and Fig. 9(b) show both concentrations of ZnO-APO paint did not show any inhibition on the bacteria tested. Commercial ZnO nps that are not combined with APO was also tested as shown in Fig. 9(c) to confirm the result. However, the observation found that there was no inhibition of the bacteria. The results obtained was contradict the tendency of antibacterial properties of ZnO. At this stage, the exact reason for no inhibition of bacteria is not yet clear. By referring to the results of the FTIR ZnO-APO paint in Fig. 4, the presence of significant organic compounds on the surface of the synthesized ZnO-APO paint can influence the results observed here. These organic compounds can easily dissolve from the surface of ZnO nps, then used by bacteria as a carbon source for growth. As such, antibacterial activity will decrease. This is in line with previous studies that have shown that the presence of organic compounds along with metal oxide nps will reduce antibacterial efficiency [27].
Moreover, the absence of antibacterial property in ZnO-APO may also be influenced by the type of paint that was used. This can be confirmed from the XRD result of ZnO-APO paint in Figure 6. (c) which shows ZnO was masked by big particles, this could be the reason of hindering the antibacterial property. Thus, this study shows that the selection of paint plays big role in surface coating as it impacts the biological properties of the nps. Alternatively, previous study shows ZnO nps that were blended with acrylic paint contained antibacterial property against gram-negative *P. aeruginosa* and gram-positive *S. aureus* [28]. Acrylic paint is categorized as water-based paint, and it is durable because it adheres extremely well. It can be applied to a lot of surfaces as it is stick so much [29].

**CONCLUSION**

The study was successful to blend ZnO nps with APO synthesized based waste cooking oil. Previous studies have shown that glutaldehyde acid, hydrogen peroxide and sulfuric acid are used when synthesizing epoxidized palm olein (EPO). However, this reaction material is incompatible with the equipment used during the experiment as it produces EPO that has too high acid value. Therefore, studies have replaced the reaction substances with hydrogen peroxide and formic acid. Next, the study was also successful to characterize ZnO-APO for surface coating by using UV-vis, XRD and FTIR spectroscopy analysis. ZnO nanomaterials show UV-vis absorption at wavelength 330 nm. XRD analysis shows ZnO-APO paint is amorphous coating and ZnO nps were masked by the big particles in the paint. The FTIR report shows that the resulting sample does not show ZnO nps bond. Analysis from SEM and EDX could confirm the result of FTIR and XRD as there was no Zn element found in the ZnO-APO paint. However, this study was unable to confirm the antibacterial property of ZnO-APO. This is because the ZnO-APO paint produced did not cause any inhibition on the MRSA and *K. pneumoniae* bacteria. Due to its natural properties, ZnO-APO paint shows a significant presence of organic compounds on its surface that are likely to cause no bacterial inhibition to occur. This result also shows the paint used was not suitable as it masked the ZnO nps. This is because the particles of the paint were very big if compared with the nps of ZnO as shown in the FESEM analysis. Based on the characterization analysis and the observations carried out clearly show that ZnO-APO paint does not show the antibacterial property in surface coating. Further research should be done to identify the suitability of the type of paint used as it will affect its properties. Other characterization work of ZnO-APO should also be examined with their potential as an anti-UV substance.

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**REFERENCES**


