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PAPER-ZNO NANO COMPOSITE PAPER FOR ANTIMICROBA PACKAGING APPLICATIONS

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ABSTRACT

Development and innovation for both antimicrobial functional packaging (active packaging and nanocomposite materials) from renewable polymers. This study aims to include ZnO nanoparticles in PLA (Polylactic Acid) paper layers in antimicrobial packaging applications. The method used for the manufacture of ZnO nanoparticles is the precipitation method and heating method in the manufacture of PLA-ZnO nanocomposite by varying 0.5%, 2% and 3.5% ZnO NP. The results obtained are in SEM images showing that the nanoparticles are distributed homogeneously on the surface. Antimicrobial tests showed that nanocomposite worked effectively in deactivating E. coli and S. aureus. Furthermore, E. coli was found to be more susceptible to this type of nanocomposite, showing a reduction of 3.4 log to 3.5% ZnO loading in the PLA layer. Based on the results, it can be explained that the ZnO nanoparticles have several active mechanisms, and different antimicrobial testing methods can only activate some of the mechanisms. In addition, nano-activated packaging materials for food contact applications and market prospects are analyzed.

Keywords: *Nanocomposite, ZnO nanoparticles, PolyLactic Acid, Antimicrobials*

INTRODUCTION

The current trend is to direct research towards developing innovative solutions both for antimicrobial functional packaging (active packaging and nanocomposite materials) and low environmental impact (biodegradable materials, packaging can be recycled by reducing size). (1-10). In this case, developing biodegradable polymers from renewable sources is highly desirable for food preservation and packaging, provided it can be effective as the current plastic or paper used in packaging, protecting food against microbial contamination, physical damage and chemical reactions (eg oxidation). Lactic acid poly (PLA) is one of the polymers naturally produced by several bacteria growing on agricultural crops that are rich in carbohydrates (sugar beets, corn). So far, PLA has attracted attention for applications in the plastic and paper industry with the fastest growing market of 10 - 30% (Javidi, Hosseini, & Rezaei, 2016; Marra, Silvestre, Duraccio, & Cimmino, 2016).

Zinc oxide nanoparticles (ZnO) as antimicrobial agents offer several advantages, such as superior antimicrobial properties, no negative impact on food sensory properties, and compatibility with harsh polymer processing conditions (Duncan, 2011; Liu et al., 2009; Llorens, Lloret, Picouet, Trbojevich, & Fernandez, 2012; Martins et al., 2013). Due to the strong antimicrobial activity of ZnO NP, which also holds potential applications not only in controlling food spoilage (Fernández, Picouet, & Lloret, 2010; Li, Xing, Jiang, Ding, & Li, 2009; Maneerat & Hayata, 2006), but also in food safety control by deactivating foodborne pathogens. Among the several advantages, it can be increased to use ZnO NP for food contact applications, the benefits are as follows:

1) The non-nano form of ZnO has been approved by EFSA (European Food Safety Authority) as an additive for plastic materials and articles, with SML (Specific Migration Limits) of 25 mg/kg of food (CEF EFSA Panel on Food Contact Materials, 2015).

2) ZnO NP shows low toxicity to biological systems (Reddy et al., 2007). In addition, zinc is an important element for human physiological activity; c.a. Required 10 mg / person / day (CEF EFSA Panel on Food Contact Materials, 2015). Toxicity studies recommend an upper limit of 25 mg /person/day (CEF EFSA Panel on Food Contact Materials, 2015).

3) In food packaging, transparency remains a determining factor for choosing packaging materials. On the other hand, some foods are susceptible to UV rays. To overcome this problem, UV inhibitors are used in polymer processing. Studies show that loading ZnO NP as low as 1% by weight enables good UV blocking performance without disrupting the transparency of the host polymer (El-Feky, Hassan, Fadel, & Hassan, 2014; Murariu et al., 2011; Therias et al., 2012).

In this study, we propose a paper-based packaging material, which is coated with ZnO-PLA nanocomposites. This application can be a paper wrapper for food because there is a relatively high risk of microbiological contamination in these cold processed foods. Focus is placed on in vitro assessment of the NP ZnO antimicrobial activity.

RESEARCH METHODS

Materials and tools

This experiment is divided into three parts. First, zinc oxide nanoparticles (ZnO NP) are synthesized. Next, the synthesized ZnO NP is used in paper coatings. Finally, both of them were synthesized ZnO NPs which were tested for compatibility and properties. The chemicals and techniques used to synthesize ZnO NP and paper coating films will be discussed. All chemicals used in the experiment were analytical reagents (AR Grade, 99.9% pure) grade. Dehydrated zinc acetate [Zn (CH3COO) 2 • 2H2O] was obtained from QReC Sdn. Bhd while the sodium hydroxide (NaOH) pellet was obtained from LabChem Sdn. Bhd. Ethanol is obtained from Sigma Aldrich. Lactic acid poly (PLA) (Nature Work TM PLA 3001D) in pellet form obtained from Nature Work ® LLC, Minnetonka, MN USA. It has a specific gravity of 1.24 g / cm 3 and a flow rate index (LKM) of 15 g / 10 minutes (190 ° C / 2.16 kg). The solvent used in this study was chloroform obtained from R&M Chemistry. de-ionized water is used during the synthesis process.

ZnO Preparation

The ZnO preparation was carried out using the precipitation method mentioned in Figure. 1 First, 0.2 M of zinc acetate dihydrate is prepared by dissolving zinc acetate dihydrate with the molecular formula Zn (CH3COO) 2 • 2H2O in de-ionized water. Then, 0.6 m of sodium hydroxide, NaOH is prepared and added dropwise in zinc acetate dihydrate solution with constant stirring at room temperature for 2 hours. A white precipitate is formed from the reaction between zinc acetate dihydrate and NaOH solution. The white precipitate is filtered and rinsed with ethanol followed by de-ionized water. This is to ensure that the remaining NaOH in the white precipitate is lost. Finally, the white precipitate was dried overnight in an oven at 60 ° C. The obtained white precipitate was sent for XRD and FTIR analysis to ensure that pure ZnO NP was obtained. ZnO NP is then stored to be used to prepare composites.

Preparation of Nanocomposite PLA / ZnO

15 g of PLA pellets (Polylactic Acid, 4060D, Natureworks) are dissolved using chloroform. Then the dissolved PLA was added with ZnO NPs at a concentration of 0.5% by weight, 2% by weight and 3.5% by weight (% by weight of the PLA) and stirred with strong stirring at room temperature until it dissolves fully. Subsequently bleached white kraft paper (base weight 106 g / m, an ash content of 7.7%, top side size) was used as a substrate for coating. The coating is carried out on the side of the size. The coating is carried out on a film lab applicator (Elcometer 4340) using a fine rod to store 50-micron wet films onto the substrate. After coating, the sample is left to dry overnight at room temperature. The structure of the final wrapping material is illustrated in Figure.2.

Figure.1 Synthesis of ZnO Nanoparticles

RESULTS AND DISCUSSION

3.1 Characteristics of ZnO Nanoparticles
3.1.1 Fourier Transform Infrared Spectroscopy (FTIR)
Figure 3 shows the FTIR spectrum of the synthesized ZnO NP obtained in the range of 4000 - 400 cm - 1. The band at 3378.49 cm - 1 is due to the stretching vibrations of the OH group in water, alcohol and phenol, possibly

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due to atmospheric humidity. The peak at 1695.5cm-1 corresponds to C = group O carboxylic derivatives, which may be due to residues of zinc acetate used in the reaction. The peak at 1413.6 cm - 1 is related to the symmetrical stretching vibrations of the carboxylic group [11]. The absorption at 832.20 cm - 1 is due to the formation of Zn tetrahedral coordination [12]. The broad absorption band found at 364.71 cm - 1 is related to the hexagonal ZnO mode (Active friendly). Similar results were also observed by other researchers for ZnO NP [13].

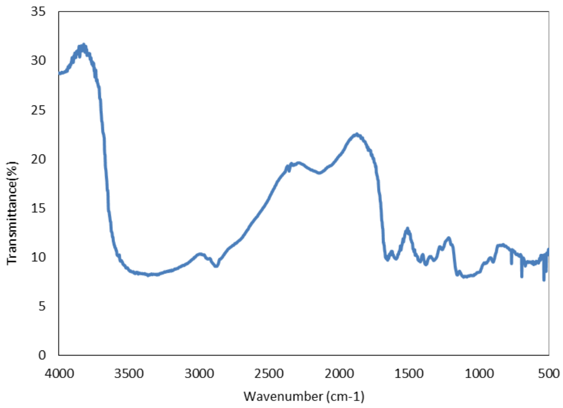

Figure.2 Spektrum FTIR ZnO NP

3.2 Characteristics of PLA-ZnO paper nanocomposites

3.2.1 SEM (scanning Electron Microscope)

Figure 4 shows the morphology of the surface of the layer by using representative SEM taken from each sample. Note that images are presented in pairs when captured at the same point of view but are produced with different detectors: secondary electrons provide more information about the morphology of the sample, while the backwards-fibre electrons contrast with the composition of the material. In a general review, the surface of the paper is well covered by layers, showing good smoothness and the absence of surface pores. This is important for the following antimicrobial tests with the JIS Z 2801. Also, ZnO is distributed homogeneously, which is clearer in backscattering images (small white dots); on the other hand, some ZnO aggregates survive in the layers (larger white dots). Clearly, with increasing NP loading, more NPs appear on the surface, and thus an antimicrobial activity that is stronger than the material can be expected.

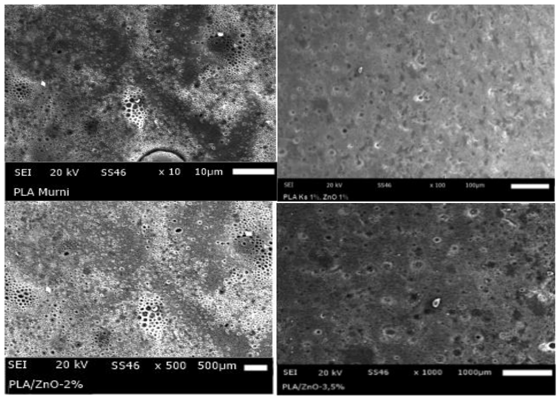

Figure.3 SEM of PLA-ZnO coating

3.2.2 Characteristics of Antibacterial Test

The S. aureus (Gram-positive) susceptibility test with respect to the active ingredient is shown in Figure 5. For convenience comparison, the concentration of control bacteria at 0 hours was used as a baseline. As expected, S. aureus susceptibility follows ZnO NP concentrations - higher concentrations provide stronger antimicrobial effects. If in log reduction, this corresponds to 1.16, 1.66, and 5.18. A log reduction greater than 2 indicates a killing success greater than 99%, and therefore the material can be described as "antimicrobial" (Murariu et al., 2011; Pantani, Gorrasi, Vigliotta, Murariu, & Dubois, 2013). So, in this sense, only a 3.5% -ZnO NP sample can be said to be antimicrobial against S. aureus. These results are comparable to those reported in previous publications: for example in the study of Martins et al. (2013), starch-based coatings containing 1.37% by weight of ZnO NPs induced 1.6 log reduction of S. aureus; in a similar study (Murariu et al., 2011), 3% by weight NP achieved a 4.3 log reduction in the same bacterial strain; whereas in the work of Pantani et al. (2013), it takes longer (7 days, not 24 hours) to achieve a satisfactory log reduction. The difference between results from different sources can be attributed to his microbic activity. ZnO NP in certain morphologies has stronger activity than others (Esmailzadeh, Sangpour, Shahraz,

Hejazi, & Khaksar, 2016). In addition, the smaller the particle size the stronger the antimicrobial efficacy (Yamamoto, 2001).
For the E. coli susceptibility test, as shown in Figure 6, a stronger inhibitory effect was observed with all samples containing ZnO NP, each of which induced 3.15, 3.58 and 4.30 log reduction. Clearly, this test provides evidence that E. coli (Gram-negative) is more susceptible to ZnO NPs than S. aureus (Gram-positive). Note that the detection limit of the agar layer method used is 3.4 log (CFU / mL).

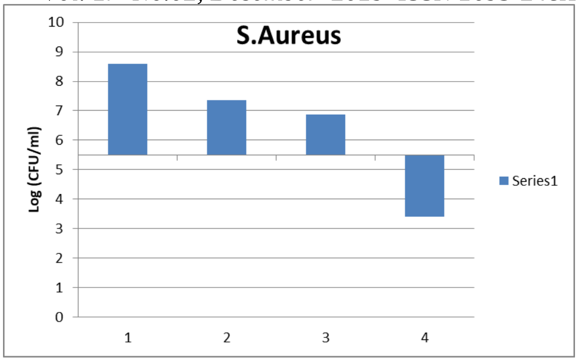

Figure.5 Antimicrobial test to determine S. Aureus

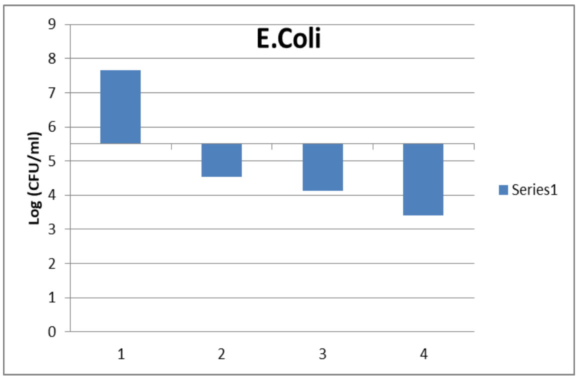

Figure.6 Antimicrobial Test to determine E.Coli

CONCLUSION

In this study, ZnO was included in the PLA layer for antimicrobial packaging applications. Surface-coated nanoparticles with 1.24% by weight organosilane, which is thermally stable in the PLA extrusion temperature range as suggested by TGA analysis. Packaging materials characterized by SEM were found to be homogeneously distributed on the surface thanks to surface modification, although some aggregates remain. Antimicrobial tests show that the incorporation of ZnO makes the surface of the antimicrobial material against S. aureus and E. coli. In addition, the agent was found to be stronger against E. coli, giving a reduction of 3.15 log at 2.5% by weight of the loading agent. For further research, the following improvements should be considered. First, materials can be produced with an extrusion coating, which better reflects the case in industrial applications. Second, apart from in vitro testing, the antimicrobial performance of the material must be validated by testing with real food.

REFERENCE

[1] S. Khalloufi, J. Giasson, C. Ratti, activity of freeze-dried mushrooms and fruit, Can Agr Eng, 42 (2000) 51-56.
[2] A. Cagri, Z. Ustunol, ET Rysers, antimicrobial edible films and coatings, J Food Protect, 67 (2004) 833-848.
[3] M. Vargas, A. Albors, A. Chiralt, C. Gonzalez-Martinez, Characterization of chitosan-oleic acid composite films, Food Hydrocolloids, 23 (2009) 536-547.
[4] G. Findenig; S. Leimgruber; R. Kargl; S. Spirk; K. Stana-Kleinschek; V. Ribitsch, Making Water Barrier Coatings from Hydrophilic Components. ACS Appl. Mater. Interface 2012, 4, 3199-3206.
[5] T. Bourtoom, MS Chinnan, Preparation and properties of rice starch-chitosan mixed biodegradable film, LWT-Food Sci Technol, 41 (2008) 1633-1641

[6] MA Bertuzzi, EF Castro Vidaurre, M. Armada, JC Gottifredi, water-permeability edible starch-based films, Journal Of Food Engineering, 80 (2007) 972-978.

[7] M. Perez-Mateos, P. Montero, MC Gomez-Guillen, Formulation and stability of biodegradable films made from cod gelatin and sunflower oil mixtures, Food Hydrocolloids, 23 (2009) 53-61.

[8] T. Sivarooban, NS Hettiarachchy, MG Johnson, physical and antimicrobial properties of grape seed extract, nicin, and EDTA incorporated edible film soy protein, International Food Research, 41 (2008) 781-785.

[9] MA Del Nobile, A. Conte, AL Incoronato, O. Panza, antimicrobial efficacy and release of thymol kinetics from zein films, Journal of Food Engineering, 89 (2008) 57-63.

[10] P. Suppakul, J. Miltz, K. Sonneveld, SW Bigger, Active packaging technology with an emphasis on antimicrobial packaging and application, Journal of Food Science, 68 (2003) 408-420.

[11] Javidi, Z., Hosseini, S. F., & Rezaei, M. (2016). Development of flexible bactericidal films based on poly(lactic acid) and essential oil and its effectiveness to reduce microbial growth of refrigerated rainbow trout. LWT – Food Science and Technology, 72, 251– 260.

[12] Marra, A., Silvestre, C., Duraccio, D., & Cimmino, S. (2016). Polylactic acid/zinc oxide biocomposite films for food packaging application. International Journal of BiologicalMacromolecules, 88, 254–262.

[13] Duncan, T. V. (2011). Applications of nanotechnology in food packaging and food safety: Barrier materials, antimicrobials and sensors. Journal of colloid and interface science, 363(1), 1-24.

[14] Liu, Y., He, L., Mustapha, A., Li, H., Hu, Z., & Lin, M. (2009). Antibacterial activities of zinc oxide nanoparticles against Escherichia coli O157: H7. Journal of applied microbiology, 107(4), 1193-1201.

[15] Llorens, A., Lloret, E., Picouet, P. A., Trbojevich, R., & Fernandez, A. (2012). Metallic-based micro and nanocomposites in food contact materials and active food packaging. Trends in Food Science & Technology, 24(1), 19-29