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Coláiste na hEolaíochta, na hInnealtóireachta agus Eolaíocht Bhia
College of Science, Engineering and Food Science

Manufacture of Metal-Based Nanoparticles and Their Incorporation into Plastic Materials for the Development of Active Antimicrobial Food Packaging

A Thesis submitted in the Fulfilment of the Requirements for the Degree of Doctor of Philosophy

Presented by
Azlin Shafrina Hasim, MSc., BSc.

Under the supervision of
Prof. Joseph P. Kerry
Dr. Malco Cruz-Romero
Prof. Michael A. Morris
School of Food and Nutritional Sciences, UCC
Head of School – Prof. Yrjo Roos

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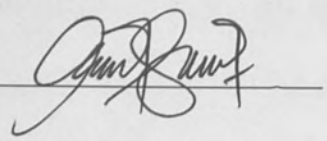
Declaration

I hereby declare that this thesis is my own work and contains no material that has been accepted for the award of any degree in University College Cork or elsewhere.

Signature: 

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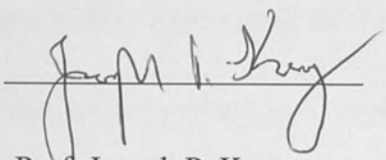
Certified by: 

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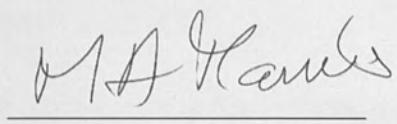
Certified by: 

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Thank You Almighty Allah for uncountable blessing....

"الحَمْد لله"

"Tidak ada kemudahan kecuali apa yang Engkau jadikan mudah. Sedang yang susah dapat Engkau jadikan mudah, apabila Engkau menghendakinya."

Go Raibh Maith Agat, Thank You, Terima Kasih

Abstract

Silver (Ag), copper (Cu) and zinc oxide (ZnO)) nanoparticles (NPs) were synthesized and antimicrobially assessed. Subsequently, Ag NPs showed the best antimicrobial effects against a wide range of test microorganisms: *Staphylococcus aureus*, *Bacillus cereus, Escherichia coli* and *Pseudomonas fluorescens* as well as microflora isolated from raw chicken breast fillets (CBF), raw beef and cooked ham. Ag NPs were then employed to manufacture antimicrobial films *via* solvent casting, extrusion or coating techniques. Subsequently, the resulting films were assessed in terms of their mechanical, thermal, barrier and antimicrobial properties. Surface modification of commercial polymer films (low density polyethylene (LDPE), composite LDPE with 4% ethylene vinyl acetate (LDPE-EVA) or polypropylene (PP)) using strong oxidising solutions (piranha solutions) or UV/ozone treatment was carried out to increase wettability and attachment of Ag. In general, the mechanical and thermal properties of the active films were dependent upon the type of polymer and method employed to incorporate Ag NPs. The manufactured Ag-active films were then tested on CBF and results showed that, regardless of the method used (solvent casting, extrusion or coating), the shelf-life of CBF was significantly extended. UV/ozone treatment increased the wettability of commercial polymer films compared to piranha solutions as shown by toluidine blue O (TBO) assay and FTIR analysis. Furthermore, antimicrobial activity of the Ag-coated LDPE films increased with increased exposure time to UV/ozone.

Novel methods to manufacture Ag- coated films were developed using self-assembled polystyrene-*b*-polyethylene (PS-*b*-PEO) block copolymer (BCP) and layer-by-layer (LbL) application. *In-vitro* antimicrobial testing showed that Ag-active films had good antimicrobial activity against Gram-positive and Gram-

negative bacteria. However, these methods were not easy to scale-up for shelf-life testing purposes. For this reason, a simple process for producing robust Ag-coated films was developed that allowed surface-modification of commercial LDPE films so that a well-defined antimicrobial surface could be prepared using Pluronic™ surfactant and PS-*b*-PEO BCP. The Pluronic™ surfactant acts to provide a surface that is more readily functionalised, whilst BCP provides a reactive interface which is important in providing a route to Ag NPs that are well adhered to the film surfaces. Because of the simplicity of the methods developed, this technique did not have a film size limitation. The resulting active films showed good antimicrobial activity, but results obtained were dependent upon the initial concentration of Ag precursor used and the number of Ag coatings applied. Generally, Gram-negative bacteria were more susceptible to Ag NPs compared to Gram-positive bacteria and that pure culture bacteria were more susceptible than microflora isolated from meat products. The Ag-active films developed in this thesis have the potential to be used as antimicrobial packaging in food packaging applications.

Keyword: silver nanoparticles; antimicrobial activity; shelf-life; antimicrobial packaging; surface modification.