UNIVERSITI PUTRA MALAYSIA

PRODUCTION, CHARACTERIZATION AND MIGRATION OF MELTBLENDED AND LAYER-DEPOSITED POLYETHYLENE SILVER NANOCOMPOSITE AS ANTIBACTERIAL FOOD PACKAGING

MARYAM JOKAR

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By

MARYAM JOKAR

Thesis Submitted to the School of Graduate Studies, Universiti Putra Malaysia, in Fulfillment of the Requirements for the Degree of Doctor of Philosophy

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DEDICTED TO MY KIND FAMILY

Abstract of thesis presented to the Senate of Universiti Putra Malaysia in fulfillment of the requirement for the Degree of Doctor of Philosophy

PRODUCTION, CHARACTERIZATION AND MIGRATION OF MELT-BLENDED AND LAYER-DEPOSITED POLYETHYLENE SILVER NANOCOMPOSITE AS ANTIBACTERIAL FOOD PACKAGING

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August 2012

Chairman: Professor Russly Abdul Rahman, PhD

Faculty: Faculty of Food Science and Technology

Antimicrobial packaging, a promising form of active packaging, is an innovative concept which has been the subject of substantial research for only the last two decades. The aim of this study was to incorporate silver nanoparticles into polyethylene films and to investigate physical and antimicrobial properties and silver ion migration of polyethylene nanocomposite. Silver nanoparticles with a uniform size of 5.5±1.1 nm were prepared by chemical reduction using polyethylene glycol (PEG) as stabilizer as well as reducing agent of silver nitrate. Silver colloid dispersion showed typical visible spectra band at 447 nm and also significant ($p<0.05$) antimicrobial effects on *Escherichia coli*, *Staphylococcus aureus* by agar plate test. Low density polyethylene (LDPE) was used as polymer matrix. LDPEsilver nanocomposites produced by two methods of (i) melt blending and (ii) layer by layer (LBL) self assembly deposition. In melt blending, silver nanoparticles

at five concentration levels were added into low density polyethylene (LDPE) pellets by melt blending and subsequent hot pressing at 140 °C. Melt blended LDPE silver nanocomposites were characterized by atomic force microscopy (AFM) and X-ray diffraction (XRD) for morphology and size feature and then mechanical, thermal and barrier properties were investigated. Silver nanoparticles did not influence mechanical and thermal properties of melt blended LDPE silver nanocomposite significantly ($p>0.05$). Melt blended LDPEsilver nanocomposite showed clear zone and significant effect on the growth kinetic parameters of *S. aureus* and*E. coli.*

In LBL deposition method, nanocomposite films were prepared by sequential dipping of a LDPE film in either anionic silver colloid dispersion or cationic chitosan with the thickness of 2, 4, 8, 12, 16 and 20 layers. LBL deposited silver nanocomposite films were characterized by electron microscopy and then mechanical, thermal and barrier properties of LBL deposited silver nanocomposites were also investigated. Silver nanoparticles increased crystallinity of LDPE films which was determined by differential scanning calorimeter (DSC) and resulted in improving barrier properties. Chitosan coating increased mechanical elongation strength significantly ($p<0.05$). Antimicrobial efficiency of LBL deposited silver nanocomposites was considerably higher than melt blended ones because silver nanoparticles are trapped in melt blended polymer composites but could release easier in LBL coated nanocomposites. It can be concluded that LBL deposition is preferable than the melt blending processing to produce LDPE silver nanocomposite due to more antimicrobial activity and improved mechanical and barrier properties against water vapor and oxygen.

The silver ion released from either melt blended or LBL deposited silver nanocomposites into EU standard food stimulants (deionized water, 3% acetic acid and 10% ethanol alcohol) and apple juice during 30 days at 4 and 40 °C was determined by atomic absorption spectroscopy(AAS) and analyzed using factorial and response surface designs. Production method, silver concentration, temperature, time and contact media showed significant effect ($p<0.05$) on silver ion migration, respectively. The quantity of silver ion migration from nanocomposites into food stimulants and apple juice was less than allowable concentration (10 ppm) at all cases over 30 days. LBL deposition method, more silver concentration in the polymer, higher temperature and acidic property of contact liquid promote more silver ion release from nanocomposite films. Migration of silver ions from nanocomposites obeyed first order diffusion kinetic.

Abstrak tesis yang dikemukakan kepada Senat Universiti Putra Malaysia sebagai memenuhi keperluan untuk ijazah Doktor Falsafah

PENGHASILAN, PENCIRIAN DAN MIGRASI POLIETILINA NANOKOMPOSIT PERAKMELALUI ADUNAN LEBUR DAN LAPISAN TERDEPOSIT SEBAGAI PEMBUNGKUSAN MAKANAN ANTIBAKTERIA

Oleh

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Pembungkusan antimikrub, sebagai satu bentuk pembungkusan aktif yang berpotensi, merupakan satu konsep inovatif dimana penyelidikan yang menyeluruh hanya dilakukan dalam dua dekad yang lalu. Tujuan kajian ini adalah untuk menginkorporasi nanopartikel perak kedalam filem polietilina dan untuk menhkaji sifat-sifat fizikal dan antimikrob dan perpindahan ion perak nanokomposit polietilina. Nanopartikel perak dengan saiz yang seragam (5.5 ± 1.1 nm) telah disediakan melalui kaedah pengurangan kimia menggunakan glikol polietilina (PEG) sebagai agen penurunan dan pada masa yang sama bertindak sebagai penstabil. Taburan koloid perak menunjukkan spektrum yang visibel pada 447 nm dan kesan antimikrob terhadap *Escherichia coli* serta*Staphylococcus aureus* yang signifikan ($p<0.05$) menggunakan plat agar nutrient. Polietilina ketumpatan rendah (LDPE) telah digunakan sebagai matriks polimer. LDPE-perak nanokomposit yang dihasilkan oleh dua kaedah (i) pencairan adunan dan (ii) lapisan dengan lapisan

(LBL) pemendapaniaitu pengumpulan sendiri. Dalam pemprosesan pencairan, lima tahap konsentrasi nanopartikel perak disediakan sebelum di campur ke dalam pellet polietilina ketumpatan rendah (LDPE) dengan mencampurkan polimer dan nanopartikel menggunakan penekanan panas pada suhu 140 °C. Nanokomposit LDPE- nanopartikel perak dicirikan untuk morfologidan saiz menggunakan mikroskop daya atom (AFM) dan pembelauan sinar-X (XRD) dan kemudian sifat-sifat mekanikal, terma dan halangan di kaji.Nanopartikel perak tidak mempengaruhi sifat dan fungsi mekanikal dan haba adunan filem LDPE secara signifikan ($p>0.05$). Adunan LDPE nanokomposit perak menunjukkan zon pencerahan dan kesan yang besar ke atas parameter pertumbuhan kinetik *S. aureus* dan *E. coli*.

Dalam kaedah pemendapan LBL, filem nanokomposit telah dibuat melalui pencelupan filem LDPE sama ada dalam penyebaran koloid anion perak atau kation kitosan dengan ketebalan 2, 4, 8, 12, 16 dan 20 lapisan. Filem LBL nanokomposit perak terdeposit telah dicirikan melalui mikroskopi elektron dan kemudiannya sifat-sifat mekanikal, terma dan halangan LBL nanokomposit terdeposit telah juga dikaji. Nanopartikel perak meningkatkan penghabluran filem LDPE yang dikira melalui pengimbas beza kalorimeter (DSC) dan menghasilkan fungsi halangan yang lebih baik.Lapisan kitosan meningkatkan kekuatan pemanjangan mekanikal dengan signifikan ($p<0.05$). Kecekapan antimikrob LBL nanokomposit perak terdeposit adalah lebih tinggi daripada dibandingkan dengan kaedah adunan lebur, kerana nanopartikel perak terperangkap di dalam komposit adunan lebur tetapi boleh dilepaskan dengar lebih mudah dalam kaedah nanokomposit LBL. Ini boleh disimpulkan bahawa pemendapan LBL adalah lebih baik dari pemprosesan adunan

lebur untuk menghasilkan LDPE nanokomposit perak kerana sifat-sifat mekanikal dan halangan yang bertambah baik dan aktiviti yang lebih antimikrob.

Ion perak yang di lepaskan melalui kedua dua kaedah ini di nilai berdasarkan standard rangsangan makanan EU (air ternyahion, 3% asid asetik dan 10% etanol) dan jus epal dalam tempoh 30 hari pada suhu 4 dan 40 °C ditentukan dengan menggunakan spektroskopi penyerapan atom (AAS) dan dianalisis menggunakan reka bentuk factorial dan rangsangan permukaan.Kaedah pengeluaran, kepekatan perak, suhu, masa dan media persentuhan menunjukkan kesan yang signifikan ($p<0.05$) terhadap penghijrahan ion perak. Kuantiti penghijrahan ion perak dari nanokomposit kepada perangsang makanan dan jus epal adalah kurang daripada tahap kepekatan yang dibenarkan (10 ppm) delam semua kosselama 30 hari. Kaedah pemendapan LBL, kepekatan perak yang lebih dalam polimer, suhu yang lebih tinggi dan sifat keasidan cecair yang bersentuhan menggalakkan pembebasan ion perak dari filem nanokomposit. Penghijrahan ion perak dari nanokomposit mematuhi kinetik serapan peringkat pertama.

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I certify that a Thesis Examination Committee has met on 2th August 2012 to conduct the final examination of Maryam Jokar on his thesis entitled "Production, Characterization and Migration Study of Melt Blended and Layer Deposited Polyethylene Silver Nanocomposite as an Antibacterial Food Packaging" in accordance with Universities and University College Act 1971 and the Constitution of the Universiti Putra Malaysia [P.U.(A) 106] 15 March 1998. The committee recommends that the candidate be awarded the relevant degree. Members of the Thesis Examination Committee were as follows:

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DECLARATION

I declare that the thesis is my original work except for quotations and citations, which have been duly acknowledged. I also declare that it has not been previously and is not concurrently, submitted for any other degree at Universiti Putra Malaysia or at any other institutions.

MARYAM JOKAR

Date:

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