UNIVERSITI PUTRA MALAYSIA

PREPARATION AND CHARACTERIZATION OF POLY(VINYL ALCOHOL)/CHITOSAN BIO-NANOCOMPOSITES REINFORCED WITH CELLULOSE NANOCRYSTALS, CELLULOSE NANOCRYSTALS/ZINC OXIDE AND CELLULOSE NANOCRYSTALS/ZINC OXIDE-SILVER NANOPARTICLES

SUSSAN AZIZY

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By

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

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PREPARATION AND CHARACTERIZATION OF POLY(VINYL ALCOHOL)/CHITOSAN BIO-NANOCOMPOSITES REINFORCED WITH CELLULOSE NANOCRYSTALS, CELLULOSE NANOCRYSTALS/ZINC OXIDE AND CELLULOSE NANOCRYSTALS/ZINC OXIDE-SILVER NANOPARTICLES

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Polymer nanocomposites are materials composed of polymer matrices and nano-sized fillers with enhanced physical and chemical properties in comparison with the pure polymers or conventional composites. Strong research attempts have been focused on the use of bio-polymers because of increasing environmental concerns of using petroleum base polymers. The present research aims to study the influence of cellulose nanocrystals (CNCs), cellulose nanocrystals/zinc oxide nanoparticles (CNCs/ZnO-NPs) and cellulose nanocrystals/zinc oxide-silver nanoparticles (CNCs/ZnO-Ag-NPs) on the properties of poly(vinyl alcohol)/chitosan (PVA/CTS), an important bio-polymer blend.

Cellulose nanocrystal was extracted by acid–catalyzed hydrolysis of cotton cellulose. ZnO-NPs and ZnO-Ag-NPs were prepared in suspension of CNCs as a stabilizer via a co-precipitation method. The samples were characterized using Fourier transform infrared (FTIR), energy dispersive x-ray spectroscopy (EDS), ultraviolet-visible (UV-vis), x-ray diffraction (XRD), transmission electron microscope (TEM), field emission scanning electron microscope (FESEM), thermogravimetric analysis (TGA) and antimicrobial tests. According to the XRD and TEM results, polygonal structured ZnO nanocrystallites with a mean size of less than 30 nm were formed. The prepared ZnO-Ag nanocrystallites were spherical with a mean size diameters in a 12–35 nm range.

The bio-nanocomposites were prepared by mixing various percentages of nano-sized fillers and PVA/CTS blends in the ratio of 3:1. The properties of the prepared bio-nanocomposites were studied by XRD, TEM, TGA, UV-vis, barrier, tensile and antimicrobial tests. The PVA/CTS/CNCs bio-nanocomposites with low percentage of the CNCs (1.0 wt%) exhibits maximum mechanical, thermal, and barrier properties.

The PVA/CTS/CNCs/ZnO 5.0 wt% bio-nanocomposite exhibits the maximum tensile, and barrier properties. TGA results show that the maximum thermal decomposition of the PVA/CTS increases by about 34 °C at 1.0 wt%. The UV–visible spectrophotometric study shows that the bio-nanocomposites display an excellent performance of absorbing UV light. The antimicrobial tests reveal a favorable antibacterial effect for those PVA/CTS blend films filled with the high levels of CNCs/ZnO-NPs content.

The PVA/CTS/CNCs/ZnO-Ag 5.0 wt% bio-nanocomposite shows the maximum tensile, thermal and barrier properties. The UV–visible measurements showed that the bio-nanocomposites display prefect absorption in the range of 300-700 nm. The all bio-nanocomposites show antibacterial power, with the maximum effect in the 7.0 wt% of CNCs/ZnO-Ag-NPs loading.

Abstrak tesis yang dikemukakan kepada Senat Universiti Putra Malaysia sebagai memenuhi keperluan untuk ijazah Master Sains

PENYEDIAAN DAN PENCIRIAN POLI(VINIL ALKOHOL)/KITOSAN BIO-NANOKOMPOSIT DIPERKUKUH DENGAN SELULOSA NANOKRISTAL, SELULOSA NANOKRISTAL/ZINK OKSIDA DAN SELULOSA NANOKRISTAL/ZINK OKSIDA-PERAK NANOPARTIKEL

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Nanokomposit polimer adalah bahan terdiri daripada matrik polimer dan pengisi bersaiz nano dengan sifat-sifat fizikal dan kimia yang dipertingkatkan berbanding dengan polimer tulen atau komposit konvensional. dipertingkatkan. Sebaliknya, dalam bidang polimer, sebahagian besar penyelidikan tertumpu kepada polimer terbiodegradasikan disebabkan kebimbangan alam sekitar menggunakan polimer asas petroleum yang semakin meningkat. Penggunaan bio-polimer telah menjadi tumpuan utama usaha penyelidikan kerana peningkatkan kebimbangan alam sekitar terhadap penggunaan polimer berasaskan petroleum. Kajian ini bertujuan untuk mengkaji pengaruh nanokristal selulosa (CNCs), nanokristal selulosa/nanozarah zink oksida (CNCs/ZnO-NPs) dan nanokristal selulosa/nanozarah zink oksida-Perak (CNCs/ZnO-Ag-NPs) terhadap sifat-sifat poli(vinil alkohol)/kitosan (PVA/CTS), satu adunan penting bio-polimer.

Selulosa nanokristal telah diekstrak keluar daripada selulosa kapas melalui hidrolisis bermangkinkan asid. ZnO-NPs dan ZnO-Ag-NPs telah disediakan dalam ampaian CNCs sebagai penstabil melalui kaedah ko-mendakan. Sampel yang telah disediakan disifatkan menggunakan jelmaan Fourier inframerah (FTIR), spektroskopi tenaga serakan x-ray (EDS), spektroskopi ultraungu/nampak (UV-vis), pembelauan sinar x-ray (XRD), mikroskop elektron transmisi (TEM), bidang pelepasan imbasan elektron mikroskop (FESEM), termogravimetri (TGA) dan antimikrob ujian. Menurut keputusan XRD dan TEM, ZnO nanokristal yang berstruktur polygonal dengan saiz purata kurang daripada

30 nm telah dibentuk. Pembentukan ZnO-Ag nanokristal adalah bulat dengan saiz purata diameter dalam julat 12-35 nm.

Bio-nanokomposit telah disediakan dengan mencampurkan pelbagai peratusan pengisi bersaiz nano dalam campuran PVA/CTS dengan nisbah 3:1. Sifat-sifat bio-nanokomposit kemudian dikaji dengan ujian XRD, TEM, TGA, UV-nampak, halangan, tegangan dan antimikrobial. PVA/CTS/CNCs bio-nanokomposit dengan peratusan CNCs yang rendah (1.0 wt%) mempamerkan sifat mekanikal, terma, dan penghalang yang maksimum.

PVA/CTS/CNCs/ZnO 5.0 wt% bio-nanokomposit mempamerkan sifat tegangan dan halangan yang maksimum. Keputusan TGA menunjukkan bahawa penguraian terma maksimum bagi PVA/CTS meningkat kira-kira 34 °C pada 1.0 wt%. Kajian spektrofotometrik UV-nampak menunjukkan bahawa bio-nanokomposit memaparkan prestasi cemerlang dalam penyerapan cahaya UV. Tambahan pula, ujian antimikrobial menunjukkan bahawa kesan antibakteria yang baik boleh dicapai pada PVA/CTS filem dengan kandungan CNCs/ZnO-NPs yang tinggi.

PVA/CTS/CNCs/ZnO-Ag 5.0 wt% bio-nanokomposit mempamerkan sifat tegangan, terma dan halangan yang maksimum. Pengukuran penyerapan UV menunjukkan bahawa bio-nanokomposit memaparkan penyerapan sempurna dalam julat 300-700 nm. Selain itu, kesemua bio-nanokomposit menunjukkan kuasa antibakteria, dengan kesan maksimum pada 7.0 wt% CNCs/ZnO-Ag-NPs.

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I certify that an Examination Committee has met on 17 June 2014 to conduct the final examination of Sussan Azizy on his Degree of Doctor of Philosophy thesis entitled "Preparation and Characterization of Poly(Vinyl Alcohol)/Chitosan Bio-nanocomposites Reinforced with Cellulose Nanocrystals, Cellulose Nanocrystals/Zinc Oxide And Cellulose Nanocrystals/Zinc Oxide-Silver Nanoparticles" in accordance with Universiti Pertanian Malaysia (Higher Degree) Act 1980 and Universiti Pertanian Malaysia (Higher Degree) Regulations 1981. The committee recommends that the candidate be awarded the Doctor of Philosophy.

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LIST OF ABBREVIATIONS

BCNC	Bacterial cellulose nanocrystal
BNCs	Bio-nanocomposites
CAB	Cellulose acetate butyrate
CCNs	Carboxylate cellulose nanocrystals
CNCs	Cellulose nanocrystals
CMC	Carboxymethyl cellulose
Cs	Chitosan
C/Z	Cellulose nanocrystals/zinc oxide
C/Z-A	Cellulose nanocrystals/zinc oxide-silver
DMF	N,N-dimethylformamide
DMSO	Dimethyl sulfoxide
EDS	Energy dispersive X-ray spectroscopy
e–h	Electron-hole
fcc	Face-center-cubic
FESEM	Field emission scanning electron microscope
FTIR	Fourier transform infrared
GPS	Glycerol plasticized-pea starch
HMDSO	Hexamethyl disiloxane
INPs	Inorganic nanoparticles
LDH	layered double hydroxide
MFC	Microfibrillated cellulose
MMT	Montmorillonite
NCF	Nano-Cellulose fibers
OT	Oxygen transmission
PA6	Polyamide6
PANI	Polyaniline
PBNCs	Polymer Bio-nanocomposites
PCL	Poly(3-caprolactone)
PEO	Polyethylene oxide
PET	Polyethylene terephthalate
PEG	Poly(ethylene glycol)
PHB	Poly(hydroxyl butyrate)
PGA	Poly(glycolic acid)
PLA	Poly(lactic acid)
PLLA	Poly(L-lactide)
PMMA	Poly(methyl methacrylate)
PNC	Polymer Nanocomposites
POE	Polyoxyethylene
Poly(S-co-BuA)	Poly butyl acrylate co-styrene
PS	Polystyrene
PUA	Polyurethane acrylate
PVA	Poly(vinyl alcohol)
PVAc	Poly(vinyl acetate)

SPR	Surface plasmon resonance
T_g	Glass transition temperature
T_m	Melting point temperature
T_{max}	Maximum degradation temperature
T_{onset}	Onset temperature
TEM	Transmission electron microscopy
TGA	Thermogravimetric analysis
TMC	Trimesoylchloride
TPS	Thermoplastic starch
UHMWPE	Ultra-high molecular weight polyethylene
UVA	Ultraviolet-A
WPU	Waterborne polyurethane

CHAPTER 1

INTRODUCTION

1.1 General Background of Research

In recent times, using petroleum based plastics has been under attack due to absence of recycling facilities or infrastructure, non-recyclability, non-renewability, non-biodegradability or using toxic additives (Tang and Alavi, 2011). As in 2005, in the USA, 28.9 million tons of plastics packaging was made and only about 5.7% of plastic waste was recycled, 94.3% was dumped in landfill and discarded or combusted into the environment (Marsh and Bugusu, 2007). Recent trends show steady growing interest in the use of biodegradable plastics with increasing accessibility of appropriate materials and owing to social and governmental pressure (Rasato, 2009).

Bio-based polymers often show greater biodegradability and biocompatibility, profiting various applications ranging from packaging to medical devices. However, some factors such as poor mechanical properties, relatively sensitivity to water (Debeaufort *et al.*, 1998), high gas permeability behaviors (Koh *et al.*, 2008) and low heat distortion temperature (Ray and Bousmina, 2005) limit their industrial applications (Zhou and Xanthos, 2009). Therefore, in order to improve and/or control properties of these polymer several methods, such as copolymerization, chain extending or blending these polymers together have been applied by researchers (Kylmä *et al.*, 2001). The use of nano-sized reinforcements to these polymers may open new possibilities for improving not only the chemical and physical properties but also the cost-price-efficiency (Sorrentino *et al.*, 2007).

Polymer nanocomposites are new materials composed of polymers and nano scale inorganic/organic fillers (Gorrasi *et al.*, 2008; Peponi *et al.*, 2009). Nanocomposites can be classified based on the dimensionality of the nano-sized fillers, one can distinguish isodimensional nanoparticles when the all three dimensions are in the nanometer scale, nanotubes or whiskers when two dimensions are on the nanometer range and the third is micrometre, and, lastly, layered minerals, existing in the form of plates of one to a few nanometers thick and hundreds to thousands nanometers in two others dimensions (Alexandre, 2000).

To obtain nanocomposites with acceptable properties, the homogeneous distribution of fillers in the polymer matrices is necessary. The size of fillers and the fillers-matrices interactions are the main parameters affecting the nanocomposite properties (Bianco *et al.,* 2009; Armentano *et al.,* 2009). Advantages of nanocomposites are claimed to be large reinforcement at very small nano-sized fillers content, but functional properties like increased thermal, mechanical, optical and conductivity are often mentioned as well. These materials are useful in various fields such as medical applications, automotive industry, higher performance electronic, magnetic and optical devices manufactories, packaging industry, etc. (Chae *et al*., 2005; Raman *et al*., 2011).

Cellulose nanocrystal (CNC) is one of the emerging renewable materials that has been extensively investigated over the past two decades as a potential nano-sized reinforcement in different polymers (Kvien *et al.,* 2005), particularly within the bio-polymer matrices. Cellulose nanocrystals (CNCs) are characteristically rod-formed monocrystals, 2 to 20 nm in diameter and from tens to hundreds of nanometers in length, and extracted after acid hydrolysis of cellulose (Habibi *et al.,* 2010). Some advantages of cellulose nanocrystal are their high aspect ratio, low density, high elastic modulus and strength (Xu *et al.,* 2013; Yu *et al.,* 2013).

Mono-functional nano-sized fillers like CNCs may only enhance a small number of properties of host polymers. To prepare polymer materials with more improved properties, mixtures of various nano-sized fillers are used into polymer matrices.

Inorganic nanoparticles (INPs) are significant kinds of nano-sized fillers which have been successfully utilized in the polymer materials. Inorganic nanoparticles give new properties to the host polymer materials. Nevertheless, the forming of aggregates will significantly decrease inorganic nanoparticles' applicability. How to synthesize inorganic nanoparticles without aggregation during their incorporation into the polymer matrices is a big challenge. The preparation of inorganic nanoparticles is mostly performed through reducing metal salts in the presence of surfactants or polymeric ligands to passivate the cluster surface. Most surfactants and polymeric ligands are prepared from nonrenewable petrochemicals, and finding a renewable biodegradable alternative is essentially important owing to exhausting fossil fuel resources. Cellulose-based materials have been widely used as templates, stabilizers, and carriers in synthesizing metallic nanomaterials (Padalkar *et al.,* 2010; Shinsuke *et al.,* 2009). Considering the functional properties of CNCs and inorganic nanoparticles, the upcoming use of CNCs/INPs nanocomposites as multifunctional nano-sized fillers in polymer matrices is possible.

Among the various types of inorganic nanoparticles, nano-sized zinc oxide (ZnO-NPs) has attained an increased interest and is extensively used in a diversity of applications including functional devices, catalysts, pigments, optical materials, cosmetics, UV-absorbers, and additives in many industrial products (Kim *et al.,* 2012). Recently, the antimicrobial activity of ZnO nanoparticles with sizes less than 100 nm has been reported (Wang *et al.,* 2012). The use of ZnO-NPs has been considered as a viable solution to stop infectious diseases due to the good antimicrobial properties of these nanoparticles (Stoimenov *et al.,* 2002). Silver has been known to be a bactericide since ancient times. Recently, nanosized silver nanoparticles (Ag-NPs) have been reported to exhibit antimicrobial properties. The outstanding antimicrobial properties of Ag-NPs have led to the development of an extensive diversity of nano-sized silver products, including nano-sized silver-coated wound dressings, contraceptive devices, surgical instruments, and implants (You *et al.,* 2012). For economical and efficient use of ZnO, ZnO nanoparticle composites have been developed and tested for antimicrobial purposes. Additionally, doped silver (Ag) reduced the ionization energy of acceptors in ZnO and thus enhanced the emission (Chen *et al.,* 2011). Therefore, Ag ions can enhance the antimicrobial activity of ZnO. Polymer–inorganic nanoparticle materials with the nanoparticles such as ZnO and Ag-NPs can have the role of antibacterial agents.

1.2 Problem Statement

Chitosan is an abundant natural bio-polymer with excellent antimicrobial activity, bio-compatibility and non-toxicity. Because of its interesting biological properties, chitosan has long been known and used in pharmaceutical and biomedical applications (Muzzarelli, 2009). Due to its unique bioactivity, the formulation of chitosan with drugs has dual therapeutic outcomes, which make chitosan a new candidate for drug carriers and antimicrobial activity (Muzzarelli *et al.,* 1990). Some synthetic polymers from non-renewable sources are also biodegradable, such as poly(vinyl alcohol). PVA is a water-soluble synthetic polymer, non-toxic with good mechanical properties, film forming, emulsifying, and adhesive properties (No *et al.,* 2007). The blend of PVA/CTS has relatively good physical and chemical properties. Therefore PVA/CTS blend becomes a good candidate to replace petroleum based polymer blends. The PVA/CTS blend has potential applications in the fields of packaging, membrane filtration, biomedical applications, etc. Therefore, scientific studies are needed to improve properties of the polymer blends to produce new products to enhance their performances.

The purpose of this study is to improve the mechanical, thermal, barrier towards oxygen gas, antibacterial, and UV shielding properties of poly(vinyl alcohol)/chitosan (PVA/CTS) blends applications by either the incorporation of mono-functional

reinforcement viz. CNCs or two types of multifunctional fillers viz. CNCs/ZnO-NPs and CNCs/ZnO-Ag-NPs disperse it.

ZnO nanoparticles, alone or coated by other metallic nanoparticles such as silver can be used as filler into polymeric materials with the aim to give UV-shielding, barrier, antibacterial, enhanced mechanical and thermal properties to the obtained nanocomposites, thus making them appropriate for a diversity of target applications such as textile, biomedical and food packaging materials. Although, the formation of particles aggregates significantly decrease their applicability. For preventing from the formation of agglomerated ZnO and ZnO-Ag particles and improve dispersion during their integration into polymer matrix cellulose nanocrystals was used as a stabilizer. Cellulose nanocrystal has plentiful hydroxyl groups on its surface which can absorb metallic ions in the synthesis process. This effect control the size by inhibiting the agglomeration of metallic particles formed in the synthesis procedure. On the other hand, the hydrophilic surface of CNCs allows proper blending with water based host polymer matrices and can provide a homogenous dispersion of inorganic particles into water based polymer. Additionally, cellulose nanocrystal is a potential nano-sized reinforcement with excellent mechanical properties. Considering to these advantages, is expected CNCs, CNCs/ZnO and CNC/ZnO-Ag fillers provide good reinforcing effects into PVA/Cs blends polymer matrices.

To date, there have been no studies based on the preparation of CNCs/ZnO and CNCs/ZnO-Ag nanocomposites, and the use of CNCs, CNCs/ZnO-NPs and CNCs/ZnO-Ag-NPs as nano-sized fillers in the PVA/CTS polymer blends matrices.

1.3 Objectives

The main objectives of this research are:

1- To extract CNCs, and prepare CNCs/ZnO and CNCs/ZnO-Ag nano-sized fillers
2- To characterize CNCs, CNCs/ZnO and CNCs/ZnO-Ag nano-sized fillers
3- To fabricate PVA/CTS/CNCs, PVA/CTS/CNCs/ZnO and PVA/CTS/CNCs/ZnO-Ag bio-nanocomposites
4- To characterize and determine properties of PVA/CTS/CNCs, PVA/CTS/CNCs/ZnO and PVA/CTS/CNCs/ZnO-Ag bio-nanocomposites

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