SYNTHESIS AND CHARACTERIZATION OF NANOPARTICLE INCORPORATED POLYMER COMPOSITE MATERIALS

MD. NAJMUL KABIR CHOWDHURY

Thesis submitted in fulfilment of the requirements for the award of the degree of Doctor of Philosophy in Chemical Engineering

Faculty of Chemical and Natural Resources Engineering

UNIVERSITI MALAYSIA PAHANG

April 2014

ABSTRACT

This thesis is composed with the aim of the synthesis of nanoparticle impregnated oil palm fibre reinforced composites. This aim is initiatedwith the synthesis of copper nanoparticles (CuNPs) at ambient condition in aqueous medium using copper chloride precursor,sodium borohydride (SBH), ascorbic acid and polyvinyl alcohol (PVA) of two different molecular weights ($M_w s$). The formationand characterization of the nano copper sols are studied. The physical appearance of prepared sol has been found to be stable for a couple of weeks when kept in ambient atmospheric condition, as confirmed by ultraviolet-visible absorption spectroscopy. Transmission electron microscopy exhibits spherical morphology of CuNPs with an average size of 3.5 ± 1.1 nm.The effect of SBH amount and PVA (wt.% and $M_w s$) on the size of CuNPs are also delineated. As a potential application of CuNPs, theywere impregnatedon/into oil palm empty fruit bunch (EFB) fibres via cationization process. Conventionally, same EFBfibres were also treated with alkali solutions. Treated fibres were characterized by Fourier transformed infrared (FTIR) spectroscopy, X-ray diffraction (XRD) study, field emission scanning electron microscopy (FESEM), energy dispersive X-ray (EDX) study and thermogravimetric analysis (TGA). Numerous physical and mechanical properties of different single fibres were measured and especially the mechanical properties were analyzed by the Griffith model and Weibull statistical distribution. The weak link scaling of Weibull analysis has provided valuable information to scale the strength of one EFB fibre to predict the strength of other one. A significant increase in mechanical property of CuNPs modified fibres with respect to the control ones has been observed. CuNPs impregnated EFB fibres show increases of tensile strength (~34%) and antifungal activity (24%) with respect to control fibres.These findings strongly suggest that CuNPs can be used as an effective agent in natural fibres to improve their mechanical property and durability. Therefore, different doses CuNPs impregnated strong and durable fibres were used to develop theCuNPs impregnated fibre reinforced unsaturated polyester resin nanocomposite. The composite behaviour, mechanical property and biodegradability have been investigated systematically by using the commonly used techniques such as FTIR, XRD, FESEM, TGA, differential scanning calorimetry (DSC), universal tensile testing tester, etc. The developed nanocomposites mechanical properties and biodegradability were optimized by response surface methodology (RSM) also. The biodegradability of the developed composites was inversely proportional to the CuNPs loadings. The change of weight gain (due to moisture absorption) for all samples is highly related with a typical Fickian diffusion behaviour. Moreover, higher mechanical (tensile and flexural) performances were obtained for CuNPs treated fibre (NF) composites compared to those of untreated fibre based composites. Among all of the fibre reinforced composites tested, NF reinforced unsaturated polyester resin composites (30% fibre) registered for the highest mechanical properties. It was found that standard micromechanical models (Rule of Mixture, Inverse Rule of Mixture and Halpin-Tsai Model) which are commonly used to predict the strength of traditional synthetic fibre composites can be applied to such natural fibre systems with mixed success. Throughout the work, three schemes were proposed.The obtained properties of the developed nanocomposites indicate that they can be considered for both indoor-outdoorapplications.

ABSTRAK

Tesis ini di jalankan bertujuan untuk memperbangunkan komposit yang di perkukuhkan dengan gentian minyak sawit bersaiz nano. Matlamat ini dimulakan dengan mengsintesis nano-zarah kuprum (CuNPs) pada keadaan ambien di dalam medium akueus menggunakan kuprum pelopor klorida , natrium borohydride (SBH), asid askorbik dan alkohol polyvinyl (PVA) pada dua berat molekul yang berbeza (MWS). Pembentukan dan pencirian sols kuprum nano telah dikaji. Penampilan fizikal sol didapati stabil selama beberapa minggu apabila disimpan dalam keadaan atmosfera ambien setelah disahkan oleh spektroskopi penyerapan ultraviolet. Transmission electron microscopy mempamerkan morfologi sfera untuk CuNPs dengan saiz purata bernilai 3.5 $\pm$ 1.1 nm. Kesan daripada jumlah SBH dan PVA (wt. % dan MWS) pada saiz CuNPs juga ditandakan. Sebagai satu aplikasi CuNPs yang berpotensi, sampel tersebut telah di terapkan pada minyak gentian tandan kelapa sawit (EFB) melalui proses cationisasi. Secara formalnya, gentian EFB tersebut dirawat dengan rawatan alkali. Gentian yang telah dirawat dianaliskan oleh Fourier transformed infrared (FTIR) spectroscopy, X-ray diffraction (XRD) study, field emission scanning electron microscopy (FESEM), energy dispersive X-ray (EDX) study dan thermogravimetric analysis (TGA). Sifat-sifat fizikal dan mekanikal gentian tunggal yang berbeza telah diukur terutamanya menggunakan sifat-sifat mekanikal yang dianalisis oleh model Griffith dan Weibull pengagihan statistik. Pautan bersisik lemah analisis Weibull telah memberikan maklumat yang penting kepada skala kekuatan satu gentian EFB untuk meramalkan kekuatan gential EFB yang lain. Peningkatan yang ketara dalam sifat mekanikal gentian CuNPs diubahsuai mengikut sample kawalan. Penerapan CuNPs kepada gentian EFB menunjukkan peningkatan kekuatan tegangan sebanyak (~ 34%) dan aktiviti antikulat sebanyak (24%) berkenaan dengan mengawal gentian. Penemuan ini mencadangkan bahawa CuNPs boleh digunakan sebagai agen berkesan dalam gentian asli untuk meningkatkan sifat mekanik dan ketahanan. Oleh itu, dos CuNPs yang berlainan menghasilkan gentian kuat dan tahan lama telah digunakan untuk menghasilkan damar nanokomposit poliester tidak tepu yang diperkukuhkan dengan gentian yang diterap dengan CuNPs. Sifat-sifat komposit seperti, sifat mekanikal dan biodegradasi telah disiasat secara sistematik dengan menggunakan teknik-teknik yang biasa digunakan seperti FTIR , XRD, FESEM , TGA , kalorimetri imbasan pembeza (DSC), mesin ujian universal, dan lain-lain lagi. Sifat mekanik dan biodegradasi nanokomposit adalah dioptimumkan dengan mengunakan response surface methodology (RSM). Sifat biodegradasi komposit adalah berkadar songsang dengan bebanan CuNPs. Perubahan jisim (disebabkan oleh penyerapan kelembapan) bagi semua sampel berkait rapat dengan tingkah laku penyebaran Fickian . Selain itu , prestasi mekanikal yang lebih tinggi (tegangan dan lenturan) telah diperolehi untuk serat yang dirawat oleh CuNPs (NF) komposit berbanding dengan komposit berasaskan gentian yang tidak dirawat. Antara semua komposit yang diperkukuhjakn oleh gentian diuji, komposit resin poliester yang diperkukuhkan oleh NF (30% serat) dikenalpasti memperoleh sifat-sifat mekanik tertinggi. Ia telah didapati bahawa piawaian model mikro mekenikal (Rule of Mixture, Inverse Rule of Mixture and Halpin-Tsai Model) yang biasa digunakan untuk meramalkan kekuatan komposit gentian sintetik tradisional boleh digunakan untuk sistem gentian semula jadi dengan jayanya. Sepanjang kerja ini, tiga

skim telah dicadangkan. Sifat-sifat yang diperolehi daripada kemajuan nano-komposit menunjukkan bahawa ia boleh dipertimbangkan untuk kedua-dua aplikasi dalaman-luaran.

TABLE OF CONTENTS

LIST OF TABLE

LIST OF FIGURES

LIST OF ABBREVIATIONS

AAS	Atomic absorption spectroscopy
AATCC	American Association of Textile Chemists and Colourists
AB	After burial
AF	Alkali treated EFB fibre
AFM	Atomic force microscopy
AMA	Allyl methacrylate
ANOVA	Analysis of variance
ASTM	American Standard Testing Method
BB	Before burial
BD	Biodegradability
C	Degree of cationization
CF	Cationized EFB fibre
CF-C	CF reinforced composite
CHPTAC	3-Chloro-2-hydroxypropyl)trimethylammonium chloride
CRP	Chemical reduction process
CRP	Chemical reduction process
CTAB	Cetyltrimethylammonium bromide
Cu	Copper
CuNPs	Copper nanoparticles

D	Coefficient of diffusion,
D_{hkl}	Average size of the cellulose crystallites
d	Diameter
DEG	Di-ethylene glycol
DI	Deionized water
DMSO	Dimethyl sulfoxide
DSC	Differential scanning calorimetry
DTG	Differential thermo gravimetry
E	Moment of inertia of the composite beam
E. coli	Escherichia coli
EB	Elongation at break
EDX	Energy dispersive X-ray
E_F	Elastic modulus of fibre
EFB	Empty fruit bunch
E_M	Elastic modulus of matrix
F	Faraday's constant
FESEM	Field emission scanning electron microscopy
FTIR	Fourier transformed infrared
FWHM	Full width at half-maximum
G	Modulus of rigidity

GDI	Gasoline Direct Injection
GHz	Gigahertz
GPa	Giga Pascals
HDEHP	Bis(ethylhexyl)hydrogen phosphate
HMP	Hexameta phosphate
IROM	Inverse rule of mixing
K	Equilibrium constant
kHz	kilohertz
l	Span of the composite beam
L	Length
MC	Moisture content
MDF	Medium density fibre
MHz	Megahertz
M_m	Moisture content at saturation point
MNP	Metal nanoparticles
MOP	Molded oil palm
MPa	Mega Pascal
MRSA	Methicillin-resistant Staphylococcus aureus
M_w	Molecular weight
m_w	Weibull modulus

NF	Nanosol treated EFB fibre
NF-C	NF reinforced composite
NFRT	Natural fibre reinforced thermoplastic
nm	Nanometer
NP	Nanoparticle
NPs	Nanoparticles
NR	Natural rubber
OPA	Oil palm ash
OPF	Oil palm fibre
OPFr	Oil Palm Fronds
OPT	Oil Palm Trunk
P	Load within the elastic range
PAA Na	Polyacrylic acid sodium salt
PCS	Photon correlationspectroscopy
PEG	Polyethylene glycol
PEI	Polyethylene imine
PF	Phenol formaldehyde
P_f	Probability of failure
PLA	Poly(lactic acid)
PP	Polypropylene
pp	Particles

ppm	Parts per million
PU	Polyurethane
PVA	Polyvinyl alcohol
PVC	Polyvinyl chloride
PVP	Polyvinylpyrrolidone
PWD	Pulsed wire discharge
PZC	Zero point charge
R	Gas constant (J/mol K)
RC	Regenerated Cellulose
ROM	Rule of mixing
RSM	Response surface methodology
S. aures	Staphylococcus aureus
SBH	Sodium borohydride
SDS	Sodium dodecyl sulfate
SEM	Scanning electron microscope
SPR	Surface plasmon resonance
SS	Sodium succinate
T	Temperature (in Kelvin)
t	Treatment time
T_0	Onset temperature
Tc	Crystallization Temperature (^oC)

TCF	Total chlorine-free
T_d	Degradation temperature
TEM	Transmission electron microscopy
TEPA	Tetraethylenepentamine
Tg	Glass Transition Temperature (^{0}C)
TGA	Thermo gravimetric analysis
T_m	Melting endotherm
Tm	Melting Temperature (^{0}C)
TM	Tensile modulus
TOAB	Tetraoctylammonium bromide
TS	Tensile strength
TX-100	Triton X-100
UF	Untreated EFB Fibre
UF-C	UF reinforced composite
USA	United States of America
UV-vis	Ultra-violet visible
V	Volt
V_F	Volume fraction of fibre
V_M	Volume fraction of matrix
VR	Unsaturated polyester resin
W_f	Weight of fibre
WL	Weight loss

W_m	Weight of matrix
XRD	X-ray diffraction
Y	Young’s modulus
β	FWHM (in radians)
ΔE	Redox potential
ΔH	Heat of fusion (J/g)
θ	Diffraction angle
λ	Wavelength of X-ray (1.541 Å)
ρ_f	Density of fibre
ρ_m	Density of matrix
σ_{ave}	Average tensile strength
∂	Total deflection
ΔG^0	Gibb's free energy
µg	Microgram
µm	Micrometer
2θ	Scattering angle