TAILORING THE PREPARATION OF PALM OIL BASED ALKYD/EPOXY RESIN COMPOSITE THROUGH COPPER OXIDE NANOPARTICLE

ONG HUEI RUEY

DOCTOR OF PHILOSOPHY

(CHEMICAL ENGINEERING)

UNIVERSITI MALAYSIA PAHANG

UNIVERSITI MALAYSIA PAHANG

DECLARATION OF THESIS AND COPYRIGHT

Author's full name : Ong Huei Ruey

Date of birth : 8th July 1986

Title : Tailoring the preparation of palm oil based alkyd/epoxy resin composite through copper oxide nanoparticle.

Academic Session : SEMESTER II 2015/2016

I declare that this thesis is classified as:

☐ **CONFIDENTIAL** (contains confidential information under the Official Secret Act 1972)

☐ **RESTICTED** (contains restricted information as specified by the organization where research was done)

☐ **OPEN ACCESS** I agree that my thesis to be published as online open access (Full text)

I acknowledge that Universiti Malaysia Pahang reserve the right as follows:

1. The Thesis is the Property of Universiti Malaysia Pahang.
2. The Library of Universiti Malaysia Pahang has the right to make copies for the purpose of research only.
3. The Library has the right to make copies of the thesis for academic exchange.

Certified By:

____________________	____________________ .
(Student's Signature)	(Signature of Supervisor)
860708-23-5463	Md. Maksudur Rahman Khan .
New IC/ Passport Number	Name of the Supervisor
Date:	Date:

Universiti Malaysia PAHANG
Engineering • Technology • Creativity

SUPERVISOR'S DECLARATION

We hereby declare that we have checked this thesis and in our opinion, this thesis is adequate in terms of scope and quality for award of the degree of Doctor of Philosophy (Chemical Engineering).

_______________________________.

(Supervisor's Signature)

Full Name : MD. MAKSUDUR RAHMAN KHAN, PHD

Position : ASSOCIATE PROFESSOR

Date :

_______________________________.

(Field-supervisor's Signature)

Full Name : RIDZUAN RAMLI, PHD

Position : PRINCIPAL RESEARCH OFFICER, MALAYSIAN PALM OIL BOARD

Date :

STUDENT'S DECLARATION

I hereby declare that the work in this thesis is based on my original work except for quotations and citation which have been duly acknowledged. I also declare that it has not been previously or concurrently submitted for any other degree at Universiti Malaysia Pahang or any other institutions.

_______________________.

(Author's Signature)

Full Name : ONG HUEI RUEY

ID Number : PKC 13001

Date :

TAILORING THE PREPARATION OF PALM OIL BASED ALKYD/EPOXY RESIN COMPOSITE THROUGH COPPER OXIDE NANOPARTICLE

ONG HUEI RUEY

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

Faculty of Chemical and Natural Resources Engineering
UNIVERSITI MALAYSIA PAHANG

AUGUST 2016

TABLE OF CONTENTS

DECLARATION	
TITLE PAGE	i
ACKNOWLEDGEMENTS	iii
ABSTRACT	iv
ABSTRAK	v
TABLE OF CONTENTS	vi
LIST OF TABLES	xi
LIST OF FIGURES	xiii
LIST OF SCHEMES	xvi
LIST OF SYMBOLS	xvii
LIST OF ABBREVIATIONS	xviii
CHAPTER 1 INTRODUCTION	1
1.1 Background	1
1.2 Problem statements	3
1.3 Objectives	4
1.4 Scopes of study	4
1.5 Novelty	6
CHAPTER 2 LITERATURE REVIEW	7
2.1 Background of alkyd resin	7
2.2 Classification of alkyd resins	9
2.3 Major components for alkyd resin preparation	13
2.3.1 Oils or fatty acids	13
2.3.2 Polyols	18
2.3.3 Polybasic acids and their anhydrides	19
2.3.4 Monobasic acid	21

2.4 Preparation of alkyd resin 21
2.4.1 Single step process 22
2.4.1.1 Reaction conditions 22
2.4.1.2 Progress in technology 24
2.4.2 Two step process 27
2.4.2.1 Reaction conditions 27
2.4.2.2 Progress in technology 29
2.4.3 Fusion method 36
2.4.4 Solvent method 41
2.5 State-of-the-art technology 52
2.5.1 Blending 52
2.5.2 Catalyst used for alkyd preparation 53
2.5.3 Addition of nanoparticles 54
2.6 Mathamatical modelling 57
2.7 Optimization of the preparation condition of polymer composite by response surface methodology 60
2.8 Application 61
2.9 Conclusion 64

CHAPTER 3 METHODOLOGY 66

3.1 Materials 68
3.2 Nanoparticle synthesis and characterization 69
3.3 Alkyd resin synthesis 70
3.3.1 Alcoholysis 71
3.3.1.1 Synthesis of MG using CuO nanoparticle 71
3.3.1.2 Synthesis of MG using hetero-homo- catalyst system 71
3.3.1.3 NMR studies 72
3.3.1.4 High performance liquid chromatography (HPLC) 72
3.3.2 Polyesterification 74
3.3.2.1 Preparation of alkyd resin 74

3.3.2.2 Determination of average degree of polymerization 75
3.3.2.3 Fourier transform infrared spectroscopy (FTIR) 75
3.3.2.4 Raman spectroscopy 75
3.3.2.5 Gel permeation chromatography (GPC) 75
3.3.2.6 NMR studies 76
3.3.2.7 Antimicrobial test 76
3.4 Preparation and characterization of alkyd/epoxy blend 76
3.4.1 Preparation of alkyd/epoxy blend 77
3.4.1.1 Mechanical properties 77
3.4.2 Characterization of alkyd/epoxy blend 78
3.4.2.1 Fourier transform infrared spectroscopy (FTIR) 78
3.4.2.2 Thermogravimetric analysis (TGA) 78
3.4.2.3 Contact angle measurement 78
3.4.3 Antimicrobial test 79
3.5 Perspectives of micromechanical models 80
3.5.1 Rule of mixtures equation 80
3.5.2 Inverse rule of mixtures equation 81
3.5.3 Takayanagi equation 81
3.5.4 Halpin–Tsai equation 81
3.6 Finite element modeling 82
3.7 Optimization of alkyd/epoxy blend using response surface methodology (RSM) 84

CHAPTER 4 PREPARATION AND CHARACTERIZATION OF ALKYD RESIN 86

4.1 Nanoparticle synthesis and characterization 86
4.1.1 Nanoparticle formation 87
4.1.2 Size and morphology determination 96
4.1.3 Determination of elemental composition: XPS 98
4.1.4 Conclusion 100
4.2 Alcoholysis of palm oil and characterization 100
4.2.1 Alcoholysis of palm oil 100

4.2.1.1 Qualitative characterization by NMR 101
4.2.2 Effect of different catalysts on the alcoholysis of oil 105
4.2.3 Mechanism of alcoholysis of oil 111
4.2.4 Stability of CuO nanoparticle 114
4.2.5 Conclusion 116
4.3 Polyesterification 116
4.3.1 Preparation of alkyd resin 116
4.3.2 Characterization of alkyd resin 121
4.3.2.1 FTIR analysis 121
4.3.2.2 Raman analysis 122
4.3.2.3 NMR analysis 124
4.3.3 Molecular weight characterization 126
4.3.4 Stability of CuO nanoparticle 127
4.3.5 Antimicrobial study 128
4.3.6 Conclusion 130
4.4 Discussion 130

CHAPTER 5 PREPARATION AND CHARACTERIZATION OF ALKYD/EPOXY BLEND 135

5.1 Mechanical properties 135
5.1.1 Effect of alkyd/epoxy ratio 135
5.1.2 Effect of molecular weight of alkyd 140
5.2 Curing behaviour: qualitatively analysis 143
5.3 Thermal stability of blend 144
5.4 Determination alkyd functional group 147
5.5 Surface wettability test 151
5.6 Antimicrobial efficiency 152
5.7 Discussion 153
5.8 Conclusion 158

CHAPTER 6 MATHEMATICAL MODELING AND OPTIMIZATION 159

6.1 Theoretical modeling of blend 159

6.2 Finite element model 162

6.3 Response surface methodology 163

6.3.1 Effects of model parameters on tensile strength 171

6.3.2 Effects of model parameters on flexural strength 174

6.3.3 Effects of model parameters on impact strength 178

6.3.4 Process optimization 182

6.4 Discussion 183

6.5 Conclusion 184

CHAPTER 7 CONCLUSION AND RECOMMENDATIONS 185

7.1 Conclusion 185

7.2 Recommendation 186

REFERENCES 188

APPENDIX A 212

APPENDIX B 214

LIST OF TABLES

Table	Title	Page
2.1	Alkyd resin based on oil length	10
2.2	Alkyd properties with respect to oil length	11
2.3	Common fatty acids, their formulas and type of saturation	16
2.4	Common vegetables and their fatty acid compositions	17
2.5	Melting and boiling points of some polyols	18
2.6	Melting and boiling points of some polybasic acids	20
2.7	Optimization of various parameters of alkyd preparation from available resources by alcoholysis-polyesterification process through fusion method for the maximum yield	38
2.8	Optimization of various parameters of alkyd preparation from vegetable oils by alcoholysis-polyesterification process through solvent method	44
2.9	Physico-chemical and mechanical properties of vegetable oil based alkyds and oil modified alkyds	47
2.10	Drying schedule of alkyds based on vegetable oils and chemical treated oils monitored both outdoor and indoor	50
3.1	List of chemicals used in this work	68
3.2	Samples prepared for the study of the effect of CuO nanoparticle, alkyd/epoxy weight ratio and molecular weight of alkyd	77
3.3	Variables for model	85
4.1	The results of deconvolution of XPS Cu $2p_{3/2}$ peaks	98
4.2	Chemical shifts and assignment of main resonances in ^{1}H–NMR spectra of palm oil and products of alcoholysis reaction (see Figure 4.7)	104
4.3	Composition of copper obtained from the linear fitting with sample CuO-nano before and after the reaction and reference spectra for Cu and CuO	115
4.4	Molecular weights and molecular weight distributions of palm oil alkyd resin with CuO (C) and without CuO nanoparticles (A) at various stage of the reaction	127
4.5	Composition of Cu/O obtained from the linear fitting with the sample CuO nanoparticle before and after the reaction	128
4.6	Antimicrobial activity of alkyd resin (A) and (C)	129
4.7	Comparison current work with literature	133
5.1	Thermal data obtained from TGA thermograms of alkyd/epoxy blend with and without CuO nanoparticle	147
5.2	Antimicrobial efficiency of the CuO incorporated blend	152
5.3	Photographs of survival bacteria colonies in diluted solutions correspond to the cell suspensions obtained after incubation at 37 ℃	153
5.4	Comparison current work with literature for tensile strength	156
5.5	Comparison current work with literature for flexural strength	156
5.6	Comparison current work with literature for impact strength	157
5.7	Comparison current work with literature for mechanical properties	157
6.1	Standard deviation of the models respected to experiment data	161
6.2	Design matrix of three level factorial	164

6.3	Model equation for each response	165
6.4	Analysis of variance (ANOVA) for quadratic model of tensile strength	167
6.5	Analysis of variance (ANOVA) for quadratic model of flexural strength	167
6.6	Analysis of variance (ANOVA) for quadratic model of impact strength	168
6.7	Optimum conditions derived by RSM design	182
6.8	Model validation	183

LIST OF FIGURES

Figure	Title	Page
2.1	The properties to be expected from an alkyd of different oil length and iodine value	12
2.2	Block diagram of alkyd preparation in various methods	22
2.3	Reaction pathway of single step reaction [R correspond to alkyl radicals of vegetable oils vary from C_8-C_{20}]	23
2.4	Preparation of waterborne alkyds	25
2.5	Reaction pathway of two step method i.e., alcoholysis followed by polyesterification [R_1, R_2 and R_3 correspond to alkyl radicals of vegetable oils vary from C_8-C_{20}]	27
2.6	Linear and cross-linked alkyd prepared by the chemo-enzymatic route	31
2.7	Synthesis of liquid crystalline pentalkyds	32
2.8	Process diagram of alkyd resin preparation by fusion method	37
2.9	Process diagram of alkyd resin preparation by solvent method	42
4.1	(a) UV-Vis spectra of $CuCl_2$ in aqueous solution (i), $CuCl_2$ in glycerol before (ii), after (iii) addition of hydrazine solution. ([$CuCl_2$] = 28.6 ppm); (b) XANES spectra of CuO standard, $CuCl_2$●$2H_2O$ in glycerol medium (precursor), 0 min sample (after addition of hydrazine solution). ([$CuCl_2$] = 200 ppm)	90
4.2	(a) UV-vis spectra of Cu sol formation, [$CuCl_2$] = 200 ppm (insert graph: [$CuCl_2$] = 28.6 ppm); (b) Normalized absorbance of peak at ■ 310 nm and ● 560 nm	92
4.3	(a) XANES spectra of copper sol formation ([$CuCl_2$] = 200 ppm); (b) XANES spectra of peak B shift of sol formation with respect to time; (c) Normalized concentration of Cu(II) complex (■), Cu^0 (●), Cu_2O (▲) and CuO (▼) during sols formation	96
4.4	TEM micrograph of CuO at low magnification (i), high magnification (ii)	97
4.5	Typical deconvolution of Cu $2p_{3/2}$ (a) and O 1s (b) main peak of 6 h sample	99
4.6	^{13}C-NMR spectra of alcoholysis reaction of palm oil with chemical shifts of the products: (a) before reaction; (b) after reaction with NaOH catalysed and (c) after reaction with CuO-nano+NaOH catalysed. A break is shown in the figure from 75 to 172.5 ppm	102
4.7	^{1}H–NMR spectra of alcoholysis reaction of palm oil with chemical shifts of the products: (a) before reaction; (b) after reaction with NaOH and (c) after reaction with CuO-nano+NaOH	103
4.8	Effect of CuO-nano loading on oil conversion, X_{TG}, MG yield, Y_{MG} and DG yield, Y_{DG} [Concentration of CuO-nano, ppm: ■ 0.00002 wt%; ● 0.00003 wt%; ▲ 0.00004 wt%; red line = oil conversion; black line = MG yield; blue line = DG yield]	106
4.9	Effect of different catalyst system on (a) oil conversion, X_{TG}, (b) selectively, $S_{MG/DG}$ and (c) MG yield, Y_{MG} [Concentration of CuO-nano = 0.00004 wt%; catalyst system: ■ CuO-nano+0.4 wt% NaOH; ● CuO-nano+0.3 wt%	

NaOH; ▲ CuO-nano+0.1 wt% NaOH; ▼ CuO-nano+0.01 wt% NaOH; ◄ 0.3 wt% NaOH; ► CuO-nano] 110
4.10 Effect of molar ratio of oil to glycerol on oil conversion, X_{TG}, MG yield, Y_{MG}, and DG yield, Y_{DG} [catalyst system = 0.00004 wt% CuO-nano+0.3 wt% NaOH ; reaction time = 40 min] 111
4.11 XANES spectra at the Cu K edge of Cu standard, CuO standard, $CuCl_2$●$2H_2O$, CuO-nano before and after the reaction 115
4.12 Effect of different catalyst system on the completion of first step 119
4.13 Plot of acid value and DP against reaction time for different catalysis systems during polyesterification process (■A, ●B, ▲C and ▼D). Table of initial reaction rates is shown inside the figure 119
4.14 Plot of acid value and DP against reaction time for different temperature during C catalysed polyesterification process (■220 °C, ●230 °C, ▲240 °C and ▼250 °C). Table of initial reaction rates is shown inside the figure 120
4.15 Infrared spectra of (i) oil, (ii) alkyd resin (A) and (iii) alkyd resin (C) 122
4.16 Raman spectra of alkyd resin (A, C) and CuO standard–alkyd 124
4.17 ^{1}H–NMR (a) and ^{13}C–NMR (b) of palm oil–based alkyd resin 125
4.18 ^{1}H-NMR (a) and ^{13}C-NMR (b) of palm oil 126
4.19 XANES spectra at the Cu K edge of Cu standard, CuO standard, $CuCl_2$●$2H_2O$, CuO nanoparticle before reaction and CuO nanoparticle after reaction 128
5.1 Tensile (a), flexural (b) and impact strength (c) of alkyd/epoxy blend with and without CuO nanoparticle (sample at 180 min) 139
5.2 Effect of polymerization reaction time of alkyd resin on tensile (a), flexural (b) and impact strength (c) of alkyd/epoxy blend (30:70) with and without CuO nanoparticle 142
5.3 The DSC curves of the alkyd/epoxy blend during cure and after cured, (a) with CuO and (b) without CuO [(i) A/E 50:50, (ii) A/E 30:70 and (iii) A/E 10:90] 143
5.4 TGA thermograph of alkyd/epoxy blends resin (a) and effect of CuO nanoparticle on A/E 30:70 blend (b) 146
5.5 FTIR spectra of alkyd (i), epoxy (ii), alkyd/epoxy blend (A/E 30:70) without CuO (iii) and with CuO (iv) 149
5.6 Contact angle images of A/E blend without CuO nanoparticle 30:70 (a), A/E blend with CuO nanoparticle 50:50 (b), 30:70 (c) and 10:90 151
6.1 Comparison of experimental tensile strength and theoretical predictions for blends, (a) without CuO incorporation (b) with CuO incorporation 161
6.2 Experimental and numerical results of alkyd/epoxy blend. [Dot = experimental data; line = FEM data; ■ = alkyd/epoxy 50:50; ● = alkyd/epoxy 40:60; ▲ = alkyd/epoxy 30:70; ▼ = alkyd/epoxy 20:80; ♦ = alkyd/epoxy 10:90; ◄ = neat epoxy] 162
6.3 Experimental and numerical results of CuO incorporated alkyd/epoxy blend. [Dot = experimental data; line = FEM data; ■ = alkyd/epoxy 50:50; ● = alkyd/epoxy 40:60; ▲ = alkyd/epoxy 30:70; ▼ = alkyd/epoxy 20:80; ♦ = alkyd/epoxy 10:90; ◄ = neat epoxy] 163
6.4 Predicted vs. experimental values (a) tensile, (b) flexural and (c) impact strength 170

6.5 Single factor plot of tensile strength on effect of (a) alkyd proportion, (b) polymerization time and (c) modification 172
6.6 Three-dimensional response surface plot of tensile strength for x_1x_2 (a) without and (b) with CuO nanoparticle 174
6.7 Single factor plot of flexural strength on effect of (a) alkyd proportion, (b) polymerization time and (c) modification 176
6.8 Three-dimensional response surface plot of flexural strength for x_1x_2 (a) without and (b) with CuO nanoparticle 177
6.9 Single factor plot of impact strength on effect of (a) alkyd proportion, (b) polymerization time and (c) modification 180
6.10 Three-dimensional response surface plot of impact strength for x_1x_2 (a) without and (b) with CuO nanoparticle 181

LIST OF SCHEMES

Scheme	Title	Page
3.1	Flowchart of the alkyd/epoxy blend preparation process	67
3.2	Synthetic pathway of palm oil–based alkyd resin (alcoholysis–polyesterification process)	70
3.3	Schematic picture of antimicrobial efficiency test	79
3.4	Stress-strain curve of plastic material	84
4.1	Proposed mechanism of copper nanoparticles formation	96
4.2	Alcoholysis reaction of palm oil with glycerol	101
4.3	Mechanism of alcoholysis of oil using homogeneous catalysis system	112
4.4	Mechanism of alcoholysis of oil over CuO-nano catalyst	114
5.1	Schematic diagram of the phenomenon occurring during the crosslinking of the blend	150

LIST OF SYMBOLS

x_1	Alkyd proportion
x_2	Alkyd polymerization time
x_3	Modification (with and without CuO nanoparticle)
Y_1	Tensile strength
Y_2	Flexural strength
Y_3	Impact strength

LIST OF ABBREVIATIONS

ΔH	Heat of fusion (J/g)
°C	Degree Celsius
µL	Microliter
µm	Micrometer
ANOVA	Analysis of variance
ATBS	Amide tertiary butane sulfonic acid
ATR	Attenuated total reflectance
AV	Acid value
BE	Binding energy
BMF	Butylated melamine formaldehyde
Ca	Calcium
$Ca(OH)_2$	Calcium hydroxide
$CaCO_3$	Calcium carbonate
CaO	Calcium oxide
CeO_2	Cerium(IV) oxide
CH_3NaO	Sodium methoxide
cm	Centimeter
CN	Carbon nanofillers
Cu	Copper
CuO	Copper oxide
CV	Coefficient of variation
DCC	Dicyclohexyl carbodiimide

DD	Deodorizer distillate
DG	Diglyceride
DMTA	Dimethyl ester of TPA
DSC	Differential scanning calorimetry
E	Strength fractions
EG	Expanded graphite
EJO	Epoxidized jatropha oil
Fe_3O_4	Iron(II,III) oxide
FID	Free induction decays
F_n	Average number of methylene groups adjacent to double bond per oil molecule
FT	Fourier transformation
FTIR	Fourier transform infrared spectroscopy
FWHM	Full width at half maximum
g	Gram
GC	Gas chromatography
GO	Graphene oxide
Gol	Glycerol
GPC	Gel permeation chromatography
h	Hour
HBUA	Hyperbranched urethane alkydresin
HPLC	High performance liquid chromatography
HRSO	Heated rubber seed oil
Hz	Hertz

IPA	Isophtalic acid
IPN	Interpenetrating polymer network
IROM	Inverse rule of mixture
J	Joule
JSO	Jatropha curcas seed oil
KOH	Potassium hydroxide
kV	Kilo-volt
L	Liter
LB	Luria Bertani
Li	Lithium
LiOH	Lithium hydroxide
LMCT	Ligand-to-metal charge transfer
m	meter
mA	Milli-ampere
MERSO	Methyl ester of rubber seed oil
MF	Melamine-formaldehyde
mg	Milligram
MG	Monoglyceride
MgO	Magnesium oxide
min	Minute
mL	Milliliter
mM	Milli mole
M_n	Number-average molar mass
MPa	Megapascal

M_w	Weight-average molar mass
MWD	Molecular weight distributions
NaOH	Sodium hydroxide
$Ni(OH)_2$	Nickel(II) hydroxide
NiO	Nickel oxide
nm	nanometer
NMR	Nuclear magnetic resonance spectrophotometer
P	Extent of the reaction
PA	Phthalic anhydride
PANI	Polyaniline
PbO	Lead(II) oxide
PDI	Polydispersity index
PMDS	Polydimethylsiloxane
ppm	Parts-per-million (10^{-6})
PVA	Polyvinyl alcohol
ROM	Rule of mixture
RSM	Response surface methodology
RSO	Rubber seed oil
s	second
T	Temperature
TEM	Transmission electron microscopy
TG	Triglyceride
TGA	Thermogravimetric analysis
THF	Tetrahydrofuran

T_i	Initial degradation temperature
TiO_2	Titanium dioxide
TLC	Thin layer chromatography
TMP	Trimethylolpropane
TPA	Terephthalic acid
UTM	Universal Testing Machine
UV-Vis	UV-visible spectrophotometer
v	Volume
V	Volume fractions
VOC	Volatile organic compounds
W	Walt
wt%	Weight percentage
XANES	X-ray absorption near edge structure spectrophotometer
XPS	X-ray photoelectron spectroscopy
X_{TG}	Conversion of TG
Y_{DG}	Yield of DG
Y_{MG}	Yield of MG
ZnO	Zinc oxide

TAILORING THE PREPARATION OF PALM OIL BASED ALKYD/EPOXY RESIN COMPOSITE THROUGH COPPER OXIDE NANOPARTICLE

ONG HUEI RUEY

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

Faculty of Chemical and Natural Resources Engineering
UNIVERSITI MALAYSIA PAHANG

AUGUST 2016

ABSTRACT

Intensive research on the development of polymers from renewable resources has been triggered due to the environmental concerns. Alkyd resin is a green polymer derived from vegetable oil with low cost and higher biodegradability mainly used for organic coating, paint or varnish. On the other hand, epoxy resin is considered as highly reactive polymer may form structural materials for indoor and outdoor applications while blended with fillers in the form of nanocomposites. The alkyd/epoxy blend can overcome the drawbacks of the individual polymers and resulted in improved mechanical properties. Conventional nanocomposites usually require 1-5 wt% filler; most commonly clay, carbon materials or metal/oxide nanoparticles. The present work is an attempt to produce alkyd/epoxy blend containing CuO nanoparticles with its homogeneous distribution to achieve higher mechanical and antimicrobial properties. In the present work palm oil and glycerol were used as starting material to produce alkyd resin. Colloidal CuO nanoparticle was prepared in glycerol and subsequently used alcoholysis–polyesterification process to produce alkyd resin. The nanoparticle formation was monitored by X–ray absorption near edge structure spectroscopy (XANES) and its particle size was confirmed by TEM in the range of ~5 nm. The formation of the alkyd resin was confirmed by FTIR, Raman, ^{1}H–NMR and ^{13}C–NMR analyses and its molecular weight were determined by gel permeation chromatograph (GPC). The antimicrobial activity of the resin was determined via Kirby–Bauer Method and the CuO stability was determined by XANES. The addition of CuO nano-sol to the conventional homogeneous base catalyzed system explored a new catalytic route for the preparation of vegetable oil based alkyd resin that reduced the reaction time from 120 min to 60 min as well as added the antimicrobial properties to the resin. Moreover, alkyd was blended with epoxy resin in order to prepare composite of desired properties and the effect of weight ratio of alkyd/epoxy blend was investigated. The formation of blend and its chemical and mechanical properties were elucidated by standard methods (ASTM). It was found that, the presence of CuO nanoparticle enhanced the mechanical properties of the blend. The CuO incorporated alkyd/epoxy blend at ratio of 30:70 was found to be optimum and its tensile (47 MPa), flexural (138 MPa) and impact strengths (101 J/m^2) were higher than the blend without CuO nanoparticle. Moreover, standard micromechanical models (rule of mixture, inverse rule of mixture, takayanagi and halpin-tsai model) and finite element modeling were used to predict the data. The effect of alkyd to epoxy ratio, alkyd polymerization time and CuO nanoparticle modification concerning the tensile, flexural and impact strength was optimized by using response surface methodology (RSM). The composite comprising of alkyd, epoxy and CuO nanoparticle exhibited better mechanical properties, thermal stability and biodegradable, can be considered for both indoor-outdoor applications.

ABSTRAK

Penyelidikan yang intensif terhadap pembangunan polimer dari sumber yang boleh diperbaharui telah dicetuskan akibat kebimbangan terhadap alam sekitar. Alkyd adalah polimer hijau yang berkos rendah dan mempunyai keboleh biodigradasi yang tinggi, dihasilkan dari minyak sayur-sayuran dan telah digunakan untuk lapisan organik, cat atau varnish manakala resin epoksi dianggap sebagai polimer yang sangat reaktif dan boleh membentuk bahan berstruktur dalam bentuk nano komposit untuk aplikasi dalaman dan luaran apabila dicampur dengan pengisi. Gabungan alkyd/epoksi dapat mengatasi kelemahan polimer individu dan menghasilkan polimer yang mempunyai sifat-sifat mekanikal yang lebih baik. Nano komposit konvensional biasanya memerlukan 1-5% berat pengisi seperti tanah liat, bahan-bahan karbon atau nano partikel logam/oksida. Kajian ini adalah satu percubaan untuk menghasilkan gabungan alkyd/epoksi yang mengandungi nano partikel CuO bertaburan sekata supaya dapat mencapai sifat-sifat mekanik dan anti-mikrob yang lebih tinggi. Dalam kajian ini, minyak sawit dan gliserol telah digunakan sebagai bahan asas untuk menghasilkan resin alkyd. Nano partikel koloid CuO telah disediakan di dalam gliserol, seterusnya menggunakan proses alkoholisis-polyesterification untuk menghasilkan resin alkyd. Pembentukan nano partikel dipantau menggunakan alat penyerapan X-ray berhampiran struktur tepi spektroskopi (XANES) dan saiz partikel dalam lingkungan ~ 5 nm diperoleh melalui alat TEM. Pembentukan resin alkyd pula telah disahkan daripada analisis FTIR, Raman, ^{1}H-NMR dan ^{13}C-NMR manakala berat molekul ditentukan dengan menggunakan gel penyerapan kromatografi (GPC). Aktiviti anti mikrob resin ditentukan melalui Kaedah Kirby-Bauer dan kestabilan CuO telah ditentukan melalui XANES. Penambahan CuO nano sol terhadap sistem pemangkin konvensional homogen telah meneroka satu laluan baru dalam penyediaan alkyd resin berasaskan minyak sayuran yang dapat mengurangkan masa tindak balas daripada 120 min ke 60 min serta menambah ciri-ciri anti mikrob untuk resin. Selain itu, alkyd telah dicampur dengan resin epoksi untuk menghasilkan komposit yang mempunyai ciri-ciri yang dikehendaki dan kesan nisbah berat gabungan alkyd / epoksi dikaji. Pembentukan serta sifat kimia dan mekanikal gabungan telah dijelaskan dengan kaedah piawai (ASTM). Kajian mendapati kehadiran nano partikel CuO dapat meningkatkan sifat-sifat mekanikal campuran. Kecekapan antibakteria campuran itu juga dikaji. CuO diperbadankan alkyd / campuran epoxy pada nisbah 30:70 didapati optimum dan tegangan (47 MPa), lenturan (138 MPa) dan kesan kekuatan (101 J/m^2) adalah lebih tinggi daripada gabungan tanpa CuO nano partikel. Selain itu, model mikro mekanikal piawai (Prinsip Campuran, Prinsip Campuran Songsang, Model *Takayanagi* dan Model *Halpin-Tsai*) dan *finite element modeling* telah digunakan untuk meramalkan data kajian. Kesan alkyd kepada nisbah epoxy, masa pempolimeran alkyd dan pengubahsuaian nano partikel CuO berkaitan tegangan, lenturan dan kesan kekuatan telah dioptimumkan dengan kaedah gerak balas permukaan (RSM). The komposit terdiri daripada alkyd, epoxy dan CuO nano partikel mempamerkan sifat-sifat mekanikal yang lebih baik, kestabilan haba dan mesra alam, boleh dipertimbangkan untuk kedua-dua aplikasi dalaman dan luaran.