SYNTHESIS, CHARACTERIZATION AND EVALUATION OF NANO-MODIFIED POLYMERIC MATERIALS FROM YELLOW OLEANDA (*Thevetia peruviana*) SEED OIL

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DECLARATION

I, SIYANBOLA, Tolutope Oluwasegun, hereby declare that this thesis is a product of my own unaided research work. It has not been submitted, either wholly or in part, to this or any other institution for the award of any degree, diploma, or certificate. All sources of scholarly information that were used in this thesis were duly acknowledged.

 25 – 03 - 2014

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SIYANBOLA, Tolutope Oluwasegun

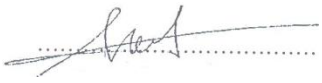
CERTIFICATION

We certify that the thesis titled "**Synthesis, Characterization And Evaluation Of Nano-Modified Polymeric Materials From *Thevetia Peruviana* Seed Oil**" is an original work carried out by Mr. Siyanbola Tolutope Oluwasegun (CUGP070185) in the Department of Chemistry, Covenant University, Ota, Ogun State, Nigeria under the supervision of Prof. E.T. Akintayo, Prof O. Olaofe, and Dr. K.O. Ajanaku. We have examined and found the research work acceptable for the award of a degree of Doctor of Philosophy in Industrial Chemistry.

26 – 03 -2014

Supervisor — Date

Prof. E.T. Akintayo



26 – 03 -2014

Co-Supervisor — Date

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Dean, College of Science and Technology — Date

Prof Loto Cleophas

DEDICATION

This research work is dedicated to God almighty, for the provision of wisdom, personalities and agencies necessary for the success of this research work. To Him alone I give all the praise and adoration.

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Siyanbola, Tolutope Oluwasegun

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REACTION SCHEMES

LIST OF ABBREVATIONS

APTMS	3-Aminopropyltrimethoxysilane
AV	Acid value
CaO	Calcium oxide
DMSO	Dimethylsulfoxide
DMTA	Dynamic Mechanical Thermal Analysis
DSC	Differential Scanning Calorimetry
ESI-MS	Electrospray ionization mass spectroscopy
FAME	Fatty acid methylesters
FT-IR	Fourier Transform Infrared Spectroscopy
HETA	N,N'-Bis (2-hydroxyethyl) *Thevetia peruviana* oil fatty amide
H^{12} MDI	4,4'-Diisocyanatodicyclohexylmethane
H.V	Hydroxyl value
HCl	Hydrochloric acid
I.V	Iodine value
ICl	Iodine monochloride
NCO	Isocyanate group
NMR	Nuclear Magnetic Resonance
N	Normality
PESA	Polyesteramide
KOH	Potassium hydroxide
MTCC	Microbial Type Culture Collection
PESAU	Polyesteramide-urethane from FAME polyol
%	Percentage
RB	Round Bottom Flask
S.V	Saponification value
SEM	Scanning Electron Microscopy
$Na_2S_2O_3$	Sodium thiosulphite
E'	Storage Modulus
TGA	Thermal Gravimetric Analysis
TEOS	Tetraethyl orthosilicate

TPPEA	*Thevetia peruviana* polyesteramide
TPPG	*Thevetia peruviana* partial glyceride
TPSO	*Thevetia peruviana*
TLC	Thin layer chromatography
TMS	Trimethylsiliane
PUD	Polyurethane Dispersion
XRD	X-ray Diffraction
ZnO	Zinc Oxide

BASIC UNITS

Å	Angstrom
cm	centimeter
^{o}C	degree celcius
g	gram
min	minutes
mL	milimeter
ppm	parts per million

ABSTRACT

The use of sustainable and biodegradable resources in the preparation of diverse industrial materials (such as organic coatings) has been revitalized due to emerging environmental challenges faced by today's world. Plant oils are considered the most available and renewable resource material, capable of replacing the petroleum feed-stock (petrochemicals), used in the preparation of most polymeric materials. The present report presents the synthesis, characterizations and evaluations of nano-modified polymeric materials from *Thevetia peruviana* seed oil (TPSO). The triglyceride based monomers were prepared through aminolysis and partial glyceride (PG) formation from TPSO. The fatty-amide of the oil (*N*,*N*-bis (2-hydroxy ethyl) *Thevetia peruviana* seed oil fatty-amide {HETA}) as well as desaturated fatty-amide methylesters of the oil (desaturated *N*,*N*-bis (2-hydroxy ethyl) *Thevetia peruviana* seed oil fattyamide {DHETA}) were treated with isophthalic acid and polyesteramides of their respective esterification were obtained. Partial glycerides polyol formation was carried out by reacting TPSO with glycerol in the presence of CaO as catalyst. These polyols were further reacted with 4,4'-diisocyanatodicyclohexylmethane (H_{12} MDI) to synthesize pristine polyurethanes. Nano particles (zinc oxide {ZnO} and 3-aminopropyltrimethoxylsilane-zinc oxide {APTMS-ZnO}) were also dispersed within the polymer matrix. The formation of monomers, pre-polymers as well as the eventual polymer composites were structurally elucidated by Fourier Transform Infrared Spectroscopy (FT-IR), Proton Nuclear Magnetic Resonance (^{1}H NMR) and Carbon 13 Nuclear Magnetic Resonance (^{13}C NMR) spectroscopic techniques. The fatty acid profile of TPSO fatty acid methyl esters (FAMEs) was examined by GC-FID. Thermal stability and curing of the hybrid composites were examined by thermogravimetric analysis (TGA), differential scanning calorimetry (DSC) and dynamic mechanical thermal analyzer (DMTA). The surface morphology and crystal/amorphous nature of the hybrid films was studied with scanning electron microscopy (SEM) and X-ray diffractometry (XRD) respectively. Anticorrosive (in acid, alkali, water, xylene and salt spray fog test), solubility test and antimicrobial (*Staphylococcus aureus, Escherichia coli, Bacillus subtilis, Aspergillus niger and Klebsiella pneumonia*) properties of the films were investigated. Results revealed that the fatty acid composition of the oil comprised mainly oleic (48.2 %), palmitic (22.3 %), linoleic (19.8 %) acids. FT-IR, ^{1}H and ^{13}C NMR confirmed the formation of the expected polymer matrices and their corresponding nano-modified composites, indicating a successful incorporation of the nano-material (APTMS-ZnO) in the pristine polymer coatings. The impregnation of the nano-material in the polymer led to curing of the polymer at room temperature. Results further revealed that as the percentage composition of the synthesized and incorporated nano-particle in the polymer matrix increased, properties such as thermal stability, anticorrosive and antimicrobial properties of the polymeric coatings also increased. However, at higher percentages, agglomeration of the nano-particle within the polymeric matrix ensued (for example in the case of PUTFA (Polyurethane *Thevetia* fatty amide)-APTMS-ZnO {15 wt %}). This made the micrograph of the film to be rough and also affect the thermal stability of the coatings. The successful incorporation of modified nano-particle within the pristine polymer had positive influence of the thermal stability, chemical resistance and antimicrobial inhibition on organisms tested. The coatings retain their photographic transparency irrespective of the varying inorganic–organic nano-particle within the polymer matrix.