SYNTHESIS, MODIFICATION, AND CHARACTERISATION OF FUNCTIONAL POLYURETHANE COATING SYSTEMS FROM CASTOR OIL

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A THESIS SUBMITTED TO THE SCHOOL OF POSTGRADUATE STUDIES IN PARTIAL FULIFILMENT OF THE REQUIREMENTS FOR THE AWARD OF DOCTOR OF PHILOSOPHY (PhD) DEGREE IN CHEMISTRY IN THE DEPARTMENT OF CHEMISTRY, COLLEGE OF SCIENCE AND TECHNOLOGY, COVENANT UNIVERSITY, OTA, OGUN STATE, NIGERIA

SEPTEMBER, 2024

ACCEPTANCE

This is to attest that this thesis is accepted in partial fulfilment of the requirements for the award of the degree of Doctor of Philosophy in Industrial Chemistry in the Department of Chemistry, College of Science and Technology, Covenant University, Ota, Nigeria.

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(Dean, School of Postgraduate Studies) **Signature and Date**

DECLARATION

I, ADEBOYE, SAMUEL ADEPITAN (20PCC02309), declare that this research was carried out by me under the supervision of Prof. Kolawole O. Ajanaku and Dr. Tolutope O. Siyanbola of the Department of Chemistry, Landmark University and Department of Chemistry, College of Science and Technology, Covenant University, Ota respectively. I attest that this Thesis has not been presented either wholly or partially for the award of any degree elsewhere. All the sources of materials and scholarly publications used in this thesis have been duly acknowledged.

ADEBOYE, SAMUEL ADEPITAN

Signature and Date

CERTIFICATION

We certify that the Thesis titled **SYNTHESIS, MODIFICATION, AND CHARACTERISATION OF FUNCTIONAL POLYURETHANE COATING SYSTEMS FROM CASTOR OIL** is the original work carried out by **ADEBOYE SAMUEL ADEPITAN (20PCC02309)** in the Department of Chemistry, Covenant University, Ota, Ogun State, Nigeria under the supervision of Prof. Kolawole O. Ajanaku and Dr. Tolutope O. Siyanbola of the Department of Chemistry, Landmark University and Department of Chemistry, College of Science and Technology, Covenant University, Ota respectively. We have examined and found this work acceptable as part of the requirements for the award of the degree of Doctor of Philosophy in Industrial Chemistry.

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Prof. Cecilia Akintayo
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Prof. Akan B. Williams
(Dean, School of Postgraduate Studies) **Signature and Date**

DEDICATION

I dedicate this work to my darling wife, Olufunke Asake Adeboye, a faithful friend and an unflinching support in this journey.

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LIST OF ACRONYMS AND ABBREVIATIONS

APTMS	Aminopropyltrimethoxysilane
AFM	Atomic Force Microscopy
ATR	Attenuated Total Reflectance
CSO	Castor Seed Oil
DSC	Differential Scanning Calorimetry
DTG	Differential Thermogravimetric Analysis
DMTA	Dynamic Mechanical Thermal Analysis
FESEM	Field Emission Scanning Electron Microscopy
FTIR	Fourier Transform Infrared Spectroscopy
FROCs	Functional Renewable Organic Coatings
GPC	Gel Permeation Chromatography
GO	Graphene Oxide
HDIT	Hexamethylene diisocyanate trimer
IPDI	Isophorone diisocyanate
JCO	*Jatropha caucus* Oil
MIBK	Methyl isobutyl ketone
NIPU	Non-isocyanate polyurethane
NMR	Nuclear Magnetic Resonance
PMAA	Polymethacrylic acid
PUs	Polyurethanes
RA	Ricinoleic Acid
RCSO	*Ricinus communis* Seed Oil
SEM	Scanning Electron Microscopy
TEOS	Tetraethoxysilane
TGA	Thermogravimetric Analysis

TPSO	*Thevetia peruviana* Seed Oil
TDI	Toluene diisocyanate
TMP	Trimethylolpropane
UV	Ultraviolet
VOCs	Volatile Organic Compounds
WPUs	Waterborne Polyurethanes
XRD	X-ray Diffraction

ABSTRACT

Environmental challenges have driven production science towards using biodegradable and sustainable feedstocks for product development. Developing sustainable and high-performance coating materials to address the environmental concerns and technical demands of modern industries has become so critical that plant seed oils are considered viable renewable feedstocks capable of substituting petrochemical-based materials in polymeric material preparation. This study reports the synthesis and characterisation of functional organic polyurethane coatings from castor bean seed oil (CSO) (*Ricinus communis* seed oil). Graphene nanoparticles were modified into graphene oxide and incorporated within the polyurethane polymer matrix in a one-pot synthesis. Also, aminopropyltrimethoxysilane (APTMS) was used to alter silica nanoparticles and was incorporated into the polyurethane system. Bisphenol A and trimethylolpropane (TMP) were used as extenders, and their influences on the coating properties were also examined in the urethane systems. Physicochemical analysis of the feedstock and prepared coating formulations was conducted. Structural evaluation of synthesised materials was performed using proton nuclear magnetic resonance (^{1}H NMR) and attenuated total reflection Fourier transform infrared (ATR-FTIR) spectroscopy. Synthesised urethane coatings were cured on silicon resin mould and mild steel. Thermal stability and crystallinity of pristine and composite films were studied using thermogravimetric analysis (TGA) and X-ray diffraction (XRD). Scanning electron microscopy (SEM) was used to analyse surface morphology. Water contact angle analysis revealed the hydrophobicity of the synthesised urethane films. Solubility, anticorrosive, and antimicrobial properties of prepared materials were evaluated. Spectroscopic analysis confirmed the structure of modified nanomaterials, pristine, and composite films. Surface morphology and photographic images showed successful incorporation of nanomaterials (graphene oxide and hybrid APTMS-modified silica) within the polymer matrix. Thermal stability, anti-corrosive, and antimicrobial properties of the coating films were enhanced with increasing percentages of nanomaterials in the polyurethane systems. Coating films exhibited improved hydrophobicity with rising percentages of modified nanoparticles. Film photographic retention tests showed no particle agglomeration and high transparency at 0.5% graphene oxide composition (0.5% PU-GO). It also shows that the polymer with 0.5% PU-GO is the most thermally stable. Similarly, composite films of modified silica in CSO showed enhanced thermal stability, hydrophobicity, antimicrobial activity, and corrosion resistance. The polymer with 5% PU-SNP was the most thermally stable at high temperatures. It also has the highest water contact angle and lowest corrosion rate, hence the most hydrophobic and corrosion resistant. In conclusion, the 0.5% loading of modified graphene oxide (0.5% PU-GO) nanoparticles is the optimum loading in applications requiring low and high temperatures. At the same time, 5% loading is the optimum loading of APTMS-modified silica (5% PU-SNP) in applications that require high temperature. These results present a viable, sustainable alternative for various industrial applications.

Keywords: renewable polymers, castor oil, polyurethane, nanomaterial, coatings.