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SYNTHESIS & CHARACTERIZATION OF STARCH BASE-POLYURETHANE COPPER NANOCOMPOSITE FOR PURIFICATION OF BIODIESEL

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ABSTRACT

This study synthesized and characterized starch-based polyurethane copper nanocomposites (CuNCs) for biodiesel purification, integrating copper nanoparticles (CuNPs) into the PU matrix to enhance adsorption properties. The synthesis involved reacting starch with diisocyanate to form PU, followed by integrating copper nanoparticles (CuNPs) within the PU matrix. Analytical techniques such as FTIR, ^{1}H NMR and TGA confirmed the successful synthesis polyurethanes. The nanocomposite exhibited excellent thermal stability, mechanical properties, and promising results in removing impurities from biodiesel, presenting a sustainable solution for the renewable energy sector.

Keywords: Starch, Polyurethane, Copper Nanocomposites, biodegradable, diisocyanate

2. INTRODUCTION

Starch, a naturally occurring, renewable, abundant, inexpensive, and biodegradable substance, serves as a storage polymer produced by a variety of plant granules. These sources include maize, wheat, cassava, rice, and potatoes, as well as stems, roots, legumes, and nuts. Starch exists as distinct particles that vary in shape from regular to irregular and in size from less than 1µm to over 100µm, depending on the source **[1-2].** Due to its structure, with more than two hydroxyl groups per repeating anhydroglucose unit, starch can react more effectively with

diisocyanate than other polyols or crosslinkers, making it useful in preparing Polyurethane. Additionally, starch has been utilized to increase the rigidity of flexible polyurethane foam **[3-4].**

Isocyanates are compounds with the functional group R-N=C=O, while diisocyanates are organic molecules containing two isocyanate groups. Diisocyanates are essential in polyurethane production, with different types imparting various properties to the polyurethane. MXD, derived from m-xylylene, is a colorless, highly flammable liquid with two isocyanate groups in the meta position, crucial for producing polyurethane foam. TDI, originating from toluene, is known for its flexibility and is widely used in flexible foams for furniture and bedding. IPDI, with a cycloaliphatic ring structure and dual isocyanate groups, is versatile in coatings, adhesives, and elastomers. MDI, characterized by two phenyl rings connected by a methylene bridge, is valued for its weather-resistant properties, making it ideal for rigid foams, surface coatings, adhesives, and sealants **[5].**

Polyurethane (PU) is a complex polymer made up of a series of organic units connected by carbamate linkages. It has a wide range of applications, including sponges, collagen tissue, hydrophobic films, synthetic rubber, acrylics, conductors, and more. Invented by Professor Dr. Otto Bayer and his students, the production of PU involves converters conducting polymerization, which differs from the large-scale pre-polymerization of thermoplastics. Chemical manufacturers provide the base materials, including blended components tailored for specific applications. The main raw materials for PU production are diols and isocyanates, which react to form urethane linkages, allowing for customized formulations based on end-user requirements **[6-9].**

Nanotechnology, the study of manipulating materials at the molecular and atomic levels (1-100 nm), is drawing significant interdisciplinary attention and is becoming integral to various aspects of daily life **[10-11].** This field offers practical and affordable solutions for environmental sustainability and renewable energy. Engineers are leveraging nanotechnology to create innovative products and processes across biomedicine, agriculture, energy, environmental health, and industry, thus shaping new scientific and technological advancements [**12].**

Nanomaterials, which include polymer nanocomposites and nanoparticles, are notable for their biocompatibility, low toxicity, and antibacterial properties. Copper oxide (CuO) nanoparticles, in particular, are used extensively in biomedical applications such as drug delivery, anti-cancer therapy, and wound healing [**13-14].** CuO nanoparticles also have diverse applications in field emission emitters, solar energy

conversion, high-temperature superconductors, batteries, gas sensors, and catalysis. Fluids containing micro CuO particles can enhance heat conductivity and fluid viscosity, highlighting their energy conservation potential. However, the increased use of nanoparticles raises concerns about their toxicity, necessitating the study of nanotoxicology to understand their impact on human health and the environment **[15-16].**

Polyurethane composition is selected for copper oxide (CuO) nanoparticle incorporation due to its exceptional properties and versatility. The segmented composition of polyurethane allows for tailored properties suited to specific biomedical needs, making it an ideal matrix. Polyurethanes are widely used in hospital beds, particularly in polyurethane foams (PUFs), which are categorized into open-cell and closed-cell types **[17-18].** Nearly 100% open-cell structures in mattress foams are essential for easy washing and maintenance in hospital settings. Integrating copper nanoparticles into polyurethane foam mattresses creates antimicrobial surfaces that effectively inhibit bacterial growth, enhancing hygiene and reducing infection risks in hospitals. This innovation promotes patient well-being and offers sustainable, long-lasting solutions for healthcare facilities **[19-20-21].**

This research involves creating an effective and sustainable substance that combines the benefits of polyurethane, copper nanoparticles, and starch to improve the purification of biodiesel. The aim of this study is to investing the structural, morphological, and functional properties of a nanocomposite through detailed synthesis and characterization. The goal to improve efficiency and selectivity in the removal of Impurities from biodiesel, which will further the development of environmentally friendly purification techniques for the biodiesel industry.

3. Experimental section

3.1 Materials

The M-Xylene diisocyanate (MXD), Toluene diisocyanate (PTD), 4,4-methlene diphenyl diisocyanate (PM_4D)), Isophorone diisocyanate (IPDI), all of which were utilized exactly as received, were provided by TCI Chemical. We bought DMSO from TCI Chemicals, which is a high-performance liquid chromatography grade. The TCI Chemicals provided copper oxide nanoparticles, which had an average particle size of 90 nm. I also used Round bottom flask, Condenser, Measuring Cylinder, Test Tube, Beaker, Magnetic Stirrer, Water Pot, Stand, Thermometer and Petry Dish.

There are four types of isocyanates

1. M-Xylene diisocyanate (MXD)
2. Toluene diisocyanate (PTD)
3. 4,4-methlene diphenyl diisocyanate (PM_4D)
4. Isophorone diisocyanate (PIPD)

Table 1: Name And Structure Of The Chemicals

NAME	IUPAC NAME	STRUCTURE	Code for polyurethane	Code for nanocomposite
M-xylene diisocyanate	1,3-bis (isocyanato methyl) benzene		PU-MXD	PU-CN-MXD
Isophorone diisocyanate	5-isocyanato-1-(isocyanatomethyl)-1,3,3-trimethylcyclohexane		PU-PIPD	PU-CN-PIPD
Toluene diisocyanate	2,4-diisocyanato1-methylbenzene		PU-PTD	PU-CN-PTD
4,4'-methylenediphenyl diisocyanate	bis(4-isocyanatophenyl) methane		PU-PM$_4$D	PU-CN-PM$_4$D

3.2. Methods

3.2.1. Synthesis of Starch Based Polyurethane (PUs-ST)

To create the composite material, begin by measuring 1 gm of starch and adding 20 ml of DMSO, stirring the mixture for approximately 15 minutes to achieve thorough blending. Next, introduce 14 microliters of tin, stirring the combination for an additional 30 minutes while maintaining a temperature of 50 degrees Celsius. Incorporate 0.7ml of isocyanate into the mixture and stir continuously for 4-5 hours, ensuring the temperature remains at 90 degrees Celsius throughout this duration. Add 50 ml of cool methanol to the mixture, inducing the formation of precipitates. Filter the resulting mixture using Whatman filter paper, a crucial step for separating solid particles from the liquid. Proceed with a drying process, drying the filtered substance until it transforms into a dry powder. This ensures the removal of any remaining liquid, leaving behind the desired composite mate.

Figure 1: Reaction setup for the synthesis of polyurethanes

3.2.2. Synthesis of Starch Based Polyurethane with Copper-Nanocomposite (PU- CNs)

To create a composite material, follow these steps: Start by mixing 1gm of starch with 20 ml of DMSO, stirring the combination for 15 minutes. Next, introduce 14 microliters of tin into the mixture and stir for an additional 30 minutes at a maintained temperature of 50 degrees Celsius. Proceed by adding 0.05 grams of copper nanoparticles, ensuring thorough distribution through stirring. Incorporate 0.7ml of isocyanate and stir continuously for 4-5 hours while maintaining the temperature at 80 degrees Celsius. Introduce 50 ml of cool methanol into the mixture to induce the formation of precipitates. Filter the resulting mixture using Whatman filter paper to separate solid particles from the liquid. Finally, undergo a drying process until the filtered substance transforms into a dry powder, ensuring the removal of any remaining liquid and leaving behind the desired composite material.

3.2.3. Synthesis of biodiesel

In the preparation of biodiesel the 6:1 ratio of methano:karanja oil and 15% H_2SO_4 (wt/wt) at 60 ^{0}C for 24 h. after this process the methanol was removed under the pressure and mixture was kept in separating funnel after that the starch was settled at the bottem of the funnel. To remove the starch and the other impurities and the crude biodiesel was dissolved in ethyle acetate and water. The other impurity was removed by the addition of charcoal.

Figure 2: Reaction setup for Synthesis of biodiesel

3.2.4. Application For Purification of Biodiesel By Starch-Based Polyurethane

Accurately measure 2 ml of biodiesel into a tiny RBF. To that, add 0.40 mg of polyurethane 1 hour of room temperature stirring was completed. Use Whatman filter paper to remove it after that. Calculate the filter's weight and record it. This is the method for purifying polyurethane with a cellulose base into biodiesel.

Figure 3: Purification of Biodiesel by ST-PU

4.2.5 Purification of Biodiesel

To calculate the acid value, use the formula given.

$$\text{Acid value } \frac{Volume\ titrant(ml) \times normality\ \ of\ KOH\ (N) \times M.W(KOH)}{Mass\ of\ sample(g)}$$

Where, a = no. of 0.1 N Potassium hydroxide
w= weight in gm of substance taken
Acid value of biodiesel
% of acid value efficiency = $(I_0 - I_p / I_0) \times 100$

Where, I_0 = acid value before purification
I_p = acid value after purification

Table 2: Biodiesel Purification result

Sr. no.	Name	Acid value of blank biodiesel	Acid value of biodiesel after treatment of Polyurethane	% of acid value efficiency of Polyurethane
1.	PU-PIPD	48.44	38.06	21.42
2.	PU-MXD		40.73	15.91
3.	PU-PM_4D		39.40	18.66
4.	PU-PTD		39.06	19.40
5.	PU-CN-PIPD		36.02	26.90
6.	PU- CN-MXD		35.41	29.64
7.	PU- CN-PM_4D		34.08	26.82
8.	PU- CN-PTD		35.45	26.90

4. RESULT & DISCUSSION

4.1. Characterisation by FTIR spectroscopy

Infrared spectroscopy employs the infrared region of the electromagnetic spectrum to quantify the light absorption of a material within this range. For a molecule to absorb light, its bonds must generate a dipole moment, indicating a non-uniform distribution of electrons within the bond. In the case of IR pallets, a salt plate and a liquid sample can be combined without introducing any lines onto the spectra, as they remain transparent to infrared light. Apply pressure at 10 to 12 atm. for two minutes, then introduce the IR pallet into the instrument post-pressure release. Initiate the IR recording and print the

resulting graph. The absorbance range of 4000 to 500 cm^{-1} was utilized for collecting IR spectra. The FT-IR spectrum was employed to identify and detect distinctive peaks and functional groups of active components based on their peak values in the infrared radiation region (4000 to 500 cm^{-1}).

4.2. Characterisation of starch by FTIR

The -OH group of PU Foam is detected at 3747.97 cm^-1 in the IR spectra.

Peaks at 2325.34 cm^{-1} correspond to the O=C=O group. From 2240 - 2275 cm^{-1}, the aldehyde group of PU Foam is discovered, demonstrating the existence of C ≡ C of PU Foam having a range of 2308.27 cm^{-1}. A peak at 2241.21 cm^{-1} reveals diisocyanate. A peak at 1077.59 cm^{-1} is the typical peak of -OH stretching. The raft's spectrum shows distinctive peaks of alkenes C=C at 994.17 cm^{-1}. These peaks and groups in the IR spectrum provide information about the chemical composition and functional groups present in the PU foam and the raft.

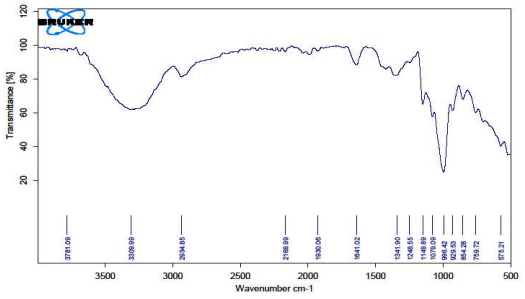

Figure 4: FTIR spectrum of starch

4.3. Overlapped FTIR of Starch & MXD & PU-MXD

The peak observed between the range of 2240 – 2275 cm^{-1} is for the isocyanates group with N=C=O stretch. Below this peak, MXD diisocyanate is observed at a range of 2241.20 cm^{-1}. The peak observed between the range of 1348.41 cm^{-1} is of the amine group C=N stretch. The range of the tertiary alcohol group is from 1100–1170 cm^{-1}, and the below-observed range is 1155.03 cm^{-1} with C–O stretch. The alkynes group range between 800 – 860 cm^{-1}, and below the observed range is 851.23 cm^-1 with C–H bend. The alkynes group range between 735 – 770 cm^{-1}, and below the observed range is 742.61 cm^-1 with C–H bend. The range stretch of cis alkenes C=C is observed at 697.14 cm^{-1}. These additional peaks and groups in the IR spectrum provide further details about the chemical composition and functional groups present in the material.

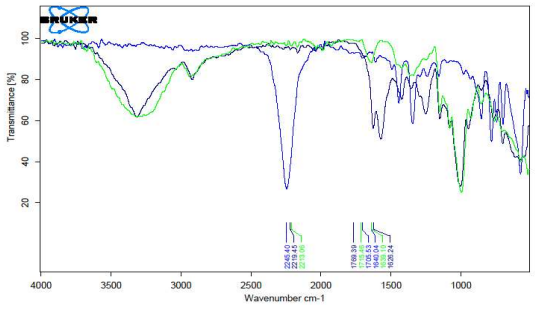

Figure 5: FTIR spectrum of ST & MXD & PU-MXD

4.4. Overlapped FTIR spectrum of Starch& PIPD & PU-PIPD

The peak observed between the range of 2240 – 2275 cm^{-1} is for the isocyanates group with N=C=O stretch. Below this peak, MXD diisocyanate is observed at a range of 2241.20 cm^{-1}. The peak observed between the range of

1348.41 cm^{-1} is of the amine group C=N stretch. The range of the tertiary alcohol group is from 1100–1170 cm^{-1}, and the below-observed range is 1155.03 cm^{-1} with C–O stretch. The alkynes group range between 800–860 cm^{-1}, and below the observed range is 851.23 cm^{-1} with C–H bend. The alkynes group range between 735 – 770 cm^{-1}, and below the observed range is 742.61 cm^-1 with C–H bend. The range stretch of cis alkenes C=C is observed at 697.14 cm^{-1}. These additional peaks and groups in the IR spectrum provide further details about the chemical composition and functional groups present in the material.

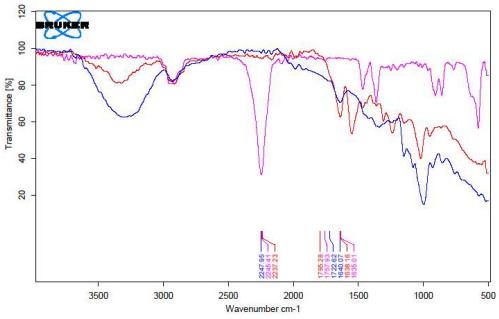

Figure 6: FTIR spectrum of ST & PIPD & PU-PIPD

4.5. Overlapped spectrum of ST & PTD & PU- PTD

In the FTIR spectrum titled "Overlapped FTIR of Toluene diisocyanate (TDI), starch, and starch-based polyurethane," key peaks are discerned: a broad signal at 3300 cm^{-1} corresponding to N-H stretching in the polyurethane's urethane group, a 2920 cm^{-1} peak indicative of C-H stretching in aliphatic groups across PTD, starch, and the polyurethane, and a 1740 cm^{-1} peak linked to C=O stretching in the urethane group of the starch-based polyurethane. Notably, the PTD peaks are PU-ST-PTD relatively weaker, suggesting a lower concentration, likely due to its role as a reactant in polyurethane synthesis with excess removed during purification. The polyurethane spectrum exhibits a broad 1740 cm^{-1} peak, hinting at diverse urethane groups. These interpretations emphasize the nuanced understanding required for FTIR analysis, where the analyst's experience plays a crucial role.

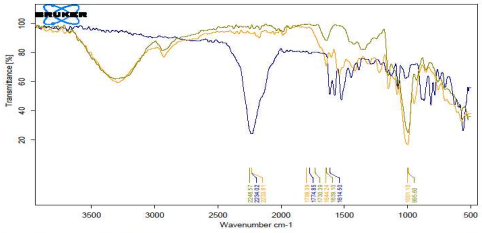

Figure 7: FTIR spectrum of ST & PTD & PU- PTD

4.6. Overlapped spectrum ST & PM_4D & PU-PM_4D

The overlapped FTIR spectrum of 4,4'-methylenediphenyl diisocyanate (M4D), stach, and starch-based polyurethane reveals key peaks, including O-H and N-H stretching (3300 cm^{-1}), C-H stretching (2920 cm^{-1}), C=O stretching (1740 cm^{-1}), N-H bending (1510 cm^{-1}), C-O stretching (1230 cm^{-1}), and out-of-plane bending vibrations of aromatic groups in PM4D (810 cm^{-1}). The relative peak intensities indicate varying concentrations of functional groups, with the polyurethane exhibiting a higher urethane content. FTIR spectra offer valuable insights into chemical

compositions and relative quantification of functional groups, but interpretation complexities and subjectivity underscore the need for expertise in chemical functional group analysis.

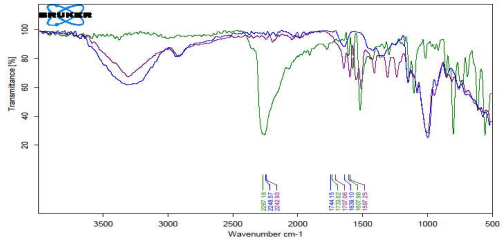

Figure 8: FTIR spectrum of ST & PM4D &PU-PM4D

5. ^{1}H NMR Starch based Polyurethane.

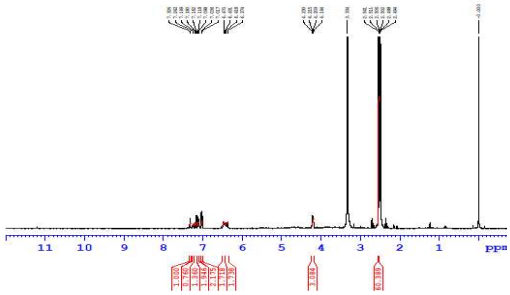

Figure 9: ^{1}HNMR spectrum PU-MXD

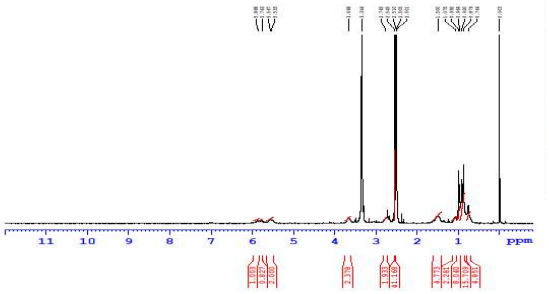

Figure 10: ^{1}HNMR spectrum PU-PIPD

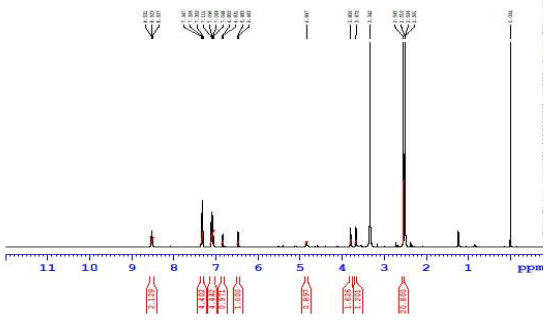

Figure 11: ^{1}HNMR spectrum PU-PM4D

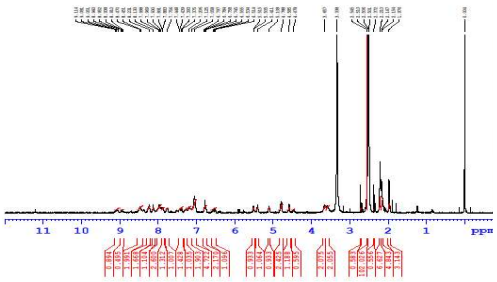

Figure 12: ^{1}HNMR spectrum PU-PTD

In the ^{1}H NMR spectrum, there are only two types of chemical environments for C-H in the benzene ring, as seen by the appearance of two peaks (δ 7.20 and 7.38 ppm) with roughly the same area corresponding to the CH with the FTIR analysis that the benzene ring is 1,4-disubstituted structure. The peaks produce the ^{1}H NMR signals at around δ 0.95–1.98 ppm for cyclic aliphatic methylene protons. The peaks seemed around at δ 3.50–3.90 and 4.55–6.02 ppm corroborated the presence of glucose units in the starch backbone. At δ 7.10 the urethenic shows N-H peak may appear in the ^{1}H NMR spectrum. At the δ 2.5 ppm the peak is showing DMSO peak.

6. TGA analysis of starch-based polyurethane nanocomposite:

6.1. TGA analysis of PU-ST-PMXD

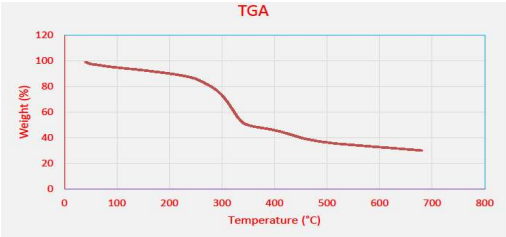

Figure 13: TGA analysis of PU-ST-PMXD

6.2. TGA Analysis of PU-ST-PIPD

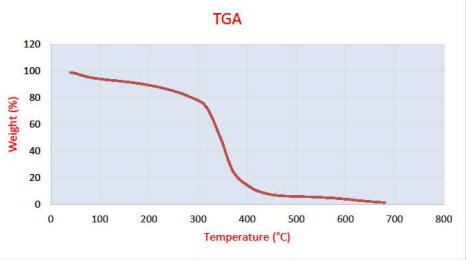

Figure 14: TGA analysis of PU-ST-PIPD

In the 270–350˚C temperature range, the TGA thermogram analysis reveals a notable weight loss. The breakdown of urethanic connections in the nanopolyurethanes composites is identified as the cause of this weight loss. Literature findings on the breakdown of urethanic connections are consistent with this phenomena. The urethane linkages have been confirmed to graft to the native structure of starch, as evidenced by the thermal properties of the composite nanopolyurethanes, as investigated by TGA thermograms. These properties reveal that the thermally decomposed state of starch differs from that of starch-based bulk and nanopolyurethanes because of structural changes like crystallinity.

7. Conclusion

A promising solution to the challenges in producing high-quality biodiesel involves creating a composite material combining starch, polyurethane, and copper. By integrating copper into the composite, we enhance its mechanical strength and adsorption capabilities, thereby improving its efficiency in purifying biodiesel. This innovative approach replaces traditional polyurethane derived from petroleum with renewable and biodegradable starch-based polymers. The potential benefits of this composite are vast, offering a sustainable alternative for biodiesel production on a large scale. Through further research and development, we can optimize the composite's performance and cost-effectiveness, paving the way for its widespread commercial use as an adsorbent. Comparative analysis reveals significant improvements in acid value efficiency between traditional polyurethane (21.42%) and nanocomposite making the latter a more promising candidate for applications in adsorption fields (26-29%). In essence, this composite material holds great promise for advancing the sustainability and efficiency of biodiesel production, presenting a compelling opportunity for industry growth and environmental stewardship.

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