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NOVEL STARCH-BASED POLYURETHANE GRAPHENE NANOCOMPOSITES FOR ADVANCED BIODIESEL PURIFICATION

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ABSTRACT

The research work has inspired the creation of a wide variety of compositions that are focused on the hunt for biodegradable polymers. Numerous combinations of biodegradable polymers have been effectively employed in the process of eliminating impurities. The nanocomposite material is synthesis by reaction of starch with (m–xylene diisocyanate to form urethanic linkage and graphene is use to form polyurethane and nanocomposite. The synthesised nanocomposite undergoes a comprehensive characterization process, utilizing techniques such as FTIR, ^{1}H NMR spectroscopy, and TGA. These analyses serve to provide valuable insights into the structural and thermal properties of the newly formed material. Particularly noteworthy is the material's potential for applications in adsorption. polyurethane and nanocomposite are applied for the purification of crude biodiesel. Synthesis of biodiesel is by acid-catalysed transesterification of Karanja oil. Nanocomposite show better result as compared to polyurethane for removal of acid value of biodiesel.

Keywords: Polyurethane, Biodiesel, Polyols, Treatment of Biodiesel, Diisocyanates, Graphene

1. INTRODUCTION:

Polymeric carbohydrates, or polysaccharides, are a class of molecule made up of long chains of carbohydrates connected by glycosidic linkage **[1]**. They might be straight or very branching, depending on their structure. They might not dissolve in water or perhaps be amorphous. Polysaccharides are one of the several natural polymers present in plants, algae, mammals, and microorganisms. The category of biopolymers made of starches, which in general have certain great qualities, has the oldest history and the most experience in terms of medicinal applications. Recent years have seen an increase in interest in the research of bioartificial materials made of polysaccharides. Many sources, including microorganisms like dextran and glean, animals like chitosan, and plants like starch, can be used to make polysaccharides, a kind of biopolymer **[2]**. Due to their biocompatibility and biodegradability, polysaccharides can be employed in medical operations with a reasonable level of safety. As delivery solutions for the treatment of many illnesses, natural polymer nano systems have attracted a lot of attention.

Green plants mostly store carbohydrates in the form of starch, which is regarded as the second largest biomass generated on earth after cellulose. A polymer made of glucose units with a six membered ring is called starch (glucopyranose). Starch having molecular weight range of 10^4 to 10^7 Daltons. The majority of starch molecules possess highly branched structures known as amylopectin, which is found in up to 100% of waxy starches, 72% of normal maize starch, and 80% of potato starch. Starch is a raw material used in the synthesis of monomers that can be non-biodegradable, such as polyethylene, or biodegradable, such as PLA (the main biodegradable commercial polymer whose monomer can be obtained from the fermentation of starch.) as a base substance for the production of biopolymers such as polyhydroxy alkanoate **[3]**. Starch is widely used in making emulsifiers, stabilizers, thickeners, and edible covering film in the food industry, as well as packaging material and functional biomaterial in the pharmaceutical or non-food sectors **[4]**.

A solid substance known as a nanocomposite is composed of many phases, at least one of which has one, two, or three dimensions, all of which are nano-meter-sized **[5]**. The aim of achieving synergy between various elements is accomplished by nanoscale phase processes. Nanoparticles, nanofibers, and nano clays are examples of nanomaterials used in nanocomposites. The preservation of key qualities to resolve defects and express certain current characteristics is another advantage of the nanocomposite material's composition of non-metallic, metallic, and polymeric components through a specific technique **[6]**. This material is an example of the multiphase crossover of matrix and reinforcing components. The matrix material is an ongoing phase made up of polymer, metallic, and inorganic non-metallic matrix materials. The dispersed phase that makes up the reinforcing material often contains fibrous substances like glass fibre, organic fibre, etc **[7]**.

A composite is a material that has reinforcement that is macroscopically integrated in or attached to a matrix with clearly defined interfaces or limits between them. A diol or polyol, a diisocyanate or poly isocyanate, and a chain extender are the three key components that makeup PUs, which are essentially block copolymers **[8]**. Polyether and polyester polyols are most commonly used in the synthesis of Pus. Micro-pumps, robotics, positioners, bioinspired robotics, electronic components, energy storage, automotive parts, light emitting diode, liquid crystal display, electromagnetic interference shielding, optoelectronic devices, flexible electronic products, and piezoelectric generator can all benefit from the better overall electrical characteristics of PU-based composites (PUC). Diisocyanate and chain extender may form a hard segment (HS) and a polyether or polyester polyol soft segment (SS). PUC has some significant limitations in high-temperature applications **[9]**. PUC has various flaws, including poor tensile strength and thermal stability in high-temperature working conditions, as well as poor anticorrosive abilities. The properties of PUC tune by alter the diols and diisocyanate. The diisocyanate is an organic molecule that has two isocyanate groups. The Diisocyanate is used the produce polyurethane. Different types of diisocyanate give different types of properties in polyurethane **[10]**. Rigid nanocopmosites and surface coating production frequently use MDI. In applications like furniture and bedding where flexible nanocopmosites are used, TDI is frequently used. Due to their resistance to the weather, TDI and MDI are both utilized to make adhesives and sealant **[11]**. m-xylene diisocyanate colourless liquid that contains two isocyanate groups on meta position. is an aromatic hydrocarbon. The m-xylene diisocyanate is colourless and very flammable. The m-xylene diisocyanate is an aromatic isocyanate that is used for the production of polyurethane nanocopmosite **[12-15]**. The research work focus on synthesis of starch-based polyurethane and nanocomposite for the purification of biodiesel.

2. MATERIALS & METHOD:

Starch is a polysaccharide which contain –OH group and was purchased from (LOBA chemicals). We have used isocyanate that contains two -NCO groups. M-xylene diisocyanate was purchased from (TCI chemicals), 1,4-diazabicyclo [2.2.2] octane (LOBA), Tin (ll) ethyl hexanoate as catalyst was used from (TCI chemicals), Graphene Platelets Nano Powder was purchased from (SRL chemicals), Polydimethylsiloxane (LOBA chemicals), Nano-calcium carbonate (MOLYCHEM chemicals), Hydrochloric acid (SRL chemicals), Methanol (SRL chemicals).

2.2. Experimental

2.2.1 Synthesis of synthesis of starch-based graphene polyurethane and nanocomposite

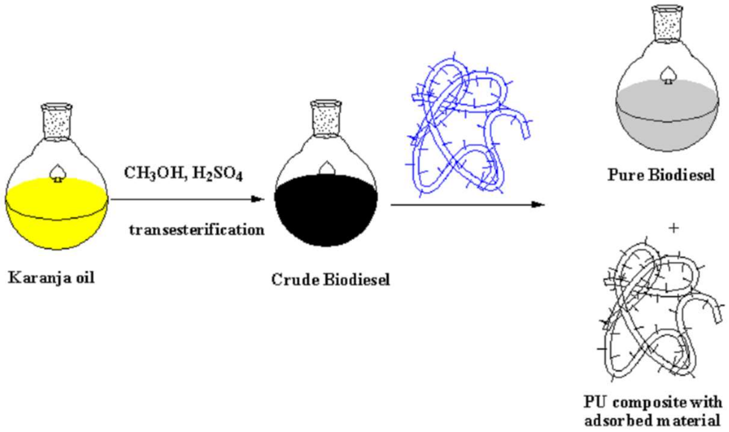
Firstly take 10 g of Diisocyanate (m–xylene diisocyanate) into RBF 1 and then add 10g of nano $CaCO_3$ to it. Then measure 1g of graphene platelets nano powder and add this to the upper mixture. After 2-3 min add the starch powder to the RBF and the mixture poured in the RBF-1 was stirred continuously until a thick layer of it was to be obtained. Then, in another RBF-2, dissolve 0.55 g of 1,4-diazabicyclo [2.2.2] octane in 12 ml of water. After that add 25 ml of starch powder to the RBF and 2-3 drops of tin (ll) ethyl hexanoate and 1 ml of silicon oil to the RBF and all the mixture components were dissolved in 25 ml of DMSO as it is used as a solvent. Next 5 g of RBF-2 mixture was added to the pre-polymer mixture of RBF-1 and stirred for 1 hour. Following 1 hour of nanocomposite, the PU sponge was submerged in 1 M HCl solution (water: alcohol 1: 1, v/v) with continuous extrusion until no bubbles were generated. After that, PU nanocomposite has been obtained.

2.2.2 Synthesis of Biodiesel:

To make biodiesel, Karanja oil and methanol are mixed together. Then, take 50 ml of dry RBF with Karanja oil. Then, while mixing, gradually add 4 ml of sulfuric acid. It was agitated for 24 hours at 60 ˚C. Glycerol and other impurities were removed using ethyl acetate and water. The sodium sulphate was used to remove the moisture. To remove any colour contaminants from the mixture, activated charcoal was added **[9]**.

2.2.3. Application in Purification of Biodiesel:

After accurately weighing out around 2ml of substance, in the event of a resin, add 5 ml of an equal mixture of alcohol and solvent ether that has been neutralized by the addition of 1-2 drops of phenolphthalein solution to 250 ml of flash. Titrate with 0.1 N potassium hydroxide while agitating the liquid ferociously until fifteen seconds-long pink colour is achieved. If necessary, gently reheat the object over until it has completely melted. Note down the reading.



Scheme 1: Synthesis and purification of biodiesel

Table 1: Purification of biodiesel by polyurethane and nanocomposite

Acid value of blank biodiesel	Acid value of biodiesel after treatme-nt with polyurethane	Acid value of biodiesel after treatment with graphene nanocomposite	% of acid value efficiency of polyurethane	% of acid value efficiency of graphene nanocomposite
48.45	**38.04**	**31.24**	**21.27%**	**35.52%**

3. RESULT & DISCUSSION:

^{1}H NMR (Proton Nuclear Magnetic Resonance Spectroscopy) technique is used to study the structure and composition of molecules by analyzing the behavior of hydrogen nuclei in a magnetic field. In this case, the text mentions that the presence of hydrogen atoms in the newly synthesized polymers is confirmed using ^{1}H NMR. The spectra were recorded at room temperature using a Bruker Avance 500 FT NMR spectrometer. The solvent used for the analysis is deuterated dimethyl sulfoxide (DMSO-d_6), which ensures that the solvent signals do not interfere with the sample signals. The chemical shifts (in ppm) are reported relative to the internal standard, which is tetramethylsilane (TMS) at 0.0 ppm.

FTIR is a technique used to identify chemical bonds and functional groups in a sample by measuring the absorption of infrared radiation. The text mentions that FTIR spectra were measured using a Perkin Elmer Model 1600 infrared spectrometer. The spectra were recorded in percentage transmittance versus wavenumber, which refers to the frequency of the infrared radiation used in the analysis. The range of wavenumbers typically covers the infrared region from 4000 to 400 cm^{-1}. To prepare the samples for FTIR analysis, solid potassium bromide (KBr) pellets were prepared using a hydraulic KBr press.

Thermal decomposition of nanopolyurethanes composite was studied with by TGA 73,000 (EXSTAR) (TGA). Thermal properties of the nanopolyurethanes composite studied by TGA thermograms have shown that the thermal decomposition of starch varies from the starch-based bulk and nanopolyurethanes due to structural changes such as crystallinity and thus confirmed the grafting of the urethane linkages to native structure of starch.

In summary, the provided text describes the methods used to analyze the newly synthesized polymers using ^{1}H NMR, FTIR and TGA spectroscopy. These techniques allow researchers to gather information about the molecular structure, composition, and functional groups present in the samples.

3.1. FTIR Spectrum Analysis of Starch Cross-linked Polyurethane:

In the FTIR spectra **(Figure 1), A, B, and C** represent respectively starch, m-xylene diisocyanate and cross-linked polyurethane Nano composite. The -OH group of PU nanocomposite is detected at 3747.97 cm^{-1} in IR spectra. The peak observed between the range of 3200 – 3400 cm^{-1} is for the Phenols group with O-H stretching. Another observed at range of 2936.62 cm^{-1} is for the Alkanes group with C–H stretching. The peak observed between the range of 2240–2275 cm^{-1} is for the Isocyanates group with N=C=O stretching. Below the peak observed is MXD diisocyanate which is at a range of 2241.20 cm^{-1}, which is clearly disappeared at polyurethane due to urethanic linkage. The peak observed between the range of 1348.41 cm^{-1} is of Amine group C=N stretching. A peak observed at 1077.73 cm^{-1} is for Tertiary Alcohol group with C–O stretching. The peak observed at 1014.79 cm^{-1} is for Primary Alcohol group with C–O stretching. The infrared spectrum of m-xylene diisocyanate is characterized by a distinct strong broad peak of approximately 2248.53 cm^{-1}, which corresponds to the presence of a -NCO group in the m-xylene diisocyanate which is veins out at cross-linked polyurethane.

3.2. ^{1}H NMR Analysis of Polyurethane:

In the ^{1}H NMR spectrum, there are δ 3.53–3.81 ppm (H2, H3, H4, H5, H6), 4.61 ppm (OH7), the peak appeared correspond to glucose units of the starch backbone present in polyurethane. 6.50–7.20 (m-xylene diisocyanate Ar protons). At δ 7.50 ppm the urethenic linkage shows N-H peak characteristic peak may appear in the ^{1}H NMR spectrum.

3.3 TGA analysis of starch-based polyurethane nanocomposite:

TGA thermogram of nanopolyurethanes composite show drastic weight loss in the range of 270-350˚C due to the urethanic linkage break down. Which is clearally reported at literature due to decomposition of urethanic linkage. Thermal properties of the nanopolyurethanes composite studied by TGA thermograms have shown that the thermal decomposition of starch varies from the starch-based bulk and nanopolyurethanes due to structural changes such as crystallinity and thus confirmed the grafting of the urethane linkages to native structure of starch.

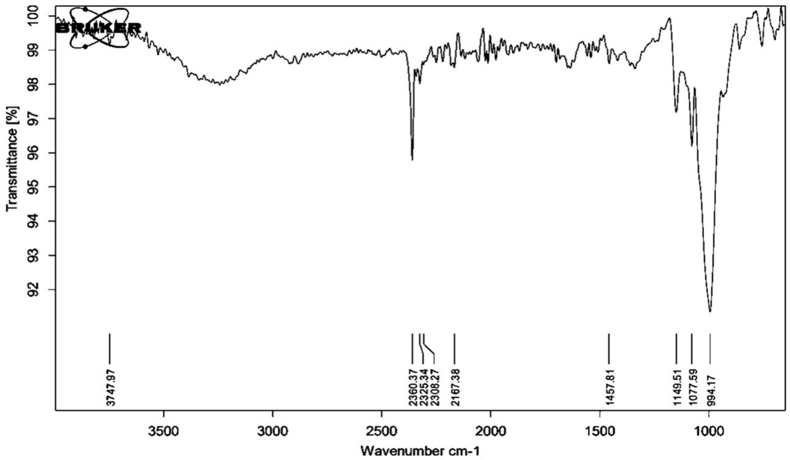


Figure 1 (A): FTIR spectra of the Starch

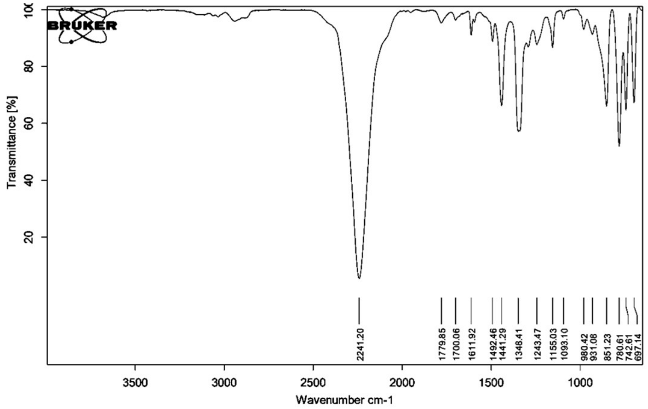


Figure 1 (B): FTIR spectrum of the m– xylene diisocyanate (MXD)

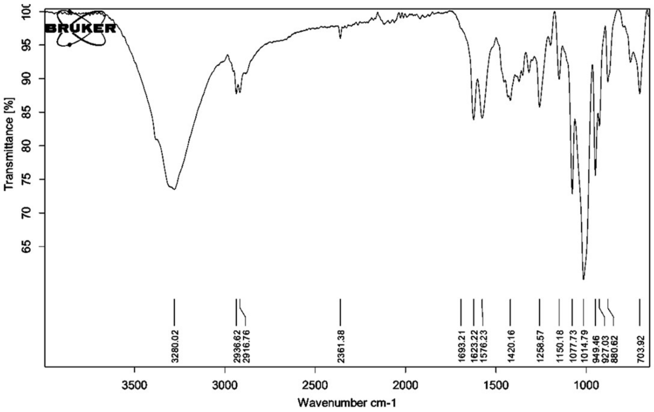


Figure-1 (C): FTIR spectra of starch cross-linked polyurethane

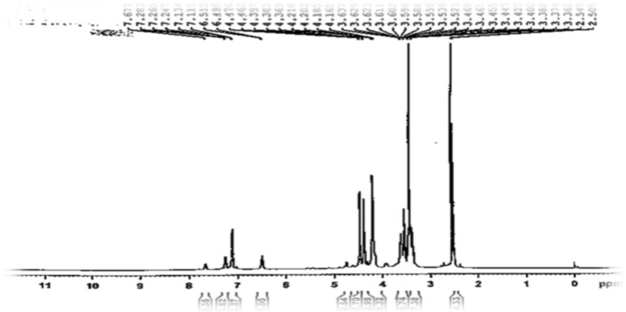


Figure 2: ^{1}H NMR spectra of Starch-Based Polyurethane Graphene Nanocomposites

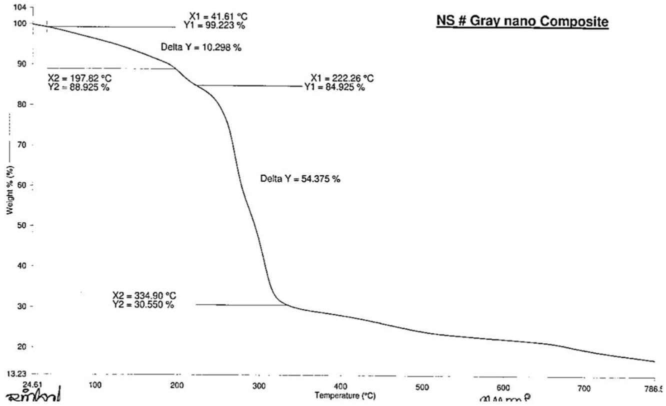


Figure 3: TGA thermograms of nanopolyurethanes composite

4. CONCLUSION:

A viable strategy for overcoming the difficulties of creating high-quality biodiesel is the creation of a starch-based polyurethane-graphene composite. The addition of graphene improves the composite material's mechanical and adsorption capabilities, which improves the effectiveness of purifying biodiesel. Traditional polyurethane materials made from petroleum can be replaced with renewable and biodegradable polymer components like starch. Overall, the use of this composite material has enormous potential for the manufacture of biodiesel on a wide scale, helping to promote the industry's sustainable growth. The composite material may be optimised for higher performance and cost-effectiveness through additional research and development in this area, opening the door for its widespread commercialization as adsorbent. The acid value efficiency of polyurethane has been reported to be 21.27%, while the acid value efficiency of graphene nanocomposite is 35.52%. The result show better candidate for the adsorption application fields.

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