A COMPREHENSIVE EXPLORATION OF BIO-BASED

NON-ISOCYANATE POLYURETHANE

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<u>CANDIDATE DECLARATION</u>

I Manpreet Kour (2k22/MSCCHE/19) hereby certify that the work which is being presented in the thesis enlightened **"A Comprehensive Exploration of Bio-Based Non-Isocyanate Polyurethane"** in partial fulfillment of the requirements for the award of the Degree of Master in Science, submitted in the Department of Applied Chemistry, Delhi Technological University is an authentic record of my own work carried out during the period from Aug 2023 to Mar 2024 under the supervision of Prof. Raminder Kaur

The matter presented in the thesis has not been submitted by me for the award of any other degree of this or any other institute.

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CERTIFICATE

Certified that Manpreet Kour (2k22/MSCCHE/19) has carried out their research work presented in this thesis entitled **"A Comprehensive Exploration of Bio-Based Non-Isocyanate Polyurethane"** for the award of Master of Science from the Department of Applied Chemistry, Delhi Technological University, Delhi, under my supervision. The thesis embodies results of original work, and studies are carried out by the students herself and the contents of the thesis do not form the basis for the award of any other degree to the candidate or to anybody else from this or any other University/Institution.

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ABSTRACT

Polyurethane in its various forms, has established dominance as a reliable material owing to its outstanding properties, including chemical resistance, weathering resilience, adhesion, mechanical strength, and durability. However, the escalating costs associated with synthetic polyurethane production, coupled with its non-biodegradable and toxic nature, along with the depletion of petrochemical-based raw materials, pose significant challenges. In response, researchers have successfully synthesized non-isocyanate polyurethane that adequately perform analogous to their petrochemical counterparts, addressing concerns such as environmental pollution, economic efficiency, and raw material sustainability. This work delves into the quest for 'greener' polyurethane materials, exploring the investigation of precursors for polyol and isocyanate synthesis. With attributes like biodegradability, cost-effectiveness, and the potential to substitute petroleum-based polyurethane, non-isocyanate polyurethane holds promising prospects for future polyurethane applications. This critical analysis provides an overview of the development, applications, and recent advancements in various non-isocyanate polyurethane polymers emerging over the last decade.

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LIST OF ABBREVIATIONS

Abbreviations	Full Form
PU	Polyurethane
PUF	Polyurethane foams
Fig.	Figure
BPU	Bio-based Polyurethane
FTIR	Fourier-transform infrared spectroscopy
XRD	X-ray diffraction
EPA	Environmental protection agency
EU	European union
REACH	Registration, Evaluation, Authorization and Restriction of chemicals
DBTDL	Dibutyltin dilaurate
NIPU	Non-Isocyanate polyurethane foams
PHMS	Polymethyl hydrogen siloxane
g-NIPU	Glucose based NIPU
DABCO	Diazabicyclo[2.2.2] octane
BCI	Bis-carbonylimidazole
SBC	Sodium bicarbonate
DMCHA	N,N- Dimethyl-cyclohexyl amine
AR	Anisotropy
MH 15	Poly(methylhydrogenosiloxane)
RDGCC	Resocrinol diglycidyl ether
TETA	Triethylene tetra amine
AOPHA	Amine-terminated oligomeric phenyl hydroxy amine

CHAPTER 1 INTRODUCTION

1.1. Background of present research

1.1.1. Polyurethane

Polyurethane (PU) is an organic polymer which consist of many urethanes bonds link together formed from combination of polyol and isocyanate. It offers a wide range of properties, which makes it a choice for a broad range of end user applications from engineering plastic to common household material. It is used to make mats, foams, plastic mugs and pots, PU pipes, adhesives, coatings etc. In addition, PU is popularly being used in biomedical, electrical and infrastructure industries. Fig.1.1 gives an overview of different uses of PU[1].
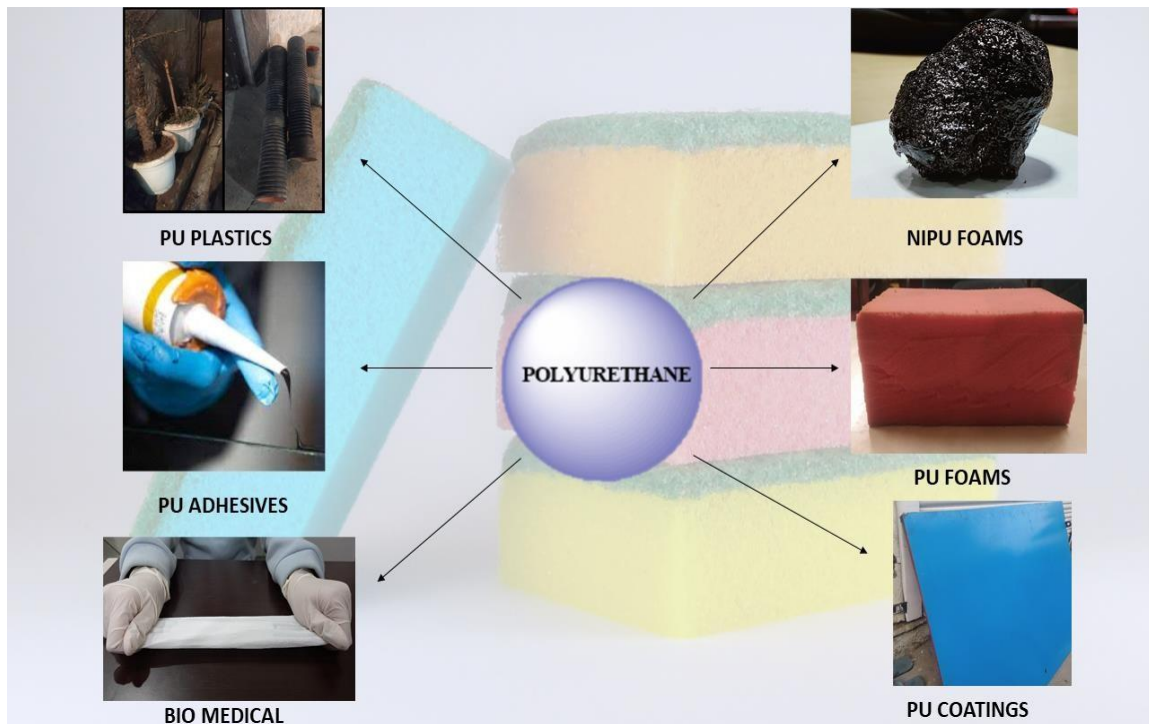
Fig.1.1: Different Uses of PU

The size of the worldwide PU market was estimated at USD 84541.58 million in 2022 and is projected to grow at a compound annual growth rate of 6.39% through 2028 to reach USD 122576.52 million. PU includes harmful chemicals that persist in the solidified foam, posing ongoing environmental risks. Shavings and dust generated during PU processing release excess chemicals, exacerbating ecological impacts, infiltrating waterways, and accumulating in aquatic organisms. Toxic compounds like isocyanates and amines, present in PU materials, can induce skin irritation, respiratory problems, asthma, and are identified as carcinogenic. Amines, acting as catalysts, pose health risks, including blurred vision and severe burns if ingested. Polyols, used in foam solidification, may accumulate in sensitive organs of organisms [2].The market share of PU encompasses a significant array of industrial sectors, with applications spanning from footwear and packaging to automotive components, furniture and interior solutions, as well as construction materials such as foams and piping systems. Fig.1.2, delineates the respective proportion of polyurethane ususage apportioned to to each industry within the fiscal year of 2021[3].

Fig.1.2: PU Market share in 2021[3]

The name "polyurethane" is derived from the formation of urethane linkages resulting from this exothermic reaction. Polyols combine with Poly-isocyanate to make Poly-urethanes. Fig.1.3. shows reaction of the same.

Fig1.3: Production of PU [4]

PU have a huge history in polymer chemistry, originating from Wurtz's synthesis of the first urethane in 1849 [1] . The year 1937 saw a monumental breakthrough when Otto Bayer introduced PU through a polyaddition reaction, forming the foundation of Polyurethane foams (PUF) production.

PUF is the third most commonly used foam for industrial and commercial application after Polyvinyl Chloride and Polystyrene foams. The demand for PU, particularly foams, has consistently grown due to their wide-ranging applications in automotive, bedding, and furniture industries[2]. Industrial PUF production involves polyaddition reactions of polyols and poly-isocyanates, facilitated by a blowing agent like CO_2. The in-situ generation of CO_2, through the reaction between water and isocyanates, allows that inside the polymer, gaseous cells be formed, result of which is foam expansion[3].This process produces a range of PUF, from rigid to flexible variants. Synthesizing PUF at an industrial scale involves simultaneous polymerization reactions and foaming reactions. Water is a common blowing agent is and its reaction to isocyanates gives urea and CO_2, facilitating foam expansion. Physical blowing agents, such as hydrofluoro olefins, hydrofluorocarbons, and hydrocarbons contribute to expansion through vaporization [1].The specific PU formulation dictates the foam's density, morphology, rigidity, physical properties, and potential applications [3]. PUF, offer superior thermal and acoustic insulation, along with impressive energy-absorbing capabilities, making them valuable in cushioning and packaging, particularly in automotive and electronics. Their cellular structure, predominantly gas, reduces the need for polymeric mass, and they can be manufactured across a range of densities (1.6 to 960 kg/m³), adapting to diverse applications. PUF classification is linked to the PU matrix's hardness influenced by factors like

crystallinity and cross-linking properties. This results in flexible, semi-flexible, semi-rigid, or rigid foams, used according to specific applications [4].

Despite its high popularity and utility, there are some challenges associated with this polymer. PU includes harmful chemicals that persist in the solidified foam, posing ongoing environmental risks. Shavings and dust generated during PU processing release excess chemicals, aggravating ecological impacts, enter waterways, and accumulate in aquatic organisms. Toxic compounds like isocyanates and amines, present in PU materials, can induce skin irritation, respiratory problems, and asthma, and are identified as carcinogenic. Amines, acting as catalysts, pose health risks, including blurred vision and severe burns if ingested. Polyols, used in foam solidification, may accumulate in sensitive organs of organisms [5].

1.1.2. Bio-based polyurethanes

In order to resolve the above challenges, PU derived from bio-based polyol was categorized under Bio-based polyurethanes (BPU), where one of the primary raw materials was replaced with the one derived from bio-mass or bio-material. In the quest to develop more sustainable forms of PU, the scientific community has been utilizing renewable resources for the synthesis of BPU foams. Over the last 5-6 decades, researchers have successfully replaced petrochemical based polyols with bio-based polyols in PU production. Plant-derived oils, cellulose, and lignin, among other biopolymers, are being employed as alternative precursors to the traditionally used petroleum-based polyols. These bio-based variants have properties such as enhanced biodegradability and a potential reduction in toxicity when contrasted with conventional foams [6].

Hydroxyl-containing bio-based compounds like alginate and other carbohydrates have been effectively incorporated into PUF structures, which enhances both the biocompatibility and the degradation rates of the materials [7].

However, the major concern associated with BPU was the use of isocyanate, which was not suitable for environment, as it released phosgene in environment. Throughout history, PUF have depended on chemical reactions involving harmful isocyanates, raising both environmental and health-related alarms. Regulatory bodies such as the United States Environmental Protection Agency (EPA) and the European Union (EU), operating under Registration, Evaluation, Authorization and Restriction of Chemicals (REACH) regulations, have intensified monitoring due to the substantial health risks linked to isocyanates. The traditional synthesis of PUF involves specific reactions employing isocyanates, polyols, and water, utilizing carbon dioxide as a foaming agent [8]

Comparative analysis between bio-based and petrochemical-based PU reveals differences in mechanical strength and thermal performance, attributed to the natural structure of the bio-derived materials. BPU typically exhibit decreased tensile strength and heat resistance. To overcome these challenges, researchers are investigating the inclusion of natural fibers, nanoparticles, and robust fillers to enhance structural integrity and thermal endurance [9].Furthermore, in pursuit of improving the quality of BPU foams, a series of approaches are being adopted. These include the refinement of the polyol blend, examination of the impacts of crosslinking within the polymer matrix, and assessment of various catalysis techniques. The ultimate aim of these research efforts is to tailor key properties such as the foam's porosity and density, as well as to substantially advance mechanical robustness and temperature robustness [9].

1.1.3. Methods of generating BPU

1.1.3.1. Utilizing Vegetable Oils as Polyols

Harvested from diverse plant sources, these oils serve as a renewable and planet-friendly foundation for PUF, potentially replacing the conventional petroleum-derived polyol. Castor oil, palm oil, soybean oil, rapeseed oil, canola oil, and tung oil stand out among these examples, offering perks like biodegradability, ecological compatibility, and compatibility with industrial solvents. The resultant PUF boast an array of coveted traits—flexibility, robust mechanical ability, resistance to abrasion, durability, adhesive strength, and resistance against chemical degradation and corrosion[10][11].

Various techniques are employed to derive polyols from vegetable oils for PUF production. These methods include epoxidation, hydroformylation, ozonolysis, and ester bond reactions like transesterification. Epoxidation involves introducing epoxy groups to carbon-carbon double bonds in oils like soybean and rapeseed, under specific conditions. Hydroformylation creates polyols with primary hydroxyl groups, offering quicker gel times and enhanced curing efficiency compared to epoxidized polyol PUF. Ozonolysis splits double bonds using ozone, resulting in longer chain polyols suitable for clear PUF with excellent mechanical properties. Transesterification, such as with castor oil, swaps alkoxy groups in triglycerides with alcohol, showing potential for applications in rigid PUF [2][10]. Fig.1.4. shows the formation of bio-based alcohol using vegetable oil.
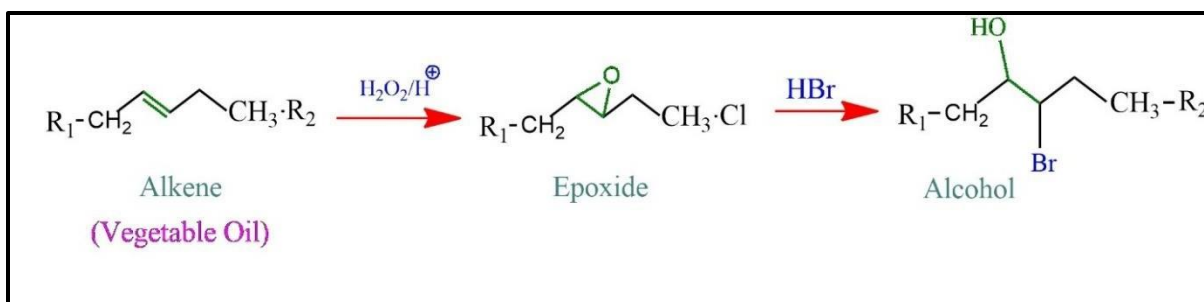
Fig 1.4: Vegetable Oil's Epoxidation[12]

The chemical composition of vegetable oils significantly shapes the resulting polyols, exercising influence over the cross-linking density and tensile strength within PUF [13]. Among these oils, castor oil stands out due to its distinguished attributes and non-competition with food resources, positioning it as a promising contender for diverse PU applications like coatings, elastomers, foams, and adhesives. Innovations involving castor oil-derived polyols, such as formulations integrating flame retardants and the introduction of expandable graphite, have yielded enhancements in thermal degradation, fire resistance, as well as improved electrical and thermal conductivities within PUF [13]. Researchers have explored the effects of rapeseed oil-based polyols for the formation of rigid PUF. Ultimately, using vegetable oil-based polyols showcases a hopeful and sustainable path in the production of PUF. Ongoing investigations aim to further perfect these techniques, developing environmentally friendly alternatives to the conventional use of petrochemical-based polyols [1][10].Utilizing castor oil, which has undergone a modification process with glycerol to yield a modified polyol, a reaction follows with methyl diisocyanate to produce a distinct variant of rigid PUF. The addition of varying ratios of silicon oil into the composition has been empirically demonstrated to yield a directly proportional enhancement in both the compressive and flexural properties of the

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resultant foam, affirming the role of silicon oil as a pivotal factor in the optimization of its mechanical characteristics. Additionally, the density of the foam demonstrates consistency with the expected parameters relevant to its formulation [14].

1.1.4. Biobased Isocyanates PU

There has been a recent surge focusing on BPU foams, with a marked emphasis on formulating PU from vegetable oils like castor, palm, sunflower, soybean, rapeseed, and neem oils. Castor oil, specifically from Ricinus Communis L, has drawn significant interest owing to its distinct triglyceride structure, low toxicity, thermal stability, cost-effectiveness, and biodegradability [15].Major focus is on crafting bio-derived isocyanates using methods that don't involve phosgene. bio-based polyols, serving as partial substitutes for petroleum-based materials in various industrial uses. In the realm of PU adhesive development, researchers have delved into diverse strategies utilizing bio-originated elements. For instance, use of a three-necked round-bottom flask to create a PU adhesive amalgamating monoglyceride, *polyethylene glycol* (PEG), and dibutyltin dilaurate (DBTDL) catalyst [16]. The mixture underwent stirring with xylene for uniformity, while Toluene diisocyanate (TDI) was meticulously added drop by drop, maintaining a viscosity of $45 \pm 2°$ C [17].

Researchers have focused on exploring an interlocking mesh of PU adhesive by blending CAPA-3050 polyol with isophorone diisocyanate (IPDI) a 1:1 molar ratio. Similarly, Somani et al. crafted PU wood adhesive, employing aromatic or aliphatic isocyanates alongside polyester polyol, experimenting with different molar ratios while employing the DBTDL catalyst. In another study, Badri et al. formulated a two-part PU adhesive by merging oil-derived polyester resin with isocyanate. This was followed by the addition of dimethyl cyclo-hexanediamine. These strides in research highlight a growing interest in harnessing bio-based resources for crafting non-isocyanate

polyurethane (NIPU), a search powered by the necessity for sustainable, eco-friendly alternatives across various industrial domains [15].

1.1.5. Non-isocyanate polyurethane

To address the environmental and resource-related concerns associated with traditional PU, the development of bio-based has been advanced, utilizing alternate reactants derived from non-fossil fuel sources for polyols, coupled with innovative non-isocyanate compounds replacing the conventional isocyanate reactants. A significant transformation is seen as NIPU enter the scene, offering an eco-friendly substitute for the conventional PU[18].To combat the toxicity of isocyanates, extensive efforts have been made to explore safer and cleaner synthetic pathways, giving rise to NIPU as a ground breaking departure from traditional PU [10][19].NIPU emerge from polyaddition reactions involving cyclic carbonates and polyfunctional amines, avoiding the necessity for isocyanates. Using blowing agents like polymethyl hydrogen siloxane (PHMS) and liquid fluoro hydrocarbons, or adopting the self-blowing technique, becomes important in generating gas for foam formation.

Biologically sourced NIPU, crafted through creative synthesis techniques and environment friendly materials, provide adaptable and sustainable alternatives, demonstrating a dedication to lessening environmental impact while upholding advantageous traits [20].The self-blowing method, enabling internal gas generation without external agents, leads to environmental sustainability within production. The considerable potential of biologically derived, whether self-blowing or using external agents, underscores their adaptability and sustainability in contrast to conventional PUF.

Table 1.1 shows a comparative analysis between BPU foams made using polyols generated from bio-based sources and BPU foams where isocyanate is generated from biological methods.Fig.1.5 portrays the developmental trajectory leading to the creation of NIPU. These innovative materials emerge as environmentally conscious alternatives to traditional PUF. In response to the hazardous nature of isocyanates, considerable research has been dedicated towards identifying greener and less harmful methods of synthesis, concluding in the beginning of NIPU.

Table 1.1: Comparative Analysis of BPU and biobased isocyanates PU

	Bio-Based PU Using Vegetables Oils (to make polyols derived from oils instead of fossil fuels but using Iso cyanate)	Bio-Based Foams (using Isocyanate as one of the reactants)
Advantages	➢ Easy access to raw material ➢ Environmental Benefits: Biodegradable, eco-friendly, and reduce the carbon footprint in foam production. ➢ Versatility: Adaptable for various applications (polyesters, epoxies, etc.) due to diverse functional groups. ➢ Improved Properties: Resulting PUFs exhibit flexibility, durability, resistance to abrasion, and enhanced thermal/electrical properties.	➢ Environmental sustainability through renewable resources. ➢ Lower toxicity compared to petroleum-based materials. ➢ Potential cost-effectiveness in the long term. ➢ Innovations in formulations for diverse industrial applications.
Disadvantages	➢ Process Complexity: The conversion methods (epoxidation, hydroformylation, etc.) might require specialized equipment and processes. ➢ Property Variation: Different vegetable oils lead to varied properties, potentially causing inconsistency across batches. ➢ Cost: Production complexity and the specific oil used might make these polyols more expensive than traditional options.	➢ Technical challenges in creating bio-derived materials. ➢ Potential inconsistencies in performance and quality. ➢ Limited availability and scalability of bio-based resources. ➢ Higher research and development costs compared to traditional processes.
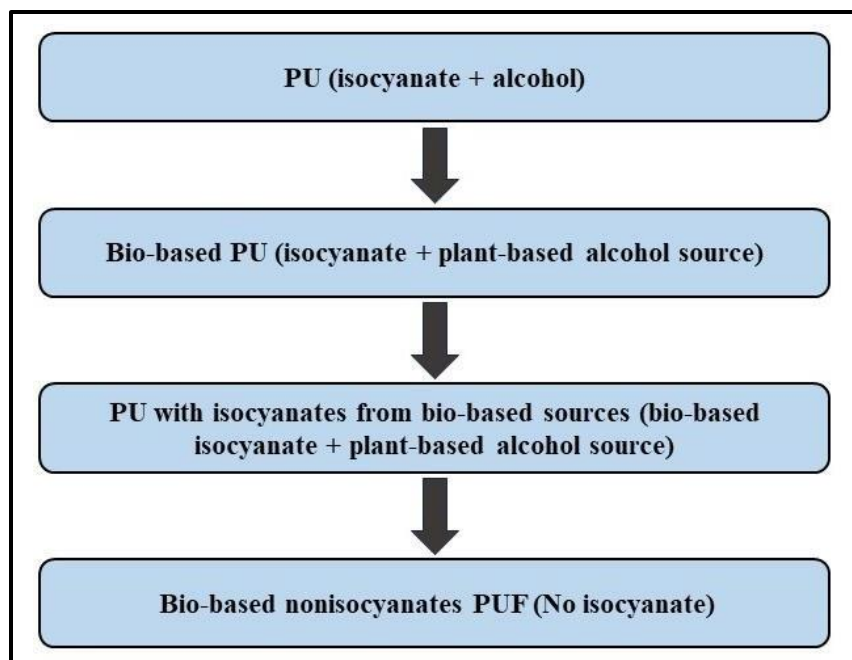
Fig.1.5: Isocyanate free foams journey

1.2. Research Objectives

The product of reacting glucose with dimethyl carbonate and hexamethyl diamine (HMDA) is glucose-based NIPU (g-NIPU), which is a partially biobased self-blowing and self-hardening polyurethane. These materials have the drawback of often requiring a high temperature. In old literature scientists have used maleic acid and glutaraldehyde and made NIPU at 150°C [21]. Here, we have used citric acid as an initiator and glutaraldehyde as a crosslinker to minimize the curing temperature and create a material based on g-NIPU.In contrast to the literature's method where they have used maleic acid and glutaraldehyde, here we demonstrated how to generate NIPU at 103 °C, the curing process in this work was done at 140°C.

PU vs   NIPU
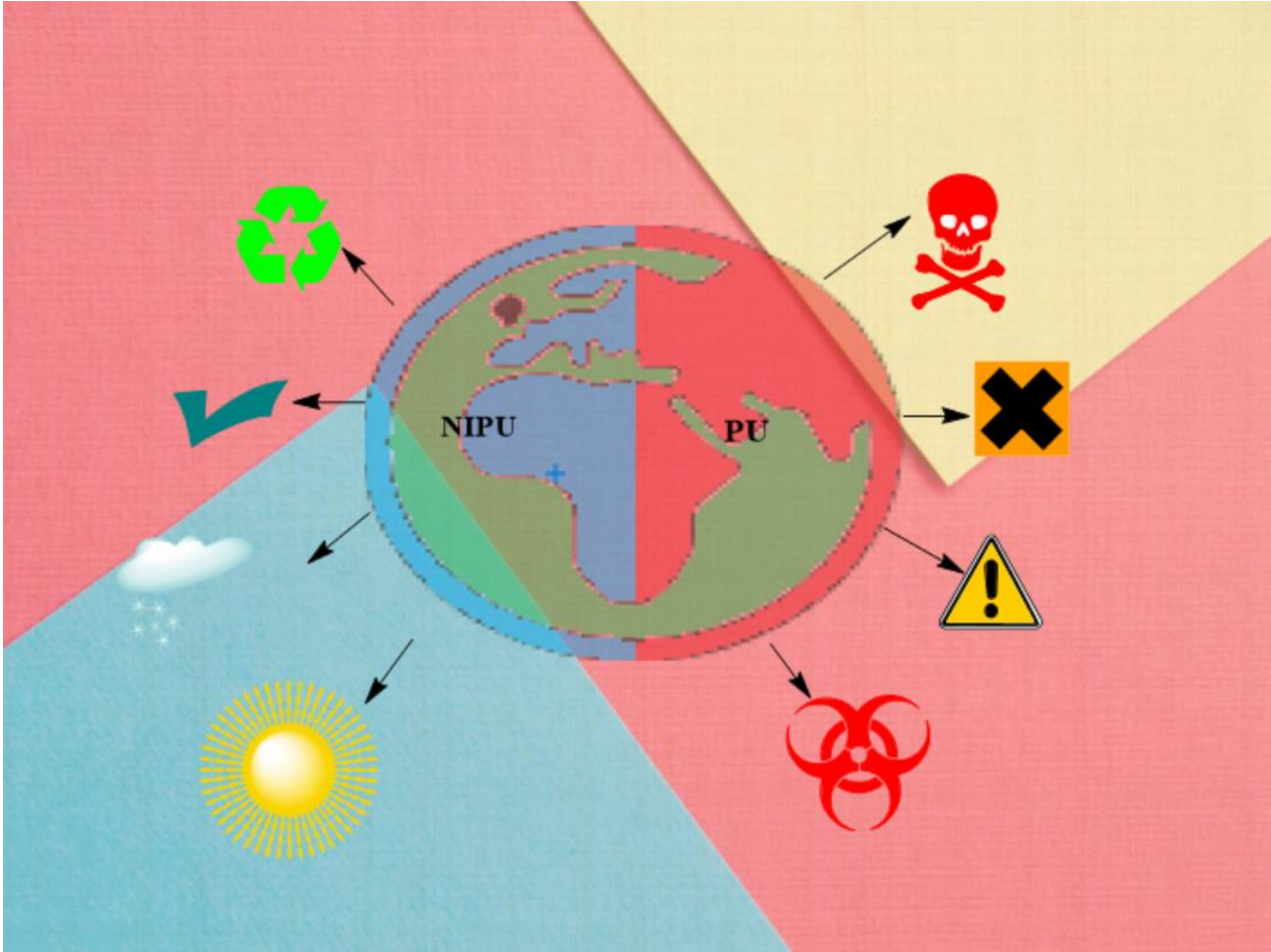
CHAPTER 2 LITERATURE REVIEW

2.1. NIPU using mechanical methods

2.1.1. NIPU using Transurethanization Approach

The chemical process of transurethane polycondensation provides an alternate method for producing PU without the use of isocyanates [21]. By combining dialkyl dicarbamates or dihydroxyethyl dicarbamates with diols and using organic or organometallic catalysts. This approach differs from the traditional step growth polymerization that uses (di-)polyamines and (di-)polycyclocarbonates. This divergence results in the formation of poly(hydroxyurethane) structures, distinguishing it from the transurethanization approach, which produces traditional PU structures. The transurethanization technique demonstrates its versatility by allowing for the option of dialkyl dicarbamate monomers, extending the range of attainable chemical structures and characteristics in the resulting PU materials [22][23].

Nonetheless, the direct synthesis of crosslinked NIPU via transurethane polycondensation has challenges due to the need for high temperatures and vacuum conditions for alcohol removal [23]. An alternative technique addresses this issue by producing telechelic NIPU oligomers, which may then be crosslinked using polyaddition processes under more moderate circumstances. Hydroxyl, allyl, and acryloyl-terminated NIPU oligomers have been successfully developed and used in the formation of crosslinked coatings [22].

A fresh avenue for NIPU flexible foams has emerged by employing bio-derived amino-telechelic NIPU oligomers, crafted through an organocatalyzed transurethane polycondensation process[22].Elements like fatty biscarbamates, fatty diols, and diamines are crucial for

synthesizing these oligomers. These subsequently underwent crosslinking with a biobased multi-epoxide compound, in association with poly(hydromethylsiloxane) or its copolymer serving as both foaming agent and surfactant. The resultant foams materialized swiftly in under 30 minutes at 100°C or over a longer duration of 14.5 hours at room temperature.

Various components were sourced for this process, including dimethyl carbonate, 1,5,7-triazabicyclo [4.4.0] dec-5-ene,poly(methylhydrosiloxane), a copolymer of poly(methylhydrosiloxane-dimethylsiloxane), polyglycerol polyglycidyl ether, and 1,10-decanediol. Crafting this involved a mechanical amalgamation of amine-terminated NIPU or NIPU urea oligomer at varied molar ratios. This mixture underwent expansion at room temperature and subsequent solidification at 100°C for 30 minutes [23].

2.1.2. Carbamate Thermal Decarboxylation for NIPU Synthesis

Ignacio Sintas et al. showed the complicated preparation of NIPU utilizing a method that involved an array of monomers.1,4-Butanediol, 1,1'-carbonyldiimidazole, 4,4'-methylenedianiline,1,4-cyclohexanedimethanol , 1,4-diazabicyclo[2.2.2]octane (DABCO,33LV), dibutyltin dilaurate, and 4,4'- dihydroxydiphenylmethane. Bis - carbonylimidazole (BCI) monomers, 1,4-butyl(bis-carbonylimidazolide), 1,4- cyclohexanedimethyl(bis-carbonylimidazolide) were synthesized using 1,1'-carbonyldiimidazole and the respective diol precursors. The synthesis involved a solvent-based reaction, filtration, and drying, yielding white powders with characteristic melting points [24].

PU foams were synthesized using BCI monomers, aromatic amines and trifunctional crosslinking agents (T-403). The reaction temperature spans 160 - 180 °C, synthesis involved melting the monomers, quick addition of reagents, and subsequent curing. The imidazole byproduct was extracted using methanol, followed by oven drying and reduced pressure treatment.The NIPU derived from BCI exhibited an extraordinary mechanism for foam formation, featuring spontaneous decarboxylation during BCI crosslinking. This novel mechanism, underwent through CO_2 detection firmly establishing the in-situ generation of CO_2 as the driving force behind foam development [25]. Fig.2.1. shows how Carbamate thermal decarboxylation takes place for NIPU generation [25]. Table 2.1 shows comparative analysis between NIPU generated using transurethanization approach and Carbamte thermal decarboxyilation method.
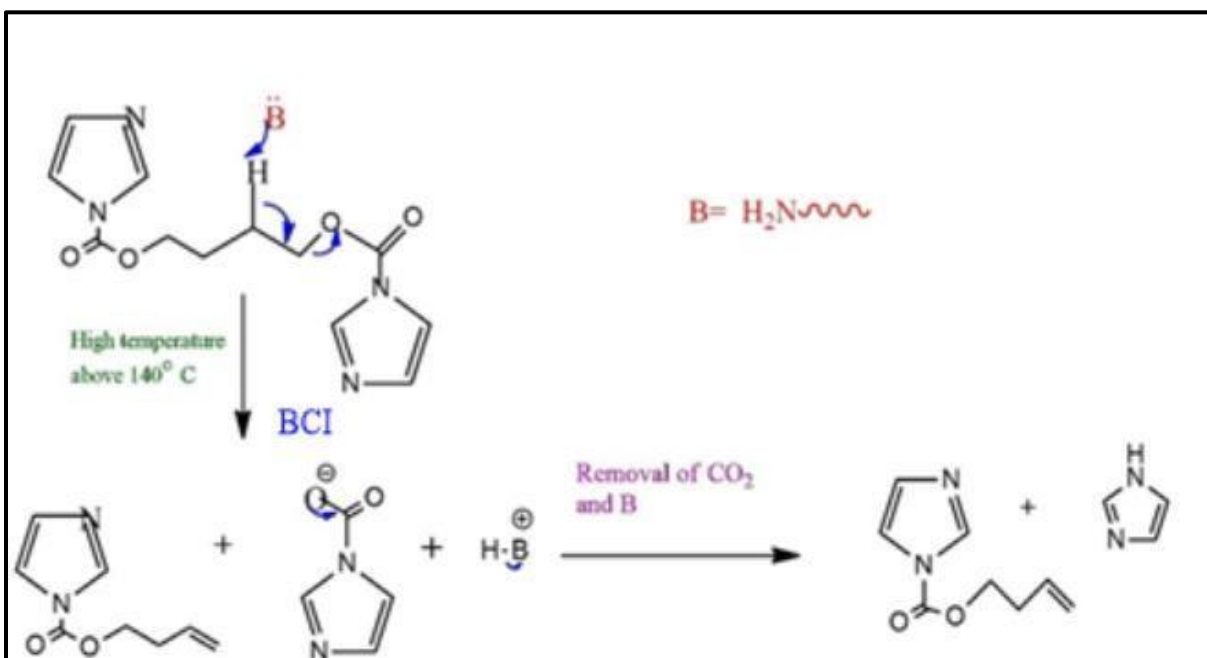
Fig.2.1: Carbamate thermal decarboxylation for NIPU [24]

Table 2.1: Comparative Analysis of NIPU using mechanistic methods

	Using Transurethanization Approach	Carbamate Thermal Decarboxylation
Advantages	➢ Versatile chemical structures ➢ Diverse material options ➢ Unique foam characteristics ➢ Formulation control ➢ Scalable	➢ Unique Foam Formation: Uses carbonate thermal decarboxylation for in situ CO_2 generation, simplifying foam creation. ➢ Versatile Temperature Range: Shows a wide range of glass transition temperatures (Tg), suitable for diverse applications. ➢ Dimensional Stability: Resilient to dimensional changes due to temperature variations, ensuring stability in different environments
Disadvantages	➢ High processing conditions ➢ Complex process ➢ Time-consuming reactions ➢ Dependency on specific components ➢ Alcohol needs to be constantly removed	➢ Complex Synthesis: Involves multiple monomers and specialized instruments, potentially limiting scalability. ➢ Byproduct Handling: Requires additional steps for extracting and handling imidazole byproducts, adding complexity to the process.

2.2 NIPU made using biobased materials

2.2.1 NIPU from Lysine and Sorbitol

Sorbitol, derived from glucose reduction, is a cost-effective and environmentally friendly feedstock [12].It is readily available as well as its non-toxic nature and commercial use in the food and cosmetic industries make it a versatile starting point for sustainable polymers. Through partial dehydration, sorbitol transforms into sorbitan, a compound with diol moieties that can be further converted into sorbitan bis-carbonate. Synthesis of sorbitan bis-carbonate directly from sorbitol, using dimethyl carbonate and catalytic base such as potassium carbonate eliminating the need for an intermediate sorbitan step. Polymerization of this bis-carbonate with petrochemically derived diamines initially yielded low molecular weight oligomers. However, the real breakthrough came when they discovered that this monomer, when polymerized under solvent-free conditions, led to the formation of rigid foams without additional blowing agents (Fig 2.2) [26].
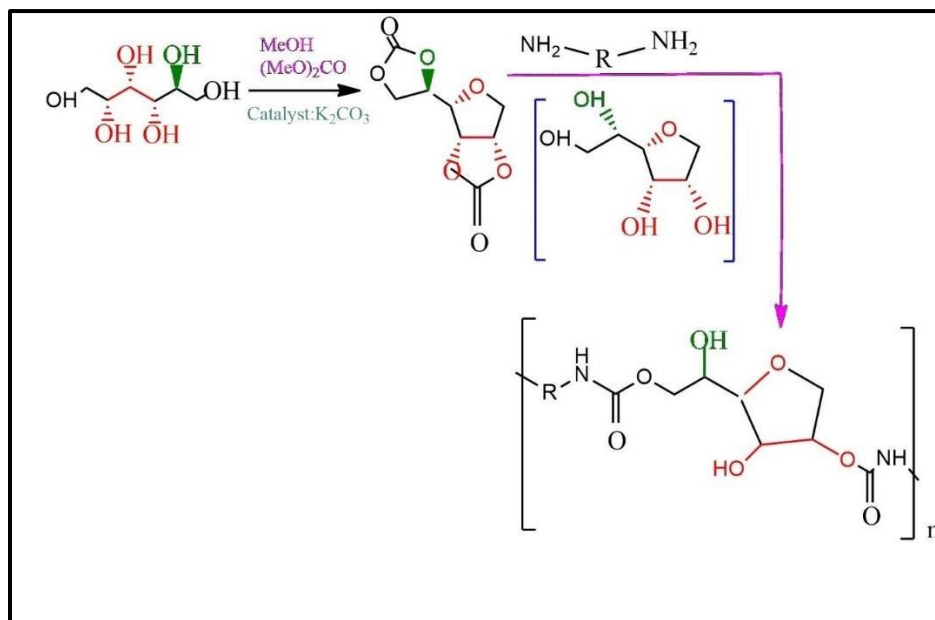
Fig.2.2: Synthesis of Polyhydroxyurethanes from sorbitol derived bicarbonate [26]

The most well-known finding of this study is the incorporation of lysine-derived cadaverine as a diamine component. Cadaverine, obtained by the decarboxylation of lysine, adds a wholly bio-based dimension to the resulting poly hydroxyurethane. This bio-derived diamine aligns with the principle of green chemistry, introducing a sustainable alternative to conventional petrochemical-based counterparts. The experimental process involves the production of sorbitan bis-carbonate, purified through washing and recrystallization. When mixed in equimolar proportions with HMDA and heated, a remarkable transformation occurs. The thoroughly mixed monomers undergo an immediate foaming reaction, as observed through microscopy [26][12][27].

2.2.2 NIPU using Carbonates

There is advancement of by innovatively crafting them using cyclic carbonates and diamines, introducing sodium bicarbonate (SBC) as a pioneering chemical foaming agent [28]. Other foaming agents can be ammonium carbonate, ammonium bicarbonate and calcium azide. The investigation precisely examines the synthesis of four unique NIPU foam variants, each with differing SBC concentrations, thoroughly inspecting their density and microstructural attributes [29].Fig.2.3. illustrates the fundamental composition of urethanes created by the reaction of Cyclic carbonates with diamines [30].
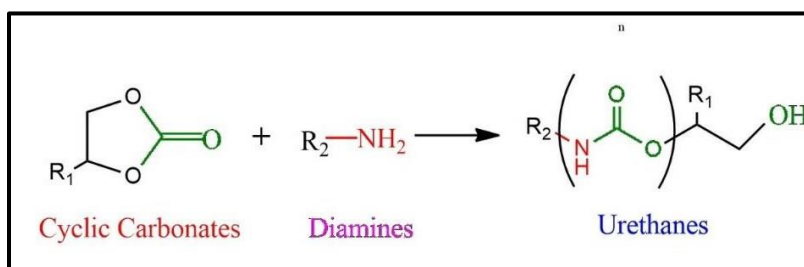
Fig.2.3: NIPU using Cyclic carbonates and diamines [30]

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The emergence of NIPU stands out as a promising substitute, involving a chemical reaction between a cyclic carbonate and a diamine, typically guided by a blowing agent either physical or chemical in nature. Here, we have used SBC as a chemical foaming agent, giving a new direction for synthesis of NIPU [28].The NIPU are made by using trimethylolpropane tris-carbonate and HMDA as the primary components. Within this synthesis, the catalytic role of N,N-Dimethyl cyclohexylamine (DMCHA) drives the reaction between tri-carbonate and HMDA [28].The NIPU production involves two core reactions. The polymerization or gelling process using cyclic tricarbonate and the diamine, using DMCHA as a catalyst. This procedure yields polyhydroxy-urethane entities, forming the complex polymeric framework. Meanwhile, during foaming or blowing reaction of foams thermal breakdown of SBC occur. At 150°C, SBC undergoes decomposition, liberating CO_2 gas, water, and SBC. The CO_2 thus formed leads to the expansion of the foam, which ultimately makes its cellular architecture[19].There is an comparative analysis between the density and cellular structure parameters of the NIPU, showcasing the variations across different SBC content (3.6, 7.1, 10.7, and 14.3 wt%).The open cell content (OC (%)), of all foams is high, since the open cell content is 79-97%. Cell size (Φ3D (μm)), is relatively small due to the higher densities of all samples and lowest value was obtained for the foam containing 7.1 wt% SBC.Finally, the last parameter to be investigated is anisotropy (AR), which indicates whether the foam cells are elongated in the direction of growth. The studies show a slight increase in the AR ratio from 1.1 to 1.3 as the SBC content increases.

The creation and analysis of NIPU through the combination of cyclic carbonates and SBC shows a prominent step towards eco-conscious foam manufacturing. The integration of SBC as a foaming agent opens fresh avenues in NIPU creation and development of more eco-friendly options within polymer manufacturing. The careful examination of foam density and microstructural surfaces leads to invaluable perspectives into the effectiveness of this method[31].

Recently, researchers have also prepared NIPU by carbonation of hydrolysable tannin followed by reaction with a primary amine. The cyclic carbonate /amine reaction avoids the use of isocyanates and diamines and permits the formation of poly(hydroxyurethane)s with hydroxyl groups. This method was tremendously studied. The main problem concerning NIPU synthesis relates to the low reactivity of carbonate/amine reaction. Many studies in the literature have been conducted to design NIPU materials from reactive cyclic carbonates bearing electro-withdrawing substituent or by using six-, seven-membered or thio-cyclic carbonate [32].In order to improve the kinetics of the carbonate/amine reaction, work had been devoted to develop novel catalysts. Blain et al. showed that the 1,5,7-triazabicyclo[4.4.0]dec-5-ene and cyclohexylphenyl thiourea are the best catalysts for carbonate/amine reaction. However, the reaction between carbonate and amine does not yield any gas, therefore cannot lead to as easily as in the case of PU [31].

Five-membered Cyclic carbonates were selected for their phosgene-free synthesis, unlike six- or seven-membered variants. resulted from step-growth polymerization of TMP-Tri-C5 and PPO-Bis-C5 Cyclic carbonates with aliphatic amines. The challenge in NIPU creation involves coordinating the gelling (carbonate/amine reaction) and the foaming process. Poly(methylhydrogenosiloxane) (MH 15), a known agent from epoxy foam production, served as

the blowing agent. MH 15 when reacted with amines, released dihydrogen, thus expanding the NIPU material. Fig.2.4 shows PUF synthesized by reacting cyclic carbonates with diamines to produce NIPU, utilizing MH 15 as a blowing agent which induced foaming through its reaction with diamines [33].
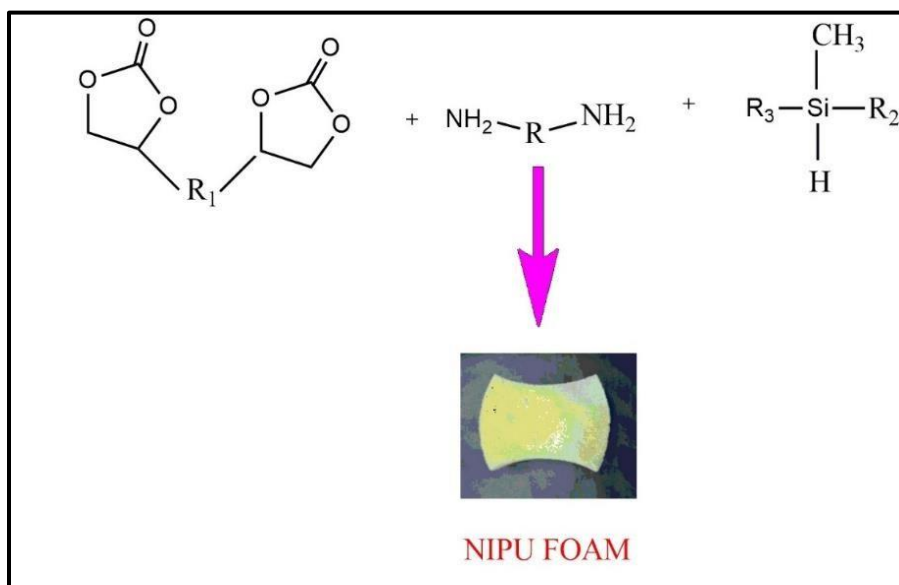
Fig.2.4: NIPU using carbonate/amine reaction and MH 15 [33]

2.2.3 Lignin-Derived NIPU

Lignin derived from Kraft pine is a diverse biopolymer which has undergone a transformative process via oxypropylation, forming liquid polyol. This breakthrough represents a significant stride within the domain of lignin-centered PUs[34]. Notably, this polyol derived from lignin was systematically evaluated against commercially accessible polyols regarding the mechanical

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attributes related to rigid PUF. This comparative investigation revealed its promising prospects as an environmentally friendly substitute [35][36].For synthesis of lignin-derived PU, the utilization of sucrose polyol and glycerol polyol (conventional industrial polyols) underwent partial substitution to assess their influence on foam characteristics. It was seen that the most favorable compressive properties were attained through exclusive implementation of lignin polyol. This outcome underscored the strength inherent in lignin's aromatic configuration and the substantial reactivity associated with lignin hydroxyl groups [36].

Recent research has highlighted the establishment of hydrogen bonds between lignin and the polymer framework, which lead to heightened thermal stability with escalating lignin concentrations, up to a threshold of 50%. Nevertheless, this concentration-imposed limitations on sustained film formation, observed to be constrained beyond the 43.3% mark [34]. The outcomes highlight the adaptability and promise inherent in lignin as a renewable reservoir for the advancement of NIPU, paving the way for eco-conscious PU materials. Table 2.2 shows comparative analysis between NIPU generated from bio-based feedstock.

Table 2.2: Comparative Analysis of NIPU made using biobased feedstock

	Cyclic Carbonates and Amines	Lysine And Sorbitol	Lignin Derived NIPU
Advantages	➢ Isocyanate Reduction: Shift from hazardous isocyanates to eco-friendly ➢ Eco-friendly: Sodium bicarbonate use reduces harmful byproducts. ➢ Property Tuning: Varying bicarbonate concentration allows tailored foam properties. ➢ Insightful Analysis: Detailed study provides insights for eco-friendly material advancement.	➢ Sustainable Sourcing: Uses renewable sorbitol and lysine-derived cadaverine. ➢ Environmental Friendliness: Cost-effective, non-toxic sorbitol from glucose reduction. ➢ Blowing Agent-Free Foaming: Forms rigid foams without additional blowing agents. ➢ Isocyanate-Free: Safer option due to the absence of isocyanates.	➢ Sustainability: Uses Kraft pine-derived lignin, reducing reliance on fossil fuels. ➢ Mechanical Strength: Shows promising strength for rigid PU foams. ➢ Renewable Resource: Lignin from the paper industry offers a sustainable source. ➢ Thermal Stability: Up to 50% concentration enhances thermal stability.
Disadvantages	➢ Density Variation: Changing bicarbonate levels leads to density fluctuations. ➢ Complex Process: Multi-step synthesis could increase production costs. ➢ Quality Control: Ensuring consistent foam quality across batches may be challenging.	➢ Structural Understanding: Requires further research for a detailed understanding of the polymerization process. ➢ Limited Information: Insufficient data on scalability, cost, and industrial challenges.	➢ Flexibility Issues: Beyond 30% concentration, leads to inflexible and fragile PU. ➢ Molecular Weight Dependency: Flexibility depends on lignin's molecular weight. ➢ Film Formation Limits: Beyond 43.3% concentration, limits sustained film formation.

2.3. Foam Synthesis Strategies

2.3.1   Self-Blowing Mechanisms in Synthesis

Clark et al. investigated the incorporation of amines and thiols into Cyclic carbonates, yielding an eco-friendly self-foaming substance derived from sorbitol and pentamethylene diamine, excluding isocyanates or inflating agents. Monie et al highlight on focusing on the expandability of their procedure [37].The experimental work was performed using resorcinol diglycidyl ether (RDGCC), benzyl triethyl ammonium chloride, CO_2, poly(propylene glycol) bis(2-amino propyl ether) , gaskamine G328, phenol, and 1,5,7-triazabicyclo[4.4.0]dec-5-ene . The study underscores the potential for scalability inherent in their methodology, aligning with prior investigations examining the integration of amines and thiols into cyclic carbonates.

Amine-terminated oligomeric phenyl hydroxy amine (AOPHA), is distinguished by the coexistence of OH and NH_2 functional groups. When subjected to temperatures below 100°C, one of the carbonates engages with the NH_2 moiety within AOPHA, initiating the establishment of urethane linkages. However, upon surpassing the 100°C, the OH group within AOPHA participates in a reaction with a second cyclic carbonate, leading to the formation of β-hydroxyether connections and the liberation of CO_2. The release of CO_2 during the curing process actively contributes to the creation of foam. Experimental validation of this mechanism involved the use of alternative amines lacking OH groups, resulting in the production of polymers devoid of foaming properties [38]. Fig.2.5. shows self-blowing strategies for NIPU formation.
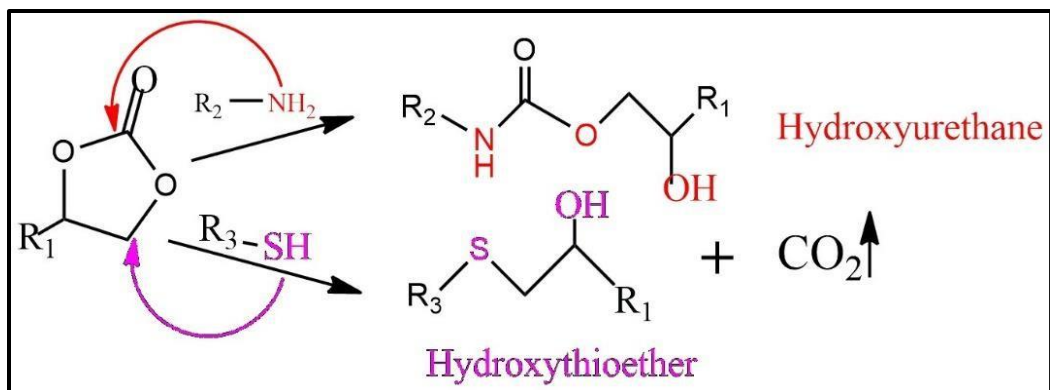
Fig.2.5 : Strategies for Self-Blowing [39]

2.4 External Blowing Agents for NIPU

2.4.1 CO₂-Blown NIPU

Ping Sen Choong et al. had introduced an innovative method based on the action of amine- CO_2 adducts and their utilization for the formation of in situ CO_2 -blown NIPU. This investigation aimed to overcome the existing limitations due to the use of combustible, hazardous, unsustainable blowing agents, or elevated temperatures within the current foaming procedures for NIPU [39][24].Major focus was on the synthesis of amine- CO_2 adducts, specifically carbamates and biscarbonates, famous for their efficacy in capturing and storing CO_2. These adducts were derived through diverse combinations of triethylenetetramine (TETA) and CO_2, in conjunction with organic bases like 1,8-diazabicyclo(5.4.0)undec-7-ene and 1,5-diazabicyclo(4.3.0)non-5-ene [40].Subsequent investigations involved the assessment of the CO_2 desorption temperatures of these adducts, revealed their potential role as both foaming agents and comonomers in the synthesis of NIPU.

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Sen Choong et al. define the remarkable CO_2 desorption capabilities of amine- CO_2 adducts, notably highlighting the efficacy of the TETA- CO_2 adduct. Upon aminolysis with Cyclic carbonates, a desorption rate of up to 87% at 60 °C was achieved. This adduct displayed favorable viscosity for blending with Cyclic carbonates /amines at ambient temperatures, laying the groundwork for its application in synthesizing NIPU under mild conditions (50−60 °C) and was termed as TCI. The utilization of TC1 facilitated the production of low-density foams, yielding densities ranging from 0.203 to 0.239 $g \cdot cm^{-3}$ following 24−48 hrs of heating [41].Comparing this study to prior work which employed thermal decarboxylation of bis- carbonylimidazolide monomers at 160 °C for CO_2 -blown underscores the significance of the current research. The former method involves the use of flammable, harmful chemicals, or high temperatures, emphasizing the imperative for sustainable alternatives in NIPU synthesis[39]. Fig.

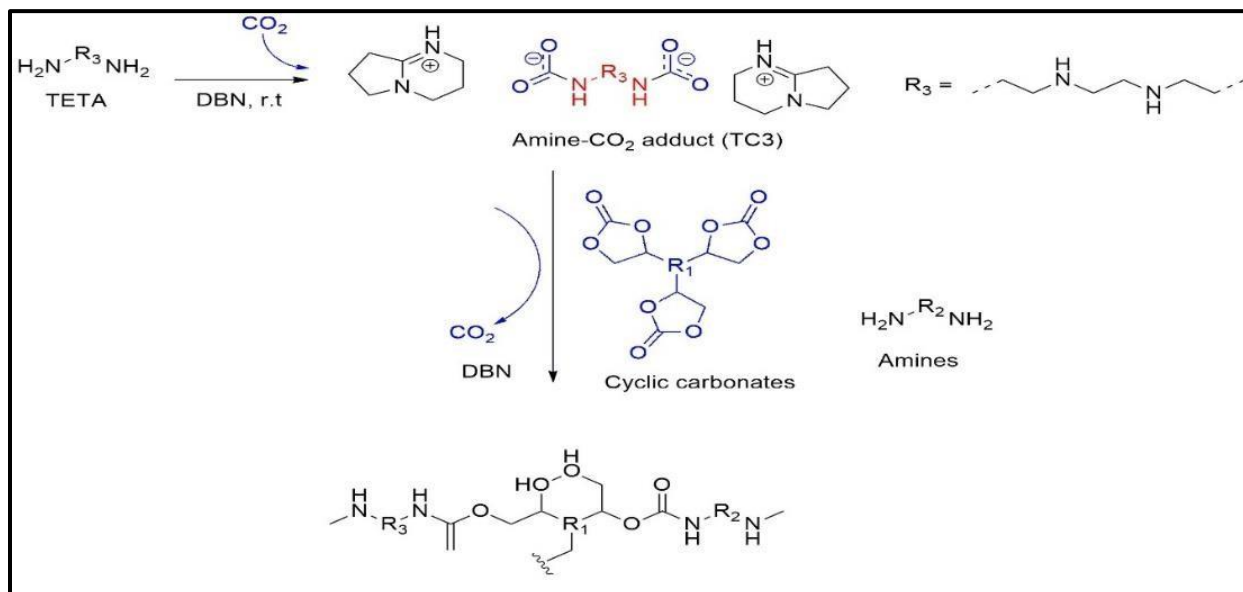2.6. shows CO_2 -blown NIPU using Amine- CO_2 adduct.

Fig.2.6.: CO_2 -blown NIPU using Amine-CO_2 adduct [40]

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2.4.2 Different External Blowing agent and their properties:

➢ **H₂ -MH15**, a blowing agent containing SiH groups that react with substances containing amines, had been combined with an equimolar quantity of amine to produce dihydrogen. The expansion of the materials to produce NIPU is caused by the release of hydrogen gas [26].

➢ **Solkane** - When creating NIPU, the hydrofluorocarbon liquid—also marketed under the name Solkane 365/227—is utilized as a physical blowing agent. It is stated that this liquid hydrofluorocarbon is non-flammable and does not deplete the ozone layer in the atmosphere. Solkane 365/227 is added in this investigation at a mass percentage of 25%. The DABCO catalyst was then mixed with the produced bio-sourced cyclic carbonates, such as carbonated trimethylolpropane glycidyl ether (TMPGC) and ethoxylated TMPGC (EOTMPGC), for 4-6 minutes at room temperature. HMDA was then added, and the mixture was mixed again before the blowing agent was added [26].

➢ **Sodium hydrogen bicarbonate (SHB)** – SBC is a chemical blowing agent that is used to create NIPU from tricarbonate and diamine. Sustainable and safe for human health and the environment. As a result, it has several uses, including those related to cooking, cleaning, and hygiene. It can also be utilized as a chemical blowing agent for thermoplastics. Due to its great availability, nonflammability, environmentally beneficial qualities, and adjustable decomposition temperatures in relation to particle size [42].

Fig 2.7 shows all methods together which generate NIPU.
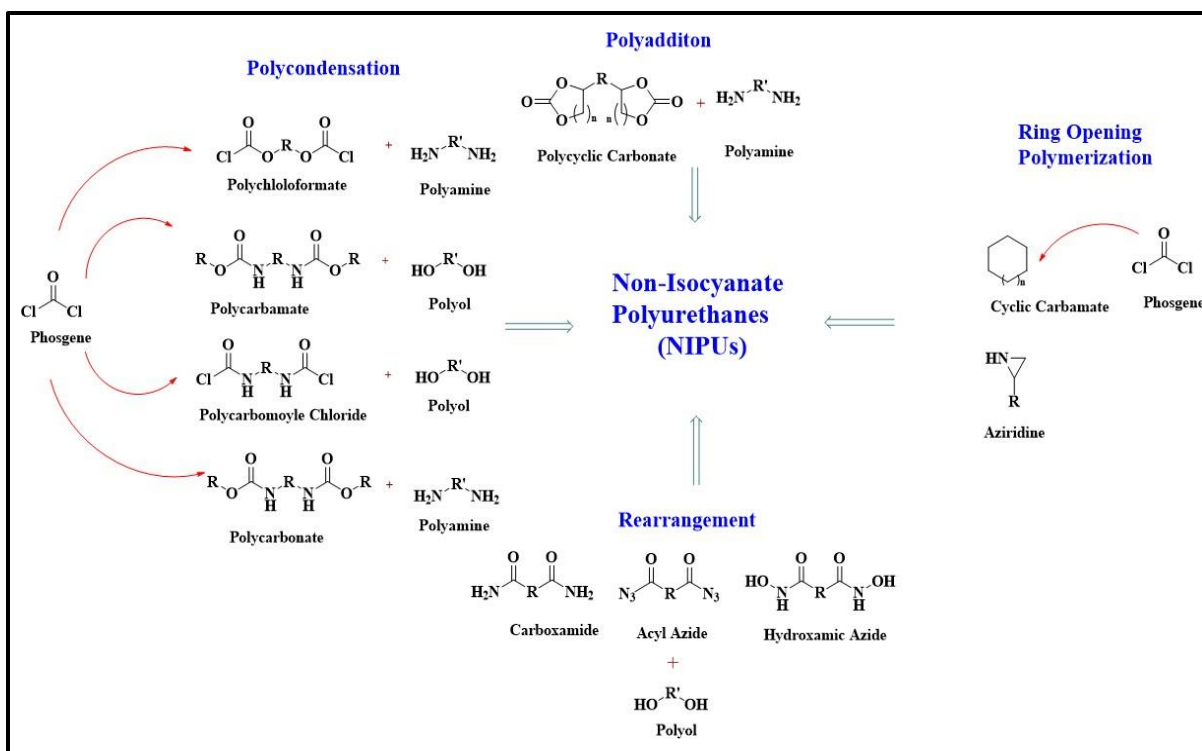
Fig.2.7: Synthesis of NIPU via different methods

2.5 Environmental Considerations

NIPU present a viable path to address ecological concerns with traditional PUF. Conventional use of isocyanate compounds in PU production has raised environmental and health-related issues [43].Given the escalating interest in sustainable materials derived from biomass, there is a pressing demand for eco-friendly substitutes. NIPU, formed by the reaction between cyclic carbonate and polyfunctional amines, stands as a promising alternative [43][44]. Used in diverse applications, such as foams in shoes, packaging materials, and construction spray foams, PU materials incorporate a complex mix of chemicals, including toxic elements[44].The

composition of spray PU, for example, includes harmful chemicals that persist in the solidified foam, posing ongoing environmental risks. Shavings and dust generated during processing release excess chemicals, exacerbating ecological impacts, infiltrating waterways, and accumulating in aquatic organisms. Toxic compounds like isocyanates and amines, present in PU materials, can induce skin irritation, respiratory problems, asthma, and are identified as carcinogenic. Amines, acting as catalysts, pose health risks, including blurred vision and severe burns if ingested. Polyols, used in foam solidification, accumulate in sensitive organs of organisms[5].

Environmental contamination is a pressing concern in PU material production, releasing pollutants affecting soil and aquatic bodies [43].Despite cost-effectiveness, PU materials have adverse effects on soil quality, leading to international regulations to lessen environmental consequences.To overcome these concerns, researches looked for solution with the discovery of polymers from renewable sources which are the alternatives for the raw materials for the plastic/polymer production, other than fossil fuels, which are degrading on daily basis and take a long time to rejuvenate. High interest in biobased polymers in recent decades leads to growing desire to diminish dependence on fossil-based products and mitigate environmental impacts. Considerable efforts have been invested in developing biobased monomers for sustainable plastics, leading to the production of common polymers like polyamides, polyesters, polyethylene, and PU.Less than 1% of the global plastics produced today is bioplastics, which are biodegradable too [8]. Under stabilized conditions microbes cause biodegradable plastics to breakdown in the form of CO_2 or methane along with water. Polycaprolactone too can be used to produce biodegradable polymers, and it looks like a good strategy to deal with bad plastics clogging the ecosystem and the seas[8][10]. Dependance on biomass and raw materials from renewable sources is not efficient to ensure complete sustainability or reduced environmental impact. Substituting traditional raw

materials with a bio-based matrix is just the start. We need a holistic, approach that considers every stage of the life cycle and potential impacts is essential to safeguard the environment. Therefore, assessing the sustainability of chemical processes, including new paths for renewable sources or fine-tuning existing methods, becomes important[8].In response to the diminishing availability of petroleum and heightened ecological consciousness, a diverse array of botanical substances— including vegetable oils, starch, cellulose, and lignin— have been explored as viable replacements for petroleum-derived polyols in the synthesis of PU materials[44].

2.6 Applications of NIPU

NIPU have expanded their industrial utility far beyond conventional realms, demonstrating versatile applications across various sectors. Within the coatings and polymer industries, NIPU systems exhibit promise in multifaceted roles, encompassing thermosetting coatings, UV-resistant coatings, and monolithic floorings. By integrating difunctional hydroxyalkyl urethane glycols, the thermal stability of NIPU is notably augmented, rendering them indispensable as diols in polymer chemistry methodologies[13][1].The technology of NIPU extends its significance to the production of hydrolysis-resistant and gasoline-resistant sealants, crucial in safeguarding electronic devices employed in aerospace construction, such as aircraft and rockets. In civil engineering, NIPU sealants demonstrate efficacy across diverse applications. The robust adhesive strength and enduring nature of NIPU glues facilitate the bonding of an extensive array of materials, encompassing metals, ceramics, and glass [1].

Furthermore, NIPU contributes significantly to advancing reinforced and highly filled polymers, aligning with the requisites of civil and chemical engineering applications. In the textile domain,

recent strides involve leveraging NIPU chemistry in UV-curable PU resin. This innovative resin, employing long-chain polyetheramine and cyclic carbonate of bisphenol-based epoxy resin, has found application in hydrophilic textile treatment. This diversification underscores the adaptability of NIPU in addressing the specific demands of various industries, solidifying its pivotal role in the ever-evolving landscape of industrial application[45].While extensive assessments have been conducted to ensure biocompatibility, concerns persist regarding the susceptibility of polyester-based PU to water and oxygen-induced degradation [46].However, advancements leveraging stable materials such as polysiloxanes and polyolefins have notably enhanced biostability. Strategies involving surface modifications and the integration of nanoparticles, such as graphene and carbon nanotubes, have significantly broadened the scope of PU applications in drug delivery systems, scaffolds, and air filters, offering increased resistance to varying pH levels, solvents, and elevated temperatures[47][48].

CHAPTER 3 MATERIALS AND METHODS

The objectives of this chapter include a thorough overview of the achievement process for the research materials, specifically outlining the chemicals involved. It will also elaborate on the methodologies employed throughout the experimentation as well as the distinctive experimental procedures undertaken to produce NIPU.

3.1 Glassware and apparatus used

The description of glassware and apparatus encompasses all the laboratory essentials, such as pipettes, graduated cylinders, beakers, and Erlenmeyer flasks, all crafted by Borosil to ensure precision and reliability. The subsequent inventory presents an exhaustive catalog of the various tools, devices, and equipment that were integral to the experimental process. This list may also detail the specifications, capacities, and manufacturers, providing a comprehensive resource for replication or further research. Maintenance and calibration protocols for the apparatus may also be included to underscore the importance of accuracy in experimental results. The inclusion of such detail seeks to provide transparency and facilitate a clear understanding of the experimental environment and the physical resources that underpin the research.

Table 3.1 List of All Instruments Used

| Glassware and apparatus	Function
OVEN	to dry samples or to maintain the temperature.
MAGNETIC STIRRER	To stir the solution
ELECTRONIC-WEIGHT BALANCE	to measure weight
X-RAY DIFFRACTION (XRD)	examining a material's atomic or molecular structure
FOURIER–TRANFORM INFRARED SPECTROSCOPY (FTIR)	to get the infrared spectrum of a solid, liquid, or gas's absorption or emission

3.2. Materials

Carbamates were produced using commercially available HMDA obtained from Sigma Aldrich. Loba Chemie (India) supplied Glucose and dimethyl carbonate. Citric acid was acquired from TCI Chemicals in Belgium. All chemicals and solvents used in the analytical measurement techniques were of analytical grade and used exactly as supplied. Glutaraldehyde ($C_5H_8O_2$, 50% water solution) used was of analytical grade (AR), obtained from Acros Organics (Illkirchn France)

3.3. g-NIPU Formation

The preparation of sample RGCA0 which is a g-NIPU follows a reported procedure. In this process, 10 g of glucose is first mixed with 7.882 g of dimethyl carbonate and water under mild heat (50 ∘C) for 40 min to promote the formation of the cyclic carbonate intermediate. Subsequently, 21.8 g of HMDA (70% solution) is added, and the mixture is heated to a higher

temperature (90 ∘C for 60 min) to facilitate the PU formation through ring-opening polymerization. After the reaction mixture is cooled to room temperature, it results in a viscous solution that can be further processed. If a quired structure is desired, additional steps involving the incorporation and reaction with crosslinking agents such as citric acid and glutaraldehyde would be necessary to achieve the porous, three-dimensional network that characterizes NIPU.The same is illustrated in Fig 3.1.
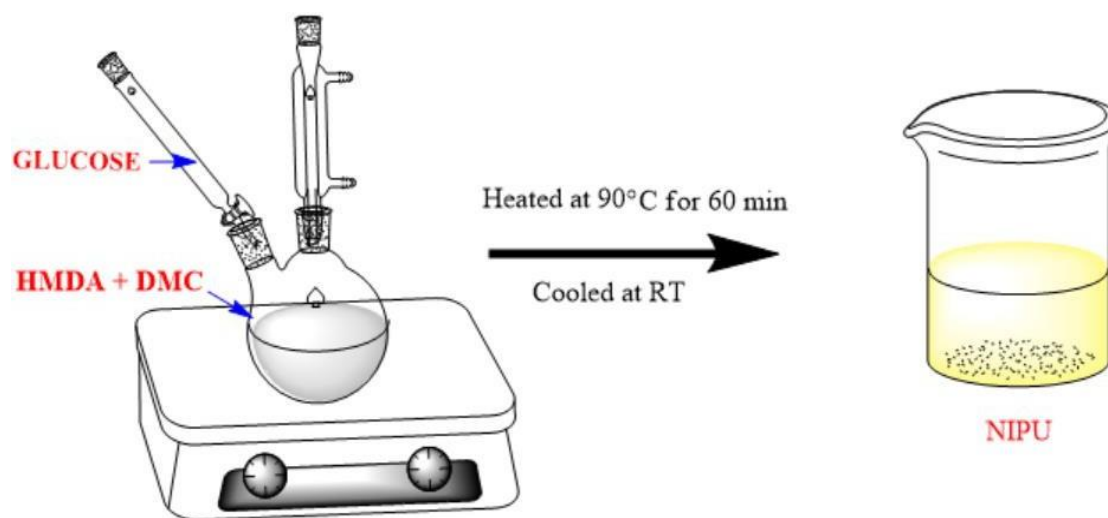
Fig.3.1: Schematic representation of NIPU formation

For, a mixture of 10g RGCA 0, 1.652 g of citric acid and 2.5 g of glutaraldehyde was used. The resulting self-sustaining soft material (Sample RGCA 1) was allowed to sit at room temperature (25 ∘C) for five hours before being dried in an oven at 150 ∘C for four hours. After being taken out of the beaker, the product was left for two days at room temperature (25 ∘C and 12% relative humidity) in order to be characterize as illustrated in Fig 3.2.
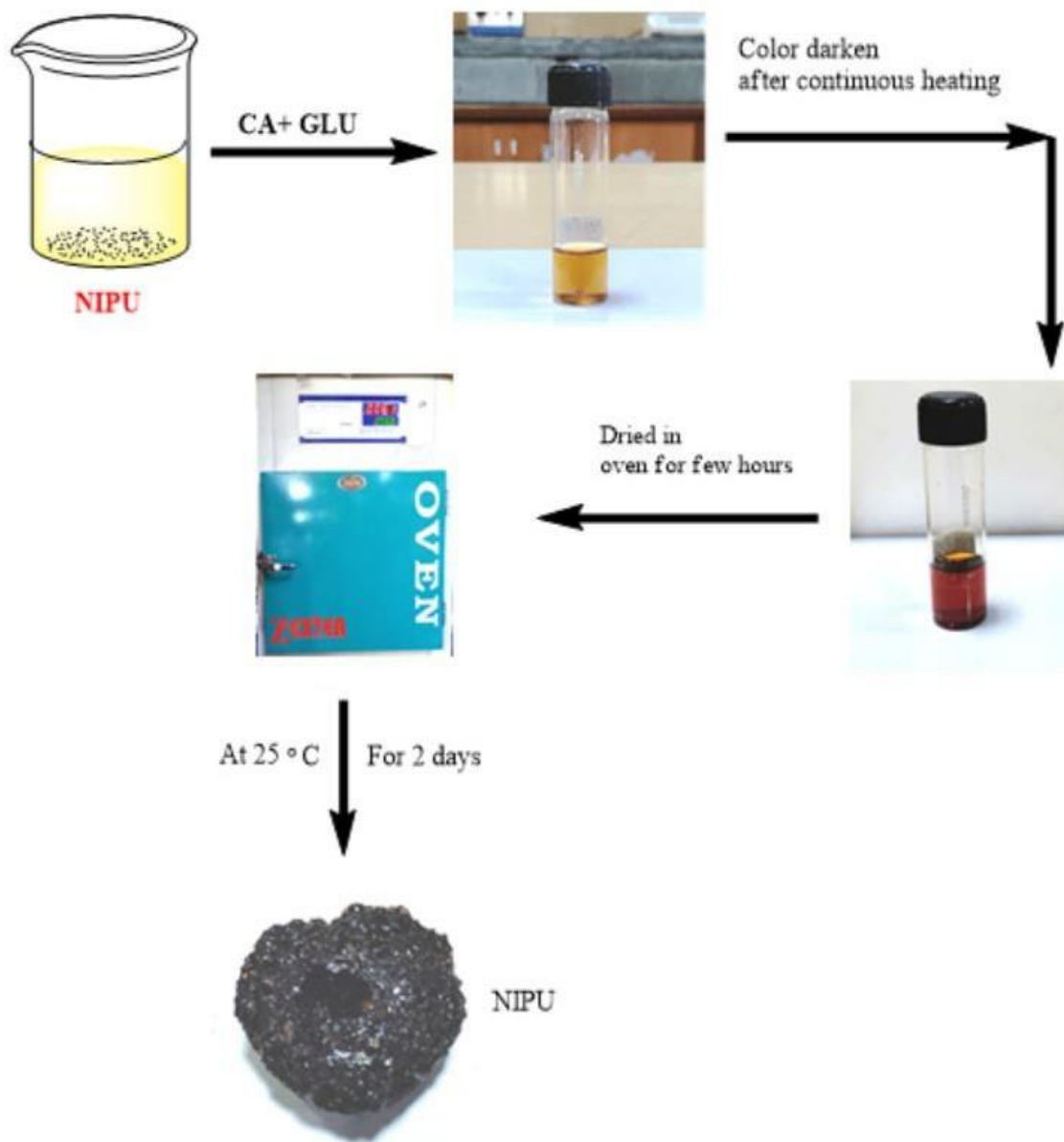
35

Fig 3.2: Schematic representation of formation of NIPU

CHAPTER 4 CHARACTERIZATION TECHNIQUE OF NIPU MATERIAL

4.1 Reactions involved in g-NIPU formation

The synthesis of NIPU requires a reaction between diamines and cyclic carbonates. To synthesize NIPU, we combine an aqueous solution of HMDA with glucose as a bio-based polyol component. Dimethyl carbonate can be used to generate the required cyclic carbonate through a reaction with the glucose polymer. The mixture is then allowed to react, facilitating polymerization to form the urethane linkages representative of NIPU structures.To create a cured structure, citric acid and glutaraldehyde can be introduced as crosslinking agents. Citric acid acts as both a catalyst and a crosslinker in the presence of polyols, while glutaraldehyde can react with amine groups from HMDA to form a more rigid three-dimensional network. The crosslinking helps to form the polymeric material with desired porosity and mechanical properties. After mixing all the components, the reaction mixture is cured, and the formation of cured structure occurs, expanding and setting into the final NIPU product.

STEP 1: Exothermic reaction occurs between citric acid and HMDA with the release of water to form citric acid diamine.
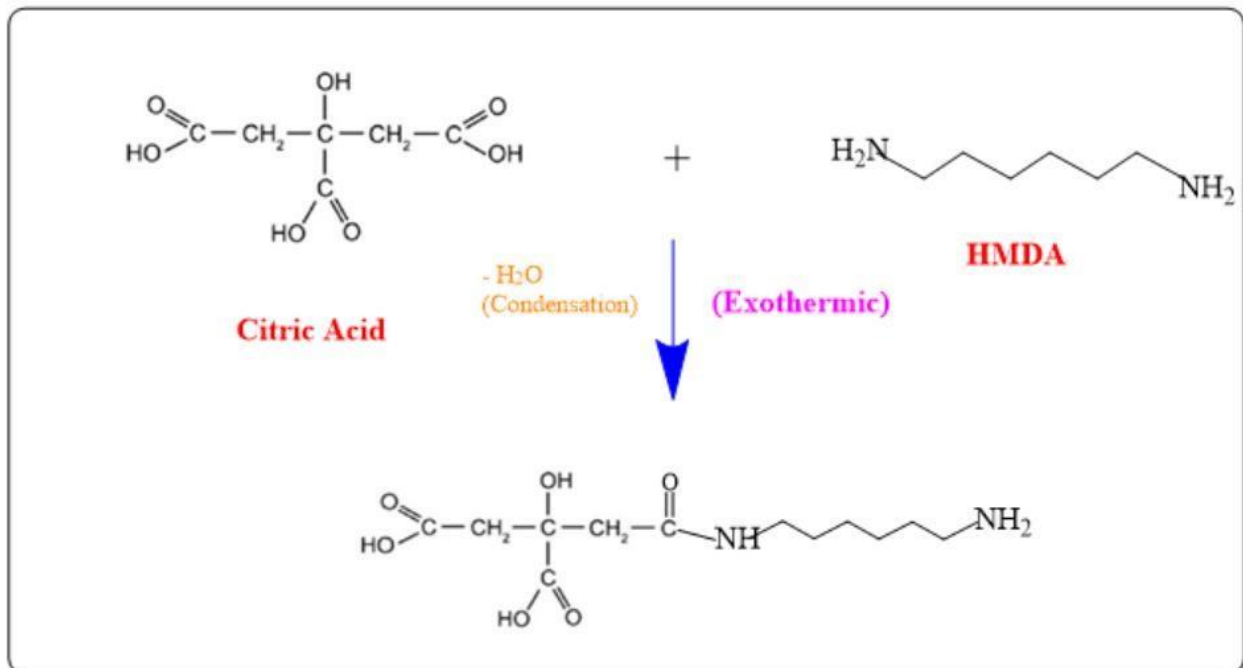
STEP 2: Glucose undergoes addition reaction with HMDA in basic medium with the release of water to form glucose carbonate diamine.

38
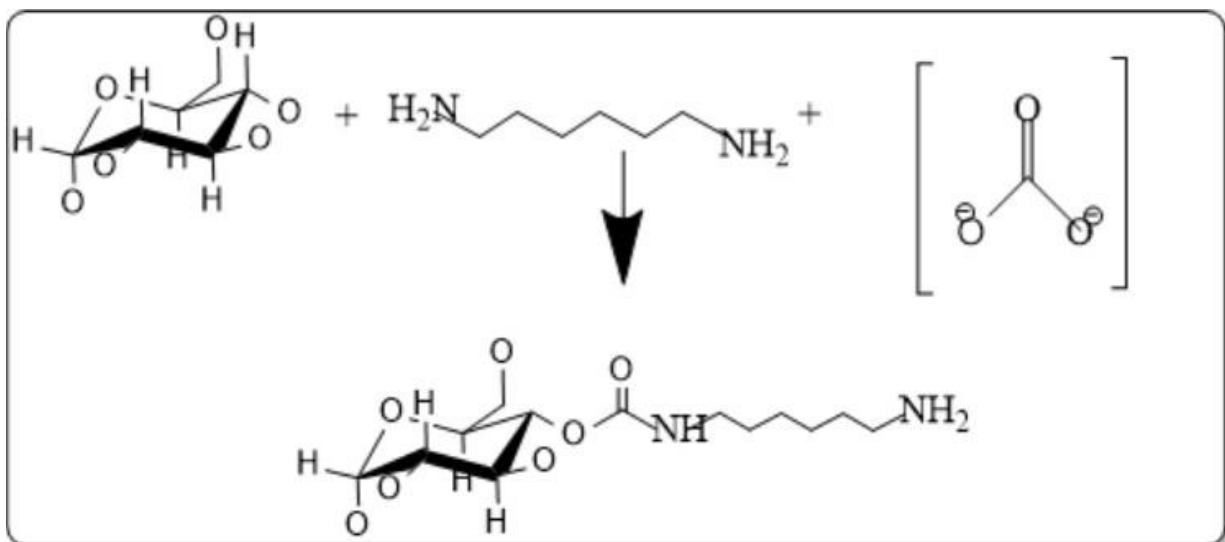
STEP 3: Condensation reaction between citric acid diamine to form added product.
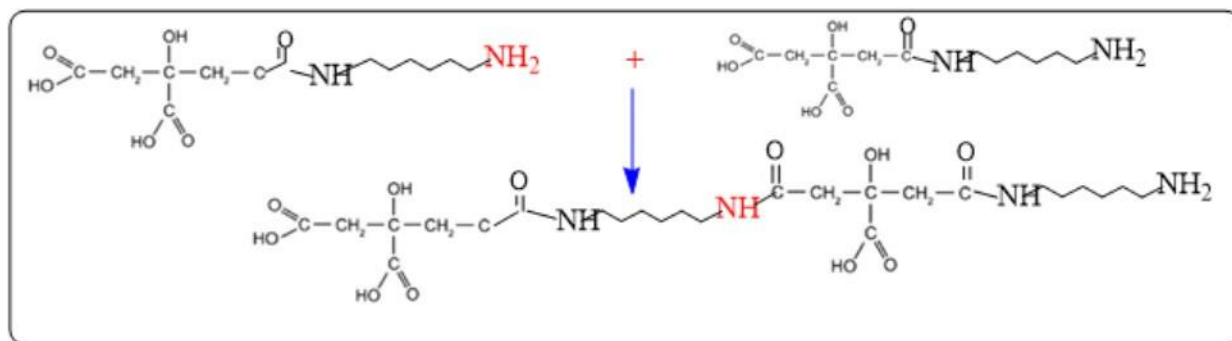
STEP 4: Glutaraldehyde reacts with glucose carbonate diamine and undergoes condensation reaction
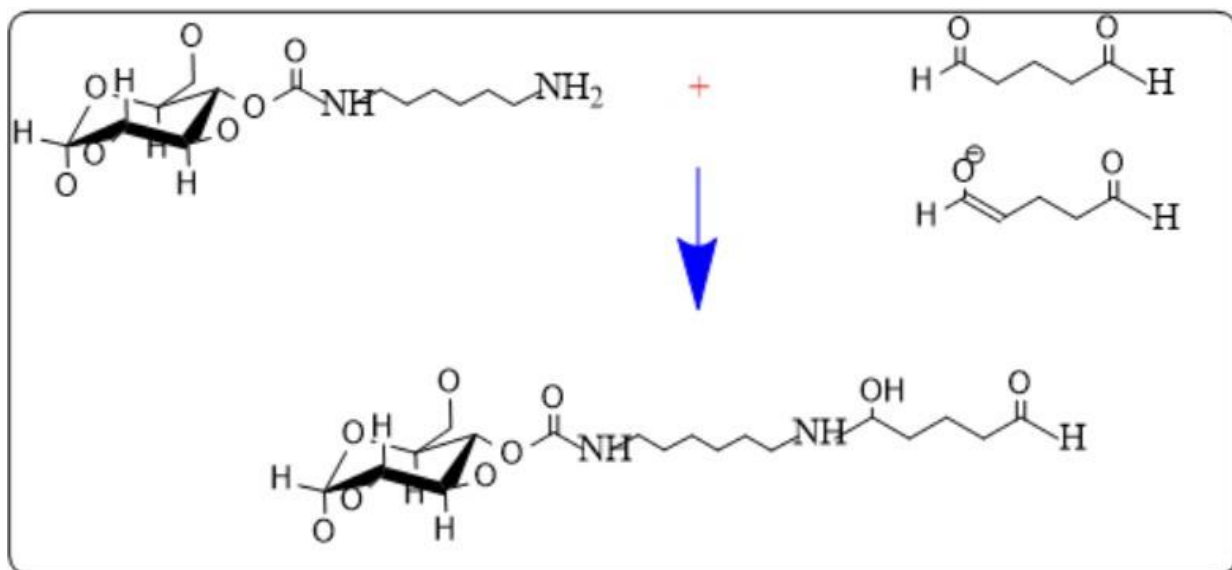
STEP 5: HMDA reacts with product form in Step 4 and undergoes condensation reaction.
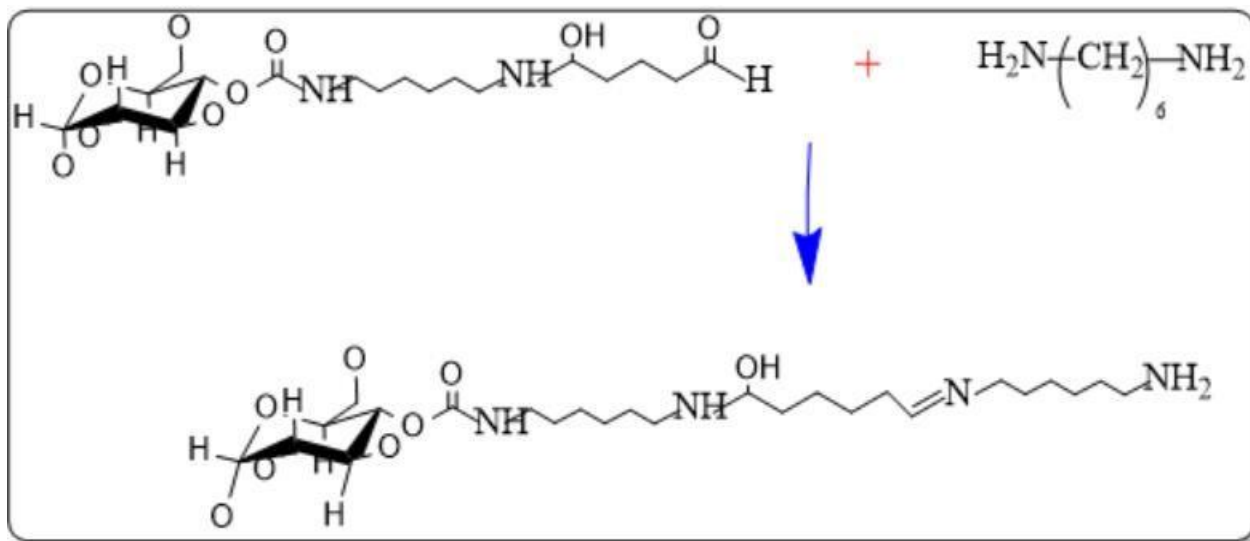
STEP 6: Citric acid diamine and glucose carbonate diamine undergoes condensation reaction to form urethane linkage.

4.2 Fourier transform Infrared (FTIR) Spectroscopy

FTIR is an analytical technique used to obtain the infrared spectrum of absorption or emission of a solid, liquid, or gas. It is one of the most powerful tools for identifying types of chemical bonds in a molecule by producing an infrared absorption spectrum that is like a molecular "fingerprint". Unlike other types of spectroscopy, FTIR spectrometers collect all wavelengths simultaneously, which ensures collection of a high-resolution spectral data over a wide spectral range in a short time.The FTIR spectra of RGCA 1 was obtained using a Perkin Elmer Frontier ATR-FTIR provided by an ATR Miracle diamond crystal.

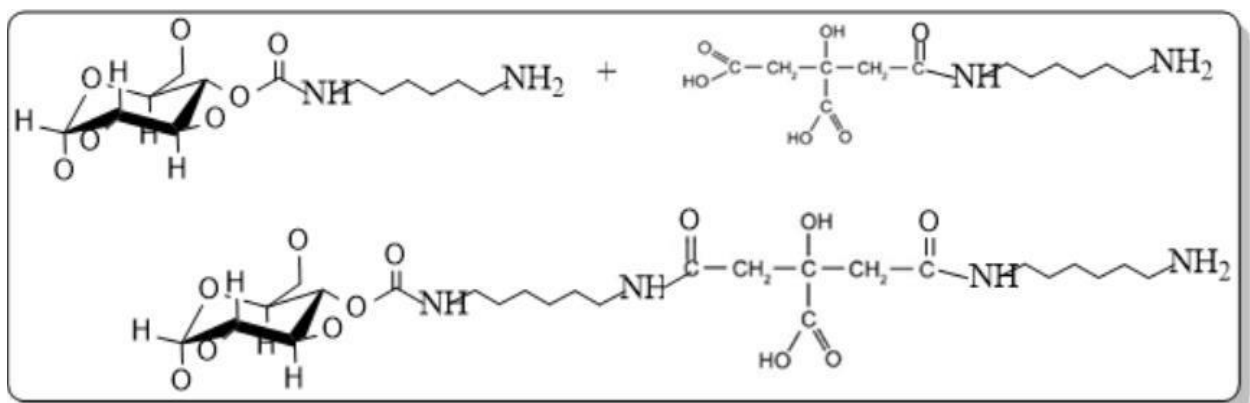**Fig.4.1- Perkin Elmer Frontier ATR-FTIR provided by an ATR Miracle diamond crystal**.

Attenuated Total Reflectance is an enhancement technique used in conjunction with infrared spectroscopy. With ATR-FTIR, the sample is placed on a crystal with a high refractive index — in this case, a diamond — allowing the infrared radiation to reflect off the internal surfaces and pass through the sample. This process results in an evanescent wave that extends beyond the surface of the crystal and into the sample. When the infrared light interacts with the sample, it can

be absorbed at specific wavelengths which correlate to the vibrational energies of the chemical bonds within the material.

Perkin Elmer Frontier ATR-FTIR provided by an ATR Miracle diamond crystal was employed to examine the functional groups of all the prepared foam samples. The powdered samples were placed on the ATR equipment's diamond eye (1.8 mm) and the sample's touch was maintained by securely screwing the clamping equipment.The powdered samples are scanned over a spectral range typically from 600 to 4000 cm−1. This range encompasses the region where most molecular vibrations occur, including stretching, bending, and combination vibrations. With 32 scans at a resolution of 4 cm−1, the FTIR technique records a spectrum.

4.3.X-ray Diffraction (XRD) Analysis

XRD is an essential tool in material science, commonly used for phase identification and to determine the crystalline structure of materials, including polymers. In the case of NIPU, XRD can provide valuable information about the material's microstructure, which is crucial for understanding its physical and mechanical properties [18].Moreover, the observed broadness ofthe peak in question is indicative of a largely amorphous constitution within the polymer matrix. It is well understood in the field of polymer science that such broad diffraction features emerge from a material wherein long-range order is not prevalent, and are symptomatic of a material wherein only short-range order exists amidst the predominantly disordered molecular chains [49].

Hybrid non isocyanate polyurethane (HNIPU) was analysed through XRD which confirmed the crystallization behavior of the samples. A 10 mm × 10 mm flakelet with a 2θ range of 5° to 50° at 5 °/min was placed on the device.The absence of noticeable diffraction peaks suggests that the HNIPU were structurally amorphous. Nonetheless, crystallization may occur, which could be accounted for by the decreased levels of secondary amines and crosslinking. Therefore, the crystallization behaviour of HNIPUs could be tailored based on the secondary content [50].

The breadth of the XRD peak not only signifies amorphicity but also has information regarding the degree of disorder. The extent to which the polymer chains are able to organize into orderly crystalline domains is inherently limited, thereby yielding a material that exhibits the enhanced flexibility and ductility often associated with amorphous polymers [51][52].To obtain crucial information regarding the solid-state structure of RGCA 1, by powder X-Ray Diffraction (PXRD), utilizing a high-resolution Bruker diffractometer.

Fig 4.2: Powder X-Ray Diffraction (PXRD), utilizing a high-resolution Bruker diffractometer

The morphology and structure of the developed foams were assessed by PXRD using a high-resolution Bruker diffractometer (D8 Discover) coupled with a point detector (scintillation counter). Cu K α radiation was received via a gobel mirror that covers the range of $2\theta=5\text{-}80°$, with a scan rate of 1.0 s/step and step size $0.02°$ at 298 K.

CHAPTER 5 RESULTS AND DISCUSSION

5.1 Characterizations

The synthesized NIPU materials (RGCA 1) were characterized by XRD and FTIR techniques.

XRD was used to determine phase composition, crystal structure, and orientation of powder,

solid, and liquid samples.FTIR is used to determine sample's functional groups.
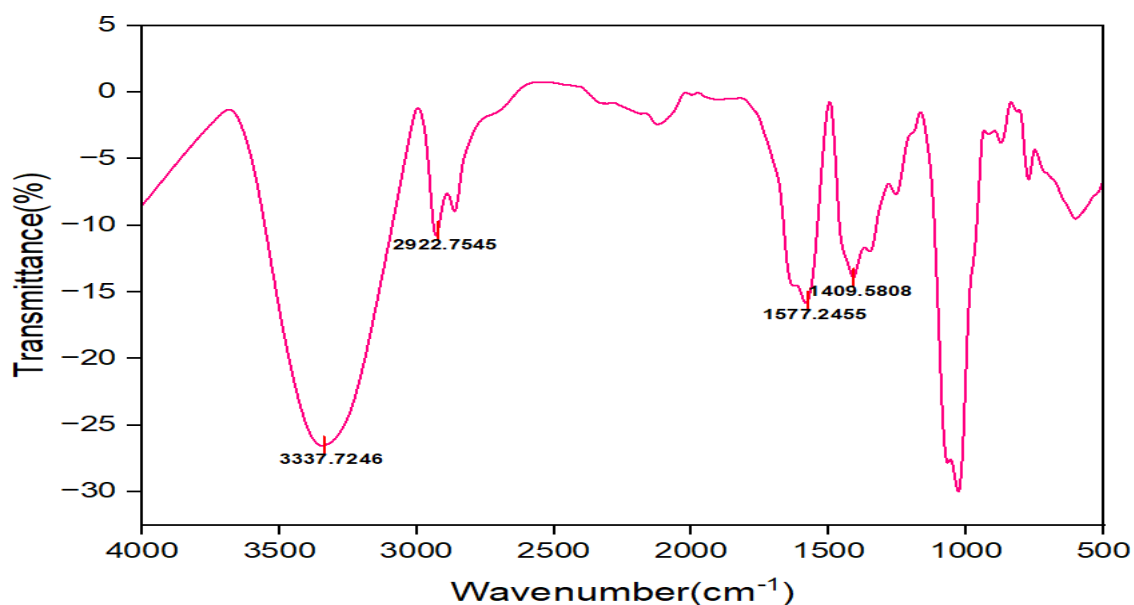
## 5.1.1. FTIR

Fig.5.1: FTIR sample of RGCA1

From fig 5.1 we can see the FTIR spectra of RGCA1 material.

In the mid-infrared region, absorption bands around 1500-1600 cm^{-1} typically arise from amine

N-H bending vibrations, indicative of primary amines, secondary amines, or amide linkages in the

structure. This feature implies the presence of nitrogen-hydrogen bonds performing a bending motion, which is common in proteins and other nitrogen-containing organic compounds.The presence of a band around 1600-1700 cm−1 is commonly attributed to the C=O stretching vibration of amide functional groups. Such a peak, often known as the Amide I band, is omnipresent in the spectra of peptides and polyamides, suggesting the material may contain polymeric features with such functional groups. The precise wavenumber within this region can also help distinguish between different types of amides or the nature of the secondary structure in a polyamide or protein.The additional peak at 1600 cm−1, attributed to urethane linkage, is another significant feature in the spectrum. Urethanes, or PU, are formed from the reaction of isocyanates with polyols and often exhibit absorbance in this range due to the presence of carbamate (urethane) groups. The linkage is indicative of PU or related materials, where the C-N stretch of the urethane linkages, often coupled with the N-H bending vibrations, gives rise to this absorption band.

Bands around 2900 cm−1 are typically associated with sp3 hybridized C-H stretching vibrations. These are indicative of aliphatic hydrocarbons, which can represent the backbone of polymers or as side chains attached to a polymeric main chain. Methane and other simple alkanes, as well as more complex organic compounds containing methyl, methylene, or methine groups, would show such vibrational characteristics.Lastly, the band at around 3400 cm−1 is a sign of hydroxyl and amine stretching vibrations. This broad absorption band can be due to the stretching of N-H bonds, O-H bonds, or both, particularly when hydrogen bonding is present.

5.1.2. XRD
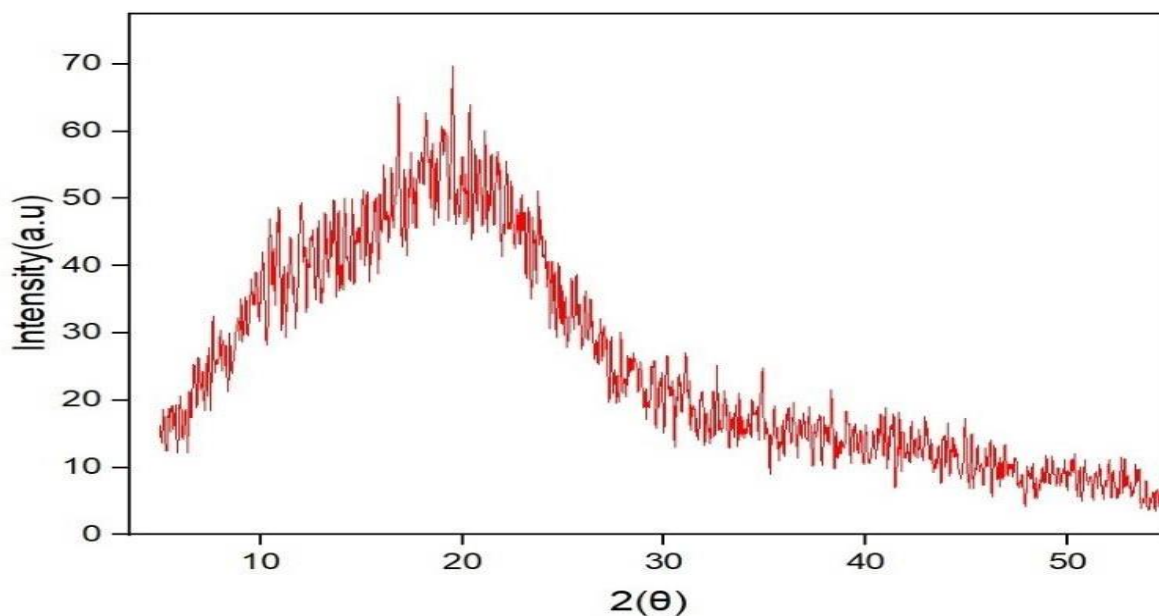
Fig.5.2: XRD plot for NIPU sample RGCA1

The data presented in the PXRD pattern of RGCA 1(Fig 5.2) suggests that knowledge of the crystalline and amorphous nature of the synthesized material can be derived. Segmented polyurethanes, like the non-isocyanate polyurethanes mentioned, often exhibit mixed phase characteristics in their PXRD patterns.

1. **Main Peak at 21°:** The highlighted main peak in the PXRD pattern at around 21° is an indicator of the characteristic arrangement of molecular chains within the material. For polyurethanes and particularly NIPUs, a peak in this region is common and may correspond to the hard segment domains or crystalline regions where the polyurethane chains pack in a regular manner.

2. **Broadness of the Peak:** The broadness of this peak signals an amorphous nature, which is typical for polymer foams and particularly for NIPUs. In polyurethanes, the amorphous character is attributed to the flexible segments in the polymer that do not attain a crystalline order. The hard segments often provide some degree of semi-crystalline behavior, but the overall dominant amorphous nature is what gives these materials their unique properties, like flexibility and elasticity.

3. **Implications for material Structure:** In the case of CA-g-NIPU foams, the PXRD pattern suggests that these materials have an amorphous matrix which is beneficial for specific applications. For example, in sound or thermal insulation, where flexibility and the ability to fill irregular spaces without losing integrity are desirable features.

The PXRD data, along with FTIR analysis, collectively provide a detailed molecular-level insight into the material's structure, guiding future material formulation and application.

Fig.5.3: Glucose based non-isocyanate polyurethane ("A" in the Mold, "B" without it).

CHAPTER 6 CONCLUSION AND FUTURE ASPECTS

6.1. Conclusion

Diverse synthesis methodologies are analyzed, detailing chemical pathways and employing techniques such as lysine, sorbitol, and transurethanization. The assessment of the structural, mechanical, and thermal properties of NIPU highlights their favorable attributes, including enhanced flexibility, durability, and insulation capabilities. Their diminished environmental impact and adherence to regulations align with sustainability goals, presenting them as an eco-friendly solution applicable across various fields. However, despite their potential, challenges such as limited fire reaction data and technical constraints persist, necessitating further investigation. This work emphasizes the significant potential of NIPU in addressing environmental concerns and advocates for their pivotal role in fostering sustainability across industries. It underscores the importance of addressing existing limitations to establish NIPU as a cornerstone material for an environmentally conscious future.

Their diminished environmental impact and adherence to regulations align NIPU with sustainability goals, presenting them as an eco-friendly solution applicable across various fields. We have emphasized the significant potential of NIPU in addressing environmental concerns and advocates for their pivotal role in fostering sustainability across industries.

6.2. Future Aspect and Challenges

Even with their potential, NIPU has obstacles like slow fire response times and ongoing technological limitations, which call for more research.The techniques employed in this literature to produce g-NIPU have a great deal of promise for producing room-temperature NIPU material. This technique for preparing g-NIPU is introduced and put into practice, doing away with the requirement for high-temperature curing hard with heat for these g-NIPUs.These materials have strong resistance to compression but still have low fire resistance. They can be used as thermal insulation materials, or as a middle layer to create a lightweight "wood– material–wood" sandwich board, or even for hydroponic applications. Future studies on the modification of these materials fire resistance are required.In the ongoing exploration of NIPU, one of the pressing obstacles involves addressing the inadequate water resistance observed in NIPU coatings. This particular challenge is attributed to the presence of pendant hydroxyl groups within their structure, contrasting with the configuration found in PU. Effectively surmounting this limitation stands as a substantial barrier in the quest to optimize NIPU coatings for more expansive applications[29].Another notable challenge within reach is the development of catalysts that facilitate curing processes at room temperature [53].Leveraging these resources, particularly derivatives of starch such as sorbitol, provides promising opportunities for transforming hydroxyl groups into carbonates, thereby establishing cross-linking sites. This innovative approach holds the potential to usher in a new era in green chemistry, unlocking pathways for environmentally conscious formulations of NIPUs [19][54].

CHAPTER 7 REFRENCES

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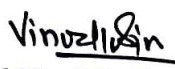## 30th November – 2nd December 2023

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Hu A COMPREHENSIVE EXPLORATION OF BIO-BASED NON-ISOCYANATE POLYURETHANE

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in

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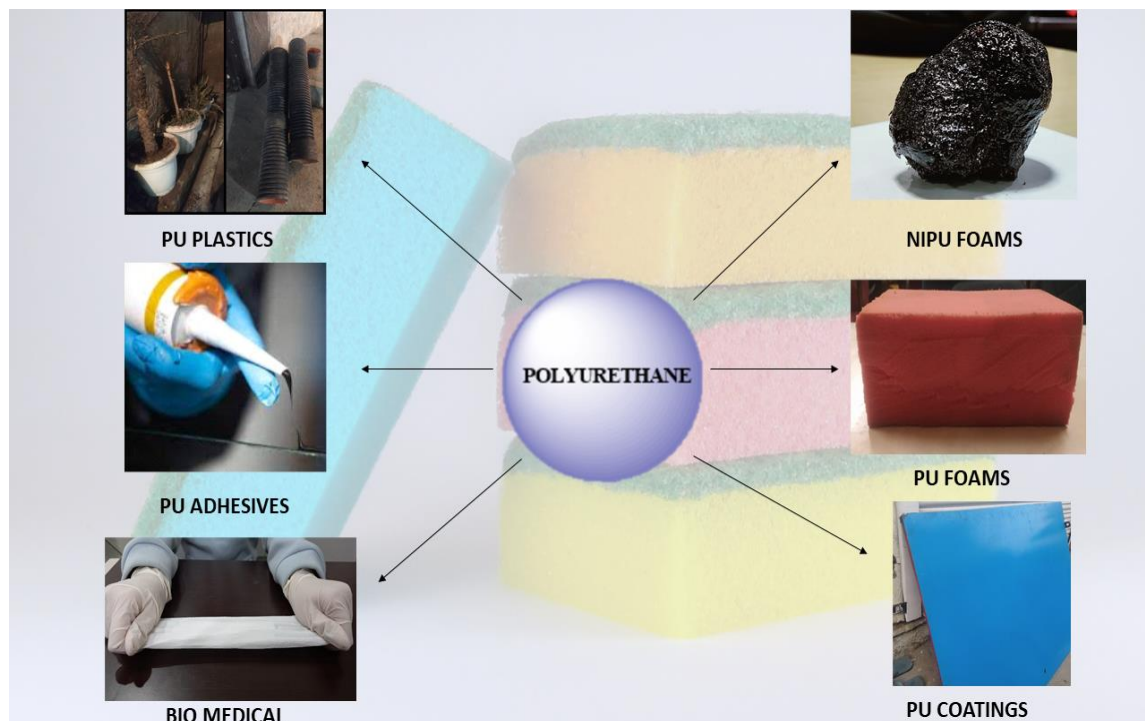**Prof. RAMINDER KAUR**

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i

CHAPTER 1 INTRODUCTION

1.1.Background of present research

1.1.1. Polyurethane

Polyurethane (PU) is an organic polymer which consist of many urethanes bonds link together formed from combination of polyol and isocyanate. It offers a wide range of properties, which makes it a choice for a broad range of end user applications from engineering plastic to common household material. It is used to make mats, foams, plastic mugs and pots, PU pipes, adhesives, coatings etc. In addition, PU is popularly being used in biomedical, electrical and infrastructure industries. Fig.1.1 gives an overview of different uses of PU[1].

Fig.1.1: Different Uses of PU

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