SYNTHESIS AND CHARACTERIZATION OF POLYURETHANE DERIVED FROM RENEWABLE SOURCES

A Thesis Submitted

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DOCTOR OF PHILOSOPHY

by

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Dedicated to my beloved family

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CANDIDATE'S DECLARATION

I **Pooja Singh** hereby certify that the work which is being presented in the thesis entitled **"SYNTHESIS AND CHARACTERIZATION OF POLYURETHANE DERIVED FROM RENEWABLE SOURCES"** in partial fulfillment of the requirements for the award of the Degree of Doctor of Philosophy, submitted in the Department of Applied Chemistry, Delhi Technological University is an authentic record of my own work carried out during the period from 14.08.2019 to 30.07.2024 under the supervision of Dr. 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.

Candidate's Signature

This is to certify that the student has incorporated all the corrections suggested by the examiners in the thesis and the statement made by the candidate is correct to the best of our knowledge.

Signature of Supervisor(s) **Signature of External Examiner**

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CERTIFICATE BY THE SUPERVISOR

This is to certify that the Ph.D thesis entitled **“Synthesis and Characterization of Polyurethane Derived From Renewable Sources”** submitted to Delhi Technological University, Delhi-110042, in the fulfilment of the requirement for the award of the degree of Doctor of Philosophy by the candidate Ms. Pooja Singh (2K19/PDHAC/08) under the supervision of Dr. Raminder Kaur, Assistant Professor, Department of Applied Chemistry, DTU. It is further certified that the work embodied in this thesis has neither partially nor fully submitted to any other university or institution for the award of any degree or diploma.

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ABSTRACT

The increasing environmental concerns and health hazards associated with conventional polyurethanes (PUs) have driven the exploration of sustainable and non-toxic alternatives. This thesis focuses on the synthesis and characterization of non-isocyanate polyurethanes (NIPUs) derived from renewable sources, aiming to address the limitations of traditional PUs while enhancing their functional properties.

Initially, NIPU foams were synthesized using xylose and dimethyl carbonate, with citric acid serving as a bio-based crosslinker. This innovative approach not only reduced the dependency on fossil fuels but also improved the flame retardancy of the foams under mild reaction conditions. The foams exhibited superior thermal stability and mechanical properties, as evidenced by comprehensive characterization techniques such as Fourier Transform Infrared Spectroscopy (FTIR), Thermogravimetric Analysis (TGA), and Differential Scanning Calorimetry (DSC).

Building on this, the synthesis methodology was further refined through a one-pot process, eliminating the need for sophisticated reaction setups and harsh conditions. This simplification aimed to make the production of porous NIPU materials more scalable and environmentally friendly. The resulting materials demonstrated enhanced flame retardancy and structural integrity, confirmed by solid-state NMR and Powder X-ray Diffraction (PXRD) analyses.

The research then progressed to the development of NIPU blends with poly(vinyl alcohol) (PVA), focusing on their rheological, thermal, and mechanical properties. These blends exhibited unique viscoelastic behavior and improved thermal stability, highlighting their potential for advanced material applications. The study of these blends was pivotal in understanding the interactions between NIPU and PVA, providing insights into the design of sustainable polymer composites.

Furthermore, the thesis explored the synthesis of NIPU-based hydrogels for environmental and biomedical applications. Utilizing water as a solvent, these hydrogels were synthesized under mild conditions, overcoming the challenges posed by traditional methods that require organic solvents. The hydrogels demonstrated remarkable efficacy in dye removal, achieving high removal efficiencies for crystal violet and malachite green dyes. Additionally, their potential for drug delivery was investigated using cefadroxil as a model drug, showcasing their capability to effectively release pharmaceutical agents.

Overall, this research presents a comprehensive study on the synthesis, characterization, and application of NIPUs derived from renewable sources. It highlights the feasibility of producing environmentally friendly and high-performance polyurethanes, paving the way for future developments in sustainable materials. The findings of this thesis contribute significantly to the field of polymer science, offering innovative solutions to the challenges posed by conventional PUs and opening new avenues for their application.

OVERVIEW OF THESIS

The objective of this thesis is to synthesize and characterization of polyurethane derived from renewable sources. The whole thesis is organized in seven chapters. **Chapter 1** of the thesis, presents the overview of PU, problems associated with its reactants, and conventional methodology. The rise of Non-isocyanate polyurethanes (NIPU) as a suitable alternative for countering pre-existing issues, followed by the research work conducted by different researchers to prepare NIPU, has also been discussed thoroughly. Furthermore, this chapter also highlights the gaps in the current state of research and the most recent developments in the subject.

Considering the fact that a significant portion of PU production is in the form of foams, it is especially necessary to synthesize porous non-isocyanate PU structures. Since a large percentage of PU materials are used as foams, which inherently exhibit a porous structure, it is imperative to develop substitute processes for making these materials without using isocyanates. These methods not only make PU production safer and more sustainable, but also create new opportunities for the development of cutting-edge materials with expanded applications. **Chapter 2** deals with the synthesis and characterisation of xylose-based NIPU foams from renewable sources, with improved flame-retardant properties. **Chapter 3** reports the modified strategy to synthesise porous NIPU materials using a novel catalyst-free one-pot synthesis method, and the impact of bio-based crosslinker on enhancing the limiting oxygen index values.

The limitations of conventional PUs necessitate the preparation of NIPU blends with polyvinyl alcohol (PVA). NIPUs provide a safer substitute for conventional PUs since they are prepared without isocyanates. The mechanical, thermal, and biodegradable qualities of the resultant material can be improved by blending NIPUs with PVA, a biocompatible and water-soluble polymer. The

PVA component can enhance the NIPU blend's hydrophilicity, tensile strength, and flexibility, which makes it appropriate for use in membranes for applications such as water treatment, scaffolds for tissue engineering, and biomedical devices. The drawbacks of conventional PUs are addressed by the synergistic combination of NIPU and PVA, which also produces a more adaptable and sustainable material. **Chapter 4** reports the synthesis of NIPU/PVA blends and their extensive characterisation using TGA, DSC, XRD, rheology, etc.

Porous NIPU hydrogels have improved toughness, flexibility, and water absorption capacity, besides presenting a safer and more environmentally friendly option. Consequently, NIPU hydrogels are appealing for various applications, such as water treatment, tissue engineering, biomedical devices, and soft robotics. NIPU hydrogels are especially well-suited for biomedical applications that demand biocompatibility because of their porous nature, which can also enhance their mechanical performance and imitate the extracellular matrix. **Chapter 5** includes the synthesis of fructose-based NIPU and its hydrogel using polysodium acrylate as a comonomer. These hydrogels exhibited excellent dye removal efficiencies for crystal violet and malachite green dye to combat water pollution. **Chapter 6** reports the pH-sensitive controlled drug delivery of cefadroxil drug using a biocompatible fructose-based hydrogel.

At last**, Chapter 7** of the thesis, where the overall conclusions of the results obtained in the above study are reported. In addition, some recommendations are made for future studies to guide researchers who want to pursue a similar kind of work on PU or wish to elaborate the studies to the next level possible**.**

The structure of the thesis is enhanced by placing references after each chapter, ensuring a clear and organized presentation of source materials. This approach allows one to easily access cited works, verify information sources, and explore topics, enhancing the overall accessibility and ease of navigation.

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LIST OF ABBREVIATIONS

PU	Polyurethanes
MDI	Methylene Diisocyanate
TDI	Toluene Diisocyanate
CMR	Carcinogenic, Mutagenic, and Reprotoxic
BPU	Bio-based Polyurethane
PUF	Polyurethane foam
NIPU	Non-Isocyanate Polyurethane
HDI	Hexamethylene diisocyante
HPMDI	1,7-heptamethylene diisocyanate
HDEDI	1,16-diisocyanatohexadec-8-ene
LLDI	L-lysine diisocyanate ethyl ester
IPDI	Isophorone diisocyanate
HAPs	Hazardous Air Pollutants
VOCs	Volatile organic compounds
TBAB	Tetra butyl ammonium bromide
EDA	Ethylene Diamine
DETA	Diethyltriamine
IPDA	Isophorone diamine
PFGC	Perfluorooctyl cyclic carbonate
CDI	Carbonyldiimidazole
BCI	Bis-carbonylimidazolide
BBCI	1,4-butyl(bis-carbonylimidazolide)
CHDMBCI	1,4-cyclohexanedimethyl(bis-carbonylimidazolide)
SEM	Scanning Electron Microscopy
FTIR	Fourier Transform Infrared

TGA	Thermogravimetric Analysis
DSC	Differential Scanning Calorimetry
PHUs	Polyhydroxyurethanes
HMDA	Hexamethylene diamine
MBA	N, N'-methylenebis(acrylamide)
AA	Acrylic acid
PXRD	Powder X-Ray Diffraction
TG Profile	Thermogravimetric Profile
DMC	Dimethyl carbonate
MG	Malachite green
CV	Crystal Violet

Chapter 1

INTRODUCTION AND LITERATURE REVIEW

1.1 Introduction

1.1.1 Polyurethanes

With the knock of the 21st century, along with vast technological advancements in the scientific field, macromolecules have made the lifestyle easier, wherein, the mankind is highly reliant on and surrounded by a diverse range of polymeric materials in the day-to-day routine. Among these materials, polyurethanes (PUs) represent nearly 8% of the total plastics production and stand tall as the 6th most widely used polymer in the world, with total production reaching 18 MTon in 2016 and still progressing [1]. The remarkable popularity of polyurethane (PU) among researchers can be attributed to its outstanding features, including but not limited to its resistance to corrosion, high automatic strength, comfortability at low temperatures, adhesiveness, and chemical structural adaptability. Urethane groups, which are produced by reacting hydroxyl (-OH) terminated chemical entities with isocyanate (-NCO) terminated compounds, are the key repeating units along the main backbone chains of PU, as illustrated by the generalized scheme given in Figure 1.1. In addition, some other functional groups may also be present in the end constitutions of the PU chains, including ethers, esters, urea, biuret, and aromatic moieties [2]. By altering the chemical compositions of PUs, researchers have been able to achieve diverse and extensive utilization of these polymers. The properties of PUs can be modified by varying the chemistry and composition of polyol, diisocyanate, and chain extender [3]. The polyol-based chain extenders are employed in the context of PUs to undergo crystallization or introduce heterogeneity which further serves the purpose of imparting enhanced rigidity and toughness to the final product. Low molecular weight aliphatic or aromatic diols with a molecular weight (Mn) less than 500 g mol^{-1} are commonly employed in conventional PUs. This is achieved by incorporating reversible chemistries into the diol structure, thereby offering chemical functionalities to PUs along with the aforementioned physical attributes.

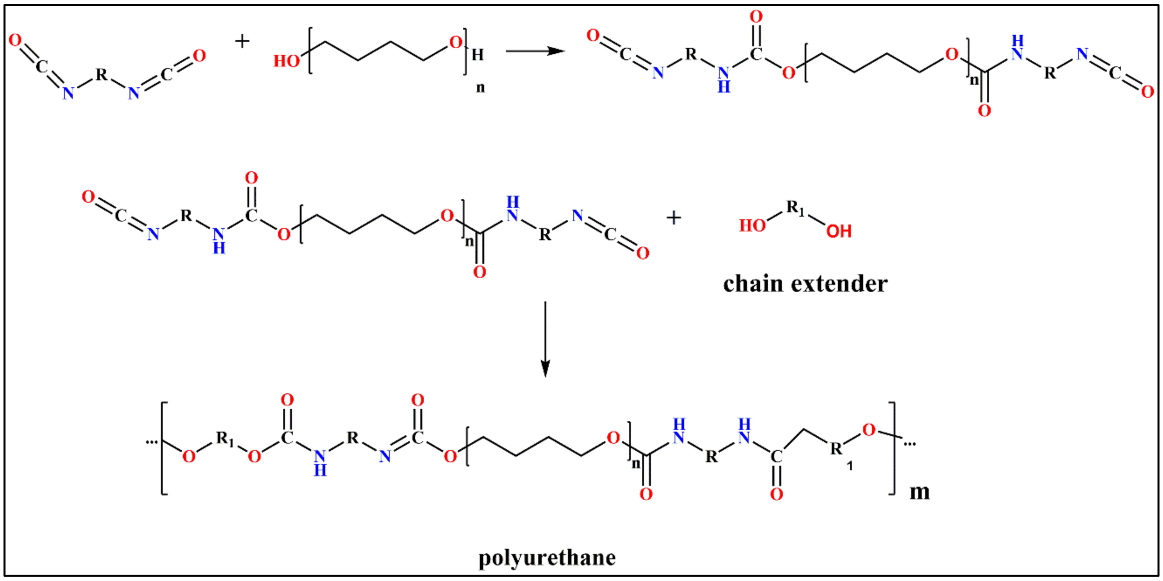
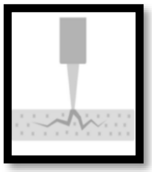


Figure 0.1 Synthesis of conventional PU via a two-step method involving the reaction of diisocyanate, polyol, and a chain extender.

PUs can be custom-made with a wide range of product implications, including foams, fibers, adhesives, coatings, elastomers, sealants, etc. by changing the raw materials, additives, and production technique. The extensive range of uses for polyurethanes is mentioned in Table 1.1. According to the latest report, the global polyurethane market will reach USD 88 million by 2026, with a compound annual growth rate of 6% [4]. However, the drawbacks associated with the preparation and usage of PUs pose a serious threat to human health and environmental hazards, which include (i) the use of petroleum sources for the preparation of polyols (ii) the use of dangerous phosgene gas for the conversion of amines into isocyanates, (iii) usage of CMR (Carcinogenic, Mutagenic, and Reprotoxic) labelled isocyanates for PU synthesis, namely Methylene Diphenyl Diisocyanate (MDI) and Toluene Diisocyanate (TDI), and the health risks associated with their long-term exposure, such as asthma, dermatitis conjunctivitis and acute poisoning (iv) post-consumption dumping (into landfills and dumping ground) or incineration of PU, leading to either hydrolytic degradation, that generates toxic amines which contaminates air and water bodies or the disintegration to yield hydrogen cyanide (HCN), during burning, which is a highly toxic chemical [5,6].

Table 0.1 Wide range of applications associated with PUs

Thermoplastic PU	**Flexible PU**	**Rigid PU**	**PU Ionomers**	**Water-Based PU**
				
Flexible and elastic with good abrasion, weather, and abrasion resistance.	Block copolymers with phase separation between soft and hard segments that are flexible.	Versatile and energy-saving insulator	Improved thermal and mechanical characteristics and greater dispersion in polar liquids due to increased hydrophilicity.	Coatings, and adhesives which use water as solvent are called water based PU .
For example, automotive instruments, footwear, medical	For example, Cushion materials, carpet underlays, furniture,	For example, Sound and thermal insulators. Used in	For example, biomedical devices, shape memory and are biocompatible.	For example, coatings, adhesives, sealants, binders

devices, film, sheets, and applications with a profile.	packaging, biomedical, and industries that use cushion materials.	commercial and residential appliances.

1.1.2 Bio-based Polyurethanes

Bio-based materials are natural, non-mineral materials that may be utilised as-is or with minor alterations to mimic the behaviour and performance of synthetic materials. One of the most adaptable materials available today is bio-based PUs, which can be very helpful in achieving environmental objectives like sustainability and waste reduction. The production of PU using renewable resources lessens harmful environmental effects, including as greenhouse gas emissions. The basic materials used to make synthetic PUs are currently depleting petrochemicals, and they are also costly, hazardous, and non-biodegradable. Therefore, issues including solid pollution, cost-effectiveness, and simple raw material availability led to the development of bio-based PU (BPU) materials. Consequently, PU has seen a significant shift from traditional petroleum-based raw feedstock toward diverse renewable alternatives like fatty acids [8], proteins [9], carbohydrates [10], vegetable oils [11], starch [12], polysaccharides [13], cellulose [14], and a variety of different agricultural products and by-products.

In the recent decade, diverse research groups have made rewarding efforts toward the synthesis of bio polyol-based PUs [13,14]. Polyols behave as soft segments in PUs responsible for transmitting flexibility, and elastomeric properties in them [15]. Polyols derived from vegetable oils have been the subject of extensive research [16,17]. Hydroformylation [18], ozonolysis [19], amidation-esterification [20], metathesis [21], and epoxidation-ring opening [22], coupling of thiol-ene with mercaptoethanol [23] have all been used to achieve this, and all have successfully provided polyol with the desired properties (as shown in Figure 1.2).

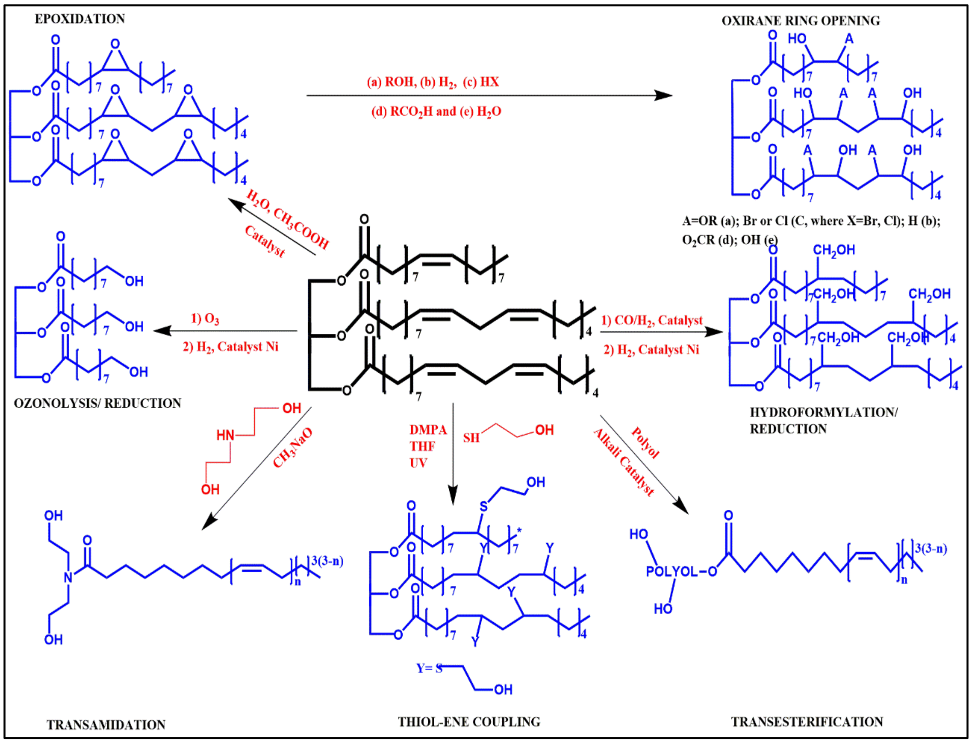


Figure 0.2 Different synthesis methods for producing polyols

Also, petrochemical-derived isocyanates are replaced by bio-based isocyanates to eliminate toxicity. These partially bio-based aliphatic isocyanates impart water resistance, good mechanical strength, and flexibility to the PU network [21]. Hence, bio-based PU materials were developed to solve empirical obstacles, particularly solid pollution, economic effectiveness, and easy availability of input materials. A comparison of the properties of bio-based PU and petro-based PU is given in Table 1.2.

Table 0.2 Comparison of the properties of bio-based polyurethane and petro-based polyurethane [16]

Properties	Bio-Based PU	Petro-Based PU
Density (kg m^{-3})	112-181	141-181
Thermal Conductivity ($Wm^{-1}K^{-1}$)	0.06-0.0540	0.0540
Compressive Strength (N mm^{-2})	111-171	58.0
Tensile Strength (N mm^{-2})	1.4-1.6	0.84
Bending strength (N mm^{-2})	2.7-3.5	1.88
Bending Stress (N mm^{-2})	1.55	1.50
Water Absorption (kg m^{-3})	0.3	0.24

Vegetable oil-derived monomers: To resolve the aforementioned challenges associated with conventional polyols, PU derived from bio-based polyols was categorized under bio-based PUs, 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 to synthesise bio-based PU foams (BPU). Among other biopolymers, plant-derived oils, cellulose, and lignin are 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 [22]. Hydroxyl-containing bio-based compounds like alginate and other carbohydrates have been effectively incorporated into PU structures, which enhances both the biocompatibility and the degradation rates of the materials [23]. Harvested from diverse plant sources, these oils serve as a renewable and eco-friendly foundation for PU, potentially replacing the conventional petroleum-derived polyol. Castor, palm, soybean, rapeseed, canola, and tung oil stand out, offering biodegradability, ecological compatibility, and compatibility with industrial solvents. The resultant PUF boasts many coveted traits—flexibility, robust mechanical ability, durability, adhesive strength, and resistance against chemical degradation and corrosion [24, 25].

Various techniques are employed to derive polyols from vegetable oils for PU 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 leads to polyols with primary hydroxyl groups, offering quicker gel times and enhanced curing efficiency than epoxidized polyol PU. Ozonolysis splits double bonds using ozone, resulting in longer chain polyols suitable for clear PU with excellent mechanical properties. Transesterification, such as with castor oil, swaps alkoxy groups in triglycerides with alcohol, showing potential for applications in rigid PU [24, 26]. Furthermore, polyester polyols that contain lactic acid units are known as lactate polyols, and they are made entirely of biorenewable material. Biodegradable and biocompatible PUs derived from lactate polyols have been observed. Two methods are commonly being reported for the synthesis of polyols from polylactic acids:- (1) ring-opening addition (Lactide is added to hydroxyl groups to open the ring.) (2) Different polyols are esterified using lactic acid or Transesterification with lactic acid esters [27].

The chemical composition of vegetable oils significantly shapes the resulting polyols, influencing the cross-linking density and tensile strength within PU [28]. Among these oils, castor oil stands out due to its distinguished attributes. The composition of castor oil consists mostly of ricinoleic acid, which makes up around 90% of the oil. The remaining components include oleic and linoleic acid in smaller quantities. Ricinoleic acid possesses a hydroxyl group on the 12th carbon atom and a double bond between the 9th and 10th carbon atoms. Castor oil typically encompasses an average of 2.7 hydroxyl groups per triglyceride and has a high OH number (160-168 mg KOH/g). Castor oil is composed of approximately 70% triols, 21% diols, and around 7% monols. 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, and improved electrical and thermal conductivities within polyurethane foams (PUF) [28].

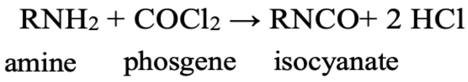
Utilizing castor oil, which has undergone a modification process with glycerol to yield a modified polyol, a reaction follows with methyl diisocyanate to produce a distinct variant of rigid PUF. The addition of varying ratios of silicon oil into the composition has been empirically demonstrated to yield a directly proportional enhancement in both the compressive and flexural properties of the resultant foam, affirming the role of silicon oil as a pivotal factor in optimising its mechanical characteristics [13]. Researchers have explored the effects of rapeseed oil-based polyols on 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 optimise these techniques, developing environmentally friendly alternatives to conventional petrochemical-based polyols [24, 29].

However, the major concern associated with BPU was the use of isocyanate, which was unsuitable for the environment, as it released phosgene into the environment. Historically, PUF has depended on chemical reactions involving harmful isocyanates, raising environmental and health-related alarms.

Bio-based Isocyanates: To further boost the renewable content of PUs, partially or potentially bio-based di-, tri- or poly-isocyanates can be utilised. Substituting petrochemical-based isocyanates with their bio-based counterparts may not be immediately practical, nevertheless it is achievable. This transition can be accomplished through a variety of methods. One approach involves the complete synthesis of PUs using solely bio-based isocyanates, which is not commonly practised. Instead, a combination of bio-based and petrochemical isocyanates is typically utilized. Both options are worthwhile. Employing a petrochemical isocyanate will decrease the overall cost of the mixture, whilst incorporating bio-based isocyanate, either fully or partially, will positively impact environmental considerations. Regrettably, bio-based isocyanates exhibit diminished reactivity due to their aliphatic nature. Nevertheless, this does not imply their use is impracticable [30]. Hojabri et al. successfully derived diisocyanate from oleic acid using the Curtius rearrangement method. They demonstrated that this diisocyanate can effectively synthesise PU by reacting it with bio-based and fossil-based polyols. Their study revealed that PUs derived from bio-HPMDI (1,7-heptamethylene diisocyanate) had comparable mechanical characteristics and thermal stability to samples based on hexamethylene diisocyante (HDI) [31]. Later on, the same group successfully produced entirely bio-based PU using HDEDI (1,16-diisocyanatohexadec-8-ene). The resulting materials exhibited improved tensile strength compared to HPMDI-based PU but lower Young's modulus and increased elongation [32]. A team of Dutch researchers successfully acquired PU using bio-isocyanate. The procedure involved the utilization of two isocyanates: L-lysine diisocyanate ethyl ester (LLDI) and L-lysine triisocyanate ethyl ester (LLTI). The resulting compounds had a faint yellow hue, as LLDI and LLTI were pigmented. PU derived from LLDI exhibited greater flexibility than those derived from petrochemical isocyanate (IPDI). Regrettably, PUs derived from bio-based isocyanates exhibit a tendency to expand in the presence of organic solvents, unlike their petrochemical counterparts. Additionally, this study successfully obtained PU by combining bio-based and petrochemical isocyanates. The mechanical properties have been observed to depend on the ratio of substrates employed. The samples with a higher concentration of IPDI were characterized by their brittleness and hardness. Including bio-isocyanate resulted in the material undergoing a softening process and becoming more susceptible to breakage. However, PUs made from the LLDI/LLTI mixture exhibited the greatest distortion when subjected to the maximum load [33]. 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 attempts in research highlight a growing interest in harnessing bio-based resources for developing NIPU, a search powered by the necessity for sustainable, eco-friendly alternatives across various industrial domains [34]. 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.

1.1.3 Non-Isocyanate Polyurethanes (NIPUs)

The isocyanates, as raw material in PU synthesis, are produced from hazardous and toxic phosgene (Figure 1.3). Phosgene is an understated toxin as the smell may not be observed and symptoms may be slow to arrive. It is known to be a widely used chemical weapon during the First World War, accounting for a significant majority of fatalities. Isocyanates are formed from amines by the process called phosgenation. Moreover, the isocyanates themselves are toxic and moisture-sensitive and cannot be prepared without sophisticated safety devices and massive investments [35].



$$\underset{\text{amine}}{RNH_2} + \underset{\text{phosgene}}{COCl_2} \rightarrow \underset{\text{isocyanate}}{RNCO} + 2\,HCl$$

Figure 0.3 Synthesis of isocyanate through phosgenation

PUF production involves the generation of gas, usually carbon dioxide, which may promote the release of isocyanates as vapours or aerosols, whose exposure may result in detrimental health effects such as asthma and skin irritation. The Bhopal Gas Tragedy of December 1984 in India was one of the deadliest industrial accidents in history that resulted in the deaths of thousands of people due to the methyl isocyanate gas leak. This chemical disaster attracted worldwide attention and demonstrated the immediate and hazardous effects of isocyanates [36]. Isocyanates enter the body primarily through inhalation or skin exposure. The most extensively used isocyanates for PU production, MDI and TDI, are categorized as “very harmful” chemicals by the European Community. Perpetual exposure to MDI and TDI vapours leads to irritation in the skin, eyes, and respiratory tract. Additionally, throughout the storage and formation processes of moisture-curing PUs, the reaction between the isocyanate and water is bothersome, as it may cause moisture curing. In such systems, careful separation of these materials from the water becomes exceptionally essential to avoid an irreversible reaction between the polyisocyanate component and water, forming CO_2 and urea, thus resulting in an unusable, hardened product [37] (Figure 1.4).

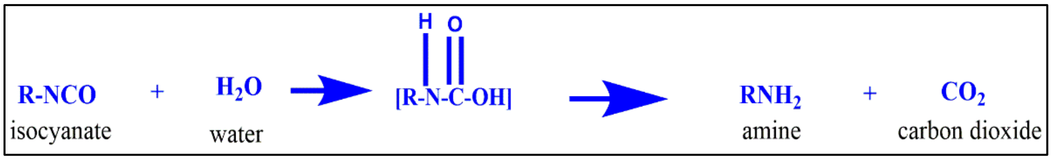


Figure 0.4 Reaction of isocyanate with water

Thus, modern researchers have recognized the need to eliminate the use of isocyanates and are looking for ways to employ environment-friendly alternatives. One such alternative is the synthesis of Non-isocyanate polyurethane (NIPU), a new type of PU that is safer and more promising than conventional PUs and is becoming a viable substitute for conventional PUs.

In 1957, Dyer and Scott documented the utilization of ethylene carbonate in the synthesis of polymeric urethanes [38]. The researchers discovered that bis(2-hydroxyethyl carbamate)s, derived from ethylene carbonate and primary diamines, have a tendency to release ethylene glycol when exposed to vacuum distillation through an alcohol at a temperature of 150 °C, in the presence of catalysts. The alcohol group could be a component of either the bis(2-hydroxyethyl carbamate) or a diol. In addition, they acquired PU derived from bis(2-hydroxyethyl carbamate), which was synthesized using ethylene carbonate and 1,6-diaminohexane. Efforts to utilize this combination in the production of N-substituted PUs using secondary diamines as a starting material were not successful. Furthermore, they synthesized N-substituted PUs using amino alcohols such as 1,10-aminodecanol or 4-aminomethylbenzyl alcohol, and ethylene carbonate by the creation of intermediates. Rokicki et al. synthesized PUs by performing a transurethanization process using bis(2-hydroxyethyl carbamate)s derived from ethylene carbonate and either 1,4-diaminobutane or 1,6-diaminohexane. They reacted these compounds with either 1,6-hexanediol or 1,10-decanediol, while employing tin catalysts [39]. The researchers analyzed the PUs and observed that, in addition to their urethane groups, the polymers also exhibited urea groups [40].

An alternative method for producing urethanes involves the transesterification process between urea and ethyl alcohol. Ethyl urethane, also known as $(C_2H_5)OCONH_2$, is a solvent used in industries. It is produced using this process and can be purchased commercially. Mandlecha et al. endeavoured to synthesize diols using ethanolamine, ethylene glycol, and urea. It was observed that carbon dioxide is the primary dicarboxylic acid. The diester of this compound is dimethyl carbonate, while its half ester half amide is urethane. As a diacid, it formed polycarbonate as one of its products, while half ester and half amides were formed as PURs. A sequence of diols through the chemical interaction of urea and monoethanolamine, as well as urea and ethylene glycol was prepared. This process resulted in the production of highly viscous diols, which could be crosslinked with melamine formaldehyde or diisocyanates. The resulting coatings were hard as well as flexible. Consequently, it is possible to create coatings that possess characteristics similar to urethane, either by completely eliminating the use of diisocyanates or by minimizing their usage, thereby significantly decreasing the associated risks [28]. Nevertheless, these reactions are also susceptible to producing unwanted byproducts, including carbamates, ethylene urea, ethylene carbonate, and 2-oxazolidone [39, 41, 42].

One example of the isocyanate-free routes of PU production is the synthesis of hydroxyurethane in the presence of cyclic carbonate and amines [43], which is regarded as the best alternative method to synthesize NIPU, as shown in Figure 1.5. Two isomers are generated in the reaction, one containing a secondary hydroxyl group and the other having a methylol group, each containing urethane and a hydroxyl group. These hydroxyl entities can develop intermolecular hydrogen bonds with the urethane group [44].

1.2 Merits of NIPU over PU

PU finds remarkable applications in paints, coatings, adhesives, and inks; for this, they are generally prepared in organic solvents. Consequently, large concentrations of hazardous air pollutants (HAPs) and volatile organic compounds (VOCs) evaporate in the atmosphere. Exposure to VOCs can cause health effects such as dizziness, headaches, cancer, irritation, etc. NIPU has many advantages over conventional PUs. Primarily, the elimination of the use of isocyanates. Besides this, the cyclic carbonates are derived from the natural sources available through epoxy resins and CO_2. Carbon dioxide is an inexpensive feedstock, and its utilization for PU production would also certainly assist to trim down Global Warming by reducing CO_2, which is a Greenhouse gas. Thus, the two problems can be solved at once- firstly the shortage of oil resources, and secondly, the greenhouse effect. So overall it stands by the laws for environmental protection [45].

1.3 Conventional Methods For Synthesis of NIPUs

It is possible to synthesize NIPUs on a laboratory and industrial scale, as they are inexpensive materials. A variety of methods can be used to synthesize NIPUs with desired physical and chemical properties for a wide range of applications. A schematic representation of the most commonly adopted methods for synthesizing NIPUs is illustrated in Figure 1.5.

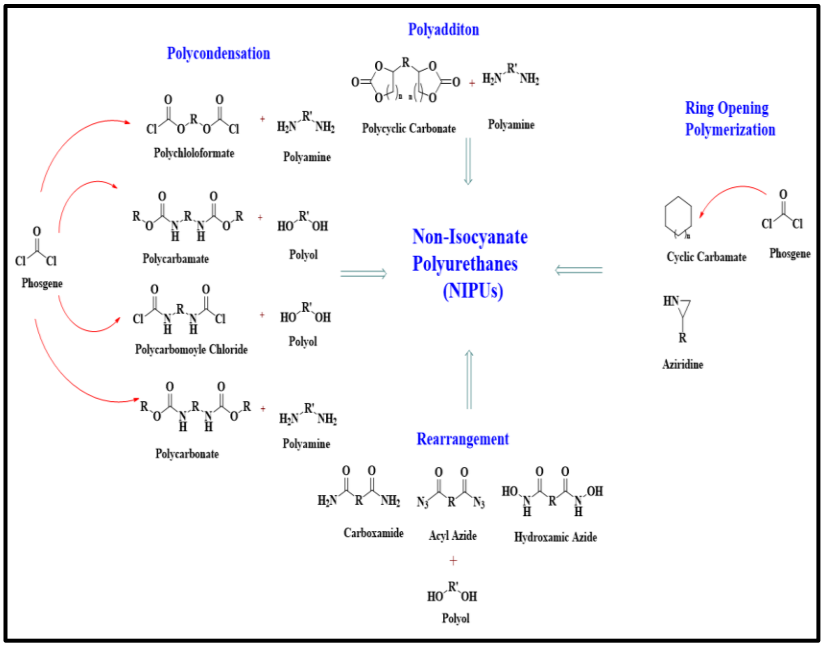


Figure 0.5 Conventional methods of synthesis of NIPUs.

1.3.1 Aminolysis Method

Aminolysis, is mainly a two-step procedure involving, (i). the development of the cyclic carbonate oligomers and then (ii) treating it with polyamines or amines resulting in the production of NIPU; as depicted in Figure 1.6. Step 1 includes the development of cyclic carbonate, i.e., one of the most competent ways of producing cyclic carbonate, by introducing the CO_2 within the epoxide group using a suitable catalyst, followed by second step, i.e., Treating this cyclic carbonate oligomer with a primary amine to provide NIPU, via an addition reaction after ring-opening. Moreover, if something more than cyclocarbonate is present in the cyclic carbonate oligomer, i.e., hydroxyl groups or epoxy groups, etc., then it is termed HNIPU, which has different properties than that acquired by NIPU [45]. This is the most widely used technique for the synthesis of isocyanate-free PUs; the procedure comprises the ring opening of a cyclic carbonate via polyamine, leading to the formation of hydroxypolyurethanes [46].

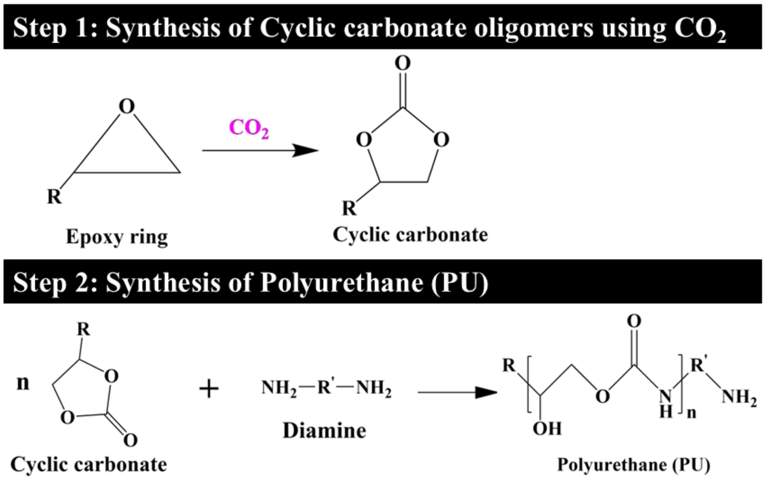


Figure 0.6 Process of aminolysis for the production of NIPU

Various attempts have been made to prepare NIPU from a wide variety of vegetable oils as shown in Table 1.3.

Table 0.3 Synthesis of NIPU from various oils

S. No	Oil	Reactants and catalyst	Reference
1	Soybean oil	CO_2, $SnCl_4.5H_2O$ and TBAB	[47]
2	Soy- and Iinseed oil	CO_2, TBAB and silica-supported 4-pyrrolidinopyridinium iodide (SiO_2 –(I))	[48]
3	Lignin and soybean oil	CO_2, TBAB	[49]
4	Soybean oil and bio-based aminated derivatives / fatty acids based oligoamides	Supercritical CO_2, TBAB	[50]
5	Jatropha curcas oil (JCO) and its alkyd resin	CO_2, TBAB	[51]
6	Sunflower oil	CO_2, solvent and catalyst free, EDA, DETA (Diethyltriamine) and IPDA	[52]
7	Canola oil	CO_2,5,10,15-tris(pentafluorophenyl)corrolato-manganese (III)	[53]

8	Jojoba and castor oils-	functionalized by thiol-ene coupling with thioglycolic acid, and then esterified with glycerol carbonate	[54]
9	Soybean Oil	CO_2, TBAB and $CaCl_2$, tetraethylenepentamine	[55]
10	Sunflower Oil	CO_2, TBAB, ZrO_2@SiO_2 nanofillers were incorporated in NIPU matrix	[56]
11	Tung Oil	Maleic Anhydride	[57]

1.3.2 Polycondensation Approach

Polycondensation approach is also a type of precipitation method. NIPUs are produced in this instance via a transurethanization reaction between polycarbamate and polyol [58]. Most commonly, phosgene is used to create polycarbamate; occasionally, alcohol and isocyanates are reacted to create the same compound [30, 59]. Therefore, the process of creating isocyanate PUs and NIPUs through transurethanization are similar. It is therefore advised to employ sustainable methods of generating polycarbamate. Using nitro chemicals [60], oxidative amines [61], and urea [62] are a few environmentally friendly methods of making this polycarbamate. The temperature at which the reaction is conducted is 130 °C. Through the poly-condensation of amines, halides, and carbon dioxide in the presence of Cs_2CO_3 and tetrabutylammonium bromide, Chen et al. recently produced NIPU that exhibited all the qualities equivalent to those of the PU made by utilizing isocyanate (the polycondensation of diols and diisocyanate) when they reacted with different diamines and dihalides at various optimum temperatures [63]. The commercial expansion of polycondensation has been restricted due to the requirement for a catalyst, longer reaction durations, product purification, low molecular weight byproduct generation, and occasionally hazardous byproducts [64].

1.3.3 Ring Opening Polymerisation

As the name implies, this process generates NIPU by polymerizing aziridine (also referred to as cyclic carbamate) [65] through ring-opening [66,67]. These are rings with six or seven members, and the polymerization process uses sodium hydride or N-acetylcaprolactam as a catalyst at a temperature of around 200 °C. Temperature determines the effectiveness of this reaction as well, which implies that the higher the temperature, the better the product is. An increasing temperature boosts the carbon dioxide content in the copolymer, which causes a corresponding increase in viscosity. A challenging aspect linked to this process isn't solely the elevated temperature but also the generation of cyclic carbamates, often originating from phosgene, consequently elevating toxicity levels to a relatively high degree [58]. The process of producing cyclic carbamates by green means is presently being investigated. Nonetheless, there isn't yet an efficient method for generating a less toxic aziridine ring.

1.3.4 Rearrangement Reactions for NIPU Synthesis

Several rearrangement reactions can be employed to synthesise NIPUs with desired properties. These rearrangements include Curtius, Hofmann, or Lossen. However, the isocyanate is produced during the course of the reaction, making these approaches equally as harmful as the conventional way of synthesising PUs [68]. In addition, halogens, particularly bromine and chlorine, augment the quantity of hazardous waste generated during the synthesis of these polymers.

In 1909, Stoermer initially synthesized aromatic PU through the thermal breakdown of p-hydroxybenzoylazide. However, no specific information regarding the experimental procedure was provided. When acyl azides are heated in a non-hydrolytic solvent, they undergo the Curtius rearrangement and form isocyanates [69]. These isocyanates then react with phenol OH groups, resulting in the formation of a PU.

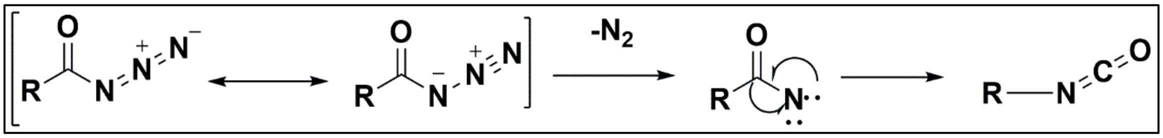


Figure 0.7 Curtius Rearrangement

A novel approach to produce PUs without harmful compounds has been suggested, involving the Lossen rearrangement. This process uses dimethyl carbonate as an activation molecule, along with methanol as the environment and a tertiary amine as the catalyst [63, 70, 71].

1.3.5 Carbamate Thermal Decarboxylation

Carbamate thermal decarboxylation is a new approach employed in the development of NIPU foams. The procedure entails utilizing monomers from carbonyldiimidazole (CDI), specifically bis-carbonylimidazolide (BCI) monomers. Bis-carbonylimidazole (BCI) monomers, 1,4-butyl(bis-carbonylimidazolide) (BBCI), 1,4-cyclohexanedimethyl(bis-carbonylimidazolide) (CHDMBCI) were synthesized using 1,1'-carbonyldiimidazole and the respective diol precursors. At temperatures above 140 °C, these monomers undergo β-hydrogen elimination, releasing a carbamic acid that then undergoes decarboxylation. This decarboxylation process generates a blowing agent on-site, and the resulting CO_2 can create a microcellular foam while also causing crosslinking. Including BCI difunctional monomers and trifunctional crosslinking agents makes producing NIPU foams with both rigid and flexible properties possible. By incorporating traditional surfactants and catalysts, it becomes possible to exercise precise control over the pore configuration of the foam. By adjusting the quantities of catalyst and surfactant, it is possible to develop a variety of foam compositions that can be either flexible or rigid. This approach follows the principles of green chemistry and enables the anticipation of performance by considering the underlying links between the structure, properties, and processes. The NIPUF derived from BCI exhibited an extraordinary mechanism for foam formation, featuring spontaneous decarboxylation during BCI crosslinking. This novel mechanism underwent CO_2 detection, firmly establishing the in-situ generation of CO_2 as the driving force behind foam development [72]. Table 1.4 shows comparative analysis between NIPUF generated using transurethanization approach and carbamate thermal decarboxylation method.

Table 0.4 Comparison between transurethanisation approach and carbamate thermal decarboxylation method

	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.

1.4 Applications of NIPU

As is widely recognized, PU, whether conventional or environmentally friendly, has a wide range of applications in the adhesive, sealant, paint, and coatings industries (Figure 1.8).

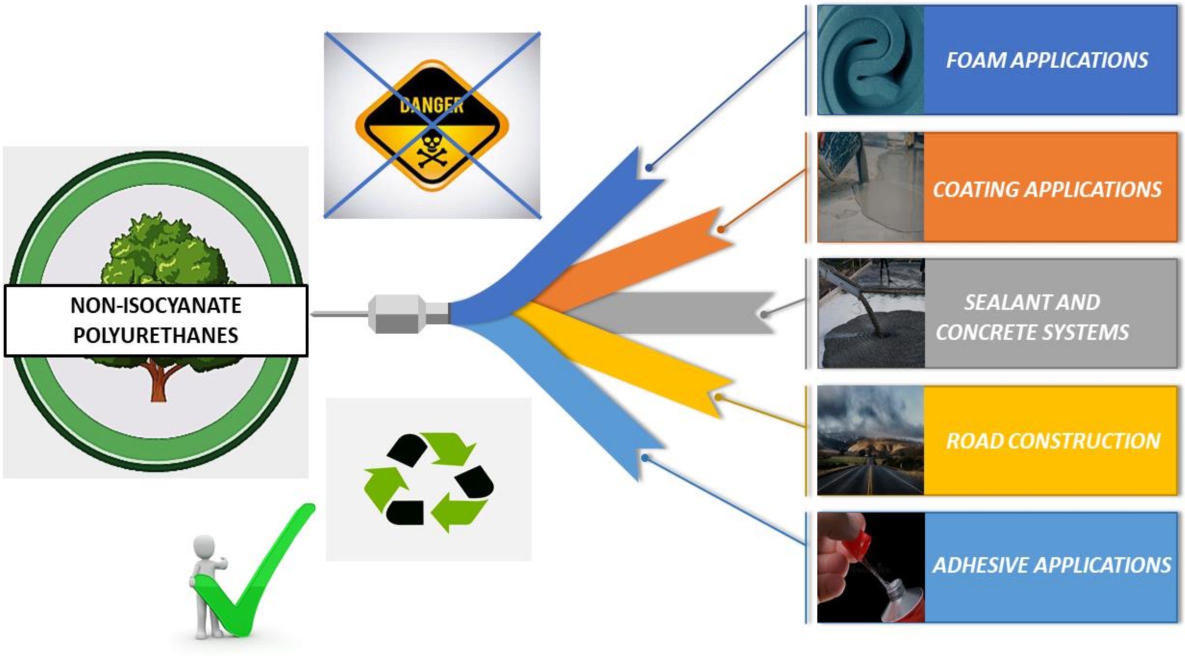


Figure 0.8 Applications of NIPU

1.4.1 NIPU Coatings

NIPU coatings, due to their impermeable structure, provide prolonged corrosion resistance against aggressive corrosive substances and offer greater durability than traditional PU coatings. Furthermore, compared to traditional PUs, NIPUs exhibit many beneficial features for corrosion protection. Unlike conventional PU, which produces isocyanurates, allophanates, urea, and biurets as byproducts (as shown in Figure 1.9), NIPU does not generate any side products. Additionally, in the case of NIPU, hydrolysis converts isocyanate into amine while simultaneously releasing CO_2. This CO_2 aids in the prevention of the formation of defects, such as pores and bubbles in coatings, which can be caused by the synthesis of VOCs [73].

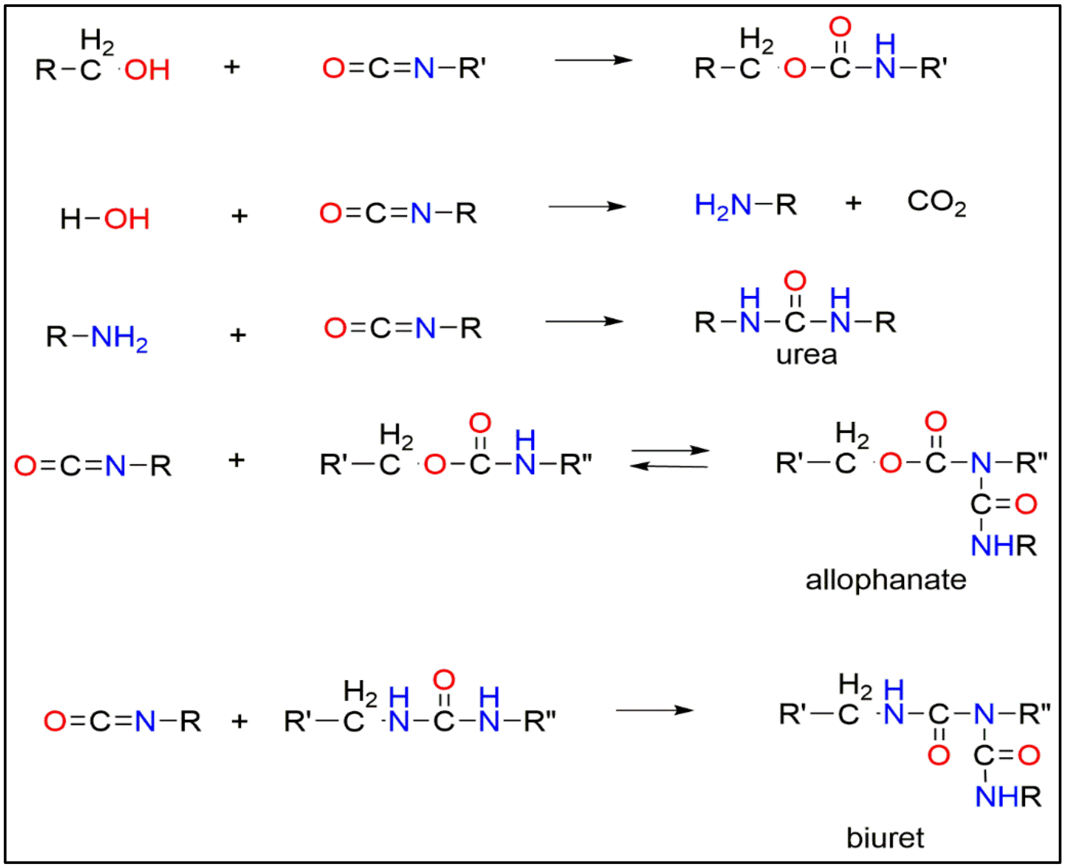


Figure 0.9 Side reactions of PU

In addition, they have superior adhesion characteristics to the metal substrate compared to traditional PU with comparable structures. This is primarily attributed to hydroxyl groups adjacent to the urethane bond. In addition, the presence of intramolecular and intermolecular hydrogen bonds results in the establishment of robust chemical bonding with the substrate, which enhances its chemical resistance. Wu et al. have produced coatings of fluorinated NIPUs by employing two cyclic carbonates, namely bisphenol AF (EC-AF) and perfluorooctyl cyclic carbonate (PFGC) [74]. Furthermore, they evaluated the coatings' hydrophobic, oleophobic, and corrosion-resistant characteristics. It has been observed that the NIPU attained from PFGC displayed excellent stain resistance and corrosion resistance capabilities, in comparison to the NIPU obtained from EC-AF. Mannari et al. have recently developed a UV-curable NIPU coating specifically designed for use in aerospace applications [75]. The performance attributes essential for aerospace applications, such as low-temperature flexibility and resistance, were assessed for the synthesized coatings. It was observed that the coatings did not develop any fractures or delamination and were able to maintain flexibility even at extremely low temperatures. Furthermore, there was no noticeable alteration in the appearance following a test of over 90 MEK double rubs, indicating excellent chemical resistance.

Kong et al. conducted a work where they synthesized a polyhedral oligomeric silsesquioxane (POSS) modified gallic acid-based NIPU (NIPU/POSS) [76]. The impact of POSS on the mechanical and thermal characteristics has been examined and revealed that the inclusion of POSS in the NIPU network enhanced the overall qualities, including water resistance, pencil hardness, and thermal stability, of NIPU/POSS. Hybrid Coating Technologies Inc., a company of PPG Industries Inc., has just introduced a new type of coating that utilizes Hybrid's zero isocyanate PU technology. These coatings have demonstrated exceptional corrosion resistance and have been determined to have superior longevity compared to those from other competitors [77].

1.4.2 NIPU Adhesives

The daily utilization of adhesives has significantly expanded across several industries such as footwear, woodworking, and automotive. Many adhesives are available in the market, mostly made from cyanoacrylate, epoxy resins, and PU. Due to their exceptional stickiness and flexibility, PU-based adhesives are currently in extensive use [78]. Nevertheless, researchers have shifted their focus towards NIPU-based adhesives due to the harmful consequences of isocyanate. These NIPU adhesives have the potential to rival traditional PU adhesives. Christophe et al. have documented the development of an adhesive from poly (hydroxyurethane) (PHU) that does not contain isocyanate. This adhesive was synthesized using a polyaddition reaction including tricyclic carbonate, hexamethylene diamine, and a catecholamine, which is a powerful adherent group [79]. The adhesion property of PHU was compared to that of standard PU, and it was observed that PHU exhibited strong adhesion but that of the synthesized PHU was poor. In a recent study, Xi et al. successfully produced a wood bonding adhesive called sucrose-based NIPU [80]. They have discovered that the product can be crosslinked by utilizing a silane coupling agent. This agent lowers the curing temperature, leading to improved adhesion properties. Furthermore, Alfonso et al. have thoroughly examined BPU and its suitability for use in adhesives [81]. In addition, Caillol and his team have successfully created PHUs without isocyanates. These PHUs have demonstrated excellent mechanical capabilities and strong adhesion to wood, aluminum, and glass surfaces [82, 83]. In addition, they have created

PU materials by polymerizing poly(propylene oxide) triol with hexamethylenediisocyante or 1, 3-bis(isocyanatomethyl)cyclohexane in order to compare their properties. Through their investigations, it was discovered that PHUs possess exceptional adhesion capabilities as a result of the hydroxyl groups attached to the primary polycarbonate chain.

1.4.3 Other Applications of NIPUs

The great potential of NIPU foams in a variety of industries, including packaging, bedding and furniture, the automotive sector, etc., has drawn attention in research and development. Only one study on linseed oil-based NIPU was published in the case of vegetable oil-based NIPU foams[84]. Apart from the restricted studies conducted on vegetable oil, there have been reports of alternative bio-material sources for the formation of NIPU foams. In a study, an aminolysis method was used to develop recyclable self-blown NIPU foams. Thiolactone and amines with cyclic carbonates have different chemistries, which are utilized in this approach. Through the reaction of a thiol with a cyclic carbonate, these reactants combine to form a polymer network, which leads to the in-situ formation of the blowing agent (CO_2). Several linkages, including primarily amides, thioethers, and hydroxyurethane, were formed inside the polymer network as a result of this process. The resulting foams displayed an open-cell shape and, depending on the formulation and reaction circumstances, can be flexible or stiff. This work showed that the foams could be easily reused by thermally treating them to produce films or structural composites. Remarkably, the foams may be formed and recycled without the need for a catalyst [85].

As a consequence of its non-toxic and biocompatible qualities, NIPU has been studied for use in biomedical applications. Regarding vegetable oil-based NIPU, Gholami and Yeganeh have developed antibacterial wound dressing membranes using soybean oil-based

NIPU that contains azetidinium groups [55]. Wang et al. recently reported the synthesis of photosensitive NIPU acrylate resin for the 3D printing of personalized biocompatible orthopedic surgical guides [86]. Higher heat stability, hemocompatibility, better biocompatibility to ME3T3-E1 bone cells and C1C12 muscle cells, and no immunogenic effect on macrophages were all displayed by NIPU acrylate in comparison to commercial photosensitive resins. Additionally, unlike the severe reaction generated by commercial resins, the NIPUA did not cause an inflammatory response following in vivo implantation. Another study conducted by Visser et al. detailed the electrospinning of NIPU using the transurethanization reaction between 1,6-hexanedicarbamate and polycarbonate diols. Primary human fibroblasts and a human epithelial cell line were used to test the cytotoxicity of these electrospun NIPU mats in order to determine their potential as biomimetic load-bearing pericardial substitutes in cardiac tissue engineering. The bare NIPU mats outperformed the collagen-functionalized NIPU mats in terms of cell adherence, showing superior performance even in the absence of further biofunctionalization. These findings suggest that the NIPU mats have a significant potential application in biomimetic scaffolds [87].

1.5 Significant Findings and Research Gap

NIPUs with varying structural properties have been synthesised using a variety of synthesis routes over the years, including aminolysis, polycondensation, ring opening polymerisation, rearrangement reactions, and thermal carbamate decarboxylation methods. However, each of these synthesis methods has its own set of drawbacks. In the case of NIPU synthesis via rearrangement reaction, the presence of harmful reactants such as hydroxamic azides, acyl azides and carboxamides makes this route less desirable. The transurethanisation method sometimes requires the employment of phosgene or isocyanate to produce carbamates. In addition, some sustainable methods of synthesis of carbamates exist such as by utilising amines, nitro compounds and urea. NIPUs with high molecular weight cannot be prepared via the polycondensation method. Also, the need for the purification of products and, at times, the production of toxic by-products hinders employing the synthesised NIPUs on a commercial scale. On the contrary, in the ring-opening polymerisation of aliphatic cyclic carbamates or aziridines, phosgene precursor is involved in the synthesis of cyclic carbamates and the toxicity of aziridines. Additionally, using extremely high temperatures can be challenging despite not generating any by-products.

Conventional methods of chemical synthesis of NIPUs are hindered by the use of extreme reaction conditions and toxic precursors. Therefore, an attempt has been made to fabricate novel NIPUs via polycondensation method without use of strong reagents and toxic precursors, under ambient conditions. To the best of our knowledge, a restricted literature is available on the synthesis of selected combinations of reactants and also their potential applications in the field of water treatment and drug delivery is not fully explored.

Aminolyis is one of the most widely used methods of synthesis for producing NIPU owing to its advantages such as high conversion rate, no involvement of hazardous isocyanates or phosgene, and enhanced resistance to organic solvents. Despite these advantages, aminolysis has limited practical applications due to its requirement of extremely high temperature and pressure, the need for a catalyst, and economic feasibility concerns. Therefore, numerous studies on the synthesis of NIPU by aminolysis have been reported during the last decades using multiple vegetable oils, including canola oil, castor oil, soyabean oil, jatropha oil, palm oil, tung oil, rapeseed oil, and cottonseed oil. However, the NIPUs, derived from different origins, exhibit incompetent mechanical strength to find any commercial applications. In light of all these limitations, as well as operational hurdles, it has been observed that such methods are required that have characteristics including low cost, high mechanical strength, and easy synthesizing and regeneration ability. Furthermore, the physicochemical properties of NIPUs and their composites suggest they are an ideal candidate for multiple applications such as coatings, adhesives, foams, blends etc.

1.6 Research Objectives

I. To Develop and optimize a novel, environment-friendly synthesis process for NIPU foams, using a bio-based crosslinker to significantly enhance flame retardancy.

II. To simplify the existing methods for the fabrication of porous NIPU materials to milder and scalable conditions, with an aim to lessen the need for sophisticated equipment and harsh processing conditions.

III. To develop and characterize NIPU blends with poly (vinyl alcohol) (PVA), with a focus on rheological and thermal properties to enhance material performance and sustainability.

IV. To design and synthesize NIPU-based hydrogels and assess their effectiveness in dye removal from wastewater and drug release applications.

1.7 References

[1] Deng Y, Dewil R, Appels L, Ansart R, Baeyens J, Kang Q. Reviewing the thermo-chemical

recycling of waste polyurethane foam. J Environ Manage 2021;278:111527. https://doi.org/10.1016/j.jenvman.2020.111527.

[2] Akindoyo JO, Beg MDH, Ghazali S, Islam MR, Jeyaratnam N, Yuvaraj AR. Polyurethane types, synthesis and applications-a review. RSC Adv 2016;6:114453–82. https://doi.org/10.1039/c6ra14525f.

[3] Pourmohammadi-Mahunaki M, Haddadi-Asl V, Roghani-Mamaqani H, Koosha M, Yazdi M. Effect of chain extender length and molecular architecture on phase separation and rheological properties of ether-based polyurethanes. Polym Bull 2022;79:8653–68. https://doi.org/10.1007/s00289-021-03907-3.

[4] Cornille A, Guillet C, Benyahya S, Negrell C, Boutevin B, Caillol S. Room temperature flexible isocyanate-free polyurethane foams. Eur Polym J 2016;84:873–88. https://doi.org/10.1016/j.eurpolymj.2016.05.032.

[5] Thébault M, Pizzi A, Essawy HA, Barhoum A, Van Assche G. Isocyanate free condensed tannin-based polyurethanes. Eur Polym J 2015;67:513–26. https://doi.org/10.1016/j.eurpolymj.2014.10.022.

[6] Kulkarni PMPA-PMPA-RD. Synthesis of Isostearic Acid/Dimer Fatty Acid-Based Polyesteramide Polyol for the Development of Green Polyurethane Coatings. J Polym Environ 2021;v. 29:54-70–2021 v.29 no.1. https://doi.org/10.1007/s10924-020-01849-x.

[7] Cheng Z, Li Q, Yan Z, Liao G, Zhang B, Yu Y, et al. Design and synthesis of novel aminosiloxane crosslinked linseed oil-based waterborne polyurethane composites and its physicochemical properties. Prog Org Coatings 2019.

[8] Kovács E, Turczel G, Szabó L, Varga R, Tóth I, Anastas PT, et al. Synthesis of 1,6-

Hexandiol, Polyurethane Monomer Derivatives via Isomerization Metathesis of Methyl Linolenate. ACS Sustain Chem Eng 2017;5:11215–20. https://doi.org/10.1021/acssuschemeng.7b03309.

[9] Liang, Haiyan; Feng, Yechang; Lu, Jingyi; Liu L. "Bio-based cationic waterborne polyurethanes dispersions prepared from different vegetable oils." AGRIS 2018;122. https://doi.org/https://doi.org/10.1016/j. indcrop.2018.06.006.

[10] Ochoa-Gómez OGA-OGA-JR. New approaches to producing polyols from biomass. J Chem Technol Biotechnol 2017; 92:705-711–2017. https://doi.org/10.1002/jctb.5149.

[11] Wang Y, Deng L, Fan Y. Preparation of Soy-Based Adhesive Enhanced by Waterborne Polyurethane: Optimization by Response Surface Methodology. Adv Mater Sci Eng 2018;2018:9253670. https://doi.org/10.1155/2018/9253670.

[12] Zuber M, Shah SAA, Jamil T, Asghar MI. Performance behavior of modified cellulosic fabrics using polyurethane acrylate copolymer. Int J Biol Macromol 2014;67:254–9. https://doi.org/10.1016/j.ijbiomac.2014.03.021.

[13] Kaur R, Kumar M. Function of silicon oil in the castor oil based rigid polyurethane foams. J Polym Eng 2013;33:875–80. https://doi.org/doi:10.1515/polyeng-2013-0083.

[14] Maisonneuve L, Chollet G, Grau E, Cramail H. Vegetable oils: a source of polyols for polyurethane materials. OCL 2016;23.

[15] Raydan ND, Leroyer L, Charrier B, Robles E. Recent Advances on the Development of Protein-Based Adhesives for Wood Composite Materials—A Review. Mol 2021;26. https://doi.org/10.3390/molecules26247617.

[16] Vanbésien, Théodore , Monflier, Eric , Hapiot F. Hydroformylation of vegetable oils: More

than 50 years of technical innovation, successful research, and development. Eur J Lipid Sci Technol 2016;118. https://doi.org/10.1002/ejlt.201500196.

[17] Paraskar PM, Prabhudesai MS, Hatkar VM, Kulkarni RD. Vegetable oil based polyurethane coatings – A sustainable approach: A review. Prog Org Coatings 2021;156:106267. https://doi.org/https://doi.org/10.1016/j.porgcoat.2021.106267.

[18] Paciorek-Sadowska J, Borowicz M, Isbrandt M, Czupryński B, Apiecionek Ł. The Use of Waste from the Production of Rapeseed Oil for Obtaining of New Polyurethane Composites. Polymers (Basel) 2019;11:1431. https://doi.org/10.3390/polym11091431.

[19] Kamairudin N, Hoong SS, Abdullah LC, Ariffin H, Biak DRA. Optimisation of Epoxide Ring-Opening Reaction for the Synthesis of Bio-Polyol from Palm Oil Derivative Using Response Surface Methodology. Molecules 2021;26:648. https://doi.org/10.3390/molecules26030648.

[20] Cao Y, Liu Z, Zheng B, Ou R, Fan Q, Li L, et al. Synthesis of lignin-based polyols via thiol-ene chemistry for high-performance polyurethane anticorrosive coating. Compos Part B Eng 2020;200:108295. https://doi.org/https://doi.org/10.1016/j.compositesb.2020.108295.

[21] Valero M, Gonzalez A. Polyurethane adhesive system from castor oil modified by a transesterification reaction. J Elastomers Plast 2012;44:433–42. https://doi.org/10.1177/0095244312437155.

[22] Delavarde A, Savin G, Derkenne P, Boursier M, Morales-Cerrada R, Nottelet B, et al. Sustainable polyurethanes: toward new cutting-edge opportunities. Prog Polym Sci 2024;151:101805. https://doi.org/10.1016/j.progpolymsci.2024.101805.

[23] Kaur R, Singh P, Tanwar S, Varshney G, Yadav S. Assessment of Bio-Based Polyurethanes:

Perspective on Applications and Bio-Degradation. Macromol 2022;2:284–314. https://doi.org/10.3390/macromol2030019.

[24] Recupido F, Lama GC, Ammendola M, Bossa FDL, Minigher A, Campaner P, et al. Rigid composite bio-based polyurethane foams: From synthesis to LCA analysis. Polymer (Guildf) 2023;267:125674. https://doi.org/10.1016/j.polymer.2023.125674.

[25] Banger A, Jangid NK, Srivastava A, Srivastava M. Polymeric Foams: Mechanisms and Properties. ACS Symp. Ser., vol. 1439, 2023, p. 43–61. https://doi.org/10.1021/bk-2023-1439.ch003.

[26] El Khezraji S, Ben youcef H, Belachemi L, Lopez Manchado MA, Verdejo R, Lahcini M. Recent Progress of Non-Isocyanate Polyurethane Foam and Their Challenges. Polymers (Basel) 2023;15. https://doi.org/10.3390/polym15020254.

[27] Wang Z, Yu L, Ding M, Tan H, Li J, Fu Q. Preparation and rapid degradation of nontoxic biodegradable polyurethanes based on poly(lactic acid)-poly(ethylene glycol)-poly(lactic acid) and l-lysine diisocyanate. Polym Chem 2011;2:601–7. https://doi.org/10.1039/C0PY00235F.

[28] Kathalewar MS, Joshi PB, Sabnis AS, Malshe VC. Non-isocyanate polyurethanes: From chemistry to applications. RSC Adv 2013;3:4110–29. https://doi.org/10.1039/c2ra21938g.

[29] Liu X, Wang X, Yao S, Jiang Y, Guan J, Mu X. Recent advances in the production of polyols from lignocellulosic biomass and biomass-derived compounds. Rsc Adv 2014;4: 49501-49520.

[30] Niesiobędzka J, Datta J. Challenges and recent advances in bio-based isocyanate production. Green Chem 2023;25:2482–504. https://doi.org/10.1039/d2gc04644j.

[31] Hojabri L, Kong X, Narine SS. Fatty Acid-Derived Diisocyanate and Biobased Polyurethane Produced from Vegetable Oil: Synthesis, Polymerization, and Characterization. Biomacromolecules 2009;10:884–91. https://doi.org/10.1021/bm801411w.

[32] Hojabri L, Kong X, Narine SS. Novel long chain unsaturated diisocyanate from fatty acid: Synthesis, characterization, and application in bio-based polyurethane. J Polym Sci Part A Polym Chem 2010;48:3302–10. https://doi.org/https://doi.org/10.1002/pola.24114.

[33] Konieczny J, Loos K. Green Polyurethanes from Renewable Isocyanates and Biobased White Dextrins. Polymers (Basel) 2019;11. https://doi.org/10.3390/polym11020256.

[34] Sahoo S, Mohanty S, Nayak SK. Biobased polyurethane adhesive over petroleum based adhesive: Use of renewable resource. J Macromol Sci Part A Pure Appl Chem 2018;55:36–48. https://doi.org/10.1080/10601325.2017.1387486.

[35] Vaish AK, Consul S, Agrawal A, Chaudhary SC, Gutch M, Jain N, et al. Accidental phosgene gas exposure: A review with background study of 10 cases. J Emerg Trauma Shock 2013;6:271–5. https://doi.org/10.4103/0974-2700.120372.

[36] Broughton E. The Bhopal disaster and its aftermath: a review. Environ Heal 2005;4:6. https://doi.org/10.1186/1476-069X-4-6.

[37] Alinejad M, Henry C, Nikafshar S, Gondaliya A, Bagheri S, Chen N, et al. Lignin-Based Polyurethanes: Opportunities for Bio-Based Foams, Elastomers, Coatings and Adhesives. Polymers (Basel) 2019;11:1202. https://doi.org/10.3390/polym11071202.

[38] Dyer E, Scott H. The Preparation of Polymeric and Cyclic Urethans and Ureas from Ethylene Carbonate and Amines. J Am Chem Soc 1957;79:672–5.

[39] Rokicki G, Piotrowska A. A new route to polyurethanes from ethylene carbonate, diamines and diols. Polymer (Guildf) 2002;43:2927–35. https://doi.org/10.1016/S0032-3861(02)00071-X.

[40] He X, Xu X, Wan Q, Bo G, Yan Y. Solvent- and Catalyst-free Synthesis, Hybridization and Characterization of Biobased Nonisocyanate Polyurethane (NIPU). Polymers (Basel) 2019;11. https://doi.org/10.3390/polym11061026.

[41] Bhanage BM, Fujita S, Ikushima Y, Arai M. Transesterification of urea and ethylene glycol to ethylene carbonate as an important step for urea based dimethyl carbonate synthesis. Green Chem 2003;5:429–32. https://doi.org/10.1039/B304182D.

[42] Ochiai B, Utsuno T. Non-isocyanate synthesis and application of telechelic polyurethanes via polycondensation of diurethanes obtained from ethylene carbonate and diamines. J Polym Sci Part A Polym Chem 2013;51:525–33. https://doi.org/https://doi.org/10.1002/pola.26418.

[43] Martínez de Sarasa Buchaca M, de la Cruz-Martínez F, Francés-Poveda E, Fernández-Baeza J, Sánchez-Barba LF, Garcés A, et al. Synthesis of Nonisocyanate Poly(hydroxy)urethanes from Bis(cyclic carbonates) and Polyamines. Polymers (Basel) 2022;14. https://doi.org/10.3390/polym14132719.

[44] Zhang T, Xue B, Yan Q, Yuan Y, Tan J, Guan Y, et al. New kinds of lignin/non-isocyanate polyurethane hybrid polymers: Facile synthesis, smart properties and adhesive applications. Ind Crops Prod 2023;199:116706. https://doi.org/https://doi.org/10.1016/j.indcrop.2023.116706.

[45] Rayung M, Ghani NA, Hasanudin N. A review on vegetable oil-based non isocyanate polyurethane: towards a greener and sustainable production route. RSC Adv 2024;14:9273–

99. https://doi.org/10.1039/d3ra08684d.

[46] Mangal M, Supriya H, Bose S, Banerjee T. Innovations in applications and prospects of non-isocyanate polyurethane bioplastics. Biopolymers 2023;114. https://doi.org/10.1002/bip.23568.

[47] Li Z, Zhao Y, Yan S, Wang X, Kang M, Wang J, et al. Catalytic synthesis of carbonated soybean oil. Catal Letters 2008;123:246–51. https://doi.org/10.1007/s10562-008-9414-8.

[48] Bähr M, Mülhaupt R. Linseed and soybean oil-based polyurethanes prepared via the non-isocyanate route and catalytic carbon dioxide conversion. Green Chem 2012;14:483–9. https://doi.org/10.1039/c2gc16230j.

[49] Lee A, Deng Y. Green polyurethane from lignin and soybean oil through non-isocyanate reactions. Eur Polym J 2015;63:67–73. https://doi.org/10.1016/j.eurpolymj.2014.11.023.

[50] Poussard L, Mariage J, Grignard B, Detrembleur C, Jéroîme C, Calberg C, et al. socyanate Polyurethanes from Carbonated Soybean Oil Using MonoNon-Imeric or Oligomeric Diamines to Achieve Thermosets or Thermoplastics. Macromolecules 2016;49:2162–71. https://doi.org/10.1021/acs.macromol.5b02467.

[51] Haniffa MACM, Ching YC, Chuah CH, Kuan YC, Liu DS, Liou NS. Synthesis, characterization and the solvent effects on interfacial phenomena of jatropha curcas oil based non-isocyanate polyurethane. Polymers (Basel) 2017;9. https://doi.org/10.3390/polym9050162.

[52] Doley S, Dolui SK. Solvent and catalyst-free synthesis of sunflower oil based polyurethane through non-isocyanate route and its coatings properties. Eur Polym J 2018;102:161–8. https://doi.org/10.1016/j.eurpolymj.2018.03.030.

[53] Malik M, Kaur R. Synthesis of NIPU by the carbonation of canola oil using highly efficient 5,10,15-tris(pentafluorophenyl)corrolato-manganese(III) complex as novel catalyst. Polym Adv Technol 2018;29:1078–85. https://doi.org/10.1002/pat.4219.

[54] Mokhtari C, Malek F, Manseri A, Caillol S, Negrell C. Reactive jojoba and castor oils-based cyclic carbonates for biobased polyhydroxyurethanes. Eur Polym J 2019;113:18–28. https://doi.org/10.1016/j.eurpolymj.2019.01.039.

[55] Gholami H, Yeganeh H. Soybean oil-derived non-isocyanate polyurethanes containing azetidinium groups as antibacterial wound dressing membranes. Eur Polym J 2021;142:110142. https://doi.org/10.1016/j.eurpolymj.2020.110142.

[56] Farid ME, El-Sockary MA, El-Saeed AM, Hashem AI, Abo Elenien OM, Selim MS, et al. An eco-friendly non-isocyanate polyurethane treated by CO2 as flame retardant nanocomposite coating/ZrO2@SiO2. Mater Res Express 2019;6. https://doi.org/10.1088/2053-1591/ab0da3.

[57] Huang Y, Pang L, Wang H, Zhong R, Zeng Z, Yang J. Synthesis and properties of UV-curable tung oil based resins via modification of Diels-Alder reaction, nonisocyanate polyurethane and acrylates. Prog Org Coatings 2013;76:654–61. https://doi.org/10.1016/j.porgcoat.2012.12.005.

[58] Figovsky O, Cornille A, Auvergne R, Boutevin B, Caillol S. Environment Friendly Polyurethanes : Nonisocyanate Synthesis 2016:1–39.

[59] Nowick JS, Powell NA, Nguyen TM, Noronha G. An improved method for the synthesis of enantiomerically pure amino acid ester isocyanates. J Org Chem 1992;57:7364–6. https://doi.org/10.1021/jo00052a069.

[60] Paul F. Catalytic synthesis of isocyanates or carbamates from nitroaromatics using Group VIII transition metal catalysts. Coord Chem Rev 2000;203:269–323. https://doi.org/https://doi.org/10.1016/S0010-8545(99)00230-1.

[61] Shi F, Deng Y. Polymer-Immobilized Gold Catalysts for the Efficient and Clean Syntheses of Carbamates and Symmetric Ureas by Oxidative Carbonylation of Aniline and Its Derivatives. J Catal 2002;211:548–51. https://doi.org/https://doi.org/10.1006/jcat.2002.3772.

[62] Chaturvedi D. Perspectives on the synthesis of organic carbamates. Tetrahedron 2012;68:15–45. https://doi.org/https://doi.org/10.1016/j.tet.2011.10.001.

[63] Chen Z, Hadjichristidis N, Feng X, Gnanou Y. Poly(urethane-carbonate)s from Carbon Dioxide. Macromolecules 2017;50:2320–8. https://doi.org/10.1021/acs.macromol.7b00142.

[64] Datta J, Włoch M. Progress in non-isocyanate polyurethanes synthesized from cyclic carbonate intermediates and di- or polyamines in the context of structure–properties relationship and from an environmental point of view. Polym Bull 2016;73:1459–96. https://doi.org/10.1007/s00289-015-1546-6.

[65] Hall HK, Schneider AK. Additions and Corrections Polymerization of Cyclic Esters, Urethans, Ureas and Imides. J Am Chem Soc 1959;81:6533. https://doi.org/10.1021/ja01533a619.

[66] Erhart K Drechsel. Polymerization of Cyclic Carbamates 1957:3.

[67] Ihata O, Kayaki Y, Ikariya T. Synthesis of Thermoresponsive Polyurethane from 2-Methylaziridine and Supercritical Carbon Dioxide. Angew Chemie - Int Ed 2004;43:717–

9. https://doi.org/10.1002/anie.200352215.

[68] Mouren A, Avérous L. Sustainable cycloaliphatic polyurethanes: from synthesis to applications. Chem Soc Rev 2023;52:277–317. https://doi.org/10.1039/d2cs00509c.

[69] Stoermer R. Umlagerung aromatischer Säureazide in Arylisocyanate. Berichte Der Dtsch Chem Gesellschaft 1909;42:3133–4. https://doi.org/https://doi.org/10.1002/cber.19090420332.

[70] Unverferth M, Kreye O, Prohammer A, Meier MAR. Renewable non-isocyanate based thermoplastic polyurethanes via polycondensation of dimethyl carbamate monomers with diols. Macromol Rapid Commun 2013;34:1569–74. https://doi.org/10.1002/marc.201300503.

[71] Kreye O, Wald S, Meier MAR. Introducing Catalytic Lossen Rearrangements: Sustainable Access to Carbamates and Amines. Adv Synth Catal 2013;355:81–6. https://doi.org/https://doi.org/10.1002/adsc.201200760.

[72] Sintas JI, Wolfgang JD, Long TE. Carbamate thermal decarboxylation for the design of non-isocyanate polyurethane foams. Polym Chem 2023;14:1497–506. https://doi.org/10.1039/D3PY00096F.

[73] Błażek K, Datta J. Renewable natural resources as green alternative substrates to obtain bio-based non-isocyanate polyurethanes-review. Crit Rev Environ Sci Technol 2019;49:173–211. https://doi.org/10.1080/10643389.2018.1537741.

[74] Wu Z, Tang L, Dai J, Qu J. Synthesis and properties of fluorinated non-isocyanate polyurethanes coatings with good hydrophobic and oleophobic properties. J Coatings Technol Res 2019;16:1233–41. https://doi.org/10.1007/s11998-019-00195-5.

[75] Zareanshahraki F, Asemani HR, Skuza J, Mannari V. Synthesis of non-isocyanate polyurethanes and their application in radiation-curable aerospace coatings. Prog Org Coatings 2020;138:105394. https://doi.org/https://doi.org/10.1016/j.porgcoat.2019.105394.

[76] Liu G, Wu G, Chen J, Huo S, Jin C, Kong Z. Synthesis and properties of POSS-containing gallic acid-based non-isocyanate polyurethanes coatings. Polym Degrad Stab 2015;121:247–52. https://doi.org/10.1016/j.polymdegradstab.2015.09.013.

[77] Boyer A, Cloutet E, Tassaing T, Gadenne B, Alfos C, Cramail H. Solubility in CO2 and carbonation studies of epoxidized fatty acid diesters: towards novel precursors for polyurethane synthesis. Green Chem 2010;12:2205–13. https://doi.org/10.1039/C0GC00371A.

[78] Sastri VR. 10 - Three-Dimensional Printing, Wearables, Medical Textiles, Adhesives, and Coatings. In: Sastri VRBT-P in MD (Third E, editor. Plast. Des. Libr., William Andrew Publishing; 2022, p. 381–421. https://doi.org/https://doi.org/10.1016/B978-0-323-85126-8.00004-7.

[79] Panchireddy S, Grignard B, Thomassin JM, Jerome C, Detrembleur C. Catechol Containing Polyhydroxyurethanes as High-Performance Coatings and Adhesives. ACS Sustain Chem Eng 2018;6:14936–44. https://doi.org/10.1021/acssuschemeng.8b03429.

[80] Xi X, Wu Z, Pizzi A, Gerardin C, Lei H, Zhang B, et al. Non-isocyanate polyurethane adhesive from sucrose used for particleboard. Wood Sci Technol 2019;53:393–405. https://doi.org/10.1007/s00226-019-01083-2.

[81] Tenorio-Alfonso A, Sánchez MC, Franco JM. A Review of the Sustainable Approaches in the Production of Bio-based Polyurethanes and Their Applications in the Adhesive Field. J

Polym Environ 2020;28:749–74. https://doi.org/10.1007/s10924-020-01659-1.

[82] Sudoł E, Kozikowska E. Mechanical Properties of Polyurethane Adhesive Bonds in a Mineral Wool-Based External Thermal Insulation Composite System for Timber Frame Buildings. Mater 2021;14. https://doi.org/10.3390/ma14102527.

[83] Cornille A, Michaud G, Simon F, Fouquay S, Auvergne R, Boutevin B, et al. Promising mechanical and adhesive properties of isocyanate-free poly(hydroxyurethane). Eur Polym J 2016;84:404–20. https://doi.org/https://doi.org/10.1016/j.eurpolymj.2016.09.048.

[84] Wang T, Deng H, Zeng H, Shen J, Xie F, Zhang C. Self-Blowing Non-isocyanate Polyurethane Foams from Cyclic Carbonate Linseed Oil. ACS Sustain Resour Manag 2024;1:462–70. https://doi.org/10.1021/acssusresmgt.3c00103.

[85] Monie F, Grignard B, Detrembleur C. Divergent Aminolysis Approach for Constructing Recyclable Self-Blown Nonisocyanate Polyurethane Foams. ACS Macro Lett 2022;11:236–42. https://doi.org/10.1021/acsmacrolett.1c00793.

[86] Wang Y, Zheng Z, Pathak JL, Feng W, Wu W, Yang C, et al. Fabrication and characterization of photosensitive non-isocyanate polyurethane acrylate resin for 3D printing of customized biocompatible orthopedic surgical guides. Int J Bioprinting 2023;9:684. https://doi.org/10.18063/ijb.684.

[87] Visser D, Bakhshi H, Rogg K, Fuhrmann E, Wieland F, Schenke-Layland K, et al. Green Chemistry for Biomimetic Materials: Synthesis and Electrospinning of High-Molecular-Weight Polycarbonate-Based Nonisocyanate Polyurethanes. ACS Omega 2022;7:39772–81. https://doi.org/10.1021/acsomega.2c03731.

Chapter 2

SYNTHESIS OF XYLOSE-BASED NON-ISOCYANATE POLYURETHANE FOAMS WITH REMARKABLE FIRE-RETARDANT PROPERTIES

2.1 Introduction

PU foams are essential materials in contemporary industry owing to their excellent adaptability, mechanical qualities, and thermal insulation capabilities. They make up 50% of the market for polymer foam and account for 67% of global PU utilization. PU foams serve many purposes such as acoustic insulation, automotive seating, mattresses, and thermal insulation [1]. Conventionally they are commonly produced by combining polyols and isocyanates through a process called polyaddition reaction. The manufacturing of PU foams is a widely recognized procedure, mainly due to their distinctive blend of qualities, including low density, high load-bearing ability, and exceptional insulation capabilities. Nevertheless, the dependence on isocyanates in conventional PU synthesis presents substantial health and environmental hazards. Consequently, there has been a notable increase in interest in the development of alternative methods for producing PU foam without the use of isocyanates [2].

An essential component of PU foam manufacture is the utilization of blowing agents. Blowing agents are necessary for forming the foam's cellular structure, offering lightweight and insulating characteristics. In earlier times, chlorofluorocarbons (CFCs) and hydrochlorofluorocarbons (HCFCs) were frequently employed as blowing agents precisely due to their high level of effectiveness [3]. Nevertheless, these compounds have been discovered to possess significant environmental consequences, such as depletion of the ozone layer and a high global warming potential [4]. Consequently, the utilization of CFCs and HCFCs has been gradually eliminated in accordance with global accords like the Montreal Protocol [5].

To address these environmental problems, the industry has transitioned to using alternative blowing agents, including hydrofluoroolefins, and natural blowing agents such as water, carbon dioxide, and hydrocarbons [6]. While natural blowing agents present a more environmentally friendly alternative, they still pose certain difficulties, such as flammability and the requirement for specific handling and equipment. Moreover, the depletion of non-renewable sources and the ramifications of global warming have prompted the innovators to create novel routes of PU production that have a minimal environmental impact and, thus, fulfilling all new environmental regulations [7]. Vegetable oil is the most often used renewable resource to generate commodities for PU products since it is widely accessible [8, 9]. Although these renewable sources have successfully yielded polyols, multiple studies have been carried out to incorporate various fillers and anti-flaming chemicals into these foams to enhance their anti-flammable, thermal, and mechanical abilities [5–12]. NIPU, a novel category of PU free from the harmful effects of isocyanates, were generated. NIPUs are traditionally synthesized in the presence of cyclic carbonate and diamines [15, 16]. The ring-opening reaction of bis-cyclic carbonates with diamines and polycondensation of carbamates are the two most frequently used approaches for producing NIPU [15]. The most promising strategy is the utilization of cyclic carbonates, which generate minimal chemical intermediates or by-products. The chemical resilience and hydrolytic stability of the polymers are enhanced, as additional hydroxyl groups are generated in the NIPU structure, in the ring-opening reaction [14]. Transurethane reactions, also called transcarbamoylation, are caused by the condensation of alcohol on carbamate, which leads to the formation of urethanes, often producing alcohols (with low molar masses) as a byproduct [16, 17]. However, there are other methods as well, which are relatively less explored; one such method involves the production of cyclic carbonates from dimethyl carbonate by reacting with o-hydroxyl compounds followed by reacting with a diamine. Since dimethyl carbonate is an environmentally compatible and non-toxic chemical, and the reaction takes place under simple circumstances, this route of manufacture is highly valued [18].

Despite the positive potential for the economic viability and environmental stewardship of NIPU, commercial production of NIPU has yet to be implemented. Research on NIPUs is currently flourishing, and the advanced characteristics of NIPUs are predominantly being used to develop coatings and cross-linked materials with prospective uses as thermosets or elastomers [19–22]. Nevertheless, due to the difficulty in foaming the NIPU matrix, existing examples of NIPU foams are relatively restricted. However, NIPU foams using tannin, glucose, lysine, and lignin have been reportedly prepared [18, 23, 24].

Due to the compelling rise in oil and natural gas prices, polymeric biomaterials, particularly agro-resource-based polymers, have progressed rapidly in recent years. After preprocessing and hydrolysis, the plant biomass hydrolyzates consist of various hexoses and pentoses. Even though the sugar content of hydrolyzates from different feedstocks varies, the dominant sugars present in most hydrolyzates from terrestrial plant biomass are glucose and xylose [25]. The motivation behind this study is to achieve an advanced understanding of how the alternative synthesis route influences the structure and properties of the PU foams, synthesized without isocyanates. Xylose is an agriculturally workable material that can be a feasible replacement for petroleum-based polymers in a life-cycle context. The prime focus of this research is to explore the viabilities of xylose in the synthesis of PU foams. The study reported here aims to employ an environmentally acceptable way to generate NIPU foams, derived from xylose. Citric acid is employed as a natural crosslinker in this study, since it is biodegradable, non-toxic, and completely safe during manufacture. Though many alternative techniques and renewable raw materials have previously been used to produce bio-based NIPU foams, no previous research has mentioned the development of xylose-based polyhydroxyurethanes (PHUs), by the processes of transcarbamoylation. Moreover, the exquisiteness of this investigation lies in the fact that these foams were synthesized at ambient pressure. Fourier transform infrared (FTIR) spectroscopy, Differential scanning calorimetry (DSC), wide-angle X-ray diffraction (WXRD), and Thermal Gravimetric Analysis (TGA), were used to explore the structure and mechanical properties of the synthesized foams. The limiting oxygen index (LOI) was used to determine the fire resistance of all foams.

2.2 Materials and methods

2.2.1 Materials

Carbamates were prepared by utilizing commercially available hexamethylene diamine (HMDA), which was acquired from Sigma Aldrich and utilized, as supplied. D-Xylose and dimethyl carbonate (DMC) were purchased from Loba Chemie (India) and utilized as received. Citric acid was purchased from TCI Chemicals (Belgium). All chemicals and solvents used in the analytical measurement procedures were of analytical grade and utilized exactly as received.

2.2.2 NIPU Foam Synthesis

In this study, NIPU foams with various combinations of precursors were prepared. The carbamates were prepared by the method already reported in the literature [26]. The reaction of DMC with HMDA was allowed to proceed for 60 minutes at 70 °C with continuous stirring, and the synthesized intermediate was termed RXCL. Further, an aqueous solution of D-xylose was added to a beaker containing RXCL and it was heated at 80 °C, with constant stirring for 20 minutes. During heating, the viscosity of the reaction mixture increased gradually, and its colour changed to dark brown. The beaker was then placed in the oven for 2 hours at 90 °C, and the resulting foamed product was labelled RXCO. A similar procedure was applied to prepare NIPU foams with citric acid. The dark brown reaction mixture was supplied with varying amounts of citric acid to prepare RXC1 and RXC2. The foaming beaker was then kept in the oven for 2 hours at 90 °C. Detailed formulations of the synthesized foams have been mentioned in Table 2.1. A schematic representation of the synthesis of Xylose-based NIPU Foam is as shown in Figure 2.1.

Table 0.1 Formulations of the synthesised products in the study

Sample	D-Xylose (g)	DMC (g)	HMDA (g)	Citric Acid(g)
RXCL	0	6	7	0
RXCO	13	6	7	0
RXC1	13	6	7	1
RXC2	13	6	7	2

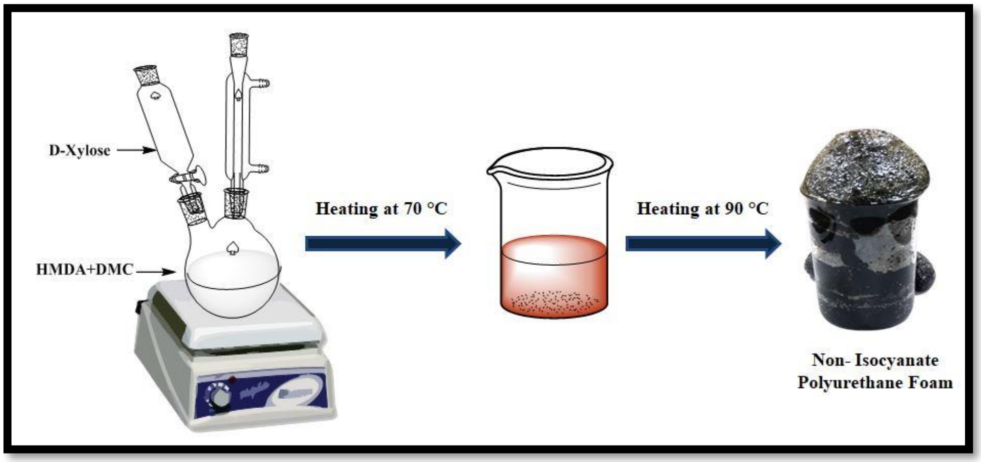


Figure 0.1 Schematic representation of the synthesis of Xylose-based NIPU Foam

2.2.3 Instrumentation

The morphology and structure of the developed foams were assessed by powder X-ray diffraction (PXRD), utilizing a high-resolution Bruker diffractometer (D8 Discover), coupled with a point detector (scintillation counter), using Cu K α radiation received via a Gobel mirror, that covers the range of 2θ = 5-80° with a scan rate of 1.0 second/step and step size 0.02° at 298 K. PerkinElmer 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. Each sample was scanned with 32 scans at a resolution of 4cm^{-1} in the wave number range of 600 to 4000 cm^{-1}, to record the spectrum. Thermogravimetric analysis (TGA) was employed to evaluate the thermal stability of the resulting NIPU foams (using TGA 4000, Perkin Elmer). Differential scanning calorimetry (DSC) was used to assess the thermal stability of the resulted foams using DSC 8000, Perkin Elmer. Nitrogen was used as a purge gas. To examine the glass transition temperature, the thermal characteristics were analyzed at 20°C min^{-1} in the range of -50 °C to 250°C. A scanning electron microscope (Jeol JSM-6610LVmodel) was used to examine the morphology and interior structure of the foams on a lateral cross-section to the rising direction of NIPU foam. Solid-state CP MAS 13C NMR was used to examine the powdered xylose foam. A Brüker AVANCE 400 MHz (Brüker, Billerica, MA, USA) spectrometer with a 4 mm probe was used to acquire the spectrum, at a frequency of 10 kHz. Chemical shifts were evaluated in comparison to tetramethyl silane (TMS). The spectrum was recorded with the spinning sideband suppression.

The rheological characteristics of pure NIPU and NIPU/Citric acid solutions were studied, at room temperature, using an Anton Paar Modular Compact Rheometer 302 (MCR). The shear-thinning behaviour was explored using a steady shear flow measurement, to determine the viscosity changes in a wide shear rate range (0.1–100 s^{-1}), using a 25 mm parallel plate geometry and 1 mm gap.

2.2.4 Apparent Density and Water Absorption Test

The apparent densities were calculated as the ratio of weight to cubic sample volume following the standards of ASTMD1622-08. Five samples were taken to determine an average. To explore the water absorption of the synthesized NIPU foams, four samples were evaluated for 24-hour water absorption and the effect of densities on water absorption was investigated [27].

2.2.5 Oxygen Index Test

The limiting oxygen index (LOI) was determined using an Oxygen index meter, according to the method described in the literature [23], (Fire Testing Technologies Ltd, United Kingdom). All of the samples were made to the specifications of 100 mm x 10 mm x 10 mm. The average LOI values for five samples of each formulation product were reported.

2.3 Results and Discussion

2.3.1 Preparation of Foams

The xylose-based NIPUs foams were prepared using a facile method at ambient pressure. The anticipated primary adducts created by various reactions that eventually lead to skeletal networks in the foam are presented in Figure 2.2. The addition of tricarboxylic citric acid serves a dual purpose as a crosslinking agent [28, 29] and a blowing agent [30] in the synthesis of NIPU. Citric acid-based foams generate their foaming energy through a relatively violent reaction between the citric acid group and the NH_2 group, which leads to self-blowing at room temperature. A three-dimensional network is formed as a result of this impact, causing the mixture's viscosity to rise sharply, followed by its gelation. The foaming action is caused by heating the reaction mixture at 70 °C in the case of foams prepared without citric acid.

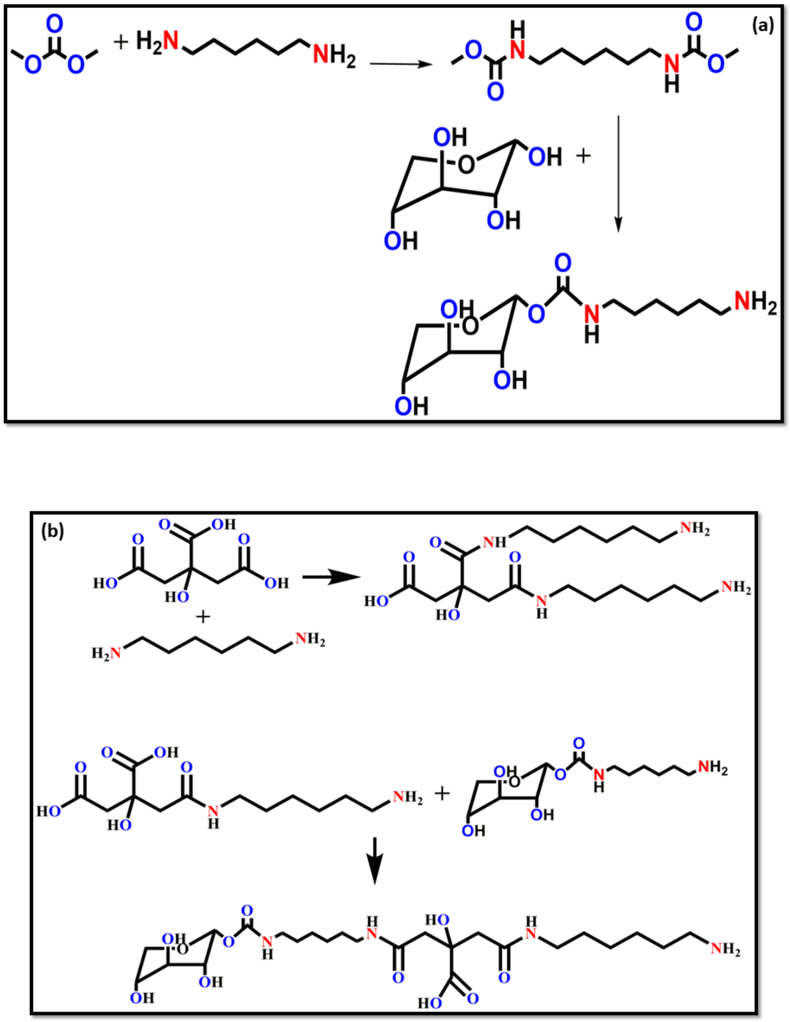


Figure 0.2 (a) Schematic representation of possible reaction mechanism for the synthesis of Xylose-based NIPU foams (b) Role of citric acid.

The prepared foams needed to be cured by heating, which is crucial for the accessability and stability of the synthesized foams and to examine their physical properties [23]. Furthermore, as the amount of citric acid increased, the apparent densities of the considered foams declined slightly, and water absorption decreased consecutively. The foaming energy generated by the interaction of citric acid with the $-NH_2$ groups is responsible for the decrease in foam density [18]. Increasing the amount of citric acid, on the other hand, can yield a smaller apparent density and, hence, a larger expansion volume, as shown in Table 2.2 [30].

Table 0.2 Apparent density and water absorption of Xylose-based NIPU foams

Sample	**Apparent Density (g/cm^3)**	**2 h Water Absorption (%)**	**Pore size Diameter (mm)**	**LOI Values (%)**
RXCO	0.974±0.13	421.246±46	1.11 ± 0.045	22.3% ± 0.11
RXC1	0.4676±0.14	353.823±35.17	1.82±0.33	23.99% ± 0.78
RXC2	0.303±0.16	319.420±31.05	1.95±0.08	26.9% ± 0.24

2.3.2 Structural Analysis

2.3.2.1 FTIR Analysis

Figure 2.3 displays the Fourier Transform Infrared (FT-IR) spectra of all foams to identify the functional groups in various foam preparations. The occurrence of a band around 1690 cm^{-1} in the FTIR spectrum of RXCL indicates the formation of carbamate linkage and confirms the methoxycarbonylation of HMDA with DMC. In the spectra of NIPU foams RXCO, RXC1, and RXC2, the occurrence of a characteristic band at 1693 cm^{-1} corresponds to urethane C=O bond formation [18, 34]. Furthermore, a band at 3340 cm^{-1} indicates the presence of hydroxyl groups and -NH-moiety of urethane groups. Additionally, the band at 1537 cm^{-1} is indicative of the urethane group, implying the formation of carbamate structures [23]. The analysis of FTIR spectra suggests that RXCL, RXCO, RXC1, and RXC2 have chemical structures that are comparable, but not identical to plain xylose and citric acid, hence indicating that the xylose-based- NIPU foams prepared using similar procedures have comparable spectra. This confirms that xylose-based NIPU foams have been successfully fabricated using a non-isocyanate method at atmospheric pressure.

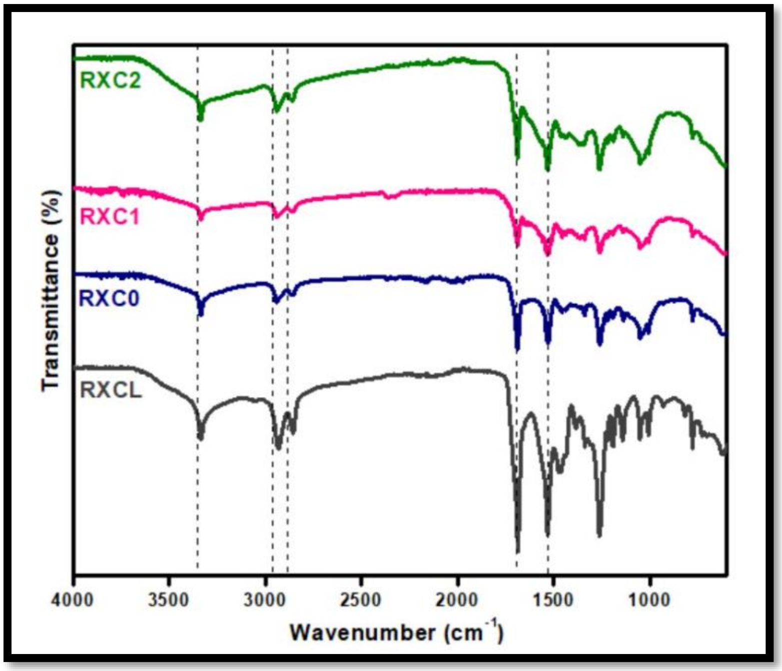


Figure 0.3 FTIR spectra of the synthesized products.

2.3.2.2 Cross-Polarisation Magic Angle Spinning ^{13}CNMR

The composition of the prepared foams was examined by solid-state Cross Polarization Magic Angle Spinning (CP MAS) ^{13}CNMR. Figure 2.4 displays the ^{13}CNMR spectrum of RXC0.The peaks at around 44.71 ppm and 30.56–28 ppm correspond to the methylene groups (–CH_2–) of the diamine chain, which are directly coupled and not attached to urethane groups, respectively. The presence of a peak at 42 ppm verifies the diamine reaction and the production of urethane groups, which is also confirmed by the FTIR spectrum of RXCO. The peak at 52.53 ppm appears due to the methyl group present in –COO–CH_3 moiety of unreacted carbonated xylose molecules. The notch around 70 ppm can be credited to the carbon atoms of the xylose ring. The peak at 158.24 ppm refers to the -C=O-linkage present in –NH–COO– moiety of the urethane bridge. This peak is extremely prominent, suggesting that the fraction of urethane produced is comparatively high in comparison to that of the 52.53 ppm peak [35].

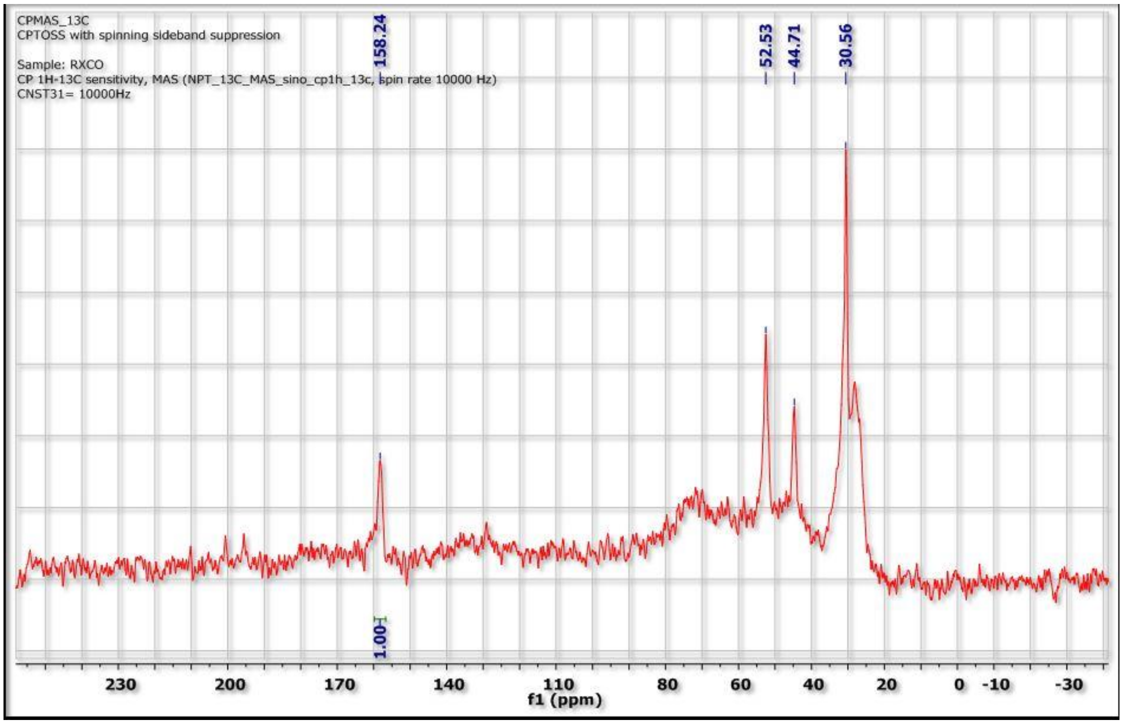


Figure 0.4 Solid State ^{13}CNMR of Xylose-based NIPU foam RXCO

2.3.2.3 Rheological Analysis

The shear-thinning characteristics were investigated by employing a steady shear flow measurement to analyze the changes in viscosity of the dark brown reaction mixture of RXCO, RXC1, and RXC2 in a wide range of shear rates (0.1-100 s^{-1}), using a 1mm gap and a 25 mm parallel plate. The steady shear profiles of samples before curing were studied at 25 °C and are presented in Figure 2.5. A significant increase in the viscosity was observed with the addition of citric acid, suggesting a resistance to the flow of the polymeric solutions.

The viscosity of polymeric solutions varied with polymer content, owing to the variation in polymer chain entanglement. RXC2, containing the highest concentration of citric acid, exhibited the highest viscosity at a low shear rate and displayed maximum shear thinning behaviour when subjected to high shear. The high viscosity may be a result of the existence of a highly entwined polymer structure in the solution due to the weak crosslinks developed by citric acid (before curing), that break down on the application of high shear and result in maximum shear thinning. While in RXCO, the low viscosity at low shear rates and the lowest shear thinning at high shear rates can be attributed to the lack of crosslinking in the absence of citric acid. The shear-thinning behaviour of these solutions demonstrates that the application of a high shear rate leads to disentanglement and even realignment of molecular chains in the blend solutions.

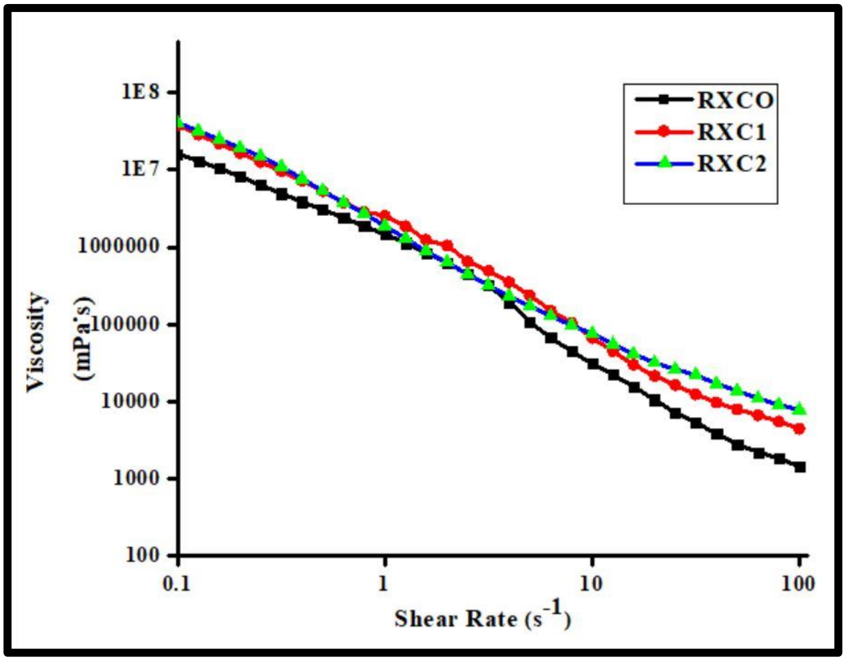


Figure 0.5 Plot of viscosity versus shear rate for the polymeric solutions of RXCO, RXC1, and RXC2.

2.3.3 SEM Analysis

The morphology of the foams synthesized with varying amounts of citric acid was examined by using SEM. Figure 2.6 displays the SEM micrographs of RXCO, RXC1, and RXC2, respectively. This suggests that all foams have a consistent cell morphology (closed cellular structure with few open cells). Figure 2.6 (b) and (c) show a considerable degree of open cell morphology in RXC1 and RXC2 compared to RXCO, which may be the result of the addition of citric acid in the resins during the preparation. The citric acid and HMDA reacted relatively vigorously producing greater energy, as a result of which more foamed material or larger foam cells appeared, as reported in other studies also [30]. A comparable pattern was observed while analyzing the apparent density of the prepared materials, which decreased with an increase in the amount of citric acid owing to the formation of larger pores, as depicted in Table 2 and Figure 2.6. In addition, some ruptures or wreckage can be seen in all prepared foams that can be attributed to the cutting step in sample preparation. It was observed that, with an increase in the citric acid concentration, the rigidity of synthesized foams increased linearly, due to the formation of stronger cell walls. Thus, the obtained products were extremely hard and exhibited resistance to mechanical force. Scattered debris can be seen in Figure 2.6 (c), and it was a result of cutting during sample preparation for SEM analysis.

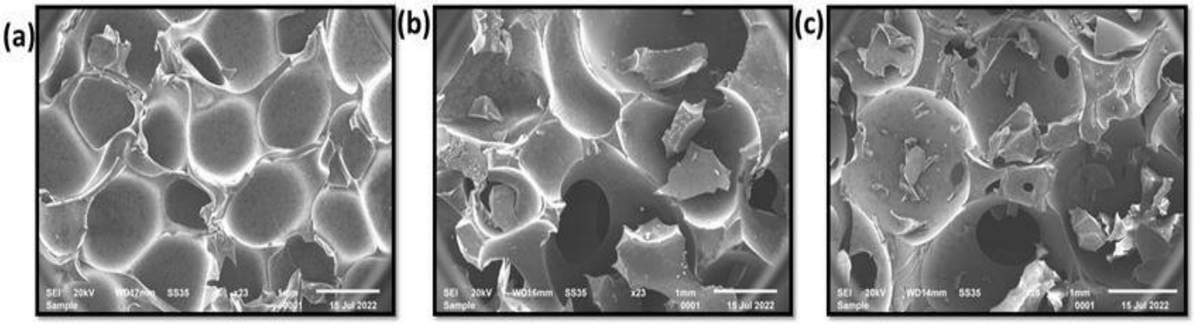


Figure 0.6 SEM images of (a) RXCO, (b) RXC1, (c) RXC2.

2.3.4 XRD Pattern Analysis

In the PXRD pattern presented in Figure 2.7, the presence of a dominant peak at 21° implies that the synthesized material is segmented PU (NIPUs in this case) and the broadness of the peak signifies the amorphous nature of the predominant phase. This is consistent with the previously reported values in the literature for segmented PUs [21–33]. This further confirms the observations drawn from DSC thermograms, as Tg is observed only in the case of polymers having an amorphous region as in the dominant phase contrary to crystalline polymers, that show sharp transitions related to melting temperature, not glass transition temperature.

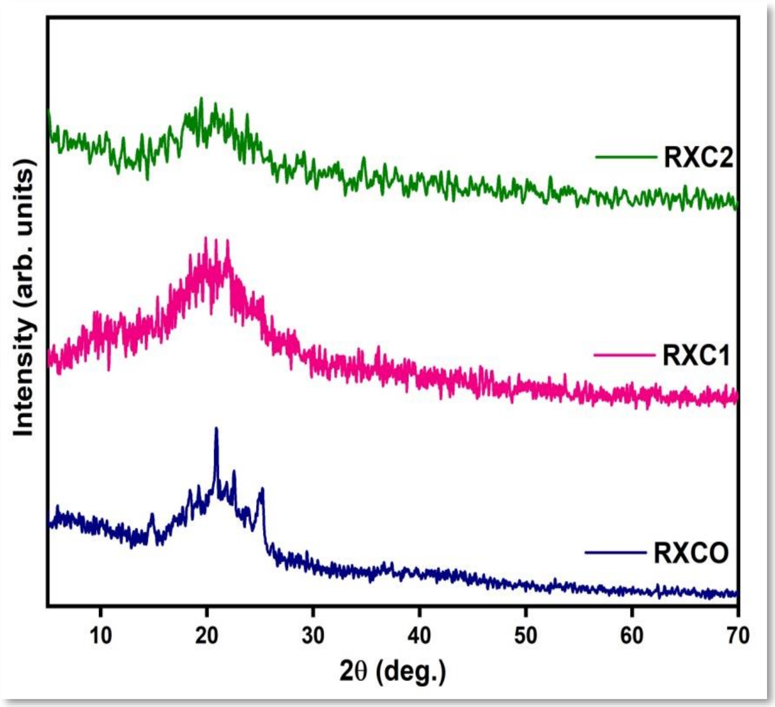


Figure 0.7 XRD pattern of the prepared NIPUs.

2.3.5 Thermal Characterisation

TGA was employed to evaluate the thermal stability of the synthesized NIPUs in a nitrogen (N_2) atmosphere across a temperature range of 25 to 900 °C and it showed a three-step mass loss, as presented in Figure 2.8 (a), (b) and (c). The initial weight loss step between 30 and 200 °C involves the decomposition of hexamine and excess acid as well as the discharge of absorbed water to 120 °C and evaporation of monomers/oligomers generated during the course of the reaction below 200°C [15, 32]. The second weight loss step observed between 200 and 275 °C occurs due to the fragmentation of the polymer backbone as a result of urethane bond cleavage. The final weight loss step occurring above 400 °C (as shown by DTG curves) involves more than 58 per cent mass loss. Possible fragmentation of C–C bonds and the degradation of pyrolysis remnant compounds from the prior two steps might have triggered this process. Similar results have been observed in the literature [38]. Figure 2.8 (a), (b) and (c) depict the respective degradation temperatures and residual masses of the prepared foams.

DSC measurements were carried out to determine the glass transition temperature (Tg) of the synthesized NIPU foams. The DSC thermogram, presented in Figure 2.8 (d), shows that the Tg of the synthesized NIPUs lies in the range of 109-112 °C and is similar to the data previously reported for NIPUs in literature [37]. Tg values of the synthesized NIPUs are higher than room temperature, suggesting a significant level of crosslinking by citric acid. Furthermore, the appearance of a singular Tg peak in the DSC curve of each sample suggests the existence of a homogenous phase in NIPU foam. Thus it can be inferred that the chemical structure of the curing agent has a considerable impact on the Tg values of NIPU foams and aids in tailoring their thermal properties [38].The role of citric acid as a blowing agent is demonstrated in the SEM micrographs of the synthesized NIPU foams (Figure 2.6) and that as a crosslinker is proven by DSC thermograms (Figure 2.8 (d)), rheology data (Figure 2.5), and also by LOI values (Table 2.2). Previous studies also suggest that citric acid is a widely reported crosslinker [23].

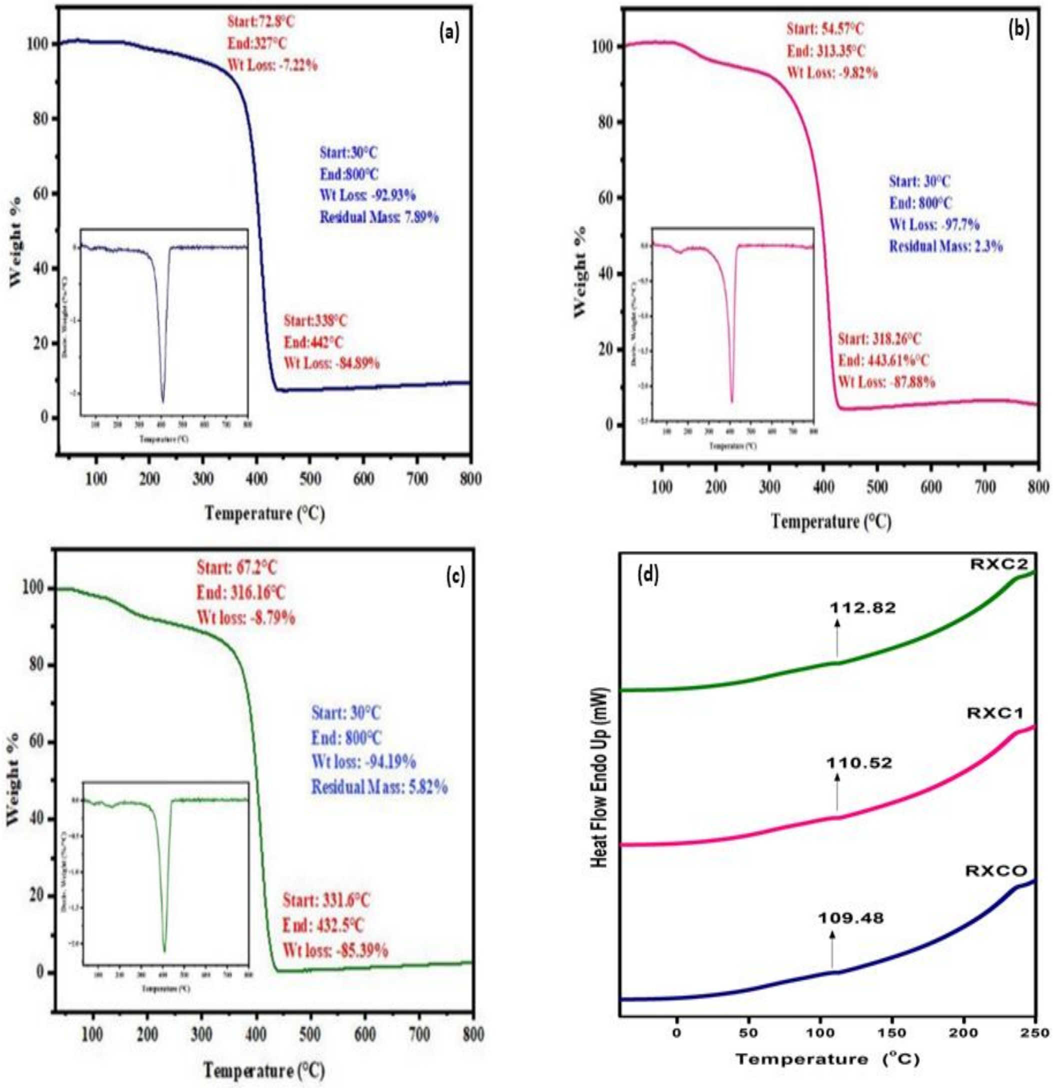


Figure 0.8 The TGA and DTG plots of (a) RXCO, (b) RXC1, (c) RXC2 and (d) DSC thermograms of the prepared foams.

2.3.6 Flame Retardant Properties

The limiting oxygen index (LOI) is used to measure the flame retardant behavior of polymeric materials by assessing the minimal oxygen concentration required for the combustion of polymer in a combined oxygen and nitrogen atmosphere. This technique continues to be one of the most crucial quality control and screening tools to evaluate both the flammability resistance and ignitability in plastics [39]. Materials exhibiting high LOI values show excellent flame retardancy. When the LOI value of a substance exceeds 27 percent, it is considered flame-retardant. Contrarily, a material is rendered inflammable, when the LOI value is less than 22 % [40]. Materials with an LOI of less than 21% are categorized as combustible, whereas those with an LOI of more than 22 are classified as self-extinguishing since their ignition cannot be perpetuated at ambient temperature without the addition of external energy [39].

The LOI values of each foam specimen were assessed, and the outcomes are presented in Table 2.2. The LOI values of plain xylose-based NIPU foam (RXCO) are around 22.3%, showing that this type of foam is not inflammable, but self-extinguishable. The LOI values of NIPU foams incorporated with citric acid were found to be 23.996% for RXC1 and 26.9% for RXC2 (Table 2.2 and Figure 2.9). The LOI values of the samples were increased markedly, as the amount of citric acid was increased. This can be attributed to the creation and densification of an isolation layer, that grew larger with increasing citric acid amount and generated a more intumescent char [41].

This phenomenon may be explained due to the shielding of the carbonaceous char layer shielding the PU surface from the flame. As a result, increasing the amount of citric acid in the foam results in a greater barrier effect, leading to the improved fire performance. This can be established by the fact that citric acid is also acting as a crosslinker here, as prior proven by DSC measurements. The higher the density of the crosslinked network, higher will be the amount of energy required to burn the sample under observation, since the three-dimensional structure will show resistance to burning [42]. As a consequence of which, RXC2 having the maximum amount of citric acid has the highest LOI value, inferring that citric acid is also enhancing the flame retardancy of the material. Similar data has already been documented in few previous studies [43, 44].

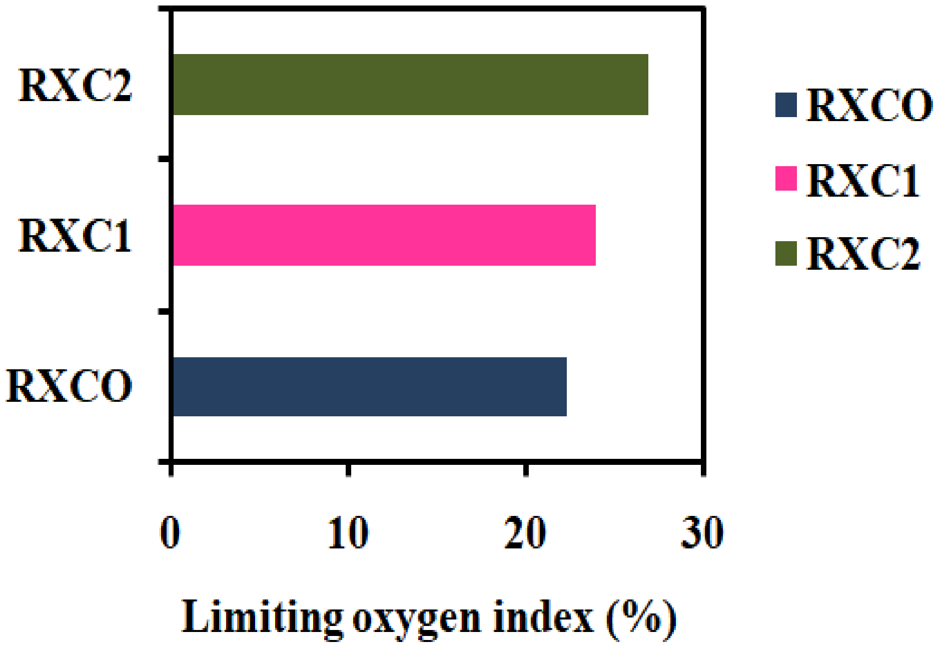


Figure 0.9 LOI values of the synthesised foams

2.4 Conclusions

Xylose-based NIPU foams have been prepared via transurethanisation (also known as transcarbamoylation). The methodology presented in this study allows for the production of sustainable PU foams using xylose as a feedstock and citric acid as a crosslinker and blowing agent, resulting in the materials with high bio-based content. It is observed that the inclusion of citric acid in various proportions in the NIPU foam can amplify the thermal stability and the fire retardancy of the xylose-based NIPU foams. According to the FTIR measurements, urethane linkages were produced in all foam compositions. Solid-state ^{13}C

NMR further confirmed the formation of the urethane bridge by displaying a distinctive apex at 158.24 ppm. The three types of foams, displayed comparable regular cell shapes, with lots of open pores visible, but the NIPU foams prepared without citric acid exhibited smaller mean cell sizes and closed cells when compared to the ones prepared using citric acid (RXC1 and RXC2); this could be due to the higher amount of foaming energy produced by citric acid.

The thermal stability of RXCO, RXC1, and RXC2 was nearly identical; however, RXC1 displayed slightly greater resistance to the applied temperature as observed in TGA data. The Tg of all the synthesized NIPU foams pertains to the range of 109-112 °C as observed from the DSC thermograms, indicating a considerable degree of crosslinking. The LOI values, determined to study the fire resistance of xylose-based NIPU foams, reported that the foam with highest citric acid content i.e., RXC2 exhibited the greatest LOI value i.e. 26.9 %, which is comparable to that of being a flame retardant (27%). In contrast, the LOI values of neat xylose-based NIPU foam (RXCO) are around 22.3%, indicating that they are inflammable.

The non-toxicity and simplicity of the methodology presented here overcomes some of the major challenges in NIPU chemistry, including low reactivity, longer reaction times, high temperature, high pressure and requirement of expensive equipments. This inexpensive, environment friendly and cost effective xylose-based NIPU is well suitable as a replacement of conventional isocyanate-based PU foams, by the incorporation of various reinforcing fillers, for commercial scale manufacturing as well as its significant potential status as "green material" for futuristic applications. As an outcome of this study, the futuristic approach can be the optimization studies focusing on more specific mechanical and physical properties. This novel, robust approach will also open up new possibilities for the construction of more sustainable PU foams and offers an alternative solution to the conventional isocyanate route due to the outstanding accessibility and diversity of the major components of the formulations.

2.5 References

[1] Kaur R, Singh P, Tanwar S, Varshney G, Yadav S. Assessment of Bio-Based Polyurethanes: Perspective on Applications and Bio-Degradation. Macromol 2022;2:284–314. https://doi.org/10.3390/macromol2030019.

[2] Datta J, Glowińska E, Wloch M. Mechanical Recycling via Regrinding, Rebonding, Adhesive Pressing, and Molding. Recycl. Polyurethane Foam., Elsevier; 2018, p. 57–65. https://doi.org/10.1016/b978-0-323-51133-9.00005-x.

[3] Albouy A, Roux J-D, Mouton D, Wu J. Development of HFC Blowing Agents. Part I: Polyurethane Foams. Cell Polym 1998;17:1–18. https://doi.org/10.1177/0262489319981702002.

[4] Kim K-H, Shon Z-H, Nguyen HT, Jeon E-C. A review of major chlorofluorocarbons and their halocarbon alternatives in the air. Atmos Environ 2011;45:1369–82. https://doi.org/https://doi.org/10.1016/j.atmosenv.2010.12.029.

[5] Simmonds PG, Rigby M, McCulloch A, O'Doherty S, Young D, Mühle J, et al. Changing trends and emissions of hydrochlorofluorocarbons (HCFCs) and their hydrofluorocarbon (HFCs) replacements. Atmos Chem Phys 2017;17:4641–55.

https://doi.org/10.5194/acp-17-4641-2017.

[6] Eling B, Tomović Ž, Schädler V. Current and Future Trends in Polyurethanes: An Industrial Perspective. Macromol Chem Phys 2020;221:1–11. https://doi.org/10.1002/macp.202000114.

[7] Maisonneuve L, Lamarzelle O, Rix E, Grau E, Maisonneuve L, Lamarzelle O, et al. Isocyanate-Free Routes to Polyurethanes and Poly (hydroxy Urethane) s To cite this version : HAL Id : hal-01365096 Isocyanate-free routes to polyurethanes and poly (hydroxy urethane) s 2019.

[8] Agrawal A, Kaur R, Walia RS. PU foam derived from renewable sources: Perspective on properties enhancement: An overview. Eur Polym J 2017;95:255–74. https://doi.org/10.1016/j.eurpolymj.2017.08.022.

[9] Agrawal A, Kaur R, Walia RS. Development of vegetable oil-based conducting rigid PU foam. E-Polymers 2019;19:411–20. https://doi.org/doi:10.1515/epoly-2019-0042.

[10] Agrawal A, Kaur R, Walia R. Flame retardancy of ceramic-based rigid polyurethane foam composites. J Appl Polym Sci 2019;136:48250. https://doi.org/10.1002/app.48250.

[11] Kaur R, Kumar M. Function of silicon oil in the castor oil based rigid polyurethane foams. J Polym Eng 2013;33:875–80. https://doi.org/doi:10.1515/polyeng-2013-0083.

[12] Kumar M, Kaur R. Glass fiber reinforced rigid polyurethane foam: Synthesis and characterization. E-Polymers 2017;17. https://doi.org/10.1515/epoly-2017-0072.

[13] Agrawal A, Kaur R. Effect of Nano Filler on the Flammability of Bio-Based RPUF. Integr Ferroelectr 2019;202:20–8. https://doi.org/10.1080/10584587.2019.1674820.

[14] Malik M, Kaur R. Influence of aliphatic and aromatic isocyanates on the properties of poly(ether ester) polyol based PU adhesive system. Polym Eng Sci 2018;58:112–7. https://doi.org/https://doi.org/10.1002/pen.24537.

[15] Malik M, Kaur R. Synthesis of NIPU by the carbonation of canola oil using highly efficient 5,10,15-tris(pentafluorophenyl)corrolato-manganese(III) complex as novel catalyst. Polym Adv Technol 2018;29:1078–85. https://doi.org/10.1002/pat.4219.

[16] Kathalewar MS, Joshi PB, Sabnis AS, Malshe VC. Non-isocyanate polyurethanes: From chemistry to applications. RSC Adv 2013;3:4110–29. https://doi.org/10.1039/c2ra21938g.

[17] Rokicki G, Parzuchowski PG, Mazurek M. Non-isocyanate polyurethanes: Synthesis, properties, and applications. Polym Adv Technol 2015;26:707–61. https://doi.org/10.1002/pat.3522.

[18] Maisonneuve L, Lamarzelle O, Rix E, Grau E, Cramail H. Isocyanate-Free Routes to Polyurethanes and Poly(hydroxy Urethane)s. Chem Rev 2015;115:12407–39. https://doi.org/10.1021/acs.chemrev.5b00355.

[19] Monie F, Grignard B, Thomassin JM, Mereau R, Tassaing T, Jerome C, et al. Chemo- and Regioselective Additions of Nucleophiles to Cyclic Carbonates for the Preparation of Self-Blowing Non-Isocyanate Polyurethane Foams. Angew Chemie - Int Ed 2020;59:17033–41. https://doi.org/10.1002/anie.202006267.

[20] Xi X, EPizzi A, Gerardin C, Lei H, Chen X, Amirou S. Preparation and evaluation of glucose based non-isocyanate polyurethane self-blowing rigid foams. Polymers (Basel) 2019;11. https://doi.org/10.3390/polym11111802.

[21] Bähr M, Mülhaupt R. Linseed and soybean oil-based polyurethanes prepared via the non-isocyanate route and catalytic carbon dioxide conversion. Green Chem 2012;14:483–9. https://doi.org/10.1039/c2gc16230j.

[22] Doley S, Dolui SK. Solvent and catalyst-free synthesis of sunflower oil based polyurethane through non-isocyanate route and its coatings properties. Eur Polym J 2018;102:161–8. https://doi.org/10.1016/j.eurpolymj.2018.03.030.

[23] Huang Y, Pang L, Wang H, Zhong R, Zeng Z, Yang J. Synthesis and properties of UV-curable tung oil based resins via modification of Diels-Alder reaction, nonisocyanate polyurethane and acrylates. Prog Org Coatings 2013;76:654–61. https://doi.org/10.1016/j.porgcoat.2012.12.005.

[24] Panchireddy S, Grignard B, Thomassin JM, Jerome C, Detrembleur C. Catechol Containing Polyhydroxyurethanes as High-Performance Coatings and Adhesives. ACS Sustain Chem Eng 2018;6:14936–44. https://doi.org/10.1021/acssuschemeng.8b03429.

[25] Chen X, Li J, Xi X, Pizzi A, Zhou X, Fredon E, et al. Condensed tannin-glucose-based NIPU bio-foams of improved fire retardancy. Polym Degrad Stab 2020;175:109121. https://doi.org/10.1016/j.polymdegradstab.2020.109121.

[26] Clark JH, Farmer TJ, Ingram IDV, Lie Y, North M. Renewable Self-Blowing Non-Isocyanate Polyurethane Foams from Lysine and Sorbitol. European J Org Chem

2018;2018:4265–71. https://doi.org/10.1002/ejoc.201800665.

[27] Kim SR, Ha SJ, Wei N, Oh EJ, Jin YS. Simultaneous co-fermentation of mixed sugars: A promising strategy for producing cellulosic ethanol. Trends Biotechnol 2012;30:274–82. https://doi.org/10.1016/j.tibtech.2012.01.005.

[28] Li HQ, Cao Y, Li XT, Wang LG, Li FJ, Zhu GY. Heterogeneous catalytic methoxycarbonylation of 1,6-hexanediamine by dimethyl carbonate to dimethylhexane-1,6-dicarbamate. Ind Eng Chem Res 2014;53:626–34. https://doi.org/10.1021/ie4029945.

[29] Xi X, Pizzi A, Gerardin C, Du G. Glucose-biobased non-isocyanate polyurethane rigid foams. J Renew Mater 2019;7:301–12. https://doi.org/10.32604/jrm.2019.04174.

[30] Yao S, Wang BJ, Weng YM. Preparation and characterization of mung bean starch edible films using citric acid as cross-linking agent. Food Packag Shelf Life 2022;32:100845. https://doi.org/10.1016/j.fpsl.2022.100845.

[31] Garcia PS, Eiras Grossmann MV, Yamashita F, Mali S, Dall'Antonia LH, Barreto WJ. Citric acid as multifunctional agent in blowing films of starch/PBAT. Quim Nova 2011;34:1507–10. https://doi.org/10.1590/S0100-40422011000900005.

[32] Chen X, Xi X, Pizzi A, Fredon E, Zhou X, Li J, et al. Preparation and characterization of condensed tannin non-isocyanate polyurethane (NIPU) rigid foams by ambient temperature blowing. Polymers (Basel) 2020;12. https://doi.org/10.3390/POLYM12040750.

[33] Rokicki G, Piotrowska A. A new route to polyurethanes from ethylene carbonate,

diamines and diols. Polymer (Guildf) 2002;43:2927–35. https://doi.org/10.1016/S0032-3861(02)00071-X.

[34] Xi X, Pizzi A, Delmotte L. Isocyanate-free polyurethane coatings and adhesives from mono- and di-saccharides. Polymers (Basel) 2018;10:1–21. https://doi.org/10.3390/polym10040402.

[35] He X, Xu X, Wan Q, Bo G, Yan Y. Solvent- and Catalyst-free Synthesis , Hybridization and Characterization of Biobased Nonisocyanate Polyurethane (NIPU) 2019. https://doi.org/10.3390/polym11061026.

[36] Lei W, Fang C, Zhou X, Li Y, Pu M. Polyurethane elastomer composites reinforced with waste natural cellulosic fibers from office paper in thermal properties. Carbohydr Polym 2018;197:385–94. https://doi.org/10.1016/j.carbpol.2018.06.036.

[37] Gandara M, Mulinari DR, Monticeli FM, Capri MR. Sugarcane Bagasse Fibers Reinforced in Polyurethane for Sorption of Vegetal Oil. J Nat Fibers 2020;00:1–12. https://doi.org/10.1080/15440478.2019.1710653.

[38] Jiao L, Xiao H, Wang Q, Sun J. Thermal degradation characteristics of rigid polyurethane foam and the volatile products analysis with TG-FTIR-MS. Polym Degrad Stab 2013;98:2687–96. https://doi.org/10.1016/j.polymdegradstab.2013.09.032.

[39] Zhang L, Luo X, Qin Y, Li Y. A novel 2,5-furandicarboxylic acid-based bis(cyclic carbonate) for the synthesis of biobased non-isocyanate polyurethanes. RSC Adv 2017;7:37–46. https://doi.org/10.1039/c6ra25045a.

[40] Eltayeb M, Li SX, Okoye PU, Wang S. Carbodiimide-Assisted Synthesis of High

Purity Bis(cyclic carbonate) Under Atmospheric Conditions for Preparation of Non-Isocyanate Polyurethane. J Polym Environ 2021;29:1880–93. https://doi.org/10.1007/s10924-020-01996-1.

[41] John MJ. Flammability performance of biocomposites. Green Compos Automot Appl 2018:43–58. https://doi.org/10.1016/B978-0-08-102177-4.00002-1.

[42] Liu J, Chen RQ, Xu YZ, Wang CP, Chu FX. Resorcinol in high solid phenol−formaldehyde resins for foams production. J Appl Polym Sci 2017;134:1–11. https://doi.org/10.1002/app.44881.

[43] Acuña P, Li Z, Santiago-Calvo M, Villafañe F, Rodríguez-Perez M ángel, Wang DY. Influence of the characteristics of expandable graphite on the morphology, thermal properties, fire behaviour and compression performance of a rigid polyurethane foam. Polymers (Basel) 2019;11. https://doi.org/10.3390/polym11010168.

[44] Liu J, Safronava N, Lyon RE, Maia J, Ishida H. Enhanced Thermal Property and Flame Retardancy via Intramolecular 5-Membered Ring Hydrogen Bond-Forming Amide Functional Benzoxazine Resins. Macromolecules 2018;51:9982–91. https://doi.org/10.1021/acs.macromol.8b02033.

[45] Mengal N, Syed U, Malik SA, Ali Sahito I, Jeong SH. Citric acid based durable and sustainable flame retardant treatment for lyocell fabric. Carbohydr Polym 2016;153:78–88. https://doi.org/10.1016/j.carbpol.2016.07.074.

[46] Kaya M. Super absorbent, light, and highly flame retardant cellulose-based aerogel crosslinked with citric acid. J Appl Polym Sci 2017;134:1–9.

https://doi.org/10.1002/app.45315.

Chapter 3

ONE POT SYNTHESIS OF BIO-BASED POROUS ISOCYANATE-FREE POLYURETHANE MATERIALS

3.1 Introduction

Porous PU materials are exceedingly versatile materials that have the potential to serve in a wide range of applications across various industries [1]. These materials are capable of offering a unique combination of properties, including high strength, flexibility, durability, and thermal stability [2]. High-density porous PU materials are suitable for applications where strength and load-bearing capacity are critical [3].

Since these compounds are detrimental to humans and the environment, hence as an outcome, the development of biomass-based polymers and the creation of ecologically benign and sustainable materials are becoming increasingly popular [4]. Extensive research has been conducted on synthesising NIPU materials due to the increasing need for sustainable and ecologically friendly PU products [5]. Conventional methods of NIPU synthesis generally involve the reaction of cyclic carbonates with amines to form urethane linkages without isocyanates [6]. Despite the growing number of articles on NIPU and polyhydroxy-urethane chemistry, limited studies focus on porous NIPU material synthesis. In the dearth of isocyanate groups, NIPU does not allow for foaming in the presence of water via the release of CO_2, as is the case with isocyanate-based PU preparation [7]. However, a simplified process for producing NIPUs is to react bio-materials including sugars [8], lignin [9], and tannins [10] just with dimethyl carbonate, which eliminates the need for cyclization of carbonate and diamine. A recent study reports the synthesis of a bio-based NIPU foam using glucose, dimethyl carbonate, and diamine as precursors [11]. Carbohydrates are an especially valuable raw material among the many renewable resources since it is cost-effective, easily accessible, and offer a wide range of stereochemical variety [12].

Despite having multiple advantages, this method often necessitates harsh reaction conditions, including high temperatures and pressures, to achieve satisfactory reaction rates and yields [7]. Furthermore, using expensive catalysts further complicates the process, making it less economically viable for large-scale production [13]. Additionally, these catalysts can pose environmental and disposal challenges, contradicting the green chemistry principles NIPU synthesis strives to uphold [14].

Extending the foundation established based on these challenges, the current chapter explores a novel, catalyst-free, one-pot synthesis method for PU-based porous materials. This method—often referred to as "one-pot"—can be used for any multi-step synthesis, reaction, or procedure. It works by avoiding many purification stages at once and allowing multiple synthetic transformations and bond-formations to be completed in a single pot. Thus, a one-pot process can minimise chemical waste, save time, and make practical aspects comparatively facile. In actuality, synthetic organic chemistry has historically employed this strategy extensively. This method addresses several key challenges of traditional NIPU synthesis by eliminating the need for catalysts and combining all reactants in a single reaction vessel. This simplification aims to enhance overall process safety, reduce production costs, and lower energy requirements. Significantly, this method has led to synthesising porous NIPU materials with high density, expanding the potential applications of these materials.

The catalyst-free one-pot synthesis method offers an efficient and sustainable substitute to traditional approaches. By eliminating the need for catalysts and consolidating the reaction into a single pot, this scheme minimizes energy consumption, reduces production costs, and enhances safety. The one-pot method involves directly mixing all reactants in a single reaction vessel, facilitating a more straightforward and efficient synthesis process [15]. This approach harnesses the inherent reactivity of the selected reactants to drive the formation of urethane linkages under milder conditions, producing high-density, porous NIPU materials. An important benefit of this approach is its capacity to be scaled up and used in industrial settings. The catalyst-free one-pot synthesis is more viable for large-scale production due to its streamlined reaction setup and less requirement for specialist equipment [16]. Moreover, the exclusion of expensive catalysts and the use of more benign reaction conditions enhance the cost-efficiency of the process, in line with the principals of sustainable manufacturing.

Another notable advantage is the decrease in environmental footprint. The catalyst-free one-pot synthesis results in a lower production of by-products and waste, hence minimizing the total environmental impact of the production process. Utilizing renewable feedstocks, such as bio-based polyols and carbonates, improves the sustainability of the products produced. This aligns with the increasing need for environmentally friendly materials in several sectors, which is being pushed by rising regulatory requirements and consumer consciousness.

A facile approach for the fabrication of bio-based porous NIPU materials with xylose has been adopted in the present study. The materials were synthesized by blowing at ambient temperature and hardening in short time intervals at a lower temperature (70 °C) with citric acid as a crosslinker, and subsequently, their flame-retardant behaviour was analyzed.

3.2 Experimental Details

3.2.1 Materials

HMDA was obtained from Sigma Aldrich and utilized exactly as supplied. DMC and D-xylose were bought from Central Drug House (India). Citric Acid was acquired from Loba Chemie (India). All these chemical reagents used in the analytical procedures were of analytical grade.

3.2.2 Synthesis of Isocyanate-Free Polyurethane-Based Porous Materials

DMC was added to D-Xylose aqueous solution and the mixture was then heated for 50 minutes, with continuous stirring. Subsequently, the reaction mixture was accompanied by HMDA. The resultant polymer mixture was stirred and heated to 70 °C, till the viscosity of the reaction mixture increased, and the color changed to dark brown, and then was allowed to cure. Table 3.1 divulges the detailed formulations of the synthesized materials. After 10-15 minutes, the appearance of pores was observed in the case of PO. The formulations P1 and P2 were further heated to 70 °C, for about 20 minutes and different amounts of 50% aqueous solution of citric acid were added in each, as crosslinkers. Figure 3.1 (a and b) shows the schematic representation of formation of porous NIPU materials.

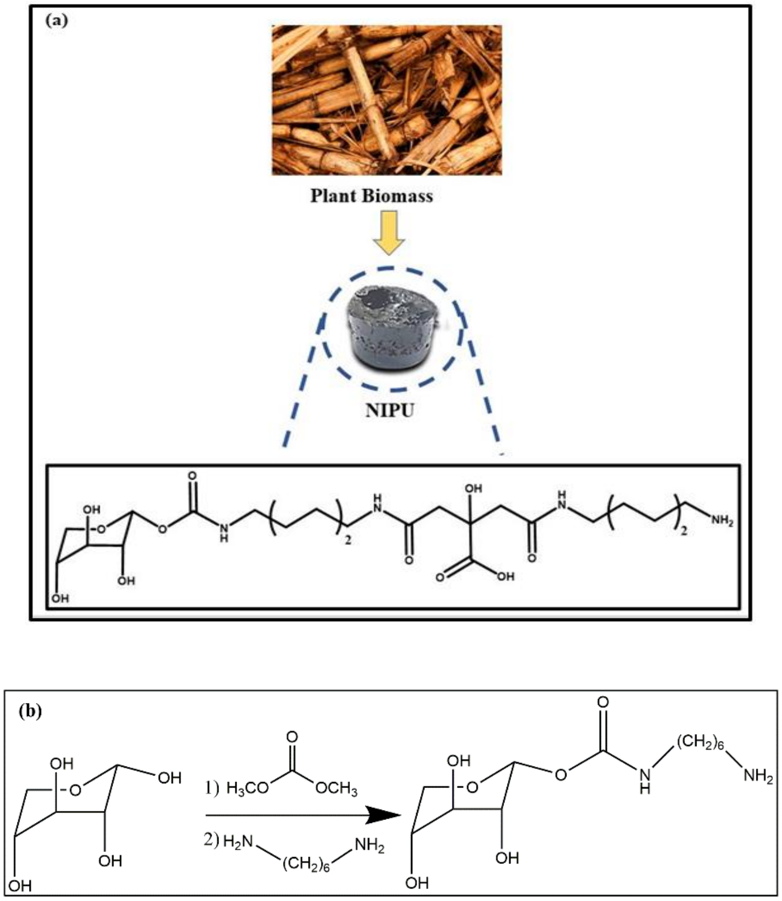


Figure 0.1 (a) Schematic representation of the formation of porous NIPU materials (b) Reaction scheme of the synthesis.

Table 0.1 Formulations of the prepared samples and their apparent densities

Sample	Xylose: DMC: HMDA: Citric Acid (weight %)	Apparent Density (g/cm^3)
PO	2:0.9:1:0	1.75
P1	2:0.9:1:0.143	2.34
P2	2:0.9:1:0.286	3.01

3.2.3 Instrumentation

The morphology and structure of the developed foams were assessed by PXRD, utilizing a high-resolution Bruker diffractometer (D8 Discover), coupled with a point detector (scintillation counter), using Cu K α radiation received via a Gobel mirror, that covers the range of 2θ = 5-80° with a scan rate of 1.0 second/step and step size 0.02° at 298 K. PerkinElmer Frontier ATR-FTIR provided by an ATR Miracle diamond crystal was employed to examine the functional groups of all the prepared foam samples. TGA was employed to evaluate the thermal stability of the resulting NIPU foams (using TGA 4000, Perkin Elmer). DSC was used to assess the thermal stability of the resulting foams using DSC 8000, Perkin Elmer. Nitrogen was used as a purge gas. To examine the glass transition temperature, the thermal characteristics were analyzed at 20 °C min^{-1} in the range of -50 °C to 250 °C. A scanning electron microscope (Jeol JSM-6610LVmodel) was used to examine the morphology and interior structure of the foams on a lateral cross-section to the rising direction of NIPU foam.

3.3 Results and Discussion

3.3.1 Structural properties of NIPU

The emergence of bands at around 1700 cm^{-1} and 1600 cm^{-1} respectively confirms the formation of urethane linkage (Figure 3.2). A band around 3370-3415 cm^{-1} suggests the presence of -NH- of urethane groups and hydroxyl groups. The role of citric acid as a crosslinker is confirmed by the linkage of COO$^-$ group of citric acid with the -NH- groups of diamine. Hence, the P2, with the maximum amount of citric acid, experiences the bands shift to a lower wavelength. In the case of P1, the formation of a sharp band at around 3400 cm^{-1} suggests the occurrence of restricted hydrogen bonding that causes a shift in the band of -C=O- linkage to 1752 cm^{-1}. With the increase in the amount of citric acid, an increase in apparent densities of the NIPUs was observed, as shown in Table 3.1. The energy generated by the interaction of citric acid with the $–NH_2$ groups is responsible for the increase in material density [11]. Also, the increase in the crosslinks developed in the polymer network could lead to such an observation. The PXRD pattern presented in Figure 3.3 exhibits the appearance of the characteristic peak of the segmented polyurethanes at around 20°, in all samples. The broadness of peaks indicates the amorphous nature of synthesized materials [9]. Hence, the results of PXRD and FTIR confirm the formation of urethane bridge in the prepared samples.

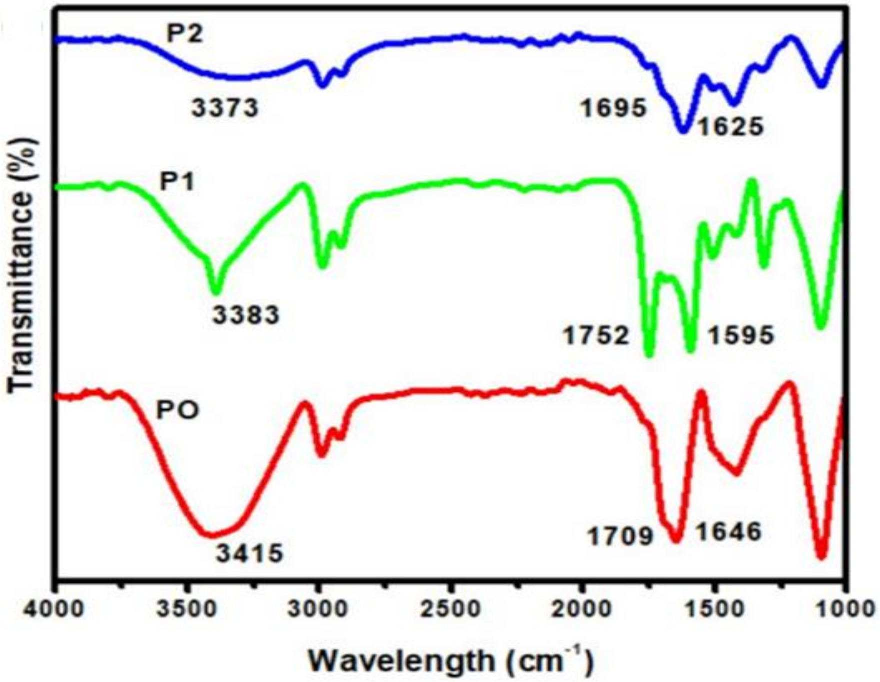


Figure 0.2 FTIR plots of the synthesised polymers.

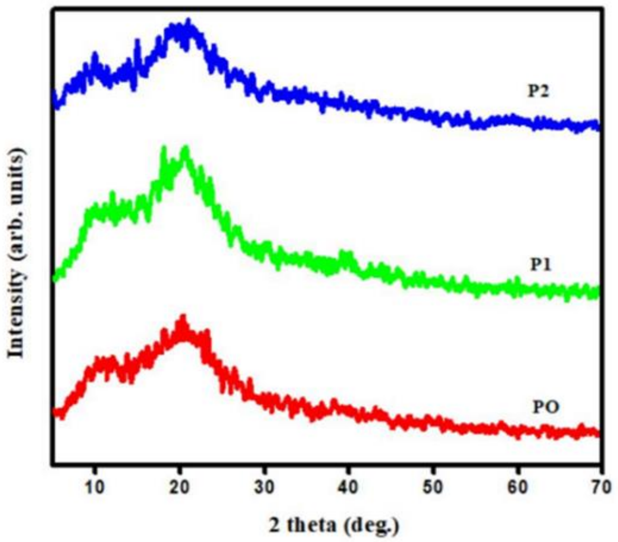


Figure 0.3 XRD pattern of the synthesised polymers

3.3.2 Morphological Properties

The morphology of the prepared materials was analyzed by scanning electron microscopy (Figure 3.4 (a-c)). Both open and closed cell structures can be observed in the shown images. Due to the action of the citric acid as crosslinker, the number of open cells decreases on moving from PO to P2 (which is an ascending order for the amount of citric acid added in the formulations) [17]. This can be attributed to an improvement in cell formation resulting from the formation of stronger cell walls, which restrict the distribution of cell size and forbid further blowing, thus opening the cells and leading to opened-celled structures.

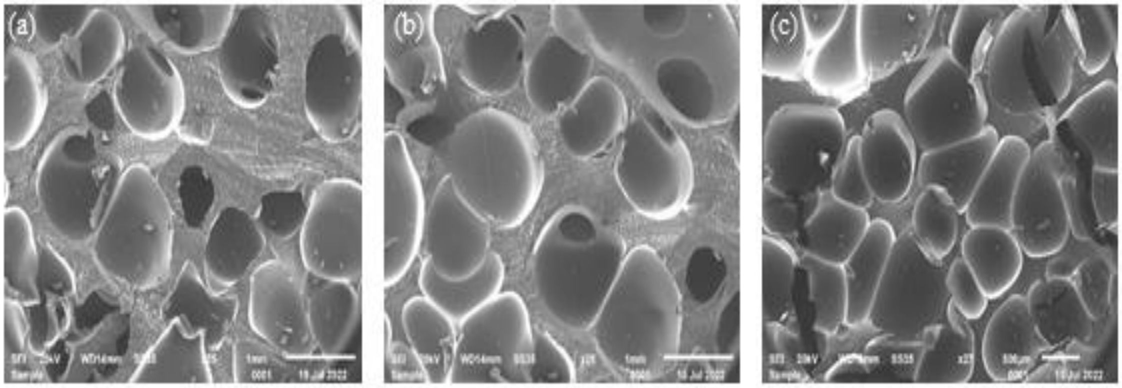


Figure 0.4 SEM images of (a) PO, (b) P1, and (c) P2

3.3.3 Thermal Characterisation

The TGA thermogram (Figure 3.5) shows that all porous NIPU materials exhibit a comparable response to pyrolysis. The first mass loss stage was observed in the range of 170-350 °C, which is attributed to the decomposition of urethane bond [10]. The second stage of mass loss was observed in the range of 370-640 °C, which could be a consequence of -C–C- bond cleavage and additional degradation of surplus products produced by the decomposition of the urethane bond in the first stage [18]. The presence of citric acid as a cross-linker in P2 (maximum amount of citric acid) explains its better stability and least mass loss at the highest temperature, as seen in the thermogram. Nevertheless, the thermal degradation of HMDA, water, and excess acid might be the reason for the small weight loss observed in the lower temperature range (<170 °C). This behaviour was analogous to the observations made by X. Chen and group [10]. Figure 3.6 represents the glass transition temperatures of the NIPU materials in a DSC thermogram. As evident, the transition temperature falls in the range of 58-76 ℃ in the increasing order of the amount of citric acid.

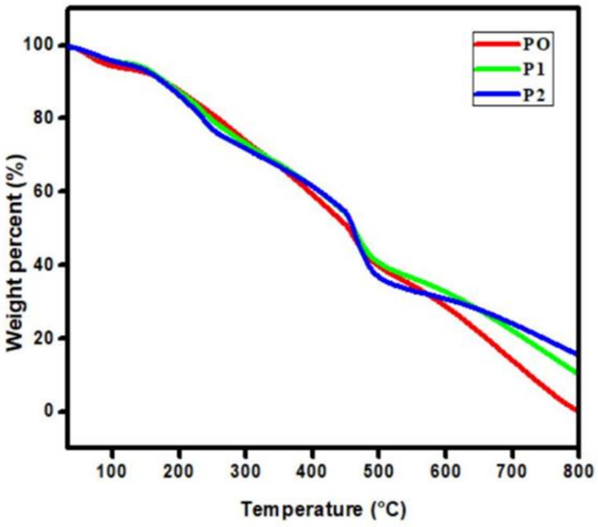


Figure 0.5 TGA thermogram of the synthesised polymer samples

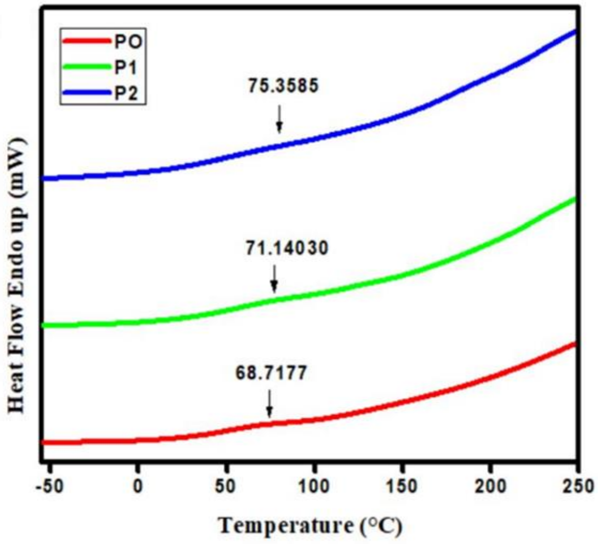


Figure 0.6 DSC thermogram of the prepared polymer samples

3.3.4 Limited Oxygen Index

A sample exhibiting an LOI value above 27% can be called a flame retardant. However, if the LOI value is below 22% the material is said to be inflammable. All the NIPU materials synthesized in this study were tested for determining their LOI values and the observations are shown in Figure 3.7. The LOI values of neat xylose-based NIPU materials (PO) are around 23.97 %. As anticipated, the LOI values of NIPU materials incorporated with citric acid (P1 and P2) demonstrated an improvement in LOI values from 23.97% for P0 to 24.01% and 24.14% for P1 and P2, respectively. This improvement in the LOI values can be a consequence of the increase in crosslinking density with the incorporation of citric acid [10].

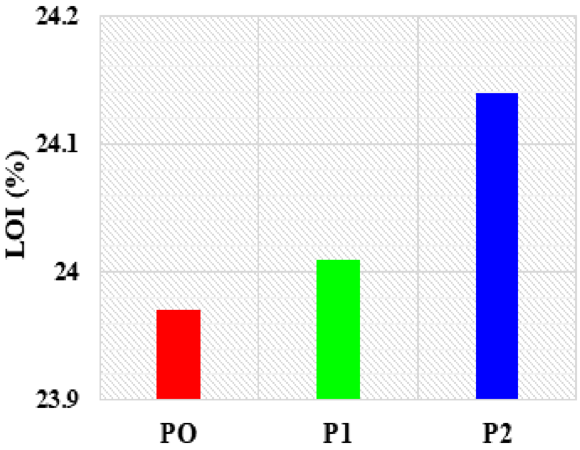


Figure 0.7 LOI of PO, P1, and P2

3.4 Conclusions

Isocyanate-free porous polyurethane materials were synthesized at 70 °C with xylose precursor, via a facile one-pot process. The prepared samples were synthesized by incorporating varying amounts of citric acid. The improvement in the thermal properties was confirmed by TGA and DSC. The thermal stability and glass transition temperature both are improved with the addition of citric acid, as it leads to the formation of a highly packed polymeric network. The NIPU materials exhibited a cell structure with varying pore sizes, that was observed to be dependent on the amount of the crosslinker added to the reaction mixture. Homogenous pore sizes were observed in case of NIPU material having maximum amount of citric acid. Citric acid, being a crosslinker, also led to an enhancement in LOI values of the prepared materials. These results validate the suitability of the synthesized porous NIPU materials in a multitude of future applications.

3.5 References

[1] Wang Z, Wang C, Gao Y, Li Z, Shang Y, Li H. Porous Thermal Insulation Polyurethane Foam Materials. Polymers (Basel) 2023;15. https://doi.org/10.3390/polym15183818.

[2] Vu V-P, Kim S-H, Mai V-D, Ra S, An S, Lee S-H. Bio-based conductive polyurethane composites derived from renewable castor oil with enhanced self-healing ability for flexible supercapacitors. J Mater Sci Technol 2024;188:44–61. https://doi.org/https://doi.org/10.1016/j.jmst.2023.12.008.

[3] Li X, Li J, Wang J, Yuan J, Jiang F, Yu X, et al. Recent applications and developments of Polyurethane materials in pavement engineering. Constr Build Mater 2021;304:124639. https://doi.org/https://doi.org/10.1016/j.conbuildmat.2021.124639.

[4] Arif ZU, Khalid MY, Sheikh MF, Zolfagharian A, Bodaghi M. Biopolymeric sustainable materials and their emerging applications. J Environ Chem Eng 2022;10:108159. https://doi.org/https://doi.org/10.1016/j.jece.2022.108159.

[5] Delavarde A, Savin G, Derkenne P, Boursier M, Morales-Cerrada R, Nottelet B, et

al. Sustainable polyurethanes: toward new cutting-edge opportunities. Prog Polym Sci 2024;151:101805. https://doi.org/10.1016/j.progpolymsci.2024.101805.

[6] Martínez de Sarasa Buchaca M, de la Cruz-Martínez F, Francés-Poveda E, Fernández-Baeza J, Sánchez-Barba LF, Garcés A, et al. Synthesis of Nonisocyanate Poly(hydroxy)urethanes from Bis(cyclic carbonates) and Polyamines. Polymers (Basel) 2022;14. https://doi.org/10.3390/polym14132719.

[7] Amezúa-Arranz C, Santiago-Calvo M, Rodríguez-Pérez M-Á. A new synthesis route to produce isocyanate-free polyurethane foams. Eur Polym J 2023;197:112366. https://doi.org/10.1016/j.eurpolymj.2023.112366.

[8] Xi X, Pizzi A, Delmotte L. Isocyanate-free polyurethane coatings and adhesives from mono- and di-saccharides. Polymers (Basel) 2018;10:1–21. https://doi.org/10.3390/polym10040402.

[9] Sternberg J, Pilla S. Materials for the biorefinery: high bio-content, shape memory Kraft lignin-derived non-isocyanate polyurethane foams using a non-toxic protocol. Green Chem 2020;22:6922–35. https://doi.org/10.1039/d0gc01659d.

[10] Chen X, Li J, Xi X, Pizzi A, Zhou X, Fredon E, et al. Condensed tannin-glucose-based NIPU bio-foams of improved fire retardancy. Polym Degrad Stab 2020;175:109121. https://doi.org/10.1016/j.polymdegradstab.2020.109121.

[11] Xi X, EPizzi A, Gerardin C, Lei H, Chen X, Amirou S. Preparation and evaluation of glucose based non-isocyanate polyurethane self-blowing rigid foams. Polymers (Basel) 2019;11. https://doi.org/10.3390/polym11111802.

[12] Galbis JA, García-Martín MDG, De Paz MV, Galbis E. Synthetic Polymers from Sugar-Based Monomers. Chem Rev 2016;116:1600–36.

https://doi.org/10.1021/acs.chemrev.5b00242.

[13] Polo Fonseca L, Duval A, Luna E, Ximenis M, De Meester S, Avérous L, et al. Reducing the carbon footprint of polyurethanes by chemical and biological depolymerization: Fact or fiction? Curr Opin Green Sustain Chem 2023;41:100802. https://doi.org/https://doi.org/10.1016/j.cogsc.2023.100802.

[14] Dannecker PK, Meier MAR. Facile and Sustainable Synthesis of Erythritol bis(carbonate), a Valuable Monomer for Non-Isocyanate Polyurethanes (NIPUs). Sci Rep 2019;9:1–6. https://doi.org/10.1038/s41598-019-46314-5.

[15] Delolo FG, dos Santos EN, Gusevskaya E V. One-Pot Reactions in Different Sites: A New Approach in Hydroformylation-Based Processes. ChemCatChem 2024;n/a:e202400273. https://doi.org/https://doi.org/10.1002/cctc.202400273.

[16] Feng Y, Man L, Hu Y, Chen L, Xie B, Zhang C, et al. One-pot synthesis of polyurethane-imides with tailored performance from castor and tung oil. Prog Org Coatings 2019;132:62–9. https://doi.org/https://doi.org/10.1016/j.porgcoat.2019.03.035.

[17] Tolinski M. Chapter 15 - Crosslinking. In: Tolinski M, editor. Addit. Polyolefins, Oxford: William Andrew Publishing; 2009, p. 215–20. https://doi.org/https://doi.org/10.1016/B978-0-8155-2051-1.00015-7.

[18] Jiao L, Xiao H, Wang Q, Sun J. Thermal degradation characteristics of rigid polyurethane foam and the volatile products analysis with TG-FTIR-MS. Polym Degrad Stab 2013;98:2687–96. https://doi.org/10.1016/j.polymdegradstab.2013.09.032.

Chapter 4

SYNTHESIS AND RHEOLOGICAL ANALYSIS OF NON-ISOCYANATE POLYURETHANES BLENDED WITH POLY(VINYL ALCOHOL)

4.1 Introduction

Materials science research remains strongly motivated by the ongoing quest for sustainable and eco-friendly polymeric materials. PUs are highly appreciated for their mechanical strength, resistance to chemicals, and ability to be used in various applications [1–4]. Nevertheless, the traditional production of PUs usually includes isocyanates, which are linked to substantial risks to both human health and the environment. As a reaction, NIPUs have developed as a possible substitute, providing decreased toxicity and environmental impact [5]. Production of hybrid NIPUs with higher performance is one strategy to counteract its lack of reactivity [6].

This chapter aims to investigate the synthesis and flow properties of NIPUs in combination with poly(vinyl alcohol) (PVA), a water-soluble polymer known for its film-forming ability, chemical resistance, and biodegradability. The aim of the method is to enhance the material properties of NIPUs and expand their scope of potential applications.

Polymers can be blended together to deliberately modify the characteristics of materials and produce composites that have combined and enhanced qualities [7]. Blending with

PVA in the context of NIPUs presents numerous possible benefits. The hydroxyl groups in PVA have the potential to engage with the urethane linkages in NIPUs, which could improve the mechanical strength and thermal stability of the blend. PVA is known for its excellent film-forming properties, water solubility, and biocompatibility. Combining these properties of PVA with the desirable mechanical strength, thermal stability and biodegradability of NIPUs via blending can lead to synergistic effects and improved performance. By adjusting the blend composition and ratio it is possible to modulate these properties to suit specific requirements for diverse applications across industries. The combined properties of NIPU and PVA blends make them suitable for applications such as coatings, adhesives, packaging materials, biomedical scaffolds, and drug delivery systems. The tailored properties of the blends can meet the specific requirements of these applications expanding the possibilities for their practical use. Furthermore, the water-repellent characteristics of PVA can enhance the ability of NIPU-based materials to resist water, which is essential for applications that necessitate moisture barrier capabilities. Furthermore, the capacity of PVA to decompose naturally enhances the overall ecological viability of the mixture. The miscibility of polymer blends can be assessed using various qualitative (namely scanning electron microscopy, FTIR) and quantitative techniques (such as DSC and rheology). Qualitative techniques such as scanning electron microscopy (SEM) and Fourier-transform infrared spectroscopy (FTIR) offer valuable information about the physical structure and chemical interactions occurring in the blend. SEM enables the examination of the morphology of blends at a very small scale, ranging from micro to nanoscale.

On the contrary, FTIR provides details on the chemical composition and the way different components in the mix are bonded together. However, quantitative methods such as differential scanning calorimetry (DSC) and rheology offer accurate measurements for evaluating the compatibility of polymer mixtures. DSC quantifies the heat transfer related to thermal changes, such as the melting or glass transition temperatures. DSC, thus, allows for the assessment of blend compatibility by analysing phase separation or mixing patterns. Rheology is a field of study that examines material flow when stress is applied to them. It provides crucial information on the viscosity, elasticity, and molecular movement of blends, which helps understand the uniformity and behaviour of different phases in the blend. It is an essential component of defining polymer blends as it offers valuable information about their flow characteristics and viscoelastic qualities. Rheology is crucial for comprehending the performance of the mix throughout processing and in its final applications. The viscosity of the blend has a direct impact on its ability to be processed in coating, moulding, and extrusion applications. The viscoelastic properties, such as the storage modulus and loss modulus, offer insights into the material's elasticity and ability to dissipate energy. These properties are crucial for applications that demand precise mechanical performance.

In this study, the glucose-based NIPU has been successfully synthesized and subsequently blended with PVA at different ratios. The objective behind blending glucose-based NIPU with PVA is to exploit their individual properties and achieve synergistic effects in the resulting blends. The rheological behaviour of these blends has been systematically investigated to assess their processability, mechanical performance, and potential applications. As rheological analysis plays a pivotal role in understanding the flow and deformation characteristics of the prepared polymer blends, the understanding gained from this study can pave the way for the design and development of innovative polymeric blends with improved performance and sustainability. In addition, this research contributes to the ongoing efforts to develop the isocyanate free PUs, thus promoting the utilisation of renewable resources resulting in reduced toxicity. The preparation of NIPU/PVA blends offers a new perspective and opportunity for the development of sustainable and versatile polymeric materials in industrial sectors.

4.2 Experimental Section

4.2.1 Chemicals

Carbamates were synthesized by employing commercially available hexamethylene diamine (HMDA), which was obtained from Sigma Aldrich. D-glucose and dimethyl carbonate (DMC) were purchased from Thermo Fisher Scientific. PVA was purchased from Central Drug House (Mw ≈ 85000-124000). All chemicals and solvents used were of analytical grade and were utilized exactly as received.

4.2.2 Preparation of Glucose-Based NIPU

The glucose-based NIPU was synthesized as has already been reported in literature [8]. Precisely, a mixture was prepared by refluxing 9.99g of glucose, 8.33g of water, and 6.71g of dimethyl carbonate in a three-necked round bottom flask for 40 minutes, at 50 °C. Afterwards, 1g of hexamethyl diamine (70% solution) was added to it. The resulting mixture was again heated at 90 °C for another 60 minutes, then cooled to ambient temperature.

4.2.3 Preparation of NIPU/PVA Solutions

To obtain the desired NIPU/PVA blended solutions, pure solutions of NIPU and PVA were prepared separately and then their 10% solutions were blended by stirring using magnetic stirrers. Pure NIPU was prepared according to the already reported study [9]. PVA solutions and NIPU were mixed and stirred for 30 minutes. The formulations of the prepared blends is as reported in Table 4.1. The prepared blends were stored at ambient temperatures for further characterizations and analysis (Figure 4.1). On exposure to 50 °C, the continuous films were formed in about 4 hours.

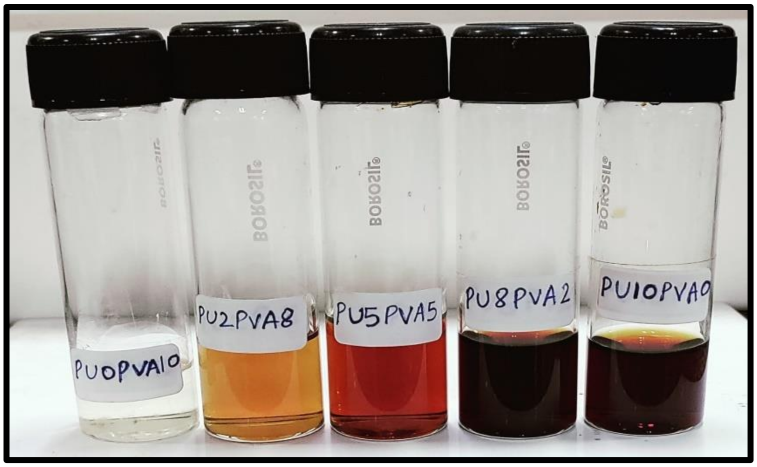


Figure 0.1 PVA-NIPU-based blends

Table 0.1 The formulation of different PVA-NIPU blends

S.No	**Sample**	**PVA (mL)**	**NIPU (mL)**
1	PU10PVA0	0	20
2	PU8PVA2	4	16

3	PU5PVA5	10	10
4	PU2PVA8	16	4
5	PU0PVA10	20	0

4.2.4 Instrumentation

The functional groups present in the polymeric blends were investigated by ATR-FTIR. The Modular Compact Rheometer 302 (MCR), manufactured by Anton Paar, was used to assess the rheological characteristics of pure NIPU, pure PVA, and their blend solutions. With a 0.5 mm gap between the cone and plate (25mm), all tests were conducted. The rheological tests under steady shear conditions were performed to measure constant viscosity, at the persistent shear rates such as 1, 50, 100, and 500 sec^{-1}. A series of oscillatory shear rheological tests were performed at different levels of strain within the linear viscoelastic region, as determined by an amplitude sweep test at a constant angular frequency of 10 rad/s. TGA (Perkin Elmer TGA 4000) was used to assess the thermal stability of the prepared NIPU/PVA blends. Nitrogen was employed as a purge gas. To identify the thermal parameters of transition, the thermal characteristics were studied at scanning rate 10 °C min^{-1} in the range of 50 to 250 °C. Both the pure polymer and the hybrid blends underwent XRD analysis to check for any morphological alterations.

4.3 Results and Discussion

4.3.1 Functional Group Analysis of the Prepared Blends

FTIR is capable of detecting any interactions that occur between the polymers in the blend. Variations in intensity, position, or emergence of peaks suggest the presence of hydrogen bonding or other interactions between the functional groups of PVA and NIPU. For instance, changes in the OH stretching bands of PVA and the C=O stretching bands of NIPU demonstrate the presence of hydrogen bonding between the hydroxyl groups of PVA and the carbonyl groups of NIPU.

The FTIR spectra of different blends have been displayed in Figure 4.2. The FTIR spectrum of PU0PVA10 displayed characteristic peaks at 3322 cm^{-1} (O–H stretching), 2858–2935 cm^{-1} (C–H stretching), 1632 cm-^{1} (residual acetate CH_3CO), 1412 cm^{-1} (C–H bending) and 1083 cm^{-1} (C–O–C stretching) respectively. In the PU spectra, small and sharp peaks at 3307 cm^{-1} (N–H and -OH stretching), peaks at 2852–2931 cm^{-1} (C–H stretching), 1742 cm^{-1} (C=O stretching), 1560 cm^{-1} and 1421 cm^{-1} (C–H bending), 1246 cm^{-1} and 1138 cm^{-1} (C–O–C stretching) were observed, which are characteristic absorptions in the PU backbone. To gain further insight into the interaction between PVA and NIPU molecules via hydrogen bonding, their FTIR spectra were analyzed. Specifically, the relative absorptions at two distinct wavenumbers were examined: 3322 cm^{-1} and 1550-1742 cm^{-1}. These absorptions correspond to the stretching vibration of the hydroxyl group (-OH) of PVA, the N-H group, and the carboxyl group (C=O) of PU in the blends. The results indicated that the addition of PU resulted in a shift of the absorption peak of PVA at 3310 cm^{-1} towards a lower wavenumber, suggesting a reduction in the intramolecular and intermolecular hydrogen bonding of PVA molecules. Nonetheless, hydrogen bonds were still observed between the molecules of NIPU and PVA. Moreover, the intensity of the absorption peak at 1632-1727 cm^{-1}, associated with the C=O group of PU gradually increased with the addition of more PU. This implies an increase in the carbonyl group content in the blends. The peak intensity of the hydrogen-bonded carbonyl group (1725 cm^{-1}) of PU8PV2 also increased, which served as a measure of the strength of the hydrogen bonding interactions. The difference in peak intensity between PU/PVA can be attributed to the variation in their structural hydrogen bonding, consistent with previous research [10].

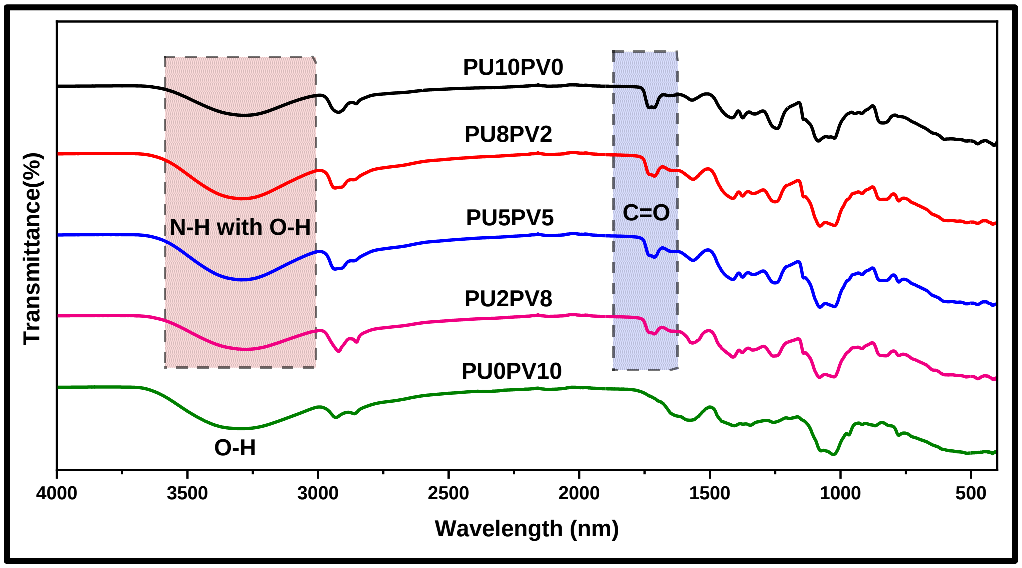


Figure 0.2 FTIR spectra of the prepared blends

4.3.2 Rheology

4.3.2.1 Steady Shear Rheological Behaviour of the NIPU/PVA Blends

As can be seen in Figure 4.3, the steady shear profiles of NIPU/PVA blend solutions were investigated at 25 °C. When shear rates ranging from 5 to 500 sec^{-1} were applied, the solution of PU10PV0 showed the lowest viscosity, while the solution of PU0PV10 exhibited the highest viscosity. It was found that the viscosities of the two materials varied depending on the amount of polymeric material present when they were blended. The blend solution with a higher content of PVA had a higher viscosity, compared to solutions with higher NIPU content. All solutions except for PU10PV0 showed Newtonian behaviour.

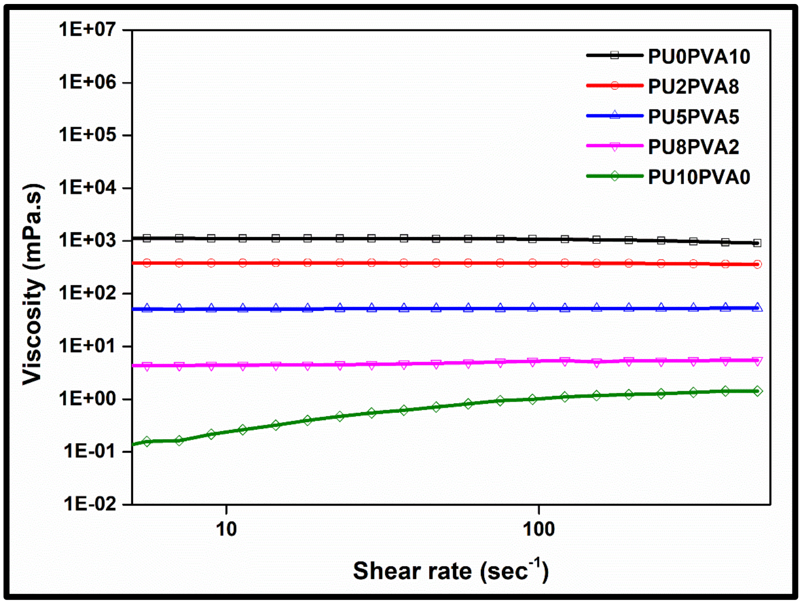


Figure 0.3 Steady shear rheological plots of the NIPU/PVA blend solution with different blending ratios at 25 °C

It was found that the viscosity of the pure polyurethane solution PU10PV0 significantly increased when the shear rate rose from 5 to 500 sec^{-1}. However, this trend was not observed in any other solutions. This behaviour is termed shear thickening, which can be attributed to either an escalation in the entanglement of molecular chains or the establishment of intricate networks and crosslinks among polymeric chains. In either case, these interactions hinder the mobility of polymer chains or particles, consequently leading to a noticeable upsurge in viscosity. This phenomenon is observed when polymer chains or particles align or undergo reconfiguration in a manner that constrains the flow of the fluid, thereby yielding an elevated viscosity. With the progressive increase in the proportion of NIPU in the blend, a notable development reveals that network formation featuring specially designed NIPU chains is established through hydrogen bonding. This transformative process results in an increased viscosity, yielding a denser and more resistant consistency in response to escalating shear rates. A similar type of thickening behaviour was observed in a study by Bercea et al. involving a PU solution in an aqueous solution [11].

The power law (Ostwald de Waele equation) regression model can be used to identify polymeric material behaviours such as shear thinning, shear thickening, and Newtonian behaviour (Figure 4.4). This can be explained using Equation (4.1), which describes the characteristics of polymeric solutions in terms of the coefficient n.

$$\eta = K(\dot{\gamma})^{n\text{-}1} \;\ldots\ldots\ldots\ldots\ldots\ldots\ldots\ldots\ldots\ldots\ldots\ldots\ldots\ldots\ldots\ldots\ldots\ldots\ldots\ldots\ldots\ldots\ldots\ldots\ldots\ldots\ldots\ldots\ldots\ldots\ldots\ldots\ldots\ldots\ldots\ldots\ldots\ldots\ldots\ldots(4.1)$$

Where η, is the viscosity in mPa.s, $\dot{\gamma}$ represents the shear rate in s^{-1}, n is the power-law constant (unitless) and K is the flow consistency index in mPa.s. [12].

Post curve fitting, the usual rheological parameters for all five solutions, including K, n, and linearity R^2, were identified. These results are displayed in Table 4.2.

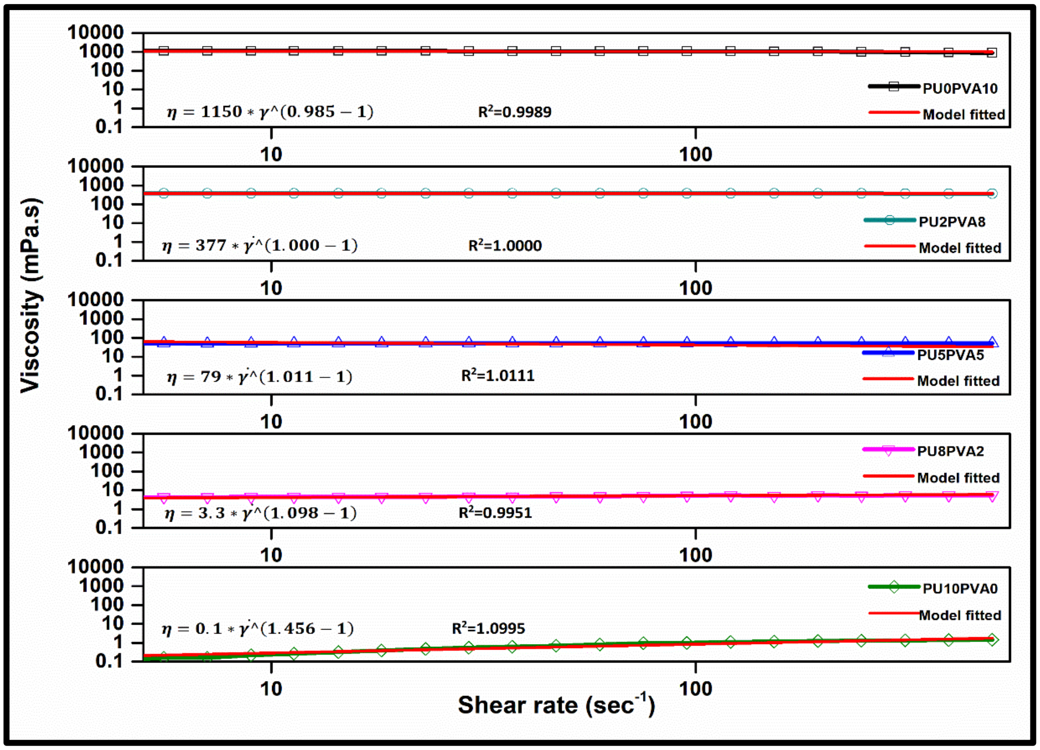


Figure 0.4 log η-log ẏ curves of NIPU/PVA blend solutions with different blending ratios

Table 0.2 Rheological parameters obtained from model fitting

S.No.	**Sample code**	K **(mPa.s)**	n	**R^2**
1	PU0PVA10	1150	0.985	0.9989
2	PU2PVA8	377	1.000	1.0000
3	PU5PVA5	79	1.011	1.0111
4	PU8PVA2	3.3	1.098	0.9951
5	PU10PVA0	0.1	1.456	1.0995

From the plot between log η **vs. log** $\dot{y}$ (Figure 4.4), the flowability of the solutions was analyzed concerning the value of power law constant n. Based on the listed parameters, the value of K is decreasing; whereas the value of n is increasing, on increasing the NIPU component in the blend solutions. The observed increase in the power law constant (n) with a higher proportion of high molecular weight glucose-based NIPU in PVA blends can be attributed to specific factors [13]. Firstly, this trend is underpinned by enhanced intermolecular interactions and chain entanglement between the NIPU and PVA components, facilitated by the longer NIPU chains. Secondly, at higher NIPU concentrations, the blend exhibits greater heterogeneity, thus, enabling the longer NIPU chains to align more effectively under applied shear forces, hence, resulting in a more structured arrangement of polymer chains. Thirdly, the increased dominance of the high molecular weight NIPU component with higher proportions leads to a shift in the blend's behaviour, as demonstrated by the higher power law constant (n) within the power law model. The viscosity response of pure PVA (PU0PVA10) solution under shear stress shows a shear-thinning behaviour, denoted by a value of n less than 1. Conversely, the pure NIPU

(PU10PVA0) solution exhibits the most pronounced shear-thickening behaviour compared to its blended counterparts. When 20% PU is added to a PVA polymeric solution (PU2PVA8), there is a shift from shear-thinning to Newtonian behaviour. Further increases in PU content (PU5PVA5 and PU8PVA2) resulted in a transition back to shear-thickening behaviour. Notably, as the PVA component increases, there is an initial trend towards more Newtonian behaviour. However, with higher NIPU quantities, the behaviour shifts from Newtonian to shear-thickening. This suggests that in PU2PVA8, a maximum alignment of chains occurs, whereas in blends like PU5PVA5 and PU8PVA2, previously disentangled chains become entangled or the interactions between NIPU and PVA chains intensify. It is important to note that the extremes of shear thickening and shear thinning were observed in pure NIPU (PU10PVA0) and pure PVA (PU0PVA10) solutions, respectively [14].

The log additivity rule (equation 4.2) can be used to calculate the viscosity and dynamic modulus of polymer blends. This applies to both NIPU and PVA polymers, assuming they are miscible. However, in immiscible blends, the viscoelastic functions deviate from this rule due to the partial miscibility of the components, and a change in phase morphology occurs at a certain blend ratio. Immiscible polymer blends can be categorized into three groups based on the blend-composition dependence of the viscoelastic functions: positive deviation, negative deviation, and positive-negative deviation. The deviation can be positive, negative, or both in different composition regions [15].

$$\log \mathrm{F} = \omega_1 \log \mathrm{F}_1 + \omega_2 \log \mathrm{F}_2 \,\ldots\ldots\ldots\ldots\ldots\ldots\ldots\ldots\ldots\ldots\ldots\ldots(4.2)$$

Where F: Viscoelastic function (such as viscosity, dynamic modulus, etc.)

ω_1 and F_l are weight fraction and viscoelastic functions of NIPU polymer in blend solution respectively. ω_2 and F_2 are weight fraction and viscoelastic functions of PVA polymer in blend solution respectively [16].

Through comparison of deviations between theoretical values and practical values, we can find that the viscosities at the shear rate 1 sec^{-1} (η_1) and shear rate 50 sec^{-1} (η_{50}) of the all-blend solutions were a bit lower than the expected value as shown Figure 4.5 (a) and (b). This phenomenon is called negative deviation which indicates the poor compatibility or uneven mixture of both NIPU and PVA polymers [17]. At higher shear rates, specifically at 100 sec^{-1} and 500 sec^{-1}, it is observed that the experimental values of all solutions exceed the estimated values, as depicted in Figure 4.5 (c) and (d). This occurrence, commonly referred to as positive deviation, may be attributed to an escalation in interface interaction [20]. A similar kind of miscibility between the blend solutions of cellulose and silk fibroin polymers in an ionic liquid solvent was investigated and reported by Yao et al. [20] and Zhang et al. [21].

As the shear rate increases, the occurrence of negative-deviation blends disappears, as shown in Figure 4.5 (a) and (b), while positive deviation is observed, as depicted in Figure 4.5 (c) and (d). The reported molecular weight of a single repeating unit in glucose-based NIPU is approximately 322.8 Da [13], whereas PVA exhibits a significantly lower molecular weight of approximately 44 Da. Specifying this substantial difference in molecular weight, the explanation for the shift from negative deviations to positive deviations at higher shear rates can be elucidated. The vanishing negative deviations can be attributed to the amplified influence of the higher molecular weight glucose-based NIPU at elevated shear rates. The intensified mixing and shear forces primarily affect the NIPU component, which, owing to its higher molecular weight, begins to exert a more prominent impact. This heightened influence effectively mitigates the dilution effect induced by PVA, causing the properties of the blend to reflect the dominance of the higher molecular weight NIPU increasingly. Consequently, the negative deviations dissipate. Conversely, the emergence of positive deviations can be ascribed to the augmentation of synergistic interactions between the PVA and NIPU chains, notwithstanding the molecular weight contrast. The higher shear rates facilitate the superior mixing and intermolecular bonding between these chains. In particular, the PVA chains become proficient at entangling with and engaging the higher molecular weight NIPU chains, fostering enhanced synergistic interactions. This heightened interplay between the components manifests in the form of positive deviations, notably impacting properties such as viscosity and viscoelasticity. In summary, all solutions remain stable at high shear rates of 100 and 500 sec^{-1}. However, if processed at low shear, they may exhibit phase separation due to poor mutual interaction between NIPU/PVA blend solutions at low shear rates. The blend solution PU2PVA8 exhibited the minimum phase separation, as evidenced by the nearly overlapping experimental and estimated data lines in negative deviation, when compared to the other blend solutions. This can be observed in Figure 4.5 (a) and (b). Conversely, the maximum gap was observed in positive deviation, as depicted in Figure 4.5 (c) and (d). As depicted in Fig. 4.5, the specific interactions, notably hydrogen bonding, exhibit improvement with increasing shear rates in the case of PU2PVA8. This observation is consistent with the outcomes derived from FTIR analysis. Notably, PU2PVA8 emerges as the most miscible blend among all blends at elevated shear rates. Remarkably, it consistently demonstrates positive deviation across the range of applied shear rates, underscoring its comparable superior miscibility characteristics [18].

After analyzing the deviation graphs, it can be deduced that the blend solution comprising 20% NIPU and 80% PVA (on a weight basis) components displayed the highest level of stability when compared to the other blends.

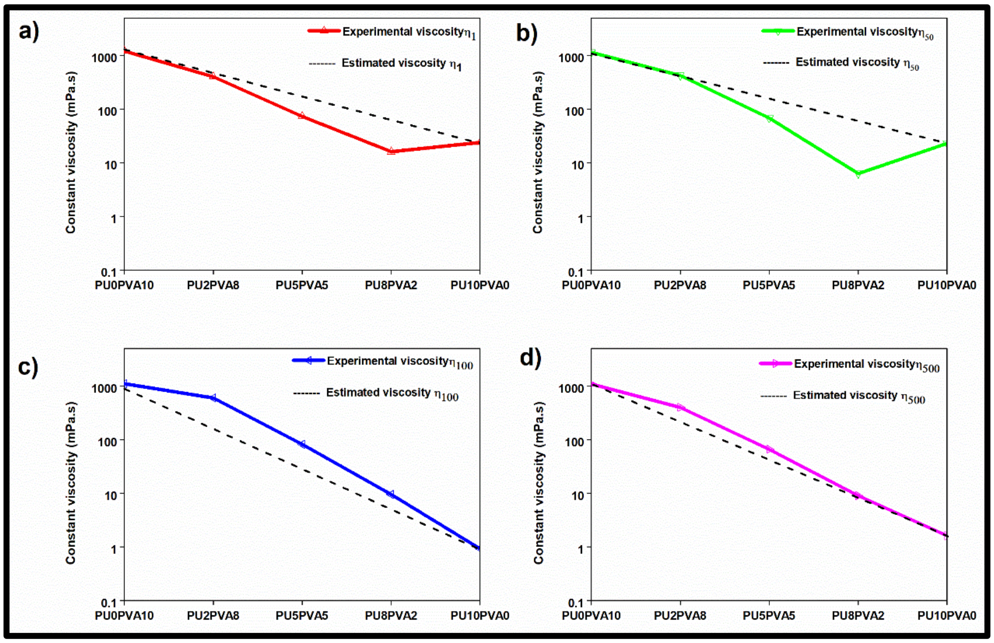


Figure 0.5 Plots of the estimated values (the black dotted lines) and experimental values of the viscosities at a shear rate of (a) 1 s^{-1}, (b) 50 s^{-1}, (c) 100 s^{-1}, (d) 500 s^{-1} for NIPU/PVA blend solutions with a different blending ratio

4.3.2.2 Dynamic Oscillation Behaviours of NIPU/PVA Blend Solutions

The study of the dynamic oscillation of polymer blends in rheology is crucial in various aspects of polymer science and engineering. This includes understanding the material behaviour, predicting processing performance, assessing mechanical properties, evaluating blend compatibility, designing tailored materials, ensuring quality control, and driving research and innovation. Understanding the dynamic oscillation of blends is fundamental in comprehending their miscibility and phase separation behaviour. This knowledge is critical to creating blends that exhibit the desired homogeneity and performance [19]. In rheology, it is mandatory to conduct an amplitude sweep before a frequency sweep to evaluate the viscoelastic properties of polymer blends. The amplitude sweep furnishes valuable insights into the reaction of the material to varying degrees of deformation, thereby facilitating the interpretation of the results obtained from the subsequent frequency sweep [19]. Identifying the linear viscoelastic region (LVR) of a material is a critical step during an amplitude sweep [20]. Within this region, the storage and loss moduli of the material remain constant and parallel under applied shear strain, effectively acting as a linear viscoelastic substance. It is essential to pinpoint the LVR to obtain accurate frequency sweep measurements. Data collected outside of this region may not accurately reflect the true viscoelastic properties, making it crucial to exercise awareness of this important aspect.

During the frequency sweep, the frequency range was adjusted from 1 to 100 rad/sec. The % shear strain of each specific blend (PU10PVA0=0.1%, PU2PVA8= 0.13%, PU5PVA5=0.1%, PU8PVA2=0.2%, and PU0PVA10=0.1%) was kept constant within the LVE region, as determined from the amplitude sweep. For analysis, G' (storage modulus) and G" (loss modulus) were plotted against angular frequency, as illustrated in Figure 4.6 (a) to Figure 4.6 (e). When testing viscoelastic materials like polymer blends using a frequency sweep, one important aspect of rheology is the crossover point. The frequency at which the storage modulus (G') and loss modulus (G") cross or intersect is known as the crossover point. As the frequency rises, the crossover point can also signify a change in behaviour from more viscoelastic solid to viscoelastic fluid, or vice versa. The crossover frequency is frequently connected to the viscoelastic transition frequency.

Based on observations from Figure 4.6 (b), (d), and (e), it can be concluded that for PU8PVA2, PU2PVA8, and PU0PVA10, G" is the dominant factor within the entire angular frequency range, indicating a viscous fluid behaviour. Furthermore, Figure 4.6 (a) clearly shows that in the case of pure polyurethane (PU10PVA0), G'' was dominant only for low angular frequency, whereas from medium to high angular frequency range, G' is dominating in nature, resulting in PU10PVA0 behaving like viscoelastic fluid at low frequency whereas viscoelastic solid for medium to high frequencies [21]. When both polymers are blended in equal parts such as PU5PVA5 solution, they exhibit viscoelastic solid behaviour at both low and high frequencies. However, at intermediate frequencies, the behaviour shifts from viscoelastic solid to viscoelastic fluid due to the dominance of loss modulus, as seen in Figure 4.6 (c).

Observations of crossover points indicate that PU10PVA0 and PU5PVA5 solutions exhibit viscoelastic behaviour. It is worth noting that the positions of their respective crossover points differ. In general, except for PU2PVA8, PU8PVA2, and PU0PVA10 solutions, the remaining two solutions, PU10PVA0 and PU5PVA5, have cross-over points at varying angular frequencies. Furthermore, their behaviour also changes when the blending ratios are adjusted. A similar kind of frequency-dependent viscoelastic behaviour of silk fibroin solution in alcohol solvent has been studied and reported [22]. The frequency dependence of viscoelastic properties of some physical gel near the gel point has been reported in the literature [23]. This suggests that materials can be prepared to be more processable by changing the blending ratio.

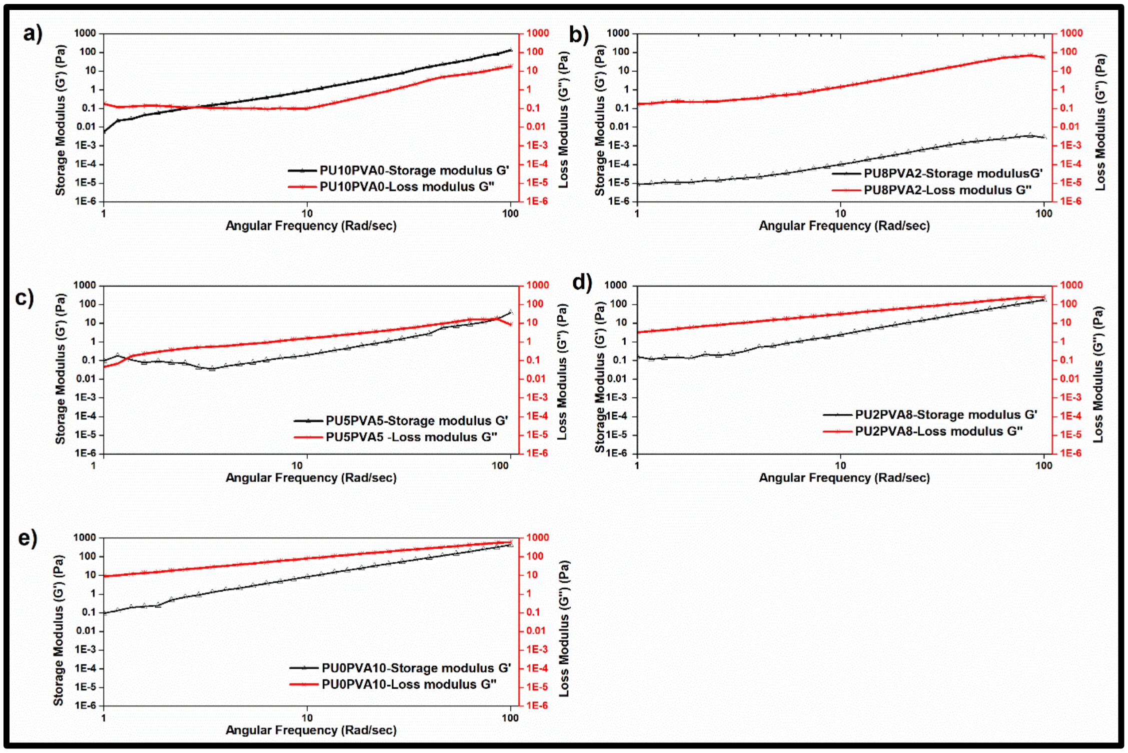


Figure 0.6 Plots of frequency sweep of NIPU (or PU) and PVA solutions with a different blending ratio

In Figure 4.7, the changes in G' and G" of NIPU/PVA solutions are displayed for three specific angular frequencies. These variations are consistent with the deviations previously discussed, concerning shear viscosities at four distinct constant shear rates (1, 50, 100, and 500 sec^{-1}). The curves show that the phase morphology of the solution changes under different shear frequencies, such positive and negative deviations confirm the phase change in NIPU/PVA solutions with a blend ratio. The study revealed that PU2PVA8 exhibited greater miscibility compared to the other solutions. The results are consistent with that of positive-negative deviation analysis (Figure 4.5), therefore validating the conclusions drawn from this experiment alone. The storage and loss moduli were analyzed and demonstrated for all the blends, as shown in Figure 4.7 (a) and (b) respectively. The moduli values were found to be either close to the estimated lines with negative deviation or showed positive deviation. Both cases show remarkable stability in the blend, a finding supported by an earlier analysis of positive-negative deviations in this study, specifically at shear rates of 1, 50, 100, and 500 sec^{-1}. This was illustrated in Figure 4.5, which is a component of the static shear rheological measurements conducted in this study.

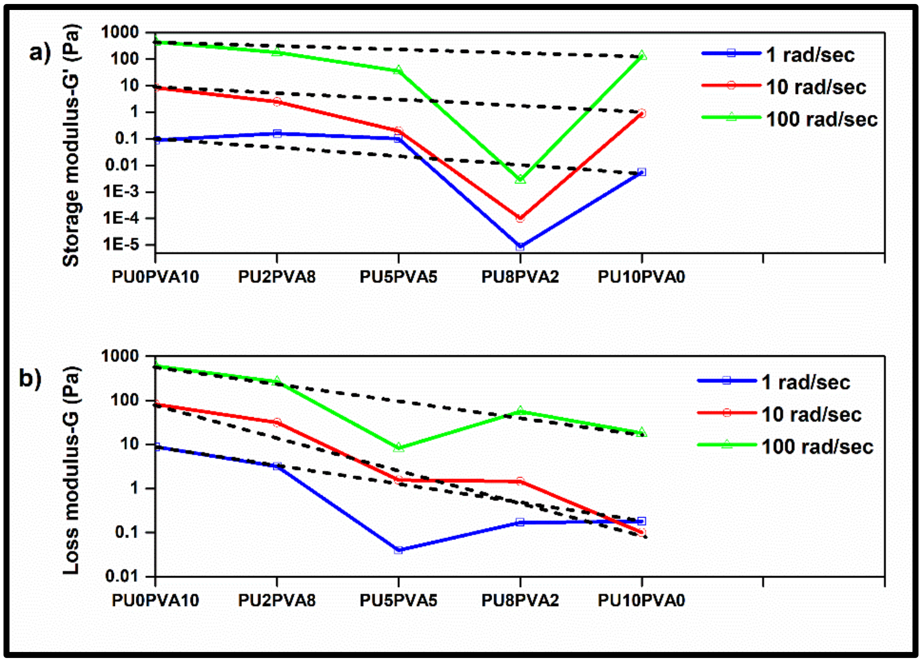


Figure 0.7 Plots of the estimated values (the black dotted lines) and experimental values of the a) storage modulus (G’) and b) loss modulus (G”) at angular frequencies 1 rad/sec, 10 rad/sec and 100 rad/sec for NIPU/PVA blend solutions with a different blending ratio.

4.3.2.3 Structure Recovery

The structural behaviour of polymeric solutions is examined by rotational shear test concerning time which provides time-dependent viscosity of the polymer solutions. In this study, a specific amount of shear is applied initially for a definite period of time, which is increased to a higher value, and then eventually brought back to the initial low shear value, and structural recovery is measured in terms of viscosity [24]. Such Behavioural change of viscosity is generally defined as Thixotropic behaviour or Rheopectic behaviour [25]. Thixotropy is the regain of initial viscosity after the removal of high shear which had caused the viscosity to reduce in the first place. Such regain of viscosity can be related to structural recovery in polymer solutions. As illustrated in Figure 4.8, the pure PVA solution (denoted as PU0PVA10) demonstrated its highest viscosity levels under conditions of low shear rates. This behaviour is chiefly attributed to the entangled structure inherent to PVA or the elevated molecular weight of the PVA component, corroborating findings from prior research [26–28] Remarkably, when subjected to high shear rates, a distinct reduction in viscosity became apparent, signifying a consequential structural alteration. This transformation was characterized by the unwinding and uncoiling of molecular chains during the high shear rate phase. Upon the removal of high shear conditions, the viscosity fully recovered, exemplifying a thixotropic response characterized by an impressive 99% structural recovery. This outcome suggests minimal, if any, likelihood of no chain breakage because of the application of high shear rates It's noteworthy that pure NIPU solution either exhibited a viscous nature or due to strong networking remained unaffected even under high shear rates, displaying no discernible alterations in viscosity during low-high-low shear sequences.

A parallel thixotropic behaviour was observed within the PU2PVA8 blend solutions, accompanied by a remarkable 99% structural recovery. Intriguingly, like pure NIPU, neither pure NIPU nor blends containing more than a 20% NIPU component in the blend solutions exhibited deformation during high-shear conditions. This robust structural resilience of NIPU is attributed to the presence of interconnections among groups of NIPU polymer chains, reinforcing its structural integrity [13, 29–32]. This was further confirmed by thermogravimetric analysis (in subsequent section), where pure NIPU polymer has the most thermally stable structure, being highly crosslinked. In the case of pure NIPU as well as NIPU concentration greater than 50% of the total blend solution, the imposed high shear was insufficient to distort or perturb the molecular chains.

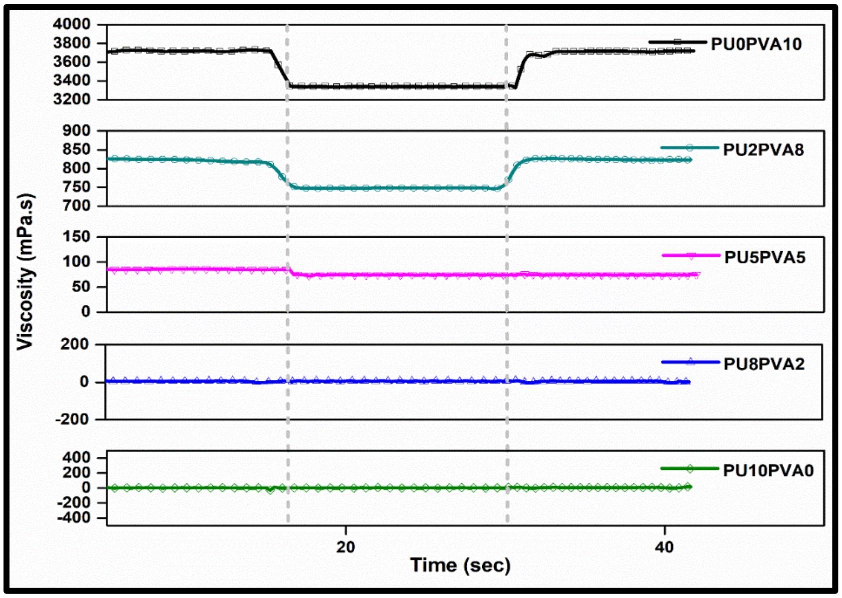


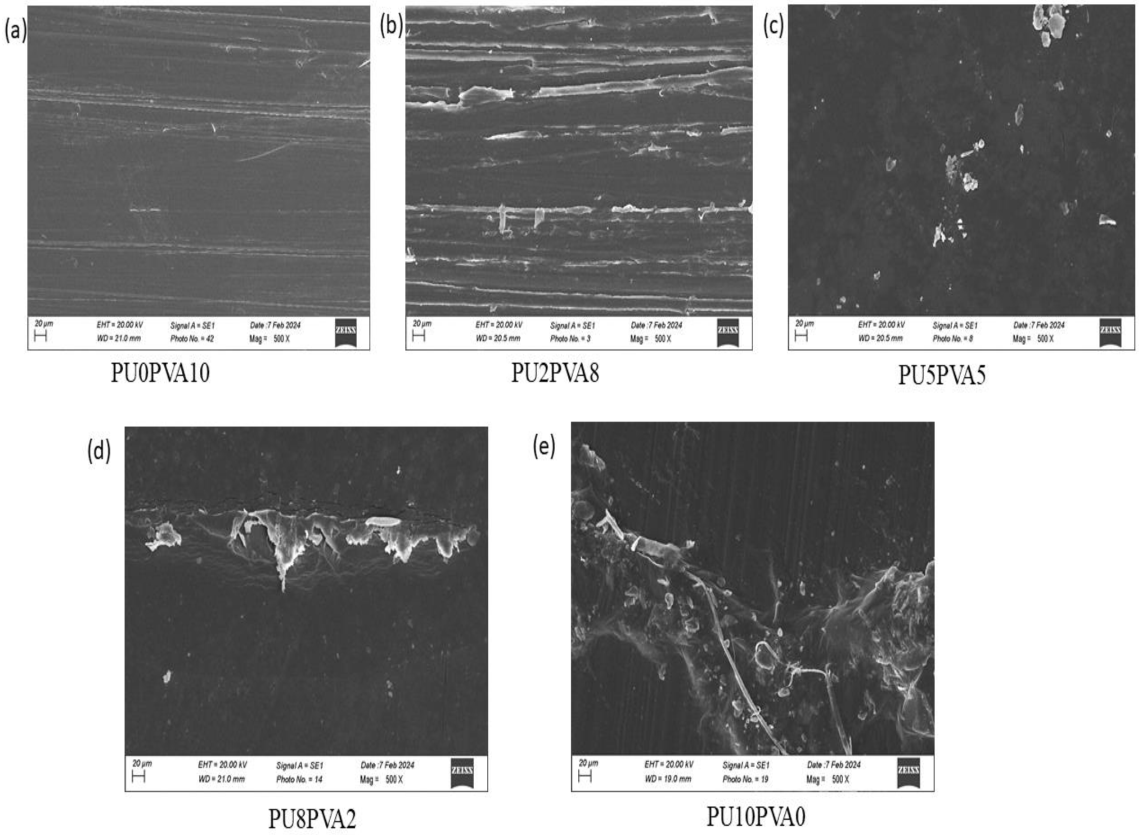
Figure 0.8 Plots of structure recovery of NIPU and PVA blend solutions

4.3.3 Scanning Electron Microscopy

SEM is a popularly employed qualitative technique to evaluate blend miscibility. It provides high-resolution imaging capabilities, allowing the observation of morphological features and phase separation within polymer blends, assisting in understanding their compatibility. SEM pictures of PU/PVA blends with different weight ratios are presented in Figure 4.9. Notably, the morphology and miscibility seen in the blend films are greatly influenced by the blend mixture.

A more thorough examination reveals that the blend designated PU2PVA8 has an incredibly homogeneous and consistent surface morphology that is dispersed equally throughout the matrix. This homogeneity indicates that the blend's NIPU and PVA components are highly miscible. This conclusion is consistent with the findings of the rheological investigation, which supports the observation of improved miscibility in this specific blend composition. On the other hand, a distinct morphology is noted for the blends designated PU5PVA5 and PU8PVA2. The blend exhibits immiscibility as the PU content increases, as evidenced by the existence of distinct or localised PU regions within the matrix. Figure 4.9(c) and (d) are clearly illustrating this occurrence, where discrete or localised regions are seen, indicating restricted blending with the PVA component.

In general, the SEM observations offer a significant understanding of the morphological traits and miscibility behaviour of blends of polyurethane and polyvinyl alcohol. While distinct PU regions in the PU5PVA5 and PU8PVA2 blends imply reduced miscibility, which is consistent with the results of the rheological data presented in this study, the uniform surface morphology observed in the PU2PVA8 mix shows its higher miscibility. The aforementioned results add to the current understanding of the structure-property interactions in polymer systems by highlighting the significance of blend content in determining the morphology and properties of polymer blends [10,11,33].



PU0PVA10 PU2PVA8 PU5PVA5

PU8PVA2 PU10PVA0

Figure 0.9 SEM image of PU/PVA blends

4.3.4 Thermogravimetric analysis

Thermogravimetric analysis was utilized to assess the thermal stability of PU0PVA10, PU10PVA0, and their blends. The study was conducted in an inert environment from 25 to 800 °C. As the temperature increased, the percentage weight of pure and blended NIPU and PVA solutions decreased, as shown in Figure 4.10. The first weight loss in all samples occurs at about 100°C due to the evaporation of adsorbed water or other volatile substances. Two distinct decomposition steps were observed, with two inflection points at approximately 350 °C and 450 °C representing the maximum loss. The thermal degradation behaviour of PU0PVA10 was investigated, and it was found that the hydroxyl groups present in the side chain of the polymer can undergo decomposition at a temperature of 350 °C, whereas the main chain of the polymer might decompose at a higher temperature of 450 °C. In a similar study conducted by Awada and Daneault on pure PVA solution, weight loss was observed at temperatures of 100 °C, 351 °C, and 423 °C [34].

The thermogram presented in Figure 4.10, indicates a multi-stage response for the decomposition behaviour of pure glucose-based NIPU i.e. the PU10PVA0 curve. The first stage of this response displays a slight weight loss at around 100 ˚C, which can be attributed to the evaporation of adsorbed water. Further, the low molecular weight substances such as hexamine and monomers/oligomers undergo evaporation, resulting in the initial degradation of samples at temperatures ranging between 100-200 ℃. A secondary peak is noticed at approximately 250 ℃, which is attributed to the breakdown of the backbone via urethane linkage. The final peak, occurs at 450 ℃, which indicates the highest degree of weight loss and may be attributed to the cleavage of C-C bonds [9]. The blend of PU0PVA10 and PU10PVA0 showed thermal behaviour that was intermediate between the two pure polymers. The curves showed a visible shift in the case of blends, and as expected, the blend samples were located between both curves. The blends displayed improved thermal stability during the primary decomposition phase compared to PU0PVA10, which can be attributed to the formation of intermolecular hydrogen bonding between NIPU and PVA chains. However, PU0PVA10 shows greater stability at lower temperatures (below 320°C), which is consistent with its distinct degradation profile.

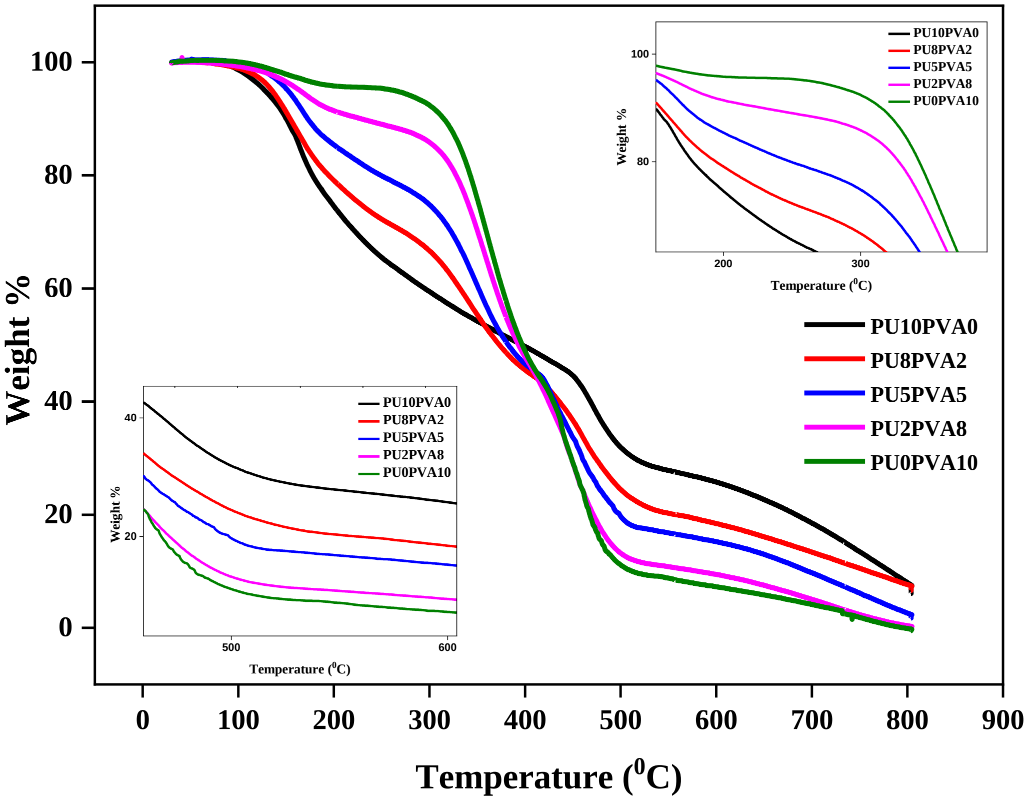


Figure 0.10 TGA of pure NIPU and PVA polymer solutions as well as their blends.

4.3.5 Differential Scanning Calorimetry

DSC is a dominant technique for evaluating polymer blend miscibility by analysing their thermal properties. It offers valuable insights into blend compatibility by detecting shifts or alterations in peaks, aiding in the comprehension of phase transitions and intermolecular interactions within the blend. The mechanical properties of semi-crystalline polymers are known to be significantly influenced by the crystallization component of those polymers, and this crystallinity may be changed by the blending with another polymer/component [36]. Figure 4.11 displayed the DSC curves of NIPU/PVA polymers. Table 4.3 provides information on the findings of various specific temperature transitions including the endothermic first glass transition temperature peak (Tg), exothermic crystallization temperature peak (Tc), and second endothermic melting temperature peak (Tm). Pure

NIPU was found to be non-crystalline since neither Tc nor Tm were observed for the tested temperature range., when compared to pure PVA, which displayed all three peaks at roughly 82 °C, 200 °C, and 222 °C, respectively, clearly indicating the presence of a crystalline component. On blending the two, some peaks disappeared, but others were found in between. The fact that the Tc and Tm peaks of PVA decreased as NIPU content increased in blends, suggests that the crystalline nature of PVA is weakening. The addition of NIPU destroyed the consistent pattern of PVA molecular chains and reduced the crystallinity of PVA, as demonstrated in Table 4.3 and by DSC curves. The blend solutions with more than 50% NIPU content, acted in a continuous phase and became non-crystalline due to the presence of PVA as a dispersed phase which led to an overall non-crystalline nature. Since only the PU2PVA8 blend solution has quantifiable peaks of Tg, Tc, and Tm in comparison to the others, this blend has the highest degree of miscibility since it has both amorphous nature (governed by NIPU) and crystalline nature (derived from PVA). Furthermore, PU5PVA5 has a much smaller peak than PU2PVA8, so it was remarkably challenging to count the peaks of each transition [10]. According to DSC, PU2PVA8 is the most miscible compound, which is also supported by the findings of the deviation curves discussed in Figure 4.5. The structure property relationship derived from DSC data can be categorised as:

1. **Effect on PVA Crystallinity:** Pure PVA exhibits well-defined peaks at 82 °C, 200 °C, and 222 °C, indicating a crystalline component. The disappearance and shifting of these peaks in the blends, especially as NIPU content increases, proclaims an interruption in the regularity of PVA molecular chains and a reduction in crystallinity.

2. **Miscibility Indicators:** The disappearing Tc and Tm peaks of PVA in the blends convey a weakening of the crystalline nature of PVA. The PU2PVA8 blend emerges as the most miscible, showcasing quantifiable peaks for Tg, Tc, and Tm. This blend demonstrates a unique combination of amorphous nature from NIPU and crystalline nature from PVA.
3. **Non-Crystalline Nature in Blends:** Blends with more than 50% NIPU content evolves into a non-crystalline phase due to the dispersed nature of PVA. The destruction of the regularity of PVA molecular chains by the addition of NIPU leads to an overall non-crystalline behaviour in these blends.

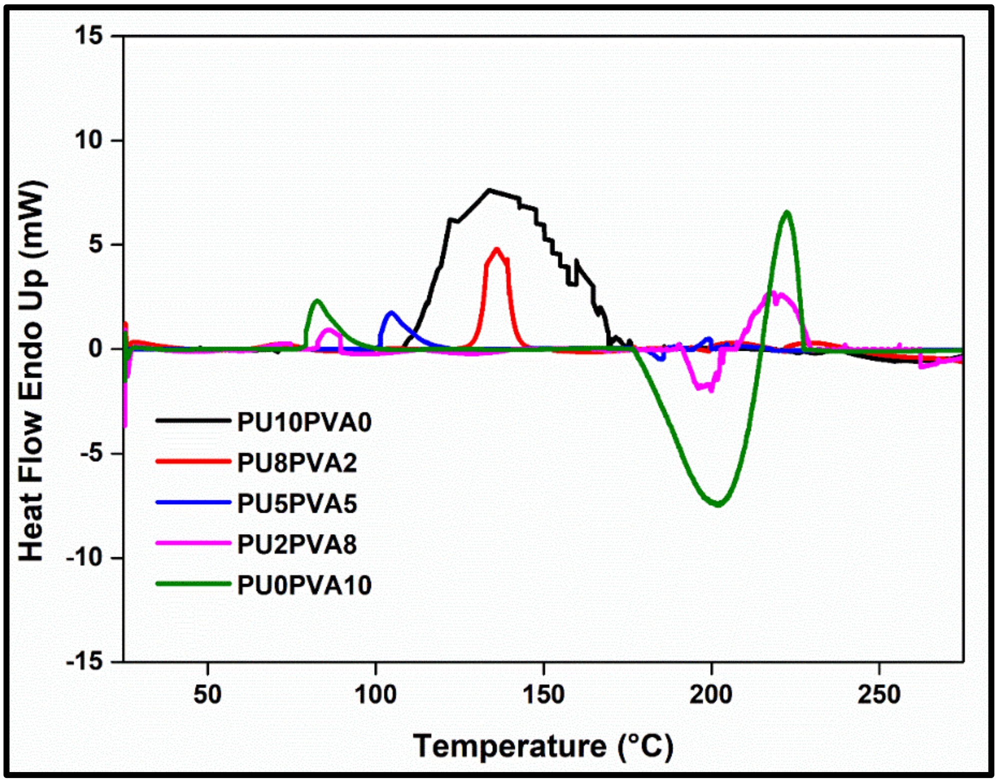


Figure 0.11 DSC curves of Pure NIPU, pure PVA, and their blends

Table 0.3 Tg, Tc, Tm, and % crystallinity of NIPU/PVA blends

S.No	Sample	%Crystallinity**	Tg (°C)	Tc(°C)	Tm(°C)
1	PU10PVA0	00.50	138	-	-
2	PU8PVA2	02.00	132	-	-
3	PU5PVA5	21.00	111	181	203
4	PU2PVA8	31.00	92	194	214
5	PU0PVA10	44.00	82	200	222

** Crystallinity was calculated from XRD curves in Figure 4.12.

4.3.6 X-Ray Diffraction

The XRD patterns for PVA, NIPU, and the blends are shown in Figure 4.12. While PU displays a wider and shallower peak at 2θ = 20°, indicating the presence of amorphous or tiny crystalline areas spread throughout the polymer matrix, PVA has a characteristic peak with a 2θ value of 20° that indicates its crystalline structure [9, 35–38] Notably, the 2θ =20° peak's loss of intensity as the content of NIPU increases points to the blends' decreased crystallinity [39]. XRD patterns were utilised to assess the amount of crystallinity in the prepared samples. It was observed that PVA exhibited maximum crystallinity (44%). On the contrary, NIPU displayed minimum crystallinity (00.50%), as observed in other reports [36]. As a consequence of blending, percentage crystallinity decreased with an increment in NIPU content, indicating a concordant trend similar to that of DSC. Also the presence of small peaks can be attributed to those impurities which have negligible influence on the primary properties of the blends. The XRD patterns accompany the DSC findings and offer supplementary insights into the crystallinity of PVA, NIPU, and their blends.

1. **Crystalline Structure Indicators:** PVA's characteristic peak at 2θ = 20° in the XRD pattern confirms its crystalline structure. The widening and shallowing of PU's peak at 2θ = 20° indicate amorphous or tiny crystalline areas within the polymer matrix.

2. **Crystallinity Changes in Blends:** The decrease in intensity of the 2θ = 20° peak with increasing NIPU content signifies a reduction in crystallinity in the blends. This trend is consistent with the DSC data, indicating a harmonious correlation between the two techniques.

3. **Quantifying Crystallinity:** PVA exhibits the highest crystallinity at 44%, while NIPU has minimal crystallinity at 0.50%. Blending leads to a reduction in the percentage crystallinity, corroborating the DSC findings.

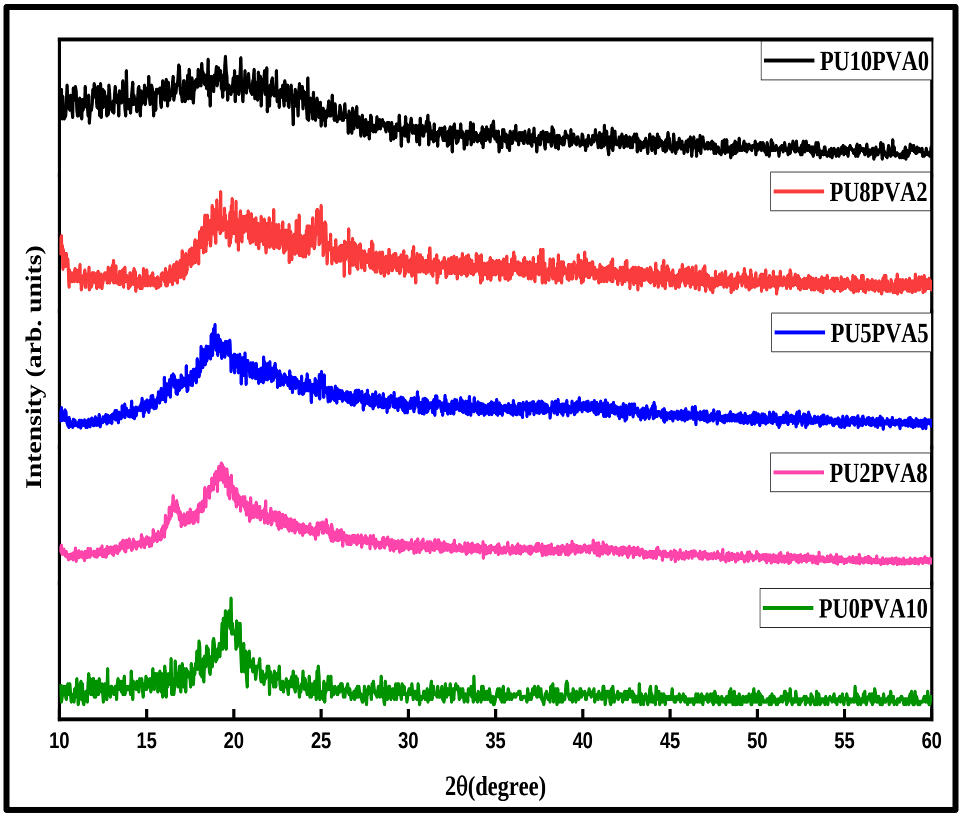


Figure 0.12 XRD pattern of NIPU, PVA and the prepared blends.

4.4 Conclusions

In order to comprehend the flow and deformation of NIPU and PVA, they were blended in different formulations. The FTIR absorption peak at 3322 cm^{-1} is attributable to the hydroxyl group of PVA being slightly moved to a lower wavenumber by the addition of NIPU, showing that the hydrogen bonding of PVA molecules was decreased. The quantity of hydroxyl groups that were available to form hydrogen bonds with the carbonyl group of NIPU increased as the blend's PVA content increased, leading to a notable rise in the total degree of hydrogen bonding and the miscibility of the two phases. The viscosity curves displayed shear thickening characteristics when the PU concentration was above 80%, which may be caused by entangled molecular chains. The two components were found to be partially miscible in the case of PU5PVA8 and PU8PVA2 as evidenced by the fact that the two Tg of PVA-rich and NIPU-rich phases in the blends migrated to the interior of their respective original Tg values. This behaviour is contrary to that observed in the case of PU2PVA8 in which both the polymers i.e., NIPU and PVA are completely miscible; corroborated by the existence of a single peak of Tg in the DSC curve. The blends became non-crystalline when the NIPU level was above 50% because PVA operated as a dispersed phase in the NIPU matrix. 99% structural recovery in thixotropic analysis showed that blend solutions containing more than 20% of NIPU did not deform under heavy shear. The addition of NIPU destroyed PVA's consistency and also led to a reduction in the crystallization ability of PVA as demonstrated by DSC and PXRD pattern.

4.5 References

[1] Malik M, Kaur R. Mechanical and Thermal Properties of Castor Oil–Based Polyurethane Adhesive: Effect of TiO2 Filler. Adv Polym Technol 2018;37:24–30. https://doi.org/https://doi.org/10.1002/adv.21637.

[2] Agrawal A, Kaur R, Walia RS. Development of vegetable oil-based conducting rigid PU foam. E-Polymers 2019;19:411–20. https://doi.org/doi:10.1515/epoly-2019-0042.

[3] Agrawal A, Kaur R. Effect of Nano Filler on the Flammability of Bio-Based RPUF. Integr Ferroelectr 2019;202:20–8.

https://doi.org/10.1080/10584587.2019.1674820.

[4] Khatoon H, Iqbal S, Irfan M, Darda A, Rawat NK. A review on the production, properties and applications of non-isocyanate polyurethane: A greener perspective. Prog Org Coatings 2021;154:106124. https://doi.org/10.1016/j.porgcoat.2020.106124.

[5] Maisonneuve L, Lamarzelle O, Rix E, Grau E, Maisonneuve L, Lamarzelle O, et al. Isocyanate-Free Routes to Polyurethanes and Poly (hydroxy Urethane) s To cite this version : HAL Id : hal-01365096 Isocyanate-free routes to polyurethanes and poly (hydroxy urethane) s 2019.

[6] Gomez-Lopez A, Grignard B, Calvo I, Detrembleur C, Sardon H. Synergetic Effect of Dopamine and Alkoxysilanes in Sustainable Non-Isocyanate Polyurethane Adhesives. Macromol Rapid Commun 2021;42:1–9. https://doi.org/10.1002/marc.202000538.

[7] Hsissou R, Seghiri R, Benzekri Z, Hilali M, Rafik M, Elharfi A. Polymer composite materials: A comprehensive review. Compos Struct 2021;262:113640. https://doi.org/https://doi.org/10.1016/j.compstruct.2021.113640.

[8] Xi X, EPizzi A, Gerardin C, Lei H, Chen X, Amirou S. Preparation and evaluation of glucose based non-isocyanate polyurethane self-blowing rigid foams. Polymers (Basel) 2019;11. https://doi.org/10.3390/polym11111802.

[9] Singh P, Kaur R. Sustainable Xylose-Based Non-Isocyanate Polyurethane Foams with Remarkable Fire-Retardant Properties. J Polym Environ 2022. https://doi.org/10.1007/s10924-022-02638-4.

[10] Wang J, Ye L. Structure and properties of polyvinyl alcohol/polyurethane blends. Compos Part B Eng 2015;69:389–96. https://doi.org/10.1016/j.compositesb.2014.10.013.

[11] Bercea M, Gradinaru LM, Plugariu IA, Mandru M, Tigau DL. Viscoelastic behaviour of self-assembling polyurethane and poly(vinyl alcohol). Polym Int 2020;69:149–55. https://doi.org/10.1002/pi.5928.

[12] Aguiar L. Composition Effects on the Morphology of PVA / Chitosan Electrospun Nanofibers 2022:1–19.

[13] Xi X, Pizzi A, Delmotte L. Isocyanate-free polyurethane coatings and adhesives from mono- and di-saccharides. Polymers (Basel) 2018;10:1–21. https://doi.org/10.3390/polym10040402.

[14] Mandru M, Bercea M, Gradinaru LM, Ciobanu C, Drobota M, Vlad S, et al. Polyurethane/poly(vinyl alcohol) hydrogels: Preparation, characterization and drug delivery. Eur Polym J 2019;118:137–45. https://doi.org/10.1016/j.eurpolymj.2019.05.049.

[15] Utracki LA. Economics of polymer blends. Polym Eng Sci 1982;22:1166–75. https://doi.org/10.1002/pen.760221717.

[16] Nandan B, Kandpal LD, Mathur GN. Poly (ether ether ketone)/ Poly (aryl ether sulfone) Blends : Polymer (Guildf) 2004:1548–63.

[17] Utracki LA, Kanial MR. Melt rheology of polymer blends. Polym Eng Sci 1982;22:96–114. https://doi.org/10.1002/pen.760220211.

[18] Utracki LA. Analysis of Polymer Blends By Rheological Techniques. Annu Tech Conf - Soc Plast Eng 1986;18:286–8.

[19] Kamkar M, Salehiyan R, Goudoulas TB, Abbasi M, Saengow C, Erfanian E, et al. Large amplitude oscillatory shear flow: Microstructural assessment of polymeric systems. Prog Polym Sci 2022;132:101580. https://doi.org/https://doi.org/10.1016/j.progpolymsci.2022.101580.

[20] Wang Y, Selomulya C. Food rheology applications of large amplitude oscillation shear (LAOS). Trends Food Sci Technol 2022;127:221–44. https://doi.org/https://doi.org/10.1016/j.tifs.2022.05.018.

[21] Priti, Batra R, Purwar R. Multifunctional Properties of Non-mulberry Silk Fibroin and Gelatin Blend Solutions: Rheological Study. In: Krupanidhi SB, Gupta V, Sharma Kaushik A, Singh AK, editors. Springer Proc. Mater., vol. 14, Singapore: Springer Singapore; 2022, p. 81–8. https://doi.org/10.1007/978-981-16-5971-3_9.

[22] Kaewprasit K, Kobayashi T, Damrongsakkul S. Thai silk fibroin gelation process enhancing by monohydric and polyhydric alcohols. Int J Biol Macromol 2018;118:1726–35. https://doi.org/10.1016/j.ijbiomac.2018.07.017.

[23] Cuvelier G, Launay B. Frequency dependence of viscoelastic properties of some physical gels near the gel point. Makromol Chemie Macromol Symp 1990;40:23–31. https://doi.org/10.1002/masy.19900400105.

[24] Paroline G. Basics of Applied Rheology 2016:21–9.

[25] Mezger T. 8. Oscillatory tests. Rheol Handb 2020:153–247.

https://doi.org/10.1515/9783748603702-009.

[26] Matsumoto A, Lindsay A, Abedian B, Kaplan DL. Silk fibroin solution properties related to assembly and structure. Macromol Biosci 2008;8:1006–18. https://doi.org/10.1002/mabi.200800020.

[27] Zhu J, Zhang Y, Shao H, Hu X. Electrospinning and rheology of regenerated Bombyx mori silk fibroin aqueous solutions: The effects of pH and concentration. Polymer (Guildf) 2008;49:2880–5. https://doi.org/10.1016/j.polymer.2008.04.049.

[28] Ross-Murphy SB. Structure and rheology of gelatin gels. Imaging Sci J 1997;45:205–9. https://doi.org/10.1080/13682199.1997.11736407.

[29] Kathalewar MS, Joshi PB, Sabnis AS, Malshe VC. Non-isocyanate polyurethanes: From chemistry to applications. RSC Adv 2013;3:4110–29. https://doi.org/10.1039/c2ra21938g.

[30] Ecochard Y, Caillol S. Hybrid polyhydroxyurethanes: How to overcome limitations and reach cutting edge properties? Eur Polym J 2020;137:109915. https://doi.org/10.1016/j.eurpolymj.2020.109915.

[31] Datta J, Włoch M. Progress in non-isocyanate polyurethanes synthesized from cyclic carbonate intermediates and di- or polyamines in the context of structure–properties relationship and from an environmental point of view. Polym Bull 2016;73:1459–96. https://doi.org/10.1007/s00289-015-1546-6.

[32] El Khezraji S, Ben youcef H, Belachemi L, Lopez Manchado MA, Verdejo R, Lahcini M. Recent Progress of Non-Isocyanate Polyurethane Foam and Their

Challenges. Polymers (Basel) 2023;15. https://doi.org/10.3390/polym15020254.

[33] Wang C, Zheng Y, Qiao K, Xie Y, Zhou X. An environmentally friendly preparation and characterization of waterborne polyurethane hydrogels by polyvinyl alcohol physical cross-linking to improve water absorption. RSC Adv 2015;5:73882–91. https://doi.org/10.1039/c5ra11109a.

[34] Awada H, Daneault C. Chemical modification of poly(vinyl alcohol) in water. Appl Sci 2015;5:840–50. https://doi.org/10.3390/app5040840.

[35] Gandara M, Mulinari DR, Monticeli FM, Capri MR. Sugarcane Bagasse Fibers Reinforced in Polyurethane for Sorption of Vegetal Oil. J Nat Fibers 2020;00:1–12. https://doi.org/10.1080/15440478.2019.1710653.

[36] Lei W, Fang C, Zhou X, Li Y, Pu M. Polyurethane elastomer composites reinforced with waste natural cellulosic fibers from office paper in thermal properties. Carbohydr Polym 2018;197:385–94. https://doi.org/10.1016/j.carbpol.2018.06.036.

[37] He X, Xu X, Wan Q, Bo G, Yan Y. Solvent- and Catalyst-free Synthesis , Hybridization and Characterization of Biobased Nonisocyanate Polyurethane (NIPU) 2019. https://doi.org/10.3390/polym11061026.

[38] Singh P, Kaur R. One pot synthesis of bio-based porous isocyanate-free polyurethane materials. Mater Lett 2023;331:133433. https://doi.org/https://doi.org/10.1016/j.matlet.2022.133433.

[39] Shirvani H, Sadeghi M, Taheri Afarani H, Bagheri R. Polyurethane/Poly(vinyl alcohol) Blend Membranes for Gas Separation. Fibers Polym 2018;19:1119–27.

https://doi.org/10.1007/s12221-018-1023-6.

Chapter 5

FRUCTOSE-BASEED NON-ISOCYANATE POLYURETHANE/POLY SODIUM ACRYLATE HYDROGELS: DESIGN, SYNTHESIS AND ENVIRONMENTAL APPLICATIONS

5.1 Introduction

PUs are versatile polymers with exceptional properties, making them ideal for use as engineering materials in various industrial applications ranging from lightweight construction materials, coatings in marine and aerospace industries, rollers, gaskets, seals, conveyor belts, flexible or rigid cellular foams, insulating components for energy conservation, and even as an ideal candidate for biomedical industries due to their biocompatibility [1]. The rapid hydrolysis of isocyanates, is a challenge in humid environments that needs to be countered for synthesizing PUs in such conditions. Some isocyanates have been linked to cancer, mutation, and reproductive harm [2]. Subsequently, the one-pot one-step synthesis of PU hydrogels in water is challenging due to the rapid hydrolysis of isocyanates [3]. They are usually synthesized in bulk or organic solvents, followed by swelling in water [4]. Subsequently, the development of alternative and sustainable approaches to polyurethane synthesis has become a significant area of research.

NIPUs can be easily fabricated from renewable resources and do not require the use of toxic isocyanates, making them environmentally-friendly and safer for production as well as for application [5]. Nearly all these reports included the reaction of synthetic cyclic or dicyclic carbonates with aliphatic diamines (via aminolysis), but only a handful of these studies reported the use of bio-based carbonates and diamines because of the complexities in the synthesis process and poor results [6, 7]. Unfortunately, problems were still found, including the use of a highly toxic reagent (epichlorohydrin), high pressure conditions, harsh reaction conditions, high temperature, and the requirement for a catalyst [8]. Potential solutions to this hindrance in the synthesis of bio-based cyclic carbonates are the conversion of epoxidized vegetable oils or the utilization of glycerin carbonate intermediates. An even better strategy for the synthesis of NIPU is the use of simpler, non-cyclic dimethyl carbonate for the initial stage of carbonation, since it is neither irritating nor mutagenic and avoids the need for ancillary steps of carbonate cyclisation. NIPU materials synthesised by these sustainable routes find application in the coatings and polymer industries, similar to PU [9]. Thermosetting coatings, UV-stable coatings, monolithic flooring, etc. could all be applied using NIPU technologies [10]. NIPUs offer distinct advantages, such as decreased toxicity and environmental impact compared to traditional PUs, yet their potential in environmental applications remains largely unexplored [11–13]. This gap in the literature highlights the need for focused investigations into the environmental applications of NIPUs, which represent a promising area for multidisciplinary research and the formation of sustainable materials with reduced ecological impact. Among the renewable precursors explored for NIPU synthesis, fructose can emerge as a promising building block due to its abundance, biodegradability, and wide availability.

A significant portion of the population faces challenges such as malnutrition, illnesses, and, in extreme cases, fatalities, primarily due to the unavailability of safe drinking water. Water contamination stands as a pressing global challenge, posing risks to ecosystems, public health, and the environment [14, 15]. The multifaceted properties of polyurethane serve as the foundation for its effectiveness in eliminating a broad range of pollutants, including oil, heavy metals, nitrates, phenols, phthalates, and dyes [16–19]. Engineered with high surface area and porosity, it effectively adsorbs pollutants such as heavy metals and dyes. Its chemical stability ensures sustained performance when exposed to different pollutants, while the ability to customize surface chemistry enhances its affinity for specific contaminants like nitrates and phthalates [20]. With robust mechanical strength and adaptable forms, polyurethane offers effective and tailored solutions for eliminating a wide range of contaminants from various environmental settings. These characteristics are enhanced when incorporated into hydrogels, attributed to physically well-defined three-dimensional porous architectures and an increased surface area-to-volume ratio, thus leading to an improved adsorption capacity [21–23]. The ability to construct a flexible network of polymer chains due to the hydrophilic nature of hydrogel adsorbents enables solutes to readily permeate the network and form stable complexes with the functional groups.

Limited research is available on the utilization of bio-based PU hydrogels for environmental applications. The first polyhydroxyurethane (PHU) hydrogels were based on a two-step process involving first the preparation of PHU in the bulk by polyaddition of a hydrophilic poly(ethylene glycol) dicyclic carbonate (PEG-diCC) to a diamine and a crosslinker; followed by their swelling in water [24]. Another example of PHU hydrogels prepared in water consisted of the aminolysis of PEG-diCC with polyethyleneimine at room temperature [25]. Fructose offers a renewable, eco-friendly source for polymer synthesis, reducing environmental impact and enabling the creation of sustainable, biocompatible materials. This facile study aimed to synthesize fructose-based NIPU by using dimethyl carbonate and hexamethylene diamine solution as precursors employing mild reaction conditions, and to study their application in the fabrication of hydrogels, having potential application in dye removal. The hydrogels were prepared (with poly sodium acrylate and N, N-methylene bisacrylamide) through a free radical polymerization method in an aqueous medium. In the process of hydrogel synthesis, sodium acrylate was synthesized by reacting acrylic acid (AA) with sodium hydroxide (NaOH). By harnessing the potential of fructose-based NIPUs and their hydrogels, this research offers valuable insights into the development of effective and eco-friendly solutions for dye removal and highlights the significance of NIPUs in addressing water pollution challenges.

5.2 Experimental Section

5.2.1 Materials and Method

Non-isocyanate polyurethane was synthesized by employing commercially available hexamethylene diamine (HMDA), which was obtained from Sigma Aldrich. D-Fructose, potassium persulphate (KPS), dimethyl carbonate (DMC), crystal violet dye (CV), and malachite green dye (MG) were purchased from Thermo Fisher Scientific. Acrylic acid (AA) and sodium hydroxide (NaOH) were acquired from CDH Pvt. Ltd whereas N, N'-

methylene bis (acrylamide) (MBA) was procured from Merck. All chemicals and solvents used in the analytical measurement trials were of analytical grade and utilized exactly as received.

5.2.2 Preparation of Fructose-Based NIPU (FNPU)

In a round bottom flask, 9.99g of fructose, 6.71g of dimethyl carbonate, and 8.33g of water were added. The reaction mixture was then refluxed at 80℃ for 60 minutes. Afterward, 1g of a 70% solution of hexamethyl diamine were added to the above solution and then the mixture was heated again at 90℃ for one hour. Finally, the solution was cooled to room temperature to obtain the desired NIPU and it was labelled as FNPU.

5.2.3 Preparation of NIPU-based hydrogel (FNHG)

NaOH was used to neutralise AA (2mL), resulting in sodium acrylate (SA), which was subsequently polymerized to produce the hydrogel. Then, an individual aqueous solution containing each FNPU and SA was mixed. Later, 0.05 g of MBA, and 0.05 g of KPS were continuously stirred into the solution. The resulted solution was then transferred into a test tube and heated for one hour in a water bath at a controlled temperature of 60 °C. The gelation process resulted in the formation of the FNHG, which was carefully removed and then further divided into tiny pellets. To make sure that all moisture had been thoroughly removed, the hydrogel pellets were subsequently dried in an oven for 48 hours at 50 °C. A schematic representation of the synthesis of NIPU-based hydrogel is shown in Figure 5.1.

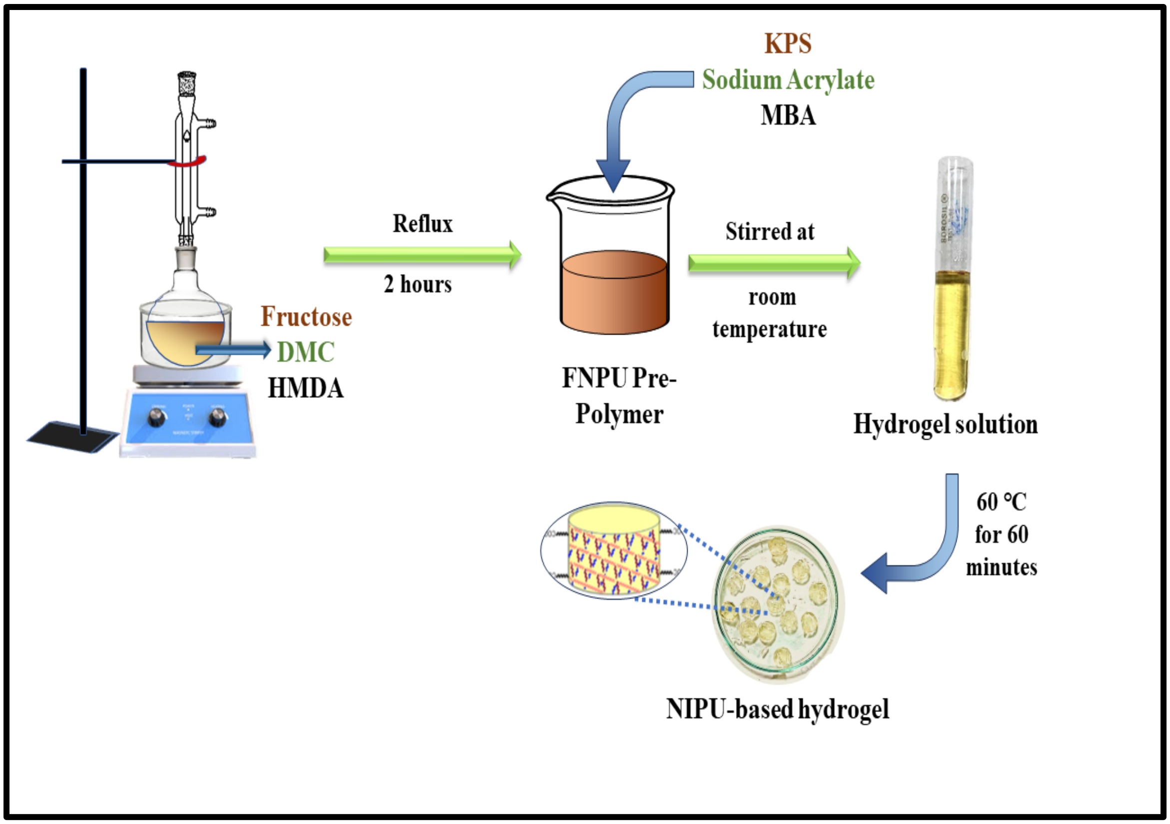


Figure 0.1 Schematic diagram for the synthesis of NIPU-based hydrogel

5.2.4 Swelling Studies

The investigation involved an examination of the swelling behaviour exhibited by synthesized hydrogels via the gravimetric approach at consistent one-hour intervals spanning 24 hours in distilled water. In the initial phase, desiccated hydrogel discs were immersed in distilled water. Any surplus fluid was blotted away using filter paper [26]. Subsequently, the swollen hydrogels were extracted after a specified interval, their mass was carefully recorded and subsequently re-immersed into the distilled water. The determination of the swelling (%) was accomplished by employing the following formula (Equation 5.1).

$$\text{Swelling (\%)} = ((W_e - W_d) / W_d) \times 100 \qquad (5.1)$$

where W_e is the weight of the swollen hydrogel at time t and W_d is the initial weight of the dried hydrogel

5.2.5 pH-Dependent Equilibrium Swelling Percent

Pre-weighed dried samples of the hydrogels were immersed in distilled water and buffer solutions of pH 2,4, 9 and 12 respectively. After a defined period of 24 hours (equilibrium state), the hydrogel samples were carefully removed and their final weights were recorded [27]. The equilibrium swelling percent (ES %) of the hydrogel samples was calculated using the equation (5.2). This calculation allows us to determine the extent of swelling exhibited by the hydrogel samples under specific pH conditions. A higher ES (%) value indicates greater swelling of the hydrogel, while a lower value suggests minimal swelling. By measuring ES (%) at different pH levels, pH sensitivity of the hydrogels can be determined.

$$ES\ (\%) = ((W_t - W_i) / W_i) \times 100 \qquad (5.2)$$

- W_t is the weight of the hydrogel sample after swelling,
- W_i is the initial dry weight of the hydrogel sample.

5.2.6 Swelling Kinetics

In order to understand the mechanism of water diffusion into the hydrogel samples, kinetic swelling studies were conducted using both the Kosmeyer-Peppas model (Equation 5.3) and the Higuchi model (Equation 5.4). Kosmeyer-Peppas model is particularly useful for hydrogels undergoing Fickian or non-Fickian diffusion, which is commonly observed in polymeric networks with complex structures. By fitting experimental swelling data to the

Korsmeyer-Peppas model, we can determine the swelling exponent (*n*), which provides the information about the mechanism of the swelling. On contrary, the Higuchi model provides insights into the kinetics of swelling by describing the swelling as diffusion mechanism. This model helps us to understand how quickly a hydrogel reaches the equilibrium swelling, under specific conditions. The most appropriate and well-fitting model for explaining the drug release mechanism is the one that shows an R^2 value approximately equal to 1.

$$\text{Log (Swelling \%)} = \text{Log K} + \text{n Log t} \qquad (5.3)$$

$$\text{Swelling \%} = K.t^{1/2} \qquad (5.4)$$

where is K is rate constant and t is time.

5.2.7 Sol-gel Analysis

The synthesised hydrogel's uncrosslinked and crosslinked fraction was determined via sol-gel analysis. A hydrogel's insoluble cross-linked portion is called a gel, while its soluble uncross-linked portion is implied by the term "sol". A sol–gel study was performed to examine the uncrosslinked portion of FNHG and control polysodium acrylate (PSA) hydrogel. Weighed (Mi) dried hydrogels were immersed in distilled water for 24 hours at room temperature. The hydrogel discs were then dried in an oven at 45 °C until a constant weight (Me) was achieved [26]. The following equations were used to calculate the sol and gel fractions:

$$\text{Sol Fraction (\%)} = \frac{M_i\text{-Me}}{M_e} \times 100 \qquad (5.5)$$

$$\text{Gel Fraction (\%)} = 100\text{-Sol Fraction} \qquad (5.6)$$

5.2.8 Dye Sorption by FNHG

Batch studies were undertaken to assess the efficacy of the synthesized hydrogel FNHG in removing malachite green (MG) and crystal violet (CV) dyes at room temperature to ensure uniform experimental conditions. In each study, 0.05 g of the testing FNHG sample was put into 25 mL aqueous solution with 20 ppm of CV and MG dye solutions at room temperature for 120 minutes, until equilibrium was reached. The dye sequestration efficiency of the synthesized hydrogel FNHG was assessed. The progression of the sorption phenomenon was precisely monitored using a UV-vis spectrophotometer at a wavelength of 617 and 582 nm for MG and CV dye, respectively. In order to assess the removal efficiency of the dyes and to ascertain the dye elimination capacity of the prepared hydrogel, the following mathematical formulation was employed:

$$\text{Removal efficiency (\%)} = \frac{\text{Co-Ce}}{\text{Co}} \text{ X } 100\ \% \qquad (5.7)$$

where C_o refers to the initial dye concentration and C_e refers to the equilibrium dye concentration.

5.3 Instrumentation

Examination of samples was conducted using an ATR Miracle diamond crystal and a Perkin Elmer Frontier ATR-FTIR. For the purpose of capturing the spectra each sample was scanned in the wave number range of 600 to 4000 cm^{-1}.

The structural analysis of FNPU was performed by employing ^{1}HNMR spectroscopy using Jeol (Model: JNM-ECZ 400S) NMR spectrometer (at 100MHz). Deuterated dimethyl sulfoxide was employed as a solvent to dissolve the sample for analysis.

The thermal stability of the NIPU and hydrogel was evaluated by TGA (Perkin Elmer TGA 4000). As a purge gas, dinitrogen was used. The thermal properties in the range of 50 to 250 °C were examined at a rate of 20 °C min^{-1} in order to determine the thermal parameters of transition.

PXRD was employed using a high-resolution Bruker diffractometer (D8 Discover), in conjunction with a point detector (scintillation counter), to analyze the morphology and structure of the developed samples.

The morphology and internal structure of the hydrogel were examined using a scanning electron microscope (Jeol JSM-6610LVmodel).

5.4 Results and Discussion

5.4.1 Mechanistic Pathway Followed for the Synthesis of NIPU and its Hydrogel

During the synthesis of fructose-based NIPU (FNPU), the fructose molecules act as the starting material for the formation of the polyurethane backbone. Non-cyclic dimethyl carbonate is utilised for the initial stage of carbonation [2], and then nucleophilic substitution is used to carboxymethylate hydroxy groups [29]. Afterward, the adduct is allowed to react with hexamethylene diamine to produce NIPU at ambient pressure as shown in Figure 5.2.

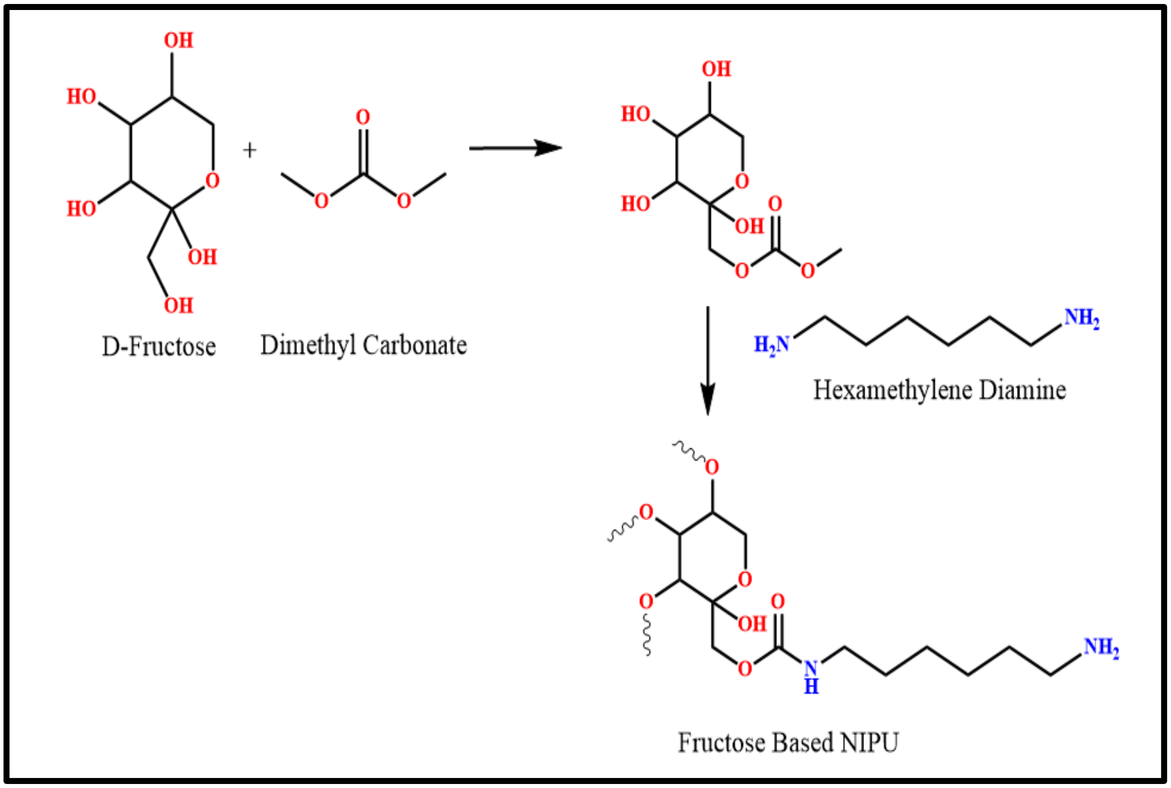


Figure 0.2 Proposed mechansim for the synthesis of fructose-based NIPU (FNPU)

The synthesized FNPU was subsequently employed as a precursor for hydrogel fabrication with SA as a co-monomer, MBA as a crosslinker, and KPS as an initiator. The various chemical interactions and reactions that occur during the synthesis process are presented in Figure 5.3.

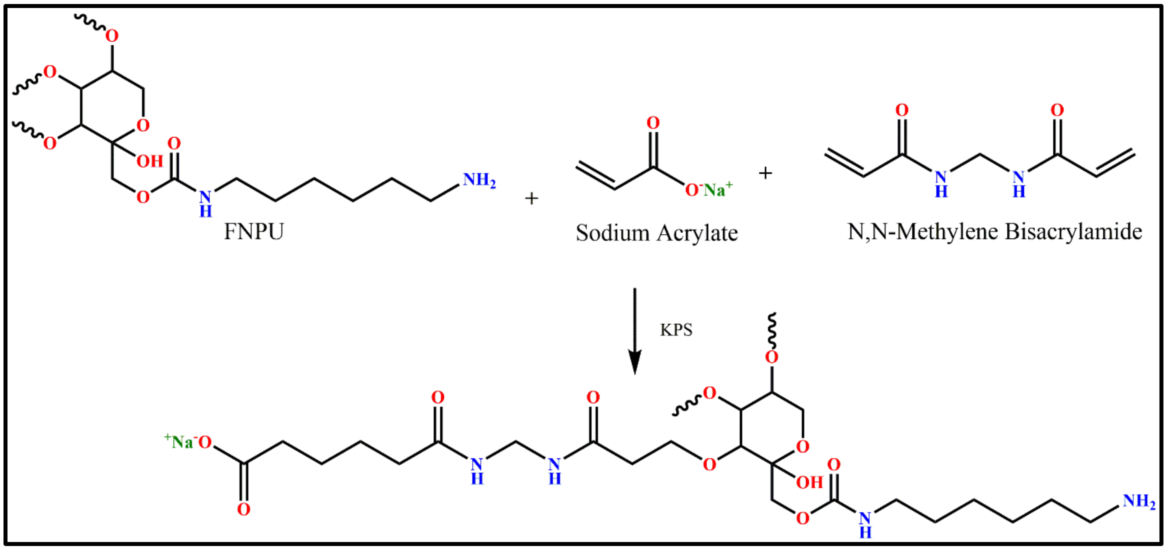


Figure 0.3 Proposed mechansim for the synthesis of fructose-based NIPU hydrogels (FNHG)

KPS serves as an initiator for the free radical polymerization of SA during the hydrogel formation. KPS dissociates in water, generating sulfate radicals ($SO_4^{\bullet -}$) through thermal decomposition. These sulfate radicals initiate the polymerization of SA monomers, leading to the formation of long polymer chains of poly sodium acrylate (PSA) that further crosslink to create the hydrogel matrix.

PSA contains a carboxylate group (–COO$^-$) that reacts with the hydroxyl groups present in the fructose-based NIPU backbone. This reaction involves a nucleophilic addition of the carboxylate group to the hydroxyl group, leading to the formation of ester linkages (–COO–) between the PSA and the NIPU backbone. In addition to the ester linkages formed between PSA and the NIPU backbone, MBA serves as a crosslinker attributing to the presence of two acrylamide groups that react with the carboxylate groups present in SA. The crosslinking reaction involves the development of amide linkages (–CONH–) between the acrylamide groups of MBA and the carboxylate groups of PSA. This crosslinking reaction reinforces the three-dimensional network structure of the hydrogels, enhancing its mechanical integrity and stability.

5.4.2 Characterisation of FNPU and FNHG

In order to study the functional group modifications occurring during the formation of FNPU, FTIR analysis was done (Figure 5.4). In the case of FNPU, the broad peak at 3332 cm^{-1} is collectively attributed to -OH and -NH stretching frequency, exhibiting extensive hydrogen bonding. The bands represented at 1709 cm^{-1} signify the presence of both carboxyl and urethane groups in the hydrogel matrix [30]. Additionally, the C-O ester groups of the network structure are associated with the unique absorption band at 1248 cm^{-1} [10–14]. In the FTIR spectra of MBA, the peak associated with the C-N bond is detected at 1311 cm^{-1}. Notably, this peak demonstrates a significant shift to 1376 cm^{-1} in the case of FNHG hydrogel, which indicates the reduction in conjugation as a consequence of the cross-linking process [34]. As a result, it can be established that the cross-linking of the FNHG has been successfully achieved. Thus, the FTIR spectra of FNPU, MBA, and FNHG confirm the successful synthesis of fructose-based NIPU/ PSA employing an isocyanate-free process at atmospheric pressure.

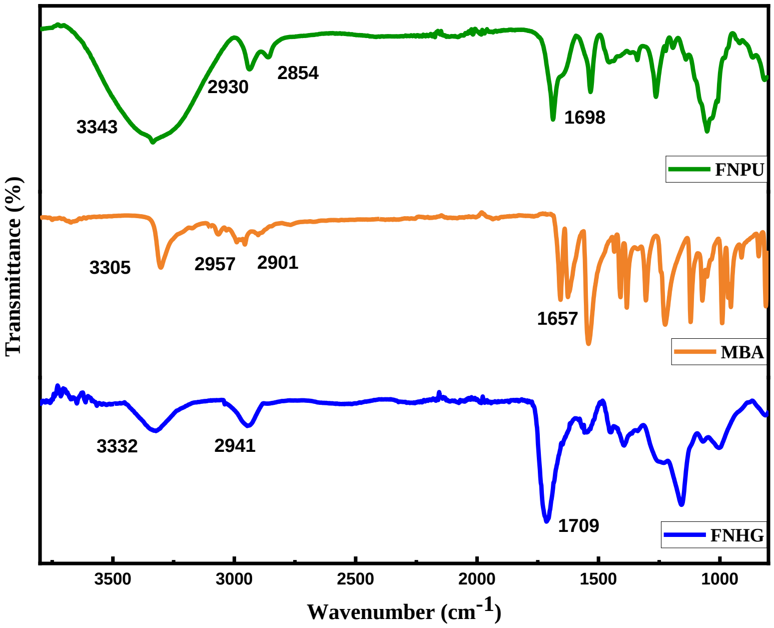


Figure 0.4 FTIR spectra of FNPU, MBA, and FNHG

To further confirm the structure of FNPU, ^{1}HNMR studies were conducted. After dissolving a predetermined amount of FNPU (about 20 mg) in deuterated DMSO, the sample solution was transferred into an NMR tube. Once the ^{1}HNMR data acquisition was completed, characteristics peaks of urethane linkage and other entities were determined. In the NMR spectra presented in Figure 5.5, peaks are observed at around 2.5 ppm and 3.3 ppm, which can be attributed to deuterated dimethyl sulfoxide (DMSO) and its water. The peak observed at 8.3 ppm in the NMR spectra corresponds to the urethane NH group, which is a crucial indicator confirming the formation of the urethane linkage. The peak observed at 4.3 ppm in the NMR spectra can be attributed to the hydroxyl (OH) group present in the synthesised polymer. The peak at δ=5.7 ppm corresponds to the methylene group adjacent to the urethane moiety, while a cluster of peaks within the δ range of 1.3-3.5 ppm arises from the protons of methylene groups in the carbon chain of hexamethylene diamine [35].

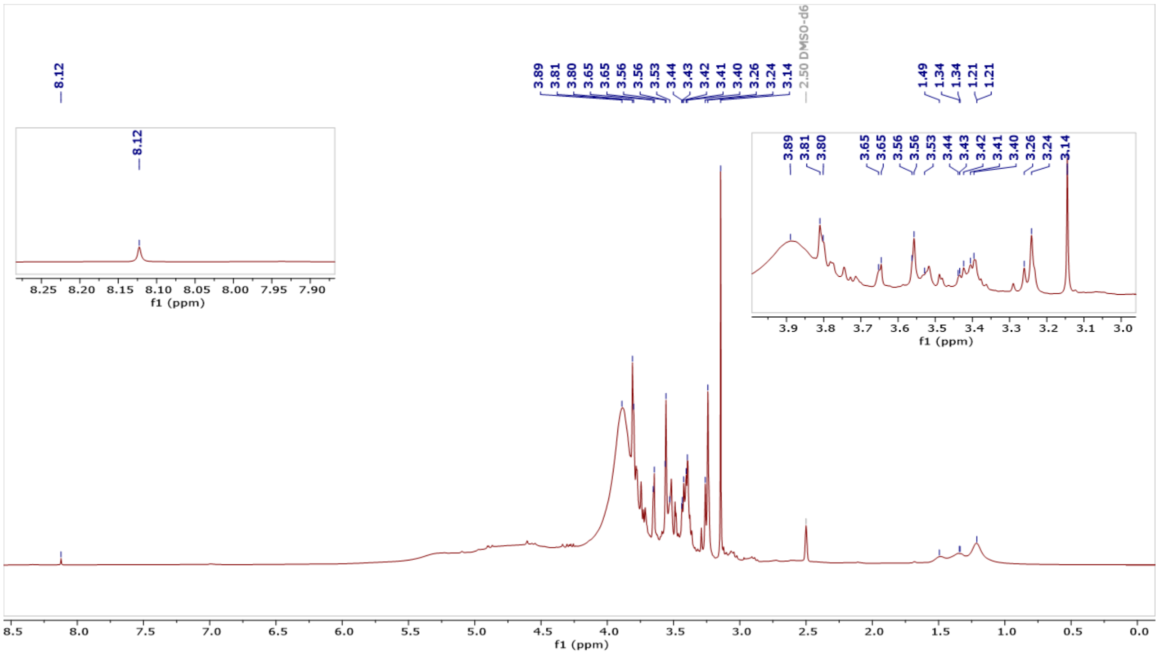


Figure 0.5 ^{1}HNMR spectra of the FNPU

In the PXRD pattern presented in Figure 5.6, the presence of a dominant peak at 20° implies that the synthesized material is segmented PU (NIPU in this case), and the broadness of the peak signifies that the FNPU has a chemical structure in accordance with the previously reported studies [16–18]. This corroborates that fructose-based NIPU has been successfully synthesized using an isocyanate-free approach at atmospheric pressure. The amorphous nature of FNPU, is reduced in the process of formation of FNHG, this could be due to the introduction of other functional groups (such as acrylate entities and amide) and an increase in the number of hydroxyl groups which may induce an ordered structure [37].

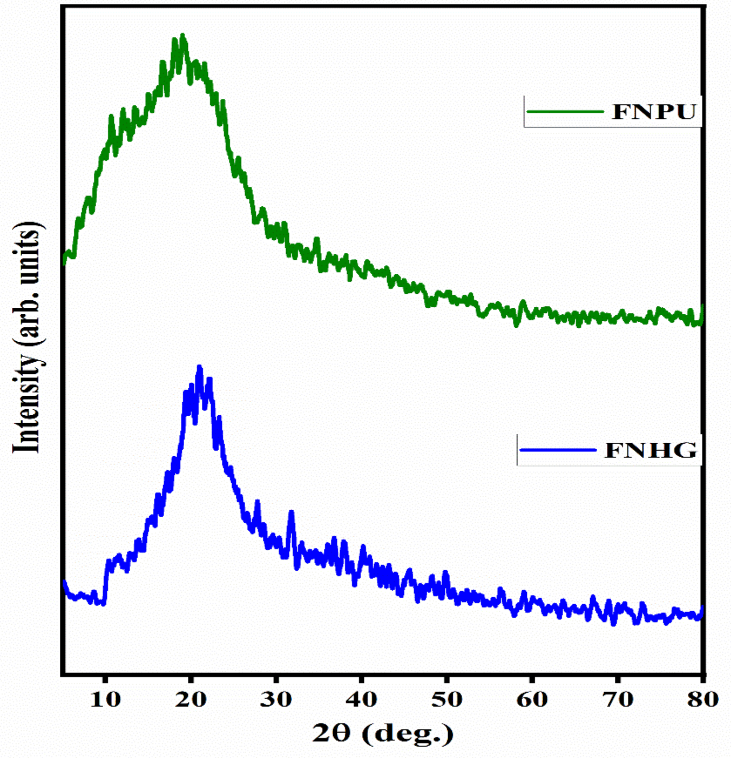


Figure 0.6 PXRD pattern of FNPU and FNHG

TGA was carried out to determine the thermal stability of the synthesized FNPU (Figure 5.7 (a)) and FNHG (Figure 5.7 (b)), in nitrogen (N_2) atmosphere across temperatures ranging from 25 to 700 °C. The TGA curve displays mass loss as a two-step process, as presented in Figure 5.7 (a). The initial weight loss step between 84-224 °C involves the decomposition of hexamine as well as the discharge of absorbed water molecules and evaporation of monomers/oligomers generated during the course of the reaction below 200 °C [24, 25]. The second weight loss step, as observed between 333 and 508 °C is a result of the collapse of the polymer backbone due to the cleavage of the urethane bond. The third and final weight loss step occurs above 500 °C and involves more than 57% mass loss, which can be credited to the possible breakdown of C–C bonds and degradation of the remnants of the pyrolysis by-products from the prior two steps.

Thermal degradation of FNHG hydrogel follows four stages of decomposition as shown in Figure 5.7 (b). The first stage occurs from 74 to 164 °C with weight loss of 0.98% indicating the vaporization of water molecules in FNHG hydrogel. The second stage indicates the loss of carboxyl and hydroxyl groups from the polymeric backbone with weight loss of 48.4% from 200 to 307 °C in FNHG hydrogel [26]. In the third weight loss step, weight loss of 35% from 333°C to 412 °C was observed and can be attributed to the breakdown of cross-links present in FNPU hydrogel. Finally, the last weight loss of 27.62% from 412 to 508 °C can be attributed to the complete degradation of FNHG hydrogel, respectively. The FNHG hydrogel showed an enhanced thermal stability as compared to that of FNPU, thus, indicating that MBA results in the formation of a chemically cross-linked PSA and NIPU network.

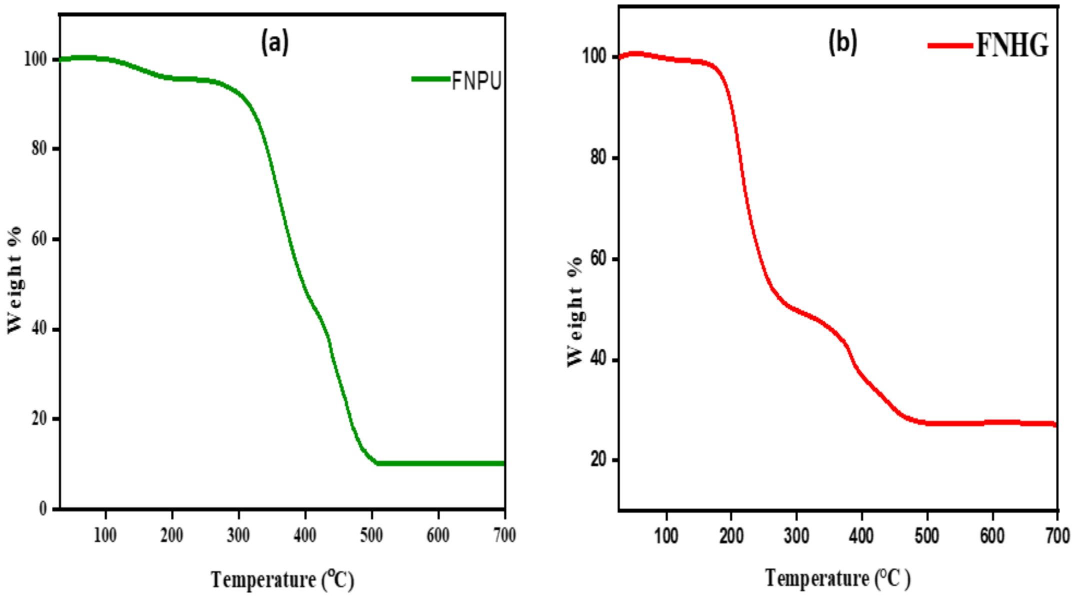


Figure 0.7 TGA thermogram of (a) FNPU and (b) FNHG

The ability of FNHG to swell by retaining water in its sponge-like structure was demonstrated by a swelling study. FNHG demonstrated the maximum swelling of 53.20%

in distilled water, as observed in Figure 5.8 (a). The ES % for FNHG was evaluated in distilled water and in pH 2,4,10, and 12, as presented in Figure 5.8 (b). The equilibrium swelling per cent was observed as maximum at pH 12 and minimum at pH 2. The ionisation characteristics of the synthesised hydrogel can be used to explain its pH-dependent swelling behaviour. At higher pH of 10 and 12, the ES % was found to have greater swelling, these values indicate that the carboxylate groups in poly sodium acrylate deprotonate, which increases ionisation and the electrostatic repulsion between polymer chains. The hydrogel network structure loosens as a result of this repulsion, allowing for increased water absorption and percent equilibrium swelling (PES) values. In contrast, the carboxylate groups are primarily protonated at low pH of 2 and 4 values, which results in less ionisation and reduced electrostatic repulsion between polymer chains. Overall, the ionisation state of carboxylate groups controls the pH-dependent swelling behaviour of the hydrogel. This eventually affects the hydrogel's capacity to swell by modifying the electrostatic interactions and hydrophilicity of the polymer chains [27].

The hydrogel samples showed behaviour that was in line with first-order kinetics and the Korsmeyer-Peppas model, according to the examination of the swelling kinetics data (Figure 5.8(c)). A moderate match of the data to the Higuchi kinetics model is suggested by the derived R^2 value of 0.73582. Furthermore, the Korsmeyer-Peppas model—which takes n to be the diffusion constant and k to be the kinetic constant—was used to examine the hydrogel samples' swelling behaviour. The obtained values of R^2 (0.98019) and n (0.64034) show that the data fit the Korsmeyer-Peppas model well, implying that non-Fickian diffusion kinetics govern the hydrogel samples' swelling behaviour. It suggests that the swelling kinetics of the hydrogel may not be entirely controlled by molecular diffusion, but rather other processes like polymer chain relaxation might also be involved [26].

The control (PSA hydrogel) and FNHG have an observed sol fraction of roughly 22.12% and 19.02% and a gel fraction of roughly 77.88% and 80.98% respectively. These results can be ascribed to the crosslinking density. The addition of NIPU improves the gel fraction by adding more crosslinks to the polymer matrix. These crosslinks aid in the development of a three-dimensional network, giving the hydrogel its structural stability. Low molecular weight species, oligomers, or unreacted monomers in the hydrogel formulation could be the cause of the observed sol fraction.

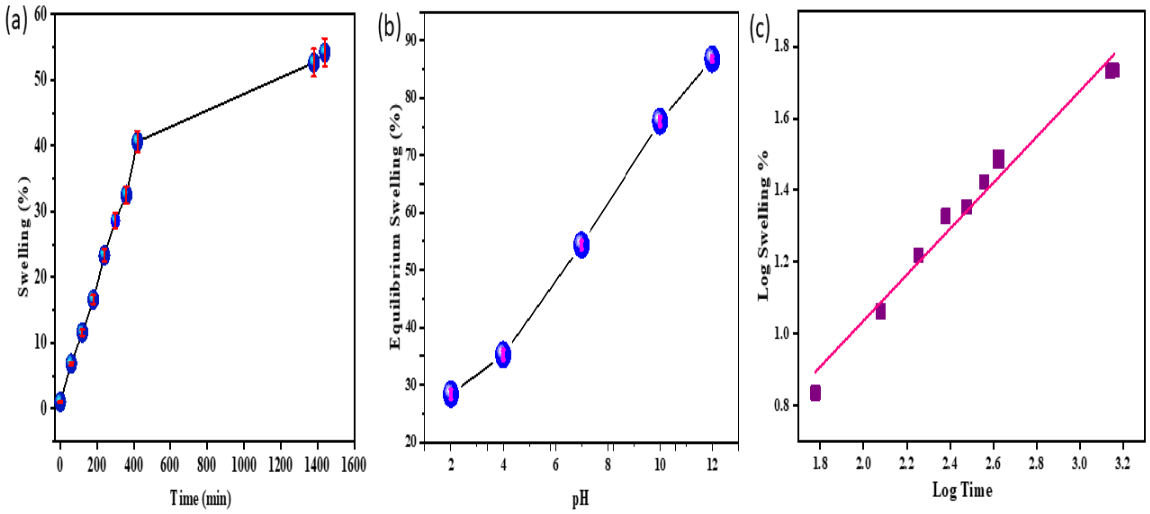


Figure 0.8 (a) Rate of Swelling of FNHG concerning time (b) Equilibrium Swelling percent at different pH and (c) Korsmeyer-Peppas Model for Swelling

Figure 5.9 illustrates the hydrogel's surface morphology before the dye removal experiments. The SEM micrograph displays that FNHG hydrogel exhibits a characteristic macroporous three-dimensional structure. A closer inspection reveals that the FNHG hydrogel has a surface that is substantially rough and contains scattered pores in comparison to the controlled hydrogel (PSA hydrogel). The surface roughness of the FNHG has significantly increased with addition of NIPU due to irregularities or changes in the surface topography of the hydrogel, as seen in Figure 5.9 (a) and (b) respectively. Changes in the crosslinking density and the incorporation of additional polymer chains, as a result of the integration of NIPU, are two reasons for this increase in surface roughness. The hydrogel's overall texture may be impacted by the surface imperfections resulting from the NIPU-polysodium acrylate interactions [38]. This feature of the hydrogel's surface morphology is beneficial for the effective collection and retention of dye molecules, which is a critical characteristic for its application in dye removal processes. The efficient removal of the dye molecules is greatly aided by this complex surface roughness. The existence of the pores and the uneven surface texture increases the surface area available for interactions between the dye molecules and the polymeric network [17]. As a result, this structural characteristic improves the hydrogel's ability to arrest molecules, which makes it suitable for removing dye molecules from the surrounding environment [39].

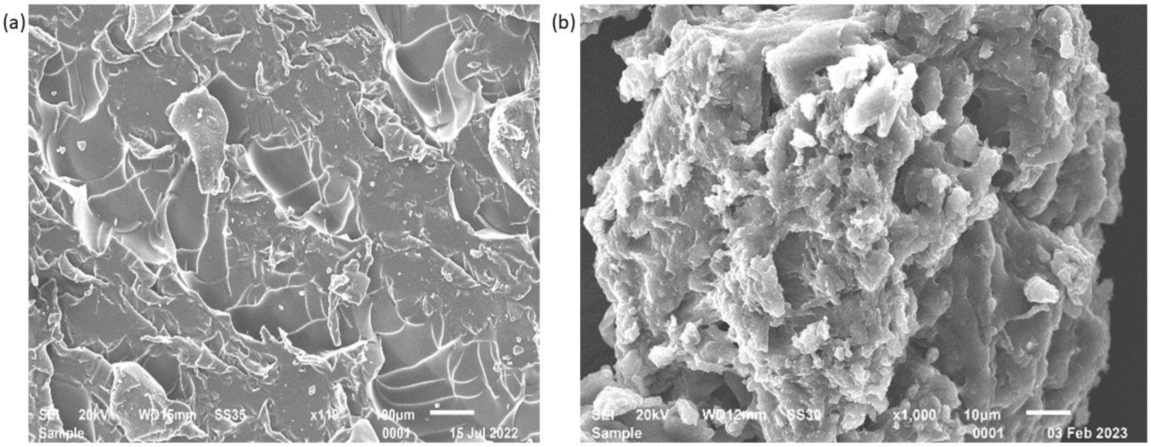


Figure 0.9 SEM image of (a) PSA hydrogel and (b) FNHG

5.4.3 Adsorption behaviour

5.4.3.1 CV and MG Dye Sequestration by FNHG

The removal efficiency of the FNHG hydrogel was assessed for the sequestration of CV and MG dyes under optimum conditions (adsorbent = 0.05 g, adsorbate solution = 25 mL, concentration of CV and MG dyes = 20 mg/L, and contact time = 120 minutes). During the process, a pattern was observed, as seen in Figure 5.10, wherein the absorbance values for both dyes show a steady fall over time, with their levels stabilizing after 120 minutes. Within the first 15 minutes of the interaction of the dye with the synthesized hydrogel, there is an abrupt and noticeable increase in dye uptake. The initial high concentrations of the dye solutions along with the availability of readily accessible adsorption sites on the hydrogel surface are responsible for this phenomenon [40]. The degree of removal, however, steadily slows down as time passes and the system gets closer to equilibrium, eventually achieving equilibrium at 120 minutes [41]. The decline in the concentration of CV and MG solution and the gradual occupation of previously available empty sites on the sorbent material are two concurrent processes that can be attributed to this slowing down of the dye removal rate.

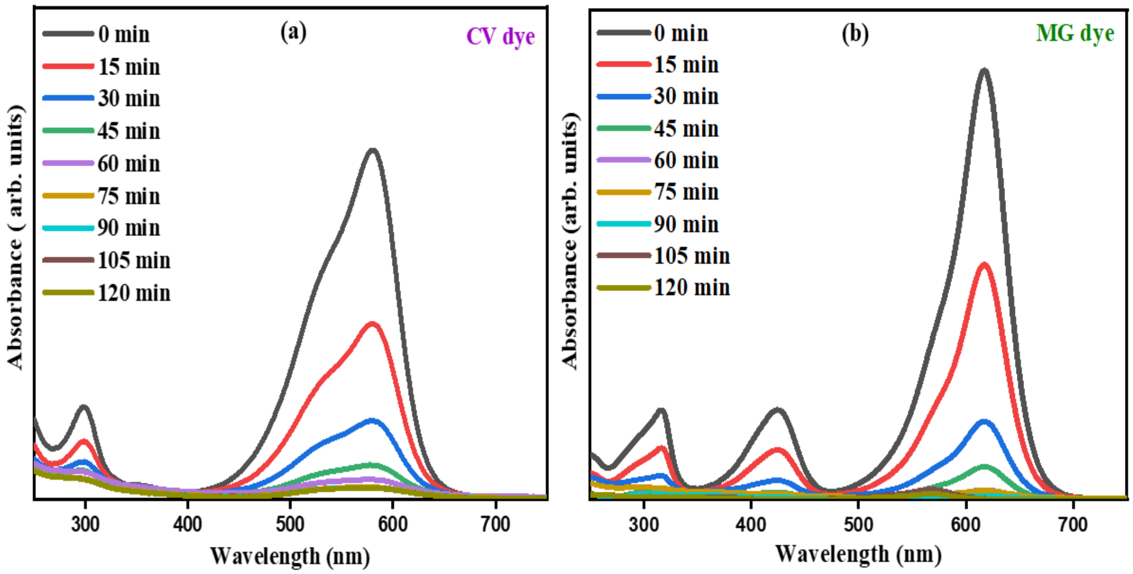


Figure 0.10 Absorbance spectra of (a) CV and (b) MG dye

The removal efficiency of controlled hydrogel was found to be around 86.84% and 90.8% for CV and MG dye, respectively whereas that for FNHG it was found to be 96.87% and 99.80% for CV dye and MG dye respectively. The removal efficiency of FNHG hydrogel (Figure 5.11 a) is significantly higher than that of the control PSA hydrogel (Figure 5.11 b). These enhanced removal efficiencies of dyes via FNHG highlight the expediency of the synthesised hydrogel as an efficient material for the uptake of dyes from wastewater.

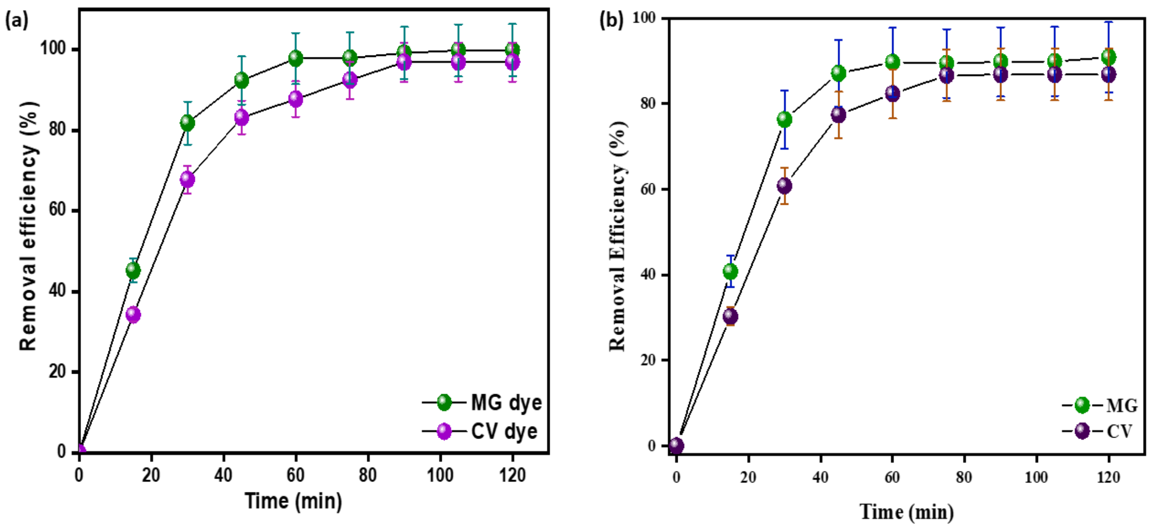


Figure 0.11 Removal efficiency of CV and MG dyes (a) FNHG and (b) Control PSA hydrogel

5.4.3.2 Possible Interaction between the synthesised hydrogel and cationic dyes

It has been reported that organic and inorganic contaminants found in wastewater can be effectively removed by polyurethane foams [6, 23–25]. However, several studies have also demonstrated that modified polyurethane-based adsorbents exhibit enhanced adsorption attributes, for example, surface area, pore size, and functional groups. These modification can be achieved through various methods, such as coating, grafting, and crosslinking; to introduce specific chemical moieties that can interact with target pollutants [42]. In this study, NIPU has been modified via crosslinking with PSA. Depending on the structure and charge of the pollutants, removal can be accomplished through a variety of interactions between the synthesized hydrogel FNHG and dye molecules, including electrostatic interactions, ion exchange, and hydrophobic interactions, etc. CV and MG dyes are water soluble and exhibit a positive charge when dissolved in aqueous solutions [44]. Negatively charged polymer entities present on the surface of hydrogel, owing to the inclusion of PSA into the matrix may have primarily facilitated the electrostatic attraction of positively charged cationic dye molecules. Leite et al studied the inclusion of sodium dodecyl sulfate (SDS) into the PU matrix which enabled the establishment of a hydrophobic ionic pairing between the cationic dye and the anionic surfactant, which displayed a strong affinity for PU [43]. Therefore, it can be suggested that poly(sodium acrylate) might be acting as a carrier to adsorb CV and MG dye molecules into the polymeric network similar to SDS. Despite the predominance of electrostatic interactions, some weaker hydrogen bonding may also occur amongst the amine groups of dye molecules and hydroxyl groups of the synthesized hydrogel [45]. The interactions between CV and MG dyes with PSA polymer lead to their attachment and probable adsorption onto the polymer surface. This property of PSA polymer makes it a useful carrier in the NIPU matrix for applications related to dye sequestration and material formulation.

5.4.3.3 Comparison with reported sorbents for CV and MG dye

In the quest to develop efficient and eco-friendly adsorbents for dye removal, the performance of fructose-based non-isocyanate polyurethane hydrogels (FNHG) was rigorously evaluated against other commonly used adsorbents. The removal efficiencies of FNHG for CV and MG dyes were compared with those of traditional adsorbents to highlight the superior capabilities of the newly synthesized hydrogels (Table 5.1).

Table 0.1 Comparison of removal efficiencies of various adsorbents for CV and MG dyes

Adsorbent	Dye	Contact time (minutes)	% Removal	Reference
Agriculture wastes residue	CV	90	82%	[46]
Gold-Silver Nanoparticles	MG	2880	90%	[47]
Cucumis sativus	CV	90	72.27%	[48]
Bentonite-Silver	MG	5	86.47%	[49]
Coniferous pinus bark powder	CV	120	87%	[50]
$ZnFe_2O_4$ nanocomposite by halloysite nanotube	CV	120	91%	[51]
This work	CV	120	96.87%	-
This work	MG	120	99.8%	-

5.4 Conclusions

The present work demonstrated the synthesis of fructose-based NIPU and then its hydrogels via a facile and novel approach. The adopted method results in the formation of hydrogel in a more ecologically friendly manner by avoiding harsh reaction conditions and by reducing gelation time to 60 minutes. The fundamental structural framework of the NIPU backbone is fructose, which was selected as a sustainable and easily accessible building element. The acquired results from FTIR and ^{1}HNMR spectroscopy confirm the formation of urethane linkages throughout the polymer matrix. The hydrogel's three-dimensional network structure is strengthened by the addition of the crosslinker MBA. Furthermore, PSA serves as a comonomer in the hydrogel formulation, facilitating the introduction of various functional groups. TGA results revealed that this structural reinforcement not only improves the hydrogel's thermal stability but also provides the mechanical resilience required for its practical applications. SEM morphology displays the presence of a rough surface, providing additional surface area. The study also demonstrated that the fabricated hydrogel can act as a potential material for the sequestration of cation dyes. The NIPU-based hydrogel exhibited high removal efficiency towards CV and MG dyes, i.e., 96.87% and 99.8%, respectively. The novel fructose-based NIPU hydrogels have enormous potential as an effective material for dye removal from aqueous solutions.

5.5 References

[1] Niesiobędzka J, Datta J. Challenges and recent advances in bio-based isocyanate production. Green Chem 2023;25:2482–504. https://doi.org/10.1039/d2gc04644j.

[2] Golling FE, Pires R, Hecking A, Weikard J, Richter F, Danielmeier K, et al. Polyurethanes for coatings and adhesives – chemistry and applications. Polym Int 2019;68:848–55. https://doi.org/https://doi.org/10.1002/pi.5665.

[3] Polo Fonseca L, Trinca RB, Felisberti MI. Amphiphilic polyurethane hydrogels as smart carriers for acidic hydrophobic drugs. Int J Pharm 2018;546:106–14. https://doi.org/10.1016/j.ijpharm.2018.05.034.

[4] Bourguignon M, Thomassin JM, Grignard B, Vertruyen B, Detrembleur C. Water-Borne Isocyanate-Free Polyurethane Hydrogels with Adaptable Functionality and Behavior. Macromol Rapid Commun 2021;42:1–13. https://doi.org/10.1002/marc.202000482.

[5] Filippova O V., Maksimkin A V., Dayyoub T, Larionov DI, Telyshev D V. Sustainable Elastomers for Actuators: “Green” Synthetic Approaches and Material Properties. Polymers (Basel) 2023;15:1–32. https://doi.org/10.3390/polym15122755.

[6] Gholami H, Yeganeh H. Soybean oil-derived non-isocyanate polyurethanes containing azetidinium groups as antibacterial wound dressing membranes. Eur Polym J 2021;142:110142. https://doi.org/10.1016/j.eurpolymj.2020.110142.

[7] Malik M, Kaur R. Synthesis of NIPU by the carbonation of canola oil using highly efficient 5,10,15-tris(pentafluorophenyl)corrolato-manganese(III) complex as novel catalyst. Polym Adv Technol 2018;29:1078–85. https://doi.org/10.1002/pat.4219.

[8] Chen X, Li J, Xi X, Pizzi A, Zhou X, Fredon E, et al. Condensed tannin-glucose-based NIPU bio-foams of improved fire retardancy. Polym Degrad Stab 2020;175:109121. https://doi.org/10.1016/j.polymdegradstab.2020.109121.

[9] Blattmann H, Fleischer M, Bähr M, Mülhaupt R. Isocyanate- and Phosgene-Free Routes to Polyfunctional Cyclic Carbonates and Green Polyurethanes by Fixation of Carbon Dioxide. Macromol Rapid Commun 2014;35:1238–54. https://doi.org/https://doi.org/10.1002/marc.201400209.

[10] Dechent SE, Kleij AW, Luinstra GA. Fully bio-derived CO2 polymers for non-

isocyanate based polyurethane synthesis. Green Chem 2020;22:969–78. https://doi.org/10.1039/c9gc03488a.

[11] Singh P, Kaur R. One pot synthesis of bio-based porous isocyanate-free polyurethane materials. Mater Lett 2023;331:133433. https://doi.org/https://doi.org/10.1016/j.matlet.2022.133433.

[12] Singh P, Kaur R. Sustainable Xylose-Based Non-Isocyanate Polyurethane Foams with Remarkable Fire-Retardant Properties. J Polym Environ 2022. https://doi.org/10.1007/s10924-022-02638-4.

[13] He X, Xu X, Wan Q, Bo G, Yan Y. Solvent- and Catalyst-free Synthesis , Hybridization and Characterization of Biobased Nonisocyanate Polyurethane (NIPU) 2019. https://doi.org/10.3390/polym11061026.

[14] Pandey B, Singh P, Kumar V. Adsorption of anionic dye from aqueous environment using surface-engineered Zn/Cu hydroxy double salt-based material: mechanistic, equilibrium and kinetic studies. J Environ Sci Heal Part A, Toxic/Hazardous Subst Environ Eng 2023;58:869–84. https://doi.org/10.1080/10934529.2023.2243193.

[15] Pathak J, Singh P. Adsorptive Removal of Congo Red Using Organically Modified Zinc–Copper–Nickel Ternary Metal Hydroxide: Kinetics, Isotherms and Adsorption Studies. J Polym Environ 2023;31:327–44. https://doi.org/10.1007/s10924-022-02612-0.

[16] Gandara M, Mulinari DR, Monticeli FM, Capri MR. Sugarcane Bagasse Fibers Reinforced in Polyurethane for Sorption of Vegetal Oil. J Nat Fibers 2020;00:1–12. https://doi.org/10.1080/15440478.2019.1710653.

[17] Qin J, Qiu F, Rong X, Yan J, Zhao H, Yang D. Adsorption behavior of crystal violet from aqueous solutions with chitosan-graphite oxide modified polyurethane as an adsorbent. J Appl Polym Sci 2015;132:1–10. https://doi.org/10.1002/app.41828.

[18] Sultan M. Polyurethane for removal of organic dyes from textile wastewater. Environ Chem Lett 2017;15:347–66. https://doi.org/10.1007/s10311-016-0597-8.

[19] Song X, Wang Y, Zhou L, Luo X, Liu J. Halloysite nanotubes stabilized polyurethane foam carbon coupled with iron oxide for high-efficient and fast treatment of arsenic(III/V) wastewater. Chem Eng Res Des 2021;165:298–307. https://doi.org/10.1016/j.cherd.2020.11.001.

[20] Barroso-Solares S, Merillas B, Cimavilla-Román P, Rodriguez-Perez MA, Pinto J. Enhanced nitrates-polluted water remediation by polyurethane/sepiolite cellular nanocomposites. J Clean Prod 2020;254:120038. https://doi.org/https://doi.org/10.1016/j.jclepro.2020.120038.

[21] Qi X, Li Z, Shen L, Qin T, Qian Y, Zhao S, et al. Highly efficient dye decontamination via microbial salecan polysaccharide-based gels. Carbohydr Polym 2019;219:1–11. https://doi.org/10.1016/j.carbpol.2019.05.021.

[22] Qi X, Wei W, Su T, Zhang J, Dong W. Fabrication of a new polysaccharide-based adsorbent for water purification. Carbohydr Polym 2018;195:368–77. https://doi.org/10.1016/j.carbpol.2018.04.112.

[23] Qi X, Wu L, Su T, Zhang J, Dong W. Polysaccharide-based cationic hydrogels for dye adsorption. Colloids Surfaces B Biointerfaces 2018;170:364–72. https://doi.org/10.1016/j.colsurfb.2018.06.036.

[24] Gennen S, Grignard B, Thomassin JM, Gilbert B, Vertruyen B, Jerome C, et al. Polyhydroxyurethane hydrogels: Synthesis and characterizations. Eur Polym J 2016;84:849–62. https://doi.org/10.1016/j.eurpolymj.2016.07.013.

[25] Bourguignon M, Thomassin JM, Grignard B, Jerome C, Detrembleur C. Fast and facile one-pot one-step preparation of nonisocyanate polyurethane hydrogels in water at room temperature. ACS Sustain Chem Eng 2019;7:12601–10. https://doi.org/10.1021/acssuschemeng.9b02624.

[26] Meena P, Singh P, Warkar SG. Development and assessment of carboxymethyl tamarind kernel gum-based pH-responsive hydrogel for release of diclofenac sodium. Eur Polym J 2023;197:112340. https://doi.org/10.1016/j.eurpolymj.2023.112340.

[27] Bajpai SK, Swarnkar MP. Controlled release of anti-diabetic drug metformin hydrochloride from cellulose/PEG/poly (SA) ter-polymeric hydrogels. J Macromol Sci Part A Pure Appl Chem 2017;54:186–93. https://doi.org/10.1080/10601325.2017.1265406.

[28] Annunziata L, Diallo AK, Fouquay S, Michaud G, Simon F, Brusson J-M, et al. α{,}ω-Di(glycerol carbonate) telechelic polyesters and polyolefins as precursors to polyhydroxyurethanes: an isocyanate-free approach. Green Chem 2014;16:1947–56. https://doi.org/10.1039/C3GC41821A.

[29] Fiorani G, Perosa A, Selva M. Dimethyl carbonate: A versatile reagent for a sustainable valorization of renewables. Green Chem 2018;20:288–322. https://doi.org/10.1039/c7gc02118f.

[30] Ghasri M, Bouhendi H, Kabiri K, Zohuriaan-Mehr MJ, Karami Z, Omidian H. Superabsorbent polymers achieved by surface cross linking of poly(sodium acrylate) using microwave method. Iran Polym J (English Ed 2019;28:539–48. https://doi.org/10.1007/s13726-019-00722-6.

[31] Xi X, Pizzi A, Delmotte L. Isocyanate-free polyurethane coatings and adhesives from mono- and di-saccharides. Polymers (Basel) 2018;10:1–21. https://doi.org/10.3390/polym10040402.

[32] Xi X, Pizzi A, Gerardin C, Du G. Glucose-biobased non-isocyanate polyurethane rigid foams. J Renew Mater 2019;7:301–12. https://doi.org/10.32604/jrm.2019.04174.

[33] Xi X, EPizzi A, Gerardin C, Lei H, Chen X, Amirou S. Preparation and evaluation of glucose based non-isocyanate polyurethane self-blowing rigid foams. Polymers (Basel) 2019;11. https://doi.org/10.3390/polym11111802.

[34] Tushar, Saraswat Y, Meena P, Warkar SG. Synthesis and characterization of novel xanthan gum-based pH-sensitive hydrogel for metformin hydrochloride release. Colloid Polym Sci 2023. https://doi.org/10.1007/s00396-023-05135-9.

[35] Eltayeb M, Li SX, Okoye PU, Wang S. Carbodiimide-Assisted Synthesis of High Purity Bis(cyclic carbonate) Under Atmospheric Conditions for Preparation of Non-Isocyanate Polyurethane. J Polym Environ 2021;29:1880–93. https://doi.org/10.1007/s10924-020-01996-1.

[36] Lei W, Fang C, Zhou X, Li Y, Pu M. Polyurethane elastomer composites reinforced with waste natural cellulosic fibers from office paper in thermal properties.

Carbohydr Polym 2018;197:385–94. https://doi.org/10.1016/j.carbpol.2018.06.036.

[37] Das M, Yadav M, Shukla F, Ansari S, Jadeja RN, Thakore S. Facile design of a dextran derived polyurethane hydrogel and metallopolymer: A sustainable approach for elimination of organic dyes and reduction of nitrophenols. New J Chem 2020;44:19122–34. https://doi.org/10.1039/d0nj01871f.

[38] Cui L, Yao Y, Yim EKF. The effects of surface topography modification on hydrogel properties. APL Bioeng 2021;5:31509. https://doi.org/10.1063/5.0046076.

[39] Salama A, Shukry N, El-Sakhawy M. Carboxymethyl cellulose-g-poly(2-(dimethylamino) ethyl methacrylate) hydrogel as adsorbent for dye removal. Int J Biol Macromol 2015;73:72–5. https://doi.org/10.1016/j.ijbiomac.2014.11.002.

[40] Pandey B, Singh P, Kumar V. Photocatalytic-sorption processes for the removal of pollutants from wastewater using polymer metal oxide nanocomposites and associated environmental risks. Environ Nanotechnology, Monit Manag 2021;16:100596. https://doi.org/10.1016/j.enmm.2021.100596.

[41] Pandey B, Singh P. Statistical Optimization of Process Parameters for Ultrafast Uptake of Anionic Azo Dyes by Efficient Sorbent: Zn/Cu Layered Double Hydroxide. Appl Organomet Chem 2023;37:1–18. https://doi.org/10.1002/aoc.7072.

[42] Selvasembian R, Gwenzi W, Chaukura N, Mthembu S. Recent advances in the polyurethane-based adsorbents for the decontamination of hazardous wastewater pollutants. J Hazard Mater 2021;417:125960. https://doi.org/10.1016/j.jhazmat.2021.125960.

[43] Leite BT, Robaina NF, Gustavo L. Removal of Malachite Green from Aqueous Medium Employing Polyurethane Foam as Adsorbent and Sodium Dodecylsulfate as Carrier Water Air Soil Pollu 2012:1303–13. https://doi.org/10.1007/s11270-011-0946-y.

[44] George G, Saravanakumar MP. Facile synthesis of carbon-coated layered double hydroxide and its comparative characterisation with Zn–Al LDH: application on crystal violet and malachite green dye adsorption—isotherm, kinetics and Box-Behnken design. Environ Sci Pollut Res 2018;25:30236–54. https://doi.org/10.1007/s11356-018-3001-3.

[45] Bekiari V, Lianos P. Poly (sodium acrylate) hydrogels as potential pH-sensitive sorbents for the removal of model organic and inorganic pollutants from water. Glob Nest J 2010;12:262–9. https://doi.org/10.30955/gnj.000720.

[46] Loulidi I, Boukhlifi F, Ouchabi M, Amar A, Jabri M, Kali A, et al. Adsorption of Crystal Violet onto an Agricultural Waste Residue: Kinetics, Isotherm, Thermodynamics, and Mechanism of Adsorption. Sci World J 2020;2020:5873521. https://doi.org/https://doi.org/10.1155/2020/5873521.

[47] Ojo SA, Lateef A, Azeez MA, Oladejo SM, Akinwale AS, Asafa TB, et al. Biomedical and Catalytic Applications of Gold and Silver-Gold Alloy Nanoparticles Biosynthesized Using Cell-Free Extract of Bacillus Safensis LAU 13: Antifungal, Dye Degradation, Anti-Coagulant and Thrombolytic Activities. IEEE Trans Nanobioscience 2016;15:433–42. https://doi.org/10.1109/TNB.2016.2559161.

[48] Smitha T, Santhi T, Prasad AL, Manonmani S. Cucumis sativus used as adsorbent

for the removal of dyes from aqueous solution. Arab J Chem 2017;10:S244–51. https://doi.org/https://doi.org/10.1016/j.arabjc.2012.07.030.

[49] Diana-Carmen M, Dumitra R, Ana-Maria G, Ana-Maria R, Andrei CV, Valentin Z, et al. Silver Nanoparticles Incorporated on Natural Clay as an Inhibitor against the New ISO SS Bacteria Isolated from Sewage Sludge, Involved in Malachite Green Dye Oxidation. Molecules 2022;27. https://doi.org/10.3390/molecules27185791.

[50] Ahmad R. Studies on adsorption of crystal violet dye from aqueous solution onto coniferous pinus bark powder (CPBP). J Hazard Mater 2009;171:767–73. https://doi.org/https://doi.org/10.1016/j.jhazmat.2009.06.060.

[51] Al-abidy M, Al-nayili A. Enhancement of photocatalytic activities of ZnFe2O4 composite by incorporating halloysite nanotubes for effective elimination of aqueous organic pollutants. Environ Monit Assess 2022;195:190. https://doi.org/10.1007/s10661-022-10811-4.

Chapter 6

DEVELOPMENT OF POLYHYDROXYURETHANE HYDROGEL FOR pH-SENSITIVE DRUG DELIVERY OF CEFADROXIL

6.1 Introduction

Polymeric hydrogels are three-dimensional structures composed of physical or chemical networks that are able to absorb and retain an enormous quantity of water. These materials are composed of hydrophilic polymer networks that have a three-dimensional structure [1]. They can be obtained from natural or synthetic sources and are categorized depending on their structure and response to environmental factors, including pH, temperature, light, and chemicals. The significant capacity to expand makes these structures highly desirable for their utilization as materials in biomedical applications [2]. The insoluble three-dimensional networks facilitate the immobilization and release of active compounds or biomolecules. The inherent characteristics of the network are established by the polymers utilized and the interactions formed within it. They have become a central research focus in recent years due to their prospective uses in the biological field. As a consequence of their biocompatibility, water absorption capacity, similarity to human tissue, amphiphilic nature, and self-assembly property, they are commonly used to design controlled drug release systems, contact lenses, wound dressings, engineering scaffolds, and biosensors [3].

One of the most significant groups of polymers is PUs. Their primary chain has a urethane linkage (-N-CO-O), which is a distinguishing property of PUs and is comparable to the peptide bonds that exist in protein structures [4]. Their resemblance to human tissue has led to their application as an integral component in various medical devices, including the dialysis membrane [5], intra-aortic balloons [6], heart valves [7], temporary scaffolds [8], and breast implants [9]. Furthermore, because of their strong mechanical properties and biocompatibility, polyurethanes have been thoroughly researched for use in biomedical applications as hydrogels, scaffolds, and electrospun fibers for the controlled release of medications and biological molecules [10]. Furthermore, synthetic polyurethane-based hydrogels have garnered increasing attention as biomaterials due to their exceptional qualities, which include biodegradability, non-toxicity, and elasticity [11].

As acclaimed, they are conventionally synthesized through the chemical reaction between diisocyanate and multifunctional polyols. In contemporary times, polyols can be readily derived from biomass feedstock and frequently possess the ability to decompose naturally and be compatible with living organisms. Nevertheless, the diisocyanate agents are derived from petroleum and are synthesized using amines and highly poisonous phosgene. Isocyanates are extremely toxic compounds with substantial health and environmental hazards [4]. Certain isocyanates have been associated with the development of cancer, genetic mutations, and reproductive damage. Furthermore, the high rate of hydrolysis poses a difficulty in areas with high humidity. Due to the quick hydrolysis of isocyanates, the one-pot, one-step synthesis of PU hydrogels in water is difficult. Typically, they are produced in large quantities or organic solvents, and then swollen in water. Therefore, investigating alternate and sustainable methods for PU synthesis has become a prominent field of study.

As a result, there has been an increasing interest in developing safer options, culminating in the emergence of Non-Isocyanate Polyurethanes (NIPUs). NIPUs are produced using methods that do not include isocyanates. These methods usually involve the reaction of cyclic carbonates with amines. This reaction leads to the creation of polyhydroxyurethanes (PHUs) with hydroxyl groups in close proximity to urethane moieties. The presence of hydroxy-urethane moieties instead of urethanes significantly affects the properties of PHUs, such as higher water absorption, improved chemical resistance, and increased hydrolytic stability compared to conventional PUs [5].

Besides reducing the health hazards associated with isocyanates, NIPUs are also more environmentally friendly and safer for biomedical applications [6]. The production of NIPU hydrogels can be challenging due to various considerations. Firstly, the rate of the aminolysis reaction of cyclic carbonates is slow, resulting in thermally activated polyadditions in organic solvents or bulk at extremely high temperatures [7]. The use of (organo)catalysts[8] can aid in this process, although the application of this method in water as the exclusive medium for polymerization is rare and primarily restricted to the production of hydrophobic PHU in aqueous dispersions with stabilizers/surfactants [9]. Recent research has utilized the crystallization process of poly(ethylene glycol) (PEG) to produce non-isocyanate poly(hydroxyurethane) hydrogels using inject printing. By meticulously manipulating the crystallization conditions, the storage modulus of these hydrogels can be modified by up to three orders of magnitude in response to changes in temperature. Surprisingly, the substance undergoes plastic deformation at a temperature of

45 °C but quickly recovers its mechanical properties when cooled down to 25 °C. This novel method emphasized the promise of PEG-based hydrogels for many applications [10]. However, ensuring that the NIPU hydrogels are responsive to specific stimuli, such as pH changes, requires thorough design and optimization of the polymer networks. One approach to enhance hydrogel performance is through the incorporation of different materials within the structure, such as the combination of NIPU with sodium polyacrylate (NaPA). NaPA is a frequently employed polyelectrolyte with high electronegativity. It is commonly utilized in the production of self-healing hydrogels and superabsorbents. The compound NaPA can be easily dissolved in an aqueous solution containing alkali or urea [11].

This study presents the successful development of bio-based NIPU (PHU) and its subsequent conversion into pH-sensitive hydrogels by combining it with NaPA. Furthermore, this work reports the synthesis of cefadroxil-loaded PHU/NaPA hydrogels for the pH-dependent controlled release of cefadroxil (CF), marking the first instance of such evaluation. Cefadroxil (first-generation cephalosporin antibiotic) has a relatively short plasma half-life, which is approximately 1-1.5 hours, thus requiring frequent dosing [12]. By incorporating cefadroxil into a smart hydrogel, it is possible to achieve a regulated and prolonged release of the drug. The synthesised hydrogels were analyzed using various techniques, including ATR-FTIR, SEM, PXRD, and TGA. This study encompasses the in vitro evaluation of cefadroxil release to quantify the percentage of CF discharged. In order to elucidate the mechanism of drug release, we employed a variety of kinetic models, including First-Order, Higuchi, Hixson-Crowell, Korsmeyer-Peppas, and Zero-Order. This finding has important implications for the advancement of tailored drug delivery systems.

Implementing this approach can enhance patient adherence, decrease the frequency of dose, and guarantee a more uniform and efficient antibiotic treatment.

6.2 Experimental Section

6.2.1 Materials

Polyhydroxyurethane was synthesized using commercially available HMDA sourced from Thermo Fisher Scientific. D-Fructose, potassium persulfate (KPS), N, N'-methylenebis(acrylamide) (MBA) and DMC were procured from Sigma Aldrich. Acrylic acid (AA) and sodium hydroxide (NaOH) were obtained from SRL Chemicals. The drug cefadroxil was purchased from Unicure India Pvt Ltd. All chemicals and solvents employed in analytical measurements were of analytical grade and used without further modification.

6.2.2 Preparation of Fructose-based PHU

To prepare the Fructose-based NIPU (PHU), a solution was created by mixing 110.90 mmol of fructose, 148.97 mmol of dimethyl carbonate, and 925.5 mmol of water in a round-bottom flask with three necks. The mixture was then refluxed at 80℃ for a short duration. Following this, 8.60 mmol of a 70% solution of HMDA was introduced, and the mixture was heated once more, this time at 90℃ for one hour. Finally, the solution was allowed to rest at room temperature.

6.2.3 Preparation of PHU based hydrogel

To synthesize NIPU based hydrogel (PHU/NaPA), initially, NaOH was dissolved in 27.75 mmol of AA, maintaining a neutral pH to produce a sodium acrylate solution.

Subsequently, a separate aqueous solution containing NIPU and SA was blended. Then, 0.227 mmol of MBA and 0.1294 mmol of potassium persulfate (KPS) were continuously mixed into the solution. Following this, the resulting mixture was poured into a test tube and heated to 60°C for one hour in a water bath. The resulting hydrogel, formed during the gelation process, was carefully extracted and subsequently cut into small pellets. These hydrogel pellets were then dried for 48 hours at 50°C in an oven to ensure the complete removal of any remaining moisture.

6.2.4 Preparation of Cefadroxil-Loaded Hydrogels

Using the in situ approach, Cefadroxil was added to the PHU/NaPA hydrogel to prepare the drug-loaded hydrogel (CF-PHU/NaPA). All of the cross-linking and polymerization processes were allowed to occur at 25 °C. During the addition of KPS and MBA to the reaction mixture of PHU/NaPA, 0.1375 mmole of CF was added to synthesise the CF-PHU/NaPA hydrogels. Aside from the addition of the drug-containing ethanol solution, the rest of the hydrogel synthesis procedure remained the same as described previously.

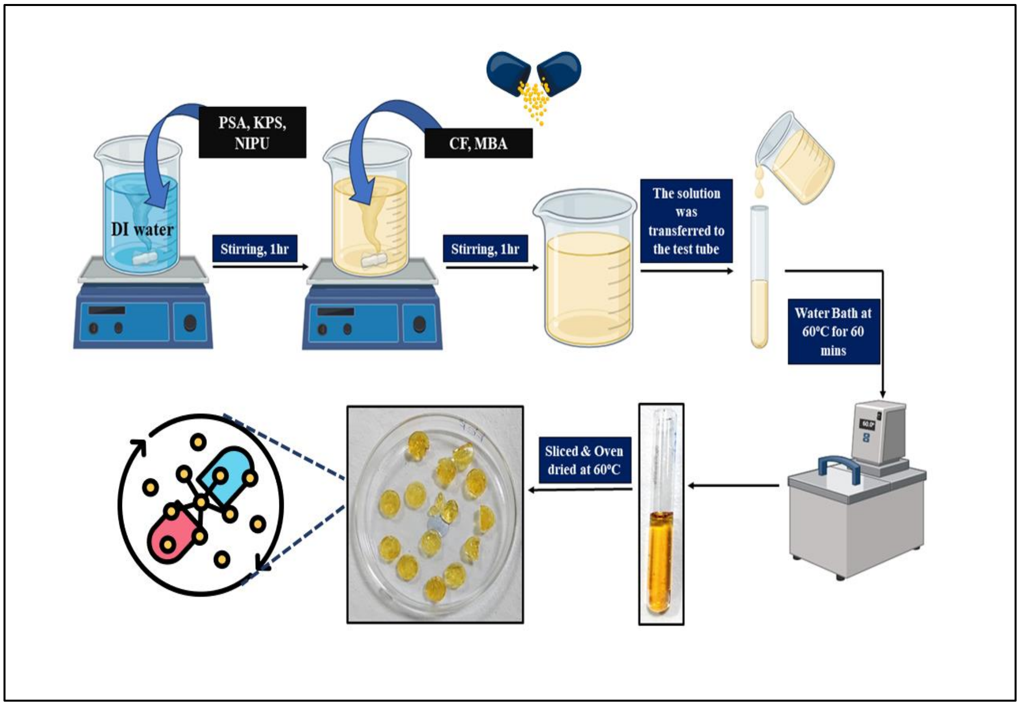


Figure 0.1 Preparation of CF-PHU/NaPA hydrogel

6.2.5 Swelling Studies

The study focused on analyzing the swelling characteristics of the produced hydrogels using a gravimetric method over a 24-hour period with consistent one-hour intervals. Initially, dehydrated hydrogel pellets were placed in distilled water. Excess liquid was removed by blotting with filter paper. After specific time intervals, the swollen hydrogels were removed, their weight was meticulously measured, and they were then placed back into the distilled water. The swelling ratio was calculated using the following formula.

$$\text{Swelling (\%)} = ((W_e - W_d) / W_d) \times 100 \qquad (6.1)$$

where W_e is the weight of the swollen hydrogel at time t, and W_d is the initial weight of the dried hydrogel.

6.2.6 Drug Entrapment Efficiency

The predetermined amount of hydrogel pellet (0.1 g) was immersed in a 100 ml buffer solution with a pH of 7.4 for 24 hours. A UV-visible spectrophotometer (model: Cary 300 UV-Vis) was used to measure the absorbance of the sample at a maximum wavelength of 271 nm for cefadroxil [13]. The provided equation was used to compute the entrapment efficiency of the drug (DEE) (%)

$$\text{DEE}\ (\%) = \frac{\text{Drug amount in hydrogel}}{\text{Theoretical drug content in hydrogel pellet}} \times 100 \qquad (6.2)$$

6.2.7 In vitro release study of Cefadroxil

The phosphate buffer saline and HCl-KCl buffer were used to conduct the drug release analysis. To ascertain the release pattern of both drugs, the weighted hydrogel discs (0.1 g) were placed in 100 ml of pH 1.2 and 7.4 at 37 °C in an orbital incubator shaker at 200 RPM. 3 ml samples were taken after a certain amount of time, and to keep the volume constant, an equal volume of new buffer was added. A UV-visible spectrophotometer (model: Cary 300 UV-Vis) was used to measure the release of cefadroxil at a maximum wavelength of 271 nm. A calibration curve was created to determine the drug content after the technique was completed in triplicate.

6.2.8 Release Kinetics of Cefadroxil

To assess the release mechanism of both drugs from the synthetic hydrogel, the Hixson-Crowell, Higuchi, zero-order, Korsmeyer-Peppas, and first-order models were used to kinetically simulate the release data. Each model's coefficient of determination (R^2) values were compared, and the model with an R^2 value closest to 1 was deemed the best fit.

6.2.9. Characterisation

PXRD was carried out utilising a Bruker D8 diffractometer with CuK radiation at a temperature range between 5 and 70 °C. The ATR-FTIR spectrophotometer (Model: Nicolet iS50 FTIR) was used to record ATR-FTIR spectra. The PerkinElmer TGA 4000 was used for the thermogravimetric analysis, which was conducted between 30 and 850 °C at a heating rate of 10 °C/min in a N_2 environment. SEM was used to investigate the surface morphology (Model: JEOL Japan Mode: JSM 6610LV). The morphology of PHU/NaPA and CF-PHU/NaPA hydrogels was examined using a scanning electron microscope (Jeol JSM-6610LVmodel).

6.2.10. Cytotoxicity Studies (MTT Assay)

The cytotoxicity of the synthesized PHU/NaPA hydrogel on the L929 cell line (obtained from NCCS Pune) was assessed using the MTT Assay. The cells were cultivated in a 96-well plate with a density of 10,000 cells per well. The culture was maintained for 24 hours in RPMI 1640 media (RPMI 1640 media- AT162-1L), supplemented with 10% FBS (Fetal Bovine Serum - HIMEDIA-RM 10432) and 1% antibiotic solution. The culture was incubated at a temperature of 37°C with a 5% CO_2 atmosphere. The following day, cells were treated with various concentrations. The untreated cells were designated as the control group, whereas the cells without MTT were designated as the blank group. Following a 24-hour incubation period, MTT Solution (with a specified concentration) was introduced to the cell culture and incubated for an additional 2 hours. After completing the experiment, the liquid above the culture was taken out, and the layer of cells was dissolved in 100 µl of

Dimethyl Sulfoxide. The dissolved cells were then analyzed using an Elisa plate reader (iMark, Biorad, USA) at wavelengths of 540 nm and 660 nm.

6.3 Results and Discussion

6.3.1 Mechanism of Synthesis of PHU, PHU/NaPA and CF-PHU/NaPA

For the synthesis of fructose-based non-isocyanate polyurethane (PHU), fructose molecules serve as the foundational material for forming the polyhydroxyurethane backbone. Initially, dimethyl carbonate is employed in the carbonation stage, facilitating the introduction of carbonate groups [4]. Subsequently, carboxymethylation of the hydroxyl groups present in fructose occurs as a consequence of nucleophilic substitution [6]. The resulting adduct is then reacted with hexamethylene diamine under ambient pressure conditions to produce the PHU.

The fabricated hydrogel, derived from the synthesized fructose-based NIPU (PHU), utilizes Sodium Acrylate as a co-monomer, N,N’-Methylenebisacrylamide (MBA) as a crosslinker, and Potassium Persulfate (KPS) as an initiator. KPS triggers the free radical polymerization of SA during the hydrogel formation. Upon dissociation in water, KPS generates sulfate radicals ($SO_4^{\bullet-}$) via thermal decomposition. These radicals instigate the polymerization of sodium acrylate monomers, culminating in the development of elongated polymeric chains of Sodium Polyacrylate (NaPA) . These chains subsequently crosslink to form the hydrogel matrix. NaPA, containing a carboxylate group ($–COO^-$), interacts with the hydroxyl groups present in the PHU backbone. This interaction involves a nucleophilic addition of the carboxylate group to the hydroxyl group, forming ester linkages (–COO–) between NaPA and the PHU backbone. Along with the ester linkages existing between NaPA and the PHU backbone, MBA aids as a crosslinker, which can be attributed to the presence of two acrylamide groups that react with the carboxylate groups present in NaPA. The crosslinking reaction involves the formation of amide linkages (–CONH–) between the acrylamide groups of MBA and the carboxylate groups of NaPA [14]. This crosslinking reaction strengthens the three-dimensional network structure of the hydrogels, thereby enhancing their mechanical integrity and stability. This study provides a comprehensive understanding of the synthesis process, offering valuable insights into the design and development of robust hydrogels for potential in pH-sensitive drug delivery applications.

Furthermore, hydrogen bonding between cefadroxil and NaPA facilitates the successful synthesis of a Cefadroxil-loaded PHU/NaPA hydrogel (CF-PHU/NaPA), as depicted in Figure 6.2.

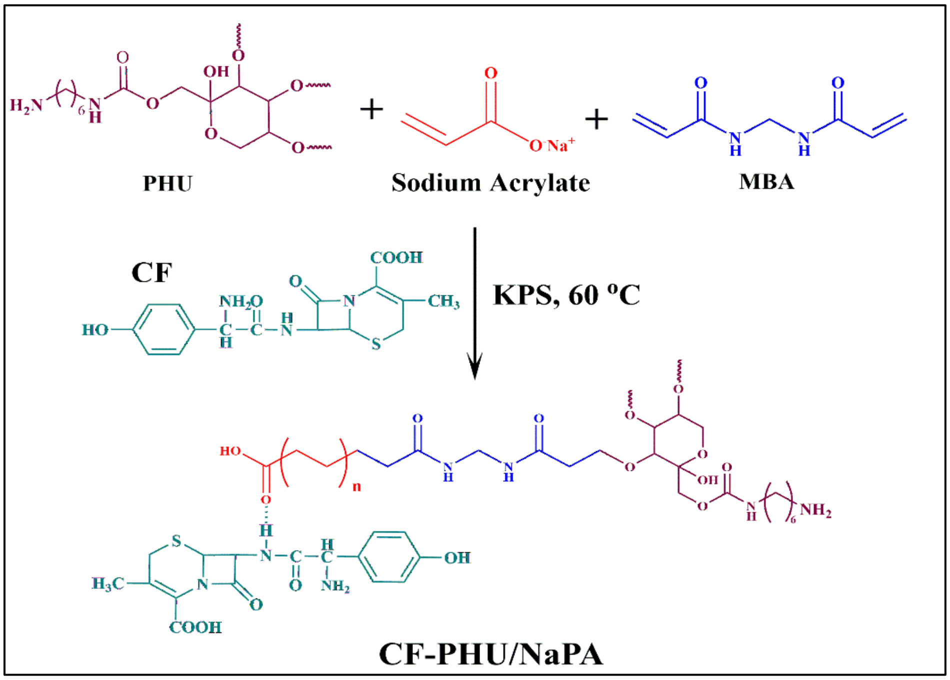


Figure 0.2 Proposed mechanism for the synthesis of CF-PHU/NaPA

6.3.2 Structural and Morphological Properties

In the spectra of NIPU (PHU), the presence of a distinctive band at 1694 cm^{-1} indicates the formation of urethane C=O bonds [17]. In addition, a band was observed at a wave number of 3343 cm^{-1} which signifies the existence of hydroxyl groups and -NH- moiety of urethane groups. Furthermore, the presence of a band at 1532 cm^{-1} suggests the existence of the urethane group, indicating the presence of carbamate structures [18]. The examination of FTIR spectra indicates that PHU has chemical structure that is similar, but not identical, to pristine fructose and dimethylene carbonate. This shows that the fructose-based NIPU (PHU) generated using similar processes also have similar spectra. These findings confirm the successful production of PHU utilizing a method that does not need isocyanate and is carried out at normal atmospheric pressure.

On the other hand, the FTIR spectrum of MBA exhibits a distinct peak at 1316 cm^{-1}, which is attributed to the C-N bond [19]. Nevertheless, after cross-linking, the formation of PHU/NaPA results in a significant shift of this peak to 1368 cm^{-1}, which suggests a decrease in conjugation, indicating the successful crosslinking of PHU/NaPA. Therefore, suggesting that the cross-linking of the PHU/NaPA has been successfully accomplished. Furthermore, the existence of carboxyl and urethane groups in the hydrogel matrix is confirmed by the appearance of bands at 1715 cm^{-1}. Furthermore, the C-O ester groups within the network structure are linked to the distinct absorption band at 1250 cm^{-1}. The FTIR spectra of PHU, MBA, and PHU/NaPA (Figure 6.3) provide evidence that the fructose-based PHU/NaPA was successfully synthesized using a technique that does not use isocyanate and was conducted at atmospheric pressure.

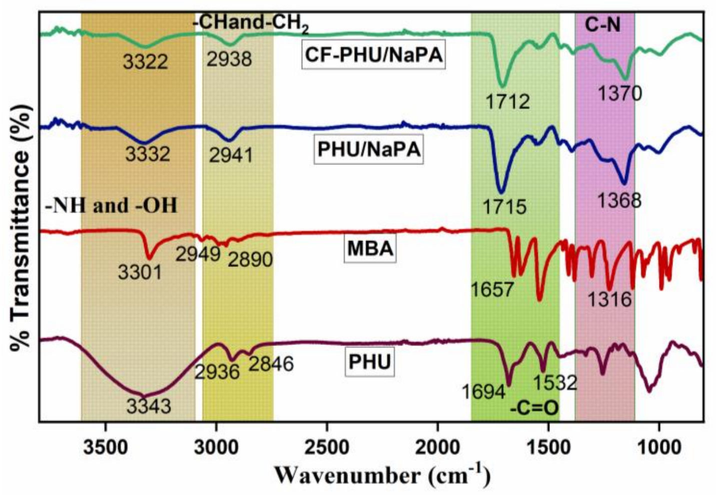


Figure 0.3 FTIR spectra of PHU, PHU/NaPA, and CF-PHU/NaPADH.

The PXRD pattern in Figure 6.4 indicates that the PHU is segmented PU as suggested by the presence of a prominent peak at 20° [20], [4]. Additionally, the broadness of the peak indicates that PHU has a chemical structure consistent with earlier findings [14]. The PXRD curves of cefadroxil exhibited distinct peaks at values of 10.2, 12.5, 14.7, 16.86, 21.81, 23.67, and 25.9, indicating the crystalline form of the drug [21]. The PXRD curve of the CF-PHU/NaPA hydrogel exhibited a broad band, indicating the amorphous nature of the synthesized hydrogel. However, the PXRD curve of the drug-loaded hydrogel does not exhibit any peak associated with CF, suggesting that both medicines are uniformly dispersed inside the cross-linked polymer network. Despite the addition of NaPA and medicines, the produced hydrogel exhibited amorphous characteristics.

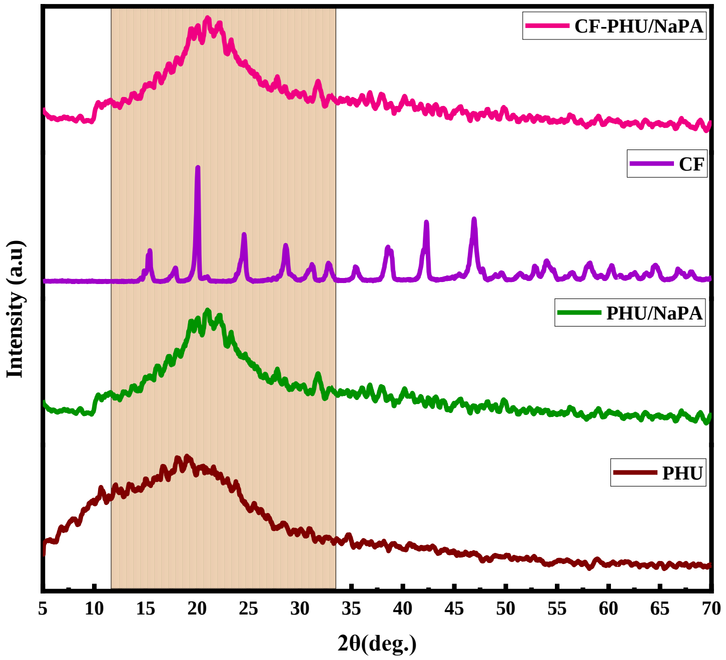


Figure 0.4 XRD pattern of PHU, PHU/NaPA, CF, CF-PHU/NaPA

Micrograph of the PHU/NaPA hydrogel (Figure 6.5 (a)) exhibits an uneven surface morphology and a porous structure, suggesting excellent water retention and drug-loading capabilities. Conversely, micrograph of the CF-loaded CF-PHU/NaPA hydrogel (Figure 6.5 (b)) reveals a smoother surface with fewer pores. This indicates that the drug has been successfully incorporated into the hydrogel matrix, reducing interstitial voids within the hydrogel [24].

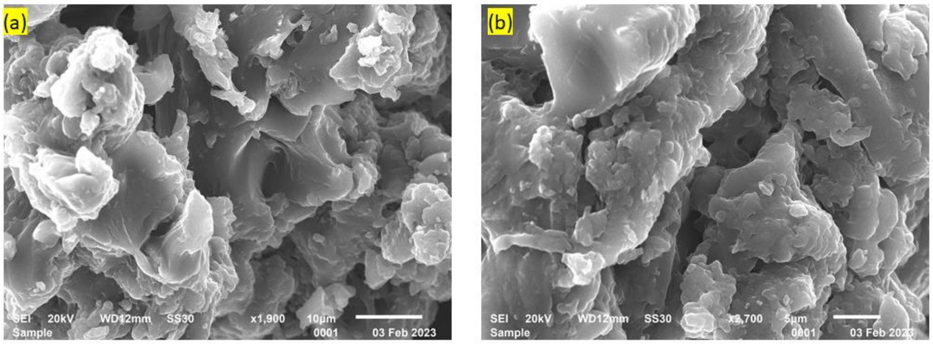


Figure 0.5 SEM image of (a) PHU/NaPA hydrogel and (b) CF-PHU/NaPA hydrogel

6.3.3 Thermal Properties

The thermogravimetric analysis (TGA) of the synthesized products namely; PHU, PHU/NaPA, CF-PHU/NaPA has been demonstrated in Figure 6.6. The thermogram of PHU reveals a three-step degradation process. The initial weight loss step observed between 91-152 °C can be attributed to multiple factors, including the decomposition of hexamine and excess acid, discharge of absorbed water up to 120 °C and the evaporation of monomers or oligomers generated during the course of the reaction below 200 °C [22]. The second weight loss step, occurring between 220 and 290 °C, is likely due to the fragmentation of the polymer backbone as a result of the cleavage of urethane bonds. The final weight loss step, observed above 570 °C, involves more than 60% mass loss [23]. This significant mass loss can be attributed to the possible fragmentation of carbon-carbon bonds and the degradation of pyrolysis remanent compounds from the prior two steps.

In the case of PHU/NaPA, the initial phase takes place between 98 and 148 °C, during which there is a 3.41 % reduction in weight. This indicates the evaporation of water molecules in the hydrogel. The second stage signifies the removal of hydroxyl and carboxyl groups, as demonstrated by a weight loss of 46.10% between temperatures of 199 and 280

°C. During the third phase of weight loss, there was a significant reduction in weight of 29.61% between temperatures of 362 °C and 488 °C [14]. This decrease can be due to the degradation of the cross-links developed in the PHU/NaPA hydrogel. The final weight loss from 688 to 723 °C can be attributable to the entire disintegration of the PHU/NaPA hydrogel, leaving a residual mass of 20.88%. The synthesized pH-sensitive PHU/NaPA hydrogel exhibited superior thermal stability compared to PHU, suggesting that the inclusion of MBA led to the development of a chemically cross-linked NaPA and PHU network.

The TGA thermogram of the CF-PHU/NaPA hydrogel is nearly identical to that of the PHU/NaPA hydrogel. This suggests that CF has minimal effect on the thermal stability of the hydrogel, indicating the absence of any chemical interaction. However, there is evidence of a physical interaction, specifically hydrogen bonding, between CF and the polymeric network. The respective degradation temperatures and residual masses of the prepared materials are depicted in Figure 6.6, which provide valuable insights into the thermal stability and decomposition behaviour of these materials.

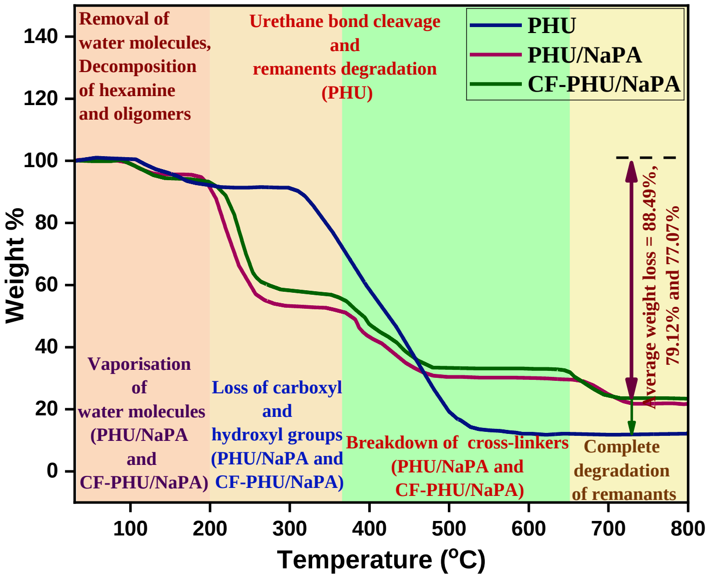


Figure 0.6 TGA curve of PHU, PHU/NaPA, CF-PHU/NaPA

6.3.4 Swelling Studies

The swelling capacity of CF-PHU/NaPA, which can retain water within its 3-dimensional porous structure, was analysed by a swelling study (Figure 6.7). According to Figure 6.7, the maximum equilibrium swelling percentage was measured at pH 7.4, while the least was observed at pH 1.2. The ionization properties of the synthesized hydrogel help elucidate its swelling behaviour, which is dependent on pH. At a pH level of 7.4, the percentage of swelling was shown to be higher. This suggests that the carboxylate groups in NaPA lose protons, leading to increased ionization and electrostatic repulsion between polymer chains. This repulsion makes the hydrogel network structure less dense, enabling greater water absorption and higher swelling per cent (524.5%) [15]. Conversely, the carboxylate groups undergo protonation predominantly at a low pH value of 1.2, leading to less ionization and diminished electrostatic repulsion across polymer chains. The pH-dependent swelling behaviour of the hydrogel is mostly determined by the ionization state of carboxylate groups [16]. This ultimately impacts the hydrogel's ability to expand by altering the electrostatic interactions and hydrophilicity of the polymer chain, thus demonstrating a value of 524.5%.

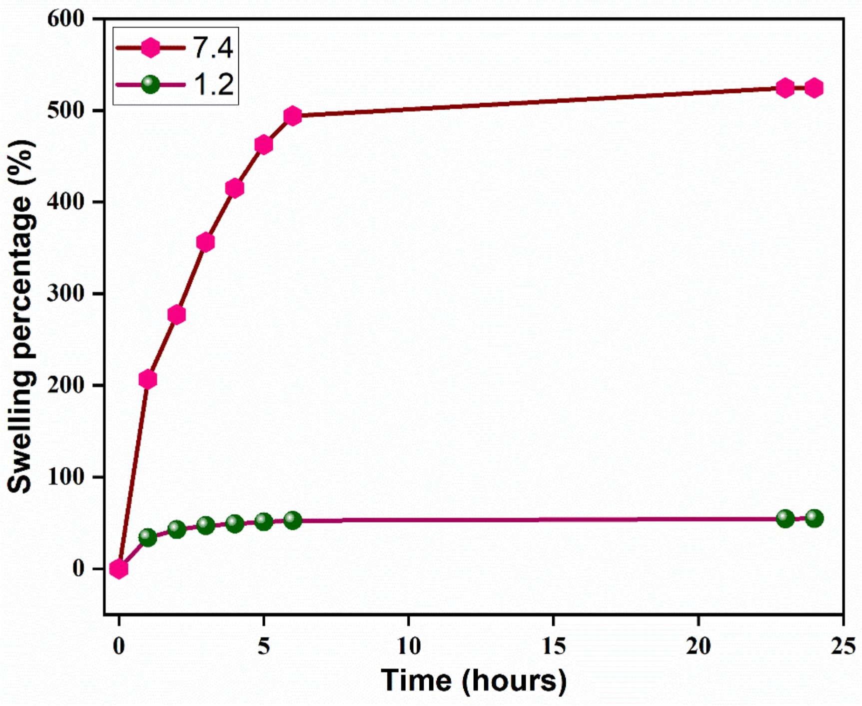


Figure 0.7 The swelling curve of CF-PHU/NaPA hydrogel

6.3.5 Drug Entrapment Efficiency

For the PHU/NaPA hydrogel loaded with CF (CF-PHU/NaPA), the drug encapsulation efficiency (DEE) (%) was found to be 63.703%.

6.3.4 In vitro release study of CF-PHU/NaPA

The release analysis of CF-loaded PHU/NaPA hydrogel was conducted in vitro using pH 1.2 and pH 7.4 buffers for 24 hours at 37 °C, as illustrated in Figure 6.8. The release of drugs from hydrogels is influenced by various factors, including the pH of the surrounding environment. In this case, the release percentage of CF from the hydrogel is higher at pH 7.4 than at pH 1.2. The increased swelling of the hydrogel at pH 7.4 compared to pH 1.2 results in a greater rate of diffusion of the drug molecules from the hydrogel [25]. Deprotonated COO^{-} groups repel one another at pH 7.4, which causes the polymeric chain to expand, increasing swelling and, as a result, drug release. The ionization of the carboxylic acid groups in the polyurethane and poly sodium acrylate hydrogel at pH 7.4 could also contribute to the higher release of the drug, as it leads to an increase in the electron charge density and water diffusion into the polymer network [26]. At pH 1.2, however, the hydrogel network contracts as a result of the protonation of the COO^{-} ions and the development of hydrogen bonds between NaPA and PHU. As a result, the swelling ratio decreases, which tends to reduced loading (%) and drug release. Thus, it can be said that the pH-dependent release of CF may be achieved by using CF-PHU/NaPA hydrogel respectively.

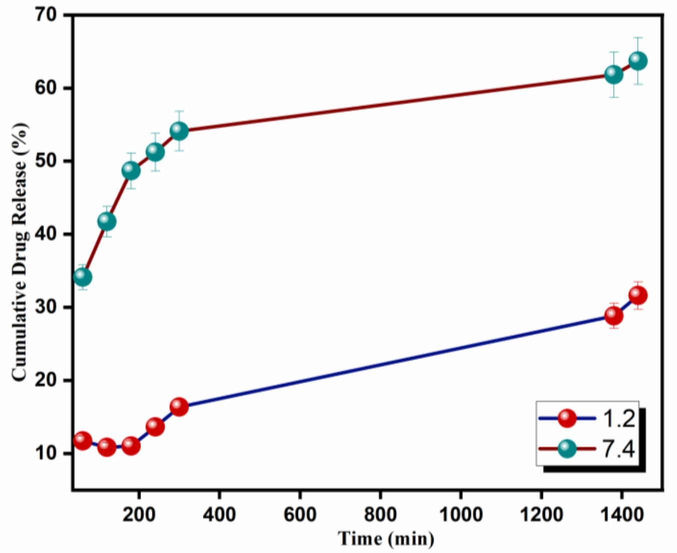


Figure 0.8 The drug release profile for CF-PHU/NaPA hydrogel in pH 7.4 and 1.2

6.3.5 Release Kinetic Modelling of Cefadroxil

The release mechanism of a drug can be identified by fitting the release data to several mathematical models such as Zero-Order, Hixson-Crowell, Higuchi, Korsmeyer-Peppas, and First-Order [27–30]. The regression coefficient (R^2) values are compared for all the models. The model with an R^2 value closer to 1 is considered the best-fit model (Table 6.1).

Table 0.1 Kinetic modelling data of CF release for PHU/NaPA hydrogel

Kinetic Model	**Equation**	**Associated Constant/ Exponent**	**pH 1.2**		**pH 7.4**	
			n	**R^2**	**n**	**R^2**
Zero Order Kinetics	$M_t=M_\infty + k_ot$	K_o = rate constant		0.8783		0.7244
Higuchi Model	$F=M_t/M_\infty = k_Ht^{1/2}$	K_H = kinetic constant		0.9798		0.9802
First Order Kinetics	$\log M_t = \log M_\infty + (kt)/2.303$	K = first order rate constant		0.7487		0.6402
Hixson-Crowell	$(M_t)^{1/3}- (M_\infty)^{1/3} = k_{HC}.t$	K_{HC} = Hixson Crowell Constant		0.8619		0.7244
Korsmeyer-Peppas	$F= M_t/M_\infty = kt^n$	K = kinetic constant n=diffusion constant	0.3579	0.9803	0.175	0.9909

At pH 1.2, the R² value for the Korsmeyer-Peppas model was found to be 0.9803, demonstrating an excellent fit to the experimental data. The release exponent (n) was determined to be 0.3247, indicative of the diffusion mechanism. Similarly, at pH 7.4, the R² value was 0.9909, and the n value was 0.175. The n values at both pH levels suggest a Fickian diffusion mechanism, as they are less than 0.5. The graphs of this model have been displayed in Figure 6.9. This implies that the drug release from the polymeric network is primarily controlled by the diffusion process [16]. This indicates that the release of CF from the hydrogel matrix depends solely on the concentration gradient and is not influenced by swelling or relaxation of the polymer chains.

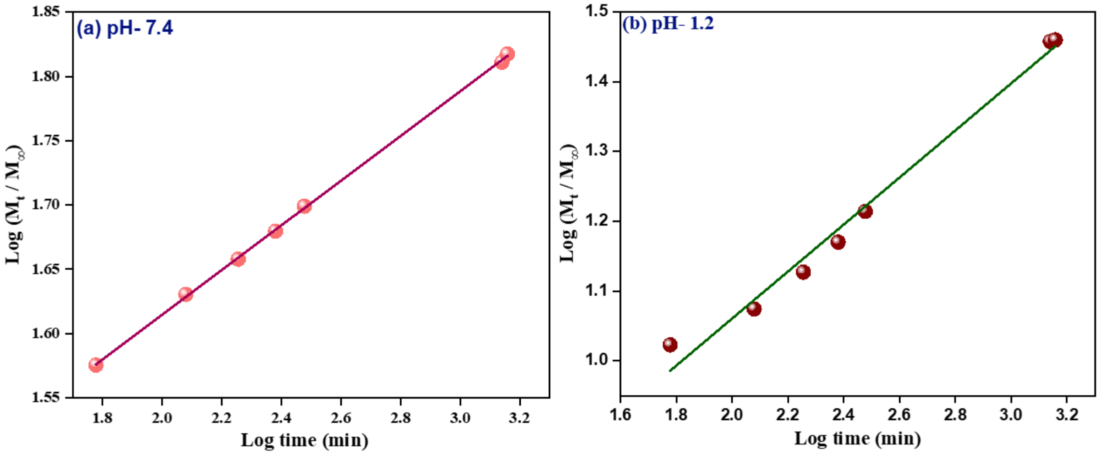


Figure 0.9 Release kinetics of CF from CF-CF-PHU/NaPA hydrogel based on the Korsmeyer–Peppas model in (a) pH-7.4, (b) 1.2

6.3.6 Cytotoxic Studies (MTT Assay)

The cytotoxic activity of the PHU/NaPA hydrogel was evaluated by subjecting the L929 cell line to different concentrations of the sample, based on the results obtained from the MTT assay. The results indicated that the hydrogel had non-toxic behaviour at all evaluated concentrations as shown in Figure 6.10. The absence of toxicity in the hydrogel can be ascribed to the biocompatible properties of non-isocyanate polyurethane [31] and NaPA [32], which are the main constituents of the hydrogel.

PU is widely recognized for its biocompatibility and non-toxic characteristics, making it desirable for various biomedical applications. The hydrogel's capacity to function in cellular settings promotes cell survival and growth, hence enhancing the hydrogel's safety and efficacy. Moreover, NaPA is renowned for its non-toxic properties, hence enhancing the biocompatibility of the hydrogel. The incorporation of these two substances in the PHU/NaPA hydrogel yields a product that is not only effective in its designated function but also biocompatible. The lack of cytotoxic effects on the L929 cell line indicates that this hydrogel has potential as a viable option for various biological uses, such as medication delivery and tissue creation. The study highlights the significance of utilizing biocompatible materials in developing secure and efficient biomedical goods.

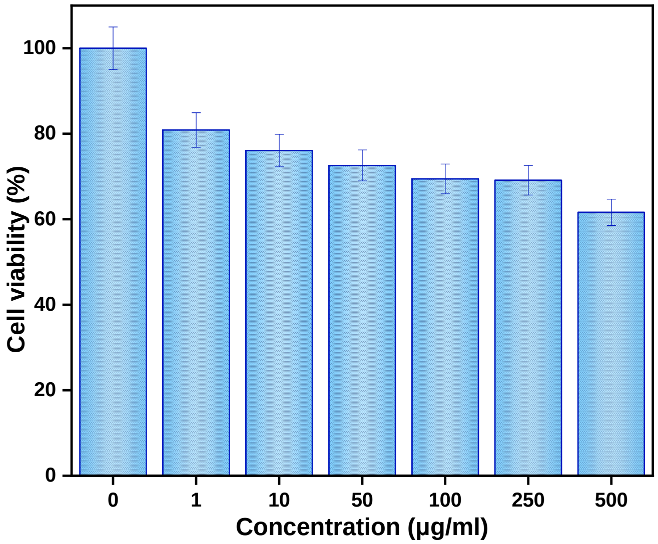


Figure 0.10 MTT assay results showing cell viability percentages to varying PHU/NaPA hydrogel concentrations

6.4 Conclusions

This study presents the effective development of an intelligent hydrogel containing CF, using PHU as a foundation polymer. The selection of NaPA with carboxylate groups at the ends of the polymer chain allowed the synthesis of pH-sensitive smart hydrogels. This hydrogel has the ability to release CF in a regulated manner. The swelling and drug release were assessed in alkaline and acidic pH conditions and were observed to be more pronounced in the alkaline environment. This can be related to the significant electrostatic repulsion between the COO– anion of the NaPA. The drug release kinetics were accurately associated with the Korsmeyer-Peppas model, indicating that the release of the drug from the hydrogel is solely based on diffusion, following the Fickian diffusion mechanism. The aforementioned results allow for the use of CF-loaded PHU/PHU hydrogel as a viable substance for the controlled release of cefadroxil, dependent on pH.

6.5 References

[1] Thang NH, Chien TB, Cuong DX. Polymer-Based Hydrogels Applied in Drug Delivery: An Overview. Gels 2023;9. https://doi.org/10.3390/gels9070523.

[2] Bashir S, Hina M, Iqbal J, Rajpar AH, Mujtaba MA, Alghamdi NA, et al. Fundamental Concepts of Hydrogels: Synthesis, Properties, and Their Applications. Polymers (Basel) 2020;12. https://doi.org/10.3390/polym12112702.

[3] Gennen S, Grignard B, Thomassin JM, Gilbert B, Vertruyen B, Jerome C, et al.

Polyhydroxyurethane hydrogels: Synthesis and characterizations. Eur Polym J 2016;84:849–62. https://doi.org/10.1016/j.eurpolymj.2016.07.013.

[4] Cherng JY, Hou TY, Shih MF, Talsma H, Hennink WE. Polyurethane-based drug delivery systems. Int J Pharm 2013;450:145–62. https://doi.org/10.1016/j.ijpharm.2013.04.063.

[5] Ma L, Su B, Cheng C, Yin Z, Qin H, Zhao J, et al. Toward highly blood compatible hemodialysis membranes via blending with heparin-mimicking polyurethane: Study in vitro and in vivo. J Memb Sci 2014;470:90–101. https://doi.org/https://doi.org/10.1016/j.memsci.2014.07.030.

[6] Brash JL, Fritzinger BK, Bruck SD. Development of block copolyether-urethane intra-aortic balloons and other medical devices. J Biomed Mater Res 1973;7:313–34. https://doi.org/https://doi.org/10.1002/jbm.820070405.

[7] Kütting M, Roggenkamp J, Urban U, Schmitz-Rode T, Steinseifer U. Polyurethane heart valves: past, present and future. Expert Rev Med Devices 2011;8:227–33. https://doi.org/10.1586/erd.10.79.

[8] Pedersen DD, Kim S, Wagner WR. Biodegradable polyurethane scaffolds in regenerative medicine: Clinical translation review. J Biomed Mater Res Part A 2022;110:1460–87. https://doi.org/https://doi.org/10.1002/jbm.a.37394.

[9] Santanelli di Pompeo F, Paolini G, Firmani G, Sorotos M. History of breast implants: Back to the future. JPRAS Open 2022;32:166–77. https://doi.org/https://doi.org/10.1016/j.jpra.2022.02.004.

[10] Kamaci M. Polyurethane-based hydrogels for controlled drug delivery applications.

vol. 123. Elsevier Ltd; 2020. https://doi.org/10.1016/j.eurpolymj.2019.109444.

[11] Mandru M, Bercea M, Gradinaru LM, Ciobanu C, Drobota M, Vlad S, et al. Polyurethane/poly(vinyl alcohol) hydrogels: Preparation, characterization and drug delivery. Eur Polym J 2019;118:137–45. https://doi.org/10.1016/j.eurpolymj.2019.05.049.

[12] Singh P, Kaur R. Sustainable Xylose-Based Non-Isocyanate Polyurethane Foams with Remarkable Fire-Retardant Properties. J Polym Environ 2022. https://doi.org/10.1007/s10924-022-02638-4.

[13] Łukaszewska I, Bukowczan A, Raftopoulos KN, Pielichowski K. ‘Spider-like’ POSS in NIPU webs: enhanced thermal stability and unique swelling behavior. J Polym Res 2023;30:1–16. https://doi.org/10.1007/s10965-023-03834-z.

[14] Singh P, Kaur R. Synthesis and Rheological Analysis of Non-Isocyanate Polyurethanes Blended with Poly (vinyl alcohol). J Ind Eng Chem 2024:1–12.

[15] Bourguignon M, Thomassin JM, Grignard B, Jerome C, Detrembleur C. Fast and facile one-pot one-step preparation of nonisocyanate polyurethane hydrogels in water at room temperature. ACS Sustain Chem Eng 2019;7:12601–10. https://doi.org/10.1021/acssuschemeng.9b02624.

[16] Blain M, Yau H, Jean-Gérard L, Auvergne R, Benazet D, Schreiner PR, et al. Urea- and Thiourea-Catalyzed Aminolysis of Carbonates. ChemSusChem 2016;9:2269–72. https://doi.org/https://doi.org/10.1002/cssc.201600778.

[17] Ochiai B, Satoh Y, Endo T. Nucleophilic polyaddition in water based on chemo-selective reaction of cyclic carbonate with amine. Green Chem 2005;7:765–7.

https://doi.org/10.1039/B511019J.

[18] Fanjul-Mosteirín N, Aguirresarobe R, Sadaba N, Larrañaga A, Marin E, Martin J, et al. Crystallization-Induced Gelling as a Method to 4D Print Low-Water-Content Non-isocyanate Polyurethane Hydrogels. Chem Mater 2021;33:7194–202. https://doi.org/10.1021/acs.chemmater.1c00913.

[19] He M, Shi L, Wang G, Cheng Z, Han L, Zhang X, et al. Biocompatible and biodegradable chitosan/sodium polyacrylate polyelectrolyte complex hydrogels with smart responsiveness. Int J Biol Macromol 2020;155:1245–51. https://doi.org/https://doi.org/10.1016/j.ijbiomac.2019.11.092.

[20] La Rosa F, Ripa S, Prenna M, Ghezzi A, Pfeffer M. Pharmacokinetics of cefadroxil after oral administration in humans. Antimicrob Agents Chemother 1982;21:320–2. https://doi.org/10.1128/AAC.21.2.320.

[21] Khalid A.M.Attia, Mohammed W.I.Nassar, Ahmad A.Mohamad AHA. Quantitative analysis of cefadroxil in presence of its degradation product by various spectrophotometric techniques. Anal Chem an Indian J 2013;13:69–76.

[22] Singh P, Kaur R. Fructose-Based Non-Isocyanate Polyurethane/Poly (Sodium Acrylate) Hydrogels: Design, Synthesis and Environmental Applications. J Polym Environ 2024. https://doi.org/10.1007/s10924-024-03317-2.

[23] He X, Xu X, Wan Q, Bo G, Yan Y. Solvent- and Catalyst-free Synthesis , Hybridization and Characterization of Biobased Nonisocyanate Polyurethane (NIPU) 2019. https://doi.org/10.3390/polym11061026.

[24] Fuensanta M, Khoshnood A, Rodríguez-Llansola F, Martín-Martínez JM. New

Waterborne Polyurethane-Urea Synthesized with Ether-Carbonate Copolymer and Amino-Alcohol Chain Extenders with Tailored Pressure-Sensitive Adhesion Properties. Mater (Basel, Switzerland) 2020;13. https://doi.org/10.3390/ma13030627.

[25] Shahrousvand M, Mirmasoudi SS, Pourmohammadi-Bejarpasi Z, Feizkhah A, Mobayen M, Hedayati M, et al. Polyacrylic acid/ polyvinylpyrrolidone hydrogel wound dressing containing zinc oxide nanoparticles promote wound healing in a rat model of excision injury. Heliyon 2023;9:e19230. https://doi.org/https://doi.org/10.1016/j.heliyon.2023.e19230.

[26] Singh P, Kaur R. One pot synthesis of bio-based porous isocyanate-free polyurethane materials. Mater Lett 2023;331:133433. https://doi.org/https://doi.org/10.1016/j.matlet.2022.133433.

[27] Lehto V-P, Laine E. Assessment of physical stability of different forms of cefadroxil at high humidities. Int J Pharm 1998;163:49–62. https://doi.org/https://doi.org/10.1016/S0378-5173(97)00366-9.

[28] Tushar, Saraswat Y, Meena P, Warkar SG. Synthesis and characterization of novel xanthan gum-based pH-sensitive hydrogel for metformin hydrochloride release. Colloid Polym Sci 2023. https://doi.org/10.1007/s00396-023-05135-9.

[29] Xi X, EPizzi A, Gerardin C, Lei H, Chen X, Amirou S. Preparation and evaluation of glucose based non-isocyanate polyurethane self-blowing rigid foams. Polymers (Basel) 2019;11. https://doi.org/10.3390/polym11111802.

[30] Chen X, Pizzi A, Essawy H, Fredon E, Gerardin C, Guigo N, et al. Non-furanic

humins-based non-isocyanate polyurethane (NIPU) thermoset wood adhesives. Polymers (Basel) 2021;13:1–13. https://doi.org/10.3390/polym13030372.

[31] Kajal, Kumar R, Meena P, Warkar SG. Development and characterization of pH-responsive CMTKG/PAM/PEG hydrogel for oral administration of etophylline. Colloid Polym Sci 2023. https://doi.org/10.1007/s00396-023-05152-8.

[32] Meena P, Singh P, Warkar SG. Fabrication and evaluation of stimuli-sensitive xanthan gum-based hydrogel as a potential carrier for a hydrophobic drug ibuprofen. Colloid Polym Sci 2024;302:377–91. https://doi.org/10.1007/s00396-023-05198-8.

[33] Demir S, Cini N, Gölcü A. Drug release profiles of Atenolol and Benidipine from pH-responsive polymeric hydrogel matrix. Chem Pap 2023;77:4519–29. https://doi.org/10.1007/s11696-023-02802-7.

[34] Tan RYH, Lee CS, Pichika MR, Cheng SF, Lam KY. PH Responsive Polyurethane for the Advancement of Biomedical and Drug Delivery. Polym 2022;14. https://doi.org/10.3390/polym14091672.

[35] Bruschi MLBT-S to M the DR from PS, editor. 5 - Mathematical models of drug release, Woodhead Publishing; 2015, p. 63–86. https://doi.org/https://doi.org/10.1016/B978-0-08-100092-2.00005-9.

[36] Pourtalebi Jahromi L, Ghazali M, Ashrafi H, Azadi A. A comparison of models for the analysis of the kinetics of drug release from PLGA-based nanoparticles. Heliyon 2020;6:e03451. https://doi.org/10.1016/j.heliyon.2020.e03451.

[37] Ekenna IC, Abali SO. Comparison of the Use of Kinetic Model Plots and DD Solver Software to Evaluate the Drug Release from Griseofulvin Tablets. J Drug Deliv Ther

2022;12:5–13. https://doi.org/10.22270/jddt.v12i2-s.5402.

[38] Bayer IS. Controlled Drug Release from Nanoengineered Polysaccharides. Pharmaceutics 2023;15. https://doi.org/10.3390/pharmaceutics15051364.

[39] Wang Y, Zheng Z, Pathak JL, Feng W, Wu W, Yang C, et al. Fabrication and characterization of photosensitive non-isocyanate polyurethane acrylate resin for 3D printing of customized biocompatible orthopedic surgical guides. Int J Bioprinting 2023;9:684. https://doi.org/10.18063/ijb.684.

[40] Khanlari S, Tang J, Kirkwood KM, Dubé MA. Synthesis and properties of a poly(sodium acrylate) bioadhesive nanocomposite. Int J Polym Mater Polym Biomater 2016;65:881–7. https://doi.org/10.1080/00914037.2016.1180608.

Chapter 7

CONCLUSIONS, FUTURE SCOPE AND SOCIAL IMPACT

7.1 Conclusions

This research intended to develop sustainable, NIPU materials using renewable resources, addressing the noteworthy environmental and health challenges presented by conventional PU production. Throughout this work, various innovative approaches were explored to synthesize NIPU foams, blends, and hydrogels, emphasizing their potential for a diverse array of applications. All the prepared NIPU materials and their synthesis were established using a wide array of techniques such as FTIR, XRD, TGA and SEM.

A major focus of this research was the development of NIPU foams utilizing a bio-based crosslinker under mild reaction conditions. Conventional methods for NIPU foam production often require high temperatures, pressures, and synthetic crosslinkers, resulting in materials with limited flame retardancy. By employing xylose and dimethyl carbonate with citric acid as a natural crosslinker, NIPU foams were successfully synthesized, that demonstrated enhanced flame retardancy (with an LOI of 26.9%) and favorable thermal properties. This method not only simplified the synthesis process but also provided an eco-friendly alternative to conventional PU foams.

To further streamline the synthesis process, a one-pot synthesis method was developed for porous NIPU materials. Traditional NIPU synthesis methods often involve multiple steps and sophisticated equipment, which significantly hinders their scalability. The one-pot approach significantly reduced complexity and facilitated the production of NIPU materials with excellent structural and thermal properties. This innovative method underscores the feasibility of scalable and sustainable NIPU production.

Furthermore, the research investigated NIPU blends with PVA to enhance material properties. Blending NIPU with PVA aimed to combine the beneficial attributes of both polymers, resulting in materials with improved rheological behaviour, mechanical performance, and thermal stability. The blends exhibited shear-thickening behaviour and increased thermal stability, indicating their potential for applications requiring advanced material properties and sustainability.

Additionally, the study also explored the synthesis and application of NIPU-based hydrogels for environmental and biomedical applications. Owing to the prevalent use of organic solvents in existing methods of NIPU hydrogel production, a green synthesis approach was developed using water as a solvent. The resulting fructose-based NIPU hydrogels demonstrated exceptional efficiency in removing crystal violet and malachite green dyes from wastewater, achieving remarkable removal efficiencies of 96.87 % and 99.8%, respectively. Furthermore, these hydrogels exhibited excellent drug loading and release properties at a pH of 7.4, with cefadroxil as a model drug, showcasing their potential for pH-sensitive controlled drug delivery applications. The drug release kinetics were studied, and it was observed that the release of the drug followed the Kosmeyer - Peppas model at pH 1.2 and 7.4.

Overall, this research has made significant contributions to the field of sustainable polyurethane materials by developing novel synthesis methods for NIPU foams, blends, and hydrogels. These methods address the environmental and health concerns associated with traditional PU production, such as the use of toxic isocyanates and the depletion of fossil fuels. The findings demonstrate the viability of using renewable resources to produce high-performance NIPU materials, offering a sustainable alternative for various industrial and biomedical applications.

7.2 Future prospects

The findings from this work lay a strong foundation for the continued development of eco-friendly and sustainable PU technologies, contributing to a greener and more sustainable future. Future studies can focus on exploring other methods of synthesising NIPU foams with enhanced mechanical properties. Investigating alternative bio-based crosslinkers and green catalysts could lead to improved reaction kinetics and material properties.

Furthermore, the miscibility and interaction of NIPU blends with PVA warrant a more detailed investigation. Future studies should employ advanced characterization techniques such as small-angle neutron scattering, atomic force microscopy, and NMR spectroscopy to gain a comprehensive understanding of the phase behaviour, microstructure, and molecular interactions within these blends.

The demonstrated efficacy of NIPU hydrogels in dye removal suggests significant potential for environmental remediation applications. Future studies should explore the adsorption capabilities of NIPU hydrogels for a wider range of pollutants, including heavy metals and emerging contaminants. Additionally, evaluating the reusability and regeneration of NIPU hydrogels will be crucial for practical environmental applications.

Conducting comprehensive lifecycle assessments and evaluating the environmental impact of NIPU materials from synthesis to disposal will provide valuable insights into their sustainability. Comparing the carbon footprint, energy consumption, and environmental emissions of NIPU materials with traditional polyurethanes will help quantify their ecological benefits.

LIST OF PUBLICATIONS, CONFERENCES AND WORKSHOPS

Publication from the Thesis

1. Raminder Kaur, **Pooja Singh,** Surya Tanwar, Gunjan Varshney and Sarla Yadav (2022), "Assessment of Bio-Based Polyurethanes: Perspective on Applications and Bio-Degradation", *Macromol,* 2, 284–314, DOI: https://doi.org/10.3390/macromol2030019 **(Scopus)**
2. **Pooja Singh,** Raminder Kaur (2023), "Sustainable Xylose-Based Non-Isocyanate Polyurethane Foams with Remarkable Fire-Retardant Properties", *Journal of Polymers and the Environment*, 31, 743–753, DOI: https://doi.org/10.1007/s10924-022-02638-4 **(I.F. = 4.7) (SCIE)**
3. **Pooja Singh,** Raminder Kaur (2023), "One-pot synthesis of bio-based porous isocyanate-free polyurethane materials", 331, 133433, *Materials Letters*, DOI: https://doi.org/10.1016/j.matlet.2022.133433 **(I.F. = 2.7) (SCI)**
4. **Pooja Singh,** Priti, Raminder Kaur (2024), "Synthesis and Rheological Analysis of Non-Isocyanate Polyurethanes Blended with Poly(vinyl alcohol)", *Journal of Industrial and Engineering Chemistry*, DOI: https://doi.org/10.1016/j.jiec.2024.04.050 **(I.F.=5.9) (SCIE)**
5. **Pooja Singh,** Raminder Kaur (2024), "Fructose-Based Non-Isocyanate Polyurethane/Poly (Sodium Acrylate) Hydrogels: Design, Synthesis and Environmental Applications", *Journal of Polymers and the Environment*, DOI: 10.1007/s10924-024- 03317- 2 **(I.F.=4.7) (SCIE)**
6. **Pooja Singh,** Raminder Kaur, "Fabrication of Advanced Non-Isocyanate Polyurethane based Hydrogels for Applications in pH-sensitive Drug Delivery" **(communicated)**

7. **Pooja Singh,** Raminder Kaur, "Advancements in Sustainable Non-Isocyanate Polyurethanes: Insights into Synthesis, Applications, and Circular Economy Perspectives" **(communicated)**
8. **Pooja Singh,** Raminder Kaur, "Recent developments in Polyurethane-based drug delivery systems: An Overview" **(communicated)**

Additional Publications

1. Sonia Khanna, **Pooja Singh,** Harsimrut Kaur, Antima Joon, (2019) Synthesis, characterization and antimicrobial investigation of mixed ligand complexes of Cobalt(II) and Nickel(II) with p-dimethylaminobenzaldehyde thiosemicarbazone, *Malaysian Journal of Chemistry,* 21(3), 100–109 **(Scopus)**

2. Sachin Kumar, Aizak Debbarma, **Pooja Singh,** Raminder Kaur (2022), "Metal-organic framework for energy applications'', *Invertius Journal of Renewable Energy* 12(4), 177-194, DOI: 10.5958/2454-7611.2022.00016.9

3. **Pooja Singh,** Gunjan Varshney, Raminder Kaur (2024), "Primary Microplastics in the Ecosystem: Ecological Effects, Risks, and Comprehensive Perspectives on Toxicology and Detection Methods", *Journal of Environmental Science and Health*, Part C, Taylor & Francis, **(IF.= 2.5)** **(SCIE),** DOI: http://dx.doi.org/10.1080/26896583.2024.2370715

4. **Pooja Singh,** Manpreet Kour, Gunjan Varshney, Raminder Kaur, "Non-Isocyanate Polyurethane (NIPU) Foams: Exploring Sustainable Synthesis Routes, Biomass Sources, and Technological Advancements", *Environmental Science and Pollution Research* (under review)

5. Gunjan Varshney, **Pooja Singh,** Sarla Yadav, Raminder Kaur, "Unleashing the potential solution of thermal comfort: Review on Advanced Engineering Application of Phase Change Material (PCM) incorporated textile" **(communicated)**

6. Saurabh, **Pooja Singh,** Sarla Yadav, Gunjan Varshney, Raminder Kaur, " Revolutionizing beverage preservation: Eco- friendly pH- Sensitive film for Intelligent Packaging" **(communicated)**

7. Sarla Yadav**, Pooja Singh,** Gunjan Varshney, Saurabh, Raminder Kaur, Poonam Singh, "Efficient photocatalytic Degradation of Crystal violet dye using Phytofabricated Zinc oxide nanoparticles from Anthocyanin extract" **(communicated)**

Book Chapters:

1. **Pooja Singh,** Gunjan Varshney, Raminder Kaur**,** Book: Arsenic Toxicity Remediation - Sustainable Nexus Approach, Chapter 21: Arsenic Contamination in Drinking Water and Health, Springer Nature, Series E-ISSN: 2524-6410, (2024).
2. Gunjan Varshney, **Pooja Singh,** Book: Advances in Fermentation Technology and their Practical Implications, Chapter: Oleaginous Yeasts: Single Cell Oil from Lignocellulosic Biomass as a Feedstock for Biofuels, **(accepted).**

Conferences

1. **Pooja Singh,** Raminder Kaur (2022), oral presentation, 6th International e-Conference on Recent Advances in Science (ICRAS-2022), organized by Invertis University Bareilly (UP), India in association with Institute of Advanced Materials, Sweden, April 1-2, 2022, **2nd Position in Oral Presentation Chemistry**.
2. **Pooja Singh,** Raminder Kaur (2022), oral presentation, International Conference on Advances in Chemical Sciences and Nanocomposites (ACSN-2022), jointly organized by Zakir Hussain Delhi College, Delhi University and Indian Society of Analytical

Scientists, (ISAS) Delhi Chapter, New-Delhi, India in association with DRDO , April 1-2,2022.

3. **Pooja Singh,** Raminder Kaur (2022), oral presentation, International Conference on Emerging Trends in Biotechnology and Sustainable Chemistry: (ETBSC-2022), Baba Farid College, Bathinda in collaboration with Central University of Punjab, Bathinda, India, April, 27-29, 2022.
4. **Pooja Singh,** Raminder Kaur (2022), poster presentation, 2nd Indian Analytical Congress (2nd IAC-2022), jointly organised by Indian Society of Analytical Scientists Delhi Chapter (ISAS-DC), Graphic Era University, and CSIR Indian Institute of Petroleum, Dehradun, Uttarakhand, India, May 26-28, 2022.
5. **Pooja Singh,** Raminder Kaur (2022), oral presentation, 2nd International Conference on Green and Sustainable Chemistry Conference-2022 organized by Department of Chemistry, Manav Rachna University, Faridabad, Haryana, India, November 17-19, 2022.
6. **Pooja Singh,** Raminder Kaur (2022), participated in the International Conference on “Nanotechnology: Opportunities & Challenges (ICNOC-2022)”, organized by Jamia Millia Islamia University, New Delhi, India, November 8-30, 2022.
7. **Pooja Singh,** Raminder Kaur (2023), oral presentation, International Conference on “Chemical and Allied Science and their Applications” organized by Department of Applied Chemistry, Delhi Technological University, January 20, 2023.
8. **Pooja Singh,** Raminder Kaur (2024), oral presentation, International Conference on Emerging Techno-Economic Development for Sustainable Environment (ETDSE-2024) organised by IPS Academy Institute of Engineering & Science, Indore, Madhya Pradesh, India, January 12-13, 2024.

Workshops and Seminars

1. Attended national seminar on “National Science Day (NSD-2023)”, organized by the Human Resource Development Centre in association with the Instititution’s Innovation Council & Department of Applied Physics, Delhi Technological University, held on 28th February 2023.

2. Attended a five-day annual information literacy workshop on “E-Resources: A Gateway for Research”, 7th Edition (2023) organized by the central library, Delhi Technological University, held from 25th -29th September 2023.

3. Attended workshop on “Intellectual Property (IP) Awareness Programme” organized by IPR cell, Delhi Technological University, Delhi, held from 12-14th December 2022.

4. Attended INUP-i2, 6th user awareness workshop on “Fabrication and characterization facility for nanotechnology”, organized by Indian Institute of Technology Delhi, held from 4th-5th March 2023.

PROOF OF PUBLICATIONS

Publications from the thesis

macromol

MDPI

Review

Assessment of Bio-Based Polyurethanes: Perspective on Applications and Bio-Degradation

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Abstract: Among numerous synthetic macromolecules, polyurethane in its different forms has proven its sheer dominance and established a reputation as a reliable and trusted material due to its proficiency in terms of superior properties, which include: high mechanical strength and abrasion resistance, good durability, good adhesion, good thermal stability, excellent chemical and weathering resistance. Synthetic polyurethane materials are non-biodegradable, poisonous, and use petrochemical-based raw materials, which are now depleting, leading to a surge in polyurethane production costs. Bio-based polyurethanes (PU) have been synthesized by researchers in recent decades and have mostly overtaken petrochemical-based PU in terms of challenges such as solid pollution, economic effectiveness, and availability of raw materials. Enormous kinds of available bio-renewable sources as predecessors for the production of polyols and isocyanates have been explored for the development of "greener" PU materials; these bio-based polyurethanes have significant potential to be used as future PU products, with a partial or total replacement of petroleum-based polyurethanes, due to increasing concern about the environment, their relatively low cost and biodegradability. This critical review concentrates on the possibilities of renewable sources to be used for polyurethane production and gives a clear perspective on the journey, utilization, and recent advancements in the field of different bio-based polyurethane polymers that have arisen over the last decade.

Keywords: polyurethanes; non-isocyanate polyurethanes; adhesives; coatings; recycling; biodegradation

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1. Introduction

Polyurethanes (PU) represent nearly 8% of the total plastics production and stand tall as the 6th most widely used polymer in the world, with total production reaching 18 MTon in 2016 [1] and still progressing. The superior properties of PU, such as flexibility, corrosion, resistance to chemicals, high automatic strength, low-temperature comfortability, adhesiveness, and chemical structure adaptability, etc. account for their considerable popularity among researchers. PU have urethane groups as major repeating units along their main backbone chains, which are derived by reacting hydroxyl (-OH) terminated chemical entities, with isocyanate (-NCO) terminated compounds, as represented by a generalized scheme shown in Figure 1. In addition, some other functional groups may also be present in the end constitutions of the PU chains, including ethers, esters, urea, biuret, and aromatic moieties [2].

$$\boxed{\text{R-NCO} + \text{HO-R'} \longrightarrow \text{R-NHCOO-R'}}$$

Figure 1. Formation of Urethane Linkage.

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ORIGINAL PAPER

Sustainable Xylose-Based Non-Isocyanate Polyurethane Foams with Remarkable Fire-Retardant Properties

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Accepted: 10 October 2022

Abstract
Self-blowing non-isocyanate polyurethane foams have been synthesized by reacting xylose with dimethyl carbonate and hexamethylene diamine using citric acid as a natural crosslinker via the process of transurethanisation. The resulting foams exhibit exceptional flame retardancy in comparison to conventional PU foams. The structure of the foam cells was examined using scanning electron microscopy. Solid-state NMR and infrared spectroscopy were used to analyze the functional groups present in the products formed. The formation of the urethane bridge was confirmed by the emergence of peaks at 158.24 ppm and 1693 cm^{-1} respectively. The thermal properties were evaluated by using TGA and DSC, which further indicated a glass transition temperature of around 112.82 °C. The dependence of viscosity of polymeric solutions on the different shear rates was also studied using a parallel plate rheometer. Limiting Oxygen Index was employed to study the flammability of the prepared foams, and it was observed that they exhibit considerable fire resistance (26.9%),which is quite comparable to the fire resistance offered by the isocyanate-based polyurethane foams with added fire retardants. The diffraction pattern of the prepared NIPU was analyzed by PXRD.

Keywords LOI · NIPU foams · rheology · solid-state NMR · xylose

Introduction

Polyurethanes (PU) are among the most extensively used polymer globally, with a broad array of applications in both academic and industrial settings, mainly attributed to their abrasion resistance, high flexibility, and other desirable characteristics. PU foams are an important class of polymers that make up 50% of the market for polymer foam and account for 67% of global PU utilization. PU foams serve many purposes such as acoustic insulation, automotive seating, mattresses, and thermal insulation [1]. However, there are a few concerns associated with the preparation and use of PU. They are typically synthesized by polyaddition of a polyol to a polyisocyanate, which, along with its precursor phosgene, is exceedingly hazardous. Research groups are now aiming to divest from the usage of hazardous chemicals and severe reaction conditions in PU production with the use of greener intermediates and procedures, considering the current state of sustainable chemistry development. Moreover, the depletion of non-renewable sources and the ramifications of global warming have prompted the innovators to create novel routes of PU production, that have a minimal environmental impact and fulfill all new environmental regulations [2]. Vegetable oil is the most often used renewable resource to generate precursors for PU products, since it is widely accessible [3, 4]. Although these renewable sources have successfully yielded polyols, multiple studies have been carried out to incorporate various fillers and anti-flaming chemicals into these foams to enhance their anti-flammable, thermal, and mechanical abilities [5–12]. In addition, as the toxic polyisocyanates used to make PU could be dangerous to humans, researchers are seeking a green and sustainable route of producing PUs from renewable sources, without the use of polyisocyanates [3]. Consequently, Non-isocyanate polyurethanes (NIPU), a novel category of PU free from the harmful effects of isocyanates, were generated. NIPUs are traditionally synthesized by using cyclic carbonates and amines [13]. The reaction produces two isomeric products, one with a secondary hydroxyl group and the other with a

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One pot synthesis of bio-based porous isocyanate-free polyurethane materials

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ABSTRACT

In the current study, synthesis of porous isocyanate-free polyurethane materials derived from xylose is reported through a one-pot process, and the impact of varying amounts of crosslinker is studied. The synthesized materials were characterized using various techniques. The formation of the urethane bridge was confirmed using Fourier Transform Infra-Red (FTIR) spectra that exhibited characteristic bands around 1700 cm^{-1}, 1600 cm^{-1}, and 3400 cm^{-1}. The characteristic peak observed at 21° (2θ value) in Powder X-ray (PXRD) diffractogram further confirms the synthesis of segmented polyurethane porous materials. Thermogravimetric Analysis (TGA) and Differential Scanning Calorimetry (DSC) thermograms indicate that thermal stability and glass transition temperature (Tg) of synthesized non-isocyanate polyurethane (NIPU) materials increase with increase in the amount of crosslinker. The increase in Limiting Oxygen Index (LOI) values with an increment in the amount of crosslinker suggests improvement in flame retardant behavior of NIPU material due to formation of highly crosslinked network in the polyurethane matrix. These porous NIPU materials align well with the principles of sustainable development.

1. Introduction

Polyurethanes (PUs) are one of the most pragmatic materials available today due to their broad array of structure and properties, as well as their capability of demonstrating elastomeric, thermoplastic, and thermoset behavior. PUs are branched, linear, or cross-linked polymers formed by addition reactions between poly-isocyanates and polyols. While polyols are petroleum by-products that contribute to the consumption of fossil fuels and require high energy for processing [1]. Polyisocyanates are synthesized from incredibly toxic isocyanate precursors that are derived from lethal phosgene gas, whose excessive exposure can cause serious health problems [2]. Thus, a need arises to find a replacement, for both economic and ecological reasons. Few reports describe the use of vegetable oils modified as polyols for commercial PU synthesis [3]. Nevertheless, even when combined with bio-sourced polyols, polymeric isocyanates have consistently been utilized in industries to produce polyurethanes. Since these compounds are detrimental to humans and the environment, hence as an outcome, the development of biomass-based polymers and the creation of ecologically benign and sustainable materials are becoming increasingly popular. To address this issue, multiple pathways have been investigated; one promising option is the use of Non-Isocyanate Polyurethane (NIPU), produced via reaction between cyclic carbonate and polyfunctional amines. Despite the growing number of articles on NIPU and polyhydroxy-urethane chemistry, only few studies focus on NIPU foam synthesis. In the dearth of isocyanate groups, NIPU does not allow for foaming in the presence of water via the release of CO_2, as is the case with isocyanate-based PU preparation. However, a simplified process for producing NIPUs is to react bio-materials including sugars [4], lignin [5], and tannins [6] just with dimethyl carbonate, which eliminates the need for cyclization of carbonate and diamine. A recent study reports the synthesis of a bio-based NIPU foam using glucose, dimethyl carbonate, and diamine as precursors [7]. Carbohydrates are an especially valuable raw material among the many renewable resources since it is cost-effective, easily accessible, and offer a wide range of stereochemical variety [8]. A facile approach for the fabrication of bio-based porous NIPU materials with xylose has been adopted in the present study. The materials were synthesized by blowing at ambient temperature and hardening in short time intervals at a lower temperature (70 °C) with citric acid as a crosslinker, and subsequently, their flame-retardant

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Full Length Article

Synthesis and Rheological Analysis of Non-Isocyanate Polyurethanes Blended with Poly(vinyl alcohol)

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A R T I C L E I N F O

Keywords:
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Structure recovery
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A B S T R A C T

This study investigated the blending of non-isocyanate polyurethanes (NIPUs) with poly(vinyl alcohol) (PVA) at various ratios, with specific emphasis on ratios such as 20%, 50%, 80%, and 100% NIPU content. Focus has been made on assessing their rheological behaviour, mechanical performance, and thermal stability. As the NIPU content surpassed 50%, a shear-thickening trend emerged, suggesting a highly interwoven molecular structure. Rheological studies demonstrate viscosity variations dependent on blend composition and shear rate, with pure NIPU solution exhibiting shear thickening behaviour suggestive of network formation facilitated by the application of shear. Dynamic modulus analysis revealed viscoelastic properties in blends containing 50% and 100% NIPU. Thixotropic analysis showcased a remarkable structural recovery of 99% in solutions with over 20% NIPU, emphasizing the resilience of NIPU-rich blends to shear-induced alterations. Thermogravimetric analysis (TGA) and differential scanning calorimetry (DSC) demonstrate thermal stability and crystallinity, with blends exhibiting intermediate behaviour and reduced crystallinity compared to pure PVA due to NIPU incorporation. Blends exceeding 10% PVA displayed reduced consistency and diminished PVA crystallization ability, corroborated by DSC and wide-angle X-ray diffraction (WXRD) results. Thermal stability increased with NIPU integration, and blends demonstrated intermediate thermal behaviour between the pure polymers. Notably, the PU2PVA8 blend demonstrates the highest miscibility and a unique combination of amorphous and crystalline nature, showcasing its potential for tailored material design with enhanced structural and thermal properties.

Introduction

Polyurethanes (PUs) have demonstrated a wide range of applications in various industries, including construction, automotive, footwear, and furniture, for insulation, sealants, coatings, and structural components, due to their exceptional physical and mechanical properties, including elasticity, adhesion, hardness, and durability. The remarkable attributes of PU, such as its ability to adapt to varying chemical structures, its flexibility, resistance to corrosion, high tensile strength, and comfort in low temperatures, significantly contribute to its immense popularity among researchers [1]. Conventionally, PUs are derived via the polyaddition reaction between polyols and isocyanates, which are highly toxic and have adverse health effects, as they are synthesised from poisonous phosgene and amine. Furthermore, the petro-based precursors for the production of polyols (ethylene and propylene oxides) are scarce and are anticipated to be exhausted shortly [2]. In spite of their numerous applications, PUs have been identified as a significant contributor to the accumulation of plastic waste and pollution in the environment. Researchers and technicians have thus begun to use environmentally friendly and sustainable resources as prospective replacements for Petro-based polyols (ethylene and propylene oxides) and di-isocyanates to address all of these drawbacks associated with the use of polyurethanes [1,2,3]. Manufacturing green polyurethane (GPU) entails two fundamental procedures: the eco-friendly formation of isocyanates from renewable materials, and the generation of sustainable green polyol. Yet, the fabrication of non-isocyanate polyurethane (NIPUs) is a more effective, environmentally friendly, and widely applicable approach [4,5]. One of the most promising alternatives to traditional polyurethanes produced by the hazardous isocyanate chemistry is the production of NIPUs using step-growth polymerisation of (poly)cyclic carbonates to (poly)amines [6]. The utilization of catalysts notwithstanding, the inadequate reactivity and stringent reaction

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ORIGINAL PAPER

Fructose-Based Non-Isocyanate Polyurethane/Poly (Sodium Acrylate) Hydrogels: Design, Synthesis and Environmental Applications

Pooja Singh[1] · Raminder Kaur[1]

Accepted: 8 May 2024

Abstract

Conventional methods for synthesising polyurethane hydrogels encompass toxic isocyanates and organic solvents, limiting their eco-friendliness and ease of synthesis. In response, this study introduces an innovative approach to synthesising fructose-based non-isocyanate polyurethane (NIPU) hydrogel (FNHG), eliminating the need for isocyanates. Initially, fructose-based NIPU (FNPU) was synthesised using dimethyl carbonate and hexamethylene diamine under mild reaction conditions, paving the way for a greener polyurethane variant. Subsequently, a free radical polymerization technique was employed in an aqueous medium. This process allowed for the integration of poly(sodium acrylate), and N, N-methylene bisacrylamide, leading to to the development of FNHG. Remarkably short gelation time of just 30 min at 60 °C was achieved, signifying a significant advancement in the synthesis process. The synthesized NIPU-based hydrogels exhibited outstanding efficiency in the removal of crystal violet (CV) and malachite green (MG) dyes from aqueous media. With an impressive removal efficiency of 96.87% for CV and an astounding 99.8% for MG, these hydrogels demonstrated high effectiveness in remediation efforts. The study's novelty lies in both the synthesis methodology, utilising FNPU, and the exceptional efficiency exhibited by these hydrogels in eliminating diverse dyes from contaminated water. Furthermore, the structure of FNPU was confirmed using FTIR and ^{1}H NMR spectroscopy, adding robustness to our findings. This research not only presents a solution to the limitations of traditional polyurethane synthesis but also demonstrates the potential of fructose-based NIPU hydrogels (FNHG) as eco-friendly and efficient agents for water purification.

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Additional Publications

Malaysian Journal of Chemistry, 2019, Vol. 21(3), 100-109

Synthesis, Characterization and Antimicrobial Investigation of Mixed Ligand Complexes of Cobalt(II) and Nickel(II) with P-Dimethylaminobenzaldehyde Thiosemicarbazone

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A series of cobalt(II) and nickel(II) complexes were prepared by reactions with p-dimethylaminobenzaldehyde thiosemicarbazone (Hdmbtsc) in stoichiometric ratio of 1:2 and in the presence of co-ligands pyridine, 1,10 phenanthroline and PPh_3, which yielded octahedral complexes (**1-8**). The ligand acted as uninegative and neutral bidentate ligands coordinating through its N, S donor atoms. Dimethylaminobenzaldehyde thiosemicarbazone (Hdmbtsc) is reported to form complexes with mercury and zinc [14]. The ligand and complexes were characterized using spectroscopic techniques (UV-Vis, FTIR). They were screened for antibacterial activity against Gram +ve (*Listeria*) and Gram –ve (*E. coli*) bacteria and antifungal activity against *Candida albicans* using agar diffusion method. Cobalt complexes **1**, **2** and **4** and nickel complex **8** were found to be active against Gram -ve bacteria (*E. coli*), while cobalt complexes **1-5** and nickel complex **6** showed moderate activity against fungi (*Candida albicans*). $[Co(dmtsc)_2(phen)]Cl_2$ (**4**), $[Co(dmtsc)_2(PPh_3)_2(NO_3)_2]$ (**5**) and $[Ni(Hdmtsc)_2(Cl)_2]$ (**6**) were found to be the most effective against tested bacterial and fungal strains.

Key words: Dimethylaminobenzaldehyde thiosemicarbazone; UV-Vis.spectra; antibacterial, antifungal activity, octahedral complexes

Received: July 2019; Accepted: December 2019

Thiosemicarbazone and its complexes have received substantial attention over the past few decades due to their multiple pharmacological properties, such as antibacterial, antifungal, antimalarial and antitumor [1-3]. This may be attributed to the flexibility of thiosemicarbazones to adopt different bonding modes forming complexes such as mononuclear, dinuclear as well as polynuclear complexes. Thiosemicarbazones are known to exhibit thione-thiol tautomerism by coordinating to a metal ion through the azomethine nitrogen either in the neutral thione form or in the anionic thiolate form [4-8].

Dimethylaminobenzaldehyde is a bifunctional aromatic compound having aldehyde group (CHO) para to dimethylamino group. It is also reported to have analytical properties [9-11]. The ^{1}H-NMR of Hdmbtsc and its Zn(II), Cd(II), Hg(II) and Cu(II) complexes are reported in literatures [12-14]. It also acts as a selective fluorosensor for detection of Hg(II) [15]. In an extension to the study, we report the synthesis and characterisation of Ni(II) and Co(II) complexes with p-dimethylaminobenzaldehyde thiosemicarbazone and co-ligands (py, phen, PPh_3), not reported earlier. All these complexes were characterised by spectroscopic methods (IR, UV). They were also tested for their antibacterial and antifungal activities to see their application as drugs.

MATERIALS AND TECHNIQUES

Thiosemicarbazide and p-dimethylaminobenzaldehyde were used without any further purification. Pyridine, 1,10 phenanthroline, triphenylphosphine, cobalt chloride, nickel chloride and cobalt nitrate were procured from Sigma Aldrich. All other reagents and solvents were purchased from commercial sources and were of analytical grade. The IR spectra were recorded on Agilent Carey 630 FTIR Spectrometer. The electronic spectra were recorded on UV-Visible Spectrophotometer (UV-1800).

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Metal Organic Framework for Energy Application

Sachin Kumar[1], Aizak Debbarma[1], Pooja Singh[1] and Raminder Kaur[2]*

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ABSTRACT

Researchers are diligently seeking clean, alternative energy sources to replace fossil fuels due to escalating pollution levels and the ever-expanding energy demand. Consequently, the imperative arises to develop carriers capable of storing energy or facilitating mass and electron transfer for energy storage and conversion. The ongoing advancements in metal-organic frameworks (MOFs) have engendered novel prospects for renewable energy conversion, storage, and utilization. The exceptional attributes of MOFs, alongside their composites and related compounds, have piqued significant interest, leading to augmented investments and the creation of innovative materials for the energy sector. This project presents a synopsis of the latest strides in energy storage and conversion using MOFs and their compositions, with a specific emphasis on elucidating the interplay between structure, composition, and function.

Keywords: Clean energy, Metal-organic frameworks, Energy storage, Renewable energy conversion, Innovative materials

INTRODUCTION

Recent efforts have been directed towards forging sustainable and clean energy storage solutions to counteract environmental degradation. Consequently, the development of energy carriers or transport mechanisms becomes paramount. The chemistry of metal-organic frameworks (MOFs) aligns seamlessly with this objective, owing to its inherent advantages encompassing structural diversity, functionality, and an array of practical applications [1]. MOFs amalgamate organic-inorganic constituents, resulting in highly porous frameworks distinguished by uniform constituent arrangements, variable pore sizes, topological diversity, and multifunctionality. Leveraging their properties and ongoing advancements, MOFs have found application in conventional energy domains, underscored by their remarkable gas storage capacity. The outstanding capabilities of these frameworks and related compounds have propelled the innovation of new materials for the energy sector. This overview encapsulates the configurations, components, and distinctive traits of these frameworks, rendering them conducive to energy conversion and storage. These applications encompass fuel storage, photo-induced H_2 evolution, and carbon dioxide reduction. Additionally, the spectrum extends to other technologies including fuel and solar cells, supercapacitors, Li-batteries, fuel cells, and water electrolysis.

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Primary Microplastics in the Ecosystem: Ecological Effects, Risks, and Comprehensive Perspectives on Toxicology and Detection Methods

Pooja Singh, Gunjan Varshney & Raminder Kaur

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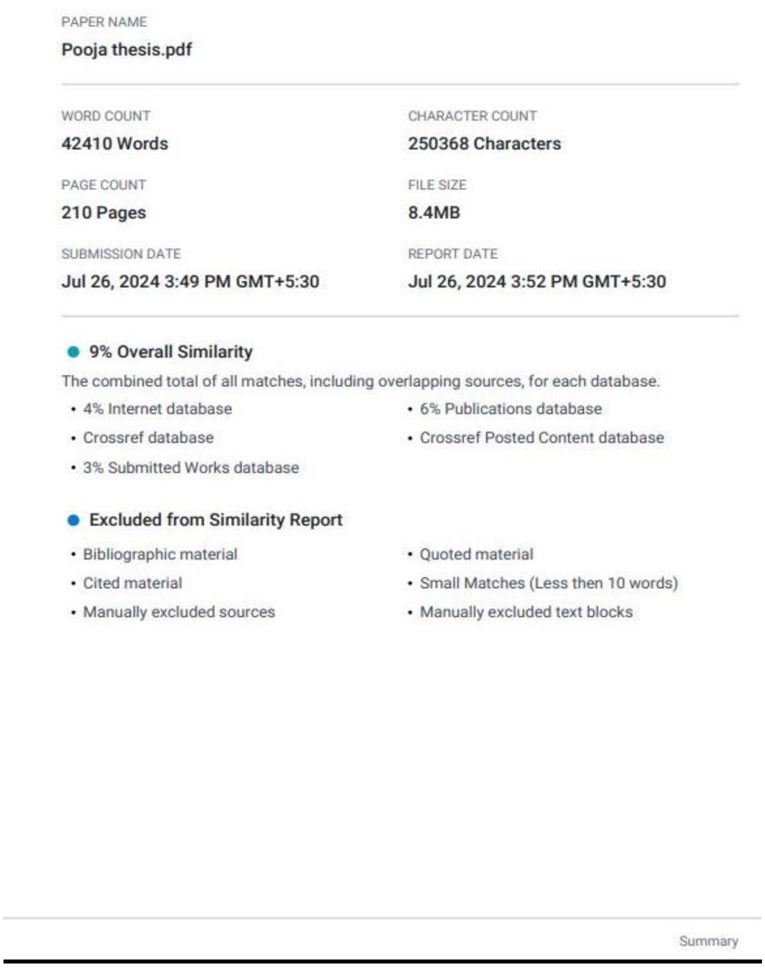

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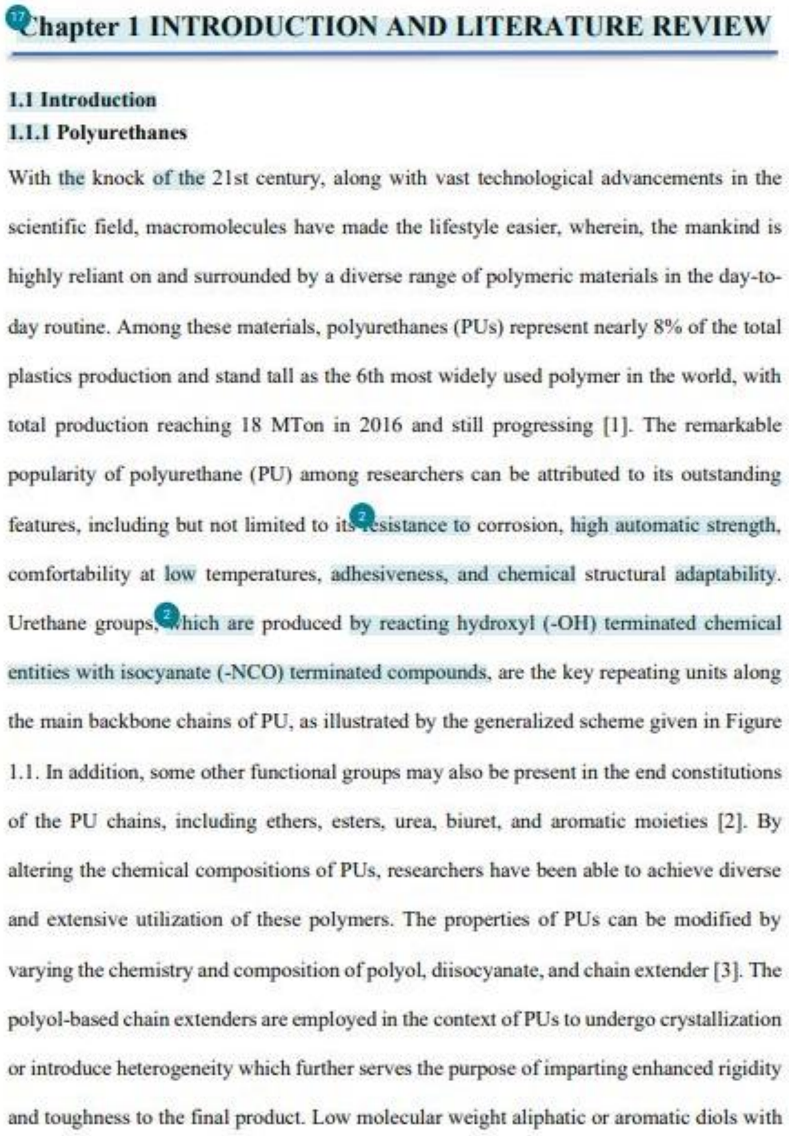
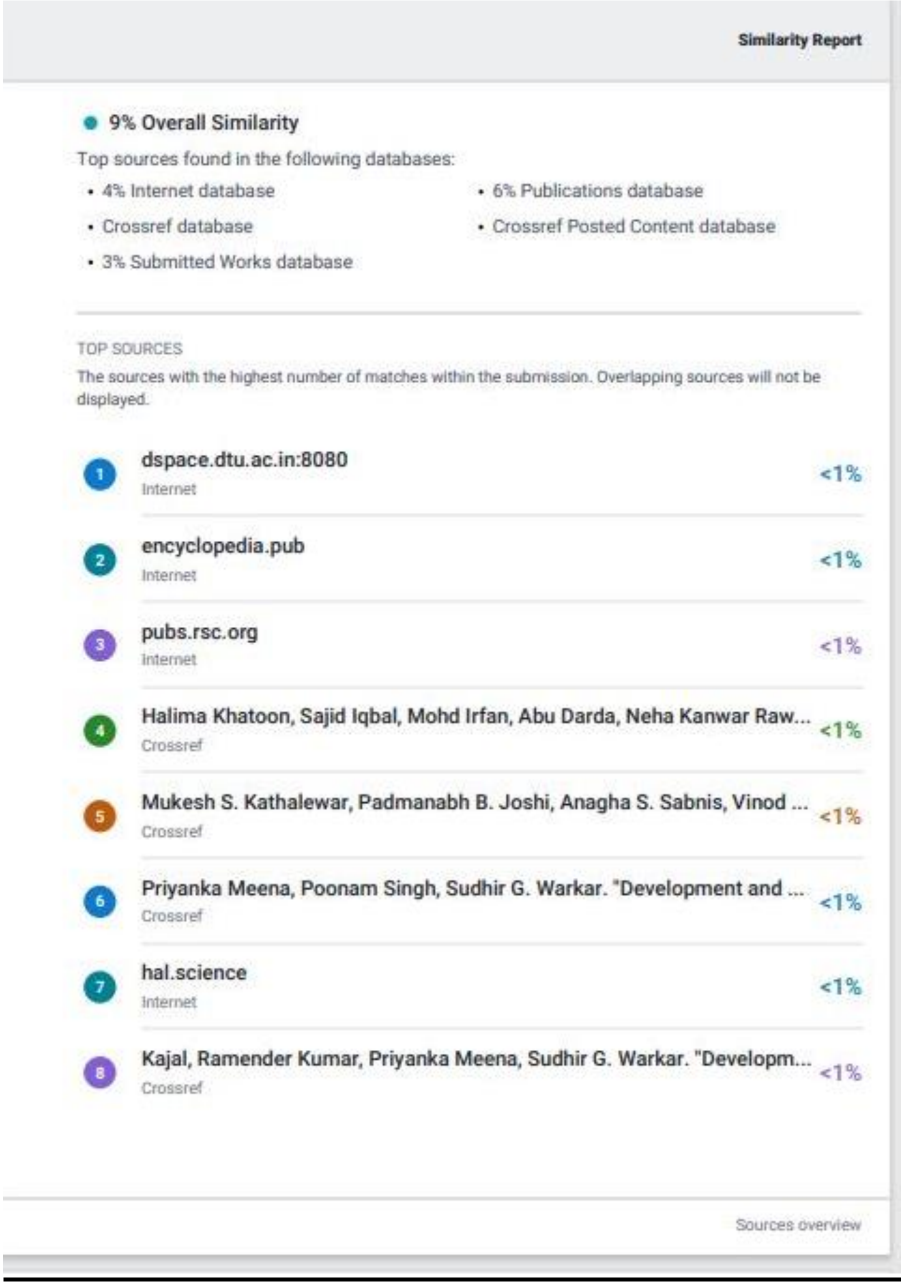


Chapter 1 INTRODUCTION AND LITERATURE REVIEW

1.1 Introduction

1.1.1 Polyurethanes

With the knock of the 21st century, along with vast technological advancements in the scientific field, macromolecules have made the lifestyle easier, wherein, the mankind is highly reliant on and surrounded by a diverse range of polymeric materials in the day-to-day routine. Among these materials, polyurethanes (PUs) represent nearly 8% of the total plastics production and stand tall as the 6th most widely used polymer in the world, with total production reaching 18 MTon in 2016 and still progressing [1]. The remarkable popularity of polyurethane (PU) among researchers can be attributed to its outstanding features, including but not limited to its resistance to corrosion, high automatic strength, comfortability at low temperatures, adhesiveness, and chemical structural adaptability. Urethane groups, which are produced by reacting hydroxyl (-OH) terminated chemical entities with isocyanate (-NCO) terminated compounds, are the key repeating units along the main backbone chains of PU, as illustrated by the generalized scheme given in Figure 1.1. In addition, some other functional groups may also be present in the end constitutions of the PU chains, including ethers, esters, urea, biuret, and aromatic moieties [2]. By altering the chemical compositions of PUs, researchers have been able to achieve diverse and extensive utilization of these polymers. The properties of PUs can be modified by varying the chemistry and composition of polyol, diisocyanate, and chain extender [3]. The polyol-based chain extenders are employed in the context of PUs to undergo crystallization or introduce heterogeneity which further serves the purpose of imparting enhanced rigidity and toughness to the final product. Low molecular weight aliphatic or aromatic diols with



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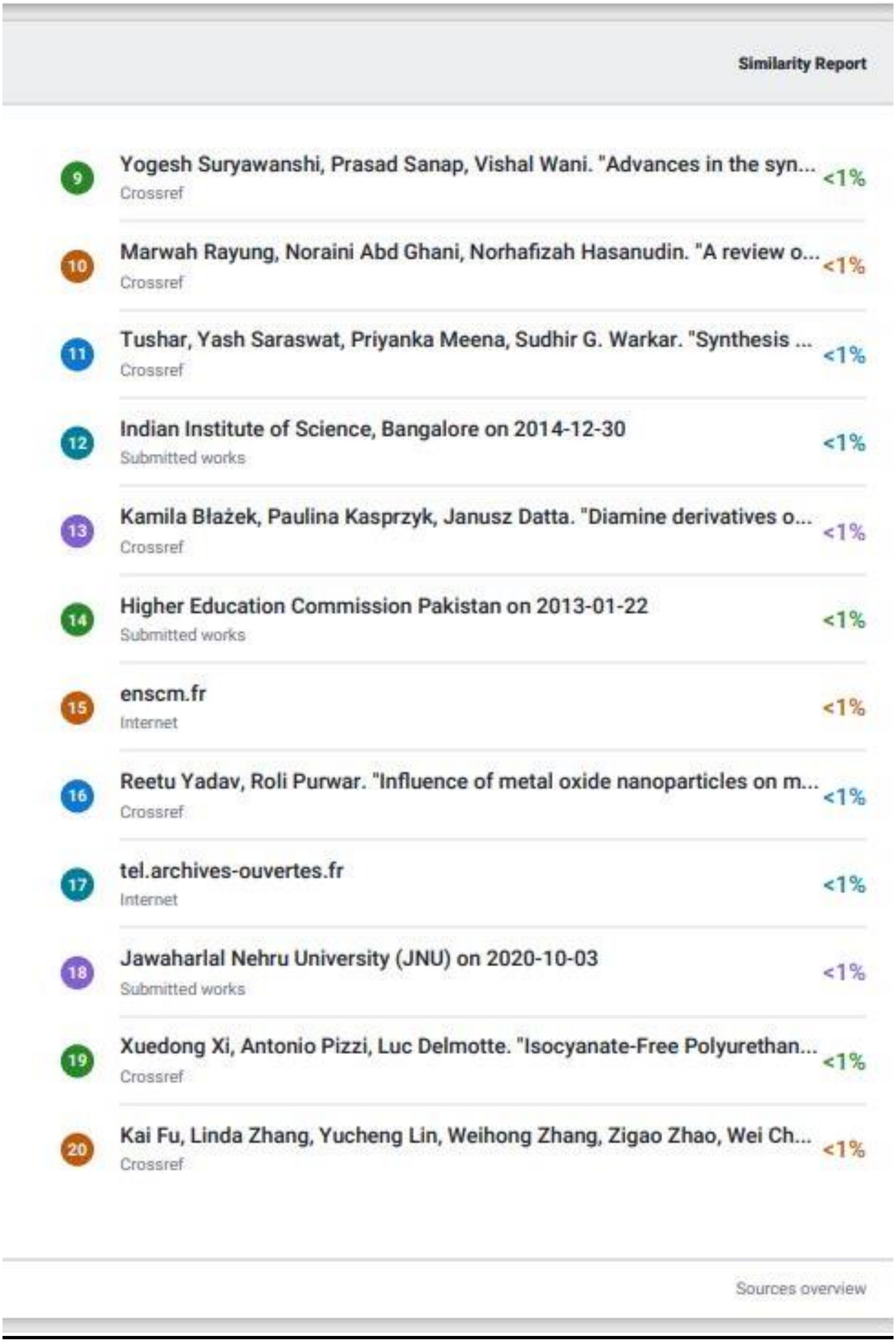

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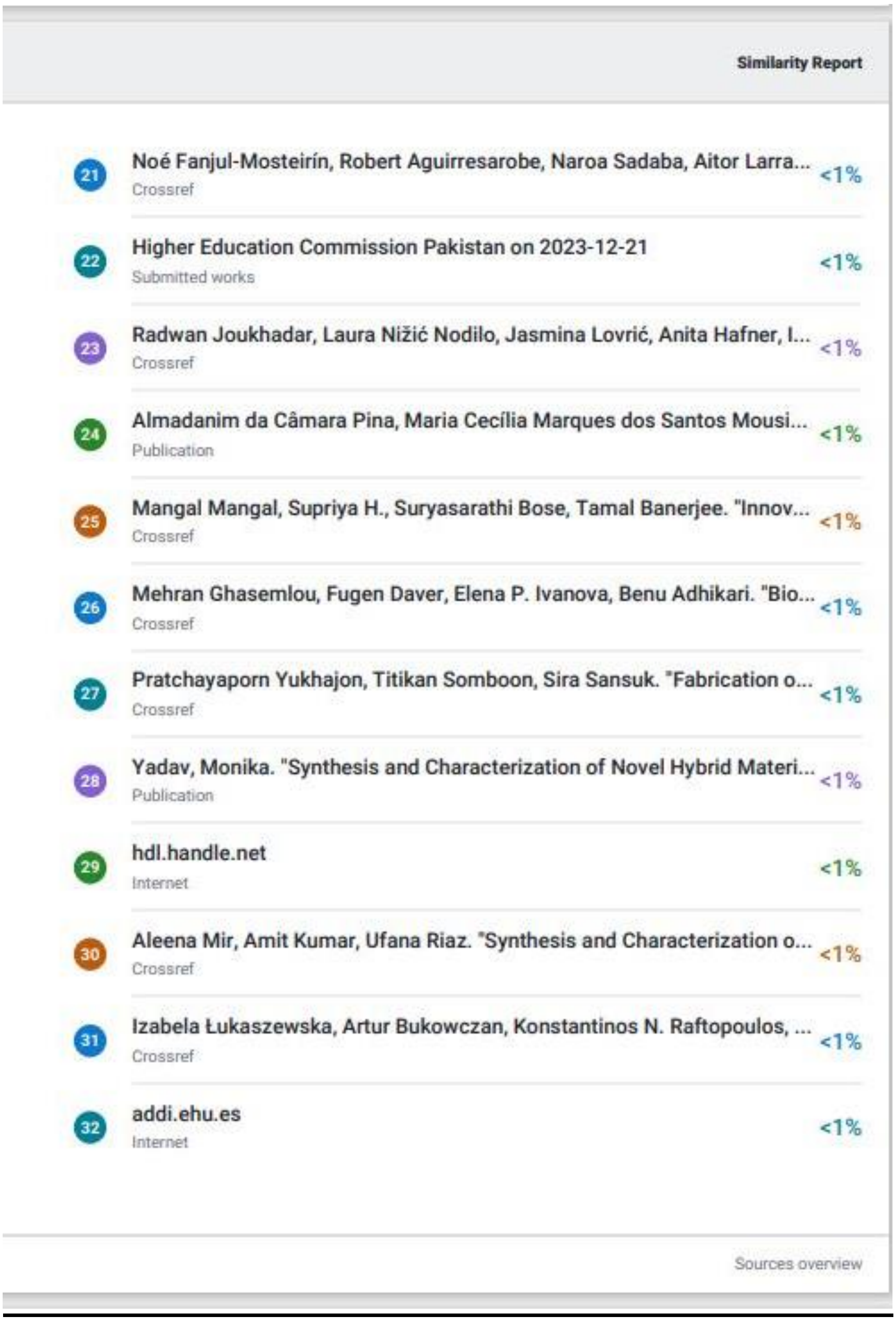

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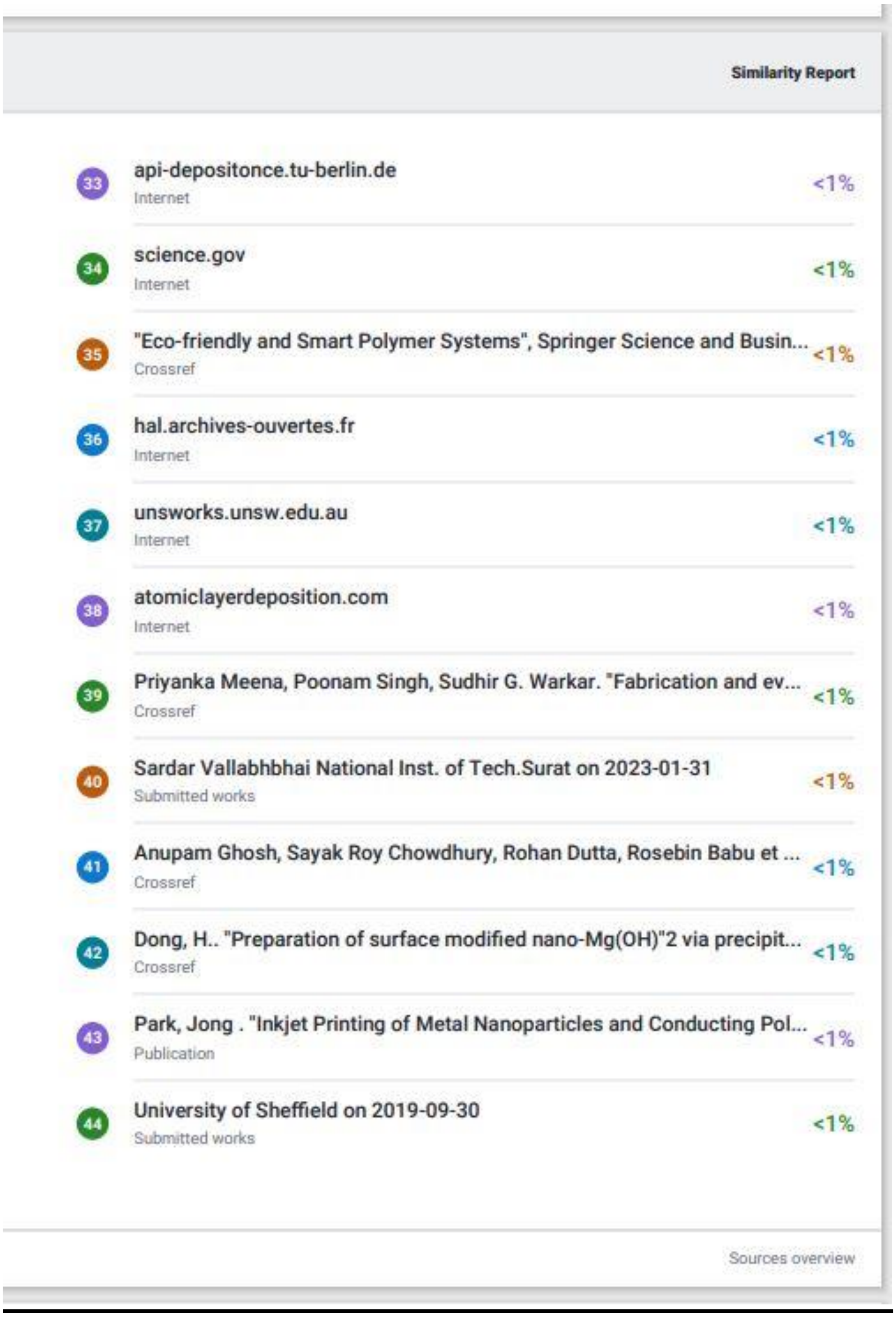

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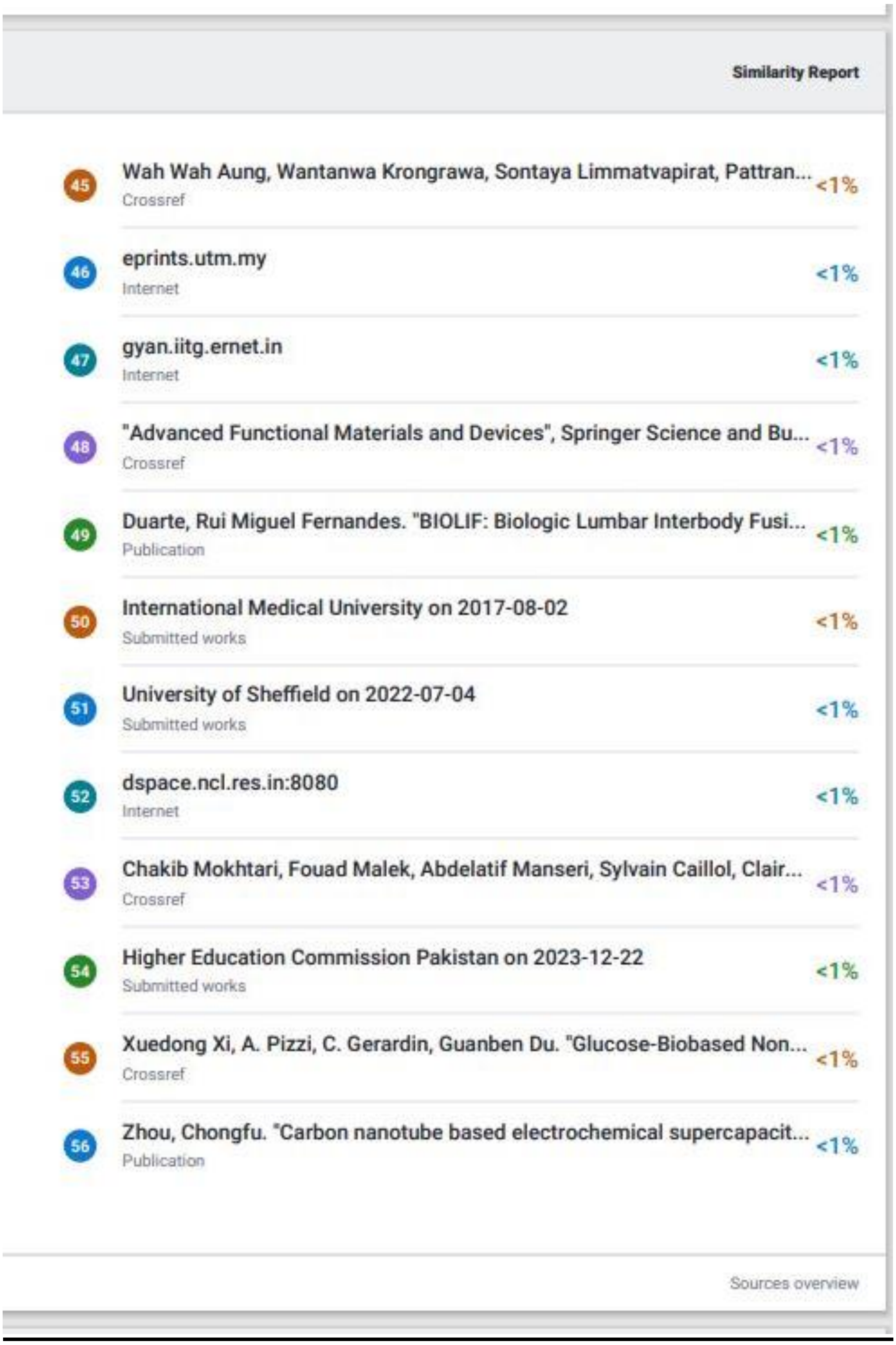

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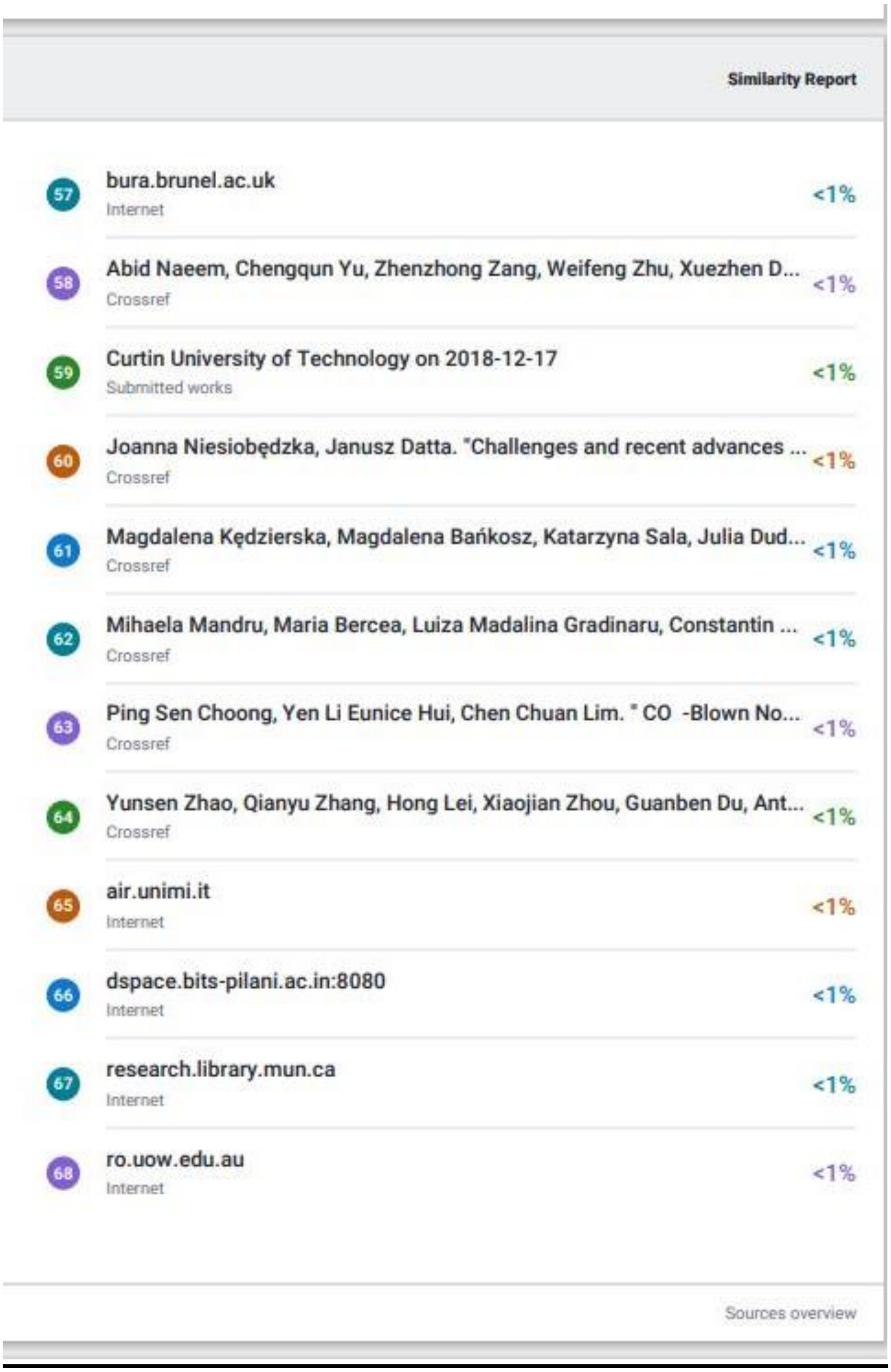

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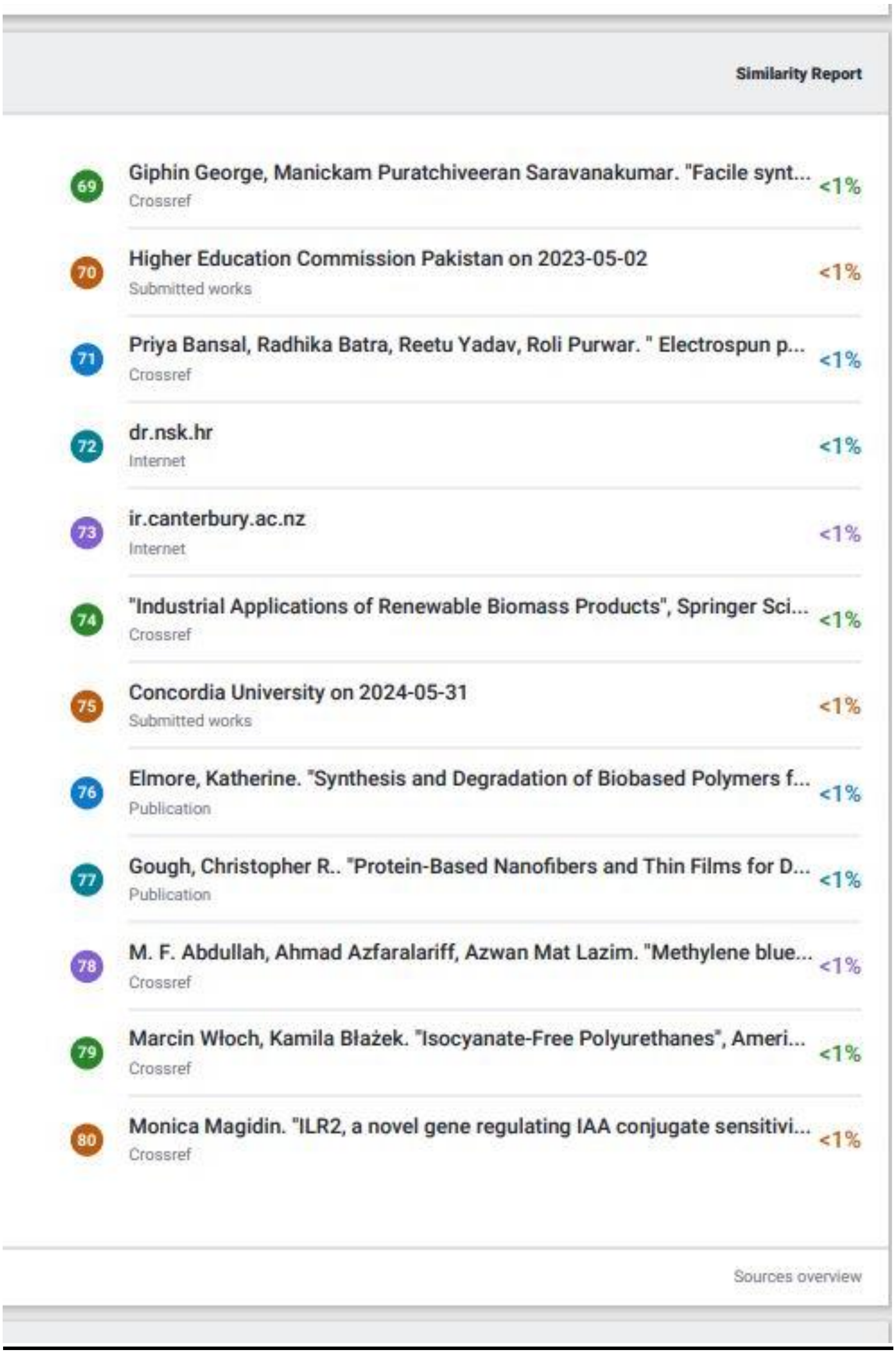

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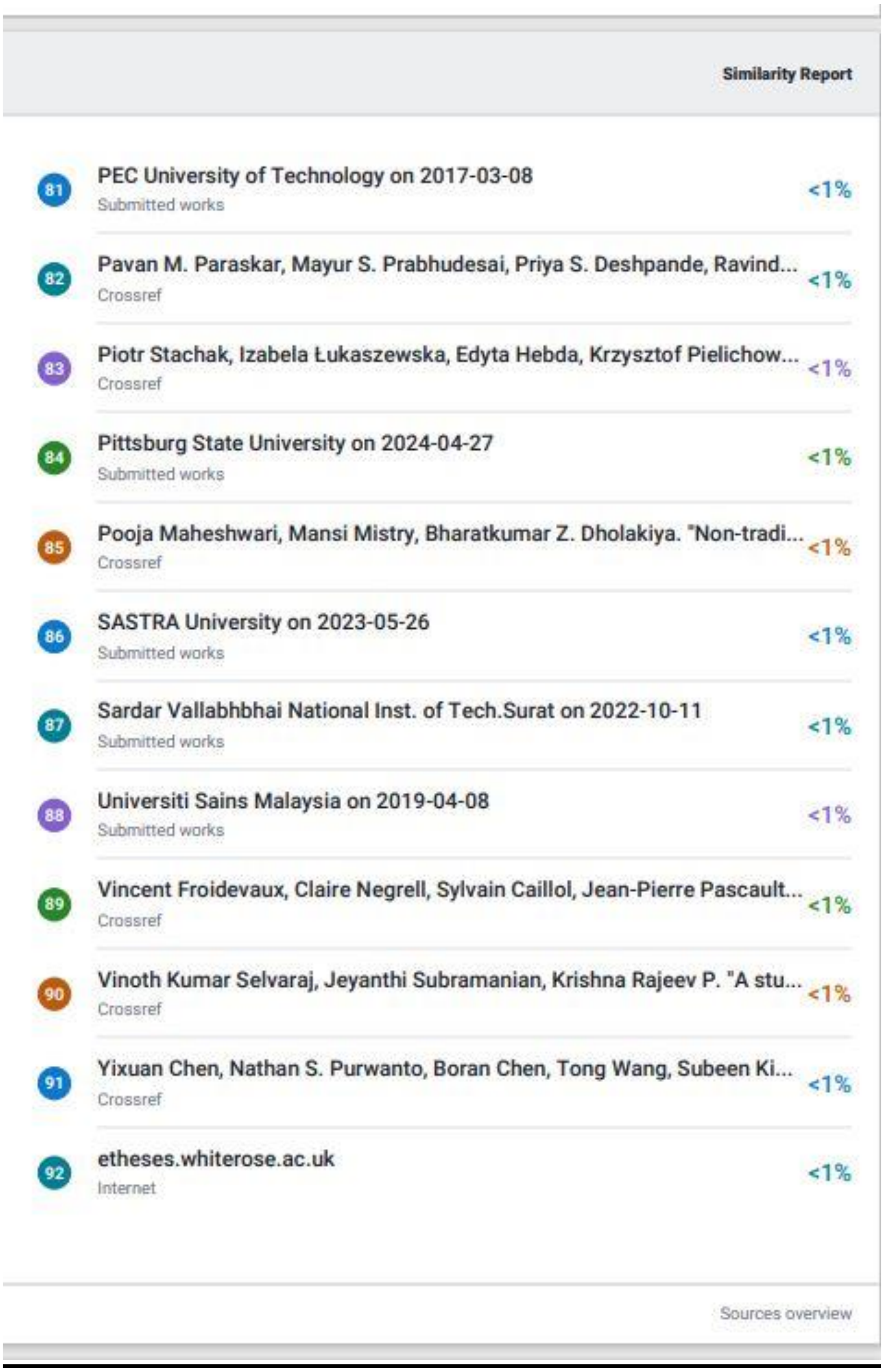

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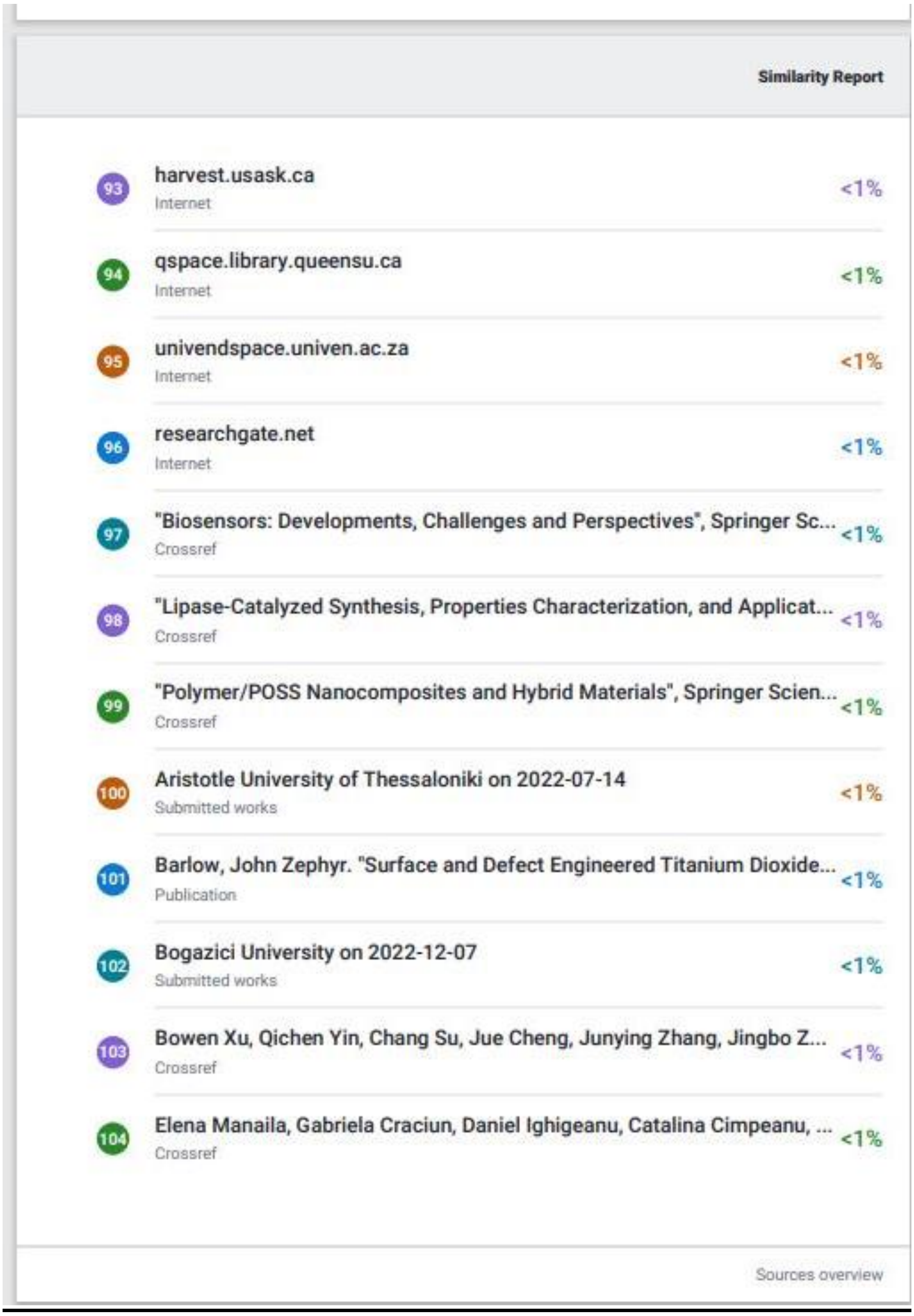

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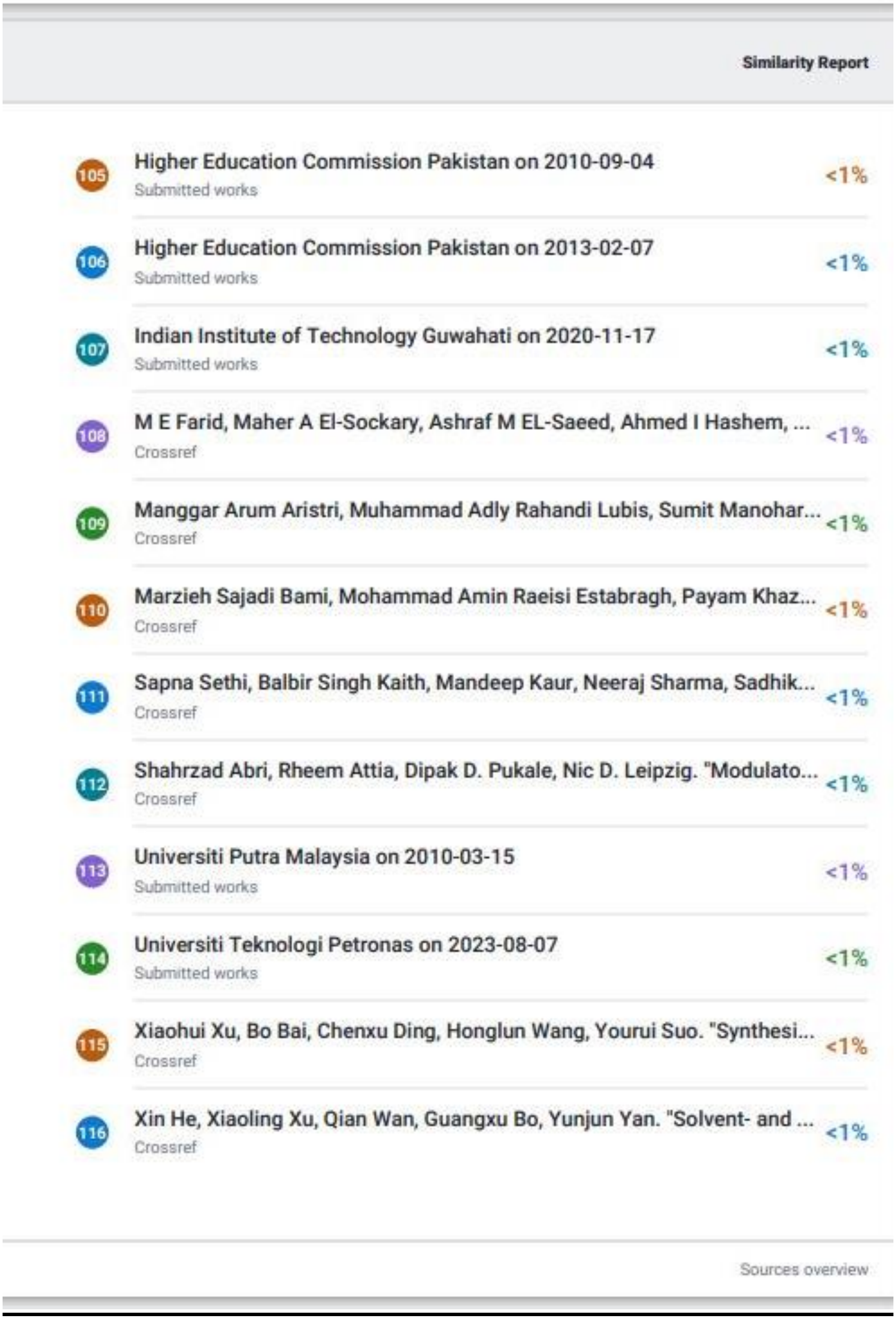

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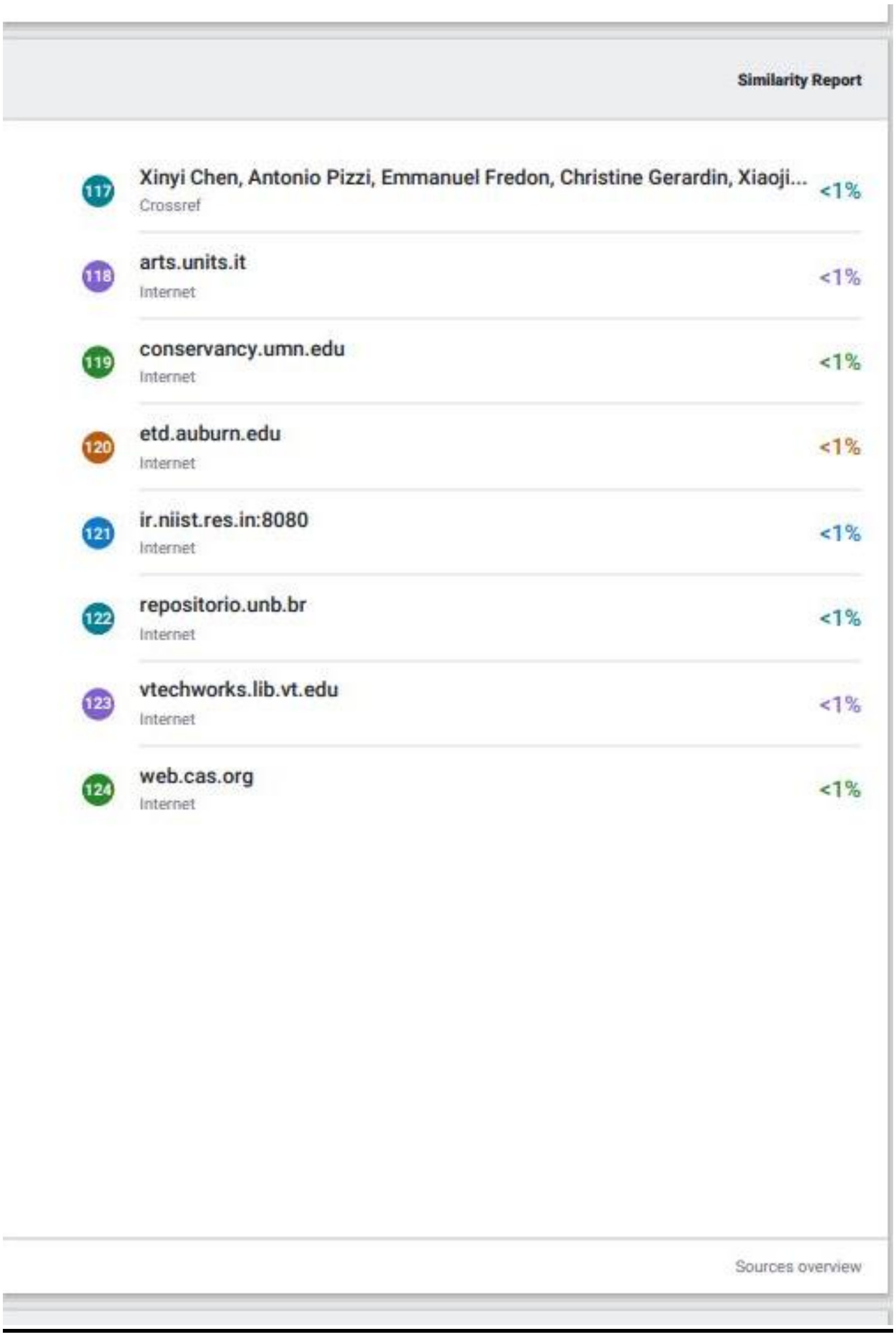

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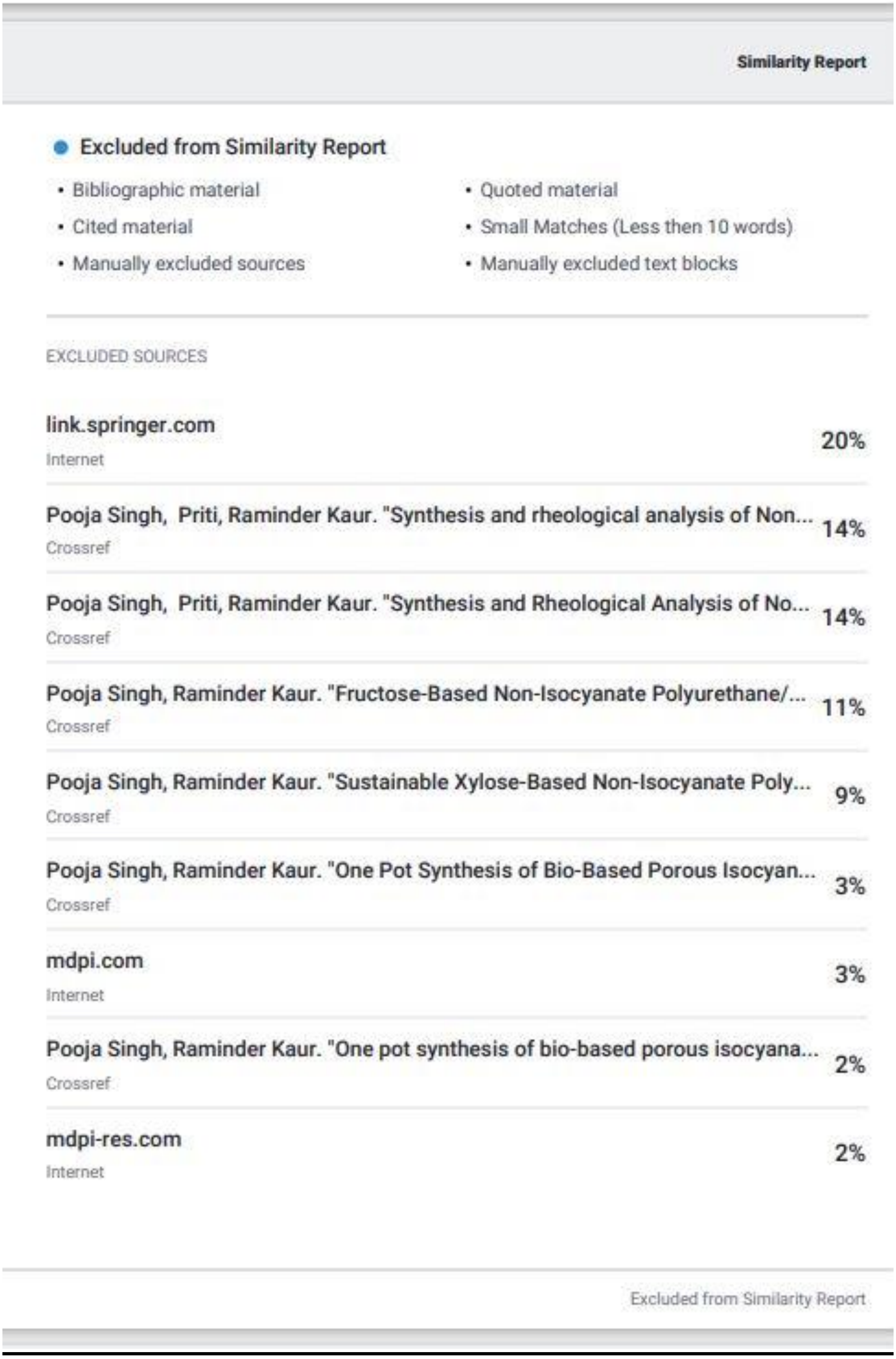

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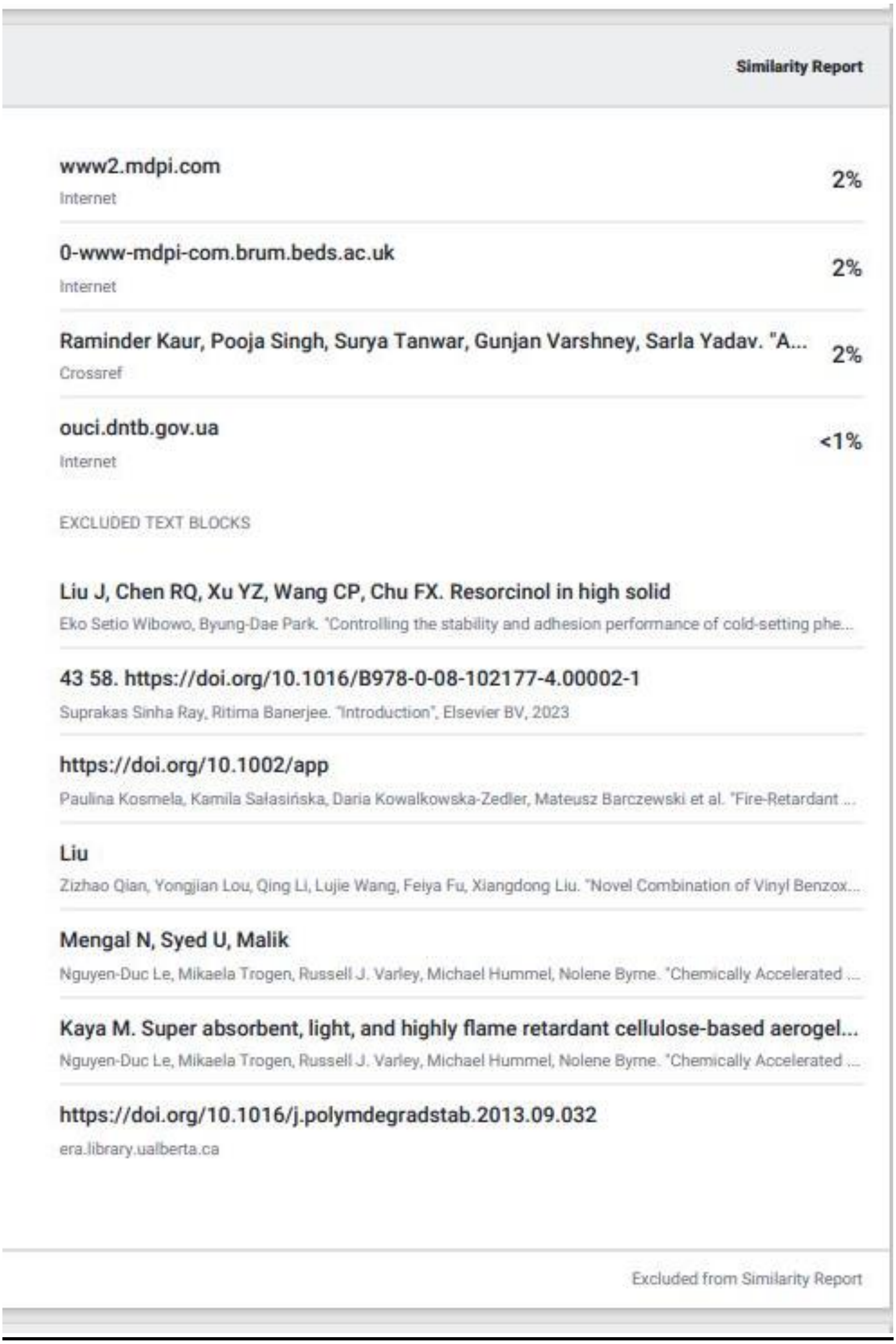

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Liu J, Chen RQ, Xu YZ, Wang CP, Chu FX. Resorcinol in high solid
Eko Setio Wibowo, Byung-Dae Park. "Controlling the stability and adhesion performance of cold-setting phe...

43 58. https://doi.org/10.1016/B978-0-08-102177-4.00002-1
Suprakas Sinha Ray, Ritima Banerjee. "Introduction", Elsevier BV, 2023

https://doi.org/10.1002/app
Paulina Kosmela, Kamila Sałasińska, Daria Kowalkowska-Zedler, Mateusz Barczewski et al. "Fire-Retardant ...

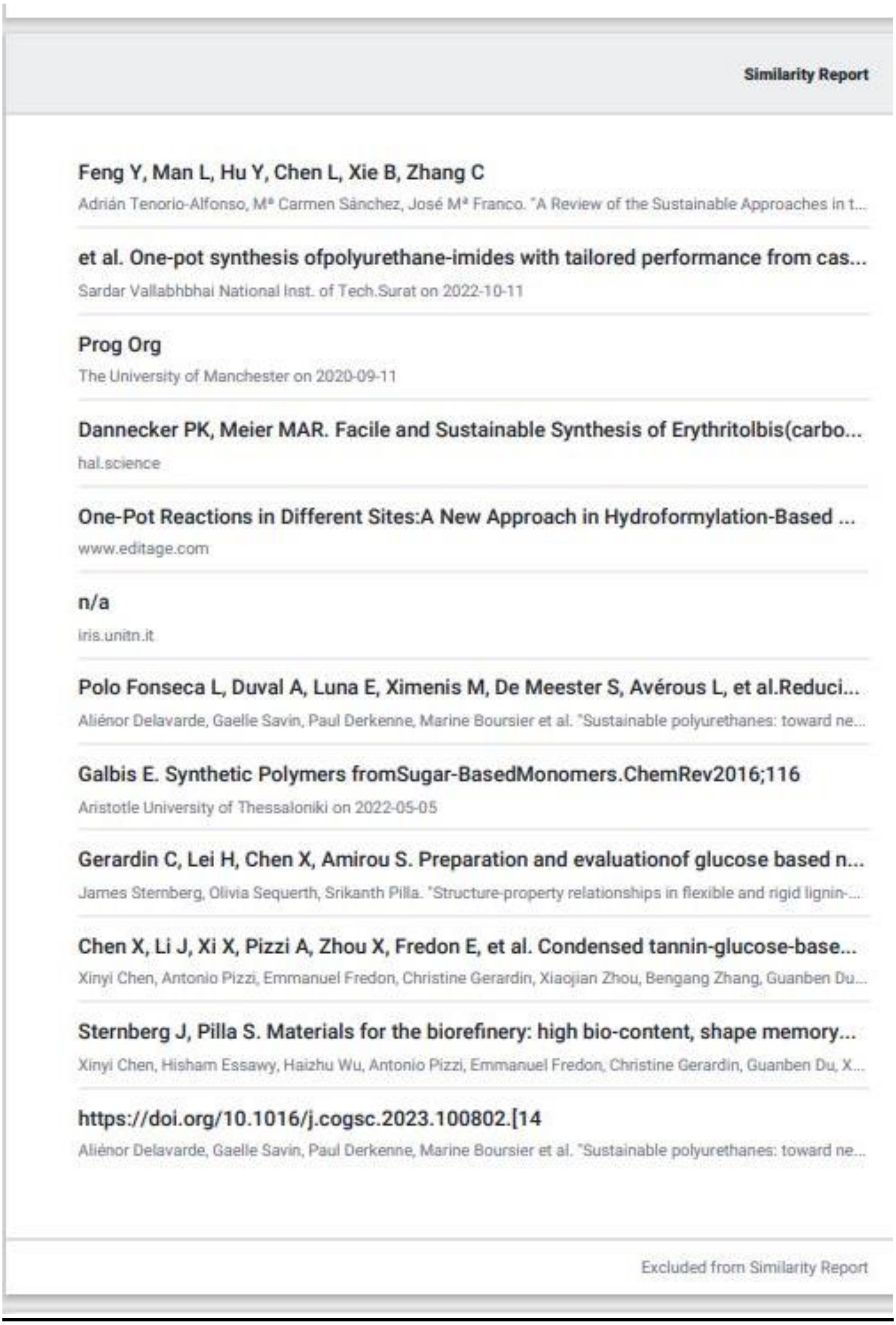
Liu
Zizhao Qian, Yongjian Lou, Qing Li, Lujie Wang, Feiya Fu, Xiangdong Liu. "Novel Combination of Vinyl Benzox...

Mengal N, Syed U, Malik
Nguyen-Duc Le, Mikaela Trogen, Russell J. Varley, Michael Hummel, Nolene Byrne. "Chemically Accelerated ...

Kaya M. Super absorbent, light, and highly flame retardant cellulose-based aerogel...
Nguyen-Duc Le, Mikaela Trogen, Russell J. Varley, Michael Hummel, Nolene Byrne. "Chemically Accelerated ...

https://doi.org/10.1016/j.polymdegradstab.2013.09.032
era.library.ualberta.ca

Excluded from Similarity Report



Similarity Report

Feng Y, Man L, Hu Y, Chen L, Xie B, Zhang C

Adrián Tenorio-Alfonso, Mª Carmen Sánchez, José Mª Franco. "A Review of the Sustainable Approaches in t...

et al. One-pot synthesis ofpolyurethane-imides with tailored performance from cas...

Sardar Vallabhbhai National Inst. of Tech.Surat on 2022-10-11

Prog Org

The University of Manchester on 2020-09-11

Dannecker PK, Meier MAR. Facile and Sustainable Synthesis of Erythritolbis(carbo...

hal.science

One-Pot Reactions in Different Sites:A New Approach in Hydroformylation-Based ...

www.editage.com

n/a

iris.unitn.it

Polo Fonseca L, Duval A, Luna E, Ximenis M, De Meester S, Avérous L, et al.Reduci...

Aliénor Delavarde, Gaelle Savin, Paul Derkenne, Marine Boursier et al. "Sustainable polyurethanes: toward ne...

Galbis E. Synthetic Polymers fromSugar-BasedMonomers.ChemRev2016;116

Aristotle University of Thessaloniki on 2022-05-05

Gerardin C, Lei H, Chen X, Amirou S. Preparation and evaluationof glucose based n...

James Sternberg, Olivia Sequerth, Srikanth Pilla. "Structure-property relationships in flexible and rigid lignin-...

Chen X, Li J, Xi X, Pizzi A, Zhou X, Fredon E, et al. Condensed tannin-glucose-base...

Xinyi Chen, Antonio Pizzi, Emmanuel Fredon, Christine Gerardin, Xiaojian Zhou, Bengang Zhang, Guanben Du...

Sternberg J, Pilla S. Materials for the biorefinery: high bio-content, shape memory...

Xinyi Chen, Hisham Essawy, Haizhu Wu, Antonio Pizzi, Emmanuel Fredon, Christine Gerardin, Guanben Du, X...

https://doi.org/10.1016/j.cogsc.2023.100802.[14

Aliénor Delavarde, Gaelle Savin, Paul Derkenne, Marine Boursier et al. "Sustainable polyurethanes: toward ne...

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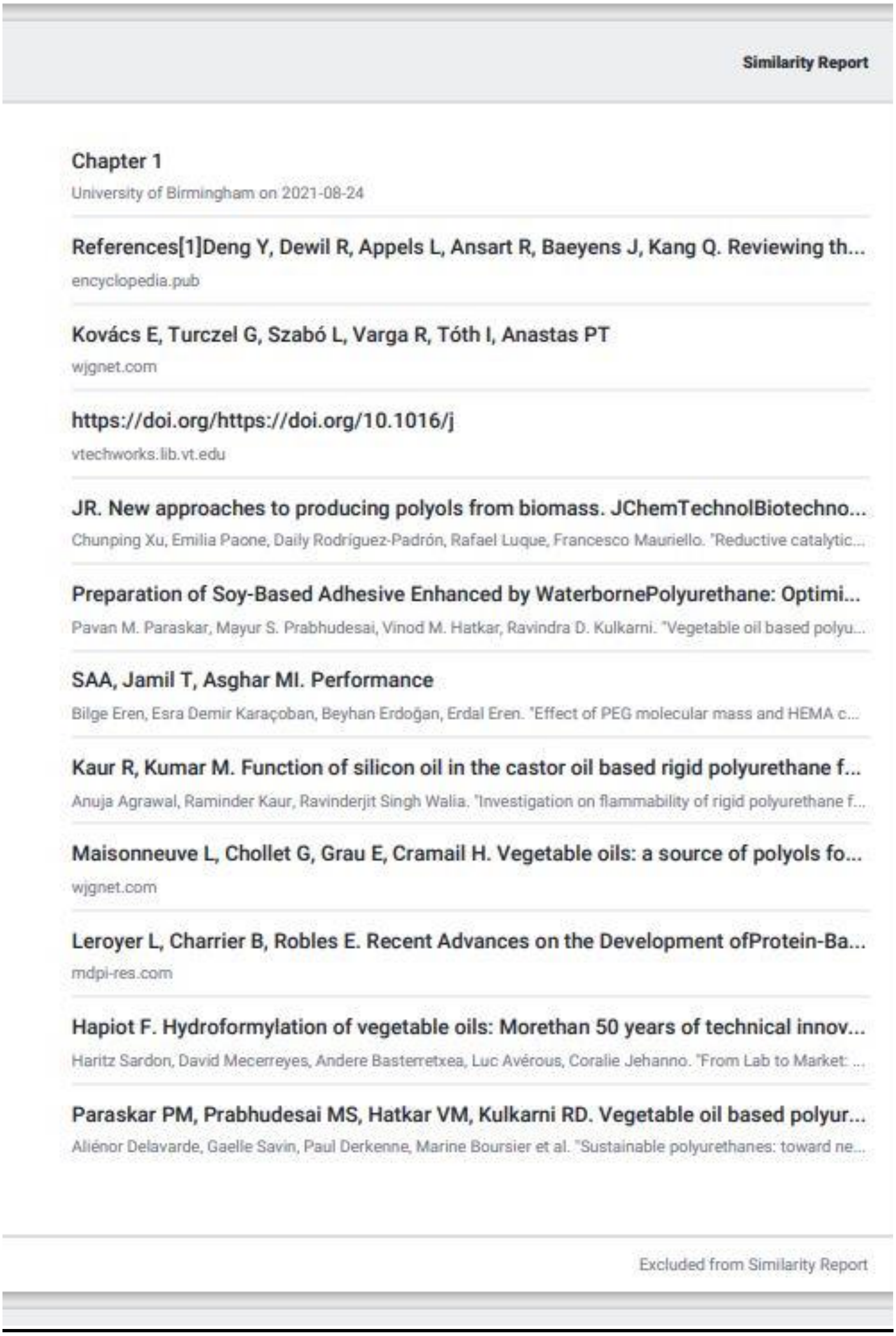


Similarity Report

Chapter 1
University of Birmingham on 2021-08-24

References[1]Deng Y, Dewil R, Appels L, Ansart R, Baeyens J, Kang Q. Reviewing th...
encyclopedia.pub

Kovács E, Turczel G, Szabó L, Varga R, Tóth I, Anastas PT
wjgnet.com

https://doi.org/https://doi.org/10.1016/j
vtechworks.lib.vt.edu

JR. New approaches to producing polyols from biomass. JChemTechnolBiotechno...
Chunping Xu, Emilia Paone, Daily Rodríguez-Padrón, Rafael Luque, Francesco Mauriello. "Reductive catalytic...

Preparation of Soy-Based Adhesive Enhanced by WaterbornePolyurethane: Optimi...
Pavan M. Paraskar, Mayur S. Prabhudesai, Vinod M. Hatkar, Ravindra D. Kulkarni. "Vegetable oil based polyu...

SAA, Jamil T, Asghar MI. Performance
Bilge Eren, Esra Demir Karaçoban, Beyhan Erdoğan, Erdal Eren. "Effect of PEG molecular mass and HEMA c...

Kaur R, Kumar M. Function of silicon oil in the castor oil based rigid polyurethane f...
Anuja Agrawal, Raminder Kaur, Ravinderjit Singh Walia. "Investigation on flammability of rigid polyurethane f...

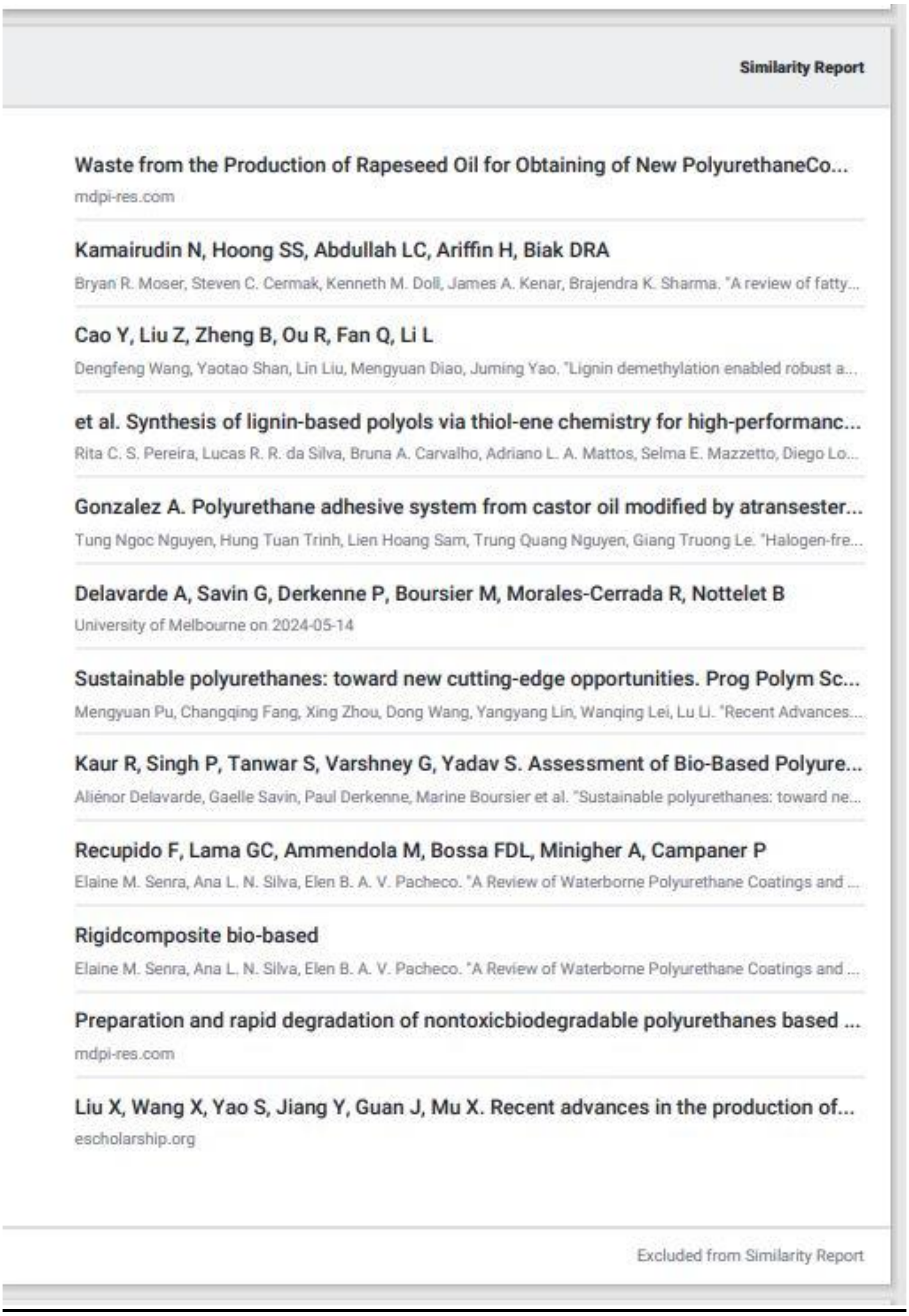
Maisonneuve L, Chollet G, Grau E, Cramail H. Vegetable oils: a source of polyols fo...
wjgnet.com

Leroyer L, Charrier B, Robles E. Recent Advances on the Development ofProtein-Ba...
mdpi-res.com

Hapiot F. Hydroformylation of vegetable oils: Morethan 50 years of technical innov...
Haritz Sardon, David Mecerreyes, Andere Basterretxea, Luc Avérous, Coralie Jehanno. "From Lab to Market: ...

Paraskar PM, Prabhudesai MS, Hatkar VM, Kulkarni RD. Vegetable oil based polyur...
Aliénor Delavarde, Gaelle Savin, Paul Derkenne, Marine Boursier et al. "Sustainable polyurethanes: toward ne...

Excluded from Similarity Report



Similarity Report

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Kamairudin N, Hoong SS, Abdullah LC, Ariffin H, Biak DRA
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Cao Y, Liu Z, Zheng B, Ou R, Fan Q, Li L
Dengfeng Wang, Yaotao Shan, Lin Liu, Mengyuan Diao, Juming Yao. "Lignin demethylation enabled robust a...

et al. Synthesis of lignin-based polyols via thiol-ene chemistry for high-performanc...
Rita C. S. Pereira, Lucas R. R. da Silva, Bruna A. Carvalho, Adriano L. A. Mattos, Selma E. Mazzetto, Diego Lo...

Gonzalez A. Polyurethane adhesive system from castor oil modified by atransester...
Tung Ngoc Nguyen, Hung Tuan Trinh, Lien Hoang Sam, Trung Quang Nguyen, Giang Truong Le. "Halogen-fre...

Delavarde A, Savin G, Derkenne P, Boursier M, Morales-Cerrada R, Nottelet B
University of Melbourne on 2024-05-14

Sustainable polyurethanes: toward new cutting-edge opportunities. Prog Polym Sc...
Mengyuan Pu, Changqing Fang, Xing Zhou, Dong Wang, Yangyang Lin, Wanqing Lei, Lu Li. "Recent Advances...

Kaur R, Singh P, Tanwar S, Varshney G, Yadav S. Assessment of Bio-Based Polyure...
Aliénor Delavarde, Gaelle Savin, Paul Derkenne, Marine Boursier et al. "Sustainable polyurethanes: toward ne...

Recupido F, Lama GC, Ammendola M, Bossa FDL, Minigher A, Campaner P
Elaine M. Senra, Ana L. N. Silva, Elen B. A. V. Pacheco. "A Review of Waterborne Polyurethane Coatings and ...

Rigidcomposite bio-based
Elaine M. Senra, Ana L. N. Silva, Elen B. A. V. Pacheco. "A Review of Waterborne Polyurethane Coatings and ...

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Liu X, Wang X, Yao S, Jiang Y, Guan J, Mu X. Recent advances in the production of...
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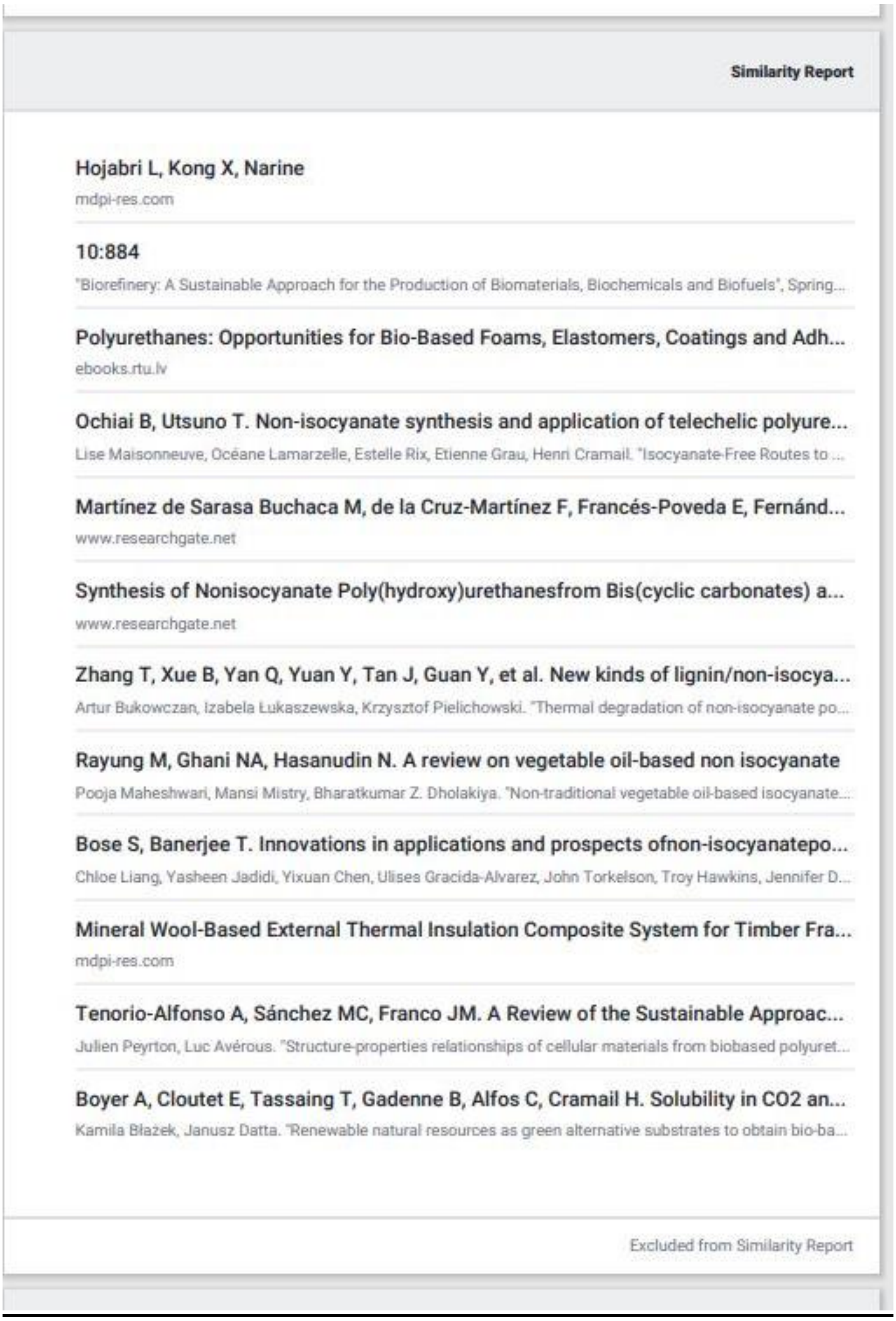

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10:884
"Biorefinery: A Sustainable Approach for the Production of Biomaterials, Biochemicals and Biofuels", Spring...

Polyurethanes: Opportunities for Bio-Based Foams, Elastomers, Coatings and Adh...
ebooks.rtu.lv

Ochiai B, Utsuno T. Non-isocyanate synthesis and application of telechelic polyure...
Lise Maisonneuve, Océane Lamarzelle, Estelle Rix, Etienne Grau, Henri Cramail. "Isocyanate-Free Routes to ...

Martínez de Sarasa Buchaca M, de la Cruz-Martínez F, Francés-Poveda E, Fernánd...
www.researchgate.net

Synthesis of Nonisocyanate Poly(hydroxy)urethanesfrom Bis(cyclic carbonates) a...
www.researchgate.net

Zhang T, Xue B, Yan Q, Yuan Y, Tan J, Guan Y, et al. New kinds of lignin/non-isocya...
Artur Bukowczan, Izabela Łukaszewska, Krzysztof Pielichowski. "Thermal degradation of non-isocyanate po...

Rayung M, Ghani NA, Hasanudin N. A review on vegetable oil-based non isocyanate
Pooja Maheshwari, Mansi Mistry, Bharatkumar Z. Dholakiya. "Non-traditional vegetable oil-based isocyanate...

Bose S, Banerjee T. Innovations in applications and prospects ofnon-isocyanatepo...
Chloe Liang, Yasheen Jadidi, Yixuan Chen, Ulises Gracida-Alvarez, John Torkelson, Troy Hawkins, Jennifer D...

Mineral Wool-Based External Thermal Insulation Composite System for Timber Fra...
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Tenorio-Alfonso A, Sánchez MC, Franco JM. A Review of the Sustainable Approac...
Julien Peyrton, Luc Avérous. "Structure-properties relationships of cellular materials from biobased polyuret...

Boyer A, Cloutet E, Tassaing T, Gadenne B, Alfos C, Cramail H. Solubility in CO2 an...
Kamila Błażek, Janusz Datta. "Renewable natural resources as green alternative substrates to obtain bio-ba...

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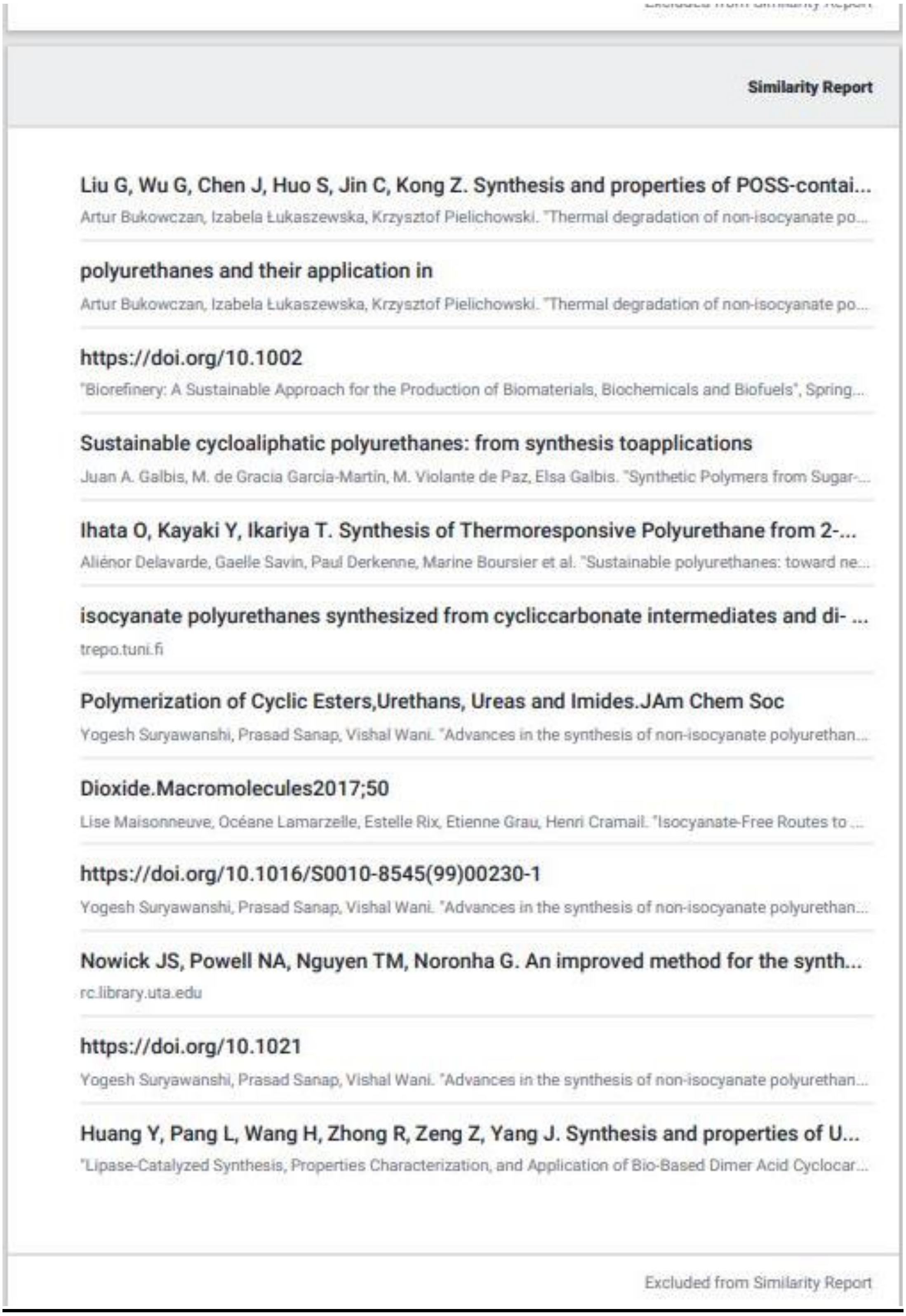

Similarity Report

Liu G, Wu G, Chen J, Huo S, Jin C, Kong Z. Synthesis and properties of POSS-contai...
Artur Bukowczan, Izabela Łukaszewska, Krzysztof Pielichowski. "Thermal degradation of non-isocyanate po...

polyurethanes and their application in
Artur Bukowczan, Izabela Łukaszewska, Krzysztof Pielichowski. "Thermal degradation of non-isocyanate po...

https://doi.org/10.1002
"Biorefinery: A Sustainable Approach for the Production of Biomaterials, Biochemicals and Biofuels", Spring...

Sustainable cycloaliphatic polyurethanes: from synthesis toapplications
Juan A. Galbis, M. de Gracia García-Martín, M. Violante de Paz, Elsa Galbis. "Synthetic Polymers from Sugar-...

Ihata O, Kayaki Y, Ikariya T. Synthesis of Thermoresponsive Polyurethane from 2-...
Aliénor Delavarde, Gaelle Savin, Paul Derkenne, Marine Boursier et al. "Sustainable polyurethanes: toward ne...

isocyanate polyurethanes synthesized from cycliccarbonate intermediates and di- ...
trepo.tuni.fi

Polymerization of Cyclic Esters,Urethans, Ureas and Imides.JAm Chem Soc
Yogesh Suryawanshi, Prasad Sanap, Vishal Wani. "Advances in the synthesis of non-isocyanate polyurethan...

Dioxide.Macromolecules2017;50
Lise Maisonneuve, Océane Lamarzelle, Estelle Rix, Etienne Grau, Henri Cramail. "Isocyanate-Free Routes to ...

https://doi.org/10.1016/S0010-8545(99)00230-1
Yogesh Suryawanshi, Prasad Sanap, Vishal Wani. "Advances in the synthesis of non-isocyanate polyurethan...

Nowick JS, Powell NA, Nguyen TM, Noronha G. An improved method for the synth...
rc.library.uta.edu

https://doi.org/10.1021
Yogesh Suryawanshi, Prasad Sanap, Vishal Wani. "Advances in the synthesis of non-isocyanate polyurethan...

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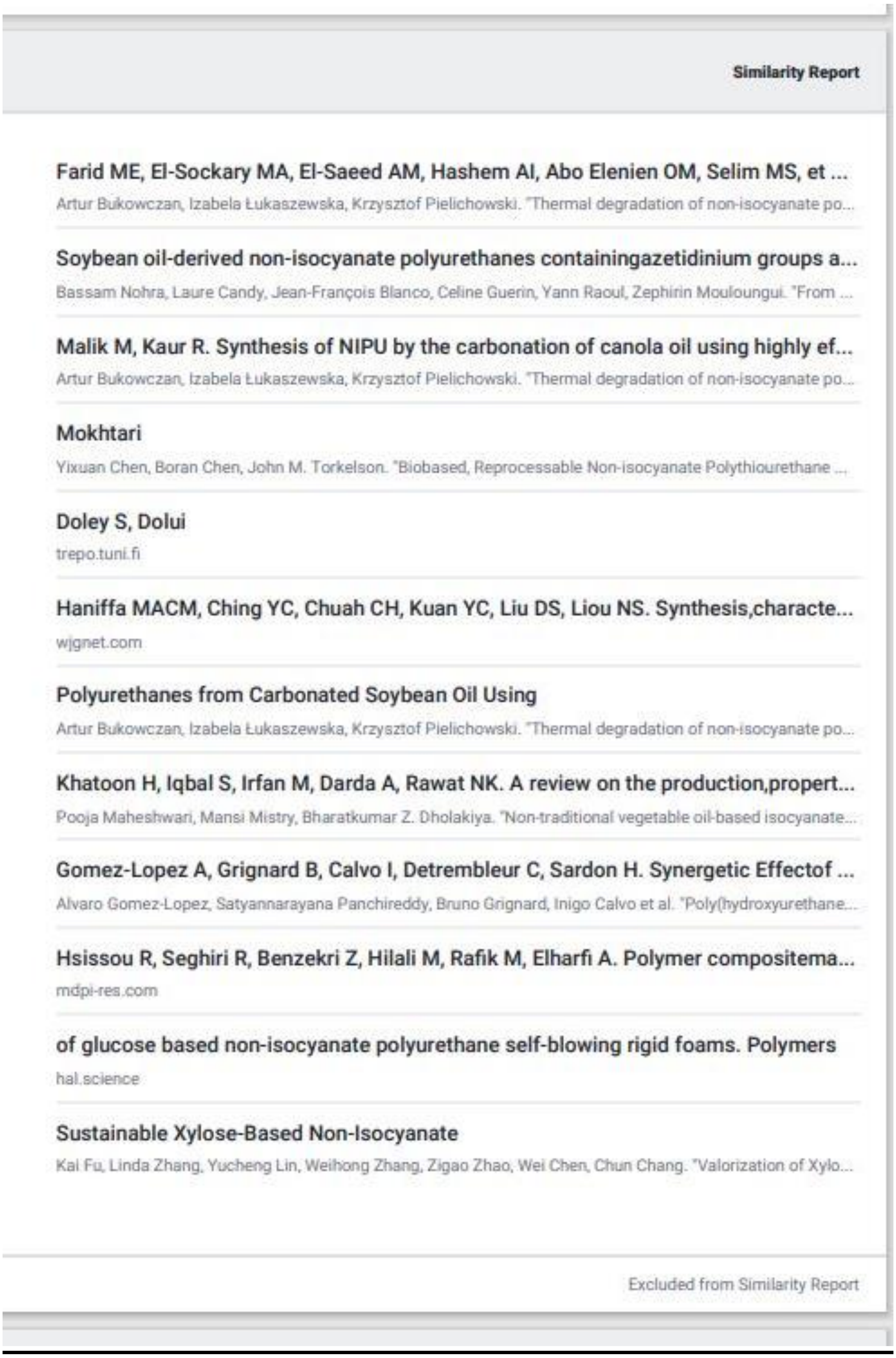

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Soybean oil-derived non-isocyanate polyurethanes containingazetidinium groups a...
Bassam Nohra, Laure Candy, Jean-François Blanco, Celine Guerin, Yann Raoul, Zephirin Mouloungui. "From ...

Malik M, Kaur R. Synthesis of NIPU by the carbonation of canola oil using highly ef...
Artur Bukowczan, Izabela Łukaszewska, Krzysztof Pielichowski. "Thermal degradation of non-isocyanate po...

Mokhtari
Yixuan Chen, Boran Chen, John M. Torkelson. "Biobased, Reprocessable Non-isocyanate Polythiourethane ...

Doley S, Dolui
trepo.tuni.fi

Haniffa MACM, Ching YC, Chuah CH, Kuan YC, Liu DS, Liou NS. Synthesis,characte...
wjgnet.com

Polyurethanes from Carbonated Soybean Oil Using
Artur Bukowczan, Izabela Łukaszewska, Krzysztof Pielichowski. "Thermal degradation of non-isocyanate po...

Khatoon H, Iqbal S, Irfan M, Darda A, Rawat NK. A review on the production,propert...
Pooja Maheshwari, Mansi Mistry, Bharatkumar Z. Dholakiya. "Non-traditional vegetable oil-based isocyanate...

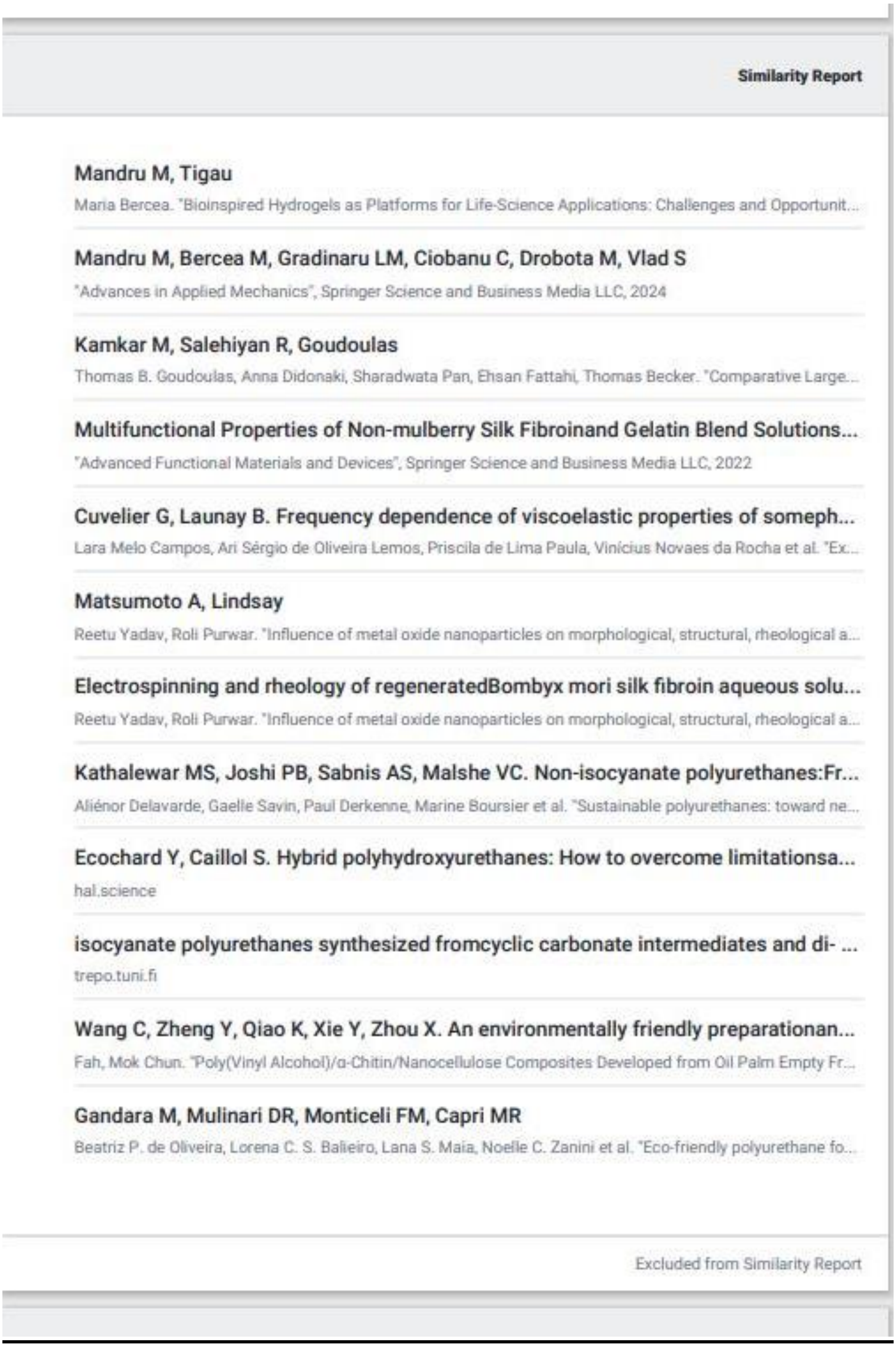
Gomez-Lopez A, Grignard B, Calvo I, Detrembleur C, Sardon H. Synergetic Effectof ...
Alvaro Gomez-Lopez, Satyannarayana Panchireddy, Bruno Grignard, Inigo Calvo et al. "Poly(hydroxyurethane...

Hsissou R, Seghiri R, Benzekri Z, Hilali M, Rafik M, Elharfi A. Polymer compositema...
mdpi-res.com

of glucose based non-isocyanate polyurethane self-blowing rigid foams. Polymers
hal.science

Sustainable Xylose-Based Non-Isocyanate
Kai Fu, Linda Zhang, Yucheng Lin, Weihong Zhang, Zigao Zhao, Wei Chen, Chun Chang. "Valorization of Xylo...

Excluded from Similarity Report



Similarity Report

Mandru M, Tigau
Maria Bercea. "Bioinspired Hydrogels as Platforms for Life-Science Applications: Challenges and Opportunit...

Mandru M, Bercea M, Gradinaru LM, Ciobanu C, Drobota M, Vlad S
"Advances in Applied Mechanics", Springer Science and Business Media LLC, 2024

Kamkar M, Salehiyan R, Goudoulas
Thomas B. Goudoulas, Anna Didonaki, Sharadwata Pan, Ehsan Fattahi, Thomas Becker. "Comparative Large...

Multifunctional Properties of Non-mulberry Silk Fibroinand Gelatin Blend Solutions...
"Advanced Functional Materials and Devices", Springer Science and Business Media LLC, 2022

Cuvelier G, Launay B. Frequency dependence of viscoelastic properties of someph...
Lara Melo Campos, Ari Sérgio de Oliveira Lemos, Priscila de Lima Paula, Vinícius Novaes da Rocha et al. "Ex...

Matsumoto A, Lindsay
Reetu Yadav, Roli Purwar. "Influence of metal oxide nanoparticles on morphological, structural, rheological a...

Electrospinning and rheology of regeneratedBombyx mori silk fibroin aqueous solu...
Reetu Yadav, Roli Purwar. "Influence of metal oxide nanoparticles on morphological, structural, rheological a...

Kathalewar MS, Joshi PB, Sabnis AS, Malshe VC. Non-isocyanate polyurethanes:Fr...
Aliénor Delavarde, Gaelle Savin, Paul Derkenne, Marine Boursier et al. "Sustainable polyurethanes: toward ne...

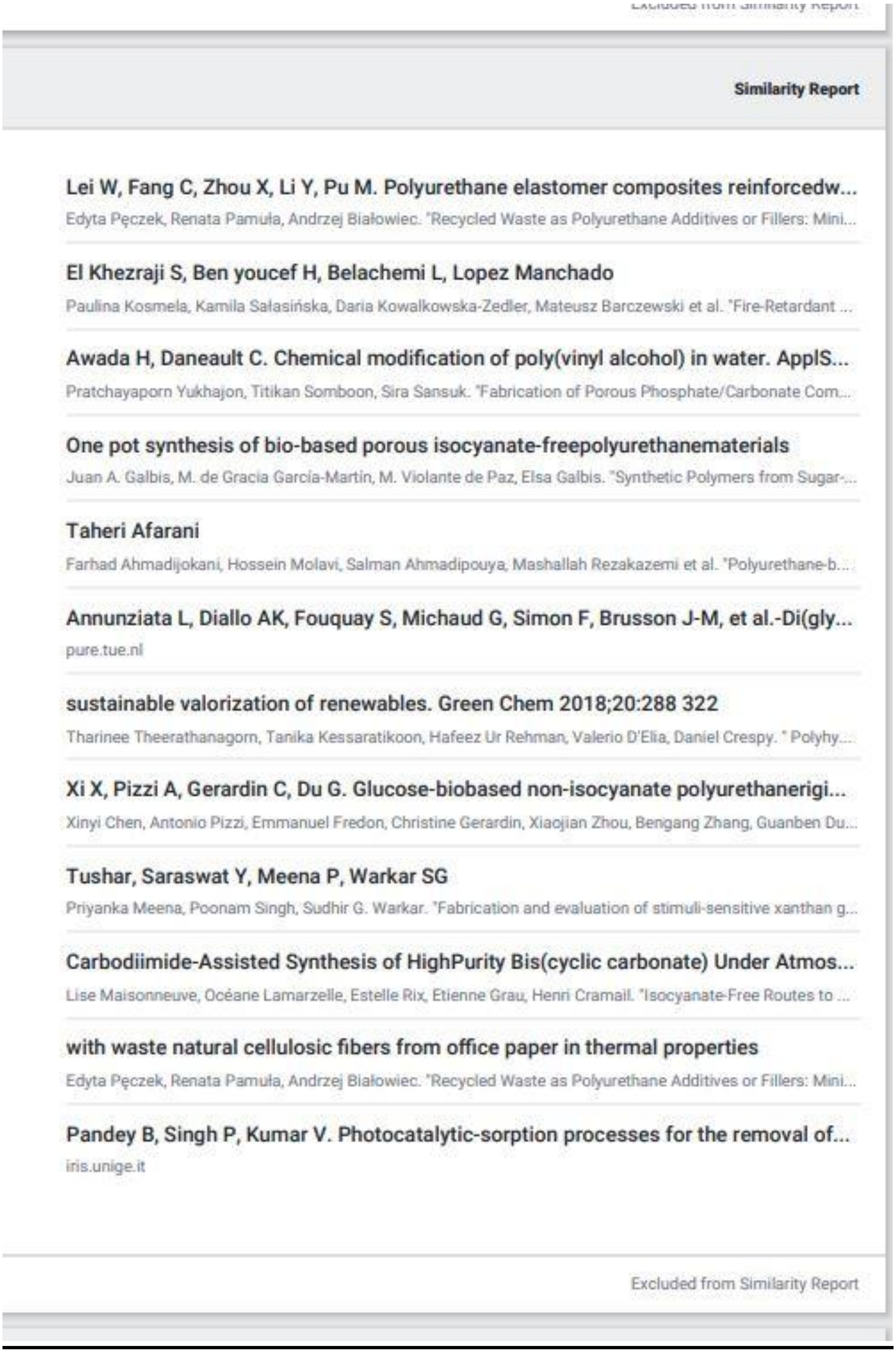
Ecochard Y, Caillol S. Hybrid polyhydroxyurethanes: How to overcome limitationsa...
hal.science

isocyanate polyurethanes synthesized fromcyclic carbonate intermediates and di- ...
trepo.tuni.fi

Wang C, Zheng Y, Qiao K, Xie Y, Zhou X. An environmentally friendly preparationan...
Fah, Mok Chun. "Poly(Vinyl Alcohol)/α-Chitin/Nanocellulose Composites Developed from Oil Palm Empty Fr...

Gandara M, Mulinari DR, Monticeli FM, Capri MR
Beatriz P. de Oliveira, Lorena C. S. Balieiro, Lana S. Maia, Noelle C. Zanini et al. "Eco-friendly polyurethane fo...

Excluded from Similarity Report



Excluded from Similarity Report

Similarity Report

Lei W, Fang C, Zhou X, Li Y, Pu M. Polyurethane elastomer composites reinforcedw...
Edyta Pęczek, Renata Pamuła, Andrzej Białowiec. "Recycled Waste as Polyurethane Additives or Fillers: Mini...

El Khezraji S, Ben youcef H, Belachemi L, Lopez Manchado
Paulina Kosmela, Kamila Sałasińska, Daria Kowalkowska-Zedler, Mateusz Barczewski et al. "Fire-Retardant ...

Awada H, Daneault C. Chemical modification of poly(vinyl alcohol) in water. ApplS...
Pratchayaporn Yukhajon, Titikan Somboon, Sira Sansuk. "Fabrication of Porous Phosphate/Carbonate Com...

One pot synthesis of bio-based porous isocyanate-freepolyurethanematerials
Juan A. Galbis, M. de Gracia García-Martín, M. Violante de Paz, Elsa Galbis. "Synthetic Polymers from Sugar-...

Taheri Afarani
Farhad Ahmadijokani, Hossein Molavi, Salman Ahmadipouya, Mashallah Rezakazemi et al. "Polyurethane-b...

Annunziata L, Diallo AK, Fouquay S, Michaud G, Simon F, Brusson J-M, et al.-Di(gly...
pure.tue.nl

sustainable valorization of renewables. Green Chem 2018;20:288 322
Tharinee Theerathanagorn, Tanika Kessaratikoon, Hafeez Ur Rehman, Valerio D'Elia, Daniel Crespy. " Polyhy...

Xi X, Pizzi A, Gerardin C, Du G. Glucose-biobased non-isocyanate polyurethanerigi...
Xinyi Chen, Antonio Pizzi, Emmanuel Fredon, Christine Gerardin, Xiaojian Zhou, Bengang Zhang, Guanben Du...

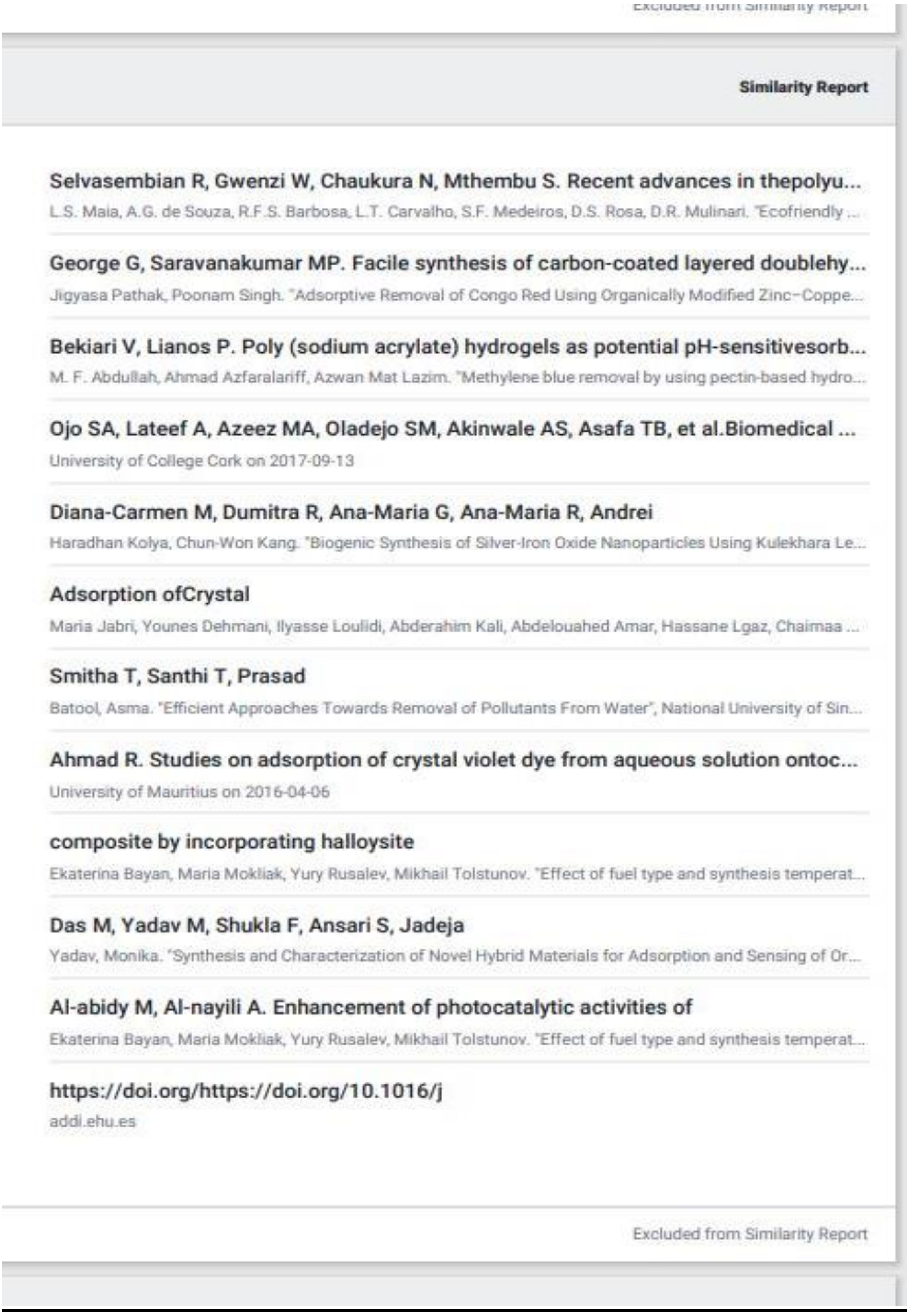
Tushar, Saraswat Y, Meena P, Warkar SG
Priyanka Meena, Poonam Singh, Sudhir G. Warkar. "Fabrication and evaluation of stimuli-sensitive xanthan g...

Carbodiimide-Assisted Synthesis of HighPurity Bis(cyclic carbonate) Under Atmos...
Lise Maisonneuve, Océane Lamarzelle, Estelle Rix, Etienne Grau, Henri Cramail. "Isocyanate-Free Routes to ...

with waste natural cellulosic fibers from office paper in thermal properties
Edyta Pęczek, Renata Pamuła, Andrzej Białowiec. "Recycled Waste as Polyurethane Additives or Fillers: Mini...

Pandey B, Singh P, Kumar V. Photocatalytic-sorption processes for the removal of...
iris.unige.it

Excluded from Similarity Report



Excluded from Similarity Report

Similarity Report

Selvasembian R, Gwenzi W, Chaukura N, Mthembu S. Recent advances in thepolyu...
L.S. Maia, A.G. de Souza, R.F.S. Barbosa, L.T. Carvalho, S.F. Medeiros, D.S. Rosa, D.R. Mulinari. "Ecofriendly ...

George G, Saravanakumar MP. Facile synthesis of carbon-coated layered doublehy...
Jigyasa Pathak, Poonam Singh. "Adsorptive Removal of Congo Red Using Organically Modified Zinc–Coppe...

Bekiari V, Lianos P. Poly (sodium acrylate) hydrogels as potential pH-sensitivesorb...
M. F. Abdullah, Ahmad Azfaralariff, Azwan Mat Lazim. "Methylene blue removal by using pectin-based hydro...

Ojo SA, Lateef A, Azeez MA, Oladejo SM, Akinwale AS, Asafa TB, et al.Biomedical ...
University of College Cork on 2017-09-13

Diana-Carmen M, Dumitra R, Ana-Maria G, Ana-Maria R, Andrei
Haradhan Kolya, Chun-Won Kang. "Biogenic Synthesis of Silver-Iron Oxide Nanoparticles Using Kulekhara Le...

Adsorption ofCrystal
Maria Jabri, Younes Dehmani, Ilyasse Loulidi, Abderahim Kali, Abdelouahed Amar, Hassane Lgaz, Chaimaa ...

Smitha T, Santhi T, Prasad
Batool, Asma. "Efficient Approaches Towards Removal of Pollutants From Water", National University of Sin...

Ahmad R. Studies on adsorption of crystal violet dye from aqueous solution ontoc...
University of Mauritius on 2016-04-06

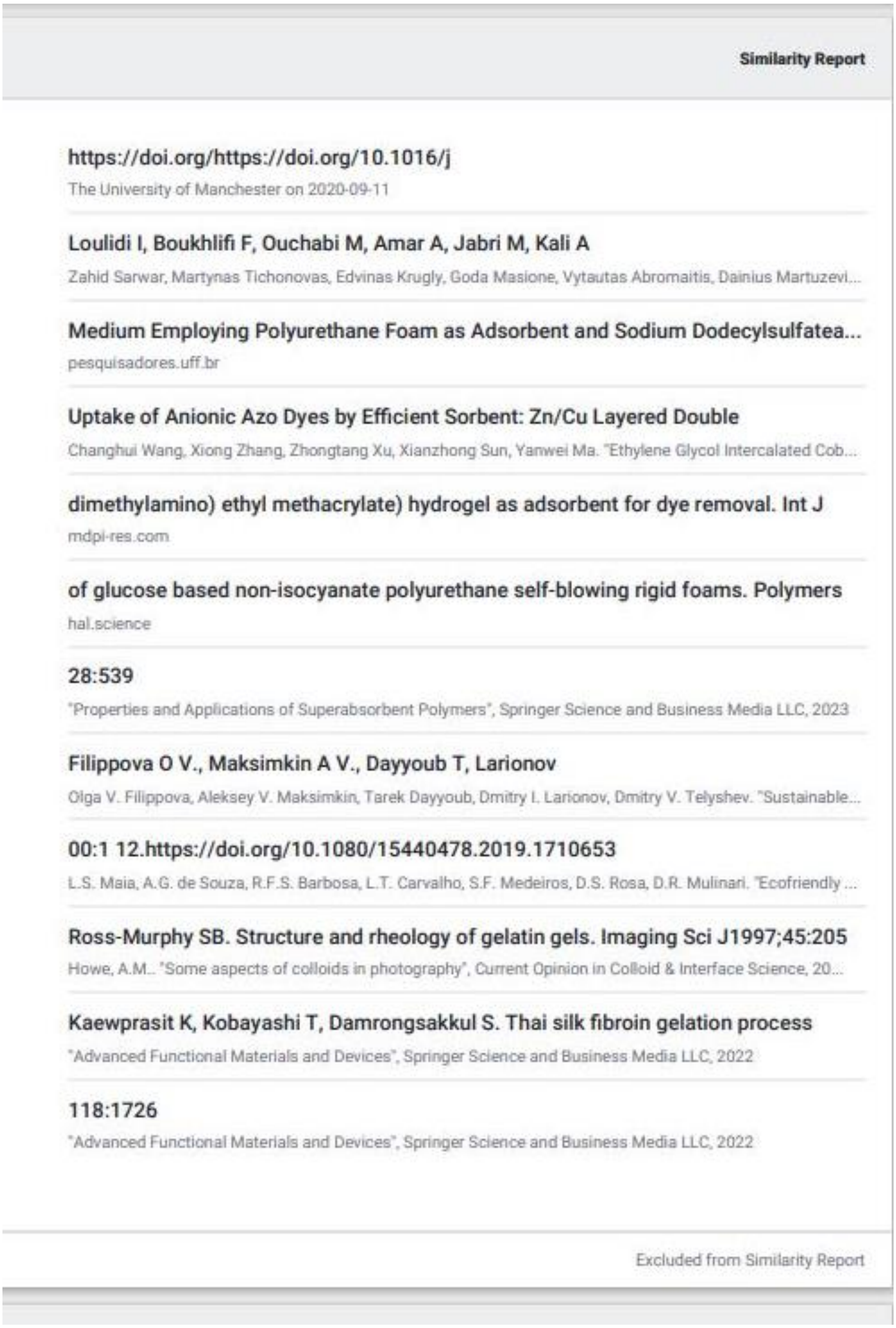
composite by incorporating halloysite
Ekaterina Bayan, Maria Mokliak, Yury Rusalev, Mikhail Tolstunov. "Effect of fuel type and synthesis temperat...

Das M, Yadav M, Shukla F, Ansari S, Jadeja
Yadav, Monika. "Synthesis and Characterization of Novel Hybrid Materials for Adsorption and Sensing of Or...

Al-abidy M, Al-nayili A. Enhancement of photocatalytic activities of
Ekaterina Bayan, Maria Mokliak, Yury Rusalev, Mikhail Tolstunov. "Effect of fuel type and synthesis temperat...

https://doi.org/https://doi.org/10.1016/j
addi.ehu.es

Excluded from Similarity Report



Similarity Report

https://doi.org/https://doi.org/10.1016/j

The University of Manchester on 2020-09-11

Loulidi I, Boukhlifi F, Ouchabi M, Amar A, Jabri M, Kali A

Zahid Sarwar, Martynas Tichonovas, Edvinas Krugly, Goda Masione, Vytautas Abromaitis, Dainius Martuzevi...

Medium Employing Polyurethane Foam as Adsorbent and Sodium Dodecylsulfatea...

pesquisadores.uff.br

Uptake of Anionic Azo Dyes by Efficient Sorbent: Zn/Cu Layered Double

Changhui Wang, Xiong Zhang, Zhongtang Xu, Xianzhong Sun, Yanwei Ma. "Ethylene Glycol Intercalated Cob...

dimethylamino) ethyl methacrylate) hydrogel as adsorbent for dye removal. Int J

mdpi-res.com

of glucose based non-isocyanate polyurethane self-blowing rigid foams. Polymers

hal.science

28:539

"Properties and Applications of Superabsorbent Polymers", Springer Science and Business Media LLC, 2023

Filippova O V., Maksimkin A V., Dayyoub T, Larionov

Olga V. Filippova, Aleksey V. Maksimkin, Tarek Dayyoub, Dmitry I. Larionov, Dmitry V. Telyshev. "Sustainable...

00:1 12.https://doi.org/10.1080/15440478.2019.1710653

L.S. Maia, A.G. de Souza, R.F.S. Barbosa, L.T. Carvalho, S.F. Medeiros, D.S. Rosa, D.R. Mulinari. "Ecofriendly ...

Ross-Murphy SB. Structure and rheology of gelatin gels. Imaging Sci J1997;45:205

Howe, A.M.. "Some aspects of colloids in photography", Current Opinion in Colloid & Interface Science, 20...

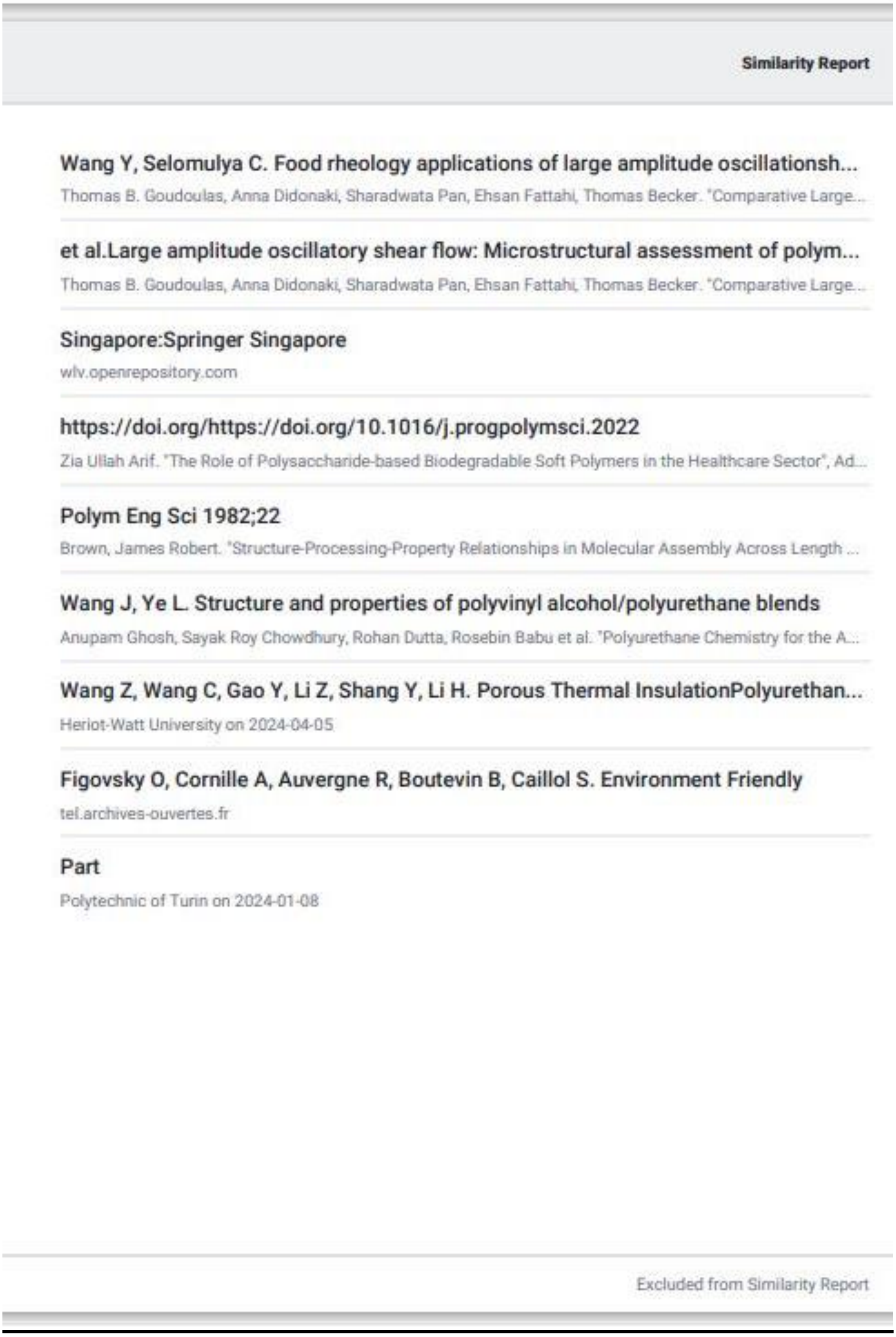
Kaewprasit K, Kobayashi T, Damrongsakkul S. Thai silk fibroin gelation process

"Advanced Functional Materials and Devices", Springer Science and Business Media LLC, 2022

118:1726

"Advanced Functional Materials and Devices", Springer Science and Business Media LLC, 2022

Excluded from Similarity Report



Similarity Report

Wang Y, Selomulya C. Food rheology applications of large amplitude oscillationsh...

Thomas B. Goudoulas, Anna Didonaki, Sharadwata Pan, Ehsan Fattahi, Thomas Becker. "Comparative Large...

et al.Large amplitude oscillatory shear flow: Microstructural assessment of polym...

Thomas B. Goudoulas, Anna Didonaki, Sharadwata Pan, Ehsan Fattahi, Thomas Becker. "Comparative Large...

Singapore:Springer Singapore

wlv.openrepository.com

https://doi.org/https://doi.org/10.1016/j.progpolymsci.2022

Zia Ullah Arif. "The Role of Polysaccharide-based Biodegradable Soft Polymers in the Healthcare Sector", Ad...

Polym Eng Sci 1982;22

Brown, James Robert. "Structure-Processing-Property Relationships in Molecular Assembly Across Length ...

Wang J, Ye L. Structure and properties of polyvinyl alcohol/polyurethane blends

Anupam Ghosh, Sayak Roy Chowdhury, Rohan Dutta, Rosebin Babu et al. "Polyurethane Chemistry for the A...

Wang Z, Wang C, Gao Y, Li Z, Shang Y, Li H. Porous Thermal InsulationPolyurethan...

Heriot-Watt University on 2024-04-05

Figovsky O, Cornille A, Auvergne R, Boutevin B, Caillol S. Environment Friendly

tel.archives-ouvertes.fr

Part

Polytechnic of Turin on 2024-01-08

Excluded from Similarity Report

Curriculum Vitae

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https://scholar.google.com/citations?user=Rlho1owAAAAJ&hl=en

Citations 118

AREAS OF INTEREST

Non-isocyanate Polyurethane Materials, Foams, Blends, Hydrogels, Drug delivery, Dye Removal, Hydrogel Nanocomposite and pH-sensitive films

EDUCATION

- Ph.D. Chemistry, Thesis Title: “Synthesis and Characterisation of polyurethane derived from renewable sources”, Delhi Technological University, Delhi, (2019 - 2024)
- M.Sc Chemistry, Sharda University, 2018 (91.05%)
- B.Sc. (Hons) Chemistry, Shyam Lal College, Delhi University, 2016 (75.07%)

Internship

- Common Effluent Treatment Plant, Mayapuri, New Delhi (2018)
- Conducted assessments such as i) Jar Test, ii) pH test, iii) TSS test, iv) TDS test, v) COD test, vi) BOD test.
- Gained practical insights into water quality assessment and environmental chemistry

Experience

- Having experience as a teaching assistant for B.Tech. Chemistry laboratories (2019-Present).
- Worked part-time as a research intern at Chem Cred Consultancy Services, synthesis of green and Bio-Based Surface and Faucet Cleaners with excellent cleaning properties (2022).

- Worked as a Tutor at Chegg India and Course Hero, Tutored students by resolving diverse academic queries posted by users. Delivered accurate and concise solutions to questions spanning various subjects and topics, ensuring clarity and comprehension for students seeking assistance (2020).

Hands-on practice and Analysis expertise:

- NMR, FTIR and XRD interpretation
- SEM and TEM analysis
- TGA (Perkin Elmer and Netzsch)
- DSC (Perkin Elmer and Netzsch)
- Zeta potential (Malvern Zetasizer Nano)
- Modular compact Rheometer 302 (MCR, Anton Paar)
- Fluorescence Microscopy (Motic Microscopes)
- Carry 300 Bio Spectrophotometer (Agilent Technologies and Shimadzu UV-2540)
- FTIR (Perkin Elmer and Agilent Technologies 600 series)
- Refractometer
- Conducting Anti-Microbial Studies