ROYAUME DU MAROC

MARRAKECH
جامعة القاضي عياض
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كليـــــة العلوم
السملالية - مراكش
FACULTÉ DES SCIENCES
SEMLALIA - MARRAKECH

UIMP
Universidad Internacional
Menéndez Pelayo

THÈSE

présentée à la Faculté pour obtenir le grade de :

Docteur

CED: Sciences et Techniques:

Spécialité: Chimie et developpement

Synthesis of environmentally friendly and non-toxic polyurethane foams and composites

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(Dernier diplôme: Master sciences et techniques)

soutenue le: devant la commission d'examen:

Preface:

The research presented in this manuscript is situated in the doctoral school of chemistry and development of Cadi Ayyad University (UCA), Instituto de Ciencia y Tecnología de Polímeros- Consejo Superior de Investigaciones Científicas (ICTP- CSIC) and University international Menendez Pelayo (UIMP). The experimental work was carried out principally at the Innovative Materials, Energy, and Development Laboratory (IMED-Lab) at the Faculty of Sciences and Techniques of Marrakech (FSTG), Cadi Ayyad University (UCA) and the Departamento de Nanomaterials Poliméricos y Biomaterials in the Instituto de Ciencia y Tecnología de Polímeros from January 2018 to January 2023.

The present research work was conducted under the supervision of Prof. Mohammed Lahcini and Prof. Belhacheni Larbi, Full Professors at the Faculty of Science and Techniques (FSTG), Cadi Ayyad University (UCA) and Dr. Raquel Verdejo and Prof. Miguel Angel Lopez Manchado, Research Scientist and Full Professor, at the Instituto de Ciencia y Tecnología de Polímeros, Consejo Superior de Investigaciones Científicas (CSIC).

The experimental results presented in this thesis were obtained from experiments achieved at different research platforms:

IMED-Lab: Innovative Materials, Energy and Development Laboratory, Cadi Ayyad University (UCA), Marrakech, Morocco.

CAC: Center of Analysis and Characterization, Cadi Ayyad University (UCA), Marrakech, Morocco.

PCG: Polymer Composite Group, Instituto de Ciencia y Tecnología de Polímeros, Consejo Superior de Investigaciones Científicas (CSIC).

Acknowledgments

Before I express my thanks and gratitude to my professors, family, and friends. I want to thank God, the Almighty, for who I am today and for His blessings throughout my life.

I would like to show my profound gratitude to Mohammed Lahcini, professor at UCA University, and Raquel Verdejo at UIMP and CSIC, who served as my research supervisors, for providing me with the opportunity to do research in their laboratories and for their helpful advice during this process. I was greatly inspired by their dynamism, vision, genuineness, and motivation. They provided me with the methods I needed to conduct the study and effectively convey my findings. Working with and learning from them was a great honor and privilege. I thank them for their time and daily advice and support during these years of my thesis. It was not easy to go through this delicate period, especially the pandemic that impacted us physically and mentally. Your calls and messages have been of significant impact. Thank you again, and I hope to live up to your expectations and trust.

I would also like to thank Miguel Angel Lopez Manchado, professor at CSIC, and Larbi Belhachemi, professor at UCA university, for their time and advice in writing good scientific papers. Working with you was a great honor for me, and I will always be grateful and proud to be a member of your team.

Special thanks to Dr. Suman Thakur for his support since my first day at ICTP-CSIC Madrid. Although we arrived in the same month, your moral and academic support has helped me achieve my goals during my thesis. Thank you for being a great colleague, a scientist who does not hesitate to share your knowledge and scientific ideas with me, and finally, for being a supportive and helpful friend.

Thank you, members of my polymer composite group. You were always present. Thank you, Javier Carretero, for your help and support in the part of bi-cyclic carbonate synthesis. Working with you was a great opportunity. Our exchanges of everything and nothing were always interesting. Thank you, Marianella for your excellent manners and your positivity. Thank you, Mario, Javier, Saul, Ornella, Nedia, Juan Carlos and all the other members of the group.

I would also like to thank the members of my laboratory (IMED Lab) at Caddi Ayad University Marrakech. I would like to thank Professor Rachid Raihane for his daily presence in the laboratory and for the common interest. I would also like to thank my friends and colleagues, Manal, Yassine, Taha, Jamal, Sara, Wafae, Jihad, Abdelghni, Asmae, Mustapha, and Hassan. Thank you all for supporting me in laboratory work, performing reactions, and for our moments of laughter. I would like to extend a special thanks to my close friends at ICTP. I know that what I am going to say will never be enough to show love and affection toward you. Without you, my four years would not have been easy to spend.

Amparo, my bestie, you were always there for me in difficult moments and whenever I needed a product, a method of characterization, or, more importantly, some advice. I will always think of our group trips, laughs, and coffee breaks to discuss everything and anything. Madrid has given me a close friend, even a second mother. The memories of Marrakech and Benidorm will permanently be engraved in my memory. Thank you for your support and for being my friend.

My dear **Moniquiti**, a spontaneous and lovely person, you were my support and my partner in padel. The memories of Marrakech and Benidorm will permanently be engraved in my memory. Thank you for your support and for being my friend.

Alberto, the big boss, the great madriléne cayetano, I thank you for all your support and help in the lab. I am delighted to have been with you during this period, and I will always be grateful for the warm welcome you have shown me since my first day at ICTP.

Sergio, mi amigo, my Spanish teacher, and my friend, thank you for your help in the lab. You were always a good person and a great support in helping me with many complex tasks. You are a lovely person, and I will never forget you.

Manal, you have the relay to optimize and innovate new methods for preparing NIPU. I thank you for your support, your help, and your support during my thesis. I was pleased to work with you in the lab and am proud to have you as a friend.

I would like to express my sincere gratitude to my boss and my brother, **Tommy**, for providing me with the opportunity to pursue my auto-financing PhD while working for his company. His unwavering trust in my abilities and his willingness to offer me a partial and freelance job has been instrumental in my success. Tommy is an outstanding leader and an excellent communicator. Working with him has been a pleasure, and I have learned a lot from his guidance and mentorship. I appreciate his unwavering support and encouragement throughout my academic journey, and I look forward to continuing to contribute to the growth of his business

I would like to thank my parents and my sister. You are great people, and I am happy to have you in my life. I won’t hide from you that I will always be grateful for your moral and financial help, and I will make all my efforts to make you proud of me. Thank you **Mamalika**, my wonderful mother, I want to take this opportunity to express my deepest gratitude and love for everything you have done for me. You have been the most incredible woman in my life, and I am eternally grateful for your unwavering presence and support. Your constant closeness and unwavering belief in me have been instrumental in my journey towards success. I firmly believe that your prayers and blessings have played a significant role in my achievements. I am overjoyed to have transformed your dreams into reality, and I promise to make every effort to continue making you proud. Your love, guidance, and unwavering faith in me have shaped me into the person I am today. Thank you for being the best mother anyone could ask for

My dad **Abdessamad**, I wanted to take a moment to express my deepest gratitude and appreciation for everything you have done for me. You have been an incredible source of support both financially and mentally, and I am truly grateful for your unwavering belief in me. The memories we have shared, particularly our joyful moments and lively discussions in front of the football matches, hold a special place in my heart. Your presence in my life has been a constant reminder of love, strength, and guidance. Thank you for being my rock, my confidant, and my biggest supporter. I am truly blessed to have you as my father.

I would like to express my heartfelt gratitude to my younger sister, **Oumaimati**, for her unwavering support both mentally and financially. Throughout my journey, she has been my rock, offering me invaluable guidance and encouragement when I needed it the most. Her selflessness and belief in my abilities have been instrumental in my success. I am truly fortunate to have such an incredible sister who has always stood by my side. Thank you, Oumaima, for your unconditional love and support; I am forever grateful.

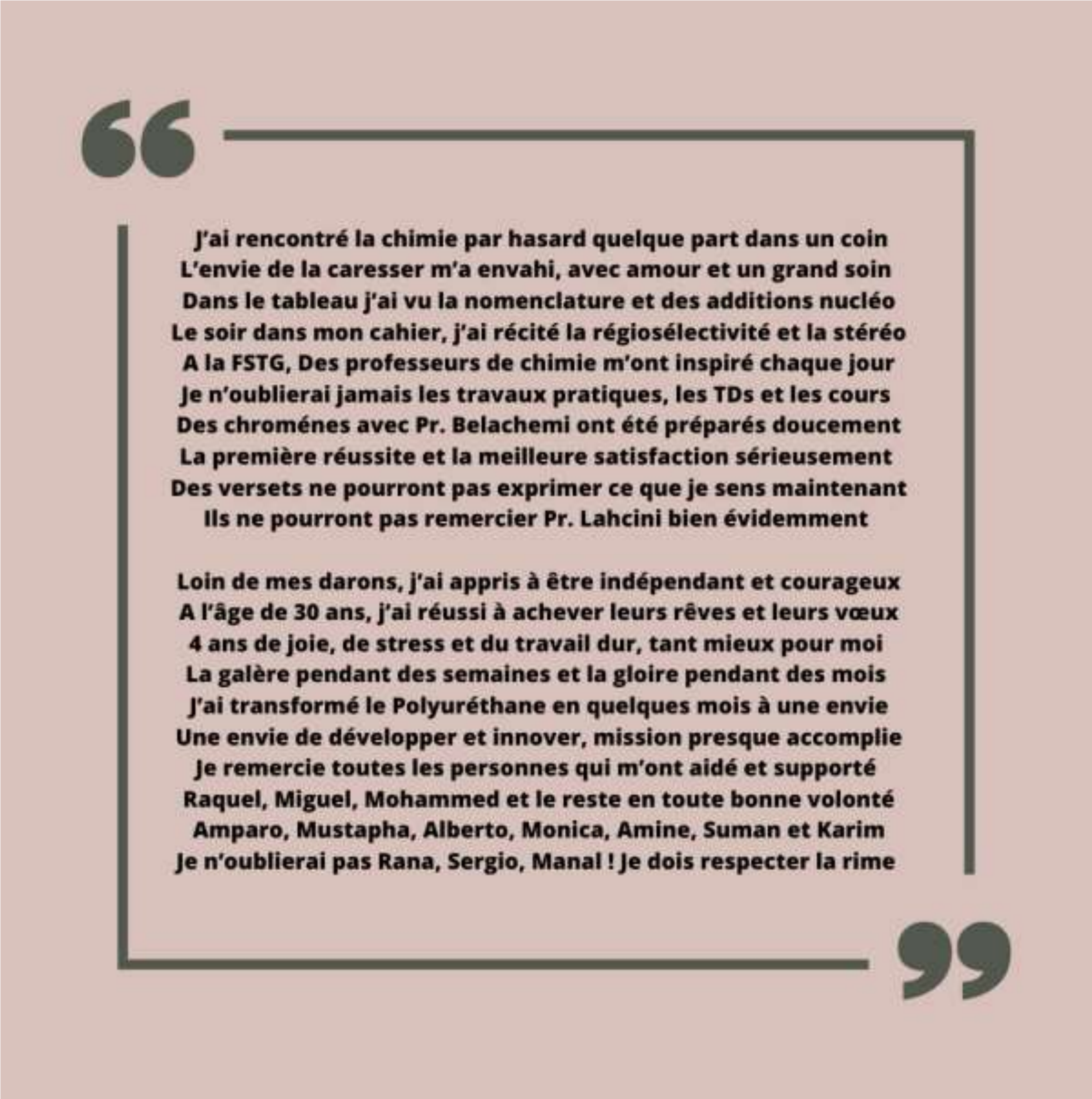
I will not forget to thank my fiancée **Rana** for her unconditional support during my thesis years. You were, for me, the motivation to reach my goals and the one who made me want to acquire new things and expand my ambitions. I can't thank you in a few lines, but we will have our whole life to celebrate our successes and love. At your side, I am the happiest and the most ambitious. “ I understand you, you understand me, we understand each other “

Thank you, my dear **Mustapha,** for our moments of joy for the pizzas and my mom’s cakes, as well as your optimism and your will that was always an inspiration. You are my brother and my friend of two decades. I am proud to call you my friend and to see your growth and development.

Karim, my close friend and confidant, we are long-time friends. Although distance has separated us for a few years, our friendship has renewed and matured. Thank you also for allowing me to know our big boss **Mouad**. You are both an example of good friends and good people.

I would also like to express my heartfelt thanks to my dear friend **Hamza**, who has been an integral part of my life for almost a decade. Hamza, your friendship has been a constant source of joy, laughter, and comfort to me. Our discussions, debates, and shared experiences have helped me to grow both personally and academically. You have always been there for me, offering your support and encouragement in every step of my journey. Your presence in my life is more than just a friendship - it's a bond of brotherhood that I treasure deeply.

I would like to express my heartfelt gratitude to my dear friends **Chaimae and Amine**, who have been an integral part of my life. Our shared political beliefs and discussions have initiated our friendship, but it is our principles and personalities that have deepened it over time. Chaimae and Amine, you both have always welcomed me with open arms whenever I visited Paris, inviting me to your home and making me feel like a part of your family. Our conversations and debates have been thought-provoking, enlightening, and enjoyable. Your friendship has been a constant source of support and encouragement to me. Chaimae and Amine, I truly cherish our friendship, and I hope to continue to grow and strengthen our bond for many years to come. Thanks to my friends Ghita, Younes, Youssef, and Marouane, you were always present to talk, discuss, and exchange. I have never hesitated to speak with you if I need your help, and I will always be at your disposal.



J'ai rencontré la chimie par hasard quelque part dans un coin
L'envie de la caresser m'a envahi, avec amour et un grand soin
Dans le tableau j'ai vu la nomenclature et des additions nucléo
Le soir dans mon cahier, j'ai récité la régiosélectivité et la stéréo
A la FSTG, Des professeurs de chimie m'ont inspiré chaque jour
Je n'oublierai jamais les travaux pratiques, les TDs et les cours
Des chroménes avec Pr. Belachemi ont été préparés doucement
La première réussite et la meilleure satisfaction sérieusement
Des versets ne pourront pas exprimer ce que je sens maintenant
Ils ne pourront pas remercier Pr. Lahcini bien évidemment

Loin de mes darons, j'ai appris à être indépendant et courageux
A l'âge de 30 ans, j'ai réussi à achever leurs rêves et leurs vœux
4 ans de joie, de stress et du travail dur, tant mieux pour moi
La galère pendant des semaines et la gloire pendant des mois
J'ai transformé le Polyuréthane en quelques mois à une envie
Une envie de développer et innover, mission presque accomplie
Je remercie toutes les personnes qui m'ont aidé et supporté
Raquel, Miguel, Mohammed et le reste en toute bonne volonté
Amparo, Mustapha, Alberto, Monica, Amine, Suman et Karim
Je n'oublierai pas Rana, Sergio, Manal ! Je dois respecter la rime

“On conquiert à force de persévérance.”

De George Matheson

"Success is not final, failure is not fatal: it is the courage to continue that counts."

Winston Churchil

"La familia es un puerto seguro en un mar tormentoso."

Incognito

Summary

Polyurethane is an extremely versatile polymer. It is widely used in many industries, including construction, automotive, textiles, and aerospace, to name a few. It is a polymer produced by the reaction between a polyol and a poly(isocyanate). The resulting material has a number of desirable properties, including durability, strength, and resistance to wear. However, the synthesis of polyurethane is fraught with problems, including the toxicity of some of the raw materials used. Isocyanates, in particular, are highly toxic and can cause severe respiratory problems, skin irritation and other health problems. In addition, the traditional method of producing isocyanates involves the use of phosgene, a highly toxic gas. To address these issues, researchers are exploring alternative methods of producing polyurethane that do not involve toxic materials.

In this thesis, the goal was to reduce the toxicity of polyurethane foam and to prepare isocyanate-free polyurethane foams and composites using less toxic commercial products and bio-based reactants. To achieve this, the classic tin octoate catalyst was replaced with the less toxic Bismuth Triflate catalyst. Additionally, two types of foams were prepared: the polyhydroxy thioether foam and the isocyanate-free polyurethane foam. The first foam was obtained using cyclic carbonate produced from the reaction of commercial epoxy with CO_2 at atmospheric pressure and tri- and tetra-thiolated monomers, which were responsible for the polymerization and release of CO_2. The second foam, the isocyanate-free polyurethane foam, was prepared in a similar manner, but with the addition of diamines for the aminolysis reaction responsible for the formation of the hydroxyurethane band. These two foams represent alternatives to conventional polyurethane foams made from toxic isocyanates and can be applied in various fields due to their unique properties.

Résumé

Le polyuréthane est un polymère polyvalent utilisé dans divers domaines tels que la construction, l'automobile, le textile, l'aéronautique et d'autres domaines. La production de ce polymère sous toutes ses formes atteint des millions de tonnes chaque année. Cependant, la synthèse et la préparation de ce polymère présentent divers problèmes, principalement dus à la toxicité des matières premières utilisées pour sa préparation. En effet, l'élément principal de cette synthèse, l'isocyanate, est produit à partir du phosgène, une substance très toxique, et le catalyseur métallique classique utilisé, le tin octoate, est également soupçonné d'être cytotoxique.

Le principal objectif de cette thèse est de préparer des mousses de polyuréthane ainsi que leurs composites en utilisant des protocoles moins toxiques et des précurseurs biosourcés sans isocyanates. Pour cela, le catalyseur toxique Tin Octoate a été remplacé par un catalyseur moins toxique voire non-toxique, le Bismuth Triflate, afin de réduire la toxicité de la mousse de polyuréthane. L'objectif n'était pas seulement de réduire la toxicité, mais aussi de préparer des mousses et des composites de polyuréthane sans isocyanate en utilisant des produits commerciaux moins toxiques et des précurseurs biosourcés tels que l'alcool vanillique.

Deux types de mousses ont été préparés au cours de cette thèse : la mousse de polyhydroxythioéther et la mousse de polyuréthane sans isocyanate. La première a été élaborée en utilisant des carbonates cycliques préparés à partir d'un époxyde commercial par condensation avec du CO2 à pression atmosphérique et des monomères tri- et tétrathiolés. Ces monomères sont responsables de la polymérisation et du dégagement de CO2, ce qui provoque la formation de la mousse. Quant à la deuxième mousse, la mousse de polyuréthane sans isocyanate, elle a été préparée en suivant le même protocole, mais en ajoutant des diamines pour la réaction d'aminolyse, qui crée la liaison hydroxyuréthane. Ces mousses visent à remplacer les mousses de polyuréthane préparées avec des isocyanates toxiques.

Resumen

El poliuretano es un polímero versátil que se utiliza en diversos campos, como la construcción, la automoción, el textil y la aeronáutica, entre otros. La producción de este polímero en todos estos campos asciende a millones de toneladas cada año debido a la excesiva demanda. Sin embargo, hay varios problemas asociados a la síntesis y preparación de este polímero, que son la toxicidad de las materias primas, por ejemplo, el isocianato que se produce con la ayuda del notoriamente tóxico fosgeno y el catalizador metálico clásico utilizado, que es el octoato de estaño. En las dos últimas décadas, los grupos de investigación han empezado a desarrollar nuevos protocolos y formulaciones para minimizar el riesgo y la toxicidad de los polímeros más utilizados, y las principales agencias sanitarias, como REACH, han publicado decenas de informes sobre la toxicidad aguda de los isocianatos y otras materias primas.

El objetivo de esta tesis doctoral era preparar espumas de poliuretano así como de compuestos poliméricos basados en PU no tóxicos y respetuosos con el medioambiente. Para ello, se sustituyó el clásico catalizador de octoato de estaño por el catalizador de triflato de bismuto, menos tóxico. Además, se prepararon dos tipos de espumas: la espuma de polihidroxitioéter y la espuma de poliuretano sin isocianato. La primera espuma se obtuvo utilizando carbonato cíclico producido a partir de la reacción de epoxi comercial con CO_2 a presión atmosférica y monómeros tri- y tetra-tiolados, responsables de la polimerización y liberación de CO_2. La segunda espuma, la espuma de poliuretano sin isocianato, se preparó de forma similar, pero con la adición de diaminas para la reacción de aminólisis responsable de la formación de la banda de hidroxiuretano. Estas dos espumas representan alternativas a las espumas de poliuretano convencionales fabricadas con isocianatos tóxicos y pueden aplicarse en diversos campos gracias a sus propiedades únicas.

ملخص

البولي يوريثين هو بوليمر متعدد الاستخدامات يستخدم في مجالات مختلفة مثل البناء والسيارات والمنسوجات والطيران وغيرها من المجالات. يبلغ إنتاج هذا البوليمر في كل هذه الدعائم ملايين الأطنان كل عام بسبب الطلب المفرط. ومع ذلك ، هناك العديد من المشاكل المرتبطة بتركيب وتحضير هذا البوليمر ، وهي سمية المواد الخام على سبيل المثال الأيزوسيانات الذي يتم إنتاجه باستخدام الفوسجين السام الشهير وكذلك المحفز المعدني الكلاسيكي المستخدم وهو أكسيد القصدير.

على مدار العقدين الماضيين ، بدأت مجموعات البحث في تطوير بروتوكولات وتركيبات جديدة لتقليل مخاطر وسمية البوليمرات المستخدمة على نطاق واسع ، وقد نشرت المنظمات الصحية الكبرى مثل REACH عشرات التقارير عن السمية الحادة للأيزوسيانات وغيرها من المواد الخام.

استندت هذه الأطروحة إلى تحضير رغاوي البولي يوريثان والمركبات القائمة على البولي يوريثين باستخدام بروتوكولات أقل سمية وأحيانًا ذات مصادر حيوية تم تطويرها للحصول على مواد خالية من الأيزوسيانات ومصدر حيوي جاهزة للاستخدام في جميع المناطق نظرًا للخصائص التي تم الحصول عليها في جميع المجالات.هذه الدراسات.

أولاً ، تم تقليل سمية رغوة البولي يوريثان عن طريق تغيير المحفز السام والكلاسيكي Tin Octoate باستخدام الحفاز Bismuth Triflate الأقل سمية أو حتى غير السام. لم يكن الهدف ذلك لأن الهدف هو أن تكون قادرًا على تحضير رغاوي البولي يوريثان والمواد المركبة بدون أيزوسيانات باستخدام طرق تعتمد على منتجات تجارية أقل سمية ومنتجات بيولوجية أخرى مثل كحول الفانيلي.

تتكون الرغوات المحضرة في هذه الرسالة من نوعين ، رغوة البولي هيدروكسي إيثيثر ورغوة البولي يوريثان الخالية من الأيزوسيانات ، الأول يتم تصنيعه باستخدام كربونات حلقية محضرة مسبقًا باستخدام إيبوكسي تجاري في وجود ثاني أكسيد الكربون تحت ضغط جوي ومونومرات ثلاثية ورباعية المونومرات المسؤولة عن البلمرة وإطلاق ثاني أكسيد الكربون المسؤول عن الحصول على الرغوة. من ناحية أخرى ، الرغوة الثانية عبارة عن رغوة بولي يوريثان خالية من الأيزوسيانات والتي يتم تحضيرها بنفس الطريقة تقريبًا باستثناء إضافة ثنائي أمين لتفاعل انحلال الأمين المسؤول عن إنشاء شريط هيدروكسي يوريثين. تهدف هذه الرغوات إلى لعب دور رغاوي البولي يوريثان التي يتم تحضيرها باستخدام أيزوسيانات

List of Abbreviations

PU: Polyurethane

PUF: Polyurethane foam

NIPU: Non-isocyanate Polyurethane

NIPUF: Nonisocyanate Polyurethane foams

PHU: Poly(hydroxyurethane)

PHUF: Poly(hydroxyurethane) foams

CC: Cyclic carbonate

CO_2: Carbone dioxide

PHMS: Poly(methylhydrogensiloxane)

TBAB: Tetrabutylammonium

BBC: Butanediol Bis Carbonate

RBC: Resocrinol Bis Carbonate

TMPTC: Trimethylpropane tris Carbonate

STC: Sorbitol Tricarbonate

SEC: Sorbitol ether carbonate

DMC: Dimetyhl Carbonatre

DBU: 1,8-Diazabicyclo(5.4.0)undec-7-ene

DMSO: Dimethyl sulfoxide

TMPGC: Carbonated Trimethylpropane glycidyl ether

EOTMPGC: Ethoxylated Carbonated Trimethylpropane glycidyl ether

MH15: Polymethylhydrogensiloxane

RDGCC: Cyclic carbonated of Resorcinol Diglycidyl ether

AOPHA: Amine-terminated oligomeric phenyl hydroxyamine

PHTE: Poly(Hydroxythioether)

NDA: 1,9-nonanediamine

TDA: 1,13- Tridecanediamine

HMDA: 1,6-Hexanediamime

h-BN: Hexagonal Boron nitride

f-BN: Fucntionnalized Boron nitride

SAMCE: Sugar-assisted Mechanochemical exfoliation

DBU: 1,8-Diazabicyclo(5.4.0)undec-7-ene

THF: Tetrahydrofuran

E’: Storage modulus

E’’: Loss modulus

SnOct$_2$: Stannous octoate

Bi(OTf)$_3$: Bismuth Triflate

PMDETA: N″,N″-Pentamethyldiethylenetriamine

SEM: Scanning Electron microscopy

TGA: Thermogravimetric analysis

DSC: Differential scanning calorimetry

NMR: Nuclear magnetic resonance

ATR: Attenuated total reflectance

FTIR: Fourier transform infrared

DMA: Dynamic mechanical analysis

DTG: Derivative Thermogravimetry

Tg: Glass transition temperature

CMR: Carcinogenic, mutagenic and reprotoxic

AlCl3: Aluminium chloride

BF3: Boron trifluoride

DBTL: Dibutyltin dilaurate

TBD: Triazabicyclodecene

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General Introduction

I. Background:

Polyurethane (PU) is typically synthesized through the polyaddition of polyols and polyisocyanates. Due to its unique molecular structure and diverse properties, it is a highly valuable material for a variety of applications, providing desirable levels of stiffness, hardness, and density [1,2]. Thus, PU is widely utilized in the manufacture of a range of products, including rigid and flexible foams, chemical-resistant coatings, adhesives, elastomers, and sealants [3–7].

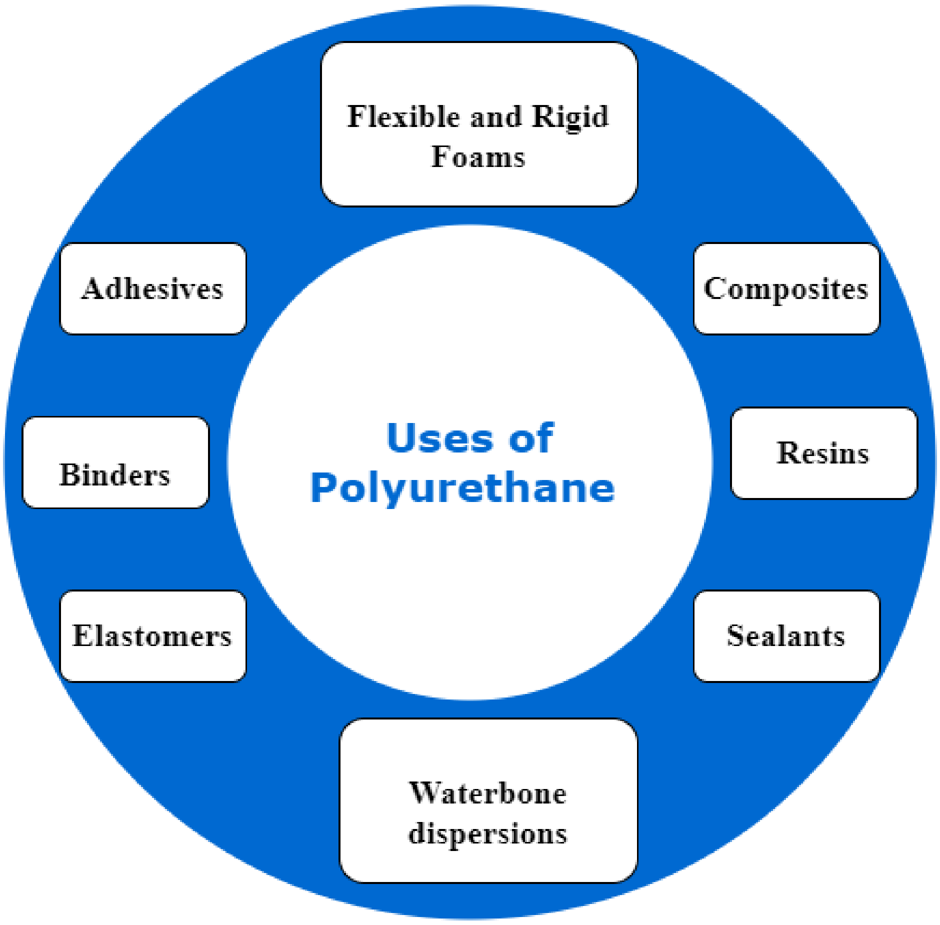

Figure 0.1: Uses of Polyurethane

The conventional and classical synthesis of PU has been known to cause significant environmental harm, affecting aquatic life, soil health, plants, and humans, for several reasons. These reasons include the difficulty of polymer degradation, the residual traces of toxic catalysts that remain in the resulting product, and also the harmful impact of the amine phosgenation reaction leading to isocyanates, which is one of the main reagents in

PU preparation [8,9]. Different synthesis routes to solve these issues are emerging such as the use of alternative non-toxic catalysts [8–10]. bio-based precursors [11,12], and non-isocyanate polyurethanes (NIPU) [13].

II. Objectives

The overall challenge of this thesis is to explore new ways to synthesize PUs that are more respectful of the environment and health. Therefore, the objectives of this PhD research work are to prepare PU foams and films under green chemistry conditions. Indeed, this has been achieved by reducing the toxicity of the conventional PU formulation and modifying the formulation itself by preparing NIPU. The obtained NIPU films and foams were analyzed and studied using different characterization methods such as chemical analysis to check the characteristic bands of each functional group, thermal analysis to study the thermal stability, morphology to observe the foam cells, degradation test in solvents to study the aspect of the foam and finally mechanical analysis to evaluate the mechanical properties of the foams and the films. This thesis is organized in 6 chapters:

Chapter 1 describes the state of the art of environmentally friendly, non-toxic polyurethane foams.

Chapter 2 describes the preparation of a reduced toxicity, conventional flexible PU foam using an alternative catalyst, in particular Bismuth Triflate. The formulation was optimized and compared with a conventional tin-catalyzed PU foam. FTIR-ATR was used to study the kinetics of isocyanate conversion of foams, ATG and DSC to study the thermal properties of the obtained foams, SEM to study the morphology, and compression test to evaluate the mechanical properties.

Chapter 3 presents the preparation and characterization of novel non isocyanate PU nanocomposite films as a way to improve current NIPU drawbacks. It first describes the synthesis and polymerization of bi-cyclic carbonate under mild conditions with high yield and, then, the preparation of the nanocomposite films with functionalised boron nitrate. This strategy reduced the heterogeneity of the polymer network, improving the thermal and mechanical properties of the films in terms of the thermal degradation temperature, glass transition temperature and the modulus.

Chapter 4 details a novel strategy to prepare a self-blowing poly(hydroxythioether) foam at room temperature using bis(cyclic carbonate) and thiol compounds, which simultaneously act as crosslinking agents and generate carbon dioxide during the reaction. This synthesis route enables foam preparation without an external blowing agent and mirrors current conventional, water blown PU foam production. A complete physicochemical study was carried out on the different foams prepared using different ratios of thiol monomers. The obtained foams were studied by FTIR, TGA, DSC, DMA, SEM, RAMAN and degradation tests in solvent.

Chapter 5 presents the preparation of non-isocyanate polyhydroxyurethane foams using a practical and novel method. The obtained foams were studied using different methods of characterization, such as thermal, mechanical, morphological, and chemical analysis.

Finally, ***Chapter 6*** details the preparation of bio-based NIPU films using vanillyl alcohol as monomer. Several reaction steps were carried out to obtain the films. The flexibility of the obtained NIPU films was studied using different diamines during their preparation. Thermal, mechanical and morphological analyses were also performed in this study.

III. References:

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Chapter 1: Bibliographic Review

Part of the work described in this chapter has been published in Polymers, 2022, 15(2), 254

I. Introduction

Polymeric foam materials are essential from an industrial and economic point of view due to their lightweight, high thermal insulation, impact resistance, and damping properties. Polymers such as polystyrene (PS) [1], polyethylene [2], polyvinylchloride (PVC) [3], and polyurethane (PU) [4], and others, have successfully been foamed and are used in diverse applications from automotive [4], packaging [5], electronics [6], aerospace [4], building construction [7], bedding [8], and medical [9]. Among these, PU is the most extensively used polymer for foam production, mainly due to the versatility of its chemistry that results in a large range of densities and stiffness [10,11]. The polyaddition of isocyanates with polyols in the presence of water is the reaction that generates polyurethane foam. However, the presence of isocyanates, which are manufactured through a process involving phosgene, makes this classical method toxic [12–14]. To overcome this issue, scientists and researchers are exploring new ways and methods to produce this polymeric foam without going through this raw material. The polymer obtained via this method is then named non-isocyanate polyurethane (NIPU) [15,16].

Since 2020, research teams around the world have been publishing more scientific papers on the NIPU topic. Figure 1.1 summarizes the number of papers published per year from 2000 to 2022, demonstrating an exponential increase in publications. Figure 1.2 displays the fields in which NIPU publications are published, with data extracted from Scopus.

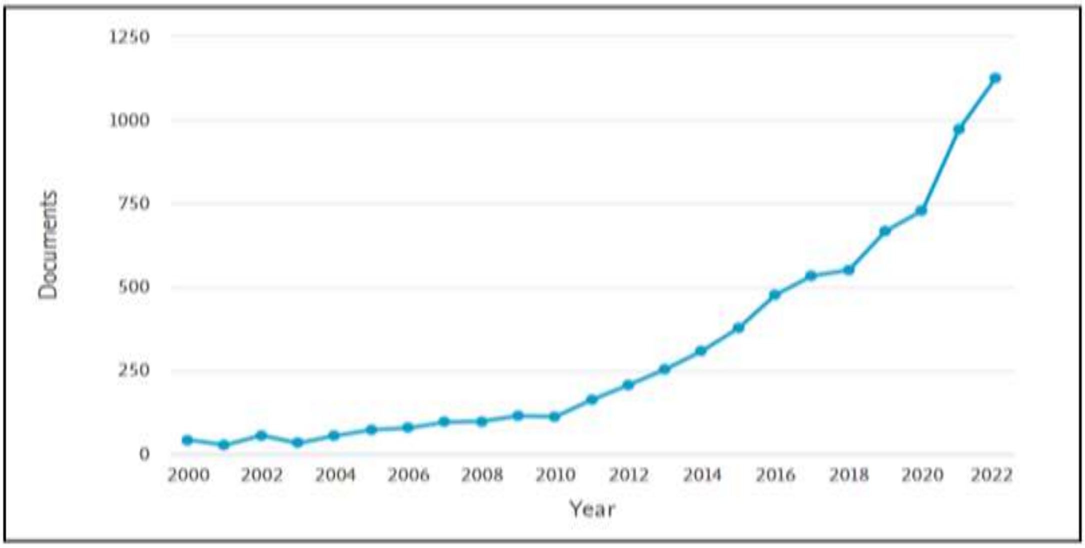


Figure 1.1: Articles published each year between 2000 and 2022 on Non isocyanate Polyurethane

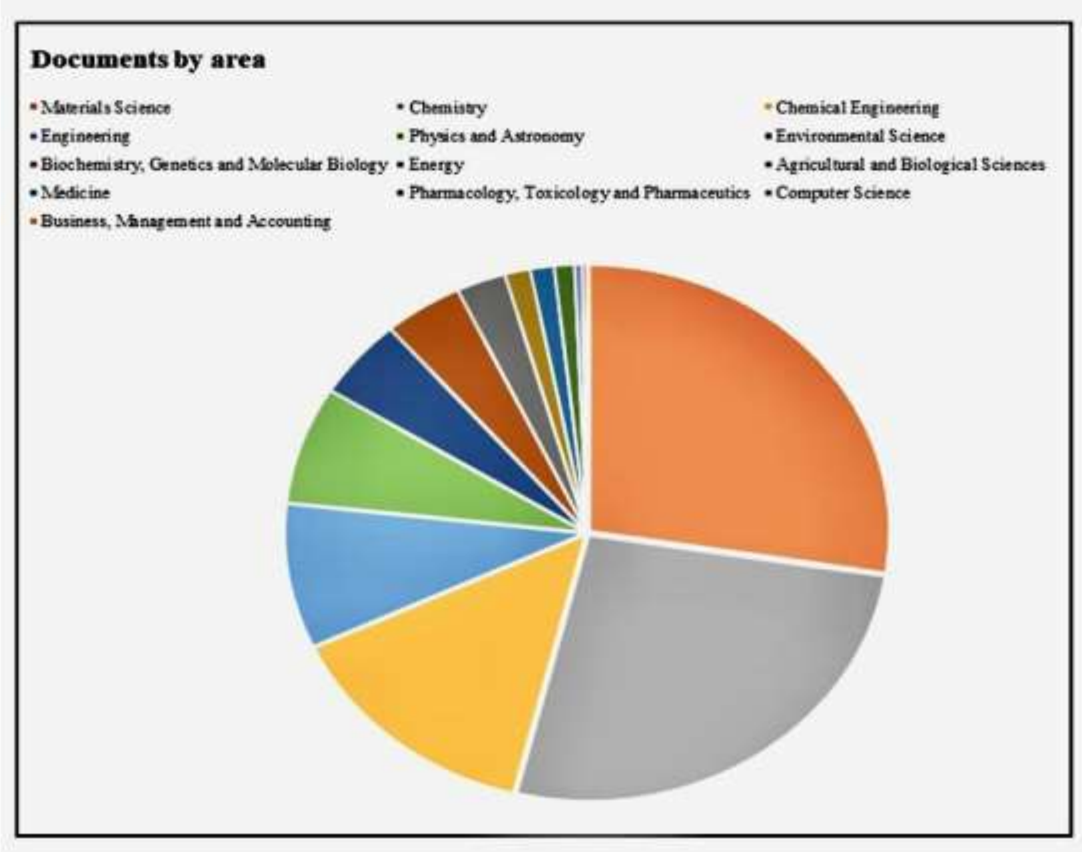


Figure 1.2: Documents by thematic areas on non isocyanate polyurethane

For the synthesis and preparation of NIPU foams (NIPUF), several methods and starting materials have been used by different research groups [12,17–19]. The primary reaction for the preparation of this foam is the aminolysis of cyclic carbonate with a diamine in the presence of a catalyst and with or without the use of an external blowing agent. The resulting NIPUFs have been prepared using bio polyols, natural monomers like glucose, vanillyl alcohol, and tannin-based compounds. For cell formation, most studies use blowing agents, while *in situ* gas generation or self-blowing foams are still rare [20].

Recent reviews have reported sustainable routes for the preparation of NIPUs via several methods as well as starting monomers [15,16]. Here, we report the synthesis procedures and the remaining challenges of NIPUFs using both an external blowing agent or self-blowing reactions.

II. The general reaction of polyurethane and challenges in non-isocyanate polyurethane.

The versatile family of polymers known as polyurethanes (PUs), which Bayer AG originally created more than 75 years ago, has a broad variety of molecular structures and polymeric characteristics [4]. The PU market is composed of foams (65%) [19], coatings (13%) [13], elastomers (12%) [21], adhesives (7%) [22], and other industries, most notably the biomedical sector (3%) [23]. By 2026, more than $61.5 billion worth of polyurethane foam is expected to be produced worldwide, up to 44 % from 2021 [24]. From soft foams, like those used in pillows or mattresses, to stiff foams, mostly found in acoustic insulation materials, a wide range of properties are needed for commercial applications [25].

PUFs are currently made by exothermically reacting formulations of polyisocyanates and polyols [26]. However, the components of isocyanate and polyisocyanate are both extremely dangerous to human health and are the root of severe asthma and other respiratory conditions [14]. As a result, regulatory bodies such as the U.S. Environmental Protection Agency and the REACH rules have increased their pressure on CMR (carcinogenic, mutagenic, and reprotoxic) substances, like methylene diphenyl diisocyanate and toluene diisocyanate.

PU foams are produced by two simultaneous processes: the polymerization or gelling reaction of polyols with isocyanates and the CO_2-producing blowing or foaming reaction from the hydrolysis of isocyanates [27]. The proper growth of the foam with the necessary features depends on the precise management of the kinetics of these two conflicting processes. The word "PU" refers to the urethane linkage resulting from the interaction of the OH (hydroxyl) groups of a polyol and the NCO (isocyanate functional group) groups of an isocyanate. This exothermic reaction creates urethane groups and shown in Figure 1.3.

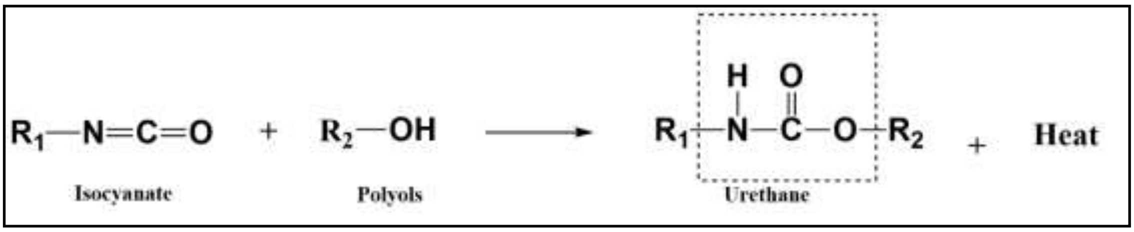


Figure 1.3: Reaction of Isocyanates and polyols for the preparation of the conventional Polyurethane

A second reaction takes place between the isocyanate and water to obtain CO_2, which is the reason for the creation of the cells and consequently the obtaining of the PU foam. This reaction produces carbamic acid, after which the acid breaks down into carbon dioxide. In the polymer precursor, the carbon dioxide dissolves and concentrates until it achieves super saturation, at which time nucleation starts [19,28,29].

Despite the yield and ease of preparing PU foams via this method, the polyisocyanates toxicity is still a major drawback to be overcome. Research efforts are devoted to find new methods of PUFs preparation excluding the use of isocyanates. Thus, non-isocyanate polyurethanes (NIPU) are appealing and promising materials towards the creation of polyurethanes that are environmentally friendly and may entirely be based on renewable raw ingredients. Among the most promising alternatives to the traditional synthesis of PU is the aminolysis reaction between a bi-cyclic or tri-cyclic carbonate monomer and a diamine.

For the synthesis and preparation of NIPU foams (NIPUF), several methods and starting materials have been used by different research groups. The primary reaction for the preparation of this foam is the aminolysis of cyclic carbonate with a diamine in the presence of a catalyst and with or without the use of an external blowing agent [30]. The resulting NIPUFs have been prepared using bio polyols, natural monomers like glucose, vanillyl alcohol, and tannin-based compounds. For cell formation, most studies use blowing agents, while *in situ* gas generation or self-blowing foams are still rare [31–33]. Five-membered cyclic carbonates (CC) are desirable monomers since they are assumably non-toxic. The most environmentally friendly method for producing cyclic carbonates from biomass involves either trans-esterifying a bio-based diol with dimethyl carbonate, which is widely regarded as a "green" reagent, or by epoxidizing olefins and reacting the resulting epoxide with carbon dioxide in the presence of a catalyst [34]. After the CC synthesis, the aminolysis reaction of the obtained CC with a diamine is the key reaction for the preparation of isocyanate-free polyurethanes. Aminolysis or polyaddition of diamines and cyclic carbonate is a direct way to obtain this type of polymer by using a suitable catalyst (Figure 1.4). The formation of every urethane linkage induces the formation of a secondary or primary hydroxyl group. Thus, NIPUs may alternatively be termed as polyhydroxyurethanes. Other reactions used to obtain the NIPU have been explored but in a lesser way than the polyaddition (e.g., the rearrangement, ring opening polymerization and the polycondensation) [35, 36].

Cyclic carbonates and amines precursors are gaining more interest for the synthesis of polyhydroxyurethane. Cyclo-carbonates have a significant advantage over several other types of reagents because of their high solubility and boiling temperatures. Various types of diamines or polyamines are used in this method, either aliphatic or aromatic amines, which gives us a wide choice of NIPUs with different structures and mechanical, thermal, and chemical properties [37–39].

Another advantage of this method is the possibility of obtaining biobased CC monomers by using natural monomers like vanillyl alcohol or biobased oils in the CO_2 fixation reaction.

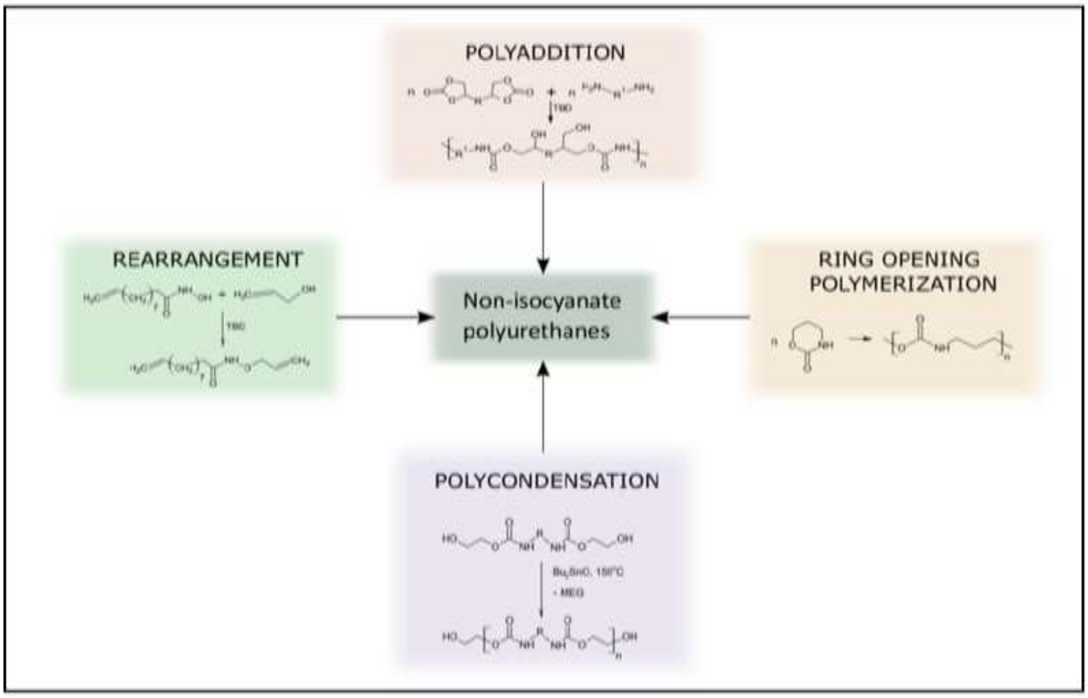


Figure 1.4: Different pathways to prepare NIPU[40]

III. External blowing agent based NIPU foams

The preparation of porous materials requires the use of blowing agents to obtain the cellular structure. External blowing agents for the creation of a gas whether it is CO_2, H_2, or others, play the primordial role in the preparation of the desired foam.

The first study to report the production of NIPU foams used polymethylhydrogensiloxane (PHMS) as blowing agent (Figure 1.5). Stefani et al. [32] synthesised NIPU foams using bi- and tri-cyclic carbonates, two amines, Jeffamine EDR-148 and Priamine 1073, and a blowing agent. The blowing reaction occurred between the amine and SiH groups of the blowing agent, resulting in the release of dihydrogen and expansion of the foam. The synthesized NIPU foams were characterized based on their structure, degree of crosslinking, and thermal properties, which were found to depend on the functionality of the cyclic carbonate and the structure of the amine [32]. Using this same blowing agent, Valette et al. [33] presented a new method based on the trans-urethane polycondensation. They prepared bio-based amino-terminated oligomers bearing urethane and/or urea functions and then used these oligomers to prepare self-supported foams by reacting their amine groups with the SiH groups of PHMS, releasing hydrogen gas as a blowing agent, and by a concomitant reaction with a multi-epoxide molecule used as a crosslinking agent. The study found that the optimal conditions for producing foams were 10 minutes at room temperature followed by 30 minutes at 100°C. The resulting foams were high-density flexible polyurethane foams with heterogeneous cell diameters and apparent densities varying from 130 to 400 kg/m^3. The study also found that the foams were thermally stable above 300 °C and had very soft physical characteristics with low Young's modulus values [33].

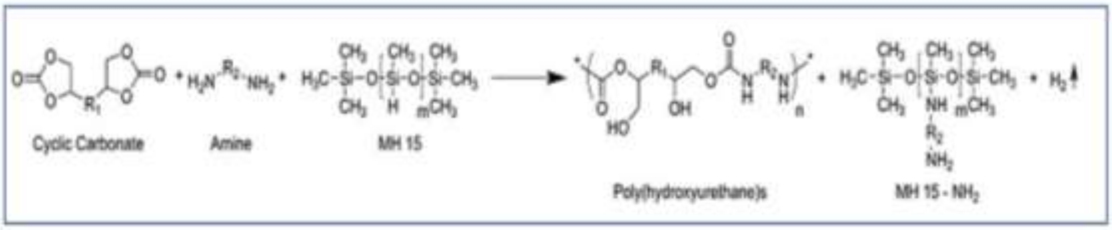


Figure 1.5: Reaction to obtain NIPUF by using MH15. Reprinted from ref [17] with permission from the publisher

Hydrofluorocarbon liquids are physical blowing agents that have a low temperature boiling point and have been used for the preparation of a NIPU biobased foam. Blattmann et al. [17] used Solkane 365/227, a third-generation hydrofluorocarbon blend manufacture by Solvay to produce a flexible and 100% bio-based NIPU foam. Their process involved curing trimethylolpropane-based cyclic carbonate blends with HMDA in the presence of the fluorohydrocarbon (Figure 1.6). The study showed that blending rigid carbonated trimethylolpropane glycidyl ether (TMPGC) and flexible ethoxylated TMPGC (EO-TMPGC) improved the foam processing and provided excellent control of the foam properties. While the use of the fluorohydrocarbon eliminated problems relating to the evolution and emission of highly flammable H_2 or the presence of residues of the chemical blowing agents [17].

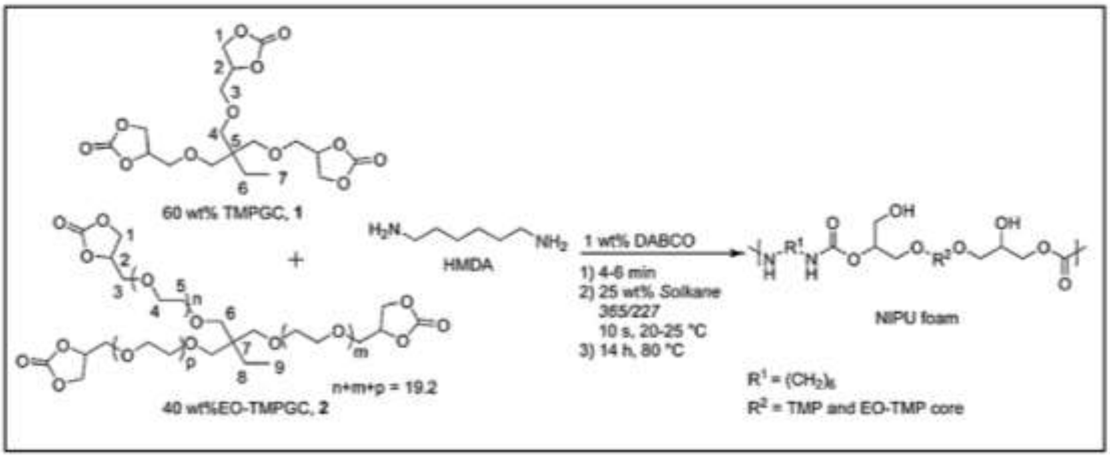


Figure 1.6: Reaction to obtain NIPUF using Solkane 365/227. Reprinted from ref [17] with permission from the publisher

Known chemical blowing agents, such as azodicarbonamide, sodium bicarbonate, and citric acid, release gas upon heating and have been widely used by the industry [41]. Although these systems have received limited attention to produced NIPUFs, both sodium bicarbonate and citric acid have been analyzed as NIPU blowing agents. Xi et al. [42] used sodium bicarbonate to prepared glucose-based NIPUF. They reacted glucose with dimethyl carbonate and hexamethylene diamine using a silane coupling agent as compatibilizer [42]. After obtaining the polymer, sodium bicarbonate was added and the mixture was placed in an oven at a temperature of 200 °C for 30 min to produce CO_2, thus creating the cells. It was also stated that sodium bicarbonate plays a role in rigidifying the cell walls, but no clear explanation of this effect has been presented Carbon dioxide released in this process is a safe and environmentally friendly external blowing agent that can produce NIPU foams with a uniform cell structure and good thermal insulation properties; however, the use of carbon dioxide can also result in foams with lower densities and lower compressive strength compared to foams produced with other external blowing agents. Meanwhile, an acid mixture composed of citric acid and glutaraldehyde has been used to develop a rigid foam made from mimosa tannin-based non-isocyanate polyurethanes (NIPUs). The study analyzed four different types of tannin-based foams with varying proportions of citric acid and glutaraldehyde, obtaining open cell structure with varying cell sizes depending on the citric acid content. The compressive mechanical properties of the foams were also found to be enhanced by the increased level of cross-linking between the tannin NIPU molecules at higher amounts of glutaraldehyde [31].

The properties of NIPUF can be influenced by the type of solvent and external blowing agent used in the synthesis process. Solvent can affect the properties of NIPU foams in several ways. For example, the choice of solvent can influence the solubility of the reactants and the rate of reaction. Solvents with a high solubility for the reactants can increase the reaction rate and the efficiency of the synthesis process. However, the use of certain solvents can also affect the final properties of the foam, such as its density, mechanical properties, and thermal stability. In contrast, external blowing agents are used to create the porous structure of polymer foams by generating gas bubbles during the synthesis process. Dallin et al. [43] discussed different external blowing agent such as water, carbon dioxide, and hydrofluorocarbons used in the preparation of NIPUFs and found that the choice of external blowing agent can significantly influence the density, cell size, and thermal insulation properties of the resulting foam.

Each external blowing agent has advantages and limitations in the preparation of NIPU foam. Water is a cheap and readily available external blowing agent that can produce NIPU foams with a uniform and closed cell structure. However, the use of water can also lead to some limitations such as the need for high processing temperatures and the risk of hydrolysis reactions. In contrast, hydrofluorocarbons are a type of fluorinated gas that can produce NIPU foams with a more open cell structure and higher thermal insulation properties. However, hydrofluorocarbons are potent greenhouse gases and are being phased out due to their high global warming potential.

IV. Self-blowing NIPU foams

Cyclic carbonate and amine groups used in PHU-based foams have weak reactivity at room temperature, making it challenging to create these types of foams. Therefore, research efforts have been focused on developing methods to allow for self-blowing of PHU-based foams.

The creation of self-blown PHU foams was proven in a very recent study conducted by Anitha et al. [20] based on selected cyclic carbonates and amines. They reported the reaction of amine terminated oligomeric phenylhydroxylamine (AOPHA) with cyclic(carbonate) of resorcinol diglycidyl ether (RDGCC), which resulted in the release of carbon dioxide, and in a parallel reaction of the hydroxyl groups and amino groups with the cyclic carbonate groups that compete during polymerization to produce PHU foams. The resulting flexible PHU foam is thermally stable and had a closed cell structure with a density of 480 kg/m3 and adhesive strength between Al-Al as 1.5 to 2.0 MPa. The CO_2 gas responsible for foaming was detected by FTIR and GC-MS [20].

Poly(thioether) foams have also been suggested as potential alternatives to PHU foams. They are produced by a click reaction from a cheaply scalable epoxy resin with thiol. The S-alkylation of thiolated monomers and tri-cyclic carbonate have been studied by Monie et al. [44] This reaction causes the release of CO_2 in the presence of 1,8-diazabicyclo(5.4.0)undec-7-ene (DBU) as catalyst (Figure 1.7) [44]. The high reactivity of thiolated monomers and cyclic carbonate makes this reaction fast and efficient. Self-blowing polyhydroxythioether (PHTE) and polyhydroxyurethane foams were synthesized with very good thermal stability and mechanical properties. Figure 1.5 shows the preparation of PHTE and PHU self-blowing foams [45,46].

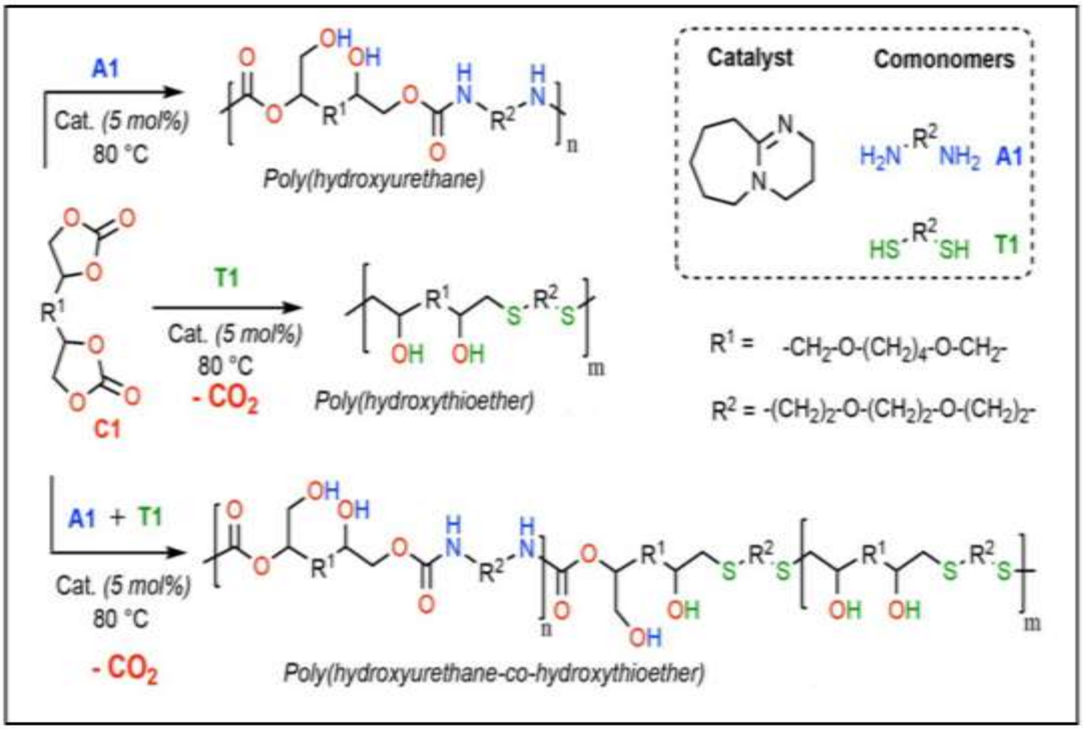


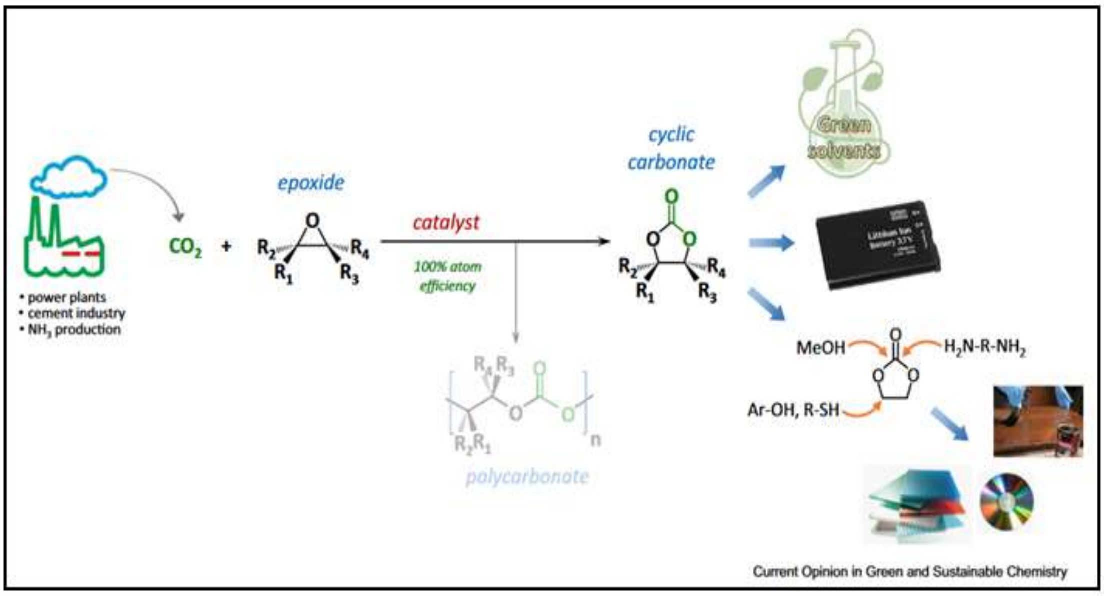
Figure 1.7: S-alkylation used to obtain NIPU foams. Reprinted from ref [44] with permission from the publisher

V. Biobased NIPU foams

Biobased non-isocyanate polyurethane foams rely on their preparation on key intermediates that are cyclic carbonate, diamines, or polyamines as well as CO_2 which is used in the preparation of CC [16]. Several studies that have attempted to prepare NIPU foams with different starting materials using different methods and operating protocols will be discussed in the following sections.

V.1. Carbon dioxide (CO_2)

The use of carbon dioxide as a substitute feedstock for the synthesis of chemicals and materials is now generating a lot of interest. The direct chemical use of CO_2 as a co-monomer in polymerization operations to produce custom materials is particularly appealing strategy (Figure 1.8). The catalytic copolymerization of epoxides and CO_2 to polycarbonates seems to be a practical technique in this case [47,48].



Current Opinion in Green and Sustainable Chemistry

Figure 1.8: The preparation of cyclic carbonate by CO_2 fixation

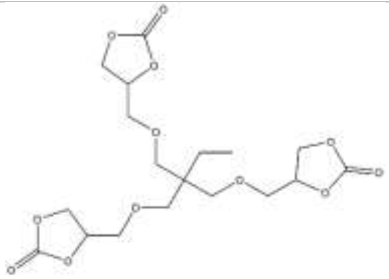
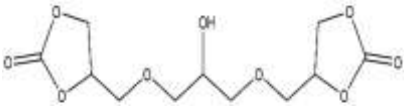
The CO_2 is used in various studies of CO_2 fixation with bis-epoxides. Different operating protocols and pressures have been reported in the synthesis of cyclic carbonate. McGuire et al. [49] presented a one-step approach for combining CO_2 with diols to form cyclic carbonates. This methodology excluded the use of potent moisture-sensitive bases and enabled the use of sublimed dry ice as a generator of CO_2. Hence, the first CO_2 based synthesis under atmospheric pressure of three new 7- and 8-membered cyclic carbonates was presented [50].

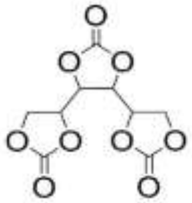
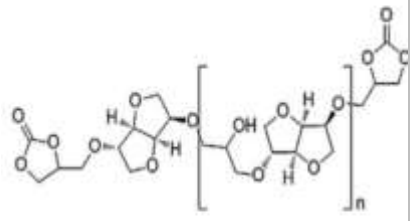
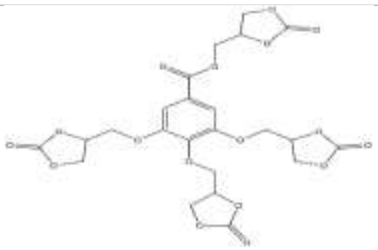
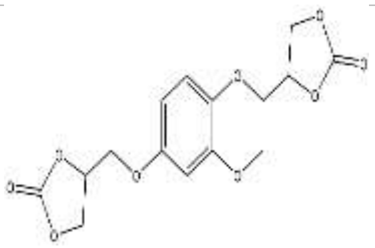
The same pressure conditions were implemented in another study reported by Das and Nagaraja [51] that use an Ag-based catalytic system. They described the sensitive synthesis of a CO_2-philic sulfonate-functionalized UiO-66 MOF with catalytically active alkynophilic Ag(I) sites and Ag(I)-anchored sulfonate functionality, designated MOF-SO_3Ag. The fixation of CO_2 involved the use of another metallic catalyst. A cobalt complex based on a carboxylic ligand with a triazole ring was investigated as an active homogeneous catalyst for the fixation of CO_2 with epoxide. The catalyst effectively converted a variety of epoxides to industrially significant cyclic carbonates at ambient pressure and without the use of solvents [52].

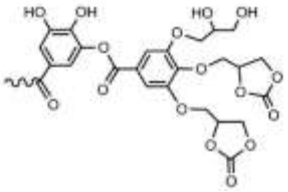
V.2. Cyclic carbonate

Five-membered cyclic carbonate is the main component in the synthesis of NIPUF via the polyaddition reaction. The synthesis of NIPUF can also be carried out by other cyclic carbonate, for example six-membered and seven-membered CC but due to the toxic method used to synthesize them, investigations are more focused on five-membered cyclic carbonate. The objective of this section is to present the different biobased monomers used for the preparation of cyclic carbonates used in the preparation of polyhydroxyurethane. The biobased monomers used as well as the synthesized CCs and some notes and remarks on the reaction and the types of NIPU prepared with these intermediates are summarized in the Table 1.

Table 1.1: Methods of preparation of biobased cyclic carbonate

Starting molecule	**Cyclic carbonates**	**Synthesis of epoxide conditions**	**Fixation conditions of CO_2**	**Ref.**
1,4-butane-diol		Commercial epoxy prepared by Butanediol (Butanediol diglycidyl ether)	LiBr as Catalyst DMF as solvent P=10 bars in reactor 80 °C, 18h	[52]
Glycerol			TBAB as catalyst Solvent-free P=30 bars in reactor 120 °C, 10h	[53]

Sorbitol		Epichlorohydrin NaOH	TBAB as Catalyst Solvent-free P=30 bars in reactor 24h	[54]
Iso-sorbide		Epichlorohydrin NaOH Water	LiBr as Catalyst DMF as solvent P=6 bars in reactor 80 ºC, 12h	[55]
Gallic acid			LiBr as Catalyst Ethylene glycol as solvent N-methyl pyrrolidone P=2MPa bars in reactor 100 ºC, 9h	[56]
Vanillin		Epichlorohydrin NaOH TEBAC	LiBr as Catalyst Acetone as solvent	[57]

			P=12 bars in Autoclave 80 °C, 12h	
Tannic acid		Epichlorohydrin NaOH TBAB	TBAB as Catalyst DMF as solvent CO_2 gently bubbled 80 °C, 2h	[58]

Camara et al. [52] synthesized three different bi-cyclic carbonates using the same process shown in Table 1.1. Butanediol bis carbonate (BBC), resorcinol bis carbonate (RBC) and trimethylpropane tris carbonate (TMPTC) were prepared by carbonation of different epoxides. The prepared cyclic carbonates were then obtained in high yields with a carbonate equivalent weight ranging between 5.05 and 5.89 mmol/g for the three synthesized carbonates. Glycidyl ethers based on trimethylpropane, glycerol and pentaerythritol were converted to cyclic carbonate with the CO_2 fixation reaction using tetrabutylammomium (TBAB) as catalyst. The absorption of the carbonate was detected in the 1780 cm^{-1} band and the FTIR spectra proved the disappearance of the epoxy signals and the appearance of the new cyclic carbonate signals [53].

Using sorbitol glicidyl ether marketed as ERYSIS GE-60, Schmidt et al. [54] prepared sorbitol ether carbonate (SEC) by solventless CO_2 fixation reaction. There are two methods for the preparation of sorbitol-based cyclic carbonate using the method described above and a second method for the preparation of sorbitol tricarbonate (STC) with the solvent DMSO. Another method was used by Besse et al. [55] in which isosorbide is converted to Epoxidized oligo-isosorbide and then carbonation is done to obtain a cyclic carbonate on the basis of isosorbide. Using LiBr as a catalyst, different cyclic carbonates have been prepared to synthesize PHUs with the help of the different amines, as an example 1,10 diaminodecane and JEFF400 [55].

In another approach, a tetracarbonate based on gallic acid in combination with ethyleneglycol and LiBr was used in an attempt to obtain satisfactory results. Using another biobased monomer which is vanillin, the classical epoxidation reaction using epichlorohydrin, NaOH and TEBAC was performed to obtain vanillin bis-epoxide, the latter underwent CO_2 fixation using LiBr metal catalyst and acetone as reaction solvent [56]. Esmaieili et al. [58] synthesized fully biobased NIPUs using tannin acid, and the epichlorohydrin used in this study is based on glycerol and CO_2 obtained under normal conditions [58].

V.3. Poly and Diamines

Polyamines or diamines are used as a curing agent in the polymerization and aminolysis reaction of cyclic carbonate in the presence of the catalyst. These chemical compounds are responsible for the creation of the hydroxyurethane bond. Due to the high reactivity and nucleophilicity of amines, the choice of this diamine has a crucial role on the final properties of the prepared polymer. Most of the amines used in this synthesis are commercial and fossil fuel-based products [59,60]. Wang et al. [61] summarised the prepared diamines based on vegetables oils as well as sugar and their derivatives in a recent review and some biobased diamines prepared by glucose, xylose, sugars and vegetable oils are presented in Figure 1.9.

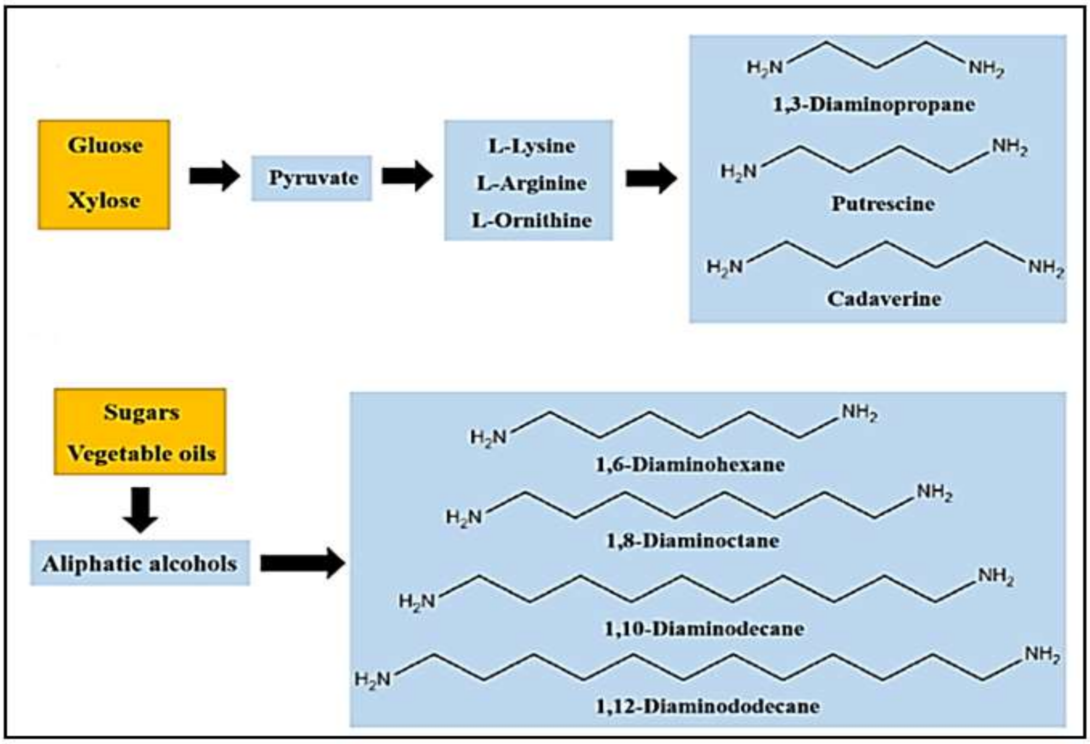


Figure 1.9: Different ways to prepare biobased diamines Reprinted from ref [61] with permission from the publisher

Classification of amines made by various research groups have resulted in 2 main types of amines. The first type is the modified biobased compounds such as oils, terpenes, fatty acids and sugar derivatives, and the second type is the amines synthesized by biobased resources that contain one or more nitrogen atoms such as polylysines, amino acids and chitosan and derivatives. Using Erucic acid and oleic acid as starting materials, Nieschlog et al. [61] succeeded in producing aliphatic diamines such as 1,9- nonanediamine (NDA), and 1,13- Tridecanediamine (TDA). Another study demonstrated the possibility to prepare 1,6- Hexanediamime (HMDA) using renewable resources such as succinic acid, glycerol, adipic acid, lactic acid and levulinic acid. Vegetable oils have been used to prepare amine-functional molecules [62].

VI. Recent studies of biobased non-isocyanate polyurethane foams

To reduced even further the toxicity and improve the sustainability of NIPU solutions, recent studies have focused biobased monomers. The use of hydrolysable tannin has been studied by Azadeh et al. [63] Tannic acid is known commercially as Chestnut wood Tannin. The method of preparation of NIPU foams in this study was based on 3 phases, the first one is the preparation of NIPU resin, then the preparation of polyurethane free-isocyanate foam and finally the heating for curing the obtained foam. The hexamethylenediamine (HMDA) was used during polymerization with dimethyl carbonate (DMC) to obtain the cyclic carbonate.

A further biobased alternative is the lignin component of biomass, which can replace the often-toxic and petroleum-derived precursors used in polymer synthesis. A recent study used lignin as a precursor for the production of NIPU foams [64]. The authors developed a process functionalizing raw Kraft lignin with green organic carbonates and solubilizing the precursors with a curing agent from renewable fatty acids to enable rapid gel-times. The resulting NIPU foam has shape memory capacity, 100% biobased carbon content and properties comparable to traditional diisocyanate-based polyurethanes. However, due to lignin's heterogeneity, the resulting material's properties may vary. Despite this, the study shows that lignin can be a promising alternative to traditional materials for creating high-performing, sustainable products.

VII. Conclusion

In the production of polyurethane, isocyanates, and polyols are frequently utilized. However, as it becomes possible to minimize the use of toxic and ecologically problematic substrates, developing cleaner synthetic pathways excluding diisocyanates is a societal must. The need for safe, and eco-friendly chemical precursors is increasing the pursuit of novel NIPUs. Those produced via the polyaddition reaction of cyclic carbonates and diamines, which results in poly(hydroxy urethanes), are of great interest.

This chapter highlights research reports on non-isocyanate polyurethane foams, either by an external blowing agent or by self-blowing. Although NIPUF is entirely green and has several advantages over isocyanate-based PUF, there is still potential for advancement and development. A safer and more innovative synthetic method can be developed under moderate reaction conditions in contrast to the majority of current NIPU that are synthesized using cyclic carbonates at high temperatures. Researchers are focusing on optimizing the preparation methods of NIPUF, aiming to scale up the technology as a significant step towards the successful implementation of NIPUF on the industrial scale.

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Chapter 2: Preparation of polyurethane foams using a non-toxic catalyst

Part of the work described in this chapter has been published in Polymers. 2021, Polymers 13 (24), 4460

I. Introduction

The versatility of polyurethane (PU) chemistry has long been recognized. It accounted for 7%, by mass, of the total polymer production in 2017 [1]. This versatility is based on the multiple chemical structures resulting from the polyaddition of di- or poly-isocyanates and di- or polyols in the presence of a catalyst. This enables the use of PUs as foams, coatings, elastomers, adhesives, and others [2]. However, their main issue is the toxicity of the isocyanate precursors and their industrial synthesis [3]. Research is therefore aimed at developing not only non-toxic synthetic routes without using isocyanates [4–6] but also "greener," sustainable PUs through the use of vegetable or renewable feedstocks [7–10].

PU foams are the result of two simultaneous reactions: the polymerization or gelling reaction, of the polyols with the isocyanates, and the blowing reaction from the hydrolysis of the isocyanates with the formation of CO_2. The kinetics of these two competing reactions have to be well controlled for the correct evolution of the foam with the desired properties. Thus, catalysts play an essential role in PU foaming by increasing the efficiency of the reactions and controlling their rate, as well as reducing the side reactions [11]. Some of these catalysts are shown in Figure 2.1. Both amine and metallic catalysts are often used together to form the foam. Amine catalyst assists in blowing reaction and contributes to the polymerization reaction. One of the most commonly used tertiary amine catalysts is 1,4-diazobicyclo[2,2,2] octane (DABCO) [11], together with the triethylenediamine, and N,N,N′,N″,N″-pentamethyldiethylenetriamine catalyst [12]. However, tertiary amines are highly volatile, causing odor problems during manufacturing and health issues such as glaucoma. Meanwhile, the metal catalyst is mainly used for the polymerization reaction, whereby it enables the reaction to achieve high reaction rates. Stannous octoate (SnOct2) is the classic metallic catalyst used in the preparation of foam for its efficiency in controlling the gelling reaction [13]. However, it has high toxicity levels on fertility and reproduction, limiting its applicability in several sectors, such as packaging and biomedical [14,15]. Thus, research efforts are focused on the use of alternative organo- [16–18], or metal catalysts [11,19–25], Among the different metal catalysts, the most studied complexes are based on iron [20,22,23,23], copper [22,25], zinc [20,23,24], titanium [20,22,23], cobalt [22,23], and zirconium [23].

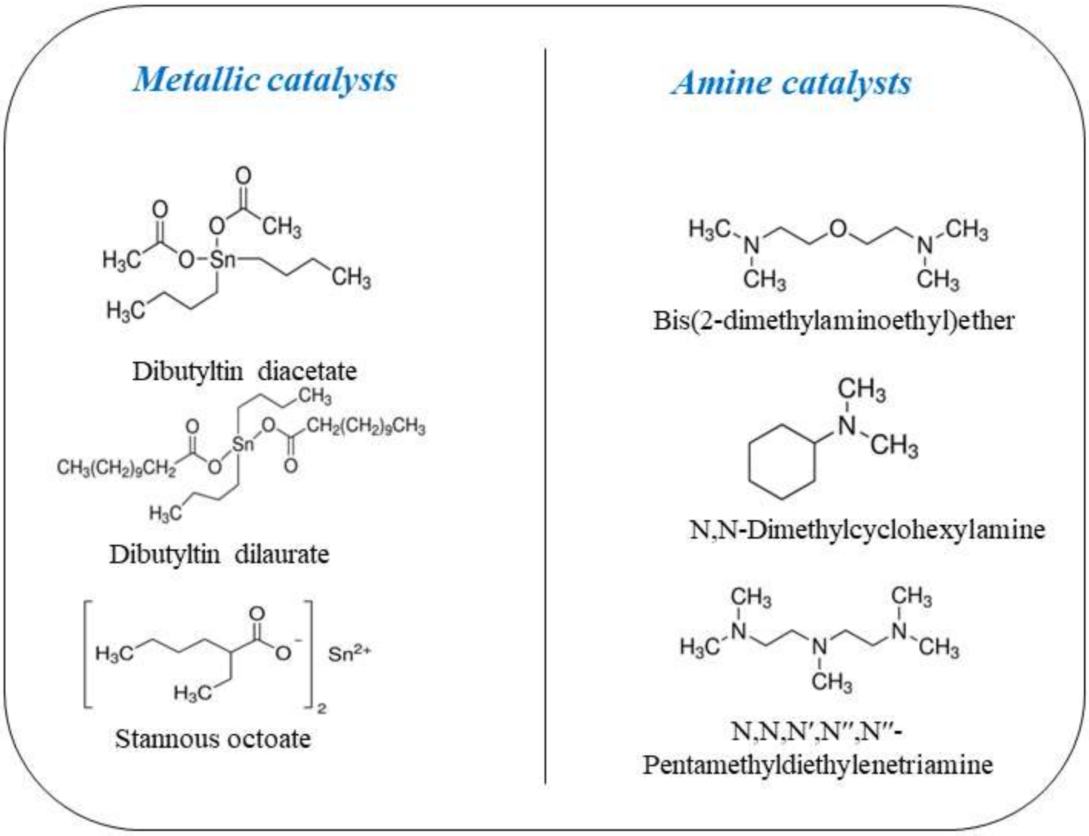

Figure 2.1: Some of the common catalysts used in PU foams production

Here, we focus on the use of bismuth-based catalyst as a possible substitute candidate. Bismuth is a unique catalyst because of its reduced toxicity, compared to many others metal salts. Additionally, Bismuth (III) salts are catalysts that play the role of a Lewis acid [26]. Moreover, bismuth sub-salicylate has been used for more than 100 years as a gastrointestinal drug, while bismuth oxide and bismuth sub-carbonate have a long tradition as ingredients of ointments [26]. The Bismuth Triflate has showed good efficiency in various reactions, such as the ring opening polymerization of cyclic esters (caprolactone and lactide) and polycondensation reaction of dicarboxylic acids and aliphatic diols [27]. Additionally, bismuth carboxylates is also good alternatives for PU systems [19,28], but their catalytic activity can insufficient for many applications and can require their combination with other metal catalysts, such as lithium carboxylates. Furthermore, the sensitivity of some bismuth catalysts to water would limit its applicability in PU foams. In this context, Bismuth Triflate may be ideal as it is soluble in water and has high reactivity in several reactions. In this study, the change of stannous octoate, the classical catalyst with Bismuth Triflate which is considered a catalyst with low toxicity aims to reduce the toxicity of the prepared foam as mentioned before, the stannous octoate in reaction with water (blowing agent) causes the oxidation of the catalyst which is toxic, as well as the increased solubility of Bismuth Triflate in water and its high reactivity make it a good candidate for use in the preparation of polyurethane foam, then, we analyse the use of Bismuth Triflate to produce flexible PU foams (F-PUF) and compare the results to traditional stannous octoate. The prepared PUFs were characterized and thermal, kinetics, mechanical, as well as morphological properties of both type PUF.

II. Materials and Methods

II.1. Materials

Lupranol 2095 (polyether polyol: hydroxyl number 35 mg KOH/g, functionality 3, viscosity (25°C) 8500 mPa.s), Lupranol 1200 (polypropylene glycol: hydroxyl number 248 mg KOH/g, functionality 2, viscosity (25°C) 72 mPa.s), Lupranate MI (a mixture of 2,4'- and 4,4'-diphenylmethane diisocyanate (MDI): NCO-content 33.5 g/100 g, viscosity at 25 °C 12 mPa·s), Lupranate M20 (MDI: NCO-content 31.5 g/100 g, viscosity at 25 °C 200 mPa·s) and DABCO DC198 (silicone glycol surfactant) were kindly supplied by BASF. N,N,N′,N″,N″-Pentamethyldiethylenetriamine (PMDETA), as amine catalysts, and Tin(II) 2-ethylhexanoate and Bismuth(III) trifluoromethanesulfonate $Bi(OTf)_3$, as metal catalysts, were purchased from Sigma Aldrich. The isocyanate index was set at 100.

II.2. Preparation of PUF with different catalyst mixture

Flexible PUFs were prepared with both tin and bismuth catalysts and with different amount of the bismuth catalyst while keeping the isocyanate index constant (Table 2.1). A premix consisting of all the products, except isocyanate, was blended using a mechanical mixer at 2000 rpm for 2 min. Then, the isocyanates were added to the premix for 10 sec at 2000 rpm. The obtained formulation was immediately poured into a mold (20x13x13 cm^3) and allowed to free rise at room temperature (Figure 2.2). Foams were left at room temperature for 24 hours prior to their characterization.

Table 2.1: Formulations of PU foams, expressed as parts per hundred of polyol

Formulation	PUF$_{S0.2}$	PUF$_{B0.2}$	PUF$_{B0.1}$	PUF$_{B0.05}$
Lupranol 1200	45.3	45.3	45.3	45.3
Lupranol 2095	55.7	55.7	55.7	55.7
DABCO DC 198	0.2	0.2	0.2	0.2
Bismuth Triflate	----	0.2	0.1	0.05
Stannous Octoate	0.2	----	----	----
PMDETA	0.5	0.5	0.5	0.5
Water	6	6	6	6
Lupranat MI	29.7	29.7	29.7	29.7
Lupranat M20s	45.3	45.3	45.3	45.3

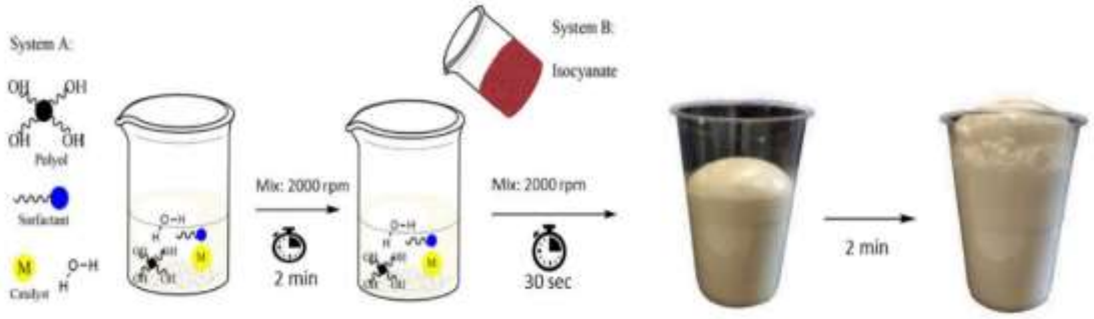

Figure 2.2: Schematic representation of the free-rise foam production.

II.3. Characterization of PU foams

The kinetics of PUF formation was monitored by infrared spectroscopy with a Fourier transform (FTIR). FTIR spectra were recorded using a Perkin-Elmer Spectrum One FT-IR Spectrometer fitted with an Attenuated Total Reflectance (ATR) accessory under unforced conditions. The reactive mixture was placed in direct contact with the diamond crystal immediately after the isocyanate was mixed with the rest of the ingredients. Measurements were collected at 8 cm^{-1} resolution and co-adding 6 scans per spectrum. The scanning time per spectrum was 2 min and the reaction was followed for 60 min. A background file was recorded prior to each run at 4 cm^{-1} resolution co-adding 6 scans per spectrum. A total of 5 spectra per sample were recorded and analysed to obtain statistically relevant data.

Density of PUF samples was measured according to ASTM D1622. Specimen of 30 × 30 × 30 mm^3 (width ×length × thickness) were cut from the middle of the foam height. The results were the average of at least three different foam samples.

Philips model XL30, with tungsten filament and accelerating voltage of 25 kV, was used to examine the morphology of the foams. Cross-sections of the samples were sliced perpendicular and parallel to the foaming direction and the fracture surface was sputter coated (Polaron SC7640) with gold/palladium, the cell size was measured by Image J software.

Compression properties were measured under uniaxial compression in a universal testing machine (Instron 3366) on cubic samples of 2.5 x 2.5 x 2.5 cm^3. All measurements were carried out at a crosshead speed of 10 mm/min. The samples were loaded to a maximum compressive strain of 75 %.

Thermogravimetric analysis was carried out using a TA-Q500 (TA-instrument, USA). Foamed samples of 10 mg were heated from room temperature to 800°C at 10 °C/min under a nitrogen atmosphere (flow rate 90 mL/min). The main degradation features, i.e., the onset of the degradation, taken at 5 % of weight loss, the maximum of the weight loss derivative curve (DTG) and the residues, are reported.

Differential scanning calorimetry was carried out using NETZSH DSC- 214 model previously calibrated with an indium standard. Foamed samples of about 10 mg (balance precision of ± 0.1 mg) were hermetically sealed in concave aluminium pans and the lid was pierced. Experiments were performed in the temperature range from -50 to 25°C, at scan rate of 10°C/min under nitrogen flux of 2 mL/min.

III. Results and Discussion

The study first compared the proposed bismuth catalyst to traditional stannous octoate using equal amounts of Bismuth Triflate and stannous octoate. Indeed, the percentage of the two catalysts is one commonly used in conventional polyurethane foam formulation [29]. We then analyzed the optimum amount of bismuth to obtain a foam with appropriate physical properties.

III.1. *Structural characterization of prepared foams*

The polymerization of PU foams is normally analyzed via infrared spectroscopy, and was used to study the catalytic performance of non-toxic bismuth catalyst. The spectra were normalized by the intensity of an internal reference band that remained constant throughout the reaction (2970 cm^{-1} corresponding to CH stretch) to compensate for the large density change of the systems [30,31]. Figure 2.3 shows a representative spectrum obtained at different reaction times showing the evolution of the carbonyl region and the isocyanate absorbance band.

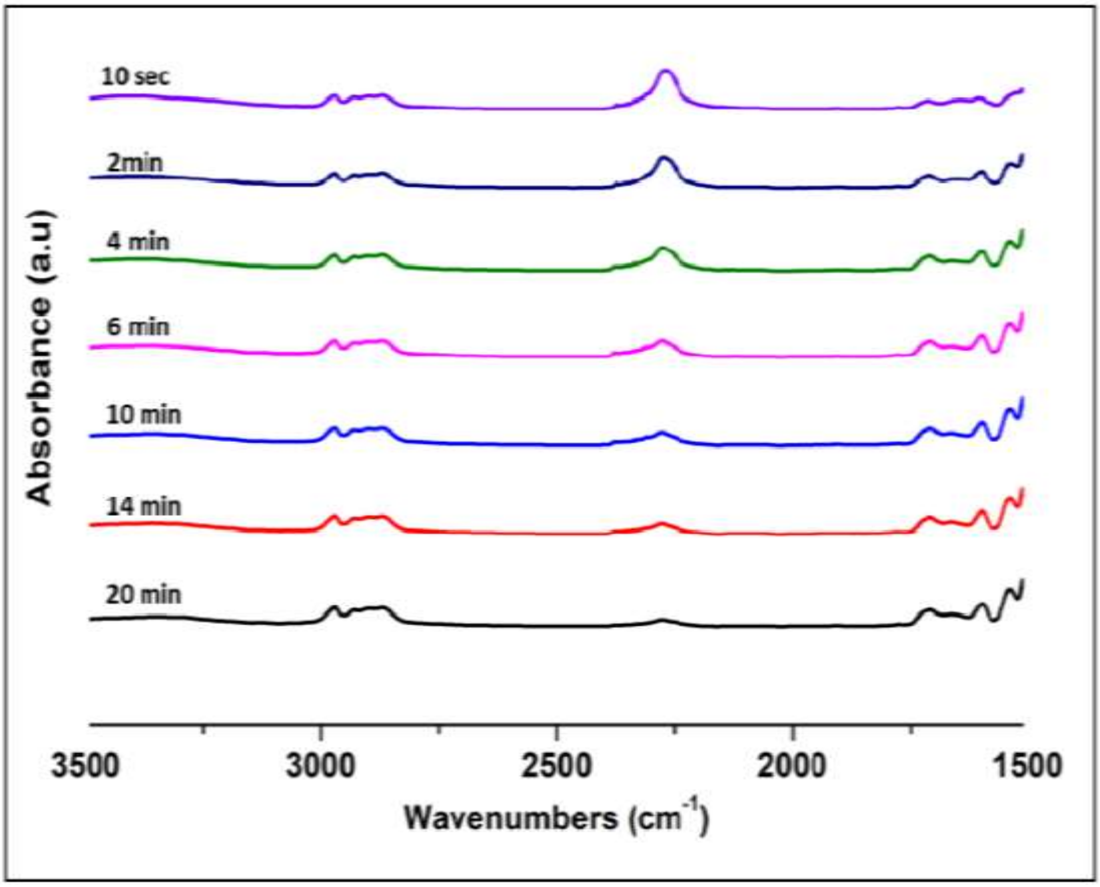

Figure 2.3: Representative FTIR spectra of PUFB0.2 formulation with time

The main regions of interest are the isocyanate absorbance band at approximately 2300 cm^{-1} and the amide I region or carbonyl region, 1800-1600 cm^{-1}. The decrease in the isocyanate absorbance as a function of reaction time informs of the reactions of the isocyanate with both the polyol and water to form urethane and urea groups, respectively. Hence, this band is used to calculate the extent of the reaction as:

$$\rho = 1 - \frac{A_{NCO}}{A_o}$$

where A_{NCO} is the ratio of the integrated absorbance of the isocyanate and that of the internal standard, and A_0 is at zero reaction time. The results shown here are the average of three experiments. Both catalysts reached approximately 80 % of isocyanate conversion, as a common practice in PU foam chemistry is to add an excess of isocyanate in the reaction over that required for chain extension and cross-linking [32]. The isocyanate conversion of the foams showed clear differences among the catalysts. Bismuth catalyst was more efficient than stannous octoate (Figure 2.4.a), reaching higher conversions at similar reaction times. Such higher conversions of Bismuth Triflate can be related to its activity towards both gelling and blowing reactions, since it has a high Lewis acidity and is soluble in water. A previous study by Arnould et al. [33] showed similar catalytic efficiency of bismuth neodecanoate compared to a Sn catalyst, in particular dioctyltin dilaurate. Meanwhile, Levent et al. [21] showed only moderate activity compared to dibutyltin dilaurate of several bismuth carboxylates towards the isocyanate/alcohol reaction that was improved using heterobimetallic complexes with lithium carboxylates. Therefore, isocyanate conversion suggest Bismuth Triflate is a strong candidate to substitute tin-based catalysts and it appears to have a better performance than other bismuth-based catalysts.

Foam samples were subsequently prepared with different concentrations of bismuth catalyst to study the minimum amount that would provide a foam with appropriate physical properties. FTIR analysis reveals similar isocyanate conversion with 0.2 php and 0.1 php, corroborating the good catalytic activity of Bismuth Triflate towards the isocyanate reaction.

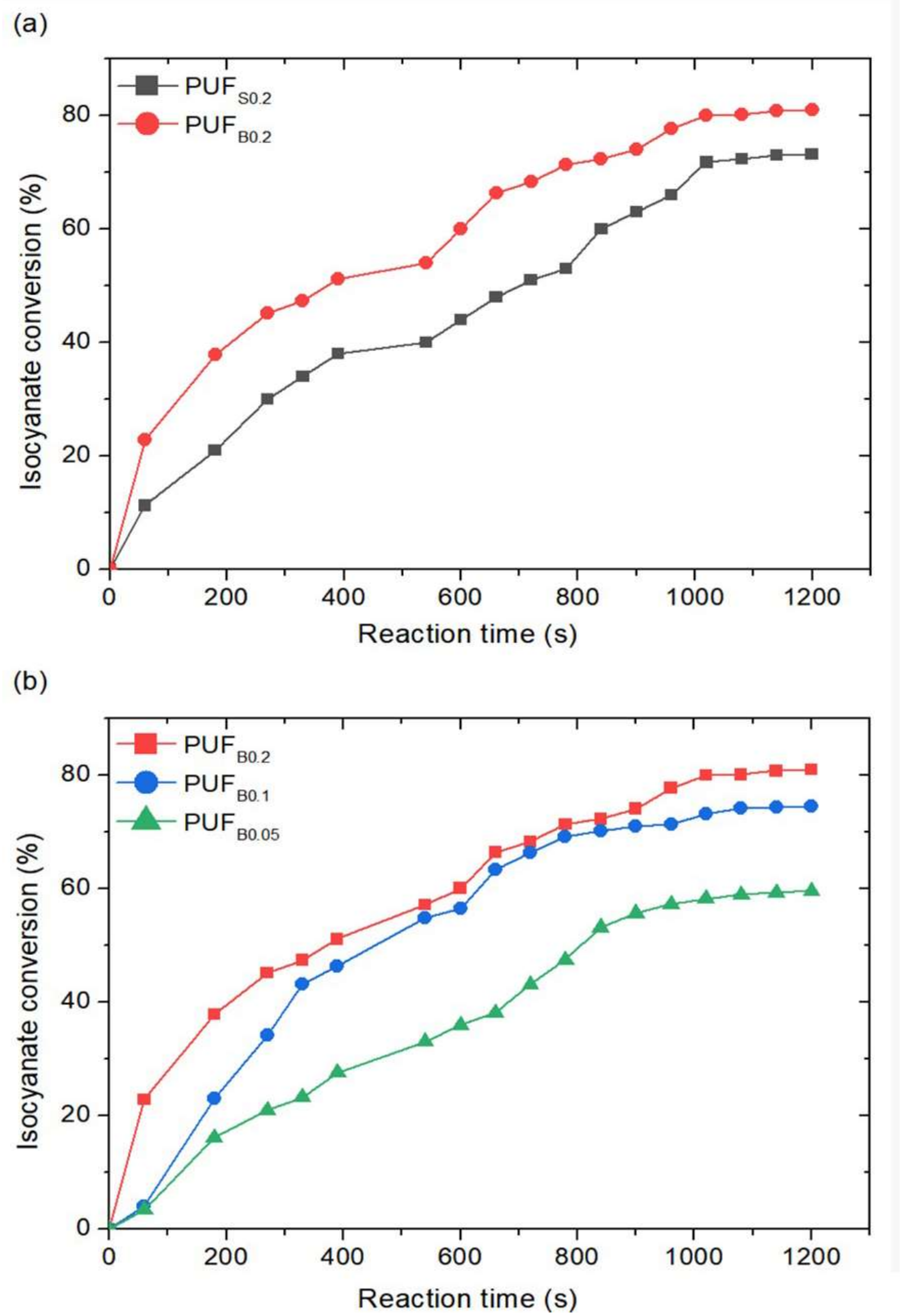

Figure 2.4: Isocyanate conversion with (a) similar concentrations of Bismuth Triflate and stannous octoate, and (b) different concentrations of Bismuth Triflate

Further analysis of the FTIR spectra analysed the carbonyl area, between 1650 and 1750 cm^{-1}, to identify the urethane compounds, formed in the gelling reaction, and the urea compounds, formed in the blowing reaction (Figure 2.5. a) [34,35]. The vibrations linked with the urea and urethane groups were identified after deconvolution of the carbonyl area. This procedure revealed the presence of free urethane (1721 - 1730 cm^{-1}), free urea (1710 cm^{-1}), monodentate urea (1664 cm^{-1}), and bidentate urea (1629 cm^{-1}). The formation of bidentate urea, or hydrogen-bonded urea, is considered as the onset of microphase separation (MST) of the segmented block copolymer and can be calculated from the bidentate urea absorbance normalised by the isocyanate conversion [32]. The MST of the samples occurred at a critical isocyanate conversion of approximately 0.33± 0.04, 0.44 ± 0.05, 0.31 ± 0.04 and 0.27 ± 0.04 for $PUF_{S0.2}$, $PUF_{B0.2}$, $PUF_{B0.1}$, and $PUF_{B0.05}$, respectively. These results are consistent with previous works for slabstock foams that reported critical isocyanate conversion in the range of 0.55 ± 0.0534, to 0.35 ± 0.0241 [36,37], except with the lower concentration of catalysts. The rapid MST of PUFB0.05 would result in an early vitrification of the polymer chains and cell opening [34], which is consistent with the observed cell sizes mentioned below. Additional analysis of the relative area percentages of urethane groups divided by the relative area percentages of urea groups provides information of both the blowing and gelling reaction [38]. Figure 2.6.b presents the urethane/urea ratio at different reaction times. The gelling/blowing reaction followed a similar trend in both tin and bismuth catalysed foams, with an inflection point at around 10 min, except for the foam with the lower concentration of bismuth catalyst. Such trend indicates that the blowing reaction dominates during the first 10 minutes, with more urea products produced, and, afterwards, it slows down. This inflection point has also been observed by Santiago-Calvo et al. [38].

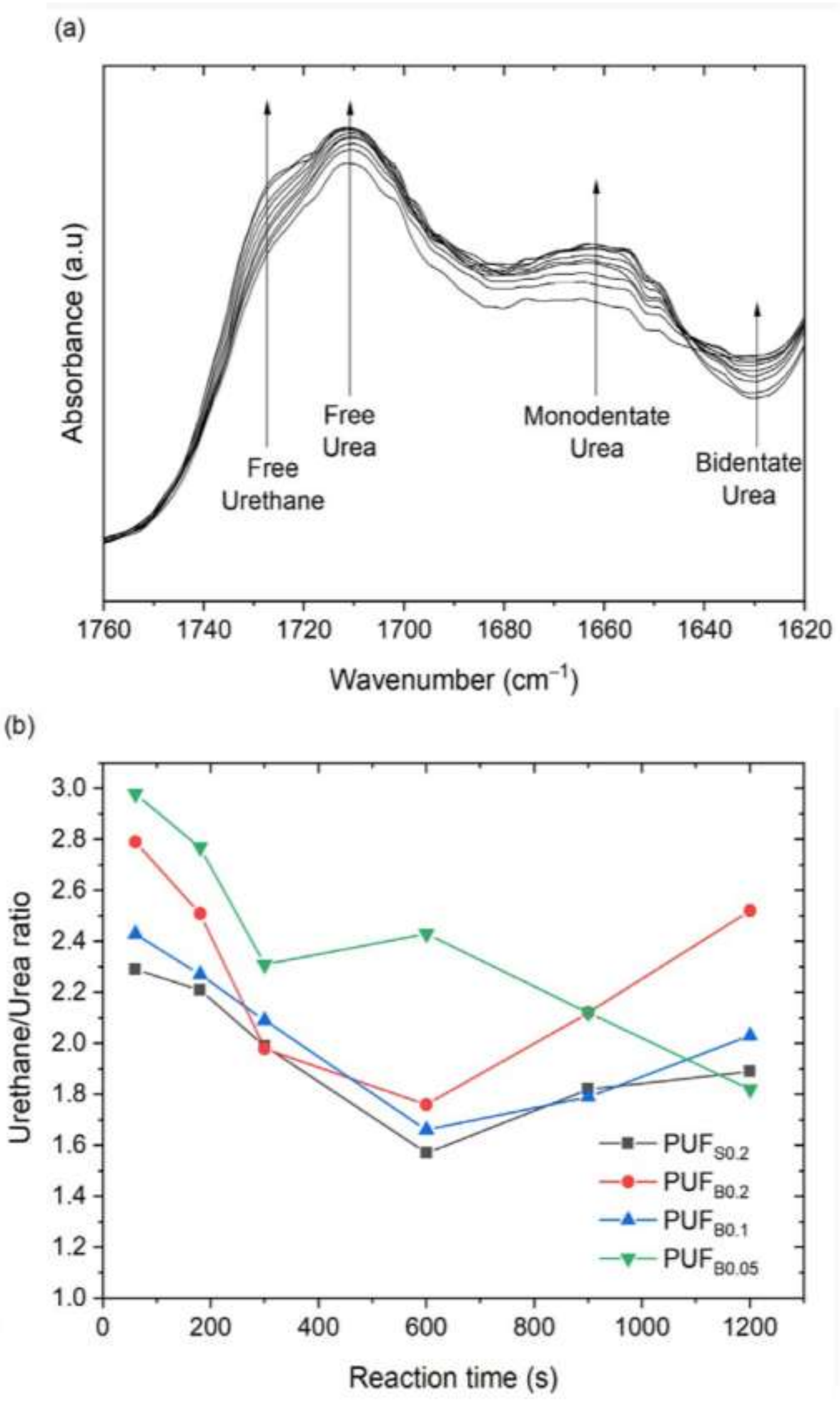

Figure 2.5: a) Infrared spectra collected at the initial stages of the reaction in the carbonyl region for PUFB0.2 sample. b) Urethane/urea ratios as a function of time

III.2. Morphological properties of PU foams

The foaming experiments reveal subtle differences in the foaming evolution. While cream and raising times of both bismuth and stannous catalysed foams were similar, around 12 s and 135 s, respectively, the final height of bismuth catalysed foam was slightly lower than the tin sample. This behaviour is also confirmed in the density differences of both types of foams (Table 2.2). Such selectivity towards the reaction between isocyanate and water is ascribed to the high solubility of Bismuth Triflate in water. SEM images of the cellular microstructure also confirm this result, as the tin-based foam has smaller cell sizes at equal catalyst content. The foams showed an open cell structure with cells elongated parallel to the foaming direction, which is consistent with free rise PU foaming (Figure 2.6). The average cells sizes (Table 2.2) are similar to those reported of foams with similar densities [39–41].

Table 2.2: Characteristics of the developed PU foams, density, average cell size and specific Young's Modulus

Sample	Apparent density (kg/m^3)	Average cell (µm)	Specific Young's modulus (kPa/kgm^{-3})
PUF$_{S0.2}$	35.6 ± 1.2	277± 83	0.42 ± 0.15
PUF$_{B0.2}$	28.2 ± 3.4	332± 97	0.40 ± 0.15
PUF$_{B0.1}$	35.8 ± 1.1	341± 99	0.61 ± 0.21
PUF$_{B0.05}$	40.2 ± 1.9	294± 86	1.09 ± 0.45

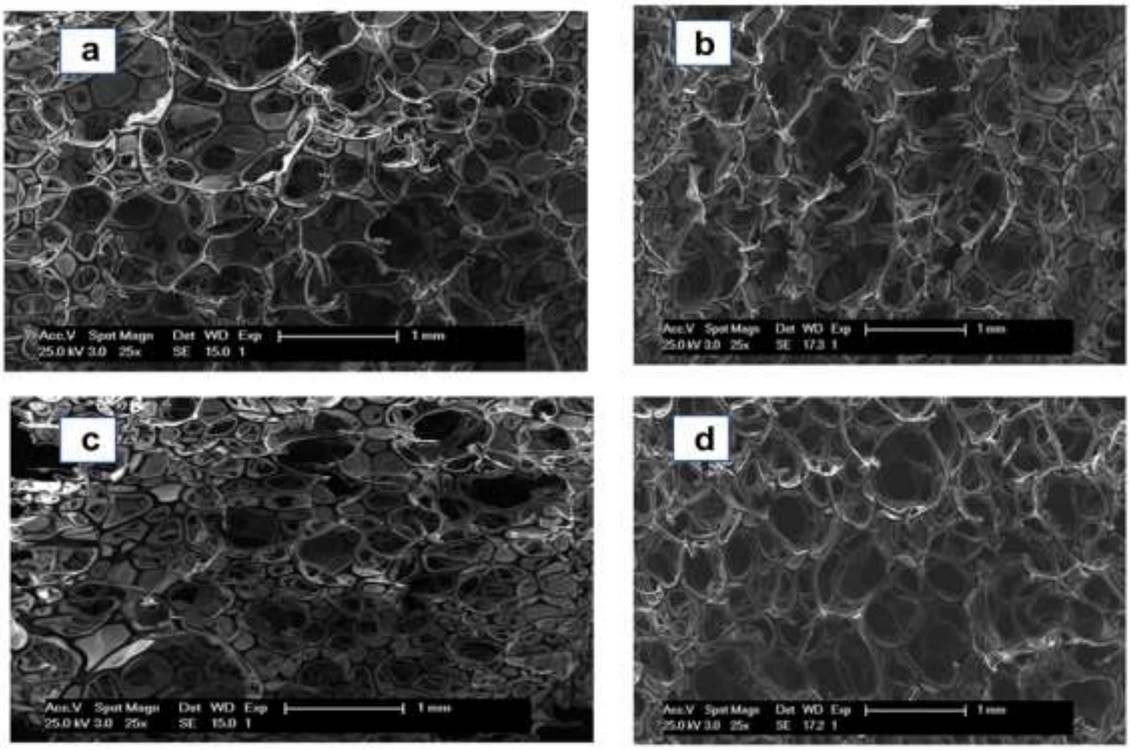

Figure 2.6: Representative SEM micrographs of catalysed with (a, parallel, and b, perpendicular) Bismuth Triflate with 0.2 php, and (c, parallel, and d, perpendicular) stannous octoate

III.3. Mechanical properties

The mechanical properties of the foams were studied in compression. Figure 2.7 shows the experimental stress-strain curves of PUF samples. All samples exhibit the typical behaviour of flexible polymeric foams, with a short linear region, related to cell wall bending and stretching, followed by a plateau, resulting from the collapse or cell wall buckling of the foam, and the densification region, which occurs at larger strains, where the foam begins to collapse [42]. The Young’s moduli were normalized by the density of the foam to compare the mechanical properties of the foams (Table 2.2), following the Gibson and Ashby theory. Comparing the samples with similar densities, bismuth-catalysed foams present better mechanical behaviour than the tin-catalysed sample. The higher modulus of the lower concentration of the bismuth catalysed foam is ascribed to the observed differences in the foaming behaviour and the cellular structure [42].

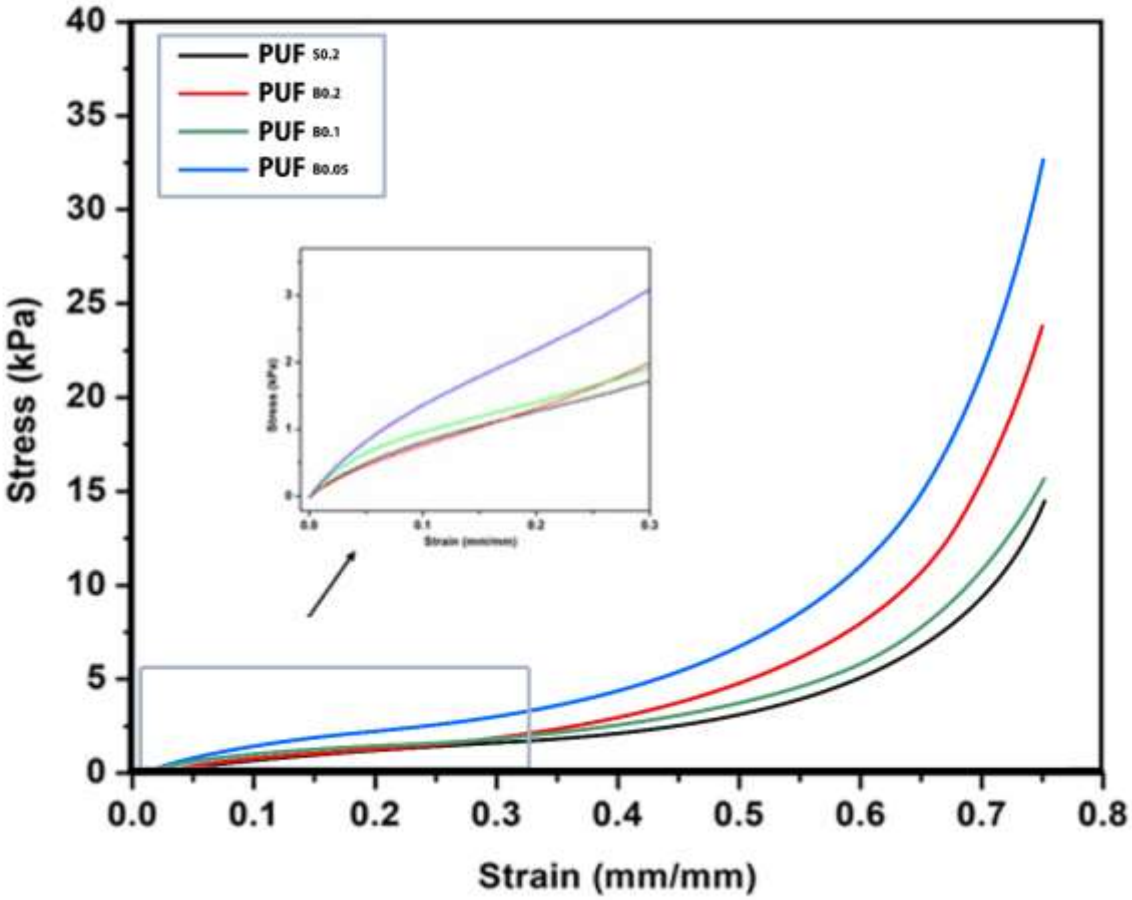

Figure 2.7: Average stress-strain curves of PUF by Bismuth Triflate and stannous octoate

III.4. Thermal properties:

The thermal degradation of PU is an heterogenous process resulting from several partial decomposition reactions [43], which presents two main steps: the first one is due to the degradation of the hard segments, resulting in the formation of isocyanate and alcohol, primary or secondary amine and olefin, and carbon dioxide, and the second step is the decomposition of the soft segments [44,45]. Figure 2.8 presents the TGA profile of the foams with both bismuth and stannous catalysts and the thermal stability data is reported in Table 3. Both foams present an almost identical behaviour of the weight loss with only small differences in their thermal stability. The samples show two main decomposition characteristic of PU systems, with the degradation of the hard segments occurring in two stages between 200 and 300 °C, and the chain scission of the polyol taking place at higher temperatures (377 and 387 °C) [46,47]. PU decomposition depends on the structure and three-dimensional arrangement of the soft segments [43,48]. Thus, the degradation behaviour suggests differences in the soft segments of the samples catalysed by bismuth and stannous. Finally, the maximum degradation temperatures of each step together with the temperature at 50 % of weight loss (Table 2.3) present similar values with the concentration of Bismuth Triflate with a slight reduction on the thermal stability behaviour with 0.05 php.

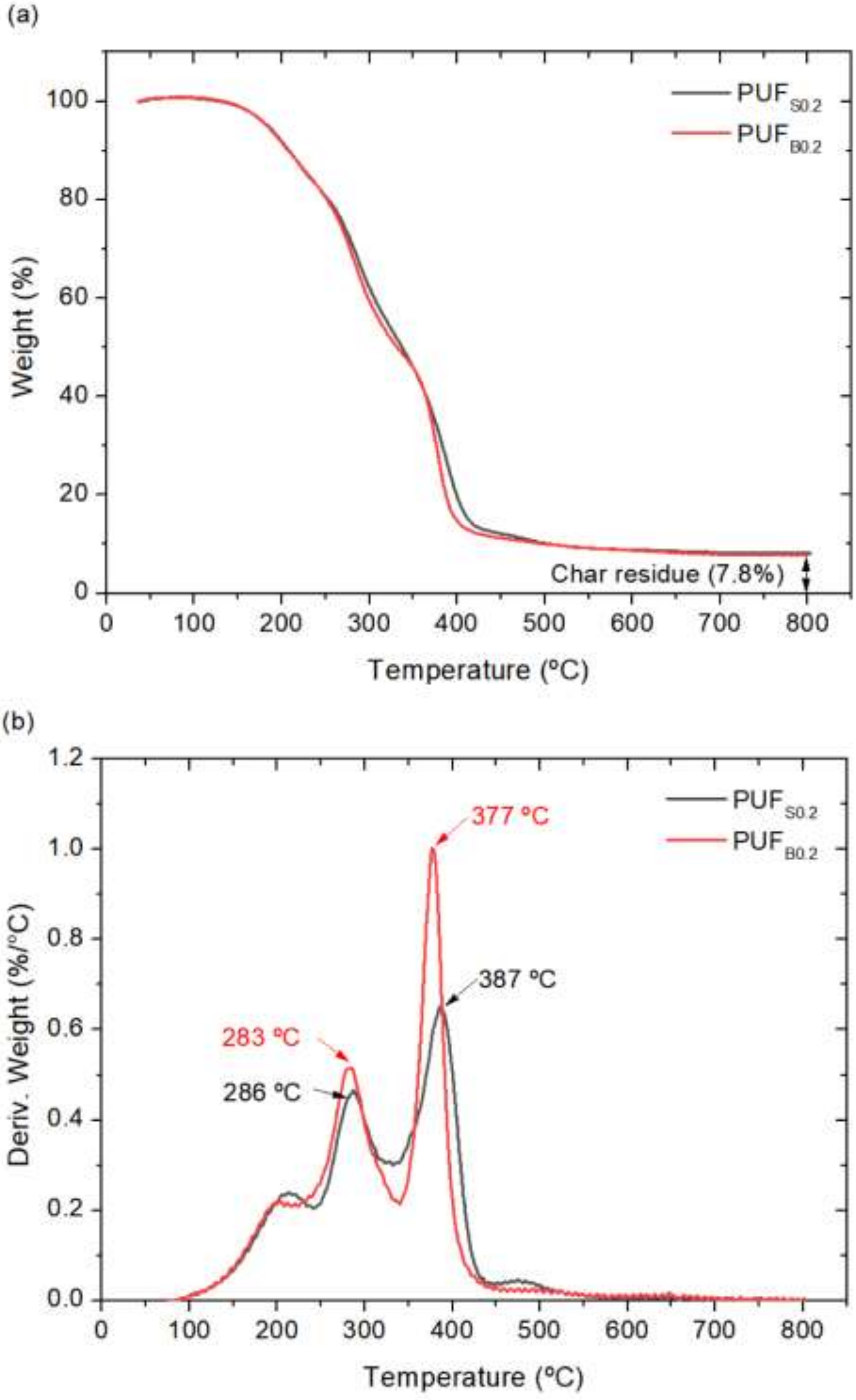

Figure 2.8: (a) TGA and (b) DTG curves of the PUF prepared with Bismuth Triflate and stannous octoate

Table 2.3: Different parameters of thermal stability of PUF prepared with different quantities of Bismuth Triflate

	5 % weight loss (°C)	50% weight loss (°C)	Residue (%)	T_{max1} (°C)	T_{max2} (°C)
$PUF_{S0.2}$	184.3	332.5	7.8	286	387
$PUF_{B0.2}$	184	330	7.8	283	378
$PUF_{B0.1}$	185	337	7.8	290	384
$PUF_{B0.05}$	179	325	6.4	270	347

Figure 2.9 shows the DSC curves of the PUF. All curves present only one glass transition temperature (T_g) around –59 °C, associated to the soft segments. The glass transition of the hard segments was not detected due to its small heat capacity change [49,50]. Both bismuth and tin catalysed foams present similar T_g values, considering the standard deviations, and no significant changes are either observed in the specific heat capacity (ΔC_p). Therefore, both catalysts promote similar structure, suggesting similar hard segment content. Furthermore, even the foam with the lowest amount of bismuth catalyst presents a similar thermogram compared to those with high amounts, which is ascribed to the high Lewis acidity effect of the Bismuth Triflate that would enable the development of foams with low quantities of catalyst.

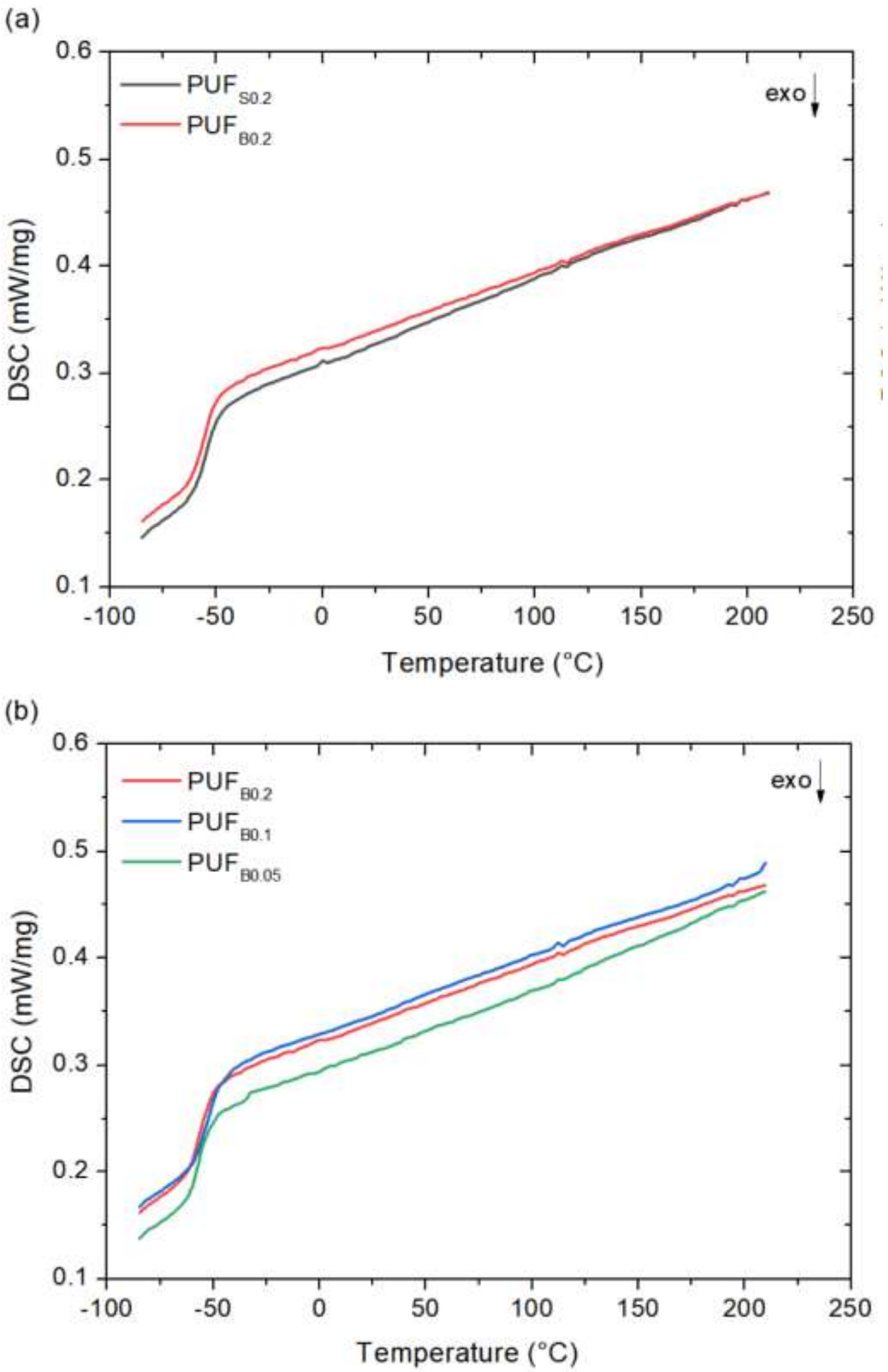

Figure 2.9: The DSC thermographs of (a) Bismuth Triflate and stannous octoate, and (b) with different amounts of Bismuth Triflate

IV. Conclusion

In this chapter, we synthesized flexible PUFs with an environmentally friendly, non toxic bismuth catalyst instead of the classical toxic stannous catalyst. The thermal stability remained almost the same for the different foams, while the mechanical properties were slightly improved compared to the stannous octoate foamed sample. The high solubility of Bismuth Triflate in water, together with its high Lewis acidity, has been shown to benefit the production of PU foams. The optimal concentration of Bismuth Triflate catalyst used is B0.2 because for most of the studies on foam properties, this concentration remains the most effective for obtaining a good flexible Polyurethane foam. Therefore, this study paves the way to show the potential of Bismuth Triflate as an alternative of toxic stannous catalysts for manufacturing PUF. However, despite using the non-toxic $Bi(OTf)_3$ catalyst for preparing PUs, the problem of using toxic isocyanate derivatives as monomers for their preparation still needs to be overcome. Thus, the next chapter will be made on a study of the preparation of thermoplastic films of non-isocyanate polyurethane in which an attempt has been made to develop a process of preparation of NIPU with the help of cyclic carbonate intermediate, which is prepared by commercial epoxy resin.

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Chapter 3: Synthesis of novel thermoplastic non isocyanate polyurethane composites

Part of the work described in this chapter has been published in Polymers. 2021, Polymers 14 (19), 3934

I. Introduction.

The increasing regulations in toxic or hazardous chemicals are driving the search for new synthetic routes to everyday materials. Among them, polyurethanes (PUs) are of particular interest for their uses as elastomer, adhesives, coatings, and foams [1]. Commonly, PUs are prepared by a polyaddition reaction of polyols and isocyanates. Isocyanates are highly toxic and cause global warming and health risks as they are obtained from amine and phosgene [2]. Therefore, research on non-isocyanate polyurethanes (NIPUs) is increasing as one of the most efficient, environmentally friendly, and applicable approaches [3].

One of the most attractive NIPU routes is the cyclic carbonate aminolysis resulting in poly(hydroxyurethane) (PHU) derivatives [2, 4–6]. PHUs are mostly synthesized from the reaction of a bis-amine with a bi-cyclic carbonate, which in turn is produced from the cyclocarbonation of a bis-epoxide with carbon dioxide (CO_2) [7–9]. A drawback of PUs is the high density of hydrogen bonds and the presence of side reactions that limits the production of high-molar mass PHUs with good mechanical properties. Thus, hybrid PHUs have been proposed to overcome these problems, ranging from copolymerization or prepolymer strategies to the preparation of composites [10, 11].

Studies of PHU nanocomposites are still scarce, but they have already shown improved thermal and mechanical properties, adhesion performances, and shape memory [10]. Although the main used fillers for PHU nanocomposites have been zero-dimensional nanoparticles (silica [12–14], polyhedral oligomeric silsesquioxanes [15], ZnO [16], and Fe_3O_4 [17]), one-dimensional nanomaterial (particularly carbon nanotubes [18, 19] and nanocellulose [20]), and two-dimensional nanomaterials (nanoclay [21, 22] and graphene [23, 24]), have also been studied. Here, we investigate the incorporation of functionalised hexagonal boron nitride (f-BN) into PHU to provide high mechanical and thermal properties. Indeed, BN nanomaterials have high Young's modulus (0.8 TPa), superior fracture strength (165 GPa), high thermal stability (up to 800 °C in the air), and outstanding thermal conductivity (300–2000 $Wm^{-1} K^{-1}$) [25–27]. Unlike graphene, BN nanomaterial is a dielectric material due to the wide bandgap (~5.6 eV) with a dielectric constant (4 ~ 8). Furthermore, nanoparticle functionalisation provides greater improvements than its non-functionalised counterparts [10]. Thus, we use a sugar-assisted mechanochemical exfoliation (SAMCE) process to ensure an improved dispersion of the filler and a covalent bond between the matrix and the filler [27]. SAMCE is an efficient, green, and low-cost process that introduces sucrose moieties and hydroxyl and amine (-OH and -NHx) groups. These PHU/f-BN nanocomposites are then characterized by means of thermal and dynamic mechanical analysis.

In this chapter, several rations of h-BN were used to prepare non-isocyanate polyurethane films, and mechanical, thermal, morphological, and chemical studies were carried out to evaluate the different products obtained in this study.

VI. Materials and Methods

I.1. Materials

Epoxy resin, EPIKOTE resin MGS RIMR135 (Bisphenol-A-(epichlorohydrin); epoxy resin (number average molecular weight ≤ 700) - 1,6-bis(2,3-epoxypropoxy) hexane), was purchased from Hexion. Tetrabutylammonium bromide (TBAB) was supplied by Sigma Aldrich and used as a catalyst for the cycloaddition of carbon dioxide (CO_2) and transfer agent for the epoxidation reaction. 1,3-diaminopropane was purchased from Merck. 1,8-Diazabicyclo[5.4.0]undec-7-ene (DBU) and hexagonal boron nitride (particle size ~ 1 µm) were acquired from Sigma Aldrich. H-Boron nitride was functionalized with commercial sugar to enhance mechanical properties.

I.2. Characterization of Bi-cyclic carbonate and PHU films

The kinetics of bi-cyclic carbonate formation were monitored by Fourier transform infrared spectroscopy (FTIR). The FTIR spectra were recorded using a PerkinElmer Spectrum One. FTIR spectrometer was fitted with an attenuated total reflectance (ATR) accessory under unforced conditions. The reactive mixture was placed in direct contact with the diamond crystal each hour. Infrared spectra for PHU films were collected in the range from 450 to 4000 cm^{-1} with a resolution of 4 cm^{-1} and co-adding 4 scans per spectrum.

Raman spectroscopy was performed on a Renishaw 2000 Confocal Raman Microprobe using a 514.5 nm argon ion laser and 0.02 cm^{-1} resolution. The spectra were recorded from 750 to 3500 cm^{-1}.

Thermogravimetric analysis was carried out using a TA-Q500. Samples of 10 mg were placed on platinum dishes and heated under a nitrogen atmosphere (flow rate 90 mL/min) from room temperature to 800 °C at 10 °C/min. The results were analysed in TA instruments Universal analysis.

Dynamic mechanical analysis was performed on a DMA Q800, TA Instruments. Temperature sweeps from −100 °C to 70 °C, heating rate of 2 °C/min were performed in tension mode with an amplitude of 15 µm and a frequency of 1 Hz. The glass transition was recorded from the maximum of the damping factor, tan δ.

Glass transition temperature (T_g) was measured on a differential scanning calorimetry (NETZSH DSC- 214 model), in the temperature range from -50 to 120 °C, and at heating rate of 10 °C/min under nitrogen atmosphere. The stability of baseline was checked before each measurement

I.3. Preparation of Bi-cyclic carbonate, h-BN functionalised and PHU films

- Preparation of bi-cyclic carbonate

Typically, a commercial epoxide (70 g) was added to a 250 mL glass flask using TBAB (3.5 g) as a catalyst and CO_2 gas is bubbled into the glass flask under atmospheric pressure and equilibrated at 105 °C, without the use of an autoclave. Vacuum distillation was used to separate the pure cyclic carbonates when the reaction was completed. The conversion of epoxides to cyclic carbonate was followed kinetically through Fourier transform infrared (FTIR) analysis to optimise the reaction conditions and therefore to obtain a high conversion rate in short reaction time.

- Functionalization of hexagonal boron nitride

Hexagonal boron nitride sheets (h-BN) were simultaneously exfoliated and functionalised by a typical sugar-assisted mechanochemical exfoliation (SAMCE) process [26]. Raw h-BN (2 g), sucrose crystals (10 g), and steel balls with diameters of 10 mm were cryo-grinded for 1 h (number of cycles = 20, grinding time = 2 min, intermediate cooling time = 1 min) in a Cryomill (Retsch, Hann, Germany). The milled mixture was washed with 200 mL deionized water and filtered through a Teflon membrane (0.2 µm pore size) under vacuum. This process was repeated 4 times to thoroughly remove free sucrose and obtained the f-BN.

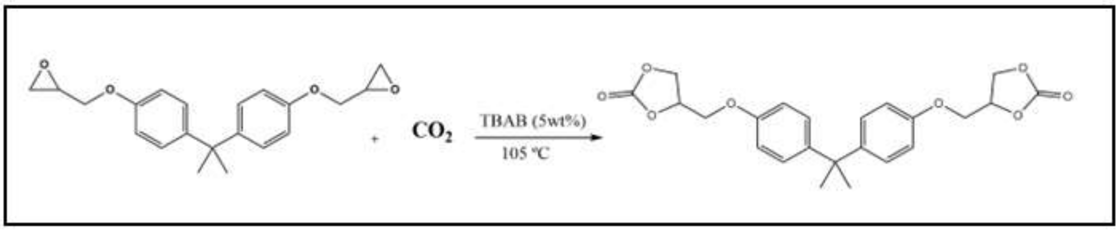
- Preparation of PHU films and nanocomposites

PHU films were produced from the reaction of the bi-cyclic carbonate, diaminopropane and DBU. The bi-cyclic carbonate (5.0 g) was added into a beaker followed by the diaminopropane (2.5 g) and the DBU (0.25 g) and blended manually. They were then vacuum degassed for 5 min and poured in a Teflon mould. Finally, the mixture is introduced in an oven at 95 ºC for 12 h. PHU/f-BN films were prepared by first solubilising the nanofiller in THF (5 mg/mL), which was added to the bi-cyclic carbonate and diaminopropane mixture prior to the inclusion of the DBU.

II. Result and discussion

II.1. Synthesis of bi-cyclic five-membered carbonate

The bi-cyclic carbonate was prepared by a reaction of commercially available epoxide and CO_2. Typically, the reaction was carried out in glass flask using TBAB as a catalyst and CO_2 gas under atmospheric pressure. The mechanism for this reaction has already been reported and is described by the ring opening of the epoxide by the bromide ion.



Scheme 3.1: Synthesis of bi-cyclic carbonate with CO2 at atmospheric pressure

FTIR analysis reveals that the conversion is almost complete after a reaction time of 4 h (Figure 3.1), from the progressive disappearance of the characteristic epoxide band at 910 cm^{-1} and the increase of the carbonyl band of the formed cyclic carbonate at 1793 cm^{-1}. Under normal pressure, the yield of the coupling of CO_2 with epoxides to cyclic carbonates after 4 h of reaction reached 82.3 % by using tetrabutylammonium bromide (TBAB) as catalyst. Further synthesis experiment carried out for a longer reaction time, 24 hours, led to a yield not exceeding 83 %. This result is comparable to previously reported works [28–30] and indicates the high activity of TBAB compared to various heterogeneous catalysts, such as Mg-Al mixed oxides [31], smectites [32], iron-based composite [33] that have shown yields between 41 % and 75 %.

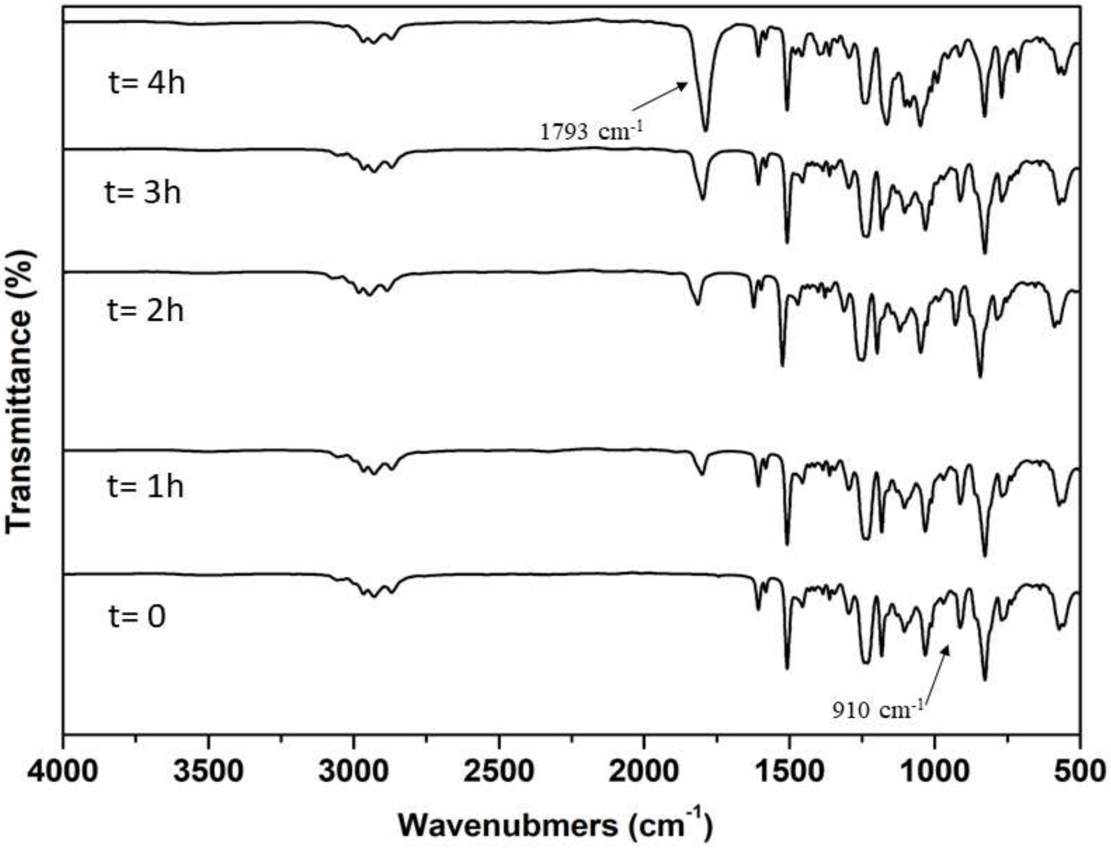


Figure 3.1: ATR-FTIR spectra of different time for the synthesis of cyclic carbonate from commercial epoxy

II.2. Functionalisation of boron nitride

Sugar assisted mechanochemical exfoliation (SAMCE) technique [27] leads to the simultaneous exfoliation and functionalisation of hexagonal boron nitride sheets. Functionalised BN (f-BN) particles present a good and stable dispersion in water and THF at concentrations up to 25.0 mg g^{-1} (Figure 3.2a). FTIR spectra of the h-BN and f-BN (Figure 3.2b) show the presence of B-N bending (≈750 cm^{-1}) and stretching (≈1320 cm^{-1}) peaks and of additional peaks of hydroxyl, amine and multiple peaks in the region of 1300–800 cm^{-1} for sugar molecules. Raman spectra of the h-BN and f-BN also suggested that the crystal and phase structures are retained after mechanochemical exfoliation (Figure 3.2c). Similar results were reported by Chen et al. [27] that suggested that ball milling in the presence of sucrose crystals cleaved the h-BN platelets into small thin flakes with active N and B edges and stabilised surfaces, all covered by sucrose molecules.

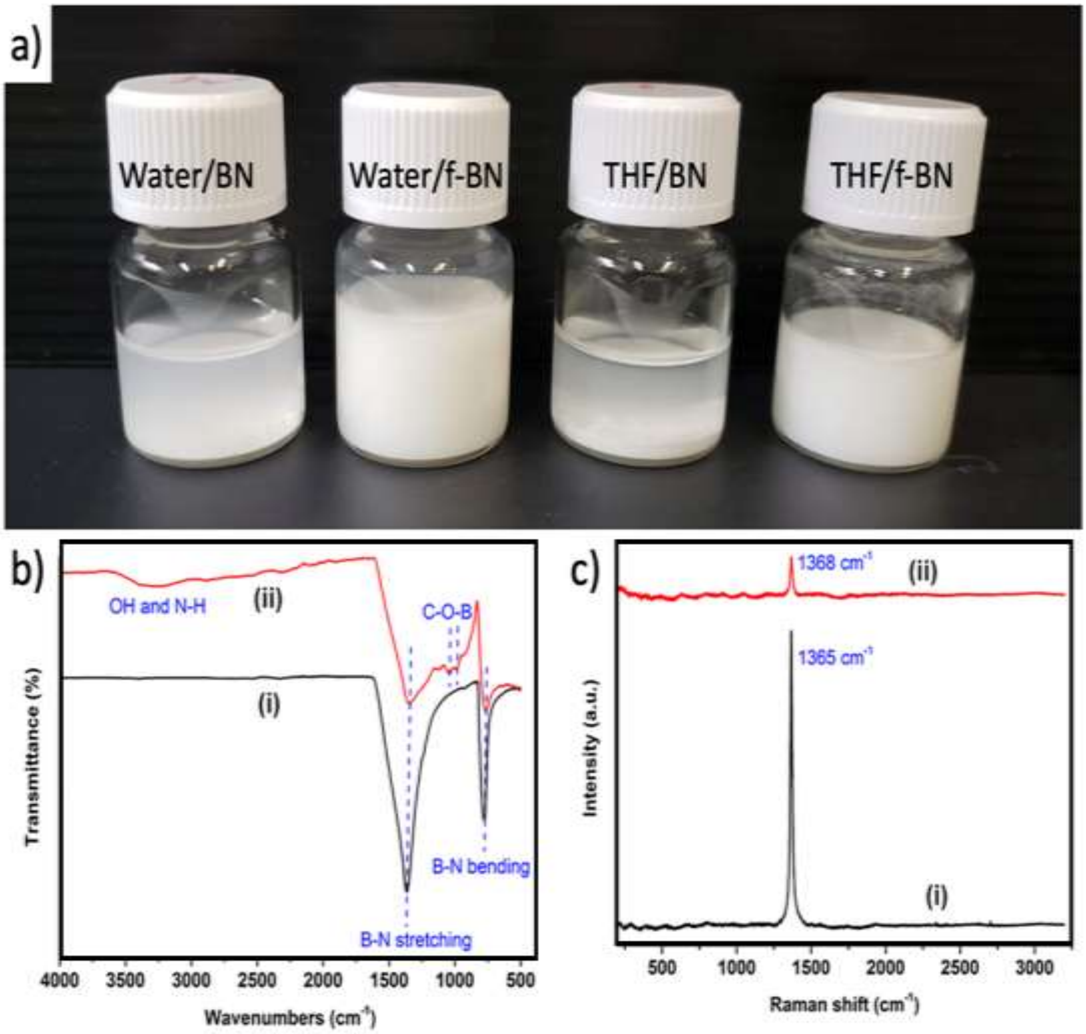


Figure 3.2: a) Dispersion of h-BN and functionalised BN in water and THF. b) ATR-FTIR and c) Raman of the i) h-BN and ii) functionalised BN

II.3. Nanocomposites PHU films

After the synthesis of bi-cyclic carbonate using epoxy resin and CO_2 and the functionalisation of hexagonal boron nitride, PHU thermoplastic films were prepared using 3 different weight percentages of functionalised h-BN (1, 2 and 3 %). The obtained nanocomposites films were studied using different characterisation methods: ATR-FTIR, TGA, DMA and DSC.

The ATR-FTIR analysis was performed to check the conversion of carbonate groups of bi-cyclic carbonate to PHU. Figure 3.3 shows the overlaid infrared spectra of all films made without and with various percentages of functionalized boron nitride. All the films have comparable spectra. Indeed, in the spectra of PHU and PHU/f-BN we observe the total absence of the peaks related to the carbonyl group of the cyclic carbonate, at 1793 cm^{-1}, indicating its complete conversion into urethane which is evidenced by the presence of the stretching of the C=O group of the urethane band at 1645 cm^{-1}. Between 3200 and 3600 cm^{-1}, a broad band is observed, indicating the presence of NH groups of the urethane functions and the hydroxyl groups resulting from the opening of the cyclic carbonate by the amine functions.

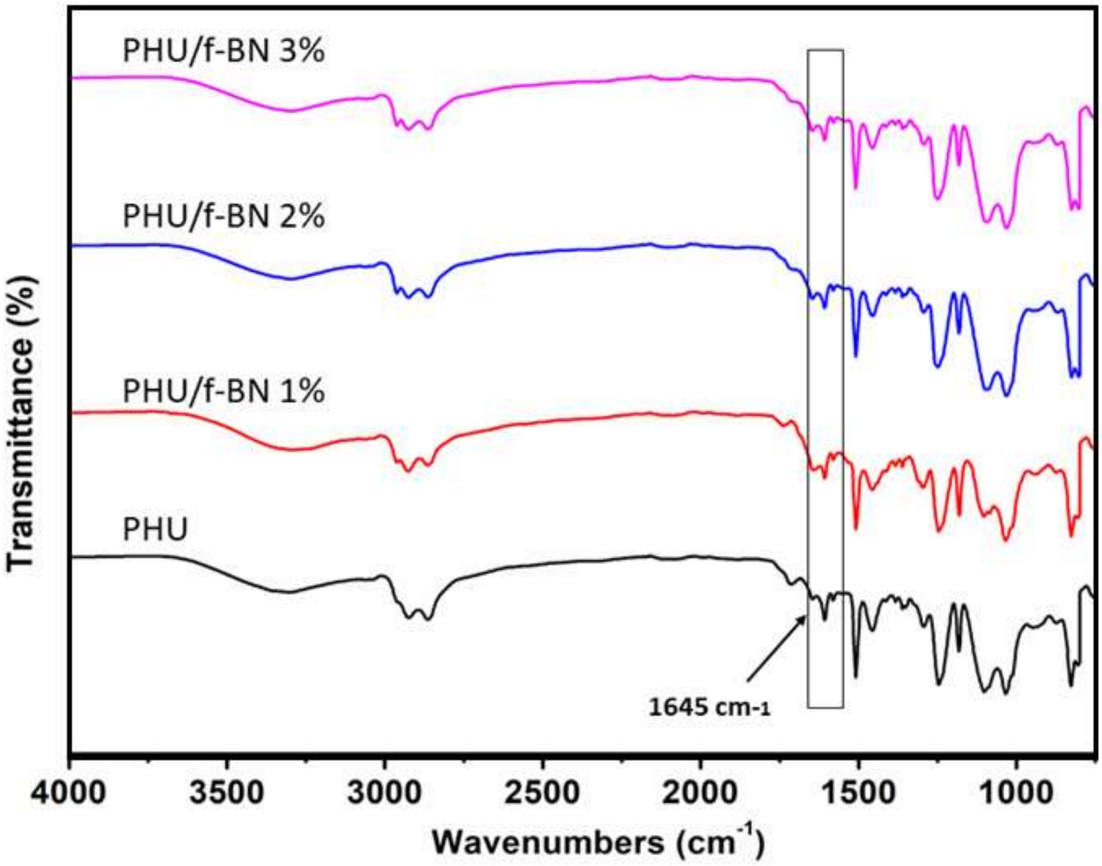


Figure 3.3: ATR-FTIR of different PHU films

II.4. Thermal properties

Thermogravimetric analysis was used to determine the thermal stability of the various nanocomposite films of PHUs compared to neat PHU. As shown by Figure 3.4, unfilled PHU sample degrades within the range 250 °C - 450 °C, with the maximum degradation rate occurring at 350 °C (Table 1). The degradation presents an initial weight loss between

100 °C and 150 °C prior to the major degradation step, which could be ascribed to the evaporation of absorbed moisture or of residual monomers [34,35]. Thermal degradation of PHUs has been reported over a wide temperature range from as low as 180 °C up to 388 °C depending on the size of the aromatic part. Thus, the synthesised PHU presents good thermal stability, which lies well within the values of conventional PU [36]. The main decomposition of PHU has been ascribed to the dissociation of the urethane bond [35]. The addition of f-BN does not modify the degradation kinetics [25] but improves the thermal stability of PHU in approximately 20 °C, increasing the maximum degradation rate temperature range to 370 °C for the 3 wt.% f-BN (Table 3.1). This effect is widely reported in the literature with improvements of up to 350 °C in PU composites filled with BN particles [25,37].

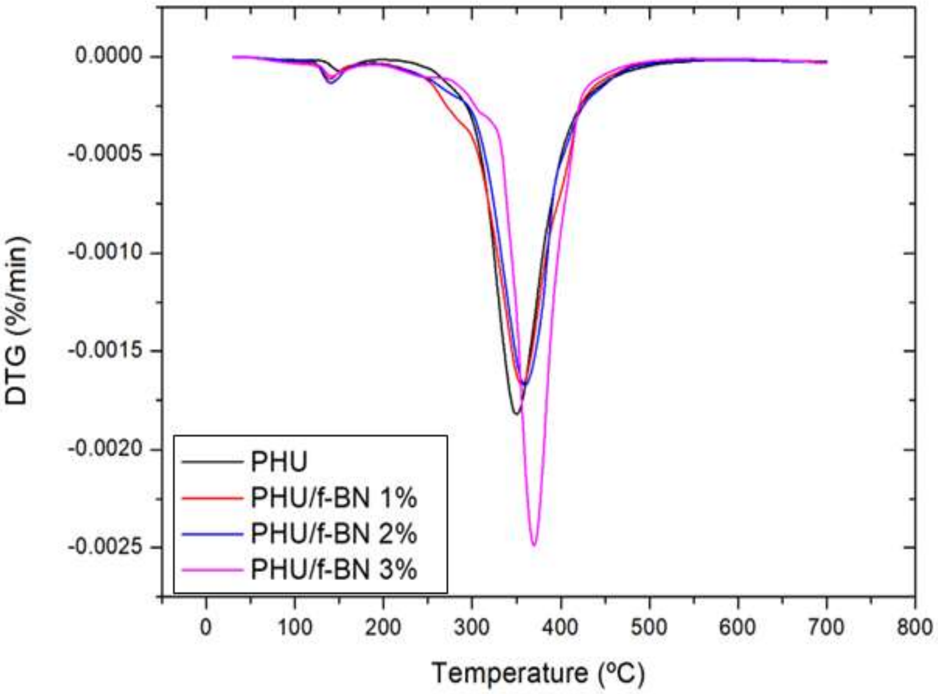


Figure 3.4: Thermogravimetric analysis (TGA) curves of different thermoplastic PHU films

II.5. Thermomechanical properties

The thermomechanical characteristics of nanocomposites PHU films were studied using DMA. Figure 3.5 shows the storage modulus (E’) and loss factor (tan d) as a function of temperature for all PHU films. At temperatures above T_g, E' increases with f-BN content from 7.8 MPa for the PHU film up to 11.6 MPa for the PHU/f-BN 3 % (Table 3.1). The presence of f-BN restricts the mobility of the rubber chains, increasing the stiffness of the polymer [23,38,39]. It is well known that the E' of a filled polymer composite is influenced by the effective interfacial interaction between the polymer matrix and the filler particles. In general, a strong interfacial interaction results in a high E' [40]. Meanwhile, the tan δ (Figure 3.5) shows a shift of the T_g from 31.7 ºC up to 49.3 ºC with increasing f-BN content (Table 3.1) indicative of a reduction of the molecular chain mobility. Furthermore, broad glass-to-rubber transition are commonly attributed to the presence of a large distribution in the molecular weight between cross-links or some other type of heterogeneity in the network structure [41]. Thus, the presence of f-BN appears to increase not only the cross-link density but also the homogeneity of the network structure. Similar shifts in T_g have been reported in PHU filled with CNTs [19], polyhedral oligomeric silsesquioxanes (POSS) [15], and graphenated ceramic fillers [23].

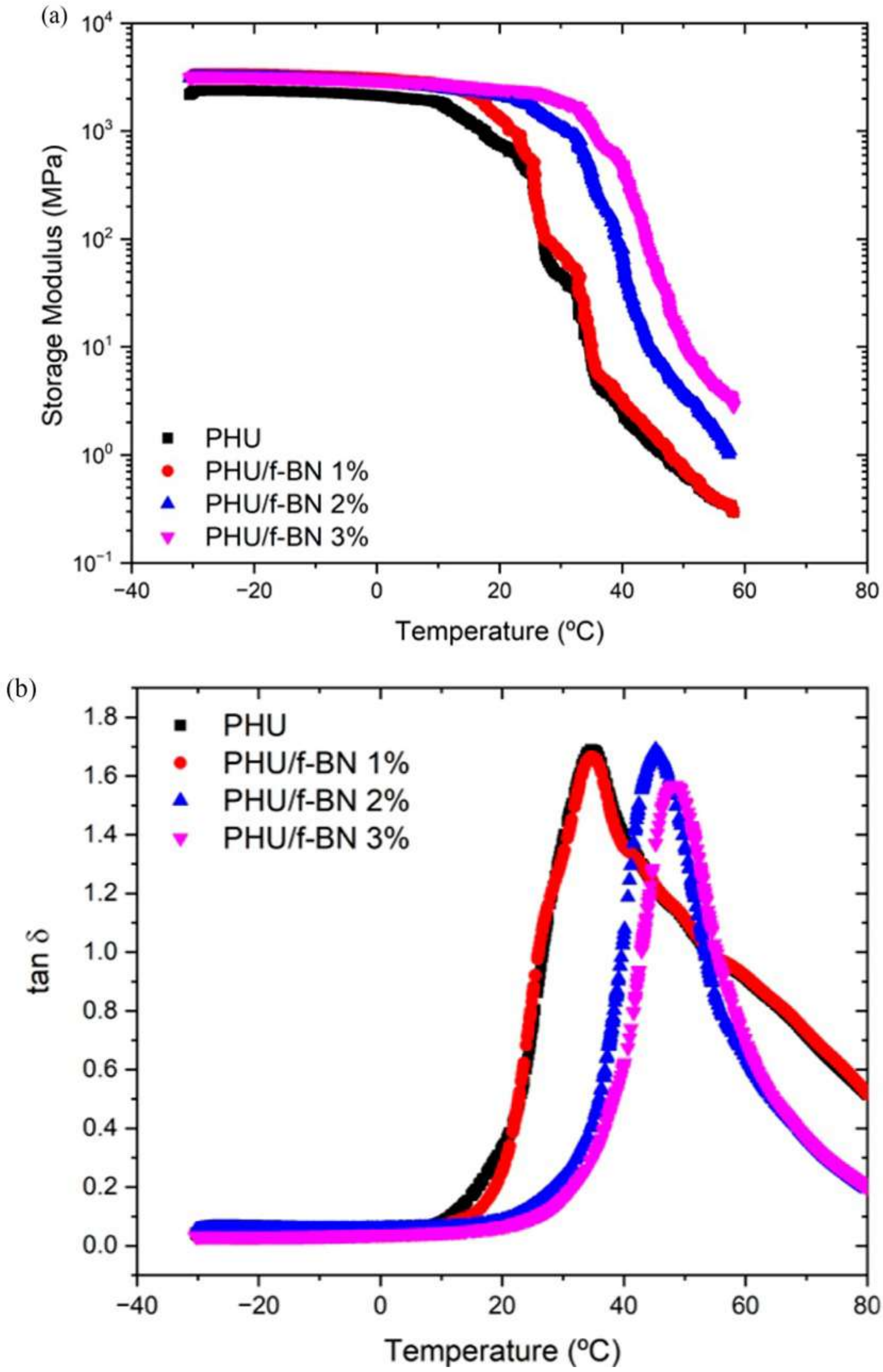


Figure 3.5: Storage modulus and damping factor of the PHUs films

The DSC curves of PHU films show comparable patterns with no melting of a crystalline phase during the second heating, suggesting that all systems are amorphous (Figure 3.6). The films with different percentages of f-BN present moderate to strong shifts in the glass transition temperatures (Table 3.1), corroborating the DMA results. As discussed previously, the shift is ascribed to both the presence of the f-BN restricting the segmental motion and cross-linking of the molecular network [17] ascribed to intramolecular hydrogen bonding between the functional groups, i.e. hydroxyl, ethers, carbonyl, and the urethane bonds [41].

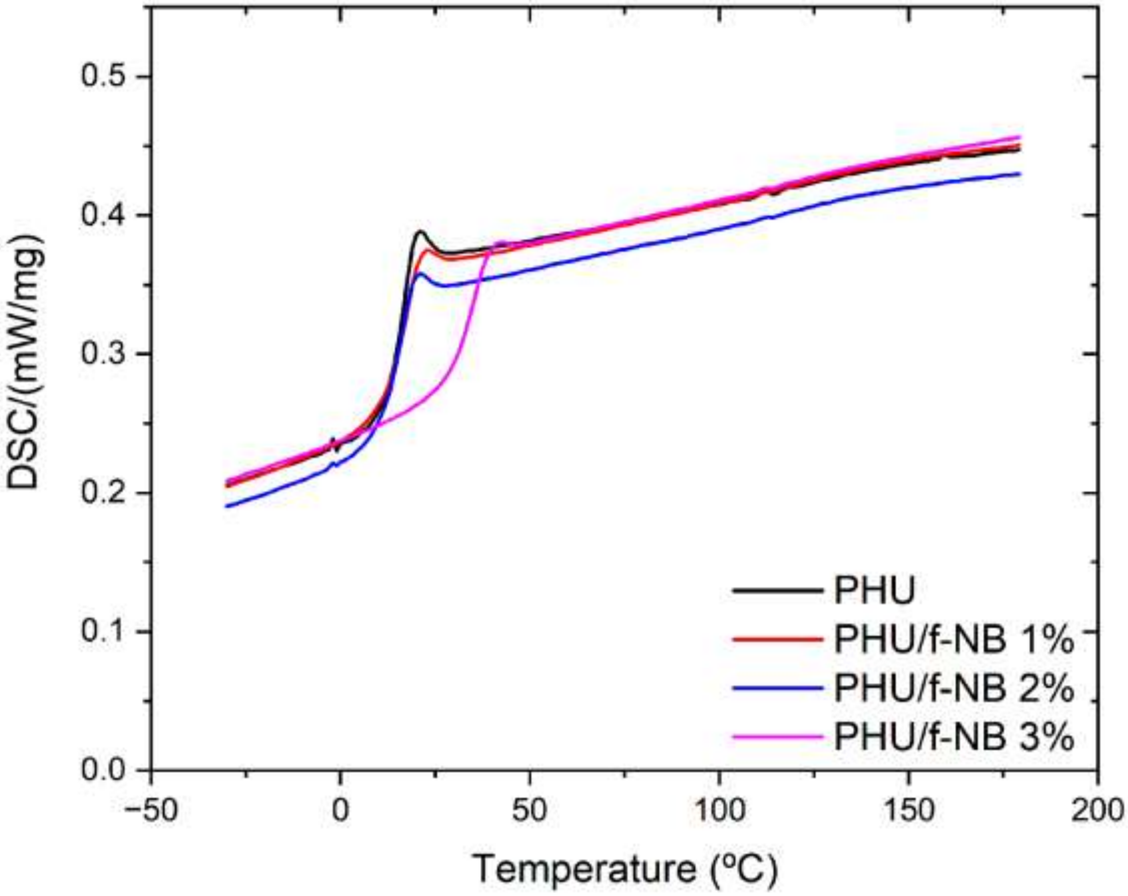


Figure 3.6: Differential scanning calorimetry (DSC) curves of all PHUs films

II.6. Morphology of PHU films

SEM images of PHU and PHU/f-BN composites are shown in Figure 3.7. Micrographs of the composites show no phase separation and agglomeration of f-BN, indicating the nanoparticles are well dispersed in the polymer matrix.

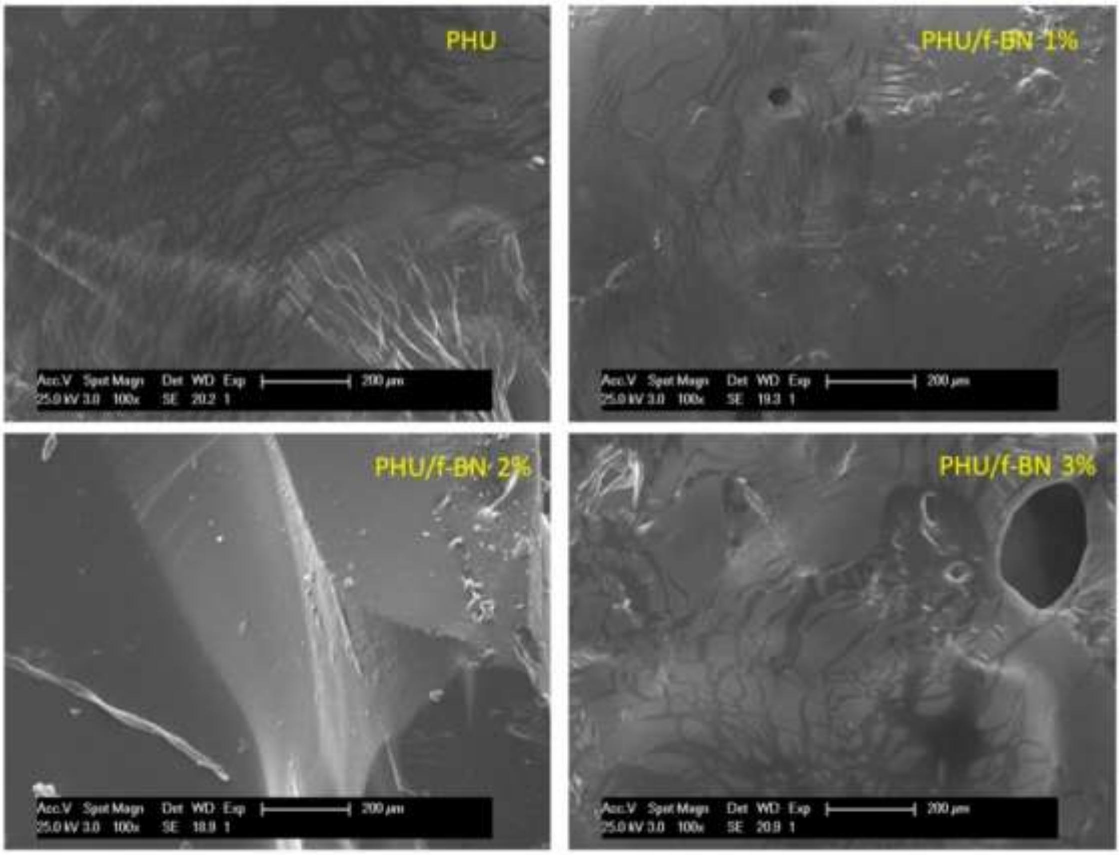


Figure 3.7: SEM images of PHU polymer and PHU/f-BN composites

Table 3.1: Different parameters of all PHU films

	T_d(ºC)*	T_g (ºC)**	T_α (ºC)***	E' (MPa)***
PHU	350	18.5	31.7	7.8
PHU/f-BN 1 %	356	19.1	31.8	8.1
PHU/f-BN 2 %	360	19.8	42.5	9.8
PHU/f-BN 3 %	370	29.2	49.3	11.6

T_d: Temperature at maximum degradation rate, E’: storage modulus at T in rubbery region, *Measured by TGA, **Measured by DSC, ***Measured by DMA

III. Conclusion

In this chapter, we have explored the synthesis of cyclic carbonate monomer and its polymerization to polyhydroxyurethane (PHU). Furthermore, we demonstrated that the use of functionalized boron nitrate is as a strategy to improve the thermal and mechanical properties of the matrix (PHU). The optimized synthesis route could be an industrially scalable process under atmospheric pressure and mild conditions, for obtaining PHU with properties comparable to those of conventional PU with high yield. Using a solvent-free, mechanochemical process provides a clean methodology to functionalise and exfoliate hexagonal boron nitrate with hydroxyl and amine groups, improving its interaction with the polymer chains. Additionally, the inclusion of f-BN appears to reduce the heterogeneity of the network, improving the thermal and mechanical properties in terms of the thermal degradation temperature, glass transition temperature and modulus. Therefore, the developed PHU composites are an efficient, environmentally friendly, and industrially scalable material that can be a suitable alternative to polyurethanes.

The preparation of thermoplastic films of non-isocyanate polyurethane allowed us to study the chemical, thermal, morphological, and mechanical properties of the obtained composites. The success of the preparation reaction of bi-cyclic carbonate using TBAB as a catalyst and atmospheric pressure as reaction conditions was also evaluated. Next, we developed foams using thiolated monomers (tri and tetrathiol) to facilitate the S-alkylation reaction that generates CO2 and creates the hydroxythioether bond. The upcoming chapter focuses on the synthesis of poly(hydroxythioether) foams, which are considered an alternative to non-isocyanate polyurethane foams.

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Chapter 4: Preparation of poly (hydroxy thioether) foams

Part of the work described in this chapter has been published in European Polymer Journal. 2023, 189,111960

I. Introduction

Foams, particularly polyurethane (PU) foams, are important materials in modern lives, with a global production anticipated to reach 12.7 million tons by 2024 [1]. They can be used for comfort and wellness (e.g., furniture, beds, chairs), shock absorption, thermal/acoustic insulation, or as sealants [2–7]. PU foams are produced at room temperature through two simultaneous reactions: a polyaddition of di- or polyisocyanates with di- or polyols [8–10] and the hydrolysis of isocyanates, which leads to the generation of CO_2 [11]. Such a process is one of the most successful and versatile foaming strategies, allowing the production of hard to soft foams due to the wide variety of polyols that can be employed. However, the health risks and regulatory restrictions associated with using hazardous isocyanates have prompted manufacturers and researchers to look for new ways to create isocyanate-free PU foams or alternatives [12,13].

Thus, the step-growth copolymerization of amines and 5-membered cyclic carbonates that leads to non-isocyanate polyurethanes (NIPU) has lately attracted considerable attention for developing PU without using isocyanate [14]. However, unlike isocyanate with water, the reaction between cyclic carbonates and amines does not produce the gas required for foaming, which limits the production of foams without any external blowing agents. Cornille et al. [15] demonstrated that NIPU foams could be made using poly(methylhydrogenosiloxane) as a blowing agent. The polymer matrix was created by reacting poly(propylene oxide) bis-carbonate or trimethylolpropane tris-carbonate with one of two amine compounds: ethylene glycol-based diamine or a derivative of C_{18} fatty acids diamine by using 1,5,7-triazabicyclo [4.4.0]dec-5-ene (TBD) as a catalyst [16]. Meanwhile, Blattmann et al. [17] also used a physical blowing agent, in particular a hydrofluorocarbon blend Solkane 365/227, to produce cellular isocyanate-free PU from carbonated polyglycidylethers of TMP (TMPGC), ethoxylated TMP (EO-TMPGC) and hexamethylene diamine.

Poly(thioether) foams have also been suggested as potential alternatives to NIPU foams. They are produced by a click reaction from a cheaply scalable epoxy resin with thiol [18] but, like NIPUs, they require external blowing agents [19,20]. King et al. [18] have developed a poly(β-hydroxythioether) foam via a rapid reaction between an epoxy and thiol monomer by using 1,8-diazabicyclo [5.4.0] undec-7-ene (DBU) as an organobase catalyst and acetone as physical blowing agent. This instantaneous reaction enables the production of poly(β-hydroxythioether) foams with controlled density and pore morphology. A recent study on the preparation of a NIPU foams using thiocyclic carbonate aminolysis, which involves the reaction of thiols, cyclic carbonates, and amines at a temperature of 50 ◦C, leading to the release of CO2. This study reports the successful preparation of NIPU foams using this method [21].

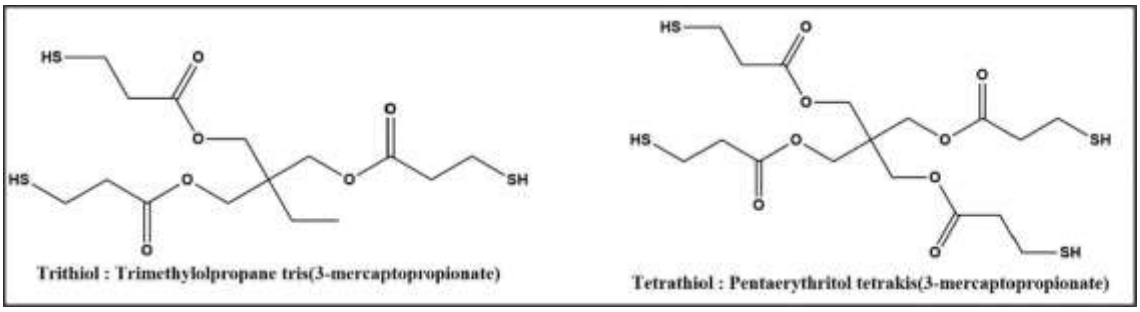
Recently, Monie et al. [22] have produced for the first time self-blowing poly(hydroxy urethane) (PHU) foams using the Pearson reaction, a reaction between a nucleophilic thiol and cyclic carbonate that creates CO_2 as a co-product. The Pearson reaction is attractive because it allows the blowing and curing reactions to coincide. Indeed, the carbonyl and methylene carbons in dialkylcarbonates have two electrophilic sites with reactivity that can be distinguished by the nucleophile's hard–soft nature. Carbonyl attack occurs with hard nucleophiles (such as amines) [23,24], whereas methylene attack happens with soft nucleophiles (for example thiols) [25]. In fact, similarities were observed with 5-membered cyclic carbonates (5CCs), but under more difficult reaction conditions. The alkylation of the soft nucleophile with cyclic carbonates results to the *in situ* release of CO_2 (i.e., via methylene attack). However, foaming had to be thermally induced with the optimum protocol lasting for more than 3 hours at temperatures of 100 °C and above [21]. Thus, greener alternatives to PU foams still need to be developed using industrially scalable and conventional reactive processes.

In this chapter, we develop rapid, self-blown poly(β-hydroxythioether) foams at room temperature by decarboxylative S-alkylation of a thiol with cyclic carbonates. Two different multifunctional and commercially available thiols were selected to leverage this highly reactive chemistry to produce unique porous foams. Thus, tetrathiol and trithiol were used to decarboxylate a thiol with cyclic carbonates in the presence of the super organobase DBU. Rheology, spectroscopy, and physical characterization were performed to demonstrate rapid foam blowing within seconds of mixing the reactants. The thermomechanical properties and degradability of the resultant materials were also investigated. To the best of our knowledge, this is the first time that this type of foam, which is produced instantaneously at room temperature, has been reported.

II. Materials and Methods

II.1. Materials

EPIKOTE™ MGS™ RIMR135, a bisphenol-A-(epichlorohydrin) resin (number average molecular weight ≤ 700)-1,6-bis(2,3-epoxypropoxy) hexane, was purchased from Hexion. Tetrabutyl ammonium bromide (TBAB), 1,8-Diazabicyclo [5.4.0] undec-7-ene (DBU), trithiol (trimethylolpropane tris(3-mercaptopropionate)), and tetrathiol (pentaerythritol tetrakis(3-mercaptopropionate)) were acquired from Sigma-Aldrich and used as received. CO_2 was purchased from Carburos Metalicos. The structure of the thiolated monomers is shown in Scheme 4.1.



Trithiol : Trimethylolpropane tris(3-mercaptopropionate)

Tetrathiol : Pentaerythritol tetrakis(3-mercaptopropionate)

Scheme 4.1: The structures of the thiols used in the S-alkylation

II.2. Preparation of poly(β-hydroxythioether) (PHTE) foams

Bi-cyclic carbonate was prepared by reacting commercial epoxide with CO_2 in the presence of a catalyst, TBAB, as previously reported in the chapter 3. Bi-cyclic was mixed with the thiol (tetrathiol or/and trithiol) at a 1:1 molar ratio in aluminum-based container, for 30 seconds at room temperature. Five formulations with varying amounts of the two thiol monomers from 0 to 1 were selected to optimize and determine the optimal PHTE foams. Then, the organobase catalyst (DBU) was added in the reaction and swiftly mixed manually for 5-10 seconds to generate uniform PHTE foam. The foams were then kept in a fume hood to eliminate of the smell of thiolated monomers. The obtained foams were cut into rectangular prisms to perform the dynamic mechanical analysis (DMA) test and the rest of the chemical, morphological, and thermal testing.

II.3. Characterization

The reaction progress was analyzed by attenuated total reflection- Fourier transform infrared (ATR-FTIR) using a spectrometer (Spectrum Two, from PerkinElmer, Waltham, MS, USA). Infrared spectra were recorded from 450 cm^{-1} to 4000 cm^{-1} wavenumbers, with a resolution of 4 cm^{-1} and co-adding 8 scans per spectrum.

Scanning electron microscopy (SEM) using a Philips model XL30, with tungsten filament and accelerating voltage of 25 kV, was carried out to examine the morphology of the foams. Cross-sections of the samples were sliced perpendicular and parallel to the foaming direction, the fracture surface was sputter coated (Polaron SC7640) with gold/palladium, and the cell size was measured using ImageJ software.

Samples viscosity was performed using a rotational rheometer (AR-G2, TA Instruments, USA) with a plate geometry (40 mm in diameter). The steady shear data were collected from shear rate tests ranging from 0.01 to 200 s^{-1}. The effect of temperature on samples viscosity was performed in the temperature range of 25-80°C.

Densities of PHTE samples were measured according to ASTM D1622. Specimens of 30 × 30 × 30 mm (width × length × thickness) were cut from the middle of the foam height. The results were the average of at least three different foam samples.

Differential scanning calorimetry measurements (NETZSH DSC- Polyma 214 model) were carried out in the temperature range from −50 to 135 °C, following a heating/cooling/heating cycle at 10 °C/min in nitrogen atmosphere.

Thermogravimetric analysis (TGA) was carried out using a TA-Q500 (TA-instrument, USA). The samples were placed on a platinum sample holder and heated under nitrogen atmosphere from room temperature up to 700 °C at 10 °C/min.

A temperature sweep from −100 °C to 70 °C, with a heating rate of 2 °C min^{-1}, was carried out in a DMA analyzer (DMA Q800 from TA Instruments, New Castle, DW, USA). An amplitude of 15 μm and a frequency of 1 Hz were set in a tension mode.

The number of moles of network per unit volume of cured polymer is known as crosslink density (ν). Crosslink density of NIPU films can be calculated from the modulus at the rubbery plateau by using the equation 1 [20,26,27]:

$$\nu = \frac{E'}{3RT} \quad \text{(eq. 1)}$$

where T is the temperature in rubbery plateau from which the elastic modulus is taken, the temperature is in Kelvin, R is the gas constant and E' is the storage modulus at T.

III. Results and discussion

Poly(hydroxythioether) foams were prepared using different formulations that employed various monomers of thiols and cyclic carbonate along with the catalyst DBU. The foams were synthesized at ambient temperature and at a rapid pace. The resulting foams were characterized by several techniques including TGA, DSC, DMA, SEM, and ATR-FTIR. These methods provided valuable information about the thermal stability, mechanical properties, morphology, and chemical structure of the obtained foams. The use of different monomers allowed for the creation of foams with varying properties, making them suitable for a wide range of applications. The synthesis of poly(hydroxythioether) foams via this method represents a promising approach for the production of high-performance and environmentally friendly materials.

III.1. Synthesis of bi-cyclic five-membered carbonate

The addition of CO_2 into oxiranes at high temperatures and pressures is the current and industrially used technique to synthesize cyclic carbonate (CC). However, we prepared the bi-cyclic at atmospheric pressure without the use of an autoclave, as previously reported [28]. The chemical structures of the cyclic carbonate and the epoxide were further confirmed by ^{1}H NMR presented in figure 4.1. It shows the disappearance of epoxide peaks that appear at 3 and 3.2 ppm and the appearance of new ones at 4.6 and 4.8 ppm related to the peaks of formed cyclic carbonate.

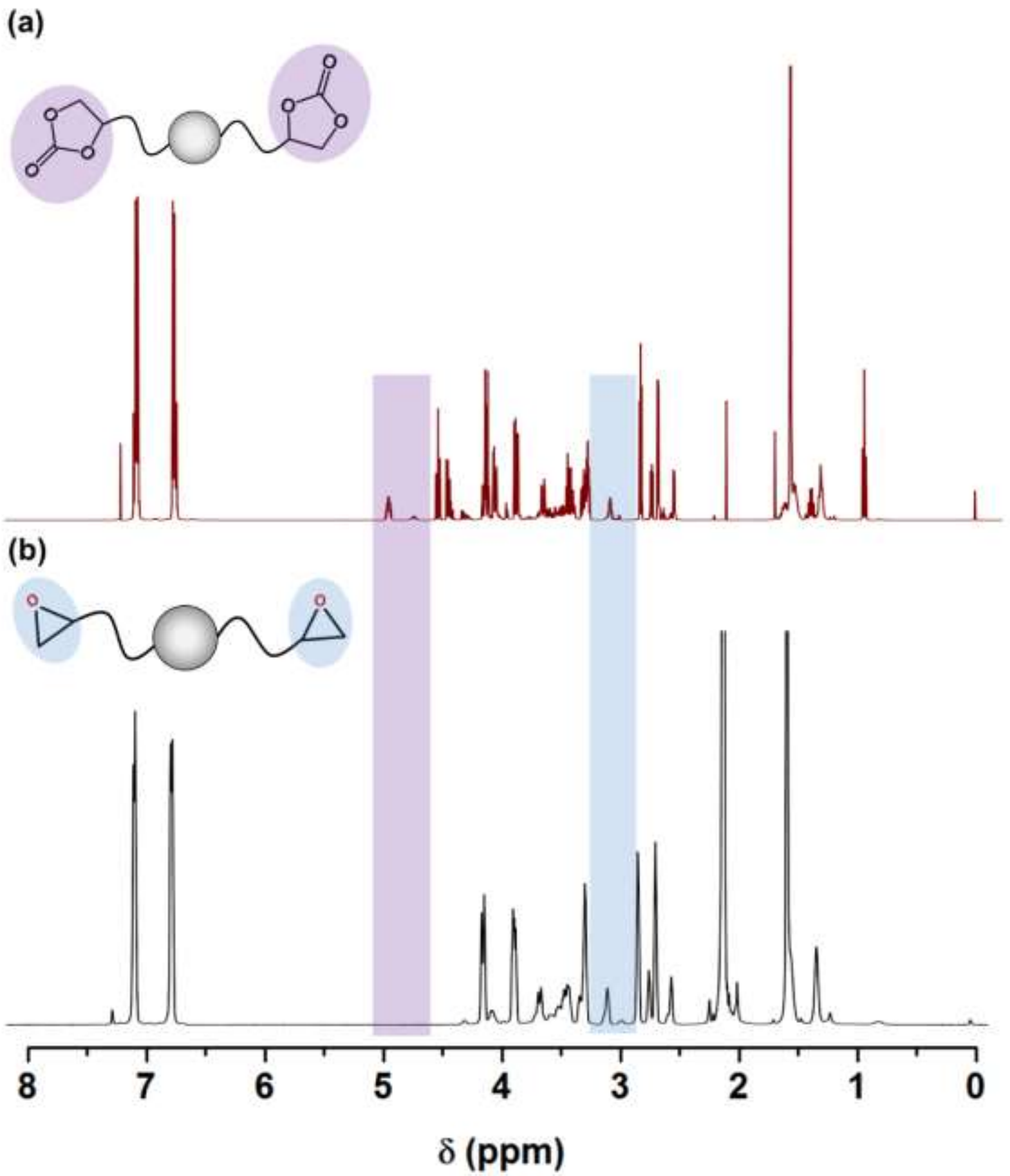


Figure 4.1: NMR of Bis epoxy and Bi-cyclic carbonate obtained

Bubble nucleation and growth is governed by several physical phenomena, such as surface tension, diffusion and viscosity [29]. Thus, the viscosity of the reactants plays a crucial role on the foaming evolution, as too low or too high viscosity will result in unstable or non-evolving foams. Additionally, as the proposed S-alkylation reaction responsible for foams formation is exothermic, a rheological study on cyclic carbonates was first carried out to evaluate their viscosity in a temperature interval from room temperature to 80 °C. As expected, the viscosity decreases with increasing temperature.

Indeed, at room temperature the viscosity of the cyclic bis carbonate is 51.3 Pa.s decreasing progressively to 0.377 Pa.s at 80 °C (Figure 4.2). While the viscosity at room temperature is high, it rapidly reaches medium viscosity values suitable for foam formation.

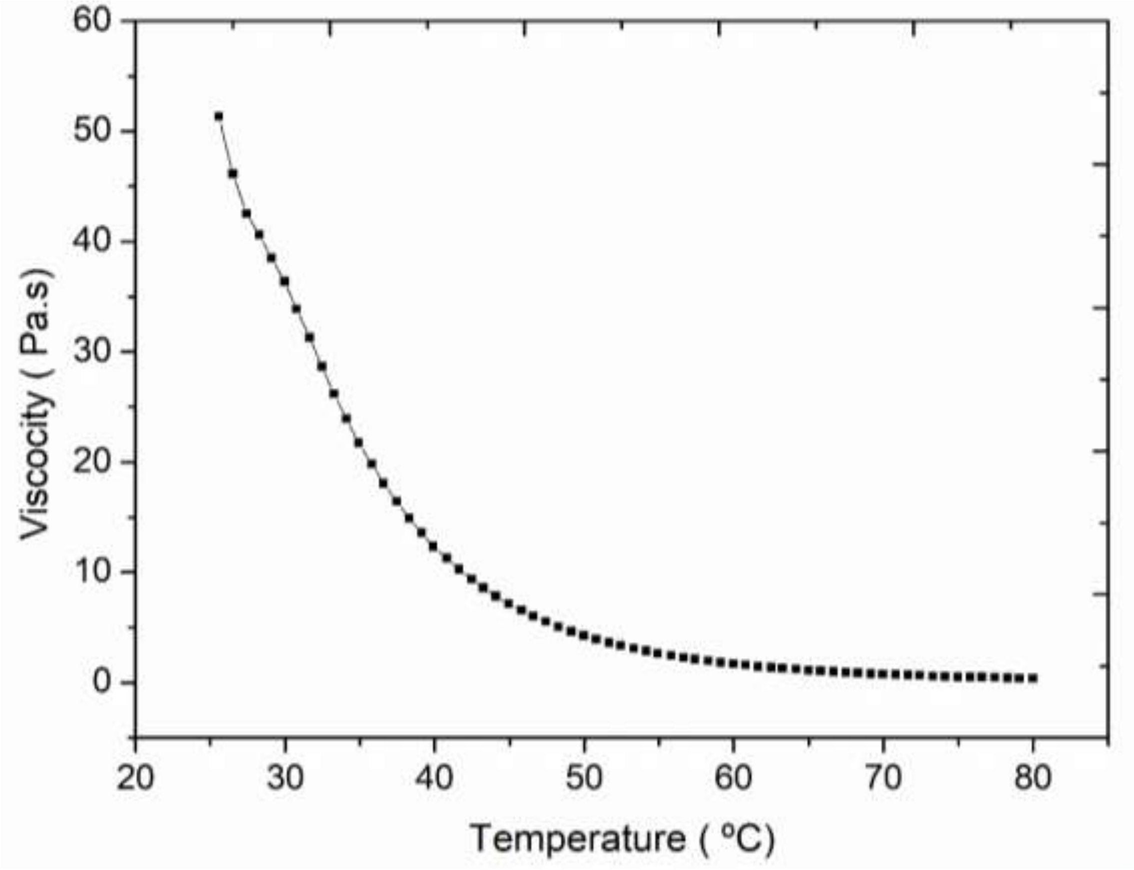


Figure 4.2: The viscosity of Cyclic carbonate in 25-80 ºC

III.2. The S-Alkylation of Trithiol and tetrathiol

It is worth mentioning that S-alkylation of trithiol and tetrathiol to generate the *in situ* CO_2 while producing thioether linkage is the basis of the self-blowing PHTE foaming process (Figure 4.4). Thus, the use of DBU as a catalyst was motivated by the fact that it enables a better control of the rate of thioether linkage synthesis and CO_2 production which is required for foam formation.

In the first step of the reaction, an interaction of the thiol with the unsubstituted carbon of the cyclic bis carbonate gave rise to the initial Van der Waals complex. The plausible mechanism of S-alkylation reaction is shown in Figure 4.4. This reaction is expected to proceed in three elementary steps. In the first step of the reaction, an interaction of the thiol with the unsubstituted carbon of the bi-cyclic carbonate resulted in the initial Van der Waals complex. In the next step, the thiol proton is transferred to the sp^2 nitrogen atom of DBU (catalyst) and 5CC ring is broken to form linear carbonate anion. The last step involves the decarboxylation of the generated linear carbonate anion, proton transfer from $DBUH^+$ to form the hydroxythioether, and regeneration of catalyst (DBU). Several studies have shown the efficiency of DBU for several alkylation reactions [30–33]. In a recent work, Tian et al. [34] demonstrated that the use of DBU as a catalyst, leads to easy and economic atomic α-alkylation of enones with electron deficient alkenes under mild conditions. This method employs a vinylogous strategy to generate dienolate intermediates, resulting in a novel way for enone regioselective -alkylation [34]. Therefore, the alkylation of alkyl phosphinates and some H-phosphonate diesters is promoted by the organobase DBU [31]. Additionally, the formation of a self-blown foam has been described from the S-alkylation of dithiols using tri-cyclic carbonates [22]. However, the reaction took 16 hours to reach an appropriate viscosity and high temperature to foam. To avoid foam collapse, the fundamental challenge in self-blowing techniques is to create polymer chains with adequate viscosity and crosslinking degree before the release of the blowing agent (CO_2). The Figure 4.3 shows the 5 steps of preparation of Poly(hydroxythioether) foam and you can also use the QR code to see the full video of the method used and the conditions to obtain the foam. In our case, the starting viscosity of the bi-cyclic carbonate was 51.3 Pa.s and the high reactivity of trithiols and tetrathiols enables both polymerization and foaming to occur simultaneously at room temperature.

Figure 4.3: The steps of the preparation of poly(hydroxythioether) foams and the QR code to see the video of the formulation

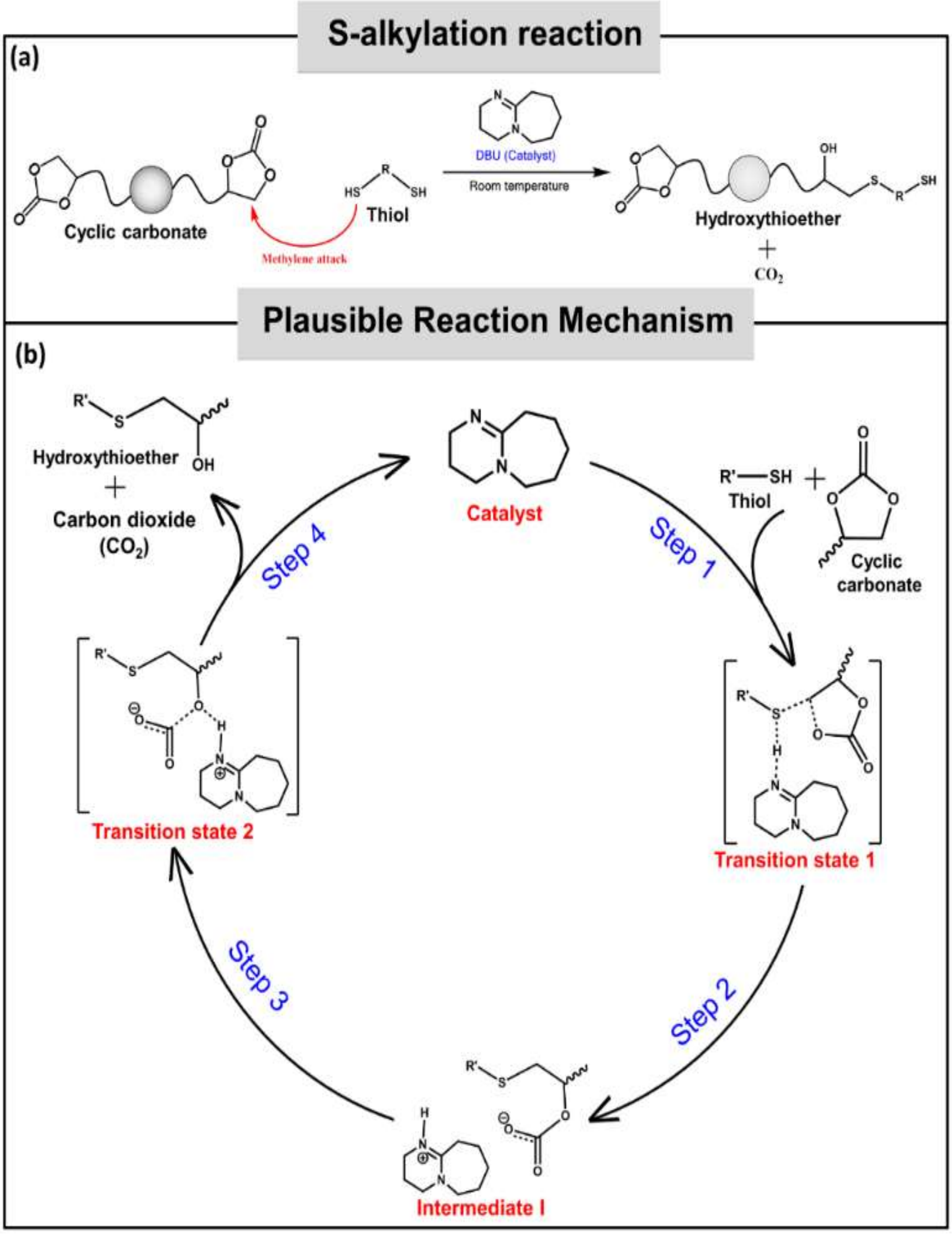


Figure 4.4: (a) The S-alkylation reaction of trithiol and tetrathiol using DBU at RT and (b) Proposed S-alkylation reaction mechanism to form self-blown foam

III.3. ATR-FTIR Analysis

The S-alkylation reaction is monitored by FTIR. Figure 4.5 shows the infrared spectra of all PHTE foams with varying molar ratio of the trithiol/tetrathiol, C3:C4, to confirm the complete reaction of carbonate groups of bis(cyclic carbonate) with thiol groups. We observe the disappearance of the band at 1790 cm^{-1}, which corresponds to the carbonyl of 5-membered bis(cyclic carbonate). Furthermore, sulfide bands (C-S) generated during the Pearson reaction between the cyclic carbonate and thiol monomers, by the consumption of carbonyl or carbonate compounds (C=O) around 1790 cm^{-1}, are revealed by a particular peak at 740 cm^{-1}. In fact, several different studies on different topics have shown the appearance of the sulfide band in the region of 690 to 730 cm^{-1} [35,36].

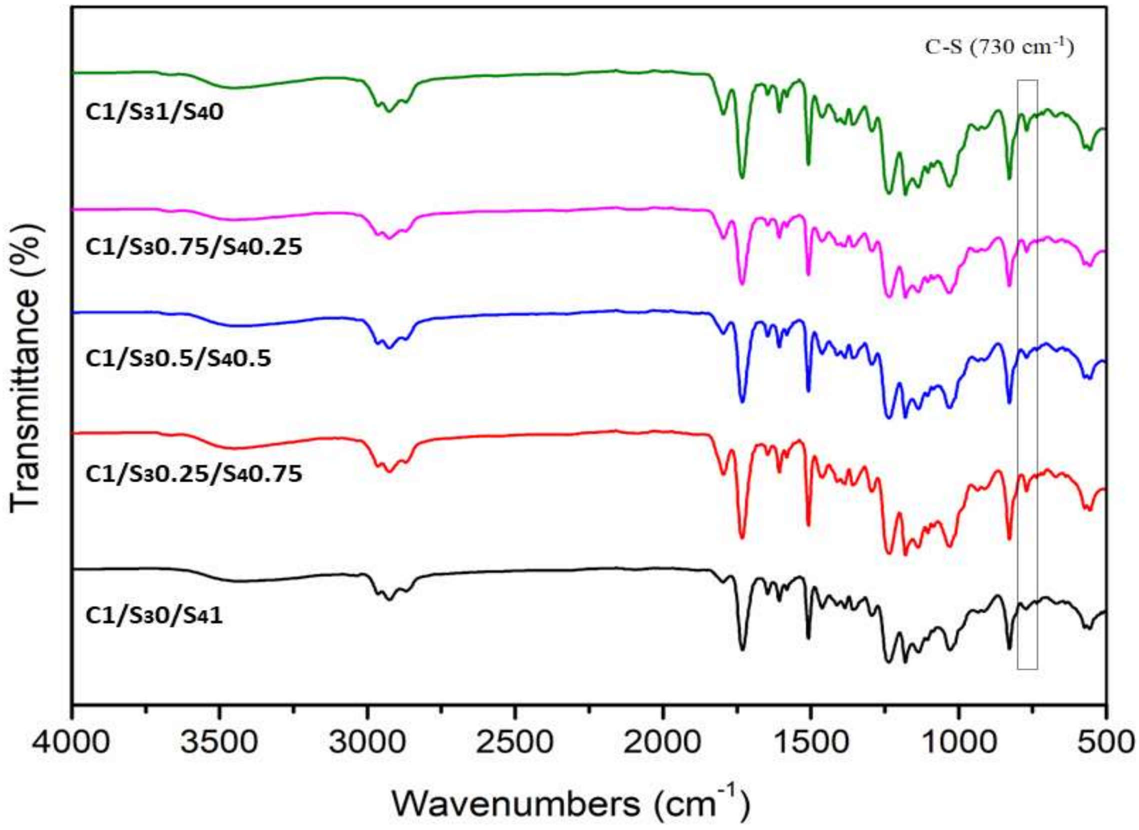


Figure 4.5: ATR-FTIR of all PHTE foams

The cellular structure of foams is a key feature that influences their final properties. Thus, the morphology and cell size of several foam formulations were studied using scanning electron microscopy (SEM) (Figure 4.6). All foams show an anisotropic structure with cells elongated parallel to the foaming direction (e.g. Figure 4.6.b) and substantially spherical perpendicular to the foaming direction (e.g. Figure 4.6.c). Such anisotropy is consistent with free-rise foams [29]. The cellular structures present typical open cells, with the presence of some partially ruptured walls. The cell size slightly varies with the trithiol/tetrathiol molar ratio, with average sizes increasing with increasing content of tetrathiol from 195 ± 74 µm up to 245 ± 81 µm (Table 4.1). Such change was ascribed to a higher CO_2 gas generation with the tetrathiol. this variation in cell size be explained by the fact that with a tetrathiol, more CO_2 is released, thereby generating higher porosity in our foams.

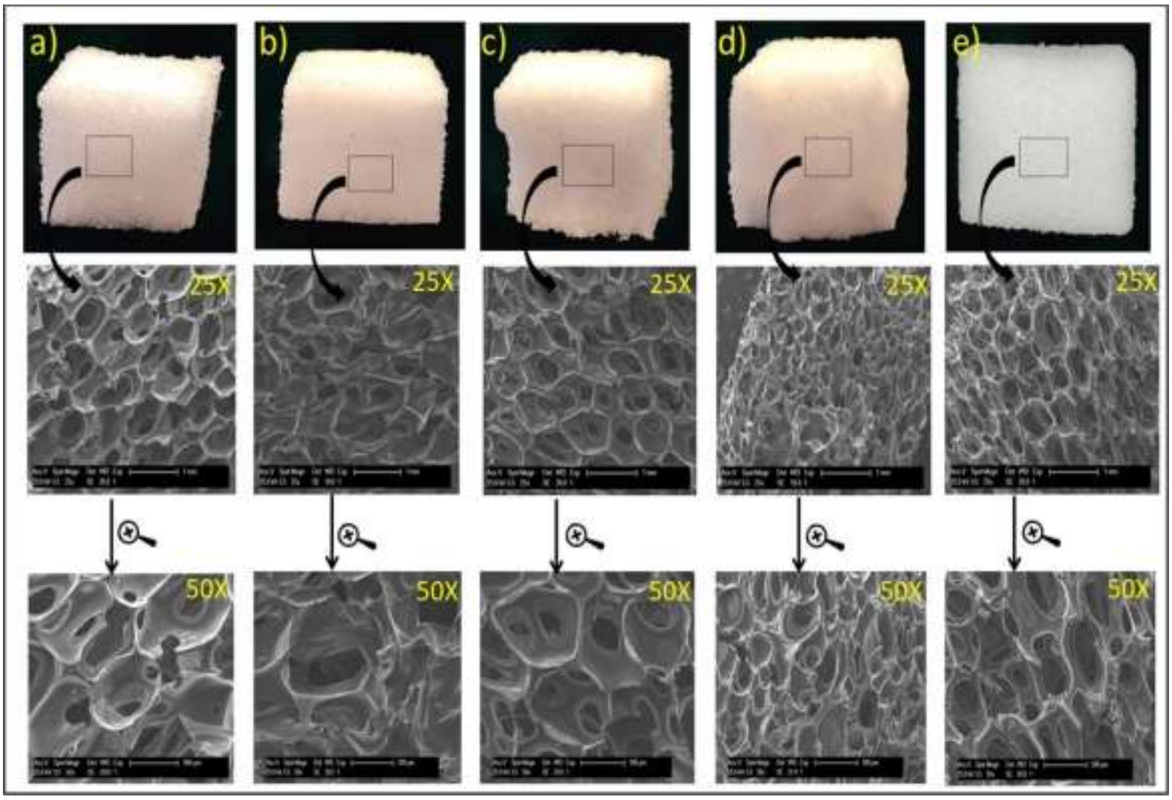


Figure 4.6: Pictures and SEM images of PHTE foams with several formulations: a) (C:S3:S4 / 1:0:1), b) (C:S3:S4 / 1:0.25:0.75), c) (C:S3:S4 / 1:0.5:0.5), d) (C:S3:S4 / 1:0.75:0.25), e) (C:S3:S4 / 1:1:0).

Table 4.1: Different parameters of PHTE foams

Molar ratio formulation (C:S3:S4)	Cell size (µm)	Apparent density ($g.cm^{-3}$)	Tg * (°C)	$T_{d5\%}$** (°C)	Crosslinking density v_e ($mol.m^{-3}$)
(1:0:1)	245±81	0.113±0.0032	28.1	251.0	37.374
(1:0.25:0.75)	201±76	0.125±0.0039	24.5	247.4	18.931
(1:0.5:0.5)	210±78	0.156±0.0043	25.2	244.1	14.667
(1:0.75:0.25)	196±74	0.193±0.0049	21.4	245.1	15.554
(1:1:0)	195±74	0.197±0.0050	18.1	242.3	8.101

* Measured by DSC

** Measured by TGA

III.4. Density of foams

Table 1 shows the apparent density of the several PHTE foams generated using the self-blowing technique. As the molar ratio of tetrathiol in the formulations decreases, the apparent density of the foam decreases, going from 0.197 $g.cm^{-3}$ to 0.113 $g.cm^{-3}$. This is due to the tetrathiol's strong reactivity, which bridges with bi-cyclic carbonate more than trithiol, resulting in a larger amount of crosslinking in the foaming process. The increase of tetrathiol helps to increase the foaming viscosity of PHTE. Moreover, the high reactivity of tetrathiol will cause a high generation of CO_2 compared to trithiol, therefore the density of the foams will have a lower density than those prepared by trithiol. Several studies have shown that the apparent density increases slightly with increasing crosslinking agent or with the use of more reactive compounds than others [26]. Indeed, in research studies reported by Chen et al. [37]. It was found that increasing the content of glutaraldehyde, used as a cross-linking agent, affects the apparent density of isocyanate-free polyurethane foams (i.e. a positive effect on gel formation, cross-linking and bonding) [37].

III.5. Thermal characterization of PHTE Foams.

Thermogravimetric analysis (TGA) (Figure 4.7) and differential scanning calorimetry (DSC) (Figure 4.8) were carried out to investigate the thermal stability and glass transition temperature of the prepared foams. Thus, it was revealed that the use of tetrathiol improves slightly the thermal stability of the resulting foam, increasing the Td5% in more than 10 ºC (Table 4.1). These PHTE foams have a better thermal stability than some of the NIPU foams prepared using bi-cyclic carbonate and diamines [38,39]. Moreover, NIPU prepared from tannin extracted of sumac leaves has shown a first degradation of 5 % at a temperature below 150 °C, this mass loss has been justified by the evaporation of volatile components from the polymer, such as unreacted hexamethylenediamine and absorbed water from the environment [40].

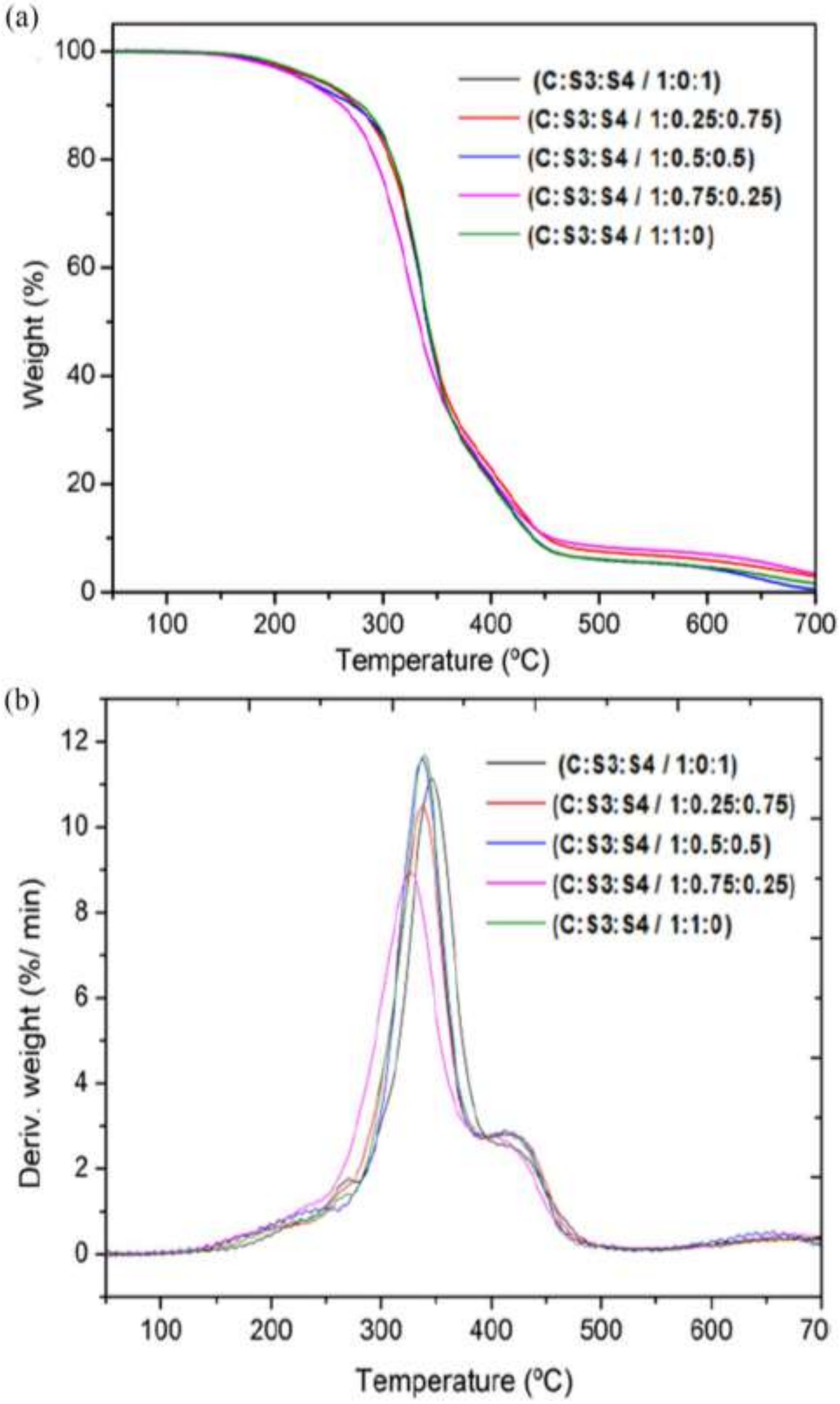


Figure 4.7: (a) TGA and (b) DTG curves of the self-blowing foam with different comonomer ratios

DSC curves (Figure 4.8) showed an increase of the foam T_g from 18 ºC to 28 ºC with increasing tetrathiol content. This result is ascribed to a higher crosslinking density in the presence of tetrathiol monomer which lead to the formation of a higher number of thioether bridges between the polymer chains (Table 4.1). Meanwhile, the PHTE foam prepared using only trithiol shows a crosslink density value of 8.101 $mol.m^{-3}$ and increases to 37.374 $mol.m^{-3}$ for the cyclic carbonate/tetrathiol (1/1) foam. This results in an improvement of the hardness and stiffness of the foam. It is important to note that the crosslinking density in PU foams using different crosslinking agents were reported to range between 9 and 102 $mol.m^{-3}$ [15].

Moreover, in a study performed on polyurethane foams with the use of lignin as cross-linking agent, it was found that when the molar ratio of lignin was higher, the glass transition temperature was slightly increased. The authors concluded that an increase in crosslinking density may limit the molecular motion of the chains in the soft segment of the PU foam increasing its T_g [26].

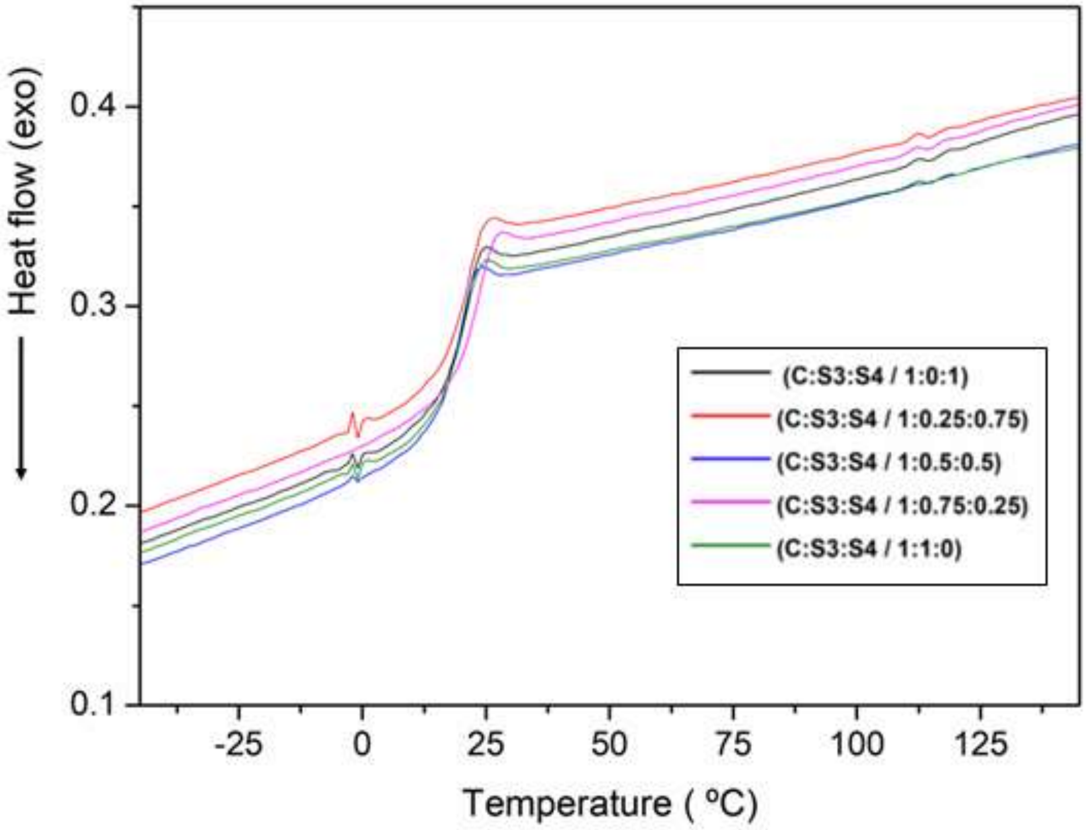


Figure 4.8: Differential scanning calorimetry (DSC) thermograms of the self-blowing PHTE foams using different compositions

III.6. Dynamic mechanical analysis

The behavior of foams under a stress in monotone tension was investigated by DMA. Figure 4.9a illustrates the storage modulus of foams as a function of trithiol:tetrathiol ratios. The storage modulus of the foams increases with increasing tetrathiol content, with E′ values of up to 93 MPa. Such result is ascribed to the higher reactivity that leads to higher crosslink density, mentioned before. The temperature associated with the peak of the tan d is taken as the T_g (Figure 4.9b). The T_g values of all materials range from 28 to 43 °C.

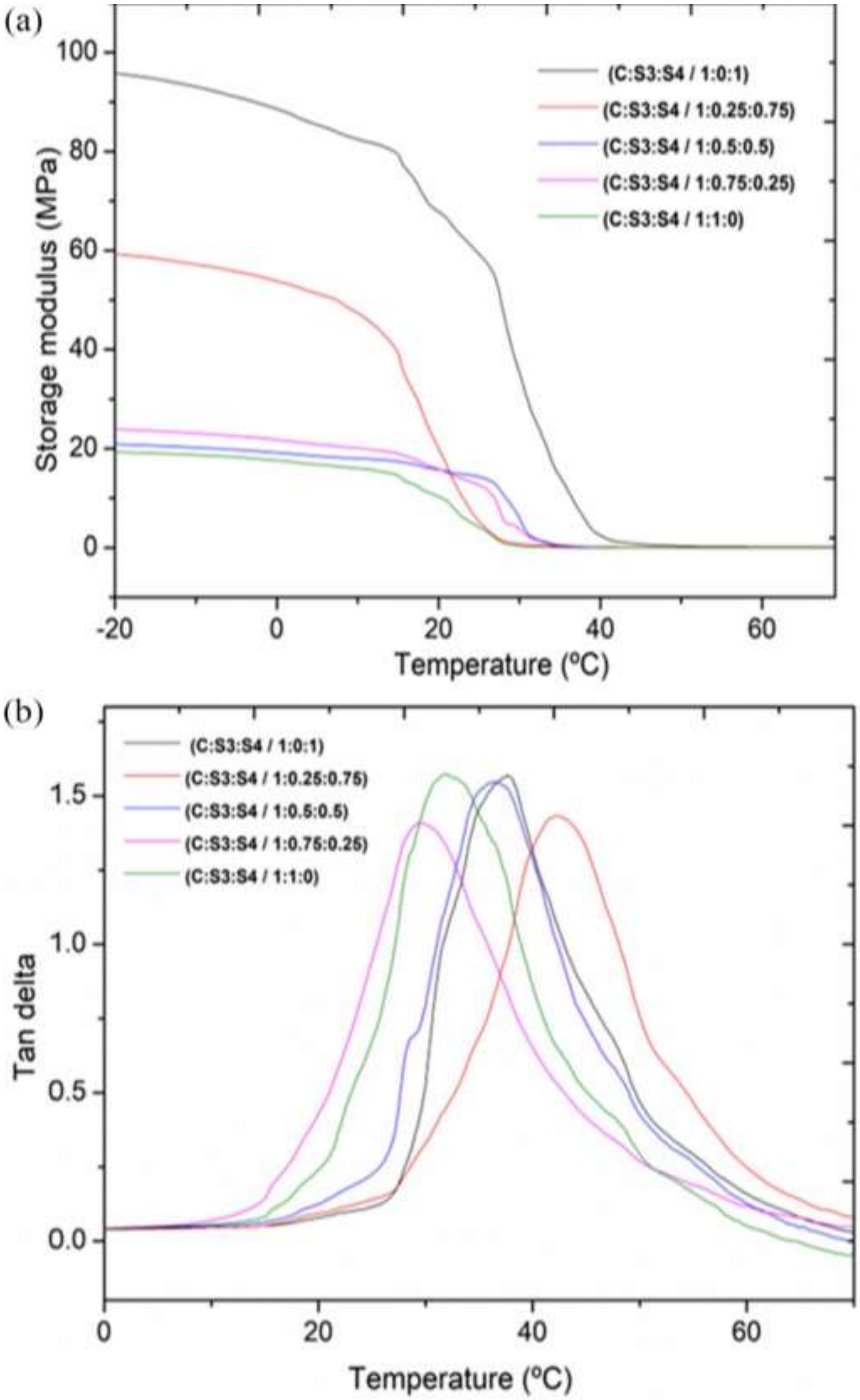


Figure 4.9: (a) Storage modulus and (b) tan delta versus temperature of self-blowing foams with different compositions

IV. Conclusion

A new strategy to prepare a microcellular self-blowing isocyanate-free poly(hydroxythioether) foams by S-alkylation of 5-membered bi-cyclic carbonate and trithiol and tetrathiol monomers was developed. Hence, formulations using DBU as an effective catalyst provided the PHTE Matrix, which we then expanded by decarboxylation. The PHTE foams are a more appealing choice than traditional commercially available polyurethane foams and non-isocyanate polyurethane foams. The study was focused on determining the best and most optimized formulation for producing uniform foams with significant mechanical and thermal properties. Therefore, we obtained a formulation that provides us with a polymer matrix that can rapidly expand and form a foam *in situ*, taking advantage of the released CO_2, but in controlled conditions. The attractiveness of this novel solvent-free approach is offering new possibilities for creating more sustainable foams with modular properties using accessible components and additives. This method and the prepared crosslinked self-blowing poly(β-hydroxythioether) foams highlight their potential to be scaled up and industrially manufactured after optimization.

The successful preparation of poly(hydroxythioether) foams has added value to the synthesis of Non-isocyanate Polyurethane foams. The use of DBU as the catalyst for the S-alkylation reaction, in combination with the addition of diamines to the reaction of thiolated monomers with bi-cyclic carbonate, led to the simultaneous formation of the urethane linkage and the release of CO2, resulting in the production of NIPU foams. This efficient method was developed after testing several catalysts for S-alkylation and demonstrates the potential for advancing the synthesis of NIPUs.

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Chapter 5: Preparation of non-isocyanate Polyurethane foams

I. Introduction

The first synthesis of non-isocyanate PU dates back to 1957 when the urethane group was formed by reacting amines with cyclic carbonates [1]. However, this synthesis route was not highly developed due to the simplicity and versatility of conventional PU [2]. The potential of that first route is now recognized and researchers are studying different products and methodologies. The favoured synthesis route is the polyaddition reaction between cyclic carbonates and diamines. These reagents are mainly produced using the following synthesis pathways: (i) diol transesterification using alkylene carbonates [3] (ii) carboxylation of epoxy precursors with CO_2 over a catalytic system [4], and (iii) the synthesis of cyclic carbonates starting from diols via CO_2 reaction using a catalytic system [3,5]. The polyaddition reactions from these precursors result in solid NIPU systems and, thus, the development of NIPU foams were iniatilly investigated using external blowing agents. The first NIPU foam was done by Cornille et al [6]. They developed a NIPU foam using bi- and tri- five-membered carbonates and diamines (EDR 148) catalysing the aminolysis reaction with 1,5,7-triazabicyclo[4.4.0]dec-5-ene (TBD). In addition, the blowing agent was polydimethylsiloxane. The H_2 gas was liberated via the reaction of SiH with the amines. Each compound was blended and filled into a silicone mold for 12 h at 80 °C, and 4 h at 120 °C and resulted in flexible open-cell foams with densities ranging from 194 to 295 kg m^{-3}, depending on the content of trifunctional reagents (cyclic carbonate and/or amine). The same authors later developed flexible NIPU foam at room temperature using thiourea as a catalyst. However, their reaction took three days to complete, resulting again in flexible foams [7]. In the same context, Blattmann et al. [8] developed NIPU foams from a combination of five-membered tri-cyclic carbonates and ethoxylated trimethylolpropane, and DABCO-catalyzed hexamethylene diamine. This initial mixture was mixed and cooled to 20-25 °C before adding the physical blowing agent, a liquid fluorocarbon mixture. Following this, the foaming procedure was attempted in a 50 °C tempered mold. They reported that the foam was formed in 20 min, followed by a long cure at 80 °C for 14 h. The densities of the flexible open-cell foam varied from 142 to 219 kgm^{-3}. Another approach reported by Grignard et al. [9] with CO_2-blown NIPU at supercritical conditions near the melting temperature of the NIPU matrix, that is, a range of 80-100 °C with 100-300 bar of CO_2. The samples were foamed within seconds with rapid depressurization with densities ranging from 110 to 176 kg m^{-3}. They also employed a two-stage process in which the reactor is cooled down to 0 °C before depressurization to avoid foaming before depressurization.

The main production route for PU foams is based on the polyaddition reaction between a polyol and a diisocyanate in the presence of water, which generates CO_2 gas. Thus, current research efforts aim to produce self-blown NIPU foams similar to PU systems. The first NIPU-based foams without an external blowing agent were reported by Monie et al. [10] through decarboxylation, which occurs via the reaction of a 5-membered cyclic carbonate and a thiol compound that generates CO_2 gas. The formulations were prepared by terpolymerization of a bis(cyclic) carbonate with dithiols and diamines. The mixtures were left to react at room temperature for 16 hours to increase the viscosity before foaming.

In our study, we describe a way of making self-blown non-isocyanate polyurethane (NIPU) foams that takes advantage of the wildly different chemistries of amines and cyclic carbonates to create the polymer network (urethan linkage) and thioether to create the blowing agent (CO_2) in situ through a reaction with a cyclic carbonate. We were able to synthesize the bi-cyclic carbonate using CO_2 at atmospheric pressure and the preparation of polyhydroxyurethane foams was in-situ and instantaneous by reacting the bi-cyclic carbonate with diamine (attack carbonyl) which generates the urethane linkage and with tetrathiol (attack methylene) which causes the release of CO_2. The obtained foams were studied chemically, thermally, and mechanically and a morphological study with the help of SEM was carried out on our obtained products.

II. Experimental part

II.1. Materials and Methods

EPIKOTE^{TM} MGS RIMR135, a bisphenol-A-(epichlorohydrin) resin (number average molecular weight ≤ 700)-1,6-bis(2,3-epoxypropoxy) hexane, was purchased from Hexion, tetrabutyl ammonium bromide (TBAB), 1,8-Diazabicyclo [5.4.0] undec-7-ene (DBU), tetrathiol (pentaerythritol tetrakis (3-mercaptopropionate)) $(HSCH_2CH_2COOCH_2)_4C$ were acquired from Sigma-Aldrich and used as received. CO_2 was purchased from Carburos Metalicos and 1,3-diaminopropane (DAP), ethylenediamine (EDA), 1,6 hexamythelendiamine (HMDA), and 1,8-diamino-3,6-dioxaoctane (DADO) were purchased from Sigma-Aldrich.

II.2. Preparation of bi-cyclic carbonate

Bi-cyclic carbonate was prepared by reacting commercial epoxide with CO_2 in the presence of TBAB, which served as a catalyst as reported in chapter 3. The conversion of epoxides to cyclic carbonate was performed using atmospheric pressure CO_2 at 105 ºC, and the reaction was monitored kinetically by FTIR analysis to optimize the reaction conditions to reach high conversion rates in a short reaction time.

II.3. Synthesis of NIPU foams

Four different formulas we employed using four diamines (DAP, EDA, HMDA and DADO) (Table 5.1). The bi-cyclic and the diamines were mixed in an aluminium container for 30 seconds at room temperature. Then, the DBU and the tetrathiol were introduced and quickly mixed with a mixer for 5-10 seconds. Figure 5.1 also shows the chemical formulas of the monomers and the reaction in general.

Table 5.1: Products and amounts used in each formulation of PHU foams

Products	*Diamines used*	*Quantity of Bi-cycic carbonate (g)*	*Quantity of diamines*	*Quantity of thiols (g)*	*Quantity of DBU (g)*
PHU1	ethylenediamine	5	2.45	1.25	0.5
PHU2	1,3 diaminopropane	5	2.55	1.25	0.5
PHU3	1,6 hexamythelendi-amine	5	2.9	1.25	0.5
PHU4	Diamino dioxocatone	5	3.2	1.25	0.5

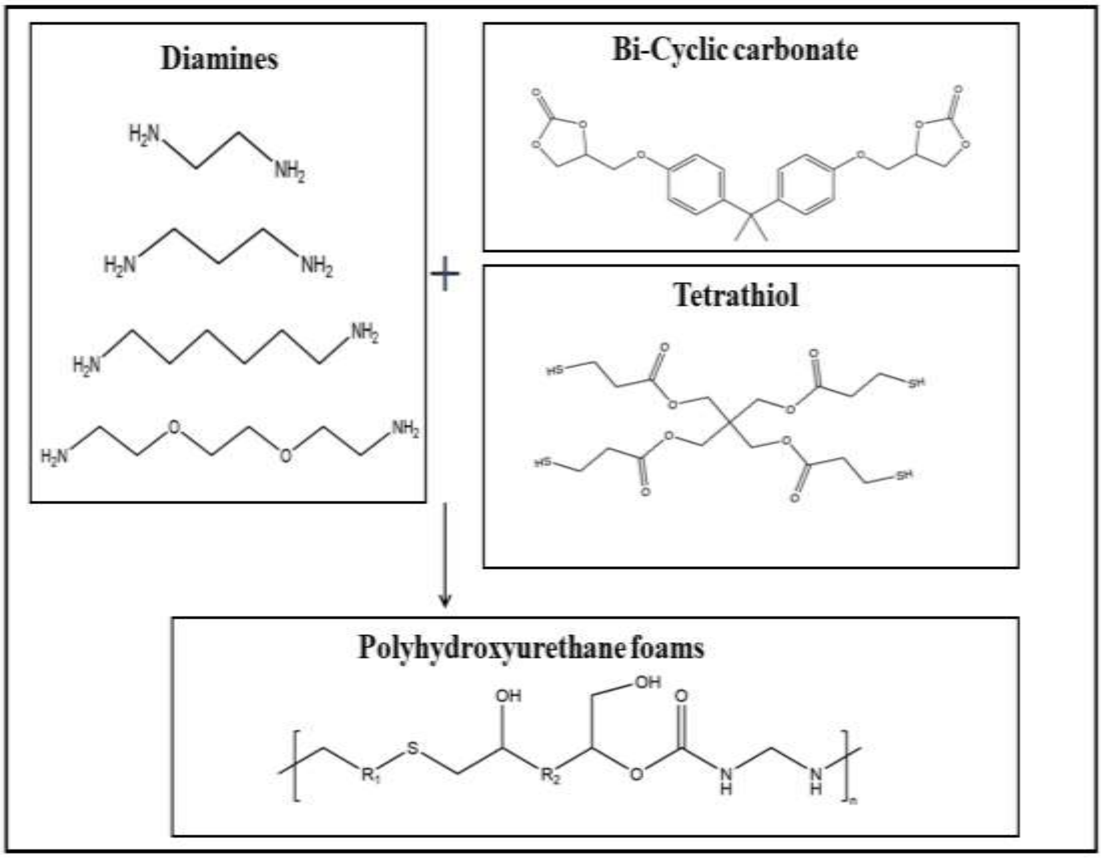


Figure 5.1: The monomers and final product obtained

II.4. Characterization

A Philips model XL30, with tungsten filament and accelerating voltage of 25 kV, was used to examine the morphology of the foams. Cross-sections of the samples were fractured perpendicular and parallel to the foaming direction, the fracture surface was sputter coated (Polaron SC7640) with gold/palladium, and the cell size was measured using Image J software.

Chemical structure of the bi-cyclic carbonate and NIPU foams were analyzed by attenuated total reflection- Fourier transform infrared (ATR-FTIR) using a spectrometer (Spectrum Two, from PerkinElmer, Waltham, MS, USA). Infrared spectra were recorded from 450 cm^{-1} to 4000 cm^{-1} wavenumber, with a resolution of 4 cm^{-1}.

Differential scanning calorimetry (DSC) measurements were carried out using NETZSH DSC- 214 model. The tests were performed in the temperature range from -50 to 175°C at a heating rate of 10°C/min under nitrogen atmosphere.

A temperature sweep from −100 °C to 70 °C, with a heating rate of 2 ◦C min^{-1}, was carried out in a DMA analyzer (DMA Q800, TA Instruments). An amplitude of 15 μm and a frequency of 1 Hz were set in tension mode.

Thermogravimetric analysis (TGA) was carried out using a TA-Q500 (TA-instrument, USA). The samples were placed on platinum sample holder and heated under nitrogen atmosphere from room temperature up to 700°C at a 10 °C/min heating rate.

The number of moles of network per unit volume of cured polymer is known as crosslink density (ν). Crosslink density of NIPU foams can be calculated from the modulus at the rubbery plateau by using the equation 1 [11–13]:

$$\nu = \frac{E'}{3RT}$$

where T is the temperature in rubbery plateau from which the elastic modulus is taken, the temperature is in Kelvin, R is the gas constant and E' is the storage modulus at T.

The NIPU foams were cut into cuboid-shaped samples. Their dimensions were measured using a calliper, and the apparent density was calculated directly from the mass and geometric volume of the samples. Three samples (30 mg each) were placed in 30 ml THF for 24 hours each to measure the swelling index (SI), which was calculated using equation 2.

$$SI = \frac{M1 - M0}{M0} * 100$$

where M0 is the initial mass of the sample and M1 is the mass after swelling in the solvent. The gel content (GC) was then calculated after drying the samples in a ventilated oven at 50°C for 24 hours using equation 3:

$$GI = \frac{M2}{M0} * 100$$

where m0 is the starting mass of the tab and m2 is the mass of the tab after drying.

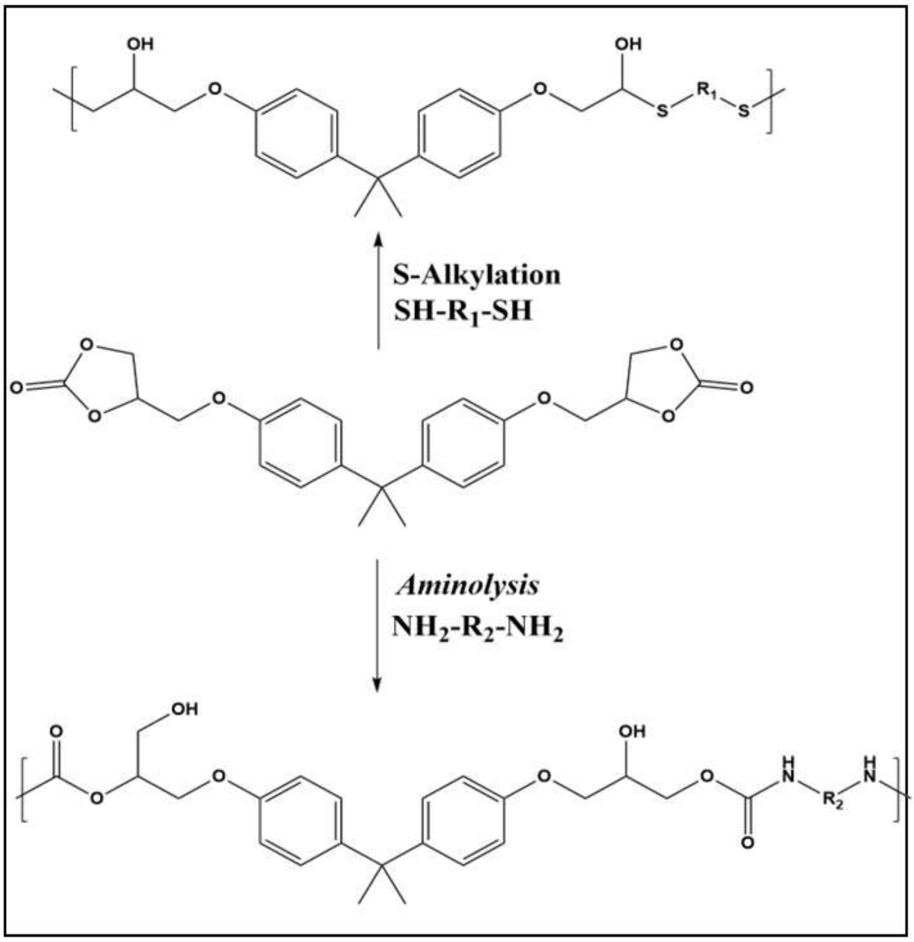
III. Results and discussion

III.1. Synthesis and characterization of bi-cyclic carbonate

Chemical fixation of carbon dioxide was used to create the cyclic carbonate monomers, which was accomplished without the need of an autoclave by reacting commercially available epoxy with carbon dioxide at atmospheric pressure. The characterization of the resulted product is described in chapter 4.

III.2. Foams preparation

Similar to conventional PU foams, the self-blowing PHU foams are based on two competitive reactions: aminolysis of the bi-cyclic carbonate to form the urethane linkage and construct the PHU network, and S-alkylation of thiols to generate the blowing agent (CO_2) while forming the thioether linkage. Four foams were made at room temperature using the bi-cyclic carbonate and four different diamines, in particular ethylenediamine (PHU_1), 1,3 diaminopropane (PHU_2), 1,6 hexamythelendiamine (PHU_3), and diamino dioxocatone (PHU_4). The DBU was used as a catalyst in the aminolysis and S-alkylation reactions, since it allows for better control of the rate of thioether linkage synthesis and CO_2 production. Several studies have shown the effectiveness of DBU on several alkylation reactions [14,15]. Scheme 5.1 summarizes both reactions as well as the various monomers and compounds used to make NIPU foams.



Scheme 5.1: S-alkylation and aminolysis reactions to prepare PHU foams

The NIPU foams evolved instantly after mixing all the reactants for less than 10 s. All four formulations foamed properly with controlled polymerization and blowing reactions, without the need for any post thermal treatment, and resulting in flexible foams (Figure 5.2, top). PHU_3 and PHU_4 samples were highly flexible foams, while PHU_1 and PHU_2 were slightly stiffer than the former. The chain length of the used amines appears to affect the flexibility of the resulting foams. One possible explanation for the effect of amine chain length on the flexibility of the resulting foams is that longer chain amines may lead to more flexible structures due to their increased flexibility and mobility. This could potentially result in a more open cell structure, which in turn can lead to increased flexibility.

It is also worth noting that the synthesis conditions, such as temperature, reaction time, and reactant concentrations, may also play a role in determining the properties of the resulting foams. These factors can influence the degree of crosslinking, the density of the foam, and the size and distribution of the cells. Therefore, it is important to consider these factors when optimizing the synthesis of NIPU foams with specific properties.

III.3. Structural characterization of NIPU foams

Low magnification SEM images show open cell structure with an anisotropic structure with cells elongated parallel to the foaming direction (Figure 5.2, middle and bottom). This morphology is consistent with self-blowing foams and resembles that of conventional low-density, flexible PU foams. The chain length of the amines used in the production of Polyurethane foams can affect the cell size of the resulting foams. The Longer chain amines may lead to more flexible structures due to their increased flexibility and mobility, which can potentially result in a more open cell structure. An open cell structure may have larger cell sizes, which can in turn increase the flexibility of the foam. However, it is important to note that the relationship between amine chain length and cell size may not be a direct one. Other factors such as the formulation of the foam, the processing conditions, and the type and amount of blowing agents used can also play a role in determining the cell size of the resulting foam [16–18].

To confirm the effect of amine chain length on cell size, further experiments may need to be conducted. This could involve varying the chain length of the amines used while keeping other factors constant, and then measuring the resulting cell size of the foams produced. There are several studies that have investigated the effect of cell size on the properties of open-cell foams, including NIFs. In the study by Pielichowska et al. [19], the authors investigated the influence of different chain extenders on the properties of polyurethane foams, including foam cell size. The results showed that the chain extender used had a significant effect on the size of the foam cells. Specifically, it was found that the use of a longer chain extender resulted in larger foam cells, while the use of a shorter chain extender resulted in smaller foam cells. The authors also noted that the choice of chain extender affected other properties of the foam, such as density and compressive strength. Overall, the study highlights the importance of selecting the appropriate chain extender in the production of polyurethane foams to achieve desired foam cell size and other properties.

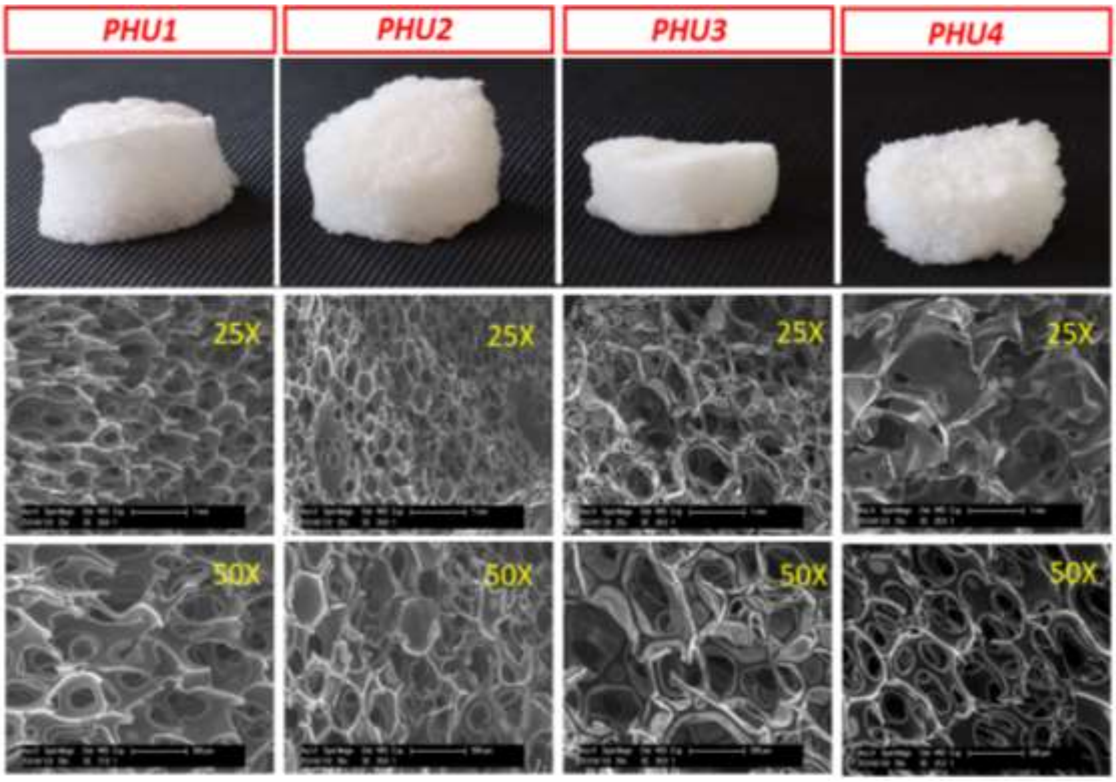


Figure 5.2: Optical and SEM images of PHU foams with the different formulations

The formation of urethane bonds was confirmed by FTIR analysis with the presence of the peak at 1640 cm^{-1} and the complete disappearance of the cyclic carbonate peak at 1780 cm^{-1} (Figure 5.3). Additionally, the success of the tetrathiol's alkylation reaction is visible in the appearance of the peak at 690 cm^{-1}, which corresponds to the stretching of the thioeter linkages C-S bond [20,21]. This alkylation produces CO_2, which is what causes the foam by the release of the gas

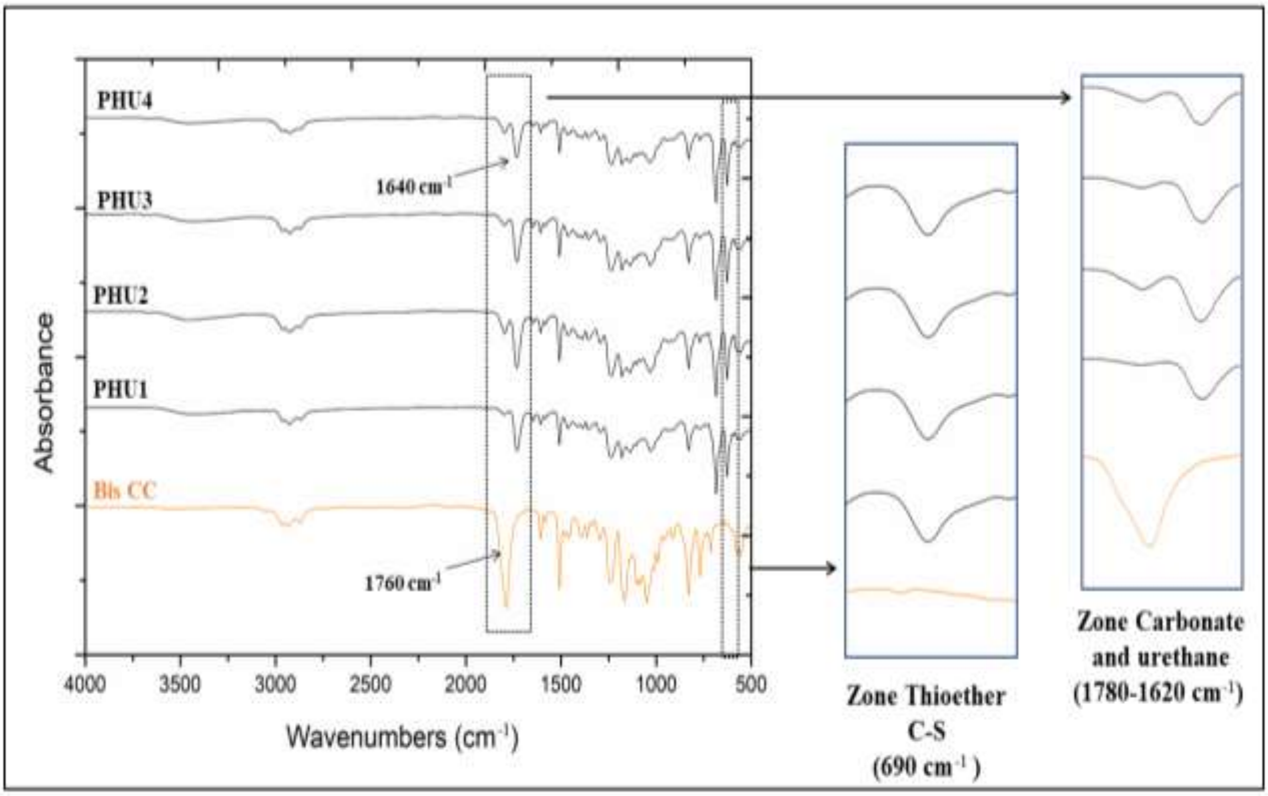


Figure 5.3: ATR-FTIR spectra of self-blowing PHU foams with different monomer composition

III.4. Thermal characterization of NIPU foams

The glass transition temperature (T_g) of PHU foams was evaluated by DSC and confirmed the observed differences in foam flexibility. PHU4 foam, prepared with diaminodioxactone, had the lowest T_g at 21ºC, followed by PHU3 foam, prepared with hexamethylenediamine, with a T_g of 23ºC, and PHU2 and PHU1 foams with T_g of 26ºC and 29ºC respectively. Thus, the longer chain of amines appeared to lower T_g confirming the already discussed influence of the chain length in the flexibility of the foams. In a similar study, NIPU foams prepared using different amines, such as HMDA, 1,9-nonanediamine (NDA), and 1,13- tridecanediamine (TDA) reported the highest T_g for the HMDA due to its lower average molecular weight and chain length [22]. Additionally, the presence of oxygen in 1,8-diamino-3,6-dioxaoctane can reduce chain mobility due to hydrogen bonding, resulting in a lower T_g. Sheng et al. [23] used EDA, PDA, and hexanediamine to prepare NIPU foams, and the highest T_g was obtained with EDA due to its smaller spacer length, which limited polymer mobility.

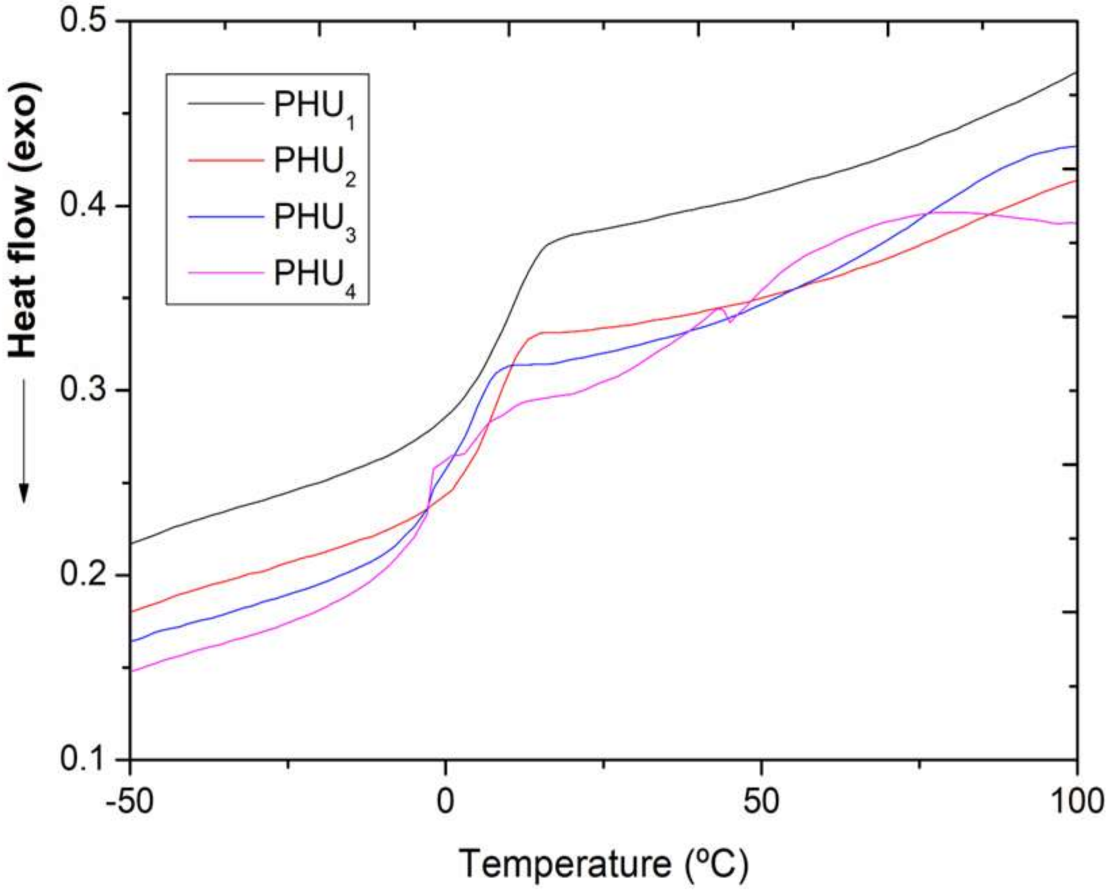


Figure 5.4: Differential scanning calorimetry (DSC) thermograms of the self-blowing PHU foams using different compositions

TGA analyses were also performed to assess thermal stability of the foam. Figure 5.5 shows the weight loss and the first derivative as a function of temperature. NIPU foams degrade start to degrade just below 235 ºC, presenting several degradation steps clearly observed in the mass loss derivative. Initial degradation steps, below 300 °C, are ascribed to the presence of unreactive diamine and degradation of aliphatic chains [4]. All samples presented two main decomposition peaks near 310 °C and 390 °C (Figure 5.5). PHUs have demonstrated thermal stability over a broad temperature range, from 180 ºC to 388 ºC, depending on the size of the aromatic component [24]. Consequently, the PHUs synthesized in this study exhibit excellent thermal stability, falling well within the range of values observed for conventional PUs. The primary degradation mechanism for PHU has been attributed to the dissociation of the urethane bond [25]. PHU1 and PHU2 presented the lowest degradation temperatures, as these formulations contain small alkyl chains. Camara et al. [26] found that the thermal stability of NIPUs varied with the length of the aliphatic chain. They reported that NIPUs prepared with hexanediamine had the highest initial degradation temperature of 266 °C, while those made with ethylenediamine had a lower temperature. They also observed that NIPUs containing the longest spacer length exhibited the highest thermal stability. Another study on poly(hydroxy urethane)s based on renewable diglycerol dicarbonate revealed that the thermal stability of the material was slightly improved with increasing chain length of the diamines [26].

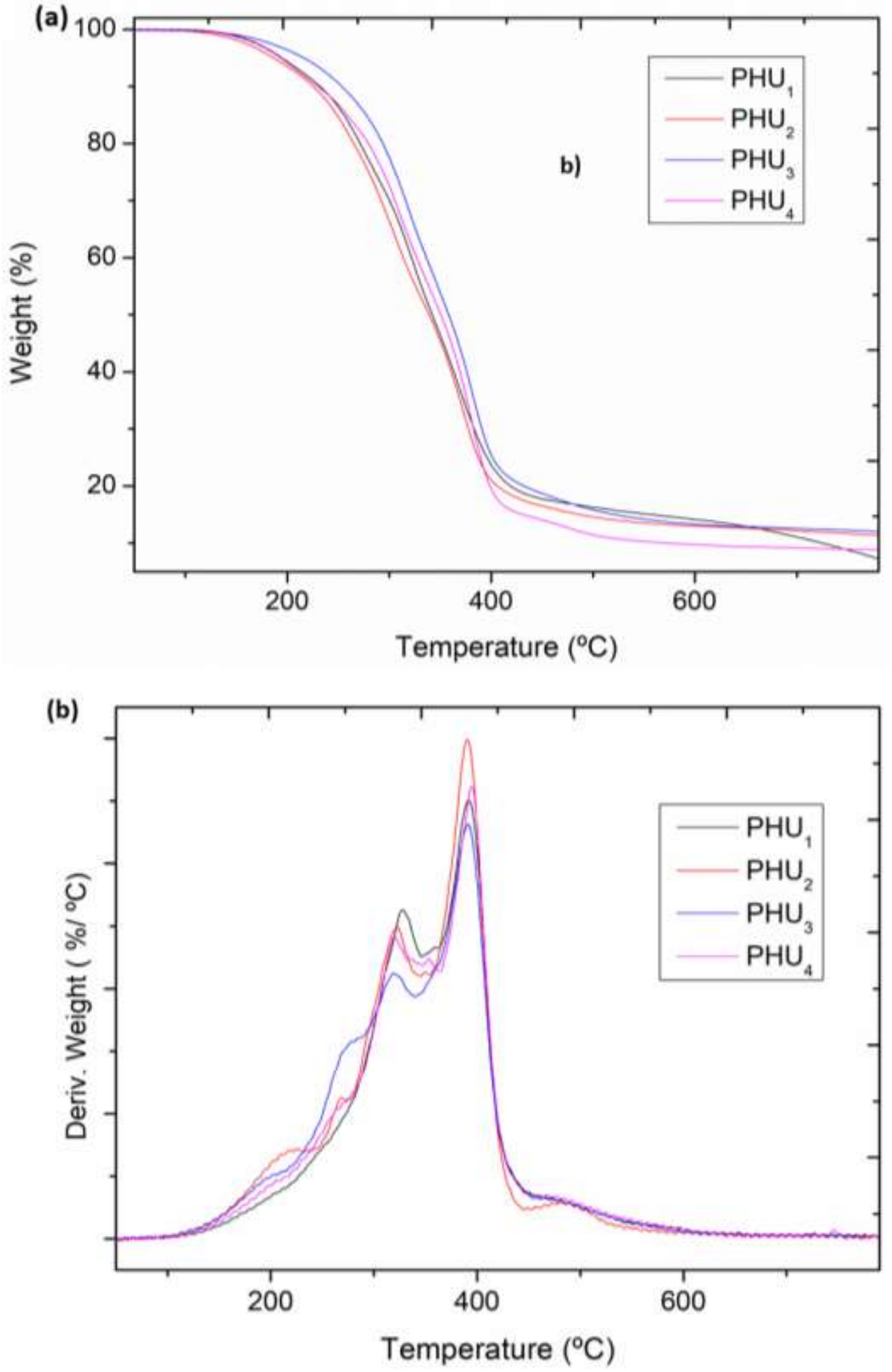


Figure 5.5: (a) TGA and (b) DTG curves of the) of self-blowing foam with different comonomer ratios

III.5. Dynamic mechanical analysis

DMA was used to investigate the thermomechanical properties of PHU foams. All PHU foams' storage modulus (E') and loss factor (tan δ) are depicted in Figure 5.6 as a function of temperature. E' decreases for PHU_4 from 97 MPa above T_g and drops for PHU_1 up to 12 MPa (Figure 5.6b and Table 5.2). Because of the short chain, the rubber chains are less mobile, making the polymer more rigid. By lowering the chain length of diamines utilized in the formulation, the tan δ (Figure 5.6) reveals a change in the T_g from 31.7 °C up to 49.3 °C, which is suggestive of a decreased molecular chain mobility.

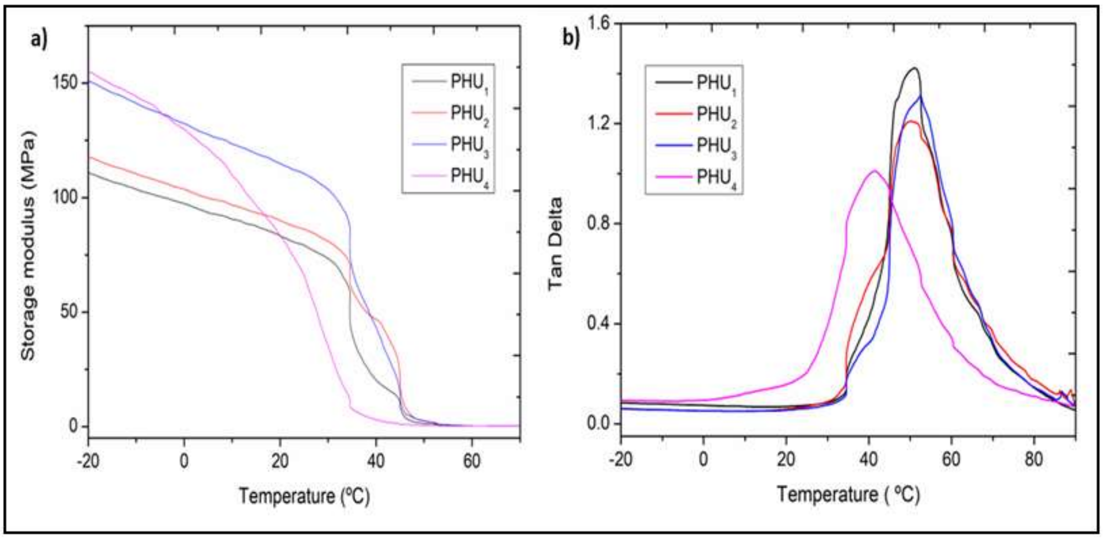


Figure 5.6: a) Storage modulus and b) Tan Delta versus temperature of self-blowing foams with different compositions

III.6. Crosslinking density and swelling index

The crosslinking density is obtained using equation 1, as you can see in table 1, the difference between PHU_1, PHU_2 and PHU_3 is quickly detected, the PHU1 foam prepared by EDA has the highest crosslinking density followed by PHU_2 and finally PHU_3. These results are interpreted by the length of the diamine chain used in the preparation of the foam and when the chain is small the degree of crosslinking is higher than the others which have longer chain lengths. On the other hand, the degree of crosslinking of PHU_4 is higher than PHU_3 and PHU_2 in spite of the big aliphatic chain that it possesses but we can explain this value of 52.317 $mol.m^{-3}$ by the hydrogen bonds that PHU4 will make with the help of the two Oxygens that they possess.

Crosslinking PHU was swelled when immerged in THF, the main reason is that the crosslinked chemical bonds can bind the molecular chains. Because the foam with a high crosslinking density contains more crosslinked chemical bonds, it has a lower swelling ratio than foams with a lower crosslinking density. Table 5.2 clearly shows that the swelling ratio of foams decreases as the diamine spacer chain length increases, except for PHU_4, which uses 1,8-diamino-3,6-dioxaoctane for the reasons already mentioned in the crosslinking density paragraph. Generally, longer chain diamines will result in NIPU foams with a higher degree of crosslinking and more compact molecular structures, which can decrease the degree of swelling in solvents like THF. On the other hand, shorter chain diamines will result in NIPU foams with a lower degree of crosslinking and more open molecular structures, which can increase the degree of swelling in solvents like THF [27].

Table 5.2: Table of different parameters of PHU foams

Sample	Density ($g.cm^{-3}$)	T_g (ºC)	T_α (ºC)	$T_{d5\%}$ (ºC)	$T_{d50\%}$ (ºC)	Cell size (µm)	Cross-linking density ($mol.m^{-3}$)	Swelling index (%)
PHU1	0.162 ± 0.0043	15.2	50.1	245	344	197	67.7	17
PHU2	0.165 ± 0.0044	11.3	48.9	259	345	205	63.9	14
PHU3	0.179 ± 0.0048	9.8	48.7	264	349	212	56.2	10
PHU4	0.213 ± 0.0052	7.5	39.2	272	354	234	52.3	9

IV. Conclusion

Nowadays, the development of NIPU materials presents a viable alternative to traditional isocyanate-based PU materials. In this chapter, NIPU foams were synthesized using tetrathiol as a crosslinker, which generates CO_2 that acts an internal blowing agent. They were prepared using cyclic carbonate derived from commercial epoxy and various diamines. The resulting PHU foams were then characterized for their structural, thermal, and mechanical properties, including SEM, apparent density, DMA, swelling index, crosslinking density, DSC, and TGA. These characterizations demonstrated that the prepared foams were highly flexible and that their structure and thermal properties were dependent on the degree of crosslinking and the chain length of the diamines used in the formulation.

The objective of our study was to prepare non-isocyanate polyurethane foams using our own method and to subject the obtained foams to several characterization tests to fully understand their chemical, morphological, thermal, and mechanical properties. In the next chapter, we focused on the preparation of biobased non-isocyanate polyurethane using Vanillyl alcohol as a biobased monomer to prepare thermoplastic non-isocyanate polyurethane films. The resulting biobased films displayed interesting properties.

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Chapter 6: Synthesis of bio-based non-isocyanate polyurethane thermoplastics

I. Introduction

Thermoplastic polyurethane (TPU) is a type of PU material that can easily be melted and reprocessed, making it suitable for a wide range of applications due to its biocompatibility, strength, elasticity, and chemical resistance [1,2]. Chemically, TPU is a multiple-phase block copolymer made by combining a polyol, a chain extender, and a diisocyanate. The TPU backbone comprises both soft and rigid segments. The soft segment made of polyols ensures flexibility, while the rigid one based on isocyanate and chain extender contributes to the mechanical and physical characteristics [3,4]. However, isocyanates face regulatory pressure due to their carcinogenic and mutagenic properties [5,6]. Additionally, conventional TPU production methods rely on fossil feedstocks, contributing to resource depletion [7,8]. Therefore, ongoing research aims to find durable, safe, and environmentally friendly approaches to obtaining TPU [9].

Over the past few years, the polymer industry has focused on the development of biodegradable polymeric materials derived from biological sources [8,10–12]. One such material that has garnered significant attention is bio-sourced thermoplastic polyurethane. This interest in biobased monomers is due to their numerous benefits, including reduced pollution, lower cost, and increased biodegradability. These monomers can be obtained through various methods, such as epoxidation of vegetable oils, terpenes, and vanillin derivatives, or glycidylation of bio-polyols [13–16]. The resulting monomers can then be carbonated with CO2.

In addition, as the use of sustainable and bio-based raw materials aligns with the principles of green chemistry, there is a growing interest in alternative pathways for producing cyclic carbonates, which traditionally have been derived from fossil fuels [16–18]. Biobased cyclic carbonates can be synthesized using a variety of methods, including epoxidation of vegetable oils, terpenes, and vanillin derivatives, as well as glycidylation of bio-polyols. These cyclic carbonates can then be carbonated with CO2 and subsequently reacted with diamines. Interestingly, aliphatic polyamines have demonstrated faster reactivity with cyclic carbonates than aromatic ones. However, aromatic amines can still be used by employing a phosphonium-based ionic liquid catalyst and elevated temperatures of around 140°C.

This study aimed to prepare biobased polyurethane films using four different diamines and to examine their flexibility, thermal stability, and mechanical properties. The focus was on determining the impact of chain length on the films' characteristics. The process involved epoxidizing vanillyl alcohol with NaOH and epichlorohydrin, followed by CO_2 fixation of the synthesized Bis epoxy at atmospheric pressure to obtain bi-cyclic carbonate. The resulting product was then polymerized in an oven to create a range of films.

II. Materials and methods

II.1. Materials

Vanillyl alcohol, which is the main raw material, tetrabutylammonium bromide (TBAB), 1,8-diazabicyclo [5.4.0]undec-7-ene (DBU), ethylenediamine (EDA), 1,6-hexamythelendiamine (HMDA), and 1,8-diamino-3,6-dioxaoctane were purchased from Sigma Aldrich. TBAB acts as a catalyst for the carbon dioxide (CO_2) cycloaddition and also as a transfer catalyst agent for the epoxidation reaction. 1,3-Diaminopropane, sodium hydroxide (NaOH) and epichlorohydrin were purchased from Merck. CO_2 was purchased from Carburos Metalicos.

II.2. Preparation of bis epoxy based vanillyl alcohol

The following approach was followed to produce a Bis epoxy resin based on vanillyl alcohol. Vanillin, TBAB, and epichlorohydrin were added in a molar ratio of 1:0.05:5 to a three-necked round bottom flask. After a progressive heating ramp, the mixture was mechanically stirred at 100 °C for 4 hours. The flask was then cooled back to room temperature. Each mole of vanillyl alcohol used in the reaction system required the addition of 0.1 mol TBAB and 5 mol sodium hydroxide with water to the flask, which was then continuously stirred for 12 hours in room temperature. The addition of sodium hydroxide is crucial in the formation of the Bis epoxy resin as it acts as a base to deprotonate the hydroxyl group of vanillyl alcohol, creating an alkoxide ion that reacts with epichlorohydrin to form the epoxy ring. During the reaction, it is important to add the sodium hydroxide drop by drop to prevent the formation of salt and any secondary reactions. The mixture is continuously stirred for 12 hours to ensure complete conversion of vanillyl alcohol to the desired Bis epoxy resin. The conditions of the reaction are carefully controlled to ensure that the reaction proceeds efficiently and yields a high-quality product. The use of a progressive heating ramp, along with continuous mechanical stirring, ensures that the reactants are mixed thoroughly and that the reaction proceeds homogeneously. Additionally, the addition of TBAB and sodium hydroxide in specific amounts and at specific stages of the reaction is critical to achieving the desired product.

The resulting solution was then washed three times using ethyl acetate and distilled water with a volume ratio of 1:1. After the separation process was achieved, the organic phase that contained the Bis epoxy resin was recovered, and then washed using distilled water. The organic phase was dried with anhydrous magnesium sulfate and the resulting precipitate was filtered. To remove excess ethyl acetate and epichlorohydrin from the organic layer, the filtrate was then evaporated using a rotary evaporator, yielding the final Bis epoxy resin. After the synthesis of the Bis epoxy resin, the resulting solution was washed three times with a mixture of ethyl acetate and distilled water in a 1:1 volume ratio. This washing process helps to remove any impurities and residual reactants that may still be present in the solution. After the separation process, the organic phase containing the Bis epoxy resin was recovered and washed again using distilled water to remove any remaining impurities.

To ensure the complete removal of any residual water, the organic phase was dried using anhydrous magnesium sulfate. The resulting precipitate was then filtered to remove any excess magnesium sulfate. To remove any excess ethyl acetate and epichlorohydrin from the organic layer, the filtrate was evaporated using a rotary evaporator. This process involves using heat and reduced pressure to remove the solvent from the organic layer, resulting in a concentrated solution of the Bis epoxy resin. The final Bis epoxy resin obtained after this purification process is of high quality and purity and is ready for use in various applications.

II.3. Preparation of bi-cyclic carbonate

In a single-necked flask, the viscous liquid Bis epoxy was mixed with TBAB (5% mw) at temperature of 105 °C under continuous stirring using the mechanical stirrer. Gaseous CO_2 was blown into the reaction mixture through a syringe for 4 hours under atmospheric pressure. Chemical analysis using NMR and FTIR-IR were performed to study the obtained results and the conversion of the epoxide to cyclic carbonate.

II.4. Preparation of NIPU films

The following method was used for the final polymerization and preparation of the films: the obtained bi-cyclic carbonate was mixed with each diamine in a beaker at room temperature for 30 minutes, and DBU was added as a catalyst for the polymerization. The specific quantities of the components used in this reaction are provided in Table 6.1. Then the beaker is put in a desiccator with vacuum by using a pump to eliminate all the bubbles in the mixture and to obtain bubble-free films. Once the beaker has been left in the desiccator for 5 minutes, the mixture of 6g is poured into a silicone mold and placed in the oven for 8 hours at 80°C. The films are then removed from the molds and left to cool to room temperature before use, the films are 5-8 mm thin.

Table 6.1: Products and quantities used in each films prepared

Products	*Diamines used*	*Quantity of Bi-cycic carbonate (g)*	*Quantity of diamines (g)*	*Quantity of DBU (g)*
TPHU1	ethylenediamine	*5*	*2.05*	*0.5*
TPHU2	1,3 diaminopropane	*5*	*2.15*	*0.5*
TPHU3	1,6 hexamythelendiamine	*5*	*2.25*	*0.5*
TPHU4	Diamino dioxocatone	*5*	*3*	*0.5*

II.5. Characterization

Chemical structure of the bi-cyclic carbonate was analyzed by ^{1}H NMR and FTIR spectroscopy. he nuclear magnetic resonance (NMR) spectra were acquired on a high-field spectrometer operating at 500 MHz, using a solution of the sample in deuterated chloroform as the solvent. The spectra were processed using standard Fourier transform methods to obtain the chemical shifts and coupling constants, which were then used to assign the proton and carbon resonances and to determine the molecular structure and composition of the sample. Chemical structure of the bi-cyclic carbonate and NIPU foams were analyzed by attenuated total reflection- Fourier transform infrared (ATR-FTIR) using a spectrometer (Spectrum Two, from PerkinElmer, Waltham, MS, USA). Infrared spectra were recorded from 450 cm−1 to 4000 cm−1 wavenumber, with a resolution of 4 cm−1.

Raman spectroscopy was performed on a Renishaw 2000 Confocal Raman Microprobe using a 514.5 nm argon ion laser. The spectra were recorded from 750 to 3500 cm^{-1}.

Differential scanning calorimetry was carried out using NETZSH DSC- 214 model, in the temperature range from -50 to 25°C at heating rate of 10°C/min under nitrogen atmosphere, the stability of baseline was checked before of each measurement. Thermogravimetric analysis was carried out using a TA-Q500 (TA-instrument, USA). 10 mg were heated under a nitrogen atmosphere from room temperature to 800°C at 10 °C/min heating rate.

A temperature sweep from −100 °to 70 °C, with a heating rate of 2 °C min−1, was carried out in a DMA analyzer (DMA Q800 from TA Instruments, New Castle, DW, USA). An amplitude of 15 µm and a frequency of 1 Hz were set in tension mode. The number of moles of network per unit volume of cured polymer is known as crosslink density (ν). Crosslink density of NIPU films can be calculated from the modulus at the rubbery plateau by using the equation 1:

$$\nu = \frac{E'}{3RT}$$

where T is the temperature in rubbery plateau from which the elastic modulus is taken, the temperature is in Kelvin, R is the gas constant and E' is the storage modulus at T [19,20].

III. Results and discussion

III.1. Preparation of Bis epoxy based vanillyl alcohol

The epoxidation reaction using epichlorohydrin and NaOH is a well-known chemical process that has been studied and mastered by many research groups [13,21,22]. This reaction involves the conversion of an olefin (a molecule with a carbon-carbon double bond) into an epoxide (a molecule with a three-membered ring containing an oxygen atom). The reaction proceeds via the formation of an intermediate chlorohydrin, which is then deprotonated by NaOH to form the epoxide. The reaction conditions, such as the temperature, pressure, and concentration of reagents, can be adjusted to optimize the yield and selectivity of the epoxidation reaction.

One of the primary uses of the epoxidation reaction is in the production of epoxy resins, which are widely used in various industries such as coatings, adhesives, and electronics. Other applications of epoxides include as solvents, as starting materials for the synthesis of pharmaceuticals and other organic compounds, and as cross-linking agents in polymer chemistry. Research on the epoxidation reaction using epichlorohydrin and NaOH continues to be of interest to the scientific community, as there is still room for improvement in terms of reaction efficiency and selectivity [22]. New catalysts and reaction conditions are being developed to achieve better yields and reduce waste, as well as to enable the epoxidation of more challenging olefin substrates [21–23].

In our study, we performed this reaction using vanillyl alcohol in order to get a vanillyl-based Bis epoxy because of the two hydroxyl groups contained in vanillyl alcohol. The composition and structure of the Bis epoxy vanillyl alcohol were evaluated by ATR-FTIR. We observe the appearance of the 910 cm^{-1} band, corresponding to the epoxy group in the prepared component of this reaction. The NMR spectrum (Figure 6.1) shows the decrease of the peaks corresponding to epoxy in 2.7 and 2.9 ppm which shows the integral consumption of epoxy following this epoxidation reaction.

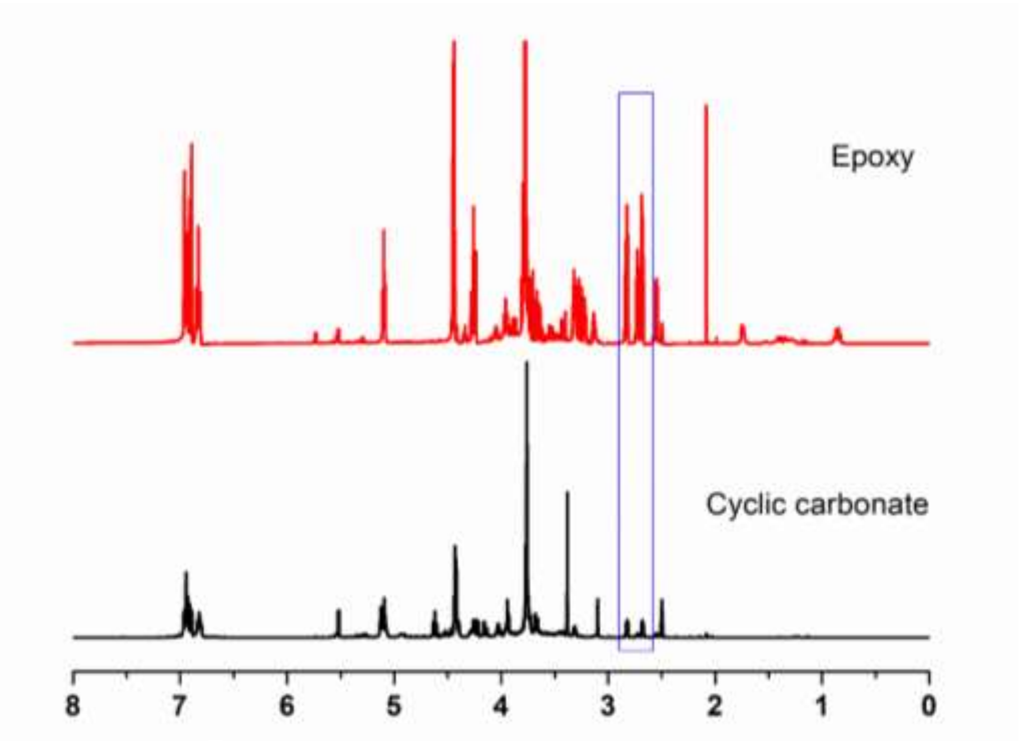
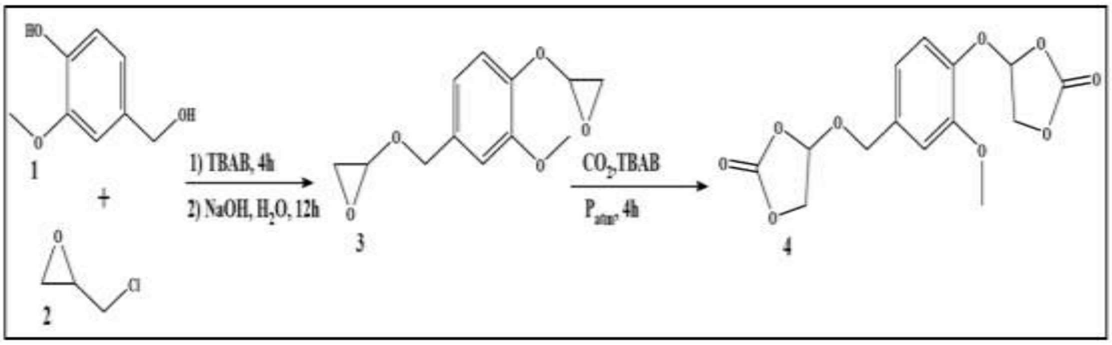


Figure 6.1: NMR of Epoxy and Cyclic carbonate prepared by Vanillyl alcohol

III.2. Preparation of Bi-cyclic carbonate

The cyclic carbonate monomers were produced by chemical fixation of CO_2, without the use of an autoclave, by reacting the previous bio-based epoxy with carbon dioxide at atmospheric pressure, as was done in the previous chapter. The chemical fixation of CO_2 has become an area of intense research interest due to the growing concerns regarding climate change. One approach to fixing CO_2 involves using epoxy and tetrabutylammonium bromide (TBAB) as catalysts to promote the reaction between CO_2 and epoxides. Under appropriate reaction conditions, the epoxide ring opens up and reacts with CO_2 to form cyclic carbonates, which can be used as valuable chemicals or monomers in the synthesis of various materials. The use of TBAB as a catalyst can enhance the reaction rate and efficiency, while the use of Bis epoxy provides a renewable and sustainable alternative to petroleum-based materials. This method has the potential to reduce the amount of CO_2 emissions by converting it into useful products and represents an important step towards mitigating the impact of climate change.



Scheme 6.1: Glycidylation reaction and chemical fixation to obtain bi-cyclic carbonate

III.3. Preparation of NIPU films

The bi-cyclic carbonate was then used to prepare bio-based thermoplastic PHU films with four different diamines. The polymerization is carried out without the use of solvents. This reduces the impact of solvents on the environment. ATR-FTIR, TGA, DMA, DSC, and SEM were some of the characterisation techniques used to examine the derived biobased films. The conversion of the carbonate groups in the bi-cyclic carbonate to PHU was examined using the ATR-FTIR technique.

The combined infrared spectra of all biobased films are shown in Figure 6.2. The spectra of all the films are similar. The complete disappearance of the peaks associated to the carbonyl group of the cyclic carbonate at 1793 cm^{-1} from the spectra of the different films indicates that the carbonate has been completely converted to hydroxyurethane, as shown by the presence of the C=O group stretch of the urethane band at 1645 cm^{-1}. A broad band is observed between 3200 and 3600 cm^{-1}, indicating the existence of NH groups of the urethane groups.

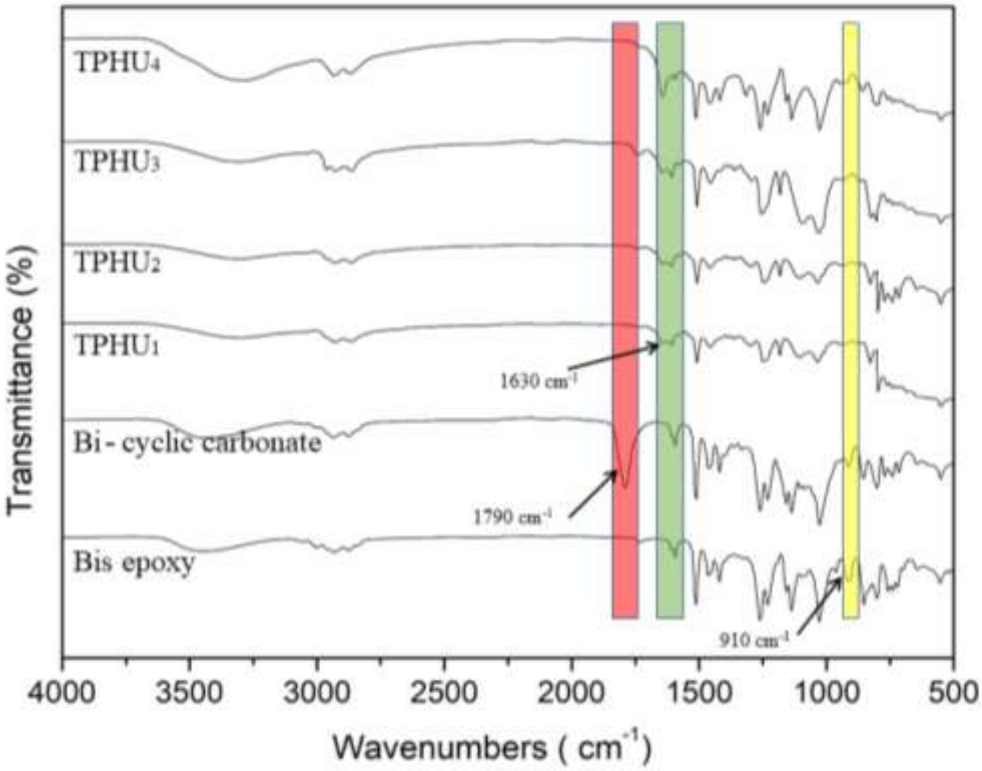


Figure 6.2: ATR-FTIR for Bis epoxy, Bi-cyclic carbonate and TPHU films

III.4. Thermal stability

The thermal stability and profile of the PHU films were analysed by TGA analyses. All samples are stable up to 265 ºC. The two films prepared by diaminopropane and hexamethylene diamine have almost the same thermal profile due to the similarity of the two despite the longer alkyl chain, but the film prepared by ethylenediamine has small Td10% and Td50% with temperatures of 317 ºC and 384 ºC respectively, on the other hand the PHU prepared by diaminodioxactone has very good profile with a $T_{d10\%}$ of 328 ºC and 388 ºC for $T_{d50\%}$ (figure 6.3). In general, polymers with longer chains tend to have higher thermal stability than those with shorter chains [24,25] This correlation has been observed in various polymers such as polyethylene [26], polypropylene [27], and polyurethane [28]. In all cases, longer chain length was found to be associated with higher thermal stability and lower rates of thermal degradation. This is because longer chains are more rigid and less able to break or degrade under the influence of heat. As a result, polymers with longer chains are less prone to thermal degradation, which is the breakdown or decomposition of a material due to the high temperatures. Sheng et al. [29]

found similar results regarding the relationship between thermal stability and the length of the aliphatic chain in a NIPU system. They reported that hexanediamine-prepared NIPU had a higher initial degradation temperature than the ethylemediamine-prepared NIPU, at 266 °C, and that the NIPU with the longest spacer length had the highest thermal stability. Others factors can also influence the thermal stability as the presence of impurities or contaminant or functional group on the polymer chain like the thermoplastic film prepared by 1,8-diamino-3,6-dioxaoctane that contain the ether functionality.

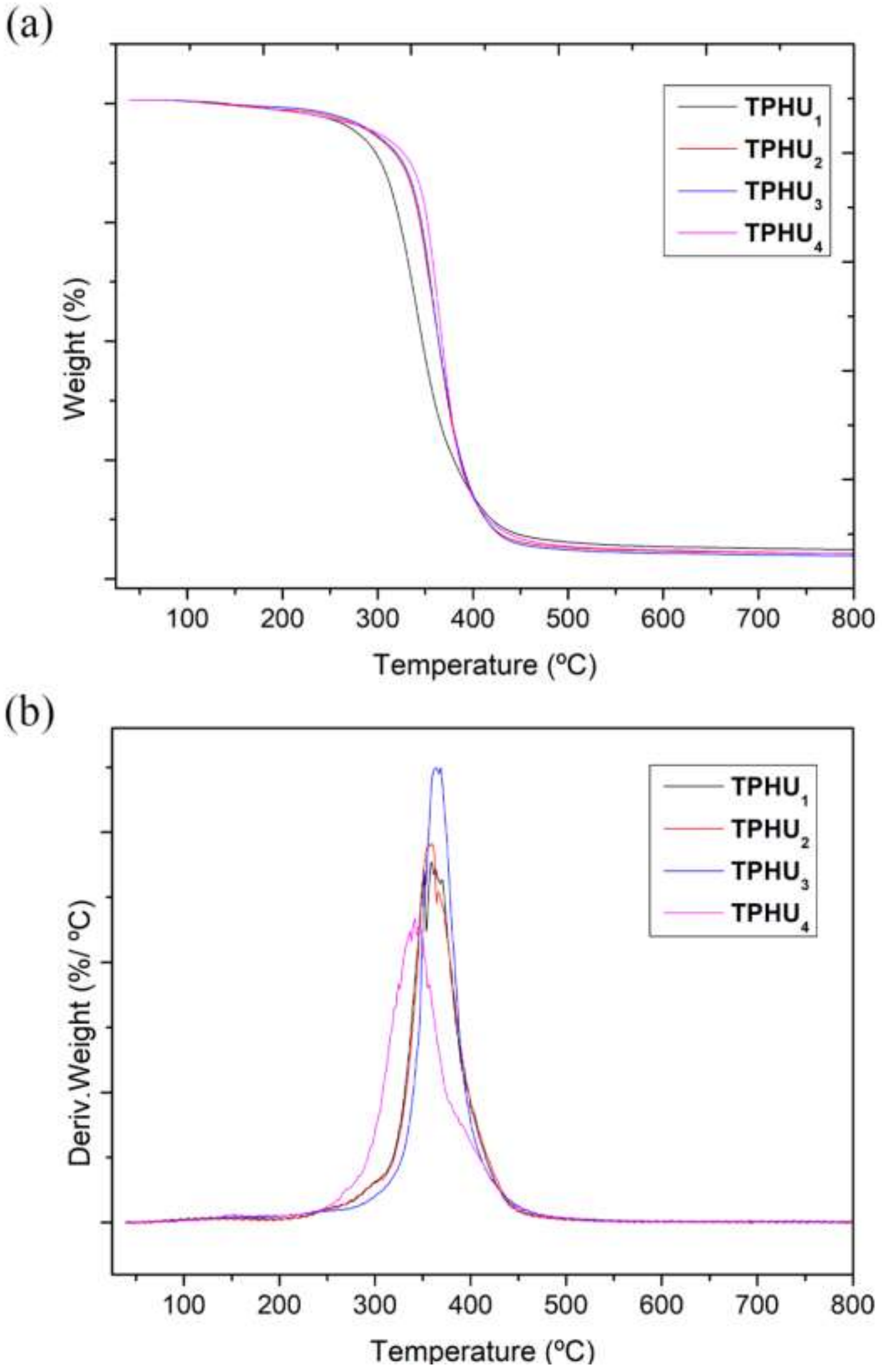


Figure 6.3: (a) TGA and (b) DTG curves of the TPHU films

With no melting of a crystalline phase during the first heating, the DSC curves of PHU films exhibit comparable patterns, indicating that all systems are amorphous (Figure 6.4). The glass transition temperature (T_g) followed the expected pattern, with the thermoplastic PHU made with diaminodioxactone having the lowest T_g (21 ºC), followed by the thermoplastic PHU made with hexamethylenediamine, which had a T_g of 25 ºC, and the TPHU made with ethylenediamine having the highest Tg. Thus, the extended chain of amines seemed to reduce T_g. The value of T_g depends on the mobility of the polymer chain and smaller chain of our films made by smaller diamine reduce the mobility and improve the T_g. In general, increasing the crosslinking density of a polyurethane film will increase its T_g. This is because crosslinking creates additional bonds between polymer chains, which increases the energy required to break these bonds and cause the material to flow. As a result, the material becomes more rigid and less flexible at higher temperatures, and the T_g increases. In a similar study, NIPU foams prepared using different amines, such as HMDA, 1,9- nonanediamine (NDA), and 1,13-tridecanediamine (TDA) reported the highest Tg for the HMDA due to its lower average molecular weight and chain length [30]. Additionally, the presence of oxygen in 1,8-diamino-3,6-dioxaoctane can reduce chain mobility due to hydrogen bonding, resulting in a lower T_g.

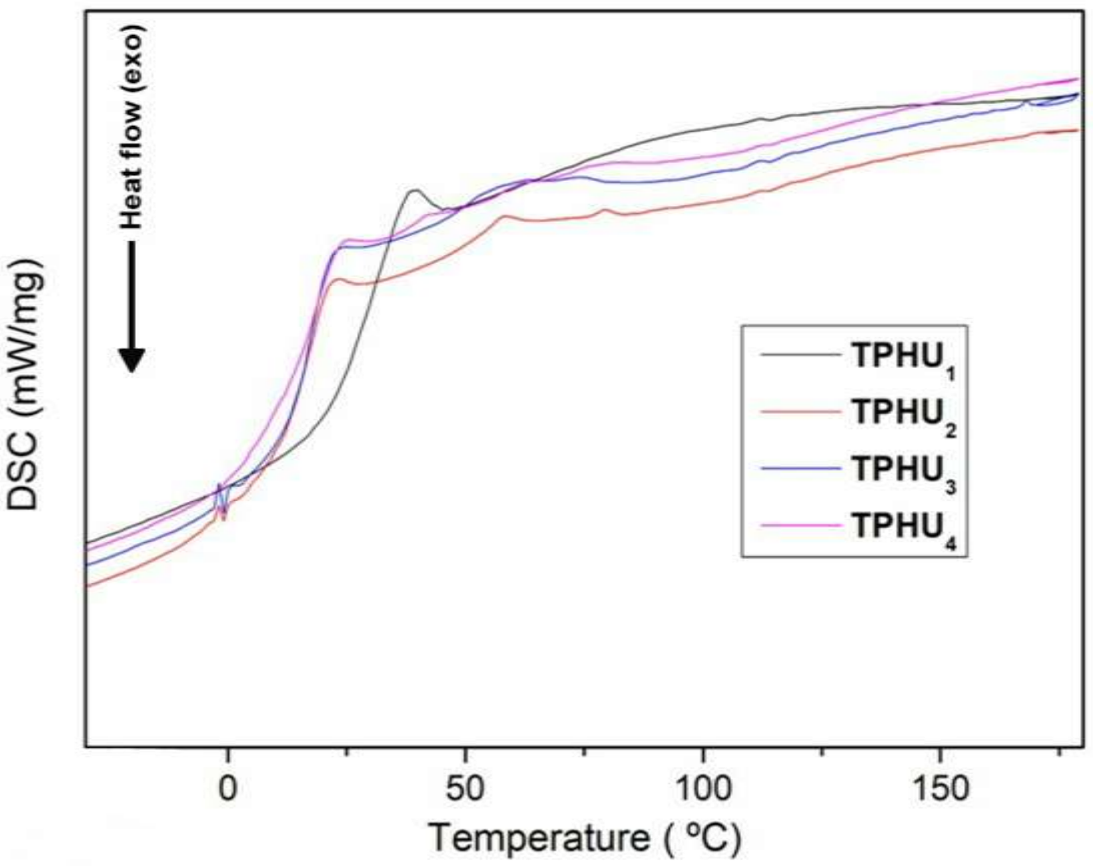


Figure 6.4: Differential scanning calorimetry (DSC) curves of all TPHU films

III.5. Mechanical properties

The thermomechanical characteristics of biobased thermoplastic PHU films were examined using DMA. The storage modulus of a polymer is a measure of the stiffness or rigidity of the material, it is one of the key mechanical properties of a polymer and is typically measured using DMA. Figure 6.5a shows the storage modulus curve, the storage modulus of TPHU4 is the largest than the other thermoplastic films prepared by different diamines due to the alkyl chain length of 1,8-Diamino-3,6-dioxaoctane diamine followed by TPHU3 which is prepared by hexamethylenediamine. The storage modulus of a polymer can be affected by various factors, including chain length. In general polymer with longer chains tend to have higher storage moduli because the longer chains are more rigid and less able to deform under an applied load. Jung et al. [31] describes a study in which the storage modulus of polyurethane elastomers was measured as a function of chain length, the results of the study showed that the storage modulus of the polyurethane elastomers increased with increasing chain length. Figure 6.4b shows tan δ of all PHU films as a function of temperature, exhibiting a shift in the T_g from 31.7 °C to 49.3 °C. This is indicatives of a decreased molecular chain mobility with decreasing chain length of the included diamines in the formulation.

Crosslinking density refers to the number of chemical bonds that exist between polymer chain in a polymer, in polyurethane films crosslinking occurs when the chains react with each other forming the covalent bonds that link the chains together. The effect of crosslinking density on the properties of polyurethane films depends on the chain length of the polymer. The crosslinking density is obtained using equation 1. The difference between TPHU1, TPHU2, TPHU3 and TPHU4 may be immediately seen in Table 6.2. The film made from TPHU1 generated with ethylenediamine has the minimum crosslinking density, followed by TPHU2 made from diaminopropane. The degree of crosslinking is lower when the diamine chain is short compared to other compounds that have larger chain lengths, which is how these results are interpreted by the length of the diamine chain utilized to make the foam. TPHU4 has a larger aliphatic chain than TPHU3 and PHU2, yet despite this, its degree of crosslinking is lower.

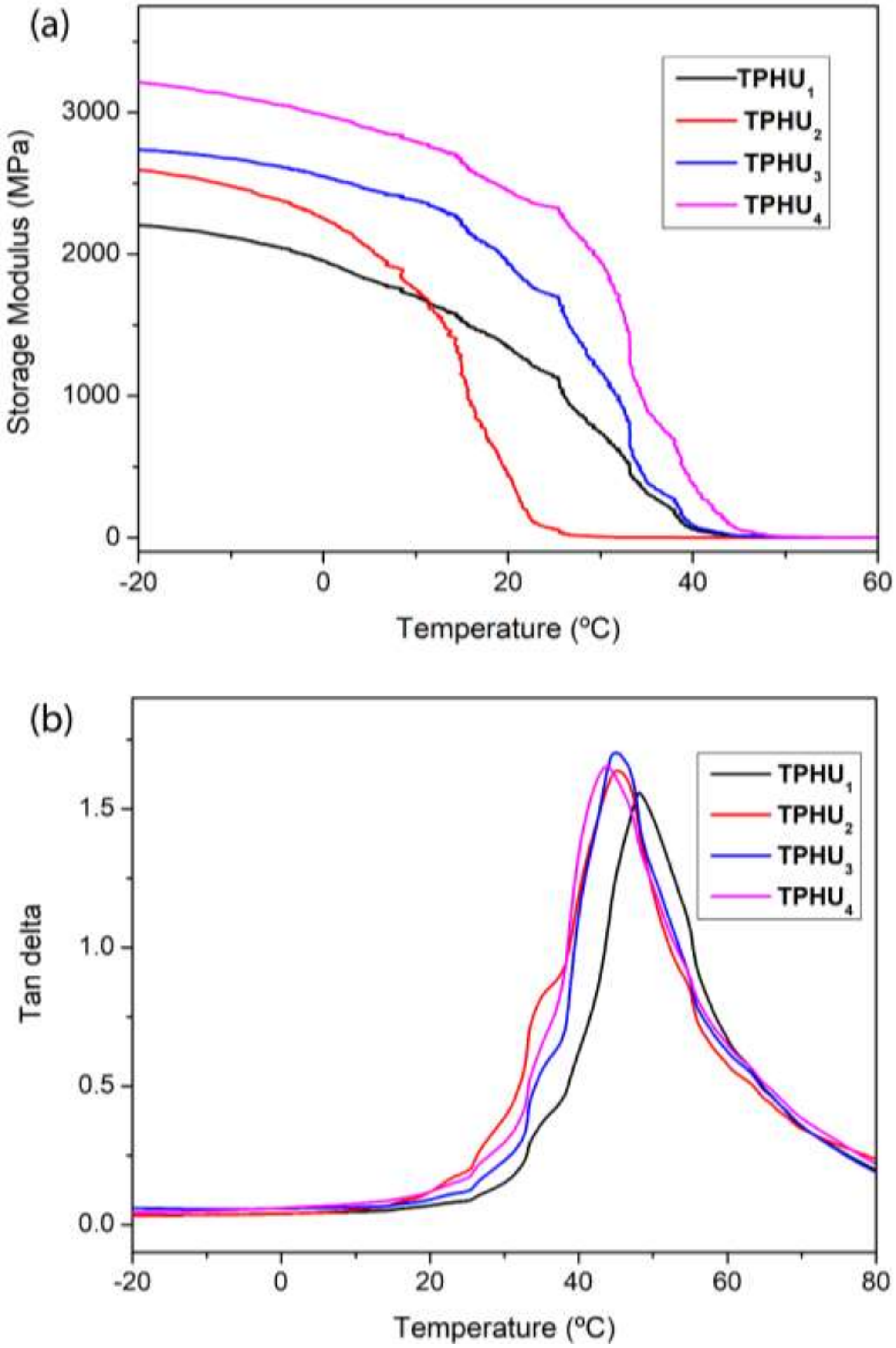


Figure 6.5: Storage modulus and damping factor of the TPHUs films

Table 6.2: Different parameters of all TPHU films

	Diamine used	$T_{d10\%}$ (°C)	$T_{d50\%}$ (°C)	T_g (°C)	T_α (°C)	V ($mol.m^{-3}$)
TPHU1	Ethylenediamine	281.4	343.5	28.9	47.3	21.3
TPHU2	1,3-Diaminopropane	291.7	359.1	27.4	42.2	23.6
TPHU3	1,6-Hexamythelendiamine	293.5	359.4	26.5	42.1	26.1
TPHU4	1,8-Diamino-3,6-dioxaoctane	298.9	362.2	22.5	41.2	27.8

III.6. Morphology of NIPU films

SEM imaging was carried out on the polyurethane film samples and no significant differences were observed between the samples (figure 6.6). The morphology of the films appeared to be consistent, with no visible defects or structural abnormalities. This suggests that the samples were homogenous and that the preparation process was successful in achieving the desired composition and structure. These results indicate that the films have a high level of reproducibility, which is a desirable characteristic for potential industrial applications.

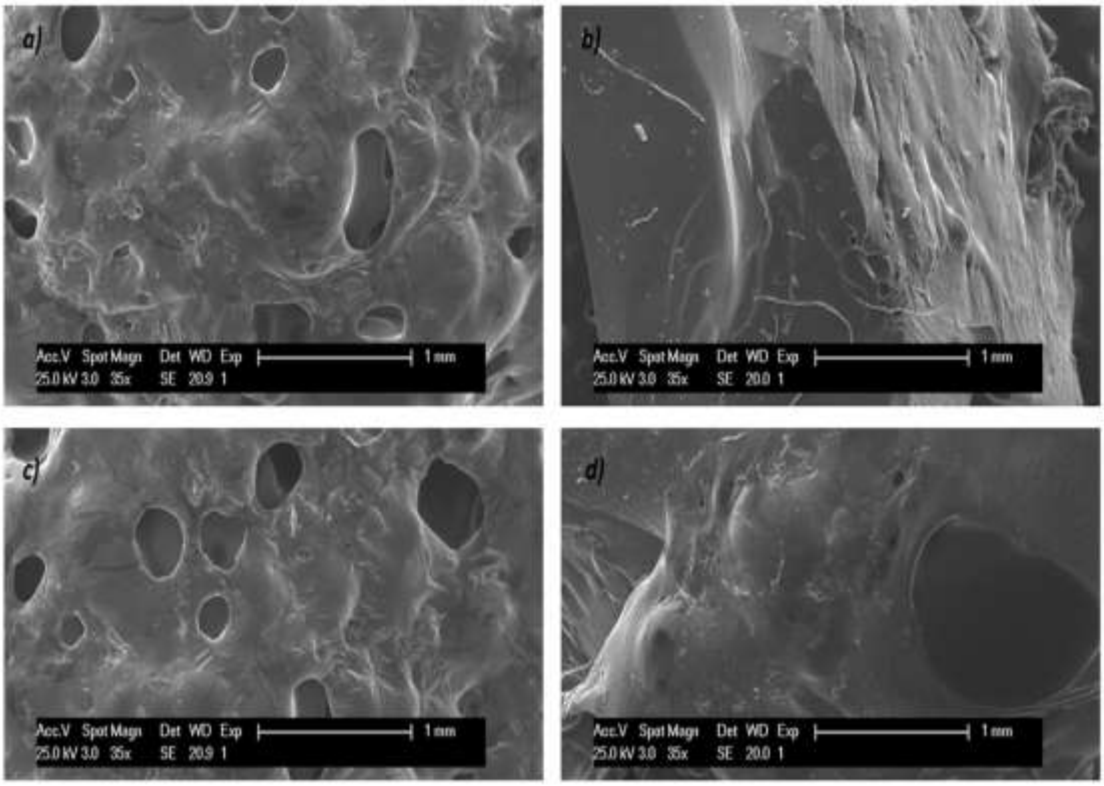


Figure 6.6: Scanning electron microscopy of the PHUs films

IV. Conclusion

In this study, we investigated the synthesis and polymerization process of bio-based cyclic carbonate monomers to produce polyhydroxyurethane (PHU). Various diamines were used to enhance the thermal and mechanical properties of the films. The synthesis technique produced PHU with qualities similar to those of conventional PU, and it is an industrially scalable technology that operates at mild conditions and atmospheric pressure. To produce biobased PU free-isocyanate, a solvent-free and biobased raw material was employed. The thermoplastic PHU produced can replace polyurethanes as it is effective, sustainable, and scalable.

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General Conclusion

This doctoral thesis has developed several synthesis routes to produce polyurethane that are safer and more sustainable. The research was carried out by first attaining a reduced toxicity formulation for PU foams using an alternative catalyst in a conventional formulation. The work then continued by developing isocyanate-free polyurethane foams and composites using less toxic commercial products and bio-based reactants. The most relevant conclusions are detailed below with possible future lines of research for this work.

Reduced toxicity of conventional PU foams

Bismuth triflate has been shown to be a potential candidate for producing less toxic PU foams using the conventional reactants. The foaming performance of the new catalyst and the resulting properties were comparable to those of a tin-catalysed foam. Thus, the use of this new catalyst can be a straightforward solution to partly reduce the health and environmental issues of the PU industry.

Non-isocyanate formulations

Non-isocyanate formulations have been studied to produce both solid and foamed polyurethanes developing two alternative formulations: poly(hydroxyurethane) and poly(hydroxythioether).

Polyhydroxyurethane (PHU) is recognised as the most promising alternative to PU and involves the reaction between multifunctional amines and cyclic carbonates. PHU was synthesized via two different approaches: the first is based on the dimethyl carbonate method (DMC), while the second on the CO_2 fixation procedure.

- The DMC method was first considered as a promising approach for the synthesis of biobased monomers. This method involves the preparation of a bi-cyclic carbonate using dimethyl carbonate and glycerol. The resulting product is considered bio-based because glycerol is derived from bio-mass. The resulting bio-based diacids can then be used to obtain NIPU product. In this thesis, both adipic acid and citric acid were used to obtain a bi-cyclic carbonate and tri-cyclic carbonate, respectively. The resulting products were purified and analyzed to evaluate their potential for use in PU foam production. However, the low molecular weight of the resulting products hindered their use for the production of polyurethane foams and has not been reported in this thesis.

- The CO_2 fixation is an approach that relies on the cycloaddition of carbon dioxide onto an epoxide. In this thesis, both commercial and bio-based synthesized epoxide were used for the production of cyclic carbonates. This methodology was suitable for the production of cyclic carbonates in high yields and large quantities to then prepare non-isocyanate polyurethane films and foams. The NIPU films were prepared with two major epoxides, the first one being the commercial epoxy, and then the biobased epoxy was synthesized using vanillyl alcohol. These two procedures gave films with attractive mechanical and thermal properties. This thesis has also analysed the relationship between thermal stability and mechanical properties with chain length of the used amines to produce PHU with the characteristic versatility of PU. Self-blowing foams were also developed using tetrathiol as a crosslinker, which generates CO_2 that acts an internal blowing agent. This approach has the potential to directly replace conventional PU foams.

Poly(hydroxythioether) have also been suggested as a potential alternative to PU foams. This thesis presented a rapid, self-blowing synthesis route at room temperature by decarboxylative S-alkylation of a thiol with cyclic carbonates leveraging this highly reactive chemistry with two different multifunctional and commercially available thiols. The proposed synthesis route produced flexible foams with appropriate thermal stability and mechanical properties.

Appendix

Publications related to this Ph.D. thesis

1) S. E. Khezraji,, S. Thakur,L.Belhachemi. M. Raihane, M. A. Lopez-Manchado, R. Verdejo and M. Lahcini, Use of Novel Non-Toxic Bismuth Catalyst for the Preparation of Flexible Polyurethane Foam. Polymers, 2021 3(24), 4460

2) S. E. Khezraji, M. Chaib, S. Thakur, M. Raihane, M. A. Lopez-Manchado, R. Verdejo and M. Lahcini, Synthesis of Novel Non-Isocyanate Polyurethane/Functionalized Boron Nitride Composites. Polymers, 2022, 3934–3934.

3) S. E. Khezraji, L.Belhachemi. H.Benyoucef, M. A. Lopez-Manchado, R. Verdejo and M. Lahcini, Recent progress of non-isocyanate polyurethane foam and Their challenges. Polymers, 2022, 15(2), 254,

4) S. E. Khezraji, S.Thakur, H.Benyoucef, M. A. Lopez-Manchado, R. Verdejo and M. Lahcini, Fast Synthesis of crosslinked self-blowing poly(β-hydroxythioether) foams by decarboxylatives-alkylation of thiols at room temperature. European Polymer Journal 189 (2023) 111960

Internships done during this Ph.D. thesis

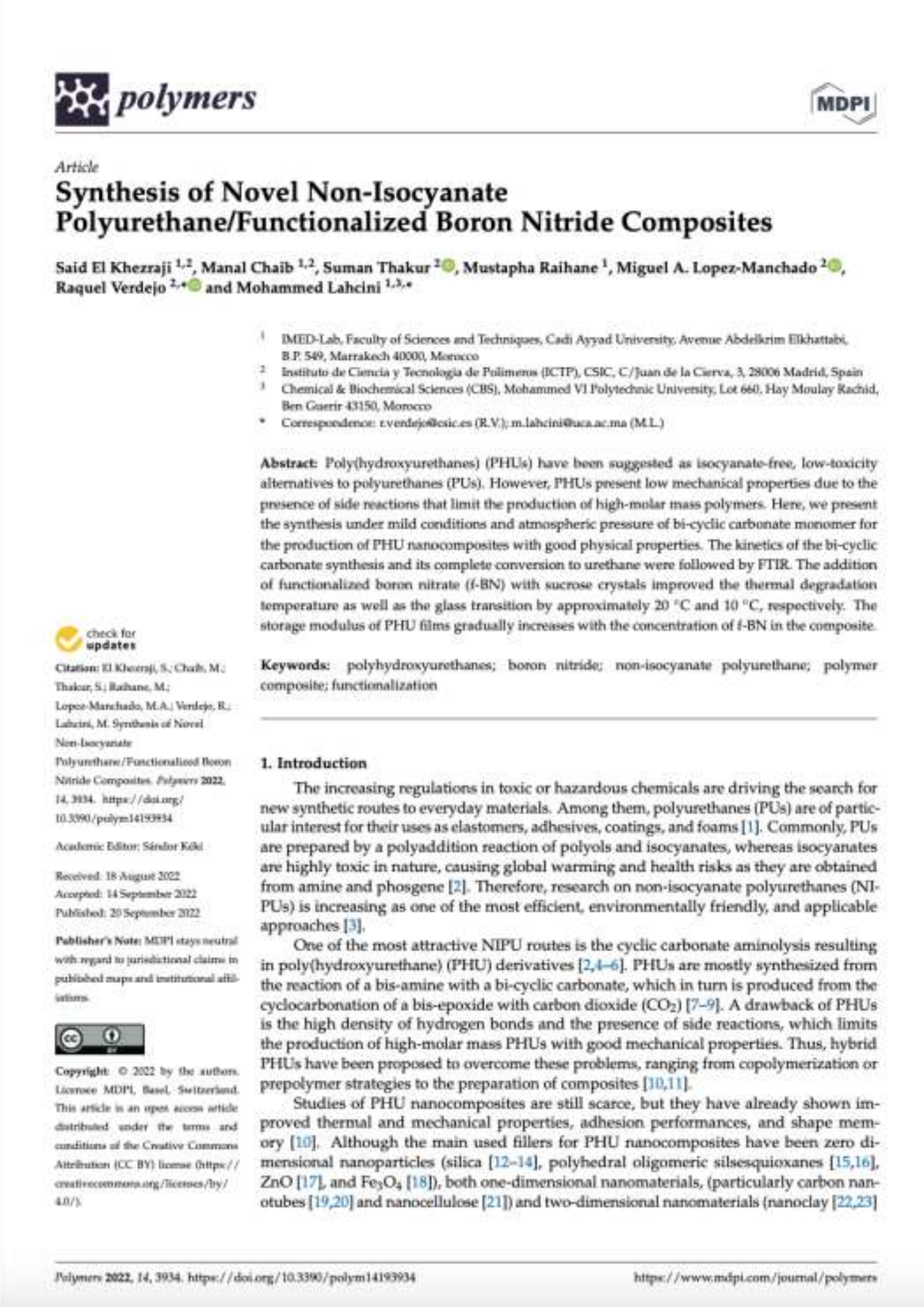
Preparation and characterization of nafion Films functionnalized for PEMFC – LISE Laboratory (Sorbonne University) – March to July 2018

Scholarships obtained during this Ph.D. thesis

Erasmus plus collaboration between UCA and Sorbonne University (March-June 2018)

Oral communications during this Ph.D. thesis

International conference of Macromolecules (Poland and India) **(Second Prize)**



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Article

Synthesis of Novel Non-Isocyanate Polyurethane/Functionalized Boron Nitride Composites

Said El Khezraji [1,2], Manal Chaib [1,2], Suman Thakur [2], Mustapha Raihane [1], Miguel A. Lopez-Manchado [2], Raquel Verdejo [2,*] and Mohammed Lahcini [1,3,*]

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Abstract: Poly(hydroxyurethanes) (PHUs) have been suggested as isocyanate-free, low-toxicity alternatives to polyurethanes (PUs). However, PHUs present low mechanical properties due to the presence of side reactions that limit the production of high-molar mass polymers. Here, we present the synthesis under mild conditions and atmospheric pressure of bi-cyclic carbonate monomer for the production of PHU nanocomposites with good physical properties. The kinetics of the bi-cyclic carbonate synthesis and its complete conversion to urethane were followed by FTIR. The addition of functionalized boron nitrate (f-BN) with sucrose crystals improved the thermal degradation temperature as well as the glass transition by approximately 20 °C and 10 °C, respectively. The storage modulus of PHU films gradually increases with the concentration of f-BN in the composite.

Keywords: polyhydroxyurethanes; boron nitride; non-isocyanate polyurethane; polymer composite; functionalization

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Citation: El Khezraji, S.; Chaib, M.; Thakur, S.; Raihane, M.; Lopez-Manchado, M.A.; Verdejo, R.; Lahcini, M. Synthesis of Novel Non-Isocyanate Polyurethane/Functionalized Boron Nitride Composites. *Polymers* **2022**, 14, 3934. https://doi.org/10.3390/polym14193934

Academic Editor: Sándor Kéki

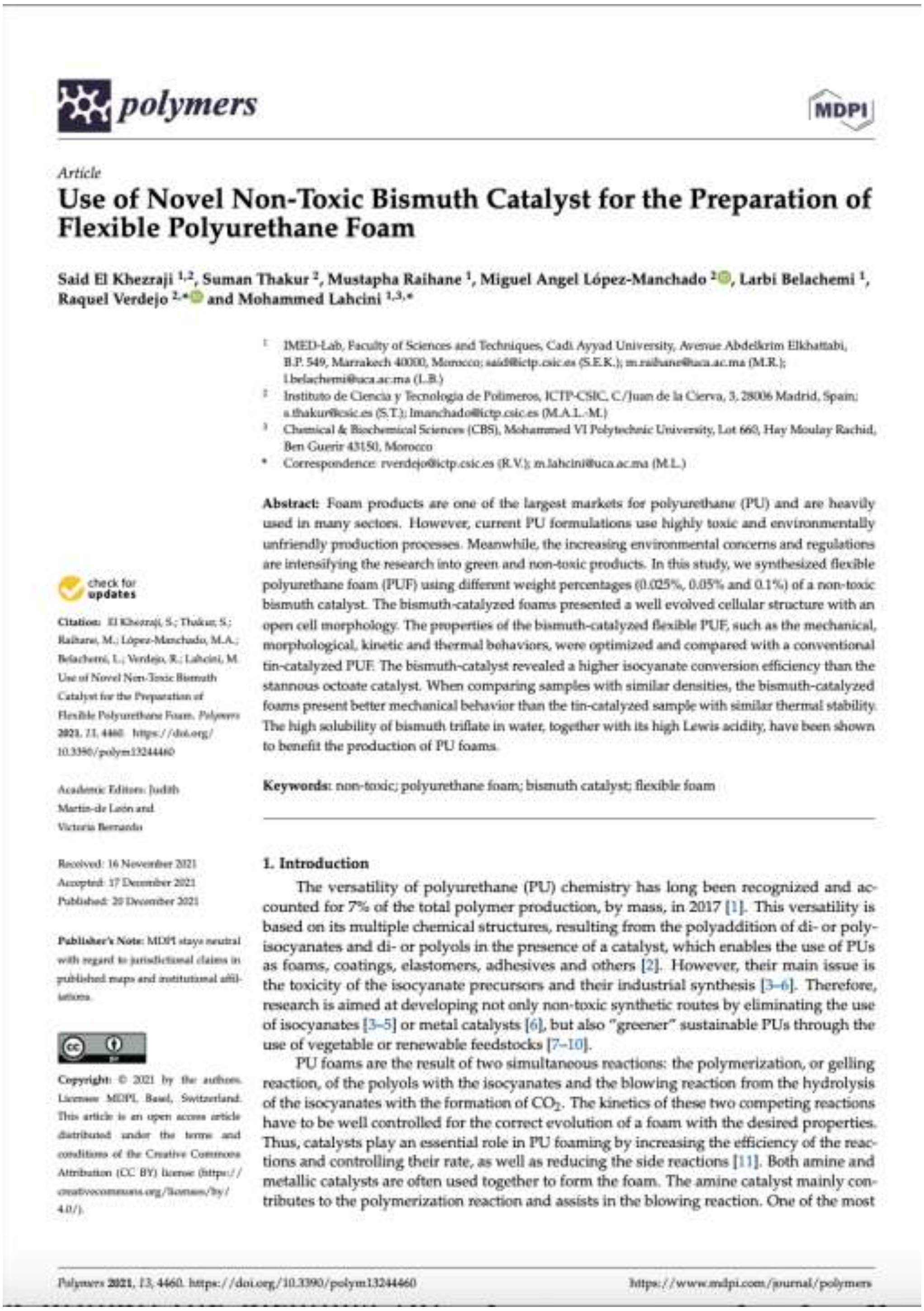
Received: 18 August 2022
Accepted: 14 September 2022
Published: 20 September 2022

1. Introduction

The increasing regulations in toxic or hazardous chemicals are driving the search for new synthetic routes to everyday materials. Among them, polyurethanes (PUs) are of particular interest for their uses as elastomers, adhesives, coatings, and foams [1]. Commonly, PUs are prepared by a polyaddition reaction of polyols and isocyanates, whereas isocyanates are highly toxic in nature, causing global warming and health risks as they are obtained from amine and phosgene [2]. Therefore, research on non-isocyanate polyurethanes (NIPUs) is increasing as one of the most efficient, environmentally friendly, and applicable approaches [3].

One of the most attractive NIPU routes is the cyclic carbonate aminolysis resulting in poly(hydroxyurethane) (PHU) derivatives [2,4–6]. PHUs are mostly synthesized from the reaction of a bis-amine with a bi-cyclic carbonate, which in turn is produced from the cyclocarbonation of a bis-epoxide with carbon dioxide (CO_2) [7–9]. A drawback of PHUs is the high density of hydrogen bonds and the presence of side reactions, which limits the production of high-molar mass PHUs with good mechanical properties. Thus, hybrid PHUs have been proposed to overcome these problems, ranging from copolymerization or prepolymer strategies to the preparation of composites [10,11].

Studies of PHU nanocomposites are still scarce, but they have already shown improved thermal and mechanical properties, adhesion performances, and shape memory [10]. Although the main used fillers for PHU nanocomposites have been zero dimensional nanoparticles (silica [12–14], polyhedral oligomeric silsesquioxanes [15,16], ZnO [17], and Fe_3O_4 [18]), both one-dimensional nanomaterials, (particularly carbon nanotubes [19,20] and nanocellulose [21]) and two-dimensional nanomaterials (nanoclay [22,23]



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Article

Use of Novel Non-Toxic Bismuth Catalyst for the Preparation of Flexible Polyurethane Foam

Said El Khezraji [1,2], Suman Thakur [2], Mustapha Raihane [1], Miguel Angel López-Manchado [2], Larbi Belachemi [1], Raquel Verdejo [2,*] and Mohammed Lahcini [1,3,*]

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Abstract: Foam products are one of the largest markets for polyurethane (PU) and are heavily used in many sectors. However, current PU formulations use highly toxic and environmentally unfriendly production processes. Meanwhile, the increasing environmental concerns and regulations are intensifying the research into green and non-toxic products. In this study, we synthesized flexible polyurethane foam (PUF) using different weight percentages (0.025%, 0.05% and 0.1%) of a non-toxic bismuth catalyst. The bismuth-catalyzed foams presented a well evolved cellular structure with an open cell morphology. The properties of the bismuth-catalyzed flexible PUF, such as the mechanical, morphological, kinetic and thermal behaviors, were optimized and compared with a conventional tin-catalyzed PUF. The bismuth-catalyst revealed a higher isocyanate conversion efficiency than the stannous octoate catalyst. When comparing samples with similar densities, the bismuth-catalyzed foams present better mechanical behavior than the tin-catalyzed sample with similar thermal stability. The high solubility of bismuth triflate in water, together with its high Lewis acidity, have been shown to benefit the production of PU foams.

Keywords: non-toxic; polyurethane foam; bismuth catalyst; flexible foam

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Citation: El Khezraji, S.; Thakur, S.; Raihane, M.; López-Manchado, M.A.; Belachemi, L.; Verdejo, R.; Lahcini, M. Use of Novel Non-Toxic Bismuth Catalyst for the Preparation of Flexible Polyurethane Foam. *Polymers* **2021**, *13*, 4460. https://doi.org/10.3390/polym13244460

Academic Editors: Judith Martín-de León and Victoria Bernardo

Received: 16 November 2021
Accepted: 17 December 2021
Published: 20 December 2021

1. Introduction

The versatility of polyurethane (PU) chemistry has long been recognized and accounted for 7% of the total polymer production, by mass, in 2017 [1]. This versatility is based on its multiple chemical structures, resulting from the polyaddition of di- or polyisocyanates and di- or polyols in the presence of a catalyst, which enables the use of PUs as foams, coatings, elastomers, adhesives and others [2]. However, their main issue is the toxicity of the isocyanate precursors and their industrial synthesis [3–6]. Therefore, research is aimed at developing not only non-toxic synthetic routes by eliminating the use of isocyanates [3–5] or metal catalysts [6], but also "greener" sustainable PUs through the use of vegetable or renewable feedstocks [7–10].

PU foams are the result of two simultaneous reactions: the polymerization, or gelling reaction, of the polyols with the isocyanates and the blowing reaction from the hydrolysis of the isocyanates with the formation of CO_2. The kinetics of these two competing reactions have to be well controlled for the correct evolution of a foam with the desired properties. Thus, catalysts play an essential role in PU foaming by increasing the efficiency of the reactions and controlling their rate, as well as reducing the side reactions [11]. Both amine and metallic catalysts are often used together to form the foam. The amine catalyst mainly contributes to the polymerization reaction and assists in the blowing reaction. One of the most

European Polymer Journal 189 (2023) 111960

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European Polymer Journal

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Fast synthesis of crosslinked self-blowing poly(β-hydroxythioether) foams by decarboxylative-alkylation of thiols at room temperature

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ARTICLE INFO

Keywords:
Polymeric foam
Poly(β-hydroxythioether)
Polyurethane
Ring-opening polymerization
S-alkylation

ABSTRACT

A novel strategy was developed to prepare a self-blowing poly(β-hydroxythioether) foam at room temperature by S-alkylation of 5-membered bis-cyclic carbonate using multifunctional thiol monomers. Two different thiol compounds, trimethylolpropane tris(3-mercaptopropionate) and pentaerythritol tetrakis(3-mercaptopropanoic acid) were used for the decarboxylative s-alkylation reaction. The thiol compounds simultaneously act as crosslinking agents and generate carbon dioxide during the decarboxylative s-alkylation reaction. This enables foam preparation without an external blowing agent. The use of tetrathiol monomer improves thermal stability, provides flexibility to the foams, and induces an increase in the glass transition temperature (*Tg*) due to a higher degree of cross-linking. The apparent density of the foams decreases with the increase of the tetrathiol ratio. This novel solvent-free approach paves the way to design sustainable foams with modular properties using accessible components and additives, as well as provides an alternative to non-isocyanate polyurethane foams.

1. Introduction

Foams, particularly polyurethane (PU) foams, are important materials in modern lives, with a global production anticipated to reach 12.7 million tons by 2024 [1]. They can be used for comfort and wellness (e.g., furniture, beds, chairs), shock absorption, thermal/acoustic insulation, or as sealants [2-7]. PU foams are produced at room temperature through two simultaneous reactions: a polyaddition of di- or polyisocyanates with di- or polyols [8-10] and the hydrolysis of isocyanates, which leads to the generation of CO_2 [11]. Such a process is one of the most successful and versatile foaming strategies, allowing the production of hard to soft foams due to the wide variety of polyols that can be employed. However, the health risks and regulatory restrictions associated with the usage of hazardous isocyanates have prompted manufacturers and researchers to look for new ways to create isocyanate-free PU foams or alternatives [12,13].

Thus, the step-growth copolymerization of amines and 5-membered cyclic carbonates that leads to non-isocyanate polyurethanes (NIPU) has lately attracted considerable attention for developing PU without using isocyanate[14]. However, unlike isocyanate with water, the reaction between cyclic carbonates and amines does not produce the gas required for foaming. This limits the production of foams without any external blowing agents. Cornille et al. [15] demonstrated that NIPU foams can be made using poly(methylhydrogenosiloxane) as a blowing agent. The polymer matrix was created by reacting poly(propylene oxide) bis-carbonate or trimethylolpropane tris-carbonate with one of two amine compounds: ethylene glycol-based diamine or a derivative of C_{18} fatty acids diamine by using 1,5,7-triazabicyclo [4.4.0]dec-5-ene (TBD) as a catalyst [16]. Meanwhile, Blattmann et al. [17] also used a physical blowing agent, in particular a hydrofluorocarbon blend Solkane 365/227, to produce cellular isocyanate-free PU from carbonated polyglycidylethers of TMP (TMPGC), ethoxylated TMP (EO-TMPGC) and hexamethylene diamine.

Poly(thioether) foams have also been suggested as potential alternatives to NIPU foams. They are produced by a click reaction from a cheaply scalable epoxy resin with thiol [18] but, like NIPUs, they require external blowing agents [19,20]. King et al. [18] have developed a poly (β-hydroxythioether) foam via a rapid reaction between an epoxy and

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https://doi.org/10.1016/j.eurpolymj.2023.111960
Received 25 December 2022; Received in revised form 26 February 2023; Accepted 28 February 2023

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Review

Recent Progress of Non-Isocyanate Polyurethane Foam and Their Challenges

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Abstract: Polyurethane foams (PUFs) are a significant group of polymeric foam materials. Thanks to their outstanding mechanical, chemical, and physical properties, they are implemented successfully in a wide range of applications. Conventionally, PUFs are obtained in polyaddition reactions between polyols, diisoycyanate, and water to get a CO_2 foaming agent. The toxicity of isocyanate has attracted considerable attention from both scientists and industry professionals to explore cleaner synthesis routes for polyurethanes excluding the use of isocyanate. The polyaddition of cyclic carbonates (CCs) and polyfunctional amines in the presence of an external blowing agent or by self-blowing appears to be the most promising route to substitute the conventional PUFs process and to produce isocyanate-free polyurethane foams (NIPUFs). Especially for polyhydroxyurethane foams (PHUFs), the use of a blowing agent is essential to regenerate the gas responsible for the creation of the cells that are the basis of the foam. In this review, we report on the use of different blowing agents, such as Poly(methylhydrogensiloxane) (PHMS) and liquid fluorohydrocarbons for the preparation of NIPUFs. Furthermore, the preparation of NIPUFs using the self-blowing technique to produce gas without external blowing agents is assessed. Finally, various biologically derived NIPUFs are presented, including self-blown NIPUFs and NIPUFs with an external blowing agent.

Keywords: biobased polyurethane; blowing agent; non-isocyanate polyurethane; polymeric foams; polyurethane foams; self-blowing

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Citation: El Khezraji, S.; Benyoucef, H.; Belachemi, L.; Lopez Manchado, M.A.; Verdejo, R.; Lahcini, M. Recent Progress of Non-Isocyanate Polyurethane Foam and Their Challenges. *Polymers* **2023**, *15*, 254. https://doi.org/10.3390/polym15020254

Academic Editor: Ru-Jong Jeng

Received: 16 December 2022
Revised: 28 December 2022
Accepted: 30 December 2022
Published: 4 January 2023

1. Introduction

Polymeric foam materials are important from both industrial and economic perspectives. These materials are lightweight and possess high thermal insulation [1,2], high sound insulation [3,4], resistance to impact, and damping properties, which allow them to fulfil the requirements for a wide range of applications. Polymer foams have been successfully implemented in the automotive industry [5], packaging, electronics [6], building construction [7], bedding [8], and medical applications [9]. Foams require the presence of a gas that is commonly introduced via blowing agents or is generated in situ during polymerization.

Among foams, polyurethanes (PUs) are one of the largest families and have widespread applications in diverse areas because they can be formulated to meet specific requirements depending on their nature, whether flexible or rigid [10,11]. PU foams (PUFs) are produced by polyaddition of isocyanates to polyols in the presence of water, which generates CO_2 gas. However, the presence of isocyanate, which is manufactured using phosgene, makes this classical method toxic [12,13]. Thus, scientists are studying new ways and methods to manufacture PUF without using this raw material. The polymer obtained via this method is then named non-isocyanate polyurethane (NIPU) or polyhydroxyurethane (PHU) [14–16].

The basic reaction for the preparation of NIPUF is the aminolysis of cyclic carbonate with a diamine in the presence of a catalyst, with or without an external blowing agent [17].