Theses of the Ph.D. Dissertation

Titled as

Data house of Polyurethane combined theoretical and experimental methods

Prepared by:

Wafaa Cheikh

Supervisor:

Prof. Dr. Béla Viskolcz

Antal Kerpely Doctoral School of
Materials Science & Technology
At the Faculty of Materials Science & Engineering

Institute of Chemistry
University of Miskolc

Miskolc, Hungary
2021

Introduction

Since the development of polyurethanes in 1937, the industrial sector started to use polyurethane in various applications: including building construction, footwear, automotive, and electronics [1][2], In 2015 the global polyurethane market size was USD 53.94 billion in 2015 in construction applications.[3] The versatility of polyurethane chemistry permits the production of a great variety of materials such depending on the initial ingredients used in the synthesis [4], polyurethane foams correspond to 67% of global polyurethane consumption. Nevertheless, other classifications can be attributed such as elastomers, coatings, adhesives, and sealants[5].

Polyurethanes also referred to as urethanes, are characterized by the urethane linkage (**Figure 1**) that is formed by the reaction of isocyanate groups with hydroxyl groups [1][6].
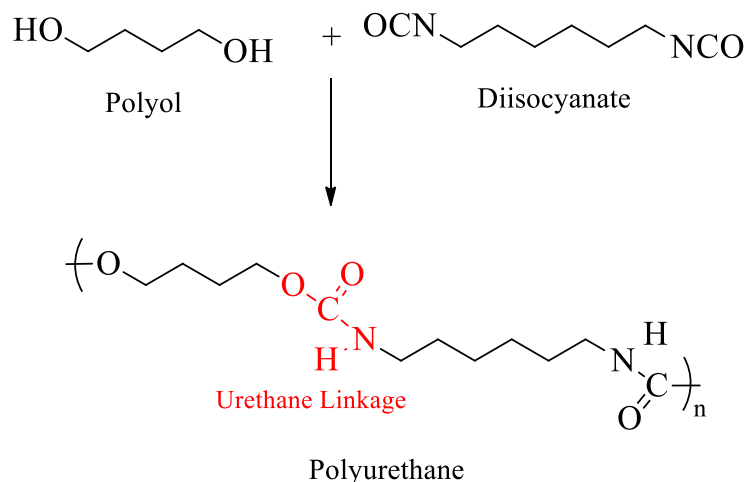

Figure 1: Polyurethane synthesis of polyols and diisocyanate.

It is produced by the simultaneous reactions between isocyanates with compounds containing at least two active hydrogens [7]. When diisocyanate and a polyol are reacted at proper ratios to form the repeating urethane linkage [8], other additives, such as catalysts, blowing agents, fillers, flame retardants, and pigments, are included in the formulation [9]. Flexible foams based on both polyether and polyester polyols are now in general use, and both types can be made in the density range of 10 to 800 $kg \cdot m^{-3}$[10][11]. The polyols have a significant impact on the foaming process of a polyurethane system and the final properties of polyurethane foams depending on their molecular weight, functionality, and the hydroxyl value [12][13]. The flexible polyurethane foams exist with a broad range of cell sizes (open-celled and closed-cells), and nowadays they are manufactured with a great variety of textures and hardness, which can

be light and resistant structures with interesting mechanical and thermal properties that we must be controlled. Moreover, the different foams are distinguished by their densities and compression deformities.

Aim

One of the first objectives of this thesis was to choose a synthesis process that is relatively simple to implement both in the laboratory and with a view to an industrial application. Based on the review of the literature, it was possible to determine the influence of the raw materials used in the synthesis on the properties of the final polymers. Thus, we have chosen to study in the influence of the two major reactants used in polyurethane synthesis: diisocyanates, and polyols. Moreover, this research was recognized that the production of polyurethane is a complicated process and requires proper control of reaction conditions. A better understanding the reaction steps of the synthetic process can promote product optimization, help find solutions to known technical problems in the laboratory or industry, and even encourage new technological developments. Computational chemistry offers the possibility of examining and determining the reaction mechanism of industrial synthesis. Nowadays, more and more experimental development is accompanied by electronic structure calculations, proving the benefits of computer calculations. The novelty of the research is supported by theoretical and experimental results, in which electronic structure calculations are used to determine possible new reaction mechanisms of urethane bond formation, and also to discover experimentally new urethane and polyurethane synthesis strategies by modifying the reactants in the mechanism. The theoretical study of this reaction mechanism requires robust quantum chemical protocol. From the results obtained from the electronic structure calculations, we will be able to guide through the experimental component of this project, and will provides valuable information for understanding the industrial reactions at the molecular level.

Methods

In this research, two methods of determining polyurethane formation are presented: a theoretical method with computational applications, and an experimental method with analysis of the kinetic of the reaction, the density, and the mechanical properties. Both procedures were used for the characterization of the urethane and polyurethane bond formation, and also to compare the energies of the reaction mechanism obtained by theory with the experimental results.

The theoretical research was studied using the computational chemistry tools implemented in the Gaussian09 program package. To make a theory more closely mimic the experiment one, it is necessary to accurately characterize the structure of the reactants, transition states (TS), complexes, intermediates (IM), and products, and this was done in order to explore the important reaction mechanisms of the urethane bond formation. All our systems were explored using *ab initio* calculations combined with accurate composite quantum chemical methods with the Solvent Model Density SMD implicit solvent model.

The kinetics of these reactions were also experimentally investigated in order to study the catalytic mechanism of the urethane bond formation. A microreactor technique has been applied to accurately determine the kinetic parameters of the reaction between phenyl isocyanate and 1-propanol using tetrahydrofuran (THF) and 1-propanol (PrOH) as the solvent at various temperatures. From the rate constants measured at different temperatures, Arrhenius activation energies of the stoichiometric reaction, the reactions in excess of alcohol, and the reactions in excess of isocyanate were experimentally determined by means of analytical HPLC.

We also investigated the influence of mono-alcohol as a reactant on polyurethane bond formation, and whether these mono-alcohols have a catalytic effect on polyurethane bond formation. Using the standard polyurethane foam reaction modified with a given amount of alcohols, the mono-alcohol components were from C1 to C8, where the experimental design based on evidence of the mechanism.

Summary

Polyurethane products are inseparable from our daily life. They are virtually everywhere and are readily available. The diversity of polyurethane synthesis is related to the diversity of the raw materials. Where these various raw materials will produce polyurethane with different properties, which play a roles in the polymer field. Polyurethane is a polymer organic material and in the future, its development can promote the rapid development of the world industry. The purpose of this research was to study the urethane bond formation and the polyurethane synthesis at the molecular level. The urethane production consists of a simple reaction between an isocyanate and alcohol; they are the essential part of the polyurethane molecules. This work focused first on the direct formation of a urethane bond with an aromatic side chain for isocyanate (phenyl isocyanate) and an aliphatic alcohol side chain (1-propanol). This research was based on theoretical and experimental studies, where the reaction mechanism of urethane bond formation was explored using *ab initio* calculations, the G4MP2 quantum chemical

method was the more accurate in the SMD implicit solvent model, whither the solvents exercised are 1-propanol and tetrahydrofuran, and the results were in good agreement with corresponding experimental results. It was found that these mechanisms of the reaction in excess alcohol and excess isocyanate were analyzed from an energetic point of view by characterizing the potential energy surface (PES). According to the newly proposed two-step mechanism for isocyanate excess, allophanate is an intermediate towards urethane formation via a six-centered transition state (TS) with a reaction barrier of 62.6 kJ·mol^{-1} in the THF solvent model. In the next step, a synchronous 1,3-H shift between the nitrogen of allophanate and cleavage of the C-N bond resulted in the release of the isocyanate and the formation of urethane bond via a low-lying TS with 49.0 kJ·mol^{-1} energy relative to the reactants. The kinetics of this reaction was also experimentally investigated using analytical HPLC. From the rate constants measured at different temperatures, Arrhenius activation energies of the stoichiometric, the reactions in excess of alcohol, and the reactions in excess of isocyanate were determined. The activation energies for both the reaction in excess alcohol and isocyanate were lower compared to that of the stoichiometric ratio (30.4 ± 1.6 kJ·mol^{-1}, 44.2 ± 4.5 kJ·mol^{-1}, 58.6 ± 6.0 kJ·mol^{-1} respectively). Theoretical calculations showed that the energy barrier needed for either the alcohol or the isocyanate catalyzed pathways to occur is lower than the barrier for the stoichiometric (bimolecular) mechanism realized from the potential energy surface see (**Figure 2**).
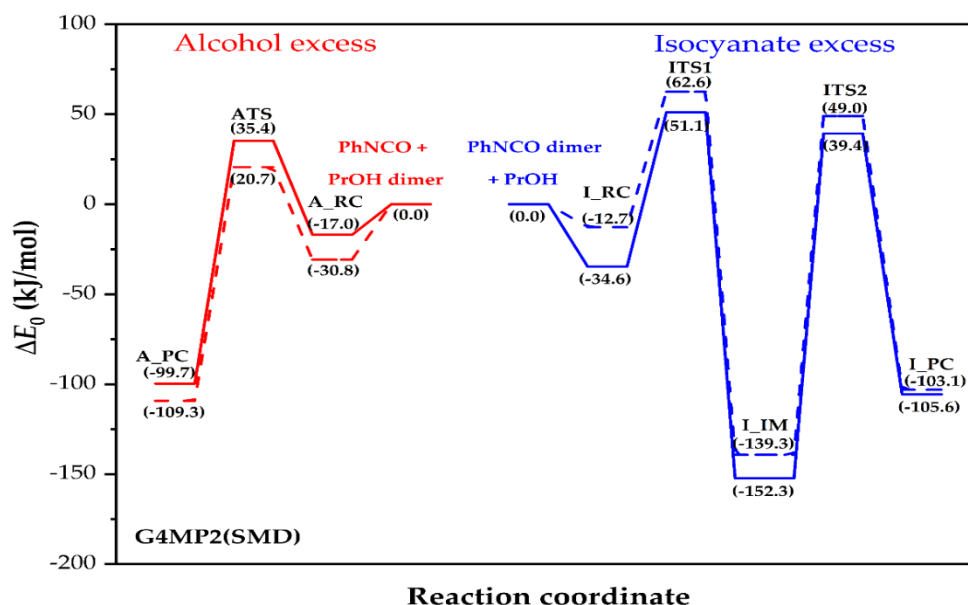

Figure 2: G4MP2 energy profile (zero-point corrected) for the alcoholic route in solvent propanol (1-PrOH) red solid line, in tetrahydrofuran (THF) red dashed line, and for the isocyanate route in propanol (1-PrOH) blue solid line, in tetrahydrofuran (THF) blue dashed line.

The urethane linkage is related to the polyurethane formation, and the results of the first study, that based on an experimental, and theoretical calculation of the urethane bond formation. Has shown the importance of the alcohol where it was noticed how the polymerization can change significantly by the presence of excess alcohol while the energy profile of the reaction has lower barrier energy and faster rate. therefore, the properties of polyurethane foams are strongly influenced by the chain length and the molecular weight of the polymeric molecules added. Mono-alcohols are capable of decreasing the molecular weight of the polyurethane and increasing the occurrence of the chain breaking. Various mono-alcohols (from C1 to C8) have been used as second alcohol in polyurethane foam synthesis and their effect on the mechanical behavior of the foams has been investigated. The alcohol concentrations were also varied between 0.2, 0.5, 1.0, to 2.0 parts by weight). The compressive strength and density of the foams have been measured, and it was found that the length of the mono-alcohol chain, especially with a shorter carbon chain, during the preparation of a flexible polyurethane foam opens a way to prepare lighter polymers without changing the mechanical properties significantly, moreover increasing the concentration of the mono-alcohol increased the flexibility of the polyurethane. Further, from the results obtained, we illustrate a new range of Young's modulus values between (0.0001-0.00002 GPa), and the density range is almost the same as other published results. Compared to the studied results case of flexible foams, this range is completely new (see Figure 3).
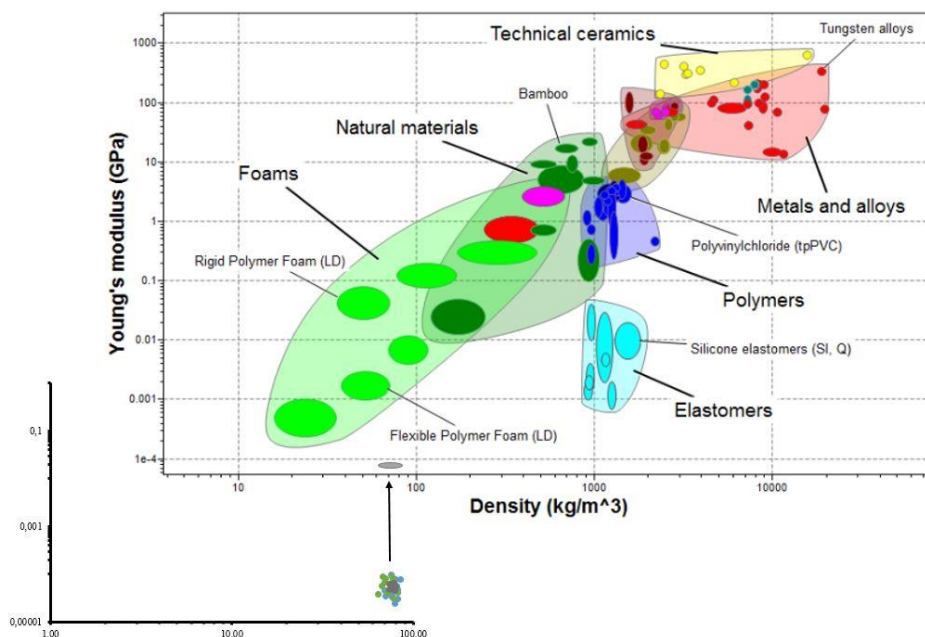

Figure 3: A chart of Young's modulus and density for materials created using the CES EduPack 2007 software with the Level 2 database.

New scientific results

Based on our combined experimental and theoretical study of polyurethane synthesis, the following main conclusions were drawn as new scientific results:

<u>Experimental and mechanistic study of urethane bond formation</u>

1st thesis

A new reaction mechanism of urethane bond formation has been proposed with excess alcohol and excess isocyanate in the liquid phase. The novelty of this theoretical study based on *ab-initio* calculation is that both the alcohol and the isocyanate can self-catalyze the urethane bond formation.

2nd thesis

The alcohol-catalyzed route was shown to be a one-step process, whereas the isocyanate-catalyzed path includes two consecutive reaction steps. The route in excess alcohol is more favorable, with a lower barrier height than that of the isocyanate route. In the case where neither the alcohol nor the isocyanate were in excess, the reaction energy barrier was the highest.

3rd thesis

The microreactor experiment was applied to study urethane bond formation for the very first time, and both catalytic routes were verified by the experiment. Moreover, the experimental parameters are in excellent agreement with the calculated ones.

<u>Experimental study of mono-alcohol</u>

4th thesis

An experimental study was carried out to determine whether the addition of mono-alcohol has a catalytic effect on polyurethane bond formation, and it was found that there is no such catalytic effect. The range of the different mono-alcohols chains used was from C1 to C8, and with different type such as linear, branched, and cyclic mono-alcohols.

5th thesis

It was found that the addition of mono-alcohols could affect the density and the Young's modulus of the foam. Where we found a new range in the Ashby plot that collects all the material data.

Publications

Publication bibliometrics

Number of papers published: 2

Number of paper: 3

Cumulative impact factor related to the thesis: 5.455

Total number of citations: 7

Scientific publications

1. Wafaa Cheikh, Zsófia Borbála Rózsa, Christian Orlando Camacho López, Péter Mizsey, Béla Viskolcz, Milán Szőri, Zsolt Fejes, Urethane Formation with an Excess of Isocyanate or Alcohol: Experimental and Ab Initio Study, *Polymers*, doi: 10.3390/polym11101543. (Q1; IF = 3.426)

2. Boros Renáta Zsanett , Koós Tamás, Wafaa Cheikh, Nehéz Károly, Farkas László, Viskolcz Béla, Szőri Milán, A theoretical study on the phosgenation of methylene diphenyl diamine (MDA), *Journal chemical physics letters,* doi: 10.1016/j.cplett.2018.06.024. (Q2; IF = 2.029)

3. Wafaa Cheikh, Zsolt Fejes, Béla Viskolcz, Light polyurethane flexible foams by using monoalcohols, *Polymers,* submitted

Oral and Poster presentations

1. 9th Visegrad Symposium on Structural Systems Biology, systematic molecular design, Szilvàsvàrad, Hungary, 2019, *Presentation.*

2. The 6th International Scientific Conference on Advances in Mechanical Engineering, Experimental study of polyurethane foams synthesis, Debrecen, Hungary, 2018, *Presentation*

3. The Scientific Conference for Ph.D. Students, The effect of mono-alcohols and diols on the properties of polyurethane foams, Miskolc, Hungary, 2018, *Poster*

4. XXIII. Bolyai Konerenciàn conference, Effect of different mono-alcohols on polyurethane foams, Budapest, Hungary, 2018, *Poster*

5. 7th Visegrad Symposium on Structural Systems Biology, Computational study of the phosgenation reaction mechanisms of the MDA, Nove Hrady, Czech Republic, 2017, *Poster*

References

[1] K. J. Saunders, *Organic Polymer Chemistry*. Springer Netherlands, 1973.

[2] S. Das, P. Heasman, T. Ben, and S. Qiu, "Porous Organic Materials: Strategic Design and Structure–Function Correlation," *Chem. Rev.*, vol. 117, no. 3, pp. 1515–1563, Feb. 2017.

[3] "Global Polyurethane (PU) Market Size & Share, 2025 | Industry Report." [Online]. Available: https://www.grandviewresearch.com/industry-analysis/polyurethane-pu-market. [Accessed: 08-Apr-2019].

[4] X. D. Smithers Rapra (Firm), L. M. Bertsch, C. Macosko, R. B. Turner, D. W. House, and R. V. Scott, *Cellular polymers.*, vol. 17, no. 5. RAPRA Technology Ltd., 1998.

[5] D. K. Chattopadhyay and K. V. S. N. Raju, "Structural engineering of polyurethane coatings for high performance applications," *Progress in Polymer Science (Oxford)*, vol. 32, no. 3. pp. 352–418, Mar-2007.

[6] E. Delebecq, J.-P. Pascault, B. Boutevin, and F. Ganachaud, "On the Versatility of Urethane/Urea Bonds: Reversibility, Blocked Isocyanate, and Non-isocyanate Polyurethane," *Chem. Rev.*, vol. 113, no. 1, pp. 80–118, Jan. 2013.

[7] D. K. Chattopadhyay and D. C. Webster, "Thermal stability and flame retardancy of polyurethanes," *Progress in Polymer Science (Oxford)*, vol. 34, no. 10. pp. 1068–1133, Oct-2009.

[8] M. Szycher, *Szycher's handbook of polyurethanes*. 1999.

[9] M. M. Bernal, M. A. Lopez-Manchado, and R. Verdejo, "In situ Foaming Evolution of Flexible Polyurethane Foam Nanocomposites," *Macromol. Chem. Phys.*, vol. 212, no. 9, pp. 971–979, May 2011.

[10] "Polyurethane Foam Properties - Technical Foam Services." [Online]. Available: https://www.technicalfoamservices.co.uk/blog/some-properties-of-polyurethane-foams/. [Accessed: 10-Dec-2019].

[11] M. Thirumal, D. Khastgir, N. K. Singha, B. S. Manjunath, and Y. P. Naik, "Effect of foam density on the properties of water blown rigid polyurethane foam," *J. Appl. Polym. Sci.*, vol. 108, no. 3, pp. 1810–1817, Mar. 2008.

[12] A. Eceiza *et al.*, "Structure-property relationships of thermoplastic polyurethane elastomers based on polycarbonate diols," *J. Appl. Polym. Sci.*, vol. 108, no. 5, pp. 3092–3103, Jun. 2008.

[13] K. Pietrzak, M. Kirpluks, U. Cabulis, and J. Ryszkowska, "Effect of the addition of tall oil-based polyols on the thermal and mechanical properties of ureaurethane elastomers," *Polym. Degrad. Stab.*, vol. 108, pp. 201–211, Oct. 2014.

[14] R. A. Friesner, "Ab initio quantum chemistry: Methodology and applications," *Proc. Natl. Acad. Sci. U. S. A.*, vol. 102, no. 19, pp. 6648–6653, 2005.

[15] L. Sinha, O. Prasad, V. Narayan, and R. K. Srivastava, "Electronic structure, non-linear properties and vibrational analysis of Acenaphthene and its carbonyl derivative Acenaphthenequinone by density functional theory," *J. Mol. Struct. THEOCHEM*, vol. 958, no. 1–3, pp. 33–40, Oct. 2010.

[16] A. Kumar, V. Narayan, O. Prasad, and L. Sinha, "Monomeric and dimeric structures, electronic properties and vibrational spectra of azelaic acid by HF and B3LYP methods," *J. Mol. Struct.*, vol. 1022, pp. 81–88, Aug. 2012.

Acknowledgment

First and foremost, praise and thank *God*, the Almighty, for His showers of blessings throughout my research work to complete my dissertation successfully.

I would like to express my deep and sincere gratitude to my supervisor Prof. Dr. Béla Viskolcz for giving me the opportunity to do research and providing invaluable guidance throughout this research.

I would like to extend my sincere and heartfelt obligation towards all members of the Institute of Chemistry and the Faculty of Materials Science and Engineering for their help, cooperation, and encouragement. A special thanks to Dr. Béla Fiser, Dr. Milán Szőri, Dr. Zsolt Fejes, and Dr. Michael Owen for conscientious guidance and encouragement to accomplish this assignment.

I also acknowledge with a deep sense of reverence, my gratitude towards *My Parents* for their love, prayers, caring, and sacrifices for educating and preparing me for the future, I hope to never disappoint you. I am very much thankful also to my sisters and brother Amel, Mohamed, Leila, sister in law Fatiha, brother in law Abdelkader, and my nieces and nephew Ines, Anes, Lilia, and Anya, who has always supported me morally and encourage me.

At last but not least, gratitude goes to all of my friends who directly or indirectly helped me: Sabah, Hanene, Bochra, Amina, Edina, Yacine, Marouane. special thanks go to Rabab Benotsmane for the keen interest shown to complete this thesis successfully.

I dedicate the fruits of this work to my grandmothers, and my Prof. Dr. R.Kessas, who I lost in 2020, and with all my love; I wish they would be in Heaven.