Theses of the Ph.D. Dissertation

Titled as

An atomistic view of polyurethane chemistry – A combined theoretical and experimental study

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 their development in 1937, the industrial sector started to use polyurethanes in various applications including construction, footwear, automotive, and electronics [1][2]. In 2015 the global polyurethane market size was 53.94 billion USD [3]. The versatility of polyurethane chemistry permits the production of a great variety of materials which depend on the initial ingredients used in the synthesis [4]. However, Foams correspond to 67% of the global polyurethane consumption. Nevertheless, other types of materials such as elastomers, coatings, adhesives, and sealants are also important [5].

Polyurethanes contain several urethane linkages **(Figure 1)** which are formed by the reaction of isocyanate groups with hydroxyl groups [1][6].

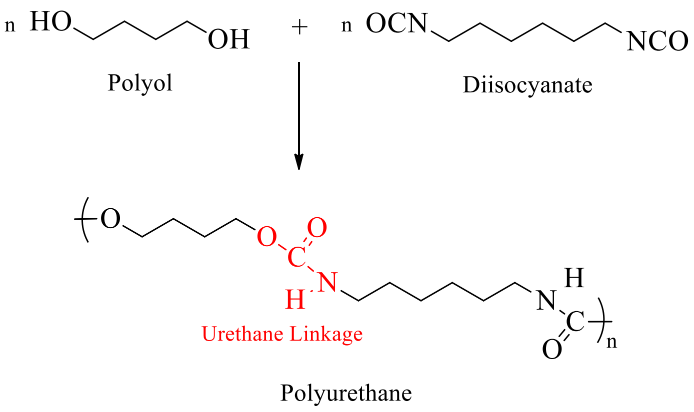

Figure 1: Polyurethane synthesis from polyols and diisocyanate.

Polyurethanes are produced by the simultaneous reactions between polyfunctional isocyanates with compounds containing at least two active hydrogens, such as polyols [7]. The reaction of diisocyanates and polyols at proper ratios to produce the repeating urethane linkage [8] is promoted by catalysts. Other additives, such as blowing agents, fillers, flame retardants, and pigments can be also included into 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. The final properties of the foam depend on their molecular weight, functionality, and the hydroxyl value [12][13]. The flexible polyurethane foams exist with a broad range of cell sizes (open-cell and closed-cell), 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 must be carefully controlled. Moreover, the different foams are distinguished by their densities and compression deformities.

Aims

The literature review revealed that polyurethane production is a complicated process and requires proper control of reaction conditions. A better understanding of the reaction steps of the synthetic process can favor product optimization and help to find further solutions to the common technical problems encountered in laboratory and industrial applications, as well as to promote new technological developments. Hence, I would like to understand more deeply this complicated process with an atomistic view, according to the following stages:

- First, to better understand urethane bond formation at an atomistic level. I would like to study the known urethane bond formation in detail by using *ab initio* electronic structure calculations. The aim is to further determine the alternative reaction pathways of urethane bond formation for both alcohol excess and isocyanate excess conditions in the liquid phase and to discover whether the alcohol or the isocyanate has the ability to self-catalyze the urethane bond formation.

- Secondly, I plan to conduct an experimental study on the kinetics of urethane bond formation to validate the results of the theoretical calculations from the first stage.

- Finally, I would like to extend the basic knowledge of urethane bond formation and apply it to polyurethane chemistry by modifying the reactants in the polyurethane synthesis by adding monoalcohols and determining if they have a catalytic effect on the polyurethane bond formation. I also aim to find out how the addition of the monoalcohols can alter the mechanical properties of the polyurethane products.

The theoretical study of this reaction mechanism requires a robust quantum chemical protocol. In the same vein, the results from the electronic structure calculations guide us through the experimental investigations including a kinetic study using a microreactor and classical laboratory experiments on foam formation. This in turn, can provide us a piece of valuable information to understand the industrial reactions at the molecular level.

Methods

In this research, two methods for the determination of polyurethane formation are presented: a theoretical method with computational chemical tools and an experimental method with the analysis of the kinetics of the reaction, and the density and mechanical properties of the products. Both procedures were used to characterize the urethane bond formation and also to compare the energetics of the reaction mechanism.

The theoretical studies were carried out using various computational methods implemented in the Gaussian09 program package [14]. The structure of reactants, transition states (TS), complexes, intermediates (IM), and products were determined, the reaction mechanisms of urethane bond formation have been described. The systems were explored by using accurate composite quantum chemical methods in combination with the implicit SMD solvent model.[15]

The kinetics of these reactions were also investigated experimentally to study the mechanism of 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 solvents at different temperatures. From the rate constants measured by analytical HPLC at different temperatures and using the Arrhenius equation, the activation energies corresponding to the reactions with excess alcohol and excess isocyanate have been determined.

The influence of various monoalcohols as reactants in the polyurethane bond formation and their catalytic effect have also been investigated. Standard polyurethane foam formulations have been modified with a certain amount of monoalcohol, these components being methanol, ethanol, 1-propanol, 2-propanol, 1-butanol, tert-butanol, 1-hexanol, cyclohexanol, and 1-octanol.

Results and Discussion

Polyurethane products are inseparable from our daily life. They are practically everywhere and are readily available. The diversity of polyurethane synthesis is supported by the diversity of raw materials. Different raw materials lead to polyurethanes with different properties. The aim of this research was to investigate urethane bond formation and polyurethane synthesis at the molecular level. Urethane bond formation involves a simple reaction between an isocyanate and an alcohol. The first part of this work focuses on the direct formation of the urethane bond. The reactants are an aromatic isocyanate (phenyl isocyanate) and an aliphatic alcohol (1-propanol). Theoretical and experimental studies were combined, and the reaction mechanism of urethane bond formation was explored using *ab initio* calculations. The quantum chemical G4MP2 method was used in combination with the implicit SMD solvent model, and the results of the calculated activation energies of ATS and ITS1 were in good agreement within 5.1 kJ·mol^{-1}, and 3.4 kJ·mol^{-1} of the average absolute deviation, respectively, with the experimental data. The reaction mechanisms were studied in excess alcohol and excess isocyanate. In the case of isocyanate excess, a new two-step mechanism was proposed. Allophanate is formed in the reaction channel leading to urethane formation. The transition state (TS) contains a six-membered ring and the corresponding barrier height is 62.6 kJ·mol^{-1} in THF. In the next step, a synchronous 1,3-H shift between the nitrogen of the allophanate and the cleavage of the C-N bond leads to the release of the isocyanate and the formation of the urethane bond via a low-lying TS with 49.0 kJ·mol^{-1} energy relative to the reactants.

The kinetics of these reactions were also studied experimentally using analytical HPLC. From the rate constants measured at different temperatures, the corresponding activation energies were determined using the Arrhenius equation in the case of stoichiometric, excess alcohol, and excess isocyanate reactions. The activation energies for both the alcohol and isocyanate excess reactions were lower compared to the stoichiometric ratio (30.4 ± 1.6 kJ·mol^{-1}, 44.2 ± 4.5 kJ·mol^{-1}, and 58.6 ± 6.0 kJ·mol^{-1} respectively). Theoretical calculations showed that the energy barrier was lower in the case of the excess systems compared to the stoichiometric (bimolecular) mechanism since alcohol or isocyanate self-catalyzed pathways took place (**Figure 2**). [*first, second and third thesis points*]

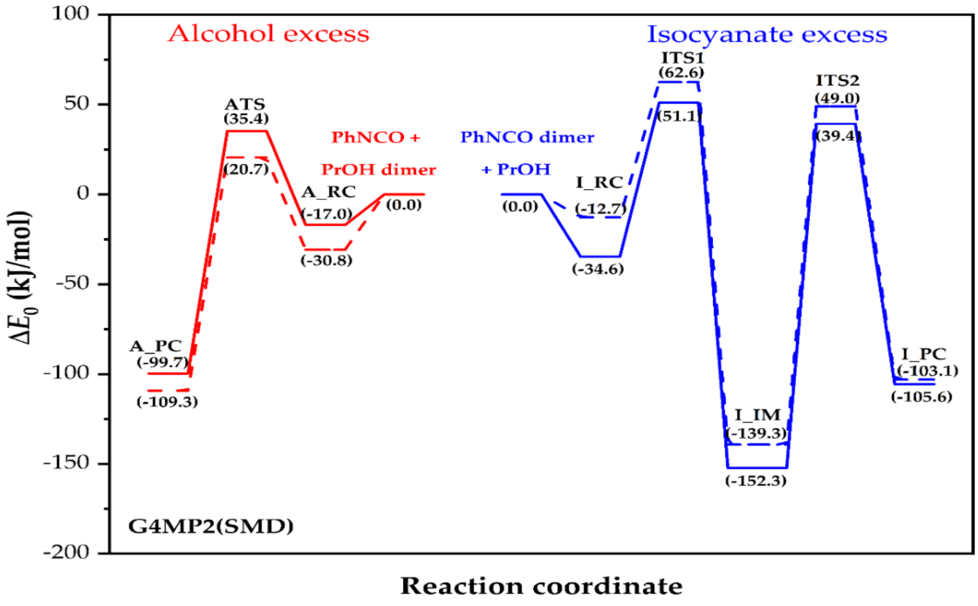

Figure 2: Energy profile (zero-point corrected) for the alcoholic urethane formation route in 1-PrOH (red solid line), and in THF (red dashed line), and for the isocyanate route in 1-PrOH (blue solid line), and in THF (blue dashed line) calculated by using the G4MP2 composite method in combination with the SMD implicit solvent model.

The importance of the alcohol was shown in the combined experimental and theoretical study.

Polymerization can be significantly altered by the presence of excess alcohol, changing the energy profile of the reaction and making the reaction faster. Therefore, the properties of polyurethane foams are strongly influenced by the chain length and molecular weight of the molecules added during synthesis. Monoalcohols are able to decrease the molecular weight of polyurethane and increase the occurrence of chain breaks. Different monoalcohols (from methanol to 1-octanol) have been used as a second alcohol component in polyurethane foam synthesis and their effect on the mechanical behavior of the foams has been investigated. The alcohol concentrations were also varied between 0.2and 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 monoalcohol chain, especially with a shorter carbon chain, during the preparation of a flexible polyurethane foam opens a way to produce lighter polymers with only slight sig changes in the mechanical properties. Moreover, by increasing the concentration of the monoalcohol, the flexibility of the polyurethane was also increased. Based on the obtained results, 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 in the case of other published materials. Compared with the literature results of flexible foams, a completely new range of properties was obtained in the present study **(Figure 3)**. [*fourth and fifth thesis points*]

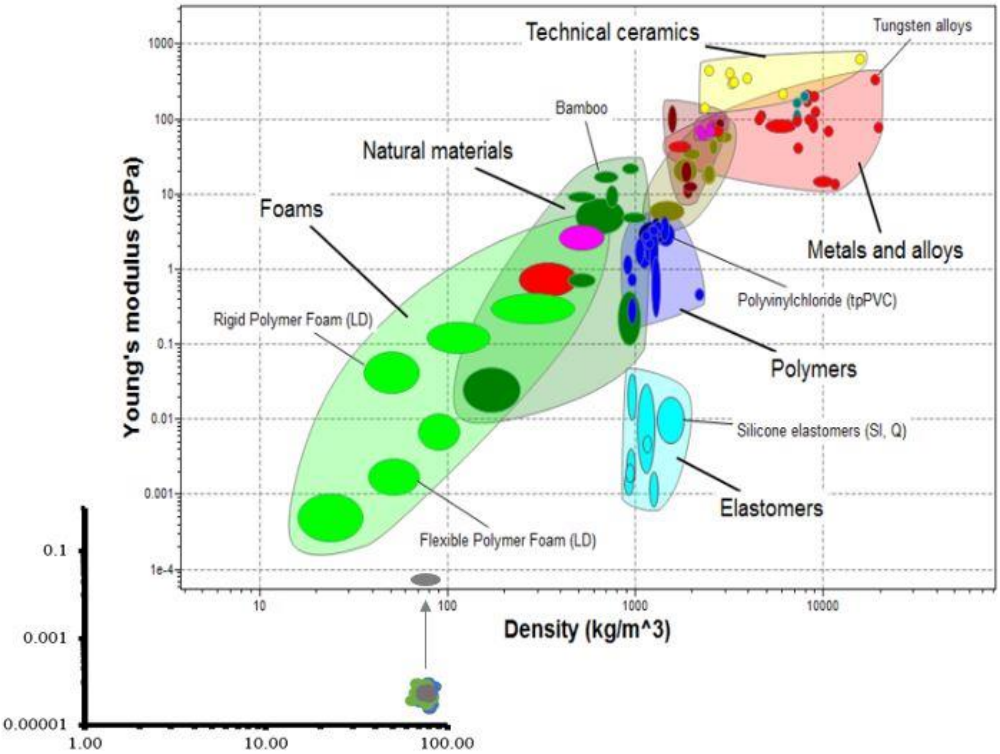

Figure 3: A chart of Young’s modulus and density.

New scientific results

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

1st thesis

A new reaction mechanism of urethane bond formation has been proposed in the case of excess alcohol and excess isocyanate in the liquid phase. Based on *ab initio* calculations and experimental measurements, it was proved 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 pathway includes two consecutive reaction steps. The route in excess alcohol is more favorable, as a lower barrier height have been found compared to the isocyanate route. In the case where neither the alcohol nor the isocyanate were in excess, the energy barrier was the highest.

3rd thesis

The experimental Arrhenius parameters for both catalytic routes are in excellent agreement with the calculated ones.

- I found the activation energies for the alcohol-catalyzed route measured and calculated equal to 30.4 ± 1.6 $kJ\cdot mol^{-1}$ and 37.7 $kJ\cdot mol^{-1}$, respectively.
- For the isocyanate-catalyzed mechanism I found that the activation energy measured and calculated is equal to 44.2 ± 4.5 $kJ\cdot mol^{-1}$ and 49.0 $kJ\cdot mol^{-1}$, respectively.

4th thesis

An experimental study was carried out to determine whether the addition of monoalcohols has an extra catalytic effect on polyurethane bond formation. The reference system were primarily catalyzed by 1.2 % DMCHA. The addition of the same amount of monoalcohol does not causes extra catalytic effect. We are concluding that the monoalcohols as self-catalysts are weaker compared with the tertiary amine DMCHA.

5th thesis

It was found that the addition of monoalcohols could affect the density and the Young's modulus of the foam. A new range of properties in the Ashby plot has been achieved.

Publications

Publication bibliometrics

Number of papers: 3

Cumulative impact factor related to the thesis: 5.455

Total number of citations: 9

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 monoalcohol–polyol mixtures*, submitted*

Oral and Poster presentations

1. 9th Visegrad Symposium on Structural Systems Biology, systematic molecular design, Szilvàsvàrad, Hungary, 2019, *Oral presentation*.
2. The 6th International Scientific Conference on Advances in Mechanical Engineering, Experimental study of polyurethane foams synthesis, Debrecen, Hungary, 2018, *Oral 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] M. J. Frisch *et al.*, “Gaussian 16, Revision B.01,” p. Gaussian 16, Revision B.01, 2016.

[15] A. V. Marenich, C. J. Cramer, and D. G. Truhlar, “Universal solvation model based on solute electron density and on a continuum model of the solvent defined by the bulk dielectric constant and atomic surface tensions,” *J. Phys. Chem. B*, vol. 113, no. 18, pp. 6378–6396, May 2009.

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 be always a pride for 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***, ***Ikram***, ***Amina***, ***Bochra***, ***Edina***, ***Yacine***, ***Marouane***. Special thanks go to ***Rabab Benotsmane***, my lovely sister in Hungary 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; May they rest in peace.

This research was supported by the European Union and the Hungarian State, co-financed by the European Regional Development Fund in the framework of the GINOP-2.3.4-15-2016-00004 project, aimed to promote the cooperation between the higher education and the industry.

The GITDA (Governmental Information-Technology Development Agency, Hungary) is gratefully acknowledged for allocating computing resources used in this work.