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Data house of Polyurethane combined theoretical and experimental methods

Ph.D. Dissertation

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“Behold! In the creation of the heavens and the earth and the alternation of the night and the day are signs indeed for those endowed of understanding.”

Quran [3:190]

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List of abbreviations

PU: Polyurethane.

MDI: Methylene diphenyl diisocyanate.

MDA: Methylene diphenyl diamine.

TDI: Toluene diisocyanate.

DMCHA: Dimethyl cyclo hexyl amine.

PhNCO: Phenyl isocyanate.

PrOH: 1-Propanol.

THF: Tetrahydrofuran.

CAN: Acetonitrile.

HPLC: High-performance liquid chromatography.

PES: Potential energy surface.

TS: transition state.

IM: intermediates.

IRC: Intrinsic reaction coordinate.

MEP: Minimal energy pathways.

DFT: Density functional theory.

MO: Molecular orbital.

QM: Quantum mechanical.

HF: Hartree-Fock.

BO: Born-Oppenheimer approximation.

MP: Moller-Plesset perturbation.

CC: Coupled-cluster.

QCISD(T): Quadratic Configuration Interaction with Single and Double substitutions.

B3LYP: Becke, 3-parameter, Lee-Yang-Parr.

HLC: Higher-level correction.

CBS: Complete basis set.

pVDZ: Double zeta basis set.

pVTZ: Triple zeta basis set.

SMD: Solvation model based on density

k_s: Rate constants for the stoichiometric reaction.

k_A: Rate constants for the reaction in excess alcohol.

k_I: Rate constants for the reaction in excess isocyanate.

E_a: Arrhenius activation energy.

ΔE₀: Zero-point corrected relative energy.

ΔH(T): Relative enthalpy.

ΔG(T,P): Relative Gibbs free energy.

ΔfH°: Heat of formation.

ΔH°_{vap}: Enthalpy of vaporization.

A_RC: Reactive complex of the reaction in excess alcohol.

ATS: Transition state of reaction in excess of alcohol.

A_PC: Product complex of reaction in excess of alcohol.

I_RC: Reactive complex of the reaction in excess isocyanate.

ITS1: First transition state of the reaction in excess isocyanate.

I_IM: Intermediate of the reaction in excess isocyanate.

ITS2: Second transition state of the reaction in excess isocyanate.

I_PC: Product complex of the reaction in excess isocyanate.

Pbw: Parts by weight.

E: Young's modulus.

ρ: Density.

1. Introduction

1.1 Synthesis process

Polyurethane (the term polyurethane having been accepted since 1988) refers to macromolecules comprising the motif constituting the chemical functional group urethane. The urethane function is more rarely called the carbamate functional group $R'-NH-CO-O-R$. This bond results from the condensation reaction between a compound with mobile hydrogen of alcohol type $R-OH$ and an isocyanate $R'-N=C=O$ (**Figure 1**). To form a polyurethane, a polyol, a compound containing two or more OH groups, must react with a polyisocyanate, which has two or more isocyanate groups. The reaction of a diol with a diisocyanate leads to a linear polyurethane. [1]

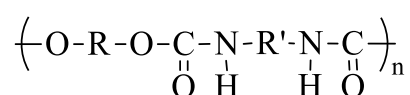


Figure 1: The main-chain structure of polyurethane.

Consequently, the way towards a new method of synthesis of macromolecular compounds was opened: the polyaddition reaction, a particular case of polycondensation. Unlike conventional polycondensation where the products formed are the polymer and an additional low molecular weight compound (water, alcohol, etc.), polyaddition only forms a polymer. The industrial manufacture of polyurethanes is almost exclusively based on a polyaddition reaction involving diisocyanates and polyfunctionalized primary alcohols. [2] They can also be obtained directly from urethanes (**Figure 2**). [3]

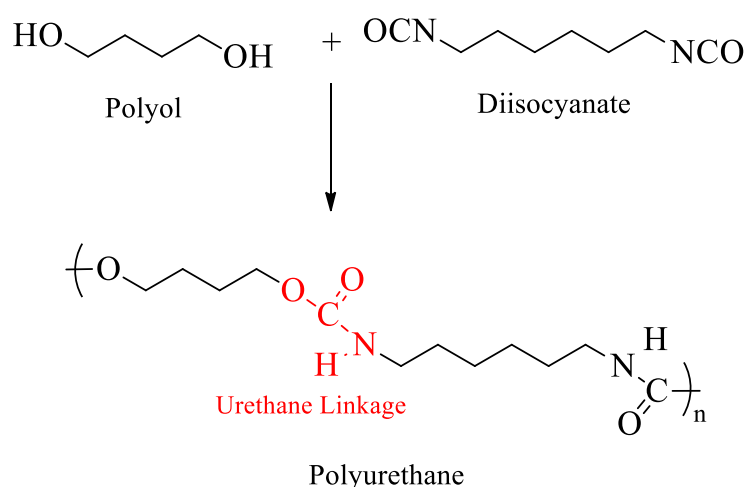


Figure 2: Polyaddition reaction.

There are several possible processes for the synthesis of polyurethanes. The most commonly applied involve a one-step synthesis and the use of a prepolymer.

The first technique consists of combining all the components of a formulation in the absence of a solvent in a single step. Its main disadvantage is the exothermicity of the reaction. If the temperature of the reaction medium is too high, the urethane functional groups may be degraded. This critical temperature depends on the structure of both the alcohol and the isocyanate and is between 170 °C and 210 °C.[4][5] Note that certain industrial processes that produce elastomer polyurethane, use polyaddition in a single step ("one-shot" process), in reason this technique is easier, faster, and more reproducible. This is particularly the case with the manufacture of foams. However, the process of using a prepolymer involves two steps. In the first step, the isocyanate prepolymer is synthesized by the reaction between diisocyanate in slightly excess and a polyol. In the second step, the isocyanate prepolymer is placed in the presence of a polyfunctional polyol (chain extending or a hydroxylated crosslinking agent of low molar mass) leading to the formation of the final polymer. The temperature of the reaction of this last step is between 80 °C and 110 °C. [6]

The use of a prepolymer makes it possible to modulate the reactivity, viscosity, functionality, the amount of free isocyanates, or even the volatility of the isocyanates. This makes it possible to overcome the problem that can arise from the difference in reactivity between macrodiol and chain extender, which enables more control of the properties of the polymer and also makes it possible to yield compounds that are less toxic than the diisocyanate starting material.

The 2-step process is detailed by Oertel [7] as follows:

a) Formation of prepolymer diisocyanate (1st step)

It is the polycondensation reaction between an alcohol compound and an isocyanate.

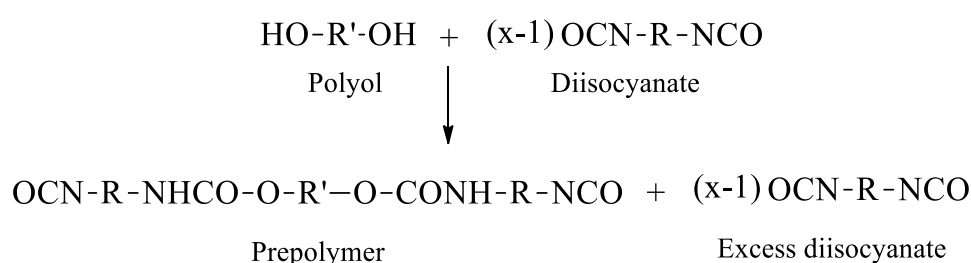


Figure 3: Polycondensation reaction of polyol and diisocyanate.

This reaction is the only one desired (**Figure 3**). It takes place between the isocyanate functional group and the active hydrogen of the alcohol resulting in the formation of a urethane bond. This

urethane bond is at the heart of a prepolymer. The prepolymer is therefore a mixture of polyol chains more or less elongated by diisocyanate molecules via urethane bonds, and excess diisocyanate.

The prepolymer is characterized by its NCO index which corresponds to the number of grams of NCO groups present in 100 grams of diisocyanate prepolymer.

b) Extension of prepolymer chains (2nd step)

This stage is known as the copolymerization phase which allows the transition from the reactive mixture to the final polymer (**Figure 4**).

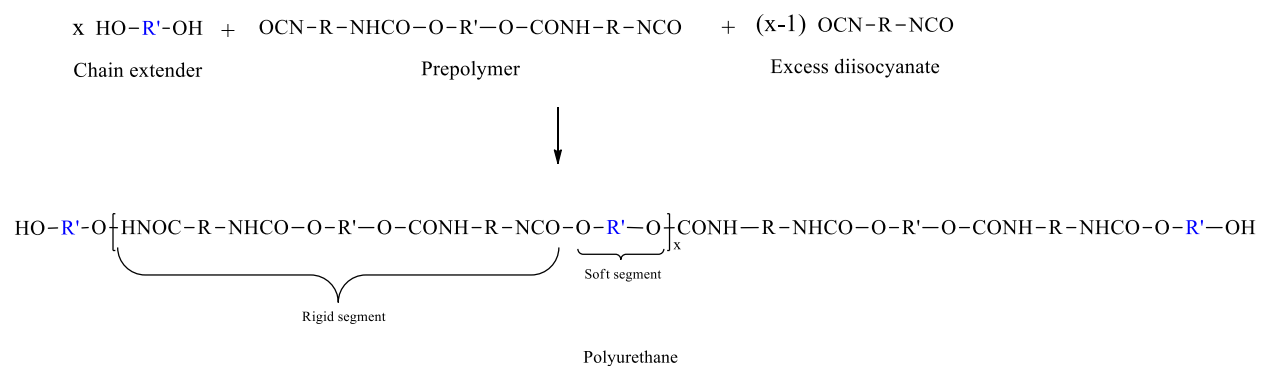


Figure 4: Copolymerization reaction.

The resulting polyurethanes consist of blocks of flexible chains with a low glass transition temperature (called flexible segments) originating essentially from macrodiol and of highly polar, relatively rigid blocks (called rigid segments). The flexible segments are generally polyesters or polyethers. The rigid segments are formed by the reaction of the diisocyanate with the chain extender. As for the final materials, the length of the rigid segments, which is linked to the amount of free diisocyanate, and the chain length of the prepolymer also directly influence the molar mass between physical crosslinking nodes formed by the rigid domains and therefore the elasticity of the final material. [8]

In addition to isocyanate, the polyol is the essential component for the formation of polyurethanes. [9][10]

The formation of the polyurethane backbone results from the reaction between an isocyanate prepolymer and a polyol of comparable mass. In the case where the isocyanate prepolymer is difunctional, the use of a macrodiol will lead to the formation of a linear polyurethane. If the functionality of the polyol, which refers to the number of OH groups per molecule, is greater than two, the polyurethane formed will be a three-dimensional network.

Starting from two difunctional alcohol and isocyanate prepolymers, it is possible to obtain a three-dimensional network by using low molecular weight polyfunctional alcohols. Glycerol is an example of such alcohol, which can act as a crosslinking agent.

Low molecular weight diols such as 1,4-butanediol are also used to control the kinetics of polyurethane formation. These alcohols are called chain extenders.

1.2 The basic chemistry of polyurethane foam

There are two main reactions important in the production of flexible polyurethane foams:

The blow reaction and the gelation reaction. For the manufacturer of flexible foams, the balance between the respective rates of these two reactions creates the open cell morphology of the foam, which is very important for its physical properties.

Polymer foams consist of a distribution of gas trapped in a solid matrix. Due to their: lightness, sound and heat insulation, and impact resistance. they are used in the transportation industry as well as in furniture or buildings. The first main characteristic of foam is its low density. The accessible density range is from 1.6 to 960 kg·m⁻³ for polystyrene and from 10 to 800 kg·m⁻³ for polyurethane [11]. This lightness is essential for aeronautical applications. Its second main characteristic is its ability to undergo large compression deformations for a relatively low level of stress [12]. In **(Figure 5)**, we qualitatively compare the compression behavior of a solid polymer to that of foam. If we can consider that the stress is a quasi-linear function of the deformation for a polymer, in the case of foam, a plateau appears. This corresponds to the crushing of the cells of foams, i.e. the compaction phase. As the magnitude of the stress further increases the deformation behavior is similar to that of the solid polymer. During deformation, a large amount of energy is absorbed by the foam, which is why these materials are used as shock absorbers in the automotive industry. This behavior is strongly influenced by the cellular structure of the foam. [13]

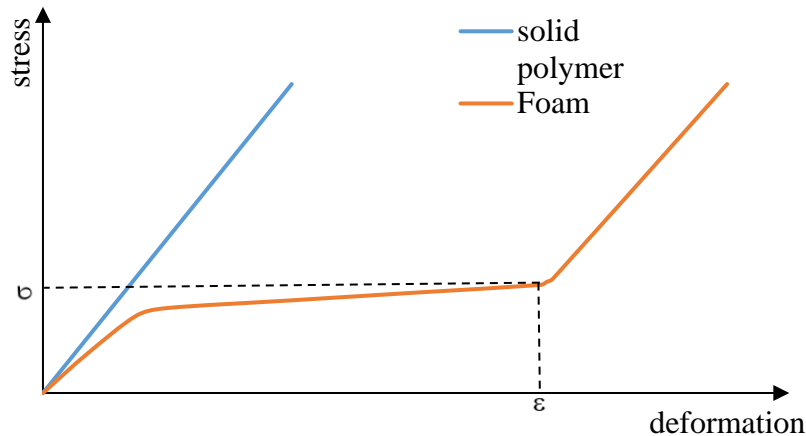


Figure 5: Variation of the stress as a function of the compression deformation of a solid polymer and a foam.

Between rigid and flexible foams, a distinction is made according to the mechanical properties of the matrix. The matrix is either made of a thermoplastic polymer such as polystyrene, or a thermoset polymer such as polyurethane. In the first case, the production of the foam is independent of the synthesis of the polymer. For thermosets, the production of foam is simultaneous with the synthesis of the polymer.[14]

The cells present in the foams are either open or closed. Where the blowing agent used can be:

- physical: a gas is injected under pressure to allow its solubilization in the polymer liquid.
- chemical: a compound will react within the polymer matrix to give gas.

The most widely used physical blowing agents were chlorofluorocarbons or CFCs. However, the use of these molecules has since been banned because of their involvement in the destruction of the ozone layer, as outlined in the (Montreal Protocol [15]). Since the early 1990s, they have mostly been replaced by hydrofluorocarbons or HFCs which do not pose any danger to the ozone layer. Unfortunately, these compounds are greenhouse gases (Kyoto Protocol [16]). Currently, polymer foams are produced with carbon dioxide under supercritical conditions [17][18][19][20].

Water presents the most common chemical blowing agent used to produce polyurethane foams, which reacts with the isocyanate functions and generates carbon dioxide. The component of water will take part in our study as the principal blowing agent.

The formation of a polyurethane foam involves two concomitant reactions: the polymerization reaction and the expansion reaction. To obtain a suitable foam, the time necessary for the

formation of the network must be similar to the time necessary for the expansion of the foam. If this condition is met, the structure of the foam will be regular and it will be possible to obtain a material with a very low density ($<50 \text{ kg}\cdot\text{m}^{-3}$) offering very good insulating and damping properties. The density value will depend on the desired foam: rigid, semi-rigid, high or low density.

1.3 Isocyanate chemistry

1.3.1 Blow reaction

The reaction of water with isocyanates is a two-step process called the blow reaction because, in addition to the production of polyurea, a gas is released which plays an essential role in the blowing of liquid. Auxiliary blowing agents can also be used to give a softer foam than is possible with water alone described in **section 1.4.7**. This reaction proceeds through an intermediate where a heat-unstable carbamic acid is generated, which spontaneously decomposes to form carbon dioxide and an amine. The diffusion of carbon dioxide into the bubbles that are already nucleated causes the foam to expand (**Figure 6**). Besides this, the heat produced will also play an important role in the expansion of the gas in the liquid to form the desired cellular morphology, where the heat of this reaction is $47 \text{ kcal}\cdot\text{mole}^{-1}$ of water. [21]

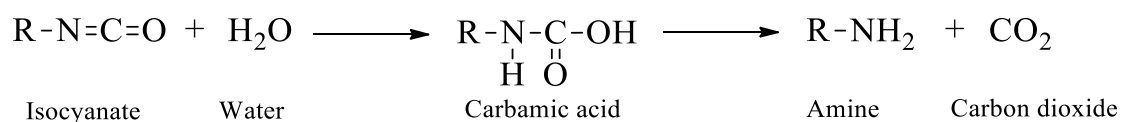


Figure 6: First step of the blow reaction of water and an isocyanate. [22]

The second step of the blow reaction is the reaction between the amine and another isocyanate group to form a disubstituted urea bond (**Figure 7**). This reaction can also be a source of covalent crosslinks if the isocyanate has more than two functional groups or if the amine is polyfunctional (e.g. diethanolamine).

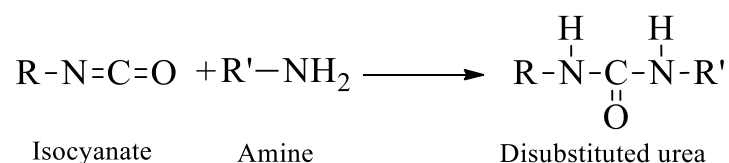


Figure 7: Second step of the blow reaction of an isocyanate with an amine. [22]

The disubstituted urea product of the second blow reaction shown in (**Figure 7**) could also react with an isocyanate functionality which produces a biuret. However, this reaction is reversible and generally does not occur below $100 \text{ }^\circ\text{C}$ (**Figure 8**).

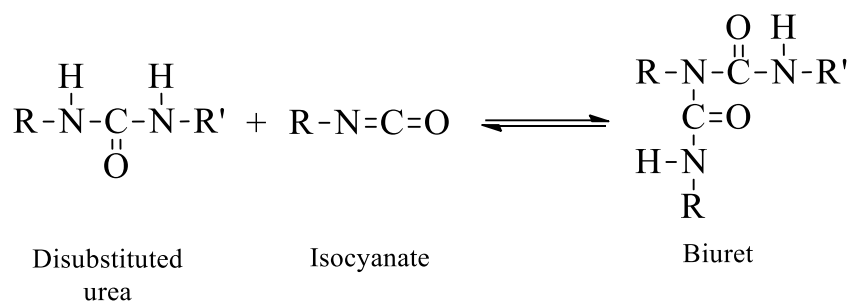


Figure 8: Formation of a biuret linkage [22].

1.3.2 Gelation reaction

Polyurethane is produced by the reaction between an alcohol and an isocyanate. This reaction is exothermic with a heat of about $24 \text{ kcal}\cdot\text{mole}^{-1}$ of urethane formed (**Figure 9**). The nature of the R groups and the R' groups can vary depending on the selection of the components of the formulation (R and R' are alkyl or aryl groups).

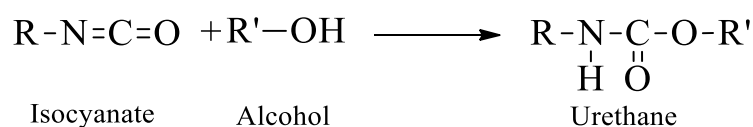


Figure 9: The gelation or cross-linking reaction of isocyanate with alcohol [22].

We have seen that isocyanates react preferentially with compounds with active hydrogen, but other reactions are possible [23][24], such as the formation of allophanates (**Figure 10**). This occurs when another free group of isocyanate reacts with the urethane bond between $100 \text{ }^\circ\text{C}$ and $140 \text{ }^\circ\text{C}$ using the hydrogen of the amine group [25][26].

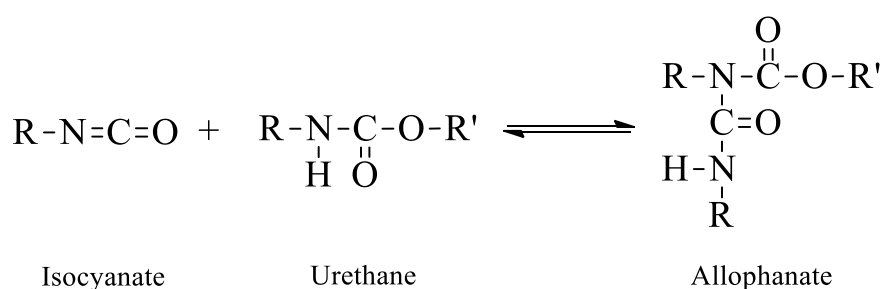


Figure 10: Allophanates formation of the reaction of an isocyanate and a urethane [22].

1.3.3 Further isocyanate reactions

a. Reaction mechanisms between an alcohol and an isocyanate

The synthesis of urethanes is based on the chemistry of the isocyanate group which has two mesomeric forms (**Figure 11**). Isocyanates are prepared by reacting phosgene with amines (**Figure 12**) where isocyanates are compounds that carry one or more $\text{N}=\text{C}=\text{O}$ functional groups

and are highly reactive [21]. The two double bonds N=C and C=O of isocyanate allow it to react with all compounds with active hydrogens such as alcohols or amines. The reactivity of isocyanates comes from the strong electrophilic nature of the carbon atom, which is enhanced in the case of aromatic isocyanates. In the absence of a catalyst, the addition reaction of a proton donor to isocyanate involves the formation of an intermediate complex. The reaction begins with a nucleophilic attack on the carbon of the isocyanate and leads to the formation of two mesomeric forms. The intermediate complex formed by the addition of a second molecule R'-H decomposes according to a proton exchange reaction. Whichever mesomer is present, the final product is no identical (**Figure 13**) [26].

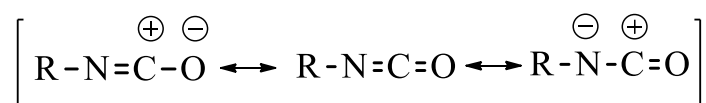


Figure 11: Mesomerism form of the isocyanate group, where either N or O carry a negative charge.

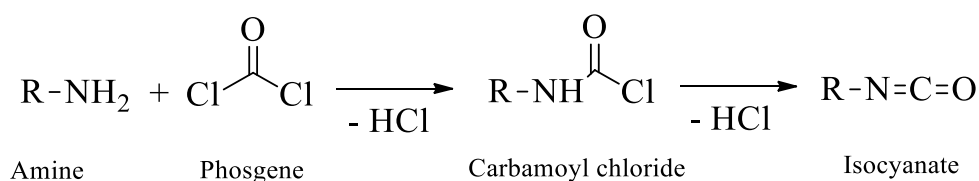


Figure 12: Production of isocyanate from a primary amine via phosgenation.

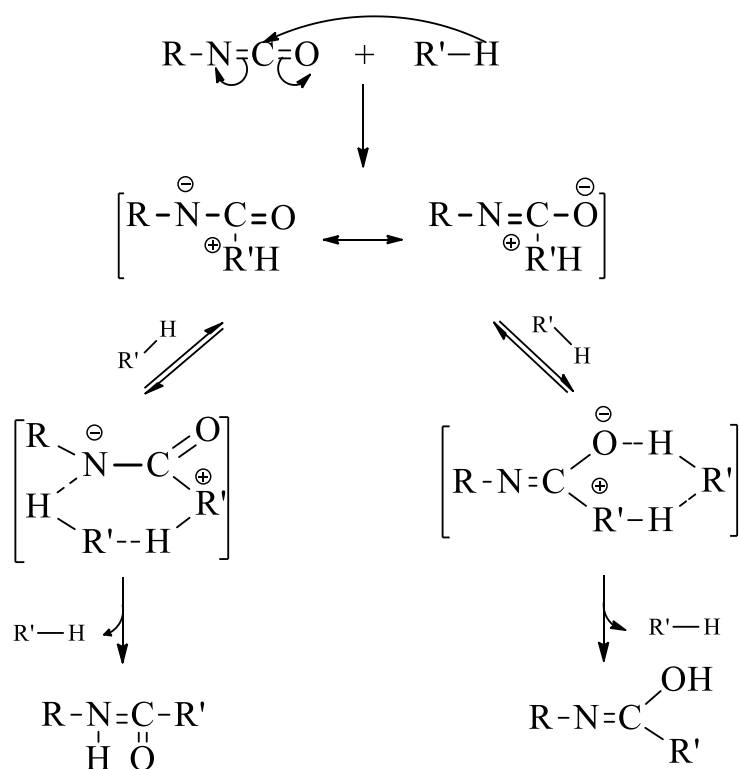


Figure 13: The reaction of an isocyanate with a nucleophilic agent.

Isocyanates can also react with each other and lead to the formation of isocyanate dimers, trimers, or even polymers. Isocyanates of high reactivity are likely to dimerize. The dimerization reaction is favored by a reaction temperature between 20 °C and 80 °C in the presence of a basic catalyst such as trialkyl phosphines[27], and leads to the formation of uretidione. Aromatic isocyanates tend to form uretidiones spontaneously, even during their storage at room temperature, in the solid-state and without a catalyst (**Figure 14**). The formation of diisocyanate dimers alters the initial stoichiometry calculated for the isocyanate unless the reaction temperature is high enough to decompose the dimers. For example, the dissociation of cyclic uretidione occurs spontaneously 150 °C and 180 °C [27].

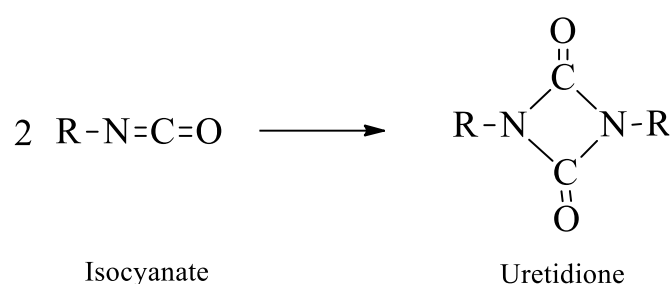


Figure 14: The spontaneous formation of uretidione from two aromatic isocyanates at 25 °C. As with dimerization, isocyanates of higher reactivity are better able to trimerize to form isocyanurates, which are characterized by high thermal stability. Moreover, due to the effective catalysts, their formation often occurs as a secondary reaction in syntheses. Trimerization is favored by harsh reaction conditions, such as the presence of strong bases, if the isocyanates used are very reactive. Trimerization is frequently accompanied by dimerization and the formation of carbodiimide, as is the case of two isocyanate molecules, which can react, between 150 °C and 300 °C, without a catalyst and yield carbodiimide bonds (**Figure 15**) [28][29].

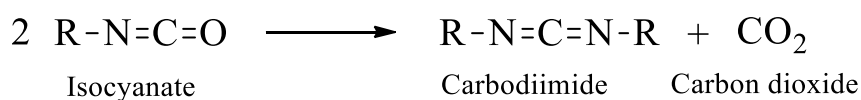


Figure 15: The carbodiimide formation from two isocyanates between 150 °C and 300 °C. If diisocyanate is the isocyanate to react with, it will yield a polycarbodiimide (**Figure 16**). Besides, a carbodiimide functional group can react again with an isocyanate and form substituted uretonimines (**Figure 17**). Isocyanurates are formed during trimerization (**Figure 18**) [30].

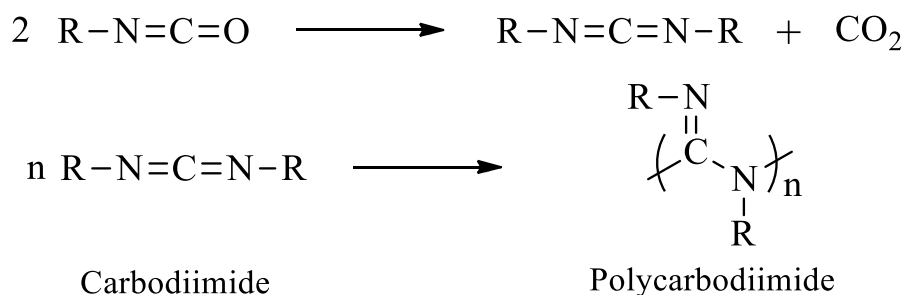


Figure 16: The polycarbodiimide formation from carbodiimide functional group.

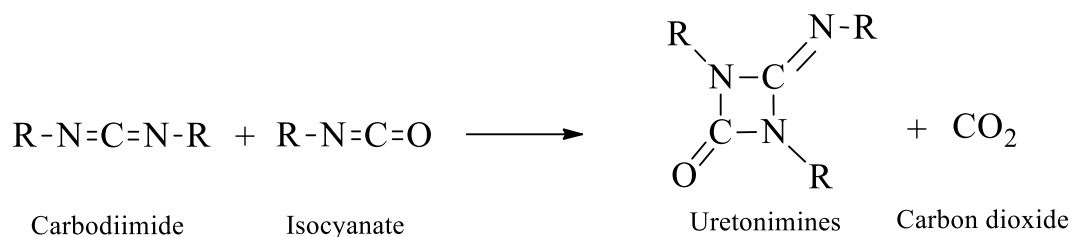


Figure 17: The formation of a substituted uretonimine from carbodiimide and isocyanate.

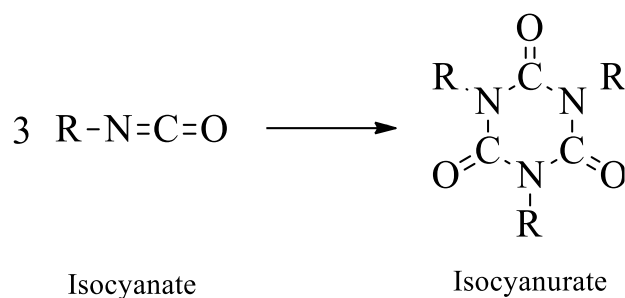


Figure 18: The isocyanurates formation of three high reactive isocyanates.

Finally, isocyanates can undergo linear polymerization at very low temperatures (-100 °C to -20 °C for certain monoisocyanates), in the presence of anionic initiators. The final polymer obtained in this case would be polyamide-1 (**Figure 19**) [30].

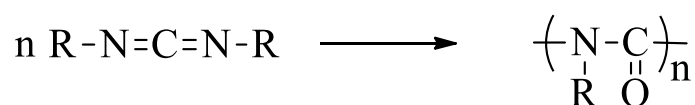


Figure 19: The polyamide-1 formation between -100 °C to -20 °C.

Studying the literature highlights the complexity of the reaction mechanisms associated with the isocyanate group. Many of these mechanisms remain hypothetical and their validation would still require years of research.

1.4 Foam formulation components

Each application of flexible polyurethane foams has specific performance criteria, thus many components are needed to ensure that the product of a typical formulation will be open-celled and still meet other requirements. For example, fillers may be added to enhance strength, or a lower potency surfactant may be used to increase cell openness. An example of the types of components that might be involved in a formulation, and some exemplary concentration ranges are provided in **Table 1**. It should be noted that, by convention, flexible polyurethane foam formulations are calculated as weight fractions based on total polyol added (termed parts per hundred polyol). The type of each component will be discussed in detail in the following subsections.

Table 1: Typical Components and their Normal Usage in Flexible Polyurethane Foam Formulations (1)

Component	Weight Added [Parts Per Hundred Polyol]
Polyol	100
Water	1.5-7.5
Inorganic Fillers	0-150
Silicone Surfactant	0.5-2.5
Amine Catalyst	0.1-1.0
Tin Catalyst	0.0-0.5
Chain Extender	0-10
Cross Linker	0-5
Additive	Variable
Auxiliary Blowing Agent	0-35
Isocyanate	25-85

1.4.1 Diisocyanates

A wide range of compounds containing the isocyanate functional group is currently used in the flexible foam industry, they carrying at least two isocyanate functions which are an aliphatic or an aromatic type.

1.4.1.1 Aromatic isocyanates

The NCO functional group is directly attached to the aromatic nucleus. This enables the delocalization of the negative charges onto the NCO group, thus making the aromatic isocyanates much more reactive than the aliphatic isocyanates [31].

Aromatic isocyanates do not require a catalyst in reactions with alcohols and are relatively inexpensive. However, they can generate materials that are sensitive to photolytic aging. Indeed, the possible oxidation of aromatic nuclei by UV radiation can cause the yellowing of these endproducts. They are instead used for polyurethanes with specific applications of adhesives or coatings for which color is not an essential aspect[32][33]. The two aromatic isocyanates used in the synthesis of polyurethane are methylene diphenyl diisocyanate (MDI) and toluene diisocyanate (TDI) [34][35].

a. Methylene diphenyl diisocyanate (MDI)

Methylene diphenyl diisocyanate, is derived from the condensation reaction of aniline with formaldehyde, which forms polymeric amines that are then phosgenated. This results in a mixture of various forms of MDI, and this process will be described in more **detail in a later chapter**. The mechanism of the phosgenation of MDA will be investigated using accurate quantum chemical calculations, and the gas phase thermodynamic profiles of the possible reaction pathways leading to the formation of the MDI will be investigated thereafter. Where MDI is generally produced in the form of 4,4-diphenylmethane diisocyanate (**Figure 20**). However, traces of the 2,4 and 2,2 isomers can be found[36].

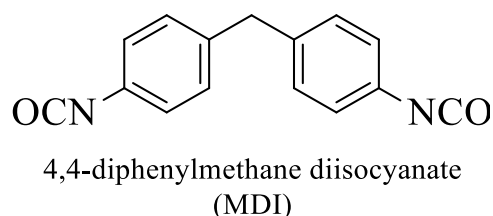


Figure 20: Chemical structure of 4,4-diphenylmethane diisocyanate.

The MDI group has a fairly rigid structure and spontaneously dimerizes at low temperatures. Although it is slow, this dimerization step alters the properties of the product. The perfect symmetry of MDI suggests that the two NCO functions should, in theory, have the same reactivity. In practice, kinetic studies have shown that the second NCO group is half as reactive once the first has reacted [37]. Indeed, at 25 °C, the reactivity ratio of the two functions is two, while it tends towards one beyond 100 °C [38]. This difference in reactivity is due to the resonance effect of the aromatic nuclei [39].

b. Toluene diisocyanate (TDI)

TDI exists in two isomeric forms, 2,4 and 2,6 toluene diisocyanate (**Figure 21**). TDI is synthesized from toluene. It includes a nitration step followed by a reduction step, which yields

either of the two aforementioned diaminotoluene isomers. A final reaction with phosgene yields the TDI end product.

In addition to its low resistance to ultraviolet radiation, the low vapor pressure of TDI makes it particularly toxic. Indeed, it causes breathing discomfort and irritation of the lungs[38][40]. The NCO group on carbon 4 of 2,4 toluene diisocyanate (**Figure 21**) is much more reactive than those on carbons 2 or 6 of 2,6 toluene diisocyanate (**Figure 21**). Once the NCO group on carbon 4 has reacted, the second NCO is approximately 8 times less reactive than the first one [41].

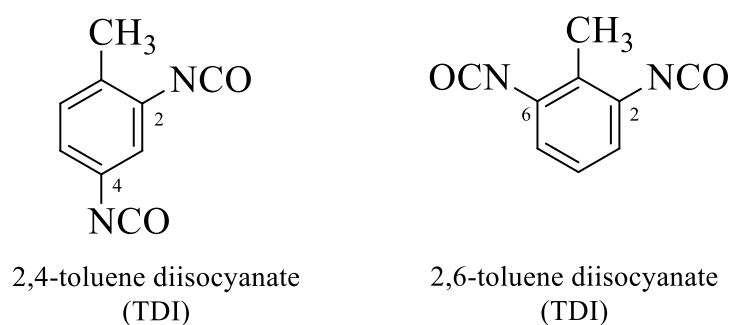


Figure 21: Chemical structures of isomeric forms of TDI.

1.4.1.2 Aliphatic isocyanates

The NCO group in aliphatic isocyanates is not directly linked to a double bond, which gives polyurethanes based on these structures excellent resistance to light and aging.

The aliphatic nature of these isocyanates leads to a lower reactivity, thus these isocyanates react more slowly and require the use of a catalyst. Their reactivity with carboxyl groups and with water is also lower and there is no self-condensation reaction. These isocyanates allow the synthesis of prepolymers at temperature ranges of 100-120 °C, compared to the 60-80 °C reaction temperature used for aromatic isocyanates [39], [42]. For all these reasons, they are generally preferred to aromatic isocyanates for the formulation of polyurethane foam, despite their much higher cost. The three aliphatic isocyanates used in the synthesis of polyurethanes are tetramethylxylene diisocyanate (TMXDI), isophorone diisocyanate (IPDI), and 4,4'-diisocyanatodicyclohexylmethane (H12MDI), see (**Figure 22**) [35].

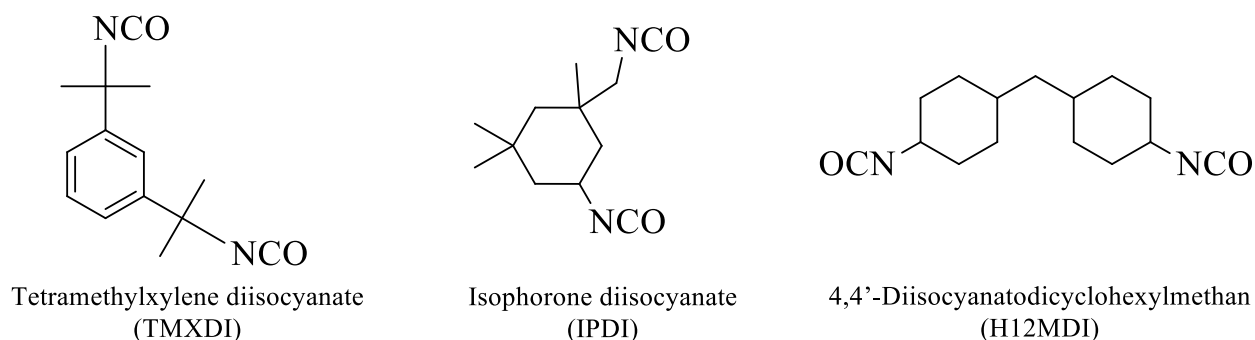


Figure 22: Chemical structures of aliphatic isocyanates tetramethylxylene diisocyanate TMXDI, isophorone diisocyanate IPDI, and 4,4'-diisocyanatodicyclohexylmethane H12MDI.

1.4.2 Polyols

The second component of polyurethane foam formulation is the polyol, which can be any molecule containing at least two hydroxyl groups. It was mainly the use of a wide range of polyols of different properties, molecular weights, and different functionalities that allowed the development of the very high diversity of polyurethanes. Polyol is generally an alcohol-functionalized low molecular weight polymer ($3,000$ to $5,000 \text{ g}\cdot\text{mol}^{-1}$) that can be classified into two categories, monomeric and polymeric polyols. Monomeric polyols are low molecular weight organic compounds, such as glycerol, ethylene glycol, propylene glycol, diethylene glycol, and 1,4-butanediol. Monomeric polyols are thus classified according to the number of hydroxyl groups in a molecule, such as diols, which have two hydroxyl groups in a molecule, triols which have three hydroxyl groups in a molecule, and so on [43][44].

Polymeric polyols are high-molecular-weight polymers obtained from ethylene oxide and propylene oxide, which are major components for the formation of polyurethane backbones. Polyether and polyester polyols are the two most common polymeric polyols [45][46]. Therefore, although about ninety percent of polyols utilized today are polyether polyols will take part in our study, their specific composition is frequently tailored to meet very specific requirements, they are cheap, easy to handle, and are more resistant to hydrolysis than polyesters are [21].

1.4.2.1 Polyethers

The hydroxylated polyethers are generally obtained by the polyaddition, either anionic or cationic, of cyclic monomers such as ethylene oxide, propylene oxide, or even tetrahydrofuran. The molar masses of the polyether polyols used in the synthesis of polyurethanes vary from 250 to $8000 \text{ g}\cdot\text{mole}^{-1}$. Their functionality can range from 2 to 7 groups depending on the nature of

the molecule used as an initiator. The terminal groups of these polyether diols can be either primary or secondary alcohols (**Figure 23**).

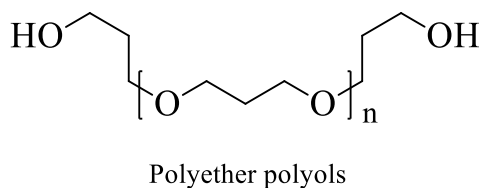


Figure 23: Chemical structure of polyether polyols.

However, the main advantage of this family of polyols is their cost, which is particularly low, because of the high availability of the raw materials used in their manufacture.

1.4.3 Water

Water (**Figure 24**) is added to these formulations to react with the isocyanate as discussed in **Section 1.1.1**. This reaction ultimately produces polyurea, carbon dioxide, and heat [47]. This carbon dioxide diffuses to existing gas bubbles in the polyol and so expands the mixture into a foam. Control of the amount of air contained in the polyol raw material is one way that manufacturers control the number of nucleation sites in the reacting mixture. These initially small bubbles quickly grow through either gaining gas from the diffusing carbon dioxide or by coalescing with other bubbles.

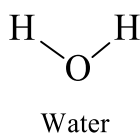


Figure 24: Chemical structure of water.

1.4.4 Catalysts

Catalysis is essential to obtain the produced material in an economically viable time. This amounts to saying that from an industrial point of view, the production of foam must be done in about ten minutes, and while the flexible polyurethane foams are the product of two competing reactions, a good balance is necessary between the two reaction speeds to obtain a good open-cell morphology at the desired density. The formation of a foam involves the synthesis of the polymer network and the release of an agent that allows it to expand [48][49][42]. The catalysts most often used for the synthesis of polyurethane foam are tertiary amines or organometallic compounds [50]. Tertiary amines behave like Lewis bases and organometallic compounds behave like Lewis acids [49][42][51]. The most commonly used type of catalyst is the tertiary amines that take part in the experimental studies.

1.4.4.1 Tertiary amines

These catalysts are generally thought of as blowing catalysts but they also enhance the gelation reaction. The lone electron pair on the nitrogen atom (**Figure 25**) provides a strong nucleophile that is capable of attacking the carbon of the isocyanate group [52].

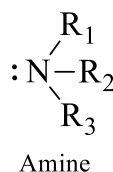
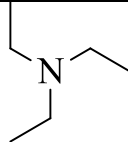
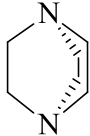
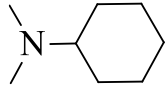
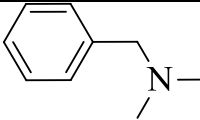
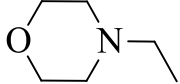


Figure 25: Chemical structure of tertiary amine.

Steric hindrance and electronic effects of the substituent groups are the two main tools used to adjust the relative catalytic activity of the various tertiary amines. In some foam systems, specific combinations of amines are used to balance the rates of the gelation and blow reactions.[53][51][54].

Table 2: The most frequently used commercial amino compounds in the production of polyurethane.

Name of amine	Abbreviation	Formula
Triethylamine	TEA	
1,4-diazabicyclo [2.2.2] octane or triethylenediamine	DABCO or TEDA	
N, N-dimethylcyclohexylamine	DMCHA	
Benzyl dimethylamine	BDMA	
N-ethylmorpholine	NEM	

There are therefore two modes of catalysis for amines. It has been shown that when they react, they create interactions with available active hydrogen and thus activate the reagent [55].

The complex between isocyanate and alcohol can then be formed more easily due to the interaction between tertiary amine and alcohol (**Figure 26**), leading to urethane bond formation.

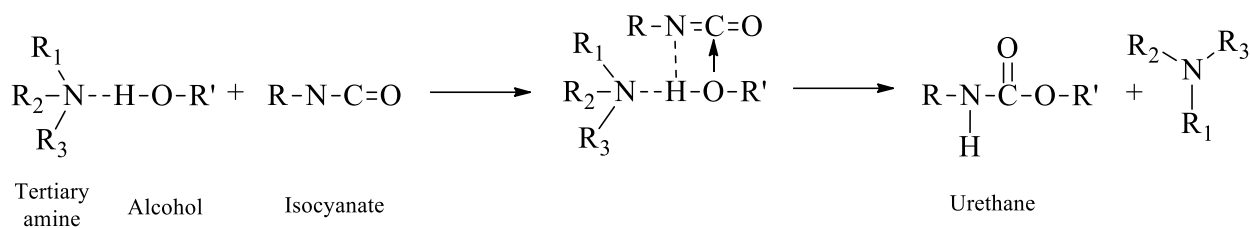


Figure 26: Activation of alcohol by an amine.

The second mode of catalysis is favored by a strong nucleophilicity induced *inter alia* by a light steric hindrance of the amine nitrogen. This can then bind to the electropositive carbon of the isocyanate and thus activate this function by increasing the partial charge of nitrogen and oxygen [56], as shown in **(Figure 27)**. The alcohol can then form a complex and react more easily.

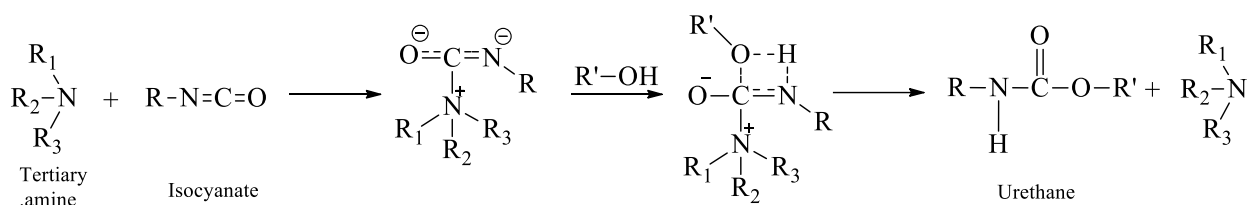
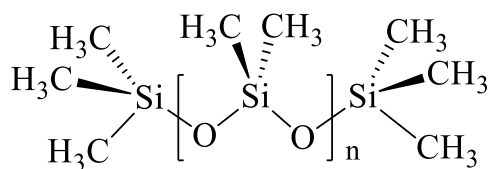


Figure 27: activation of isocyanate by an amine.

High basicity favor the isocyanate - water reaction. In addition, the increasing number of amine groups in the molecule makes it possible to increase the catalytic activity of the catalyst and to promote in particular the activation of water. In the section on the theoretical and experimental methods, we will study the association of reagents in the absence of catalysts.

1.4.5 Surfactants

Non-ionic surfactants are ubiquitous in the flexible polyurethane foam industry for the production of a good open-celled morphology. Some of the functions they perform are reducing surface tension, emulsifying incompatible ingredients, promoting bubble nucleation, stabilizing the rising foam, and reducing the defoaming effect. Of these, the most crucial to foam production is the stabilization of the cell walls. The most common surfactants in use today are graft copolymers consisting of polydimethylsiloxane **(Figure 28)** and the groups of polyethylene oxide and propylene oxide [22][21]. The mechanical properties of hard polyurethane foam such as air permeability and cell size, are greatly influenced by the structure of the silicone surfactant used in the formulation.



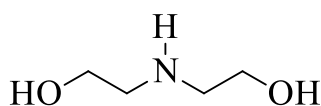
Polydimethylsiloxane

Figure 28: Chemical structure of polydimethylsiloxane.

A series of silicone surfactants with different structures have been tested. Surfactants with a higher silicone content provide a lower surface tension and help increase the number of air bubbles introduced during mixing [57].

1.4.6 Cross-linking agents

In polyurethane systems, cross-linking agents are typically short-chain molecules containing amine or hydroxyl functional groups and having a functionality greater than three. They can be added to these systems to provide increased load-bearing or initial foam stability [58]. By far, The most frequently used commercial cross-linking agents in polyurethane foam production are ethylene glycol, diethylene glycol, propylene glycol, dipropylene glycol, 1,4-butanediol, 1,6-hexanediol, glycerol, trimethylolpropane. Diethanolamine is the most common cross-linking agent used in the industry, and its structure is shown below (**Figure 29**).



Diethanolamine

Figure 29: Chemical structure of diethanolamine.

These cross-linkers are most frequently used in molded foam formulations. High molecular weight polyols and the faster reaction rates observed in those systems build viscosity so fast that the use of typical foam surfactants overstabilizes the cell walls, thus preventing many cells from opening. To allow cell opening to occur, lower-potency surfactants are utilized. However, these surfactants are not potent enough to fully stabilize the foam, and so cross-linking agents are added to provide an added dimension of stability [58][59].

1.4.7 Auxiliary blowing agents

While the water-isocyanate reaction provides the primary blowing mechanism for flexible polyurethane foams, some products require the use of auxiliary blowing agents to achieve the desired levels of density or softness. These blowing agents are low-boiling solvents which are

inert in the chemical reactions already described in **section 1.2**. As the highly exothermic foaming reactions proceed, the temperature in the mixtures reaches or exceeds 130 °C within two minutes. This large temperature increase is enough to vaporize the low boiling solvents, providing the additional gas to expand the foam. The vaporization of these additional fluids does absorb a lot of the heat needed to expand the gas into the cellular structure; therefore, these formulations generally employ higher amount of catalyst needed to increase the amount of heat generated [60][61].

1.4.8 Additives

In order to achieve desired properties, it is sometimes necessary to include an additive. Some additives are used to make the product more appealing to consumers or to achieve a design specification. For example, colorants (metal oxides, carbon black, or dyes) well we will use in one of the experimental studies the hydroquinone its structure is shown below (**Figure 30**). Other additives are included to improve product performance such as flame retardants, antistatic agents, bacteriostats, or UV stabilizers to prevent foams from yellowing. Finally, some additives may be necessary for special applications. For example, plasticizers are used to reduce in-mold viscosity, cell-openers are used to enhance the cell wall rupture mechanisms, and compatibilizers are used to enhance emulsification beyond what the standard surfactant systems can achieve [62].

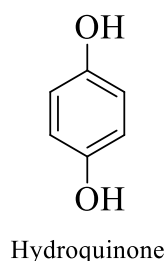


Figure 30: Chemical structure of hydroquinone.

1.5 Aim

This first bibliographic approach made it possible to highlight the interest, but above all the complexity, of polyurethane systems. One of our first objectives was to choose a synthesis process that is relatively simple to implement both in the laboratory and with a view to an industrial application, and this bibliographical research also made it possible to highlight the influence of the raw materials used on the properties of the final polymers. Thus, we have chosen to study in particular the influence of the two major reactants in the composition of polyurethane, diisocyanates, and polyols. Further, according to this approach, we recognize that

the production of polyurethane is a complicated process and requires proper control of reaction conditions. Understanding the reaction steps of synthetic products 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 this research is supported by theoretical and experimental results, in which electronic structure calculations are used to determine possible new reaction mechanisms, urethane and polyurethane foam formation processes, and discover new synthesis strategies by modifying the reactants in the mechanism. The theoretical study of the reaction mechanism requires an adequate and robust quantum chemical protocol. From the results obtained from the electronic structure calculations, we will be able to complete our research through the experimental part. The results and conclusions are described in the following sections, which provide valuable information for understanding industrial reactions at the molecular level.

2. Methods and Materials

In this research, two methods of determination of the polyurethane formation are presented: experimental method with analysis, and theoretical method with computational applications. Both procedures were used for the characterization of the urethane and polyurethane bond formation.

2.1 Experimental methods

2.1.1 Kinetic and reactivity measurement of single urethane bond formation

Stock solutions of 2.0 M phenyl isocyanate (PhNCO) and 2.0 M propanol (PrOH) in THF (for the stoichiometric runs), and 4.0 M PhNCO, and 0.2 M PrOH in THF (for the NCO excess runs) were prepared in volumetric flasks. From the pre-incubated (± 0.1 °C) stock solutions, 5.0 mL of PhNCO and 5.0 mL of PrOH solutions were pipetted into a pre-incubated glass vial which was then capped. The experiments were conducted at 30, 40, and 50 °C. At different time intervals, a 10 μ l aliquot was withdrawn from the reaction mixture and mixed into 990 μ l ACN containing 30 μ l of n-butylamine in order to quench the reaction. The amine reacts spontaneously with the isocyanate to form the adduct, *N*-butylphenylurea. The quenched samples were further diluted by a factor of 50 (for the PhNCO excess runs) or 5 (for the stoichiometric runs) with ACN:H₂O=1:1 mixture and subjected to HPLC analysis. The concentration of N,N'-diphenylurea side-product (originating from the hydrolysis of PhNCO) was also identified and was found to be a maximum of 5.6% of the starting PhNCO concentration. Further, the analytic detection technique was done on the quenched and diluted samples using a Shimadzu® HPLC equipped with LC-20AD pumps, SIL-20AC autosampler, DGU-20A3R degassing unit, CTO-20A column oven, and SPD-M20A photodiode array detector. A SunShell® C8 column (2.6 μ m, 150 x 3.0 mm) equilibrated at 40 °C was used for the separation. The injection volume was 25 μ l. The eluent was ACN:H₂O with a gradient as follows: 0–3.50 min, 42% ACN; 3.51–4.50 min, 82% ACN; 4.51–9.00 min, 42% ACN, at a flow rate of 0.6 mL·min⁻¹. The product n-propyl phenylcarbamate was quantified at 239 nm. For calibration, the reference compound was synthesized from PhNCO in PrOH and purified by flash chromatography.



Figure 31: Microreactor setup, the Asia microflow system (Syrris Ltd., Royston, UK).

2. 1. 2 Measurement of polyurethane bond formation and the analysis of mechanical properties

The synthesis of flexible polyurethane foams was based on the mixing and pouring procedure. The polyol, distilled water, mono-alcohol, and catalyst were weighed and mixed in a 500 mL plastic cup at ambient temperature (23 °C). After stirring the liquid at 2000 rpm for 1 min, the isocyanate was added and the mixture was stirred again at 3000 rpm for 10 s. The foams were obtained by free expansion.

All recipes and calculations are based on 100 total parts by weight of polyol. There may be more than one polyol in a recipe, but convention dictates that the sum of all polyols adds up to 100 parts. The amount of other ingredients are normally listed as parts per hundred parts of polyol by weight [63].

Functionality: The functionality of a B-side foam ingredient is the number of isocyanate reactive sites on a molecule. For polyols, the average functionality is generally used.

$$\text{Average Functionality} = \frac{\text{total moles OH}}{\text{total moles polyol}} \quad (1)$$

Hydroxyl Number (OH Number): Is the hydroxyl content of a polyol as determined by a wet analytical method. It is expressed as the milligrams of potassium hydroxide equivalent to the hydroxyl content in one gram of polyol or another hydroxyl compound.

$$\text{OH Number} = \frac{56.1 \cdot 1000}{\text{Equivalent Weight}} \quad (2)$$

Where 56.1 is the atomic weight of potassium hydroxide and 1000 is the number of milligrams in one gram of sample. The manufacturer provides the OH number for each lot of polyol.

Polyols are sometimes characterized by the weight percentage of hydroxyl groups. Conversion to hydroxyl number is accomplished by:

$$OH\ Number = 33 * \% OH \quad (3)$$

Where the number 33 is obtained by the reduction of constants. For a mixture of polyols, the *hydroxyl number of the mixture* (OH_m) is given by:

$$OH_m = OH\ Number_A(Wt.\ \% Polyol\ A) + OH\ Number_B(Wt.\ \% Polyol\ B) + \dots \quad (4)$$

Equivalent Weight of a Polyol: The weight of a compound per reactive site.

$$Equivalent\ Weight = \frac{Molecular\ Weight}{Functionality} \quad (5)$$

After determining the parts of each polyol, which the total polyol parts should equal 100, we then also determine the parts of other B-side components per 100 parts polyols, and finally take the sum of the parts of all B-side materials to get the total formula weight.

$$Equivalents = \frac{Parts}{Equivalent\ Weight} \quad (6)$$

After determining the equivalent weight of each B-side component, we can then calculate the equivalents of each B-side component such as water, catalysts, and other additives. In the end, we can take the sum of the reactive equivalents of each B-side component to get the total B-side equivalents. Otherwise, the A-Side represents the amount of isocyanate required to react with the polyol, water, and other reactive additives that are calculated to give the desired stoichiometry. In actual practice, the amount of isocyanate is adjusted up or down depending on the particularity of the foam system.

Isocyanate Equivalent Weight: The equivalent weight (eq. wt.) is used to calculate how many grams of a product needed for one equivalent of reactive functional groups. For an isocyanate, the equivalent weight in isocyanate is the weight of a substance that contains 42.02 grams of the reactive group, which is NCO.

$$Isocyanate\ equivalent\ weight = \frac{42.02 * 100}{NCO\ Number} \quad (7)$$

Isocyanate Index (NCO Index): The ratio of the equivalent amount of isocyanate used is relative to the theoretical equivalent amount times 100. The theoretical equivalent amount is equal to one equivalent isocyanate per one equivalent B-side compound. This is an index of 100.

$$\text{Isocyanate Index} = \frac{\text{Actual amount of Iso}}{\text{Theoretical Amount of Iso}} * 100 \quad (8)$$

After recording the isocyanate equivalent weight and selecting the desired NCO Index, we can calculate the equivalent amount of *isocyanate parts required*.

$$\text{Eq. Iso} = \frac{(\text{Equivalents B-Side}) * (\text{Isocyanate Index})}{100} \quad (9)$$

$$\text{Parts Isocyanate} = (\text{Eq. Iso}) * (\text{Iso Eq. Wt.}) \quad (10)$$

We can also calculate the *B/A ratio* according to the following equation

$$\frac{B}{A} \text{Ratio} = \frac{\text{Parts B-Side}}{\text{Parts A-Side}} \quad (11)$$

According to these calculations, we can now deduce the exact amount of each reagent needed in each experiment to produce the desired yield of polyurethane foam.

For the analysis of the Compressive test and the density, the samples having dimensions of 33 x 31 x 18 mm were cut from the prepared foams to measure the density and the compression properties of the foam. The density measurement is done by measuring the volume and the mass (the mass was determined by using an electronic weighing scale). The compression test was performed on an Instron(R) 5566 universal testing machine[64] using Instron compression plates (T1223-1021) with a diameter of 50 mm, with a 10 N or 10 kN load cell, at punch crosshead speeds (CHS) of 0.01–500 mm·min⁻¹. The testing was performed in a conditioned room at 22 °C and 50% relative humidity, using a compression rate of 10 mm·min⁻¹. The specific compressive modulus and strength of polyurethane foam were measured at 83% deformation of the original height (18 mm) to be able to evaluate the material behavior over a large deformation interval (**Figure 32**). The computer related to the software can record the on-line load-displacement data after a quasi-static compression test. The acquired data is used for drawing the load-displacement curves (stress-strain diagram), from which the yield strength, compressive strength, and Young's modulus were determined.

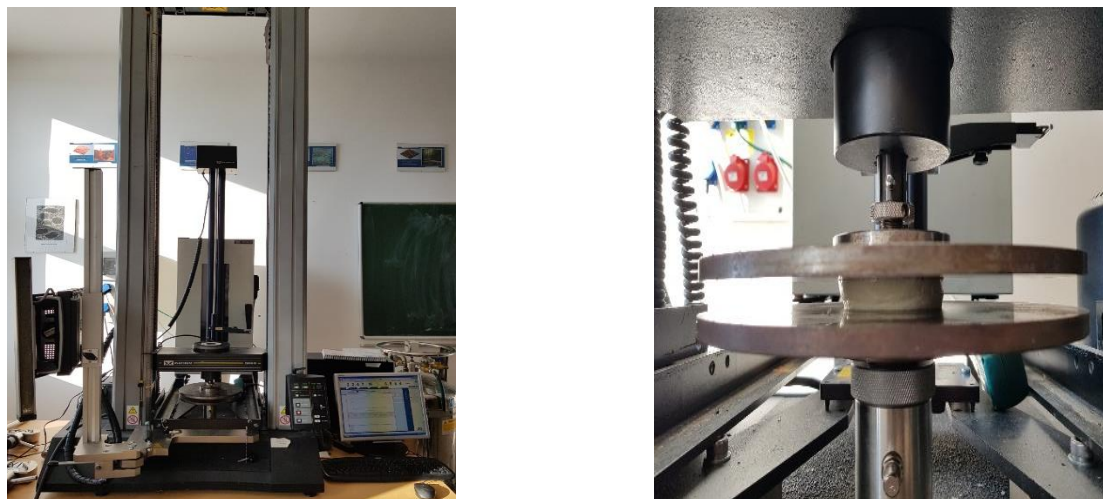


Figure 32: Compressive test of foam specimen with the Instron® 5566 universal testing machine.

2. 2 Materials

The isocyanates used in the reactions were the Ongronat® 2100, a polymeric MDI was purchased from Wanhua-BorsodChem, and phenyl isocyanate (PhNCO) ($\geq 99\%$, Acros Organics) was used as received, where the polyols used in our experiments are mostly polyether polyols based on glycerine such as Rokopol® M6000, Caradol® MC28-02, Alcupol® D-2021 and, PEG-600 were purchased from Wanhua-BorsodChem. Mono-alcohols used in the reactions were methanol and isobutanol (Molar Chemicals), ethanol and 1-propanol, 2-propanol, 1-butanol, tert-butanol ($\geq 99\%$, VWR Chemicals), 1-hexanol and cyclohexanol (Alfa Aesar), 1-octanol (Scharlab Chemicals), tetrahydrofuran (THF) ($\geq 99\%$, VWR Chemicals) were stored in 20% (m/V) activated molecular sieve (3\AA , beads, VWR Chemicals) For at least two days to reach a low water content.[65]. Catalyst, whether basic or organometallic, such as N,N-dimethylcyclohexylamine (DMCHA), Triethylaluminum (TEA), Diazabicycloundecene (DBU), N-Methylmorpholine (NMM), N-Ethylmorpholine (NEM), 1,4-Diethylpiperazine (DEPP), and n-Butylamine (BuA $\geq 99\%$) were purchased from Merck. N,N'-diphenylurea (DPU $\geq 98\%$) was purchased from Alfa-Aesar.

2. 3 Theoretical methods

Quantum chemistry “ab initio” has become a viable and powerful method for solving problems related to chemical systems. The real prospect of quantum chemical computing is to supplement experiments as a means of discovering and exploring new chemistry. It uses computer simulation technology to predict the performance of new materials, even those that have not been synthesized in the laboratory. However, the calculation cost increases greatly with the

increase of the system size and the accuracy to be achieved. Improvements in computer performance and/or theoretical performance have made computational simulation an indispensable tool in materials science. Today, even in large and complex molecular systems, more results that are accurate can be gradually obtained within a reasonable time to determine the best structure defined as having the lowest possible energy. To obtain more accurate measurement results of molecular properties, to be used in different applications, and to understand the physics of molecular systems, more reliable methods are needed [66]. The work reported in the thesis involves the use of quantum chemistry methods and experimental methods, to make a theory more closely mimic the experiment one has to consider not just one structure for a given chemical formula, but also all possible structures. That is, one characterizes the potential energy surface (PES) for a given chemical formula. Studies of the molecular, structural, vibrational, and energetic data of molecular systems are made in the gas phase and solvent phase. Density functional theory (DFT) has been used to optimize the most stable molecules and to study the ground-state properties of the molecules studied. In any quantum chemical calculation, the first step requires optimization of the molecular geometry. It is customary to assume the system in the gas phase (isolated molecule). The wave functions and energy are computed for the initial guess of the geometry, which is then modified iteratively until the identification of energy minimum and ensuring that the forces within the molecules to be zero. Using the optimized structure (minimum energy) molecular properties like polarizability, electron affinity, dipole moment, and so forth the vibrational modes can also be calculated [67][68] by computing the second derivative of the energy concerning the pairs of the atomic Cartesian coordinates. Since an optimized geometry corresponds to zero forces within the molecule, all leading force constants must be positive (that is called reaction coordinate) and therefore should not result in any imaginary vibrational wavenumber. Some infinite properties that can be calculated by quantum chemistry methods, such as the calculation of optimized ground state and transition state structure (the potential energy), molecular properties vibrational wavenumbers, rotational constants, IR and Raman spectroscopy characterization of MO reactivity prediction, dipole moment, prediction of electronic excitation, UV spectrum, NMR spectrum, reaction rate, unpaired spin density, charge distribution and thermodynamic parameters $[G(T, p), E_0, S(T, p), H(T)]$. Through the thermodynamic functions, we calculate the most important macroscopic properties in experiments, such as heat of reaction ($\Delta_r H^\circ$), the heat of formation ($\Delta_f H^\circ$), heat capacity (C_v), Gibbs free energy ($\Delta_r G^\circ$), entropy (S) and acid dissociation constant (pK_a), whence from

macroscopic properties of molecules the reaction mechanism can be predicted, and by-products and side reactions can be assumed.

2. 3. 1 Quantum Chemical Methods

The *ab initio* method uses the first principles of quantum mechanics to directly calculate the electronic structure without using experimentally derived quantities. The quantum chemistry model is derived from the Schrödinger equation that first appeared in the late 1920s. Molecules are considered to be a collection of atomic nuclei and electrons, without any form of chemical bonds.

The solution of the Schrödinger equation depends on the movement of electrons, is directly related to the molecular structure and energy between other observables, and additionally contains key information of bonding. For any system other than one electronic system, the Schrödinger equation can not be solved, so an approximation is required to deal with multi-electronic systems.

Quantum chemical models differ from each other in the form and nature of these approximations and span a wide range in terms of consistency, capabilities, and computational cost. There are two different approaches to describe the electronic structure of the Schrodinger equation of atoms and molecules: **the wave function** and **density functional based methods**. The wave function-based method expands the electron wave function, which is the sum of Slater determinants, and optimizes the atomic orbitals and its coefficients through various numerical techniques. The simplest and most fundamental electronic structure calculation from *ab initio* is the **Hartree-Fock (HF)** method.

- **The Hartree-Fock method** was first proposed in 1950 [69][70], on the premise that the N-body wave function of the system can be approximated by a single Slater determinant of N spin orbits [71]. It provides an appropriate description of equilibrium geometry, possible conformations, and provides good results for a variety of thermochemical comparisons.

Since electronic correlation is completely neglected, its use is limited. The wave function-based approach combining electron correlation is the **second-order Moller-Plesset (MP)** perturbation theory [72]. Consider the perturbation sequence to include different numbers of items (ie, different orders) to apply. The second-order MP theory (MP2) is usually used for geometric optimization [73], while the fourth-order MP4 is used to refine the calculated energy. For example, the reason why the MP3 theory is used less frequently is that the effectiveness

MP series tends to oscillate, so using even-numbered orders can give more consistent results. MP techniques are very commonly used due to the consistency of size and the highest calculation efficiency [74].

The coupled-cluster (CC) perturbation theory and quadratic CI constitute another group of related techniques for considering electronic correlation [75]. These techniques represent the corrected wave function as the result of applying the so-called cluster operator to the HF wave function. The cluster operator may consist of a series of operators that consider the excitation of one, two, three, or n electrons, where n is the total number of electrons in the molecule. Therefore, the CC technology can be truncated like the MP method, but more accurate. However, they are also more computationally expensive. CC calculations [76] using single and double excitation (CCSD) [77] are common, but usually, an additional perturbation term is used to consider triple excitations to give CCSD(T). The CCSD(T) calculation (or the closely related QCISD(T) technique) represents the best possible effect currently achieved using the HF wave function as a starting point (reference wave function) [78]. Each method has different computational scaling, depending on the number of electrons in the system.

- **Density functional theory** is very similar to the Hartree-Fock theory in computational and concept, but it provides better results, and consequently become a very popular method. Invoking the Born-Oppenheimer (BO) approximation [79] makes the Schrodinger equation easier to solve because the motion of electrons and nuclei can be separated due to their different masses. Therefore, quantum mechanical methods (ab initio, DFT, and semi-empirical methods) [80][81][82][83][84] is based on solving the time-independent Schrödinger equation related to the change of electrons in molecular systems over time and the position of the nucleus. In the classical atomistic model, atoms are regarded as basic units, and classical potential energy functions (force fields (FFs)) represent the interactions between atoms. DFT is mainly about the theory of the electronic ground state structure, implicit in the electron density distribution $n(\rho)$. Since its inception, it has become more and more useful for calculating the ground state energy of molecules/solids/clusters, or any system composed of nuclei and electrons (with or without static disturbance applied). It is an alternative to conventional quantum chemistry methods, which is implicit in terms of multi-electron wave functions.

The incorporation of the two Kohn-Sham (K-S) equations in 1965 made DFT lie on a solid theoretical foundation [85]. The first K-S theorem demonstrates that there is a one-to-one mapping between the ground state characteristics of a multi-electron system and its electron

density. The second K-S theorem gives the concept of the energy function of the system and proves that the true ground-state electron density minimizes the energy functional. To solve the forces generated by electrons as they move around the nucleus, the K-S equation relies on a mathematical tool called an **exchange-correction functional**. Currently, many such functionals can be used to describe the electronic properties of matter. Presently, two main classes of functions have been widely deployed and tested in large-scale applications and small molecule benchmark tests: gradient-correction BLYP and hybrid B3LYP functions (Becke, 3-parameter, Lee-Yang-Parr) [86][87][88][89]. The gradient-correction functional starts with a local density approximation but adds terms related to the electron density gradient ($\nabla\rho$). The **hybrid functional** also includes gradient correction but adds an accurate Hartree-Fock exchange empirically built-in blending.

- **Composite methods** The highest level of *ab initio* techniques is not even suitable for medium-sized molecules (from a practical point of view). Two classes of approximations that overcome this difficulty are basis set extrapolation techniques and the design of composite methods (including some empiricism). The former of these two classes is more accurate. It is based on the CCSD(T) calculations, extrapolates to the limit of the full basis set using a very large correlation-consistent basis set, and adds corrections for some smaller effects, which are not included in the calculation; for example, as the core valence effect, relativistic effect and atomic spin-orbit effect. This approach is limited to smaller molecules given a very large basis set must be used. Later methods are widely used in the calculation of thermochemical data. They combined methods with high levels of theory and a small basis set with methods using lower levels of theory and larger basis sets. They are often used to calculate thermodynamic quantities, such as enthalpy of formation, atomization energy, ionization energy, and electron affinity. The goal of employing these methods is to achieve chemical accuracy, usually defined as a deviation of less than 1 kcal/mol from the experimentally accepted value. One of the most popular is the Gaussian-n (Gn) theory, which uses a set of calculations with different levels of accuracy and a basis set designed to approximate accurate energy. In the Gn approach, high-level correlation calculations (such as QCISD(T) and CCSD(T) with moderate-sized basis sets) are combined with energy from lower-level calculations with large base sets (such as MP4 and MP2), To approximate the energy of more expensive calculations. Besides, assuming that they are systematic, several empirical parameters independent of the molecule, such as an advanced correction (HLC) term, are also included to estimate the remaining defects. The different steps involved in G1 [90], G2 [91],

G3 [92], and G4 [93]. An intermediate approach has recently been introduced, called the correlation consistent composite approach (ccCA) with no parametrization [94][95]. Other composite techniques related to the Gn method include the complete basis set (CBS) methods [96][97][98] and the multi-coefficient method [99][100]. In this study, G3MP2B3 is used in most cases [101][102]. In the case of this method, the geometry and zero-point energy are obtained from the B3LYP/6-31G(d) density function at a scaled frequency of 0.96, rather than from the second-order perturbation theory [MP2//FU]6-31G(d) geometries are obtained, and the Hartree-Fock theory [HF/6-31G(d)] for zero-point energy.

2. 3. 2. Basis set

Two of the major methods (*ab initio* and DFT) require some understanding of basis sets and basis functions. The atom-centered functions used to describe the atomic orbitals are known as basis functions and collectively form a basis set. Larger basis sets give a better approximation to the atomic orbitals as they place fewer restrictions on the wave function which attract a higher computational cost. The STO-3G basis set is a minimal basis set where each atomic orbital is made up of 3 Gaussians. STO-nG also exists. Split-valence basis sets model each valence orbital by two or more basis functions that have different exponents they allow for size variations that occur in bonding. Examples include the double split-valence basis sets, 3-21G and 6-31G, and triple split-valence basis sets such as 6-311G. Polarisation functions have higher angular momentum, thus they allow for anisotropic variations that occur in bonding and help model the inter-electronic cusp. These include 6-31G(d) or 6-31G*, which included functions on the heavy atoms [103]. Diffuse basis functions are additional functions with small exponents, and are therefore large, thus they allow for accurate modeling of systems, Such examples include 6-31+G which has diffuse functions on the heavy atoms. Larger basis sets can be built up from these components, for example, 6-311++G(2df,2dp). Dunning basis sets also exist, for example, pVDZ and pVTZ. For larger atoms, Effective Core Potentials (ECPs) are often used. These replace the core electrons with an effective potential and have two main advantages: They reduce the number of electrons (cheaper), and they can be parameterized to take account of relativity. The valence electrons are still modeled using Gaussian type orbitals (GTOs) [104].

2. 3. 3 Solvation models

The use of implicit solvation models is nowadays one of the most adopted strategies to include the effect of the solvent into quantum-mechanical (QM) calculations. These implicit solvation models place the molecule of interest into a cavity, whose surface charge is stabilized in

accordance with the dielectric constant of the selected solvent, thus simulating the effect of the solute being exposed to the solvent. In this approach, the Solvation Model based on Density (SMD) allows accounting for the non-electrostatic contributions, not only regarding the energy but also the geometry optimizations and frequency calculations. is a model that makes use of a smooth continuous model to assign charges on the molecular surface of the solute. For SMD, the solute is polarizable by the charge density of the solvent and the interaction between the solute, and solvent can be determined via the charge density of the former and the electric polarization field of the latter. Moreover, SMD has proven to be an effective solvation model for use in both charged and uncharged systems and can predict accurate solvation energies for various functional groups, achieving an average mean absolute error of 4 kcal•mole⁻¹ in the solvation free energies of neutral species [105].

2. 4 Computational methods application

The theoretical research was studied using computational chemistry tools with different methods applied as implemented in the Gaussian09 program package[106]. In order to explore important reaction mechanisms, it is necessary to accurately characterize the structure of the reactants, transition states (TS), complexes, intermediates (IM), and products. All our systems were explored using the B3LYP functional in combination with the 6-31G(d) basis set. As a refinement of the B3LYP/6-31G(d) level of theory, more robust and accurate the G3MP2B3, the G4MP2, and the CBS-QB3 composite methods from the Gaussian thermochemistry family were also applied. **For example**, As part of the G3MP2B3 method, the B3LYP/6-31G(d) level of theory was used for geometry optimizations [107] by applying the “tight” convergence criterion. Normal mode analysis was performed on the optimized structures at the same level of theory to characterize their identities on the potential energy surface (PES). The transition state (TS) structures were confirmed to locate at first-order saddle points on the PES by visual inspection of the intramolecular motions corresponding to the imaginary wavenumber using GaussView 5 [108]. Intrinsic reaction coordinate (IRC) calculations [109] were also attempted to map out the minimal energy pathways (MEP). Further singlepoint quantum chemical calculations of the critical points of the PES were carried out using QCISD(T)/6-31G(d) (including MP2/6-31G(d) level of theory) and MP2/GTMP2 levels of theory based on B3LYP/6-31G(d) geometries according to the G3MP2B3 composite method. Harmonic wavenumbers obtained at the B3LYP/6-31G(d) level of theory were scaled by a factor of 0.96 [110]. G4MP2 calculations have also been carried out in order to obtain accurate thermodynamic properties, such as zero-point corrected relative energy ($\Delta E_{0,G4MP2}$), relative

enthalpy ($\Delta H_{0,G4MP2}$) and relative molar Gibbs free energy ($\Delta G_{0,G4MP2}$), entropy (S°). The heat of formation value in the gas phase at 1 atm of pressure (P) and $T = 298.15$ K ($\Delta H_{f,298.15K(g)}^\circ$) for the species involved in the studied reaction mechanisms. As part of the G4MP2 protocol, the B3LYP [111], functional was applied in combination with the 6-31G(2df,p) (noted as GTBas3 in Gaussian09 [106]) basis set for geometry optimizations using ‘tight’ convergence criteria and frequency calculations. In case of the presence of solvent, each step of the G4MP2 protocol including geometry optimization and single point calculations, the SMD polarizable continuum model was used to mimic the effect of the surrounding solvent of 1-propanol (PrOH, $\epsilon_r = 20.524$) as well as of tetrahydrofuran (THF, $\epsilon_r = 7.4257$). It is worthy to note that the static relative permittivity for phenyl isocyanate (PhNCO, $\epsilon_r = 8.940$ [112]) is close to that of THF, therefore potential energy surface (PES) obtained in PhNCO and THF can be expected to be similar.

3. Results and Discussion

3. 1 Urethane Formation at Isocyanate and Alcohol Excess

A kinetic and mechanistic investigation of the alcoholysis of phenyl isocyanate using 1-propanol as the alcohol was undertaken. A molecular mechanism of urethane formation in both excess alcohol and excess isocyanate (**Figure 33**). The experimental activation energies for the reactions of aryl isocyanates with alcohols are generally in the range of 17–54 kJ·mole⁻¹. [113][114] For a given reaction the activation energy depends on the solvent and the molar ratios of the reactants. Theoretical calculations were explored using a combination of accurate composite quantum chemical methods with SMD implicit solvent model. They showed that the rather high energy barrier (>100 kJ·mole⁻¹) [115][116][117] needed for reaching the bimolecular transition state (direct addition) becomes substantially lower if one or two alcohol molecules (alcohol catalysis), or a urethane molecule (autocatalysis) are also incorporated in the transition state [115][118][119]. These mechanisms were analyzed from an energetic point of view. The kinetics of this reaction was also experimentally investigated by means of the analytical HPLC technique. From the rate constants measured at different temperatures, Arrhenius activation energies of the stoichiometric, the alcohol excess, and the isocyanate excess reactions were determined in **section 3.1.1**.

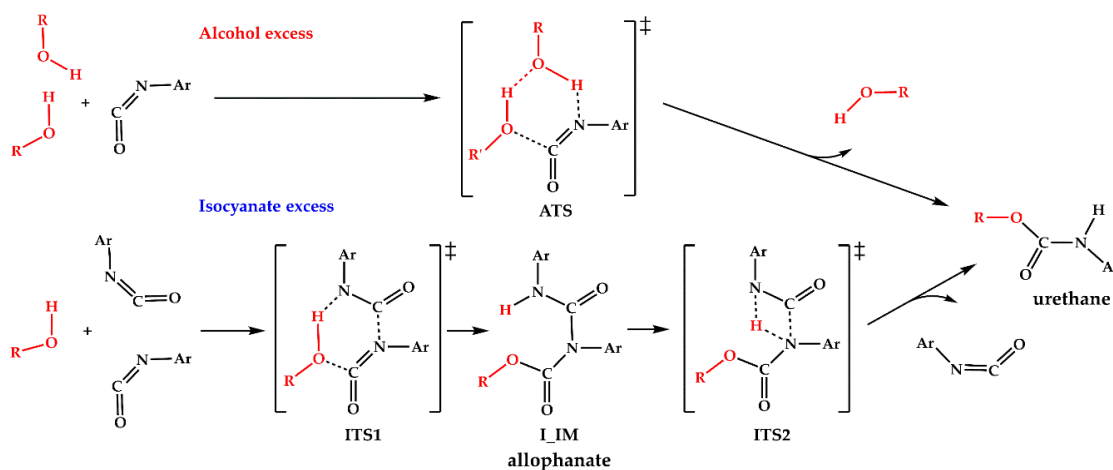


Figure 33: Elementary reaction mechanism for urethane bond formation. Alcohol excess mechanism (top) involves hydrogen-bonded alcohol associate as reactant while isocyanate excess mechanism (bottom) starts with dipole-dipole stabilized intermolecular isocyanate dimer. In the present study R = Propane and Ar = Phenyl.

3. 1. 1 Experimental results on kinetic of urethane bond formation

The rate constants (k_S for the stoichiometric reaction, $k_{I,obs}$ for the reaction running at 20-fold isocyanate excess) at different temperatures were determined by plotting the urethane

concentration versus time (**Figure 33**) and applying a non-linear fitting using the kinetic equation **Equation 12** for second-order and **Equation 13** for pseudo-first-order reactions. For the latter, because of the 20-fold isocyanate excess, the isocyanate concentration during the reaction was regarded to be constant ($[PhNCO]_0$). This way the actual rate constant k_I can be calculated from the observed rate constant k_{obs} (**Equation 14**).

$$[urethane] = [PrOH]_0 \times \left(1 - \frac{1}{1 + [PrOH]_0 \times k_S \times t}\right) \quad (12)$$

$$[urethane] = [PrOH]_0 \times (1 - e^{-k_{I,obs} \times t}) \quad (13)$$

$$k_{I,obs} = k_I \times [PhNCO]_0 \quad (14)$$

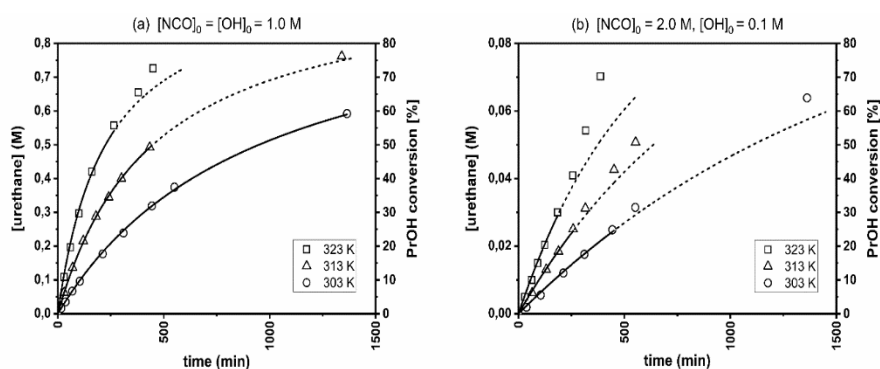


Figure 34: Experimental kinetic curves. (a) Second-order kinetics for the stoichiometric ratio (b) pseudo-first-order kinetics for the 20-fold PhNCO excess. Data points used for fitting and reaction rate constants determination are indicated by solid curve segments.

It is apparent from (**Figure 34**) that the first few data points fit well for the second-order equation **Equation 12** for (**Figure 34(a)**) and the pseudo-first-order equation **Equation 13** for (**Figure 34(b)**), but at later reaction stages a positive deviation occurs which possibly accounts from urethane autocatalysis. In the case of the stoichiometric NCO/OH ratio, the addition reaction can be described by second-order kinetics up to 50–60% conversion. When the isocyanate is in 20-fold excess, the reaction follows pseudo-first-order kinetics only up to a conversion of 25–30%. Therefore, only the initial domain of the data (see **Figure 34**) were used for non-linear fittings and reaction rate constant calculations.

(**Table 3**) summarizes the kinetic parameters of the reactions. For the reaction in excess alcohol, the rate constants (k_A) and the activation energy were measured in the previous work of our group [114]. Both at reaction in excess alcohol and reaction in excess isocyanate, the Arrhenius activation energies are lower than that of the stoichiometric reaction. From this, it is assumed that not only alcohol but also isocyanate molecules can also exert a catalytic effect and facilitate the reaction. At or near stoichiometric ratios both self-catalytic pathways can occur.

Table 3: Experimental reaction rate constants (k_A , k_S , and k_I) at different temperatures, Arrhenius activation energies (E_a), and pre-exponential factors (A). E_a and A values were obtained by the method of least squares. For $[\text{NCO}]_0 / [\text{OH}]_0 = 0.005$, data are taken from [11]. (*n.m.* = *not measured*)

Temperature, °C	Excess Alcohol	Stoichiometric ratio	Excess Isocyanate
	$[\text{NCO}]_0 / [\text{OH}]_0 = 0.005$	$[\text{NCO}]_0 / [\text{OH}]_0 = 1$	$[\text{NCO}]_0 / [\text{OH}]_0 = 20$
	$k_A \times 10^5, \text{M}^{-1} \text{s}^{-1}$	$k_S \times 10^5, \text{M}^{-1} \text{s}^{-1}$	$k_I \times 10^5, \text{M}^{-1} \text{s}^{-1}$
30	<i>n.m.</i>	1.76 ± 0.18	0.52 ± 0.04
40	0.16 ± 0.01	3.72 ± 0.32	0.91 ± 0.07
50	0.23 ± 0.01	7.41 ± 0.60	1.55 ± 0.11
60	0.33 ± 0.02	<i>n.m.</i>	<i>n.m.</i>
$E_a, \text{kJ mol}^{-1}$	30.4 ± 1.6	58.6 ± 6.0	44.2 ± 4.5
$A, \text{M}^{-1} \text{s}^{-1}$	18.8 ± 1.0	234113 ± 23971	214.9 ± 21.9

The rate constants in **Table 3** are the apparent rate constants, as the values depend on reaction conditions, such as the applied solvent and the concentrations of the reactants.

3. 1. 2 Mechanism based on theoretical calculation

Hydrogen bond stabilized alcohol associates are confirmed [120] and their role in reducing the activation barrier in urethane formation has already been accepted [115]. Therefore, in this dissertation I will focus only on the results of G4MP2 model of calculation, because in comparing with B3LYP/6-31G(d) level of theory, more robust and accurate the G3MP2B3, the G4MP2, and the CBS-QB3, the fourth generation G4MP2 quantum chemical protocol had been demonstrated that it can provide overall thermodynamic results at chemical more accuracy. Furthermore, the thermodynamic values of the stationary points of the reactive potential energy surface are summarized in (**Table 4**) and relative zero-point corrected energies in propanol (PrOH) and tetrahydrofuran (THF) are also displayed in (**Figure 35**).

Table 4: G4MP2 thermochemical properties calculated in 1-propanol (PrOH) and tetrahydrofuran (THF) including zero-point corrected relative energies (ΔE_0), relative enthalpies ($\Delta H(T)$) and relative Gibbs free energies ($\Delta G(T,P)$) at $T = 298.15$ K, and $P = 1$ atm, **A** in excess alcohol, and **I** in excess isocyanate. All values are in $\text{kJ}\cdot\text{mole}^{-1}$.

Pathway	Species	ΔE_0		$\Delta H(T)$		$\Delta G(T,P)$	
		PrOH	THF	PrOH	THF	PrOH	THF
	PhNCO + 2 PrOH	0	0	0	0	0	0
Excess alcohol (A)	A_RC	-17.0	-30.8	-14.0	-27.2	25.1	50.5
	ATS	35.4	20.7	32.7	17.0	91.4	119.2
	A_PC	-99.7	-109.3	-100.9	-109.8	-47.4	-17.2
	2 PhNCO + PrOH	0	0	0	0	0	0
Excess isocyanate (I)	I_RC	-34.6	-12.7	-33.0	-11.1	-12.7	36.9
	ITS1	51.1	62.6	44.0	55.7	62.6	141.3
	I_IM	-152.3	-139.3	-160.1	-147.2	-139.3	-59.0
	ITS2	39.4	49.0	31.5	41.2	49.0	129.4
	I_PC	-105.6	-103.1	-109.2	-106.4	-103.1	-38.4

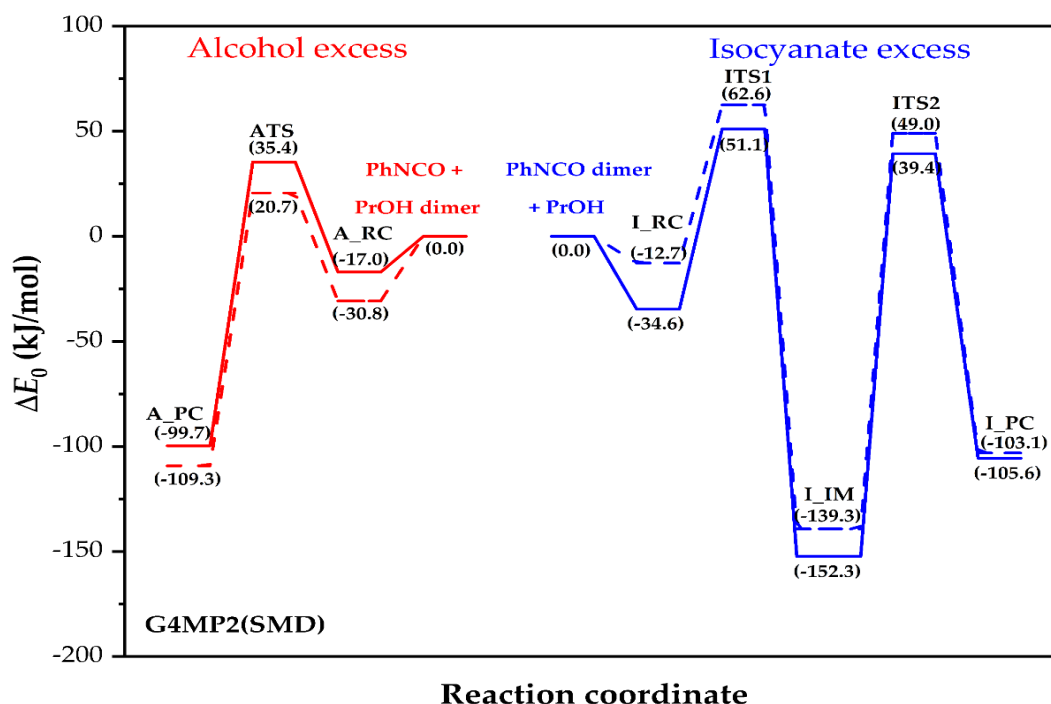


Figure 35: G4MP2 energy profile (zero-point corrected) for the alcoholic route in solvent 1-PrOH (red solid line), in THF (red dashed line), and for the isocyanate route in 1-PrOH (blue solid line), in THF (blue dashed line).

In line with the theoretical and experimental work of Raspoet et al. [115], a reactive complex of the reaction in excess alcohol (A_RC) had been characterized and its structure is shown in **Figure 36**. This structure is stabilized by three strong hydrogen bonds between the molecular moieties, and the energy gain during the complex formation is $16.9 \text{ kJ}\cdot\text{mole}^{-1}$ in propanol (PrOH) medium (values obtained in propanol solvent will be discussed further). In this concerted mechanism, the transition state structure (ATS in **Figure 36**) is a six-membered ring structure. In the ATS, the positively charged hydrogen of PrOH shifts to the electron-rich nitrogen of phenyl isocyanate (PhNCO), while the NCO group is bent, thereby activating the carbon for the formation of a new C-O bond with the other PrOH, and finally the hydrogen of this alcohol oxygen is transferred to the other alcohol in the same time. Due to the complex interaction network the transition state energy is only $35.4 \text{ kJ}\cdot\text{mole}^{-1}$ above the reactant energy level, which is consistent with the theoretical value of $27.0 \text{ kJ}\cdot\text{mole}^{-1}$ (obtained at MP2/6-311++G(d,p)//MP2/6-31G(d,p) level of theory) reported by Raspoet et al. [115] for methanol and hydrogen isocyanate. As a result of the IRC calculation, the product complex (A_PC) had been also identified and the relevant structural parameters are displayed in **Figure 36**. As shown, the formed urethane bond is strongly hydrogen-bonded to the oxygen of the remaining PrOH. This exothermic reaction releases $99.7 \text{ kJ}\cdot\text{mole}^{-1}$ energy to form A_PC. Interestingly, the relative energy of these stationary points becomes significantly lower by the changing the

solvent from PrOH to THF. Obviously, the catalytic effect of the second alcohol can only be manifested when enough PrOH dimer is accessible to the reagents for the urethane formation reaction to take place.

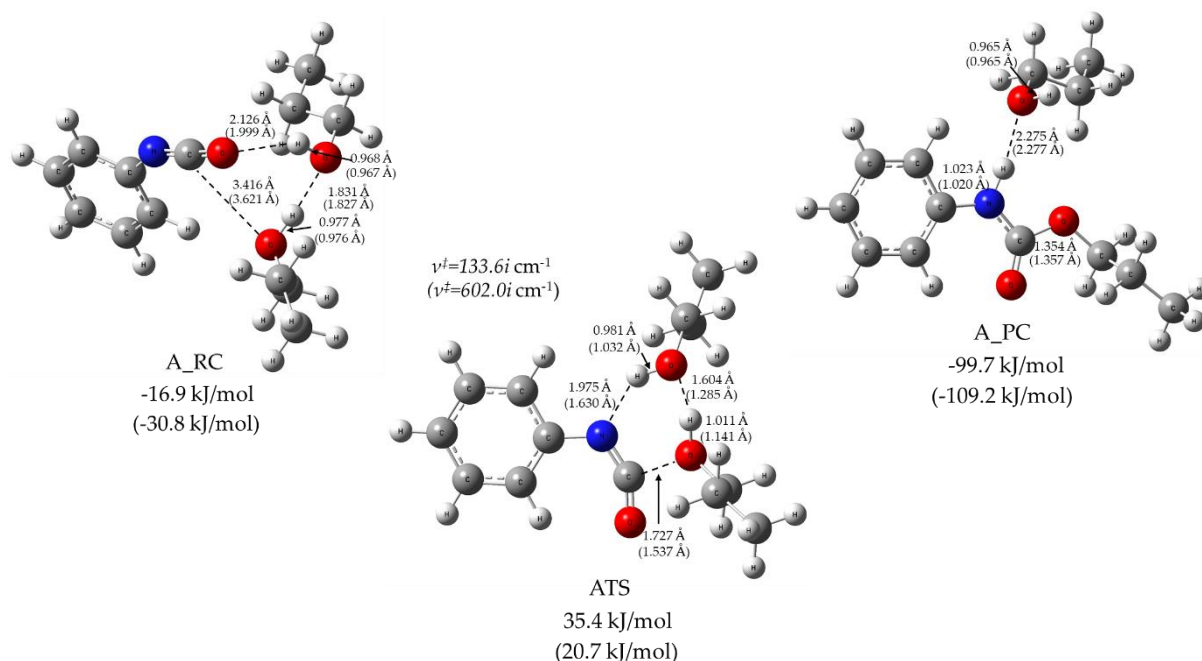


Figure 36: Reactive complex (RC), transition state structure (TS) and product complex (PC) structures (obtained at B3LYP/6-31G(2df,p) level of theory from G4MP2 calculation) for the excess alcohol reaction mechanism of urethane bond formation in solvent 1-PrOH or THF (in parenthesis). The relative zero-point corrected energies are also presented in $\text{kJ}\cdot\text{mole}^{-1}$.

Despite the extensive use of PhNCO as a proxy in mechanistic studies for urethane formation, the physicochemical properties of liquid PhNCO are scarce in the literature. For example, only a schematic representation of the intermolecular interactions between PhNCO molecules can be found in the work of Baev [121] with an enthalpy of vaporization value ($\Delta H^{\circ}_{\text{vap}} = 46.5 \pm 0.3 \text{ kJ}\cdot\text{mole}^{-1}$), while viscosity and liquid structure of PhNCO to the best of our knowledge, were never reported. This $\Delta H^{\circ}_{\text{vap}}$ value is similar to that of 1-propanol ($\Delta H^{\circ}_{\text{vap}} = 47.5 \text{ kJ}\cdot\text{mole}^{-1}$) [122]. On the other hand, the viscosity of PhNCO is $0.96 \text{ mm}^2\cdot\text{s}^{-1}$ (298 K) according to our measurement, which is about 2.76 times smaller than that of 1-PrOH ($2.65 \text{ mm}^2\cdot\text{s}^{-1}$ at 298 K). Due to the recent development of an accurate GAFF-based force field [123] for isocyanate compounds, the structural elucidation of PhNCO liquid is can be expected. Until then, as supported by the above mentioned $\Delta H^{\circ}_{\text{vap}}$ [121] and interaction energy value [124] for PhNCO similar to that of propanol, one might hypothesize that the PhNCO dimers are stable enough to act as a reactant for the urethane formation under the condition of excess isocyanate.

The reaction potential energy profile of two phenyl isocyanate molecules with PrOH is shown in **Figure 35**. The reactive complex (I_RC) is stabilized by a hydrogen bond between the nitrogen of one of the PhNCO and the hydroxyl of the PrOH molecule, as shown in **Figure 37**. In addition, the lone electron pairs of the hydroxyl point towards the positively charged carbon atom of the NCO group in the second PhNCO with a distance of 2.992 Å. These interactions can significantly reduce the relative energy of the reactive complex ($-34.6 \text{ kJ}\cdot\text{mole}^{-1}$) compared to that of the reactants. The six-membered transition state structure (ITS1) resulted in the formation of allophanate (I_IM), and has two synchronized bond-forming components that are combined with hydrogen abstraction, as shown in **Figure 37**. Here, both isocyanate groups are bent, and a new C-N bond being formed between the isocyanate groups is long (2.320 Å), while the critical distance between the alcohol oxygen and the isocyanato carbon is extremely small (1.519 Å). In the hydrogen abstraction component of the reaction coordinate, the moving hydrogen is attacked by the nitrogen of the isocyanato group from a relatively large distance ($r_{\text{H-N}} = 1.474 \text{ Å}$) and the O-H bond length is slightly elongated ($r_{\text{O-H}} = 1.067 \text{ Å}$). This motion also leads to the formation of a new C=O bond with a distance of 1.337 Å. ITS1 is $51.1 \text{ kJ}\cdot\text{mole}^{-1}$ higher in energy compared to the energy level of the reactants (PhNCO dimer and PrOH) and it is $15.7 \text{ kJ}\cdot\text{mole}^{-1}$ higher than the relative energy of ATS in the case of the excess alcohol mechanism.

As the IRC calculation starting from ITS1 confirmed, I_RC and I_IM are connected through ITS1. The formed allophanate (I_IM, propyl N,N'-diphenylallophanate) is a thermodynamically stable intermediate with the corresponding relative zero-point energy of $-152.3 \text{ kJ}\cdot\text{mole}^{-1}$. In its planar central structure, a strong intramolecular hydrogen bond can be found with a short H-O bond distance ($r_{\text{NH-O}} = 1.834 \text{ Å}$). According to the B3LYP/6-31G(2df,p) results, the N-H bond stretching mode and its rocking mode can be seen as intensive IR peaks at 3547.7 cm^{-1} and 1574.2 cm^{-1} , respectively. Furthermore, four additional high intensity IR wavenumbers can be assigned to the allophanate functional group. Symmetric and asymmetric C=O stretch modes are at 1761.2 cm^{-1} and 1713.7 cm^{-1} , respectively. The remaining two complex vibrational motions of the allophanate are at 1367.1 cm^{-1} and 1213.1 cm^{-1} . This IR spectral data may be used to monitor the components that take part in the reaction [125], although the assignment of these peaks can be difficult due to the multicomponent reaction mixtures as well as overlap amongst the IR peaks corresponding to similar functional groups (e.g. allophanate, biuret and urethane). Proper peak assignment for allophanates is still under debate [126].

Nevertheless, allophanate intermediates can further react through transition state ITS2 and lead to the urethane–phenyl isocyanate complex I_PC. As can be seen in **Figure 37**, ITS2 is a tight, four-membered transition state corresponding to a hydrogen shift from one of the allophanate nitrogen to the other. Comparing the relative energy of ITS1 and ITS2, ITS1 is found to be a bottleneck of these reaction channels since all thermodynamic parameters are higher for ITS1 than for ITS2 by at least 11.8 kJ·mole⁻¹ as shown in **Table 4**. In contrast to the mechanism in excess propanol, a change in solvent (from PrOH to THF) increased the relative energy, enthalpy, and Gibbs free energy values in the mechanism in excess isocyanate as also seen in

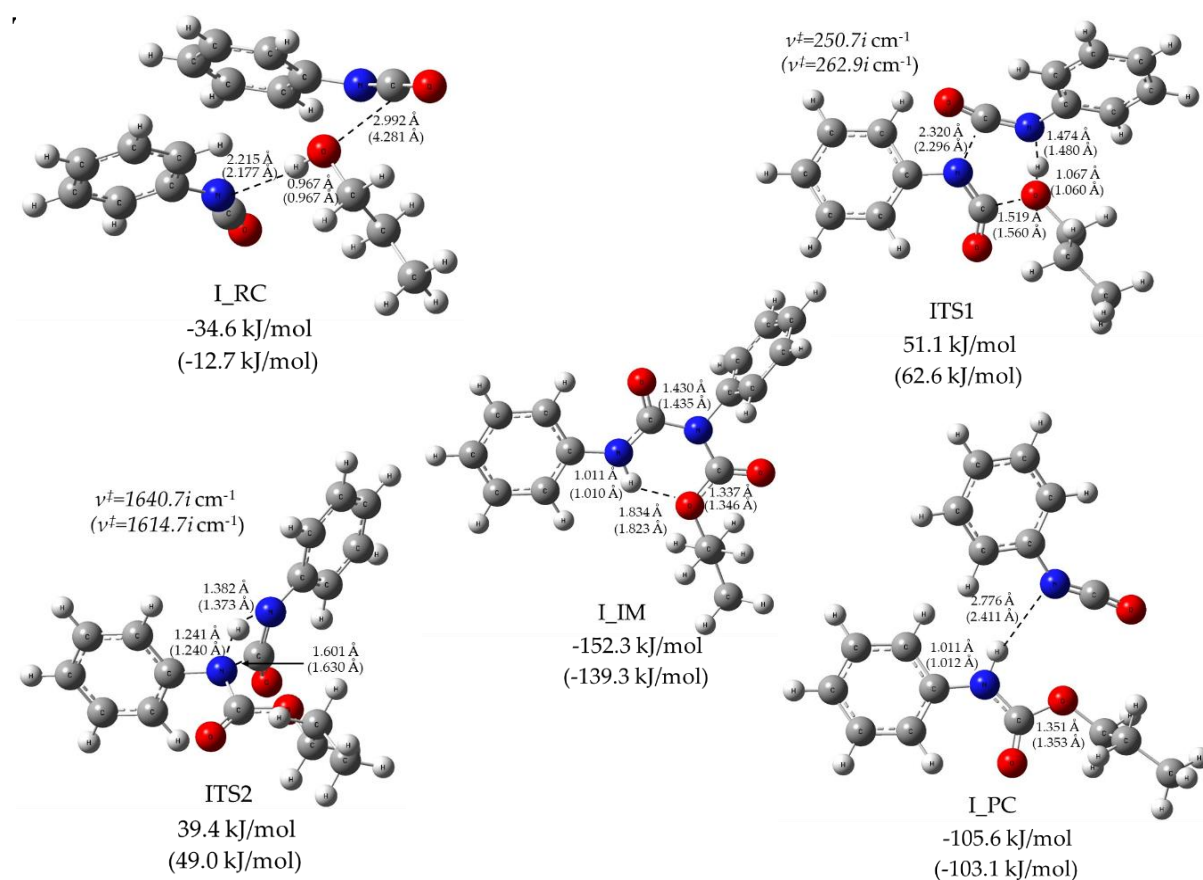


Figure 37: Reactive complex (RC), transition state structure (TS), intermediate (IM) and product complex (PC) structures (obtained at B3LYP/6 31G(2df,p) level of theory from G4MP2 calculation) for the isocyanate excess reaction mechanism of urethane bond formation in solvent 1-PrOH or THF (in parenthesis). The relative zero-point corrected prenergies are also presented in kJ·mole⁻¹.

dimer (uretdione) which then react with alcohol to give allophanate. Allophanate can then decompose to urethane and isocyanate. In contrast to this, our proposed mechanism only assumes the formation of the non-covalent dimer, which can react with alcohol through a low-lying, six-membered transition state to form an allophanate intermediate. This transition state is structurally similar to the proposed one at alcohol excess condition.

Composite method test

We used the B3LYP function combined with the 6-31G(d) basic set to explore all systems. In order to improve on the theoretical level of B3LYP/6-31G(d), more powerful composite methods such as G3MP2B3, G4MP2, and CBS-QB3 have been studied, with the purpose of comparing them and choose the more accurate method with precise thermodynamic properties, and good performance, with respect to the experimental result. (**Table 5**) shows the comparison of different barrier energies of different methods and experimental results.

Table 5: Relative enthalpies of all the transition state of the reaction at excess alcohol and excess isocyanate, obtained with different methods of calculation ($\Delta H(T)$) at $T = 298.15$ K, and $P = 1$ atm, calculated in 1-propanol (PrOH) comparing to the experimental Arrhenius activation energies (E_a), ATS according to alcohol excess, and ITS1 to isocyanate excess. All values are in $\text{kJ}\cdot\text{mole}^{-1}$.

Species	$\Delta H(T)$ (PrOH)				E_a
	G4MP2	G3MP2B3	CBS-QB3	B3LYP	Exp.
ATS	32.7	33.0	19.6	32.9	30.4
ITS1	44.0	40.6	91.3	63.5	44.2

From (**Table 5**) we deduce that the G4MP2 has an excellent agreement with the experimental results, and can be considered the best composite method. Proposing this new catalytic mechanism of urethane formation in both alcohol and isocyanate excess based on solvent, we notice that the polymerization changes significantly, and the energy profile of alcohol excess reaction has a lower barrier energy and a faster reaction comparing to isocyanate excess. Based on theoretical and experimental results, our study reveals a new possible mechanism for urethane formation, wherein two isocyanate molecules facilitate the formation of the product. Besides this new, isocyanate-catalyzed trimolecular mechanism, the applied G4MP2 composite quantum chemical method (with SMD implicit solvent model) also supports the already known hypothesis for alcohol self-catalysis. While the alcohol-catalyzed route turned out to be a one-step process, the isocyanate-catalyzed path includes two reaction steps, including the formation of an allophanate intermediate. The key step of the new mechanism is the 1,3-H shift between the nitrogen atoms of the allophanate. The potential energy surface (PES) highly depends on the applied solvent. This is in agreement with the well-known solvent dependence of the kinetics of urethane formation. The experimental finding, i.e. lower activation energies for

either the alcohol or the isocyanate-excess reactions compared to the stoichiometric reaction also suggests that both self-catalytical pathways are feasible.

3. 2 Polyurethane bond formation

The previous study concluded that the structure of the polyol (alcohol) component has a significant impact on the formation process. In this study, we used a relatively small amount of alcohol to determine whether an excessive amount of alcohol would cause some polyurethane bond formation during the polymerization process. The amount of these alcohols used for chain modification is used as the amount of catalyst, and to see if they have a catalytic effect or have an influence on other properties.

The properties of polyurethane foams are strongly influenced by the chain length, molecular weight, functionality, and hydroxyl value [128][129]. This study aims to use mono-alcohols as active additives in polyurethane foam synthesis to obtain products with high quality in terms of resistance. The use of mono-alcohols has been highlighted in several patents, and these works aim to prepare polyurethanes or polyisocyanurate–polyurethane polymers having e.g. low density, good heat adhesive properties to fibrous materials, or low viscosity with good flow characteristics. [130 and references to other patents therein]. The density range of flexible polyurethane foam based on polyether or polyester polyol is (10 – 800 kg·m⁻³). In this new study, various mono-alcohols are used to decrease the molecular weight of the polyurethane. They were added to the starting components at different concentrations in order to prepare polyurethanes with modified characteristics, the other factors in the foam formulation such as water content, catalysts, and isocyanate index were kept constant. Where the quantity of isocyanate in each formulation was based on the total hydroxyl content of Caradol® MC28-02, and mono-alcohols. The foam formulation for modified flexible polyurethane foam is shown in **Table 6**.

The addition of a small amount of the mono-alcohols on Caradol MC28-02 has a small influence on the OH number of the mixture. With 7% for the largest molecular weight, which is the 1-octanol. Well, the Hydroxyl Number of Mixture (OH_m) is given by the flowing **Equation 15** [131].

$$OH_m = OH_j * a + OH_k * (1 - a) \quad (15)$$

Hydroxyl numbers of compounds (OH_j, OH_k) and fractional weights part of each component (*a*) and (1 - *a*), where (j: Caradol® MC28-02 and k: mono-alcohol).



Figure 39: Flexible polyurethane foams, all with the concentration of mono-alcohols at the range of 0.2, 0.5, 1.0, and 2.0%.

3. 2. 1 Effect of mono-alcohols on polyurethane bond formation

a. Foam height

Figure 40 demonstrates the effect of mono-alcohol content on the height of PU foams. Increasing the chain length of mono-alcohols leads to an increase in the height of the foam, furthermore, the height of the foams is increasing as the concentration of mono-alcohols increases, which provides an additional degree of freedom to control foam volume, which can otherwise be affected by lower boiling point and volatility of these mono-alcohols. Based on the inspection, mono-alcohols appear to be more effective in forming foam, where the height is much higher than what is projected by the reference model.

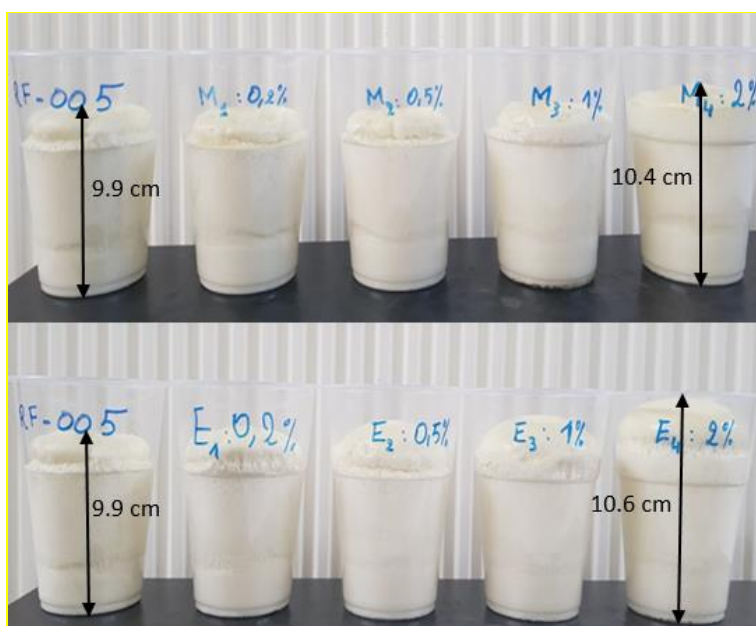


Figure 40: Height of flexible polyurethane foams with methanol and ethanol at concentrations of 0.2, 0.5, 1.0, 2.0%.

b. Foam density

The results demonstrate that with increasing concentration of mono-alcohol, the density of the foam depends on the number of carbon atoms in the alcohol (chain length) (**Figures 41** and **Figure 42**).

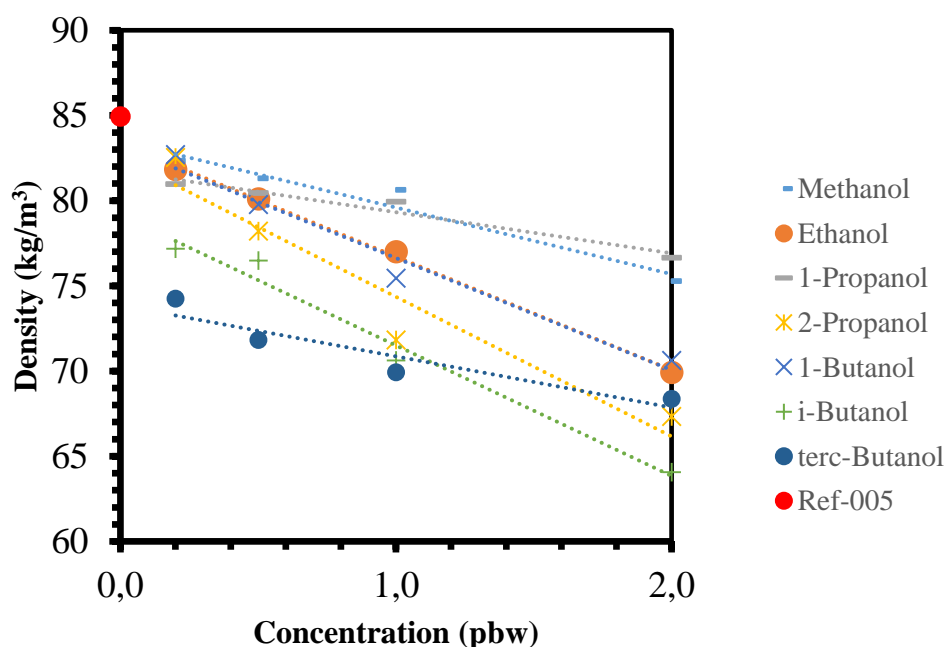


Figure 41: Densities of polyurethane foams as a function of mono-alcohol concentration.

Figure 41 describes the densities of polyurethane foams as a function of mono-alcohol

concentration, where the chain length from C1 to C4, independently of the chain type (straight or branched), the density of the foam decreases with the increasing concentration of the alcohol. In all cases, the density is lower than that of the reference foam ($84.9 \text{ kg}\cdot\text{m}^{-3}$). Among the tested alcohols, when methanol, ethanol, 1-propanol, 2-propanol, or 1-butanol were used in 0.2 pbw, the densities are similar ($81\text{--}82 \text{ kg}\cdot\text{m}^{-3}$). Besides the increased alcohol concentration, the density values start to decrease. At 2.0 pbw, the densities are lower by 82–90 % compared to the reference foam.

In the case of 0.2 pbw isobutanol, tert-butanol (**Figures 41**), 1-hexanol, cyclohexanol, or 1-octanol (**Figures 42**) the densities are in the range of $74\text{--}77 \text{ kg}\cdot\text{m}^{-3}$. Isobutanol and tert-butanol behave like the other butanol isomers, namely increasing their concentration results in decreased density, which, at 2.0 pbw corresponds to 75–80 % of the reference foam's density. Using 1-hexanol, cyclohexanol, or 1-octanol, an opposite trend can be seen: with increasing concentration the densities are also increasing, however, at 2.0 pbw the foams still have a lower density than that of the reference.

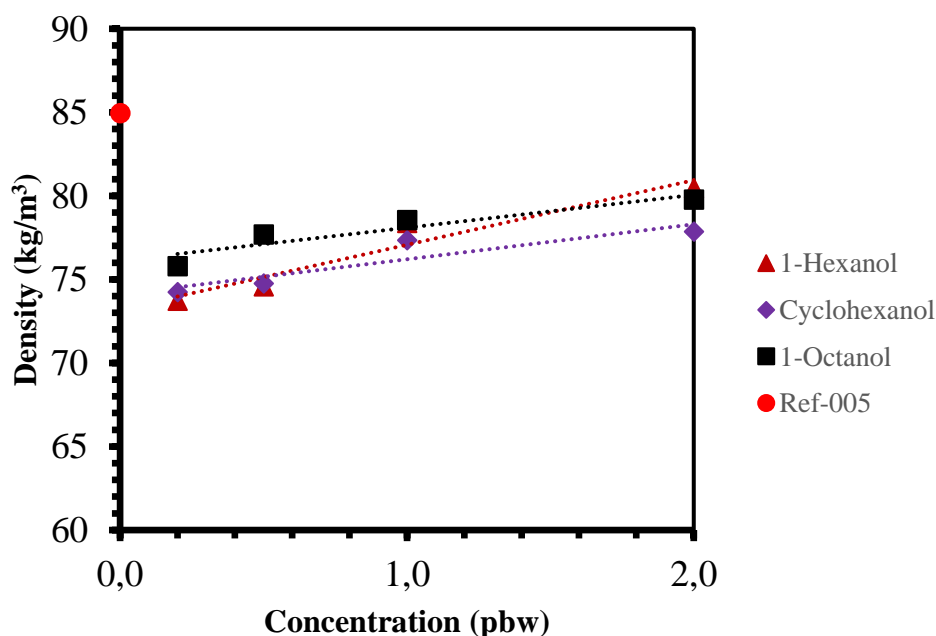


Figure 42: Densities of polyurethane foams as a function of mono-alcohol concentration.

c. Mechanical properties

Table 7 presents the compressive strength and Young's modulus of the prepared polyurethane foams with different mono-alcohols at different concentrations.

Table 7: Density and mechanical properties of polyurethane flexible foams.

mono-alcohol	mono-alcohol concentration	density	Compressive strength	Young's modulus
	pbw	kg·m ⁻³	MPa	GPa
none (Reference)	–	84.9	0.05	7.74×10^{-5}
Methanol	0.2	82.4	0.09	3.01×10^{-5}
Methanol	0.5	81.3	0.05	5.66×10^{-5}
Methanol	1.0	80.6	0.04	7.81×10^{-5}
Methanol	2.0	75.3	0.06	9.61×10^{-5}
Ethanol	0.2	81.8	0.03	4.16×10^{-5}
Ethanol	0.5	80.1	0.03	4.58×10^{-5}
Ethanol	1.0	77.0	0.10	3.25×10^{-5}
Ethanol	2.0	69.9	0.04	4.44×10^{-5}
1-Propanol	0.2	81.0	0.04	4.44×10^{-5}
1-Propanol	0.5	80.5	0.04	5.12×10^{-5}
1-Propanol	1.0	79.9	0.05	4.75×10^{-5}
1-Propanol	2.0	76.7	0.06	3.41×10^{-5}
2-propanol	0.2	82.5	0.02	4.07×10^{-5}
2-propanol	0.5	78.2	0.01	2.97×10^{-5}
2-propanol	1.0	71.8	0.04	3.86×10^{-5}
2-propanol	2.0	67.3	0.05	5.74×10^{-5}
1-butanol	0.2	82.7	0.04	4.76×10^{-5}
1-butanol	0.5	79.8	0.03	2.39×10^{-5}
1-butanol	1.0	75.4	0.02	3.83×10^{-5}
1-butanol	2.0	70.6	0.07	3.42×10^{-5}
isobutanol	0.2	77.2	0.11	7.87×10^{-5}
isobutanol	0.5	76.5	0.08	8.63×10^{-5}
isobutanol	1.0	70.6	0.05	8.18×10^{-5}
isobutanol	2.0	64.1	0.03	3.71×10^{-5}
<i>tert</i> -butanol	0.2	74.2	0.04	4.29×10^{-5}
<i>tert</i> -butanol	0.5	71.8	0.02	4.60×10^{-5}
<i>tert</i> -butanol	1.0	69.9	0.04	6.73×10^{-5}
<i>tert</i> -butanol	2.0	68.4	0.07	8.99×10^{-5}
1-hexanol	0.2	73.7	0.13	6.23×10^{-5}
1-hexanol	0.5	74.6	0.04	6.02×10^{-5}
1-hexanol	1.0	78.4	0.01	4.65×10^{-5}
1-hexanol	2.0	80.5	0.03	5.39×10^{-5}
Cyclohexanol	0.2	74.2	0.04	4.69×10^{-5}
Cyclohexanol	0.5	74.8	0.04	6.25×10^{-5}
Cyclohexanol	1.0	77.3	0.04	5.67×10^{-5}
Cyclohexanol	2.0	77.9	0.06	5.08×10^{-5}
1-octanol	0.2	75.8	0.06	5.48×10^{-5}
1-octanol	0.5	77.7	0.05	5.92×10^{-5}
1-octanol	1.0	78.6	0.06	6.59×10^{-5}
1-octanol	2.0	79.8	0.05	4.57×10^{-5}

From **(Table 7)**, a relation between density and Young's modulus can be distinguished, presented according to the Ashby plot that is a scatter plot, which displays two or more properties of many materials or classes of materials [132]. These plots are useful to compare the ratio between different properties. An example of the stiff/light part discussed above would have Young's modulus on one axis and density on the other axis, with one data point on the graph for each candidate material. On such a plot, it is easy to find not only the material with the highest stiffness, or that with the lowest density, but that with the best ratio E/ρ . Using a log scale on both axes facilitates the selection of the material with the best plate stiffness.

The benefit of this study allows us to define our target on producing optimal flexible polyurethane foams, where the cost is not the only important factor in material selection, the key design objective was the stiffness of a plate of the material, where we are looking for an optimal combination of density, Young's modulus that provides us to study the relation between these two parameters in our diagram. **Figure 43** presents a plot of Young's modulus vs density of the results with log-log scaling.

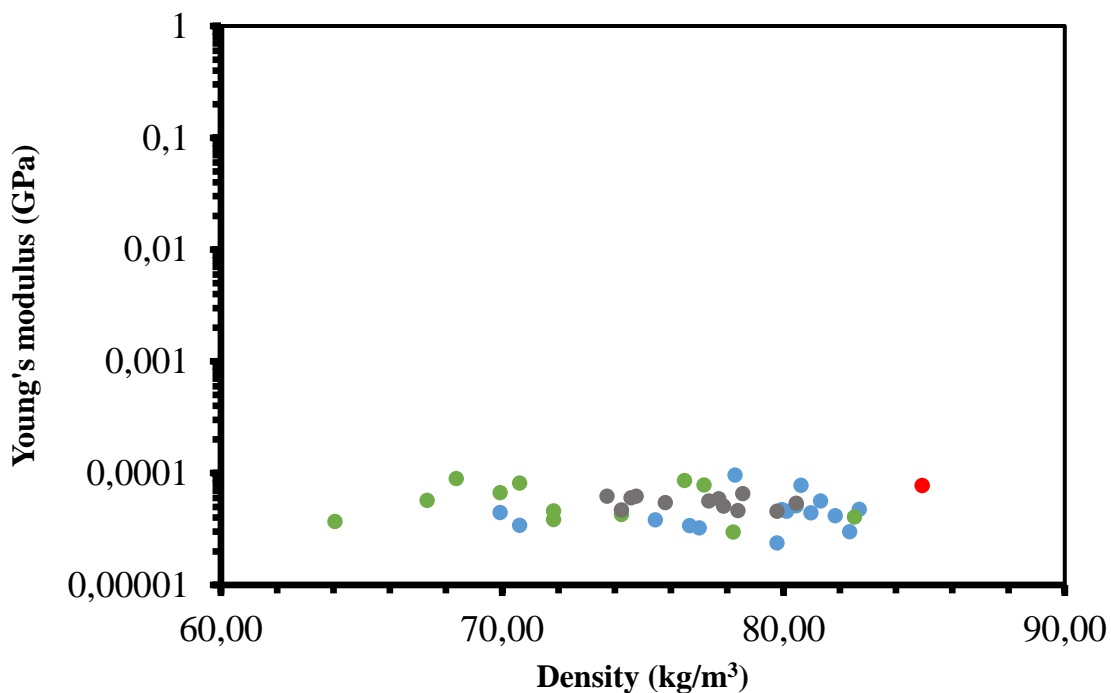


Figure 43: The Plot of Young's modulus vs density.

From the results of the diagram presented in **(Figure 43)**, we illustrate a new range for Young's modulus values between (0.0001–0.00002 GPa). This range is completely new compared to the recent research in the case of flexible foams **(see Figure 44)**. Where the range of density is almost the same as other recently published results. The gray points represent the long-chain

length, $\geq C6$, they are centered between blue and green in the density range between 73–80 $\text{kg}\cdot\text{m}^{-3}$. Moreover, the green points are mainly represented on the right with a density range between 64–82 $\text{kg}\cdot\text{m}^{-3}$. These correspond to the branched-chain with chain length $\leq C4$, as for the blue points are the majority represented on the left, correspond to the straight chain with chain length $\leq C4$, the density range along between 70–85 $\text{kg}\cdot\text{m}^{-3}$.

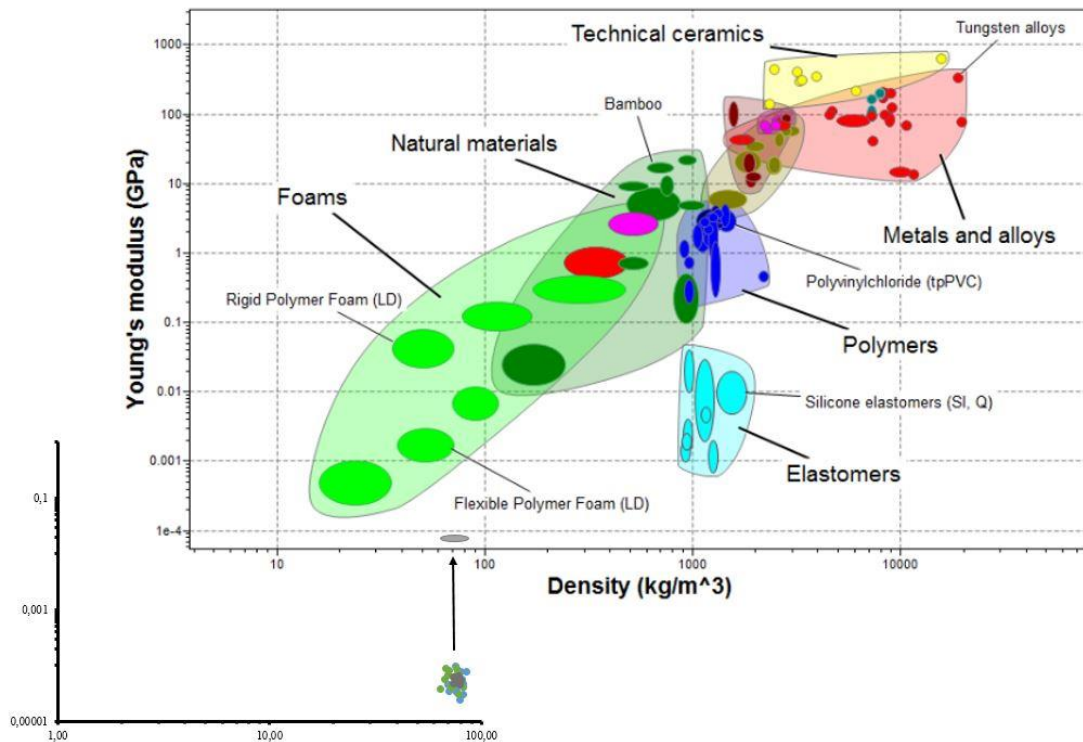


Figure 44: A chart of Young's modulus and density for materials created using the CES EduPack 2007 software with the Level 2 database.

The results showed that the addition of different mono-alcohols as a second polyol in the polyurethane composition influences selected properties of the obtained material. PU foams were made with a high concentration of mono-alcohols from C1 to C4 with a straight-chain and branched-chain; they decrease the density of foams, whereas the mono-alcohols that have a high chain length of more than six carbons increased the density of foams. The mechanical properties of these PU foams indicated that they change with the density of PU foams. By increasing the concentration of mono-alcohols, the results coming from the compressive test shows us a low deformation of the flexible PU foams, due to the high flexibility of the material. The use of mono-alcohols could represent a good alternative for a variety of industrial applications in the production of polyurethane.

4. Thesis point

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

Experimental and mechanistic study of urethane bond formation

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 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 the 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.

Experimental study of mono-alcohol

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.

5. Summary

Polyurethane products are inseparable from our daily life. They are virtually everywhere and are readily available. Polyurethane synthesis and the synthesis of raw materials are diverse. Different types of synthetic materials will produce polyurethane products with different properties. According to these characteristics, they play different roles in the field. Polyurethane is polymer organic materials 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 formation at the molecular level. The urethane production consists of a simple reaction between an isocyanate and alcohol, it is 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 in excess isocyanate were analyzed from an energetic point of view. 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 $62.6 \text{ kJ}\cdot\text{mol}^{-1}$ in the THF solvent model. In the next step, a synchronous 1,3-H shift between the nitrogens 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 $49.0 \text{ kJ}\cdot\text{mol}^{-1}$ 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 ($30.4 \pm 1.6 \text{ kJ}\cdot\text{mol}^{-1}$, $44.2 \pm 4.5 \text{ kJ}\cdot\text{mol}^{-1}$, $58.6 \pm 6.0 \text{ kJ}\cdot\text{mol}^{-1}$ 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 45**).

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.

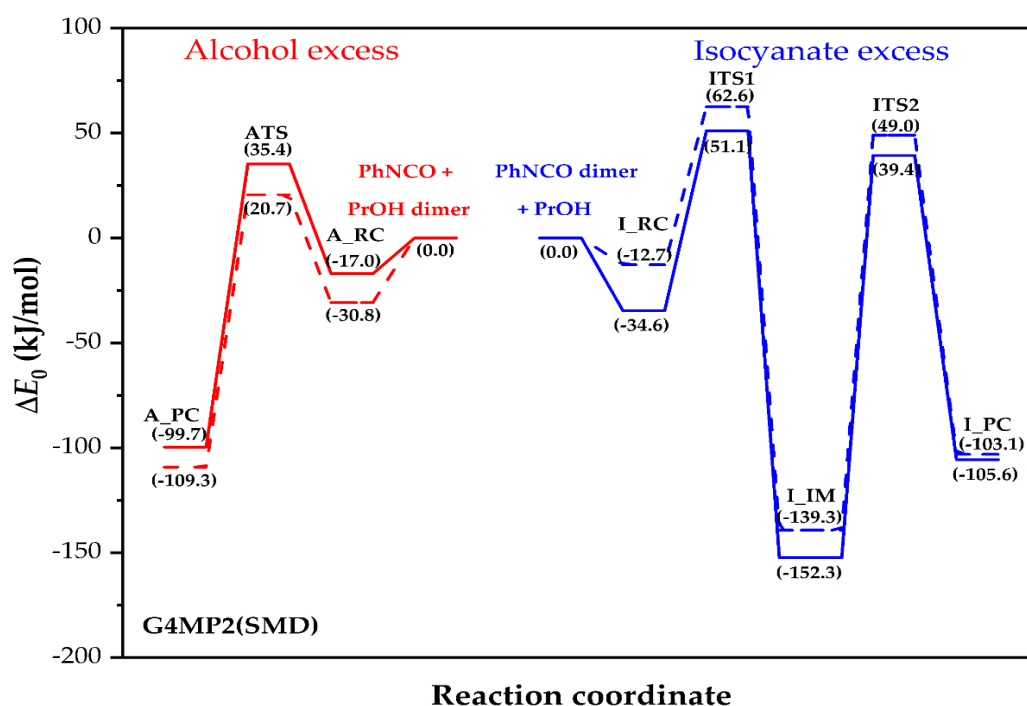


Figure 45: G4MP2 energy profile (zero-point corrected) for the alcoholic route in solvent 1-PrOH (red solid line), in THF (red dashed line), and for the isocyanate route in 1-PrOH (blue solid line), in THF (blue dashed line).

7. Scientific 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, Szilvásvarad, 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 Konferencián 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 Hradky, Czech Republic, 2017, *Poster*

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