Synthesis and characterization of a Polyurethane Prepolymer for the development of a novel Acrylate-based polymer foam

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Chapter 1. Introduction

Some years ago plastic industries were using different kinds of foam compositions to produce a variety of plastic products such as polyethylene and expanded polystyrene until they discovered polyurethane and that it could be altered in many different ways. Promising as it was, manufactures started producing and handling this material in vast amounts. Polyurethane was produced by the addition polymerization of different formulations between isocyanates and polyols to get the desired polymer. Additives were also used according to the process and type of product required. They were produced using blowing agents such as chlorofluorcarbons (CFC’s) that were substituted soon to (HCFC’s) due to the fact their toxicity was polluting the atmosphere and had an effect on the ozone layer.

The basic goal of this project is to develop a prepolymer that can substitute polyurethane polymers used for rigid insulating foams. This prepolymer will be less harmful to the environment and still maintain the basic properties and characteristics of the foam. The project will be based on the production of an acrylate-terminated prepolymer based on a commercial polyurethane prepolymer. In order to come up with the requested product, an alternative isocyanate and hydroxyl ratio should be investigated. Then the product of it, when reacted with the specific acrylate will give us the desired acrylate-terminated prepolymer that can be used for foam insulation.
Chapter 2. Foams

Foam is a colloidal suspension of a gas in a liquid created by agitation. Foams are cushiony materials formed by the creation of gas bubbles in a base material such as natural rubber, synthetic rubber or other elastomeric materials. A plastic or also known as polymeric foam material consists of a gas phase dispersed in a solid plastic phase and derives its properties from both. The dispersed phase of the foam is usually called the internal phase (air or gases), whereas the continuous phase, external (polymeric material). The solid plastic component forms the matrix. The gas phase is contained in voids or cells and is often referred to as the blowing or foaming agent. However, the blowing agent used in the production of foams is not always gaseous and chemically identical with the gas component. Some blowing agents are solids and some are liquids. The term cellular plastic, a synonym for plastic foam, is derived from the structure of the material.

The cell structure depends on the process used for the production of the foamed plastic. In some cases, both flexible and rigid foams may be produced with either open or closed cells. Generally, no foam has entirely one type of cell structure. Open- or closed-cell structure implies that the number of cells in the foam is predominantly open or closed, respectively.

Open-cell structure foam contains pores, which are connected to each other to form an interconnected network. This kind of foam has a comparatively lower density and a sponge-like appearance. Open-cell foams have sound absorbing properties and, when flexible, cushioning characteristics.

Closed-cell structure foam does not have a network of connected cells. It is a solid foam material. Normally this kind of foam has higher compressive strength due to its structure. This kind of foam has a higher dimensional stability, absorbs less moisture and has higher strength when compared to open-cell foam. Its structure makes it have a harder surface feel and makes it better at absorbing impacts. In this type, we have the syntactic foam - a special class of foam that contains hollow particles embedded in a matrix material.
Polymeric foams may be flexible, semi-flexible (or semi-rigid) and rigid, depending on chemical composition and the rigidity of the resin used as a matrix and the type of crosslinking that exists between the molecules. Flexible foams have a glass transition (Tg) below room temperature, whereas rigid foams have one above room temperature.

The matrix is made up of the base resin and other compounding ingredients that may include plasticizers, stabilizers, surfactants, dyes and pigments, fire retardants and fillers. The composition of the plastic matrix plays an important role in determining foam properties such as chemical resistance, thermal stability, flammability, specific heat, transition temperature and rigidity. With respect to the base resin of the matrix, plastic foams may be either thermoplastic or thermosetting. Thermoplastic foams are based on linear or slightly branched (non-cross-linked) polymers and thus have properties normally associated with thermoplastics. They exhibit a definite melting range and are generally susceptible to attack by organic solvents. With thermoplastic foam systems the polymerization of the base resin is generally completed first, and the polymer then compounded, melted and foamed. In contrast, thermosetting foams the matrix of these foams is based on cross-linked polymers so that, like the bulk plastics from which they are derived, they have generally good resistance to solvents and most chemicals. Although some show limited plastic flow at elevated temperatures, thermoset foams do not usually exhibit a melting range and can often be used at higher temperatures than thermoplastic foams (there are exceptions).

Thermoplastic foams include: **Polystyrene** (extruded and moulded bead) which has relatively good thermal insulation efficiency and is readily attacked by
some organic solvents (e.g., in adhesives, paints and some fuels). It is available in slabs, sheets and boards. It is used in thermal insulation for walls, roofs, ceilings and perimeter. PVC has good thermal insulation properties, very low water vapor permeability and water absorption as well as high strength and rigidity. It is available as boards and blocks with a wide range of densities. It’s used in applications for low temperature insulation and also as core material in sandwich panels. Cellulose acetate has desirable properties such good strength, solvent resistance to high temperature and slow burning. It is used in structural framing, and panels.

Thermosetting foams include: Polyurethane has very high thermal resistance for given thickness, low water absorption and low water vapor permeability; good thermal stability and good adhesion. It’s available as blocks, boards, slabs, moulded shapes, liquid prefoam mixtures. It finds its use in thermal insulation for roofs, cavity walls, perimeter, refrigeration and pipe lagging. It’s also used as a core material for sandwich panels, flotation, protective packaging and furniture. Phenol-formaldehyde (Phenolic foam) has relatively low resistance for given thickness. It has high strength and very good thermal stability. It is available as blocks, sheets and liquid prefoam mixtures for foaming-in-place. Urea-formaldehyde has high resistance for a given thickness but low mechanical strength. It has high water absorption and high water vapor permeability. It’s available as board stock, moulded shapes, liquid prefoam mixture for foaming-in-place and spraying.

Even though foams have fascinating characteristics and a number of applications, polyurethane outstands any chances with the rest. The reason for my accusation is that, although it is mentioned as one of the foam materials used in insulation, polyurethane actually is a very versatile material. Versatility of polyurethanes comes from the unique synthesis of them, which is owned to the reaction of a range of isocyanates as well as a wide range of polyols. Polyurethanes can be flexible like comfortable durable mattresses for automotive and domestic use or rigid foams, for the use in thermal insulation in construction industries or in the refrigerators, they can also be flexible of rigid integral skin foams, they can be adhesives, for making wood composite products from loading-bearing roof beams to decorative cladding panels, coatings, sealants and elastomers. It can be used and produced in anything you can imagine. They just pop up everywhere.
Chapter 3. Polyurethanes

3.1 History of Polyurethane

More than half a century ago, plastic industries were working with polymerization and polycondensation processes to produce plastics. In 1937 the German scientist Otto Bayer, also known as “father” of polyurethane, and his co-workers discovered a third process, the so called polyaddition reaction, where the polyaddition of a diisocyanate to a diol in the presence of a catalyst proceeds completely to a polyurethane under mild conditions without the formation of undesired by-products.

Since Otto’s Bayer years, plastic industries had in their disposal the third important synthesis route for the production of macromolecular organic materials. During World War II, polyurethane was used in small scale for aircraft coating, but it was not until 1952 that polyisocyanates became available in the market. In 1954, a commercial production of flexible foam began, based on toluene diisocyanate (TDI) and polyester polyols. The invention of these foams was thanks to water accidentally introduced in the reaction mix. These materials were also used to produce rigid foams, gum rubber, and elastomers. The first commercially available polyether polyol, poly (tetramethylene ether) glycol, was introduced by DuPont in 1956 by polymerizing tetrahydrofuran. In 1957, BASF and Dow Chemical introduced less expensive polyalkylene glycols. These polyether polyols offered technical and commercial advantages such as low cost, ease of handling, better hydrolytic stability and quickly supplanted polyester polyols in the manufacture of polyurethane goods. And over the years a lot of successful achievements on polyurethanes were followed.

Polyurethane, usually referred to as PU, is actually another name for the family of chemicals known as the urethane polymers, which are composed of two principal
raw materials: *isocyanates* and *polyols*, brought together with catalysts and a variety of additives as we will see further on. This reaction produces a basic material whose variations can be stretched, smashed, or scratched, and remain indestructible. Depending on the different isocyanates and polyol constituents, the resulting polyurethane might take a liquid, foam, or solid form, each with advantages and limitations.

Polyurethane might be hard, like fiberglass, squishy like upholstery foam, protective like varnish, bouncy like rubber wheels, or sticky like glue. Since its invention in the 40s, polyurethane has been used in everything from baby toys to airplane wings, and continues to be adapted for contemporary technology.
3.2 Applications of Polyurethanes

Polyurethanes are one of the most versatile materials today. Their many uses range from flexible foam in upholstered furniture to rigid foam as insulation in walls and roofs to thermoplastic polyurethane used in medical devices and footwear to coatings, adhesives, sealants and elastomers used on floors and automotive interiors. Polyurethane is a unique material that offers the elasticity of rubber combined with the toughness and durability of metal. Because urethane is available in a very broad hardness range (eraser-soft to bowling-ball-hard), it allows the engineer to replace rubber, plastic and metal with the ultimate in abrasion resistance and physical properties. Polyurethane can reduce plant maintenance and OEM product cost. Many applications using this ultra-tough material have cut down-time, maintenance time and cost of parts to a fraction of the previous product figures.

3.2.1 Rigid Foam

Rigid polyurethane foams consist of a high percent of closed cells and have unique characteristics. The characteristics are: (1) Foams can be prepared at temperatures without heating. (2) The foams adhere to many kinds of materials such as steel, wood, thermosetting resins and foams, and fibers. (3) The foam density can be varied in a wide range. (4) They are resistant to petroleum, oils and other non-polar solvents. (5) Low-density foams have high thermal insulation properties. These characteristics are quite different from thermoplastic foams such as polystyrene and polyolefin foams as well as thermosetting foams such as phenolic foam. Rigid polyurethane form one of the world's most popular, energy-efficient and versatile insulations. It significantly cuts fuel and construction costs while making commercial and residential properties safer, better utilized and more comfortable around the globe. Rigid foams can be used inside the metal and plastic walls of most refrigerators and freezers or behind paper, metals and other surface materials in the case of thermal insulation panels in the construction sector. They also have a wide application range in the automotive

Figure 4. Rigid PU Foam
industries where they are used in dashboards, exterior parts of a car like bumpers and fenders, between the doors of a car etc. They are also used in ship-building and packaging. Versatile rigid PU foam is even used in horticulture, in furniture and sports equipment, in solar technology and also for rock consolidation in mining and civil engineering.

### 3.2.2 Flexible Foam

Flexible polyurethane foam's versatility of form and function can be seen in every field of application. Foam can be created in almost any variety of shape and firmness. In addition, it's light, durable, supportive and comfortable. Flexible PU comes in many grades: from super-soft for cuddling to rock-hard for ascetics – not hard like a plank, but what the specialists call “a a harder quality” of flexible foam. Flexible slabstocks are used for upholstered furniture, mattresses, vehicle trims, textiles and other applications e.g. in the household, in packaging etc. Flexible PU moulded foams are mainly used as seats in road vehicles and aircrafts, but also in upholstered furnitureand industrial articles. A viscoelastic variant of flexible PU moulded foams provides an excellent material for sound insulation.

### 3.2.3 Thermoplastic Polyurethane

Thermoplastic polyurethane (TPU) elastomers offer a myriad of physical property combinations and processing applications. It's highly elastic, flexible and resistant to abrasion, impact and weather. TPU's can be colored or fabricated in a wide variety of methods, and their use increases a product's overall durability. In the cable and electrical industries, polyether-TPU is valued as cable sheathing material on account of its high flexibility even at below zero temperatures. Because of its advantageous combination of properties, TPU is used for many different high quality components in the automotive industry. Examples range from aerial mountings to...
snow chains and starting aids, exterior mirror housings, parts for roof racks, slide bearings, ball joint gaiters, bellows, decorative and surround strips to spoilers and automotive body-side moldings. TPU is used in various hos applications like hoses used for suction, conveying, irrigation, hydraulic and pneumatic applications. It has widely diverse uses in machine and apparatus construction as bushings, dust caps, power drill housings and battery casings, gear-wheels, clamps and hydraulic seals. Because of the wide spectrum of physical properties TPUs find use in the sports and leisure sector as well. Important examples are ski boot shells, soles for football shoes and gold shoes or ski tips.

3.2.4 Coatings, Adhesives, Sealants and Elastomers

Polyurethane coatings make a product look better and last longer. Polyurethane adhesives provide strong bonding advantages. Polyurethane sealants provide tighter seals. Polyurethane elastomers can be molded into almost any shape, are lighter than metal, offer superior stress recovery and can be resistant to many environmental factors. Polyurethane coatings and sealants are widely used in textile finishing and coating, bonding of non-woven fabrics, synthetic leather production, paper coating, gluing and for leather dressing. Polyurethane adhesives are used in the shoe and clothing industry, in plastics processing, in the production of packaging, in automotive and construction industries. Polyurethane elastomers (PU rubber) have comparable and sometimes identical applications to those of cast elastomers and TPU’s.

Figure 6. PU elastomers, coatings and sealants
Chapter 4. Polyurethane Structure

A broad spectrum of properties gives polyurethanes their versatility. Polyurethanes vary from flexible to rigid and from solid to foamed by suitable combination of the starting materials. In practice, the number of isocyanates used is limited to a few types of TDI, MDI, custom-formulated isocyanate components and in special cases aliphatic isocyanates. The broad spectrum of properties is achieved by the appropriate selection of polyols and additives.

Variations of the chain length and the degree of branching or crosslinking determine the molecular structure of polyurethanes:

The polyaddition of MDI with long chain diols and butanediol yields linear, segmented polymers typical of thermoplastic polyurethanes (TPU). Reversible crosslinking takes place by crystallization of the rigid segments consisting of MDI and butanediol. (Fig. 7)

In the reactions of long-chain triols and water with isocyanates, wide-meshed, elastic networks are formed. Crosslinking takes place both chemically (triols, polyfunctional isocyanates) and physically by phase separation into generally amorphous urea rigid segments and flexible polyol segments. This structure is characteristic of flexible polyurethane foams. (Fig. 7)

The reaction of low molecular weight polyols with three or more reactive centers (OH groups) with polyfunctional isocyanates leads to a close-meshed, crosslinked polymer structures typical of rigid polyurethane foams. The high network density is usually further increased by using excess isocyanate, which results in additional crosslinking points through allophanate, biuret or isocyanurate groups. (Fig. 8)
Figure 7. Morphology of TPU and flexible PU foam

Figure 8. Morphology of rigid PU foam
By suitable choice of ingredients, the properties such as modulus, tensile strength or elongation at break can be tailored to particular requirements through variation of molecular and phase structure. Rigid and flexible polyurethane foams, they do not only differ in molecular structure but also in the type of foam cell structure (closed cell or open cell). (Fig. 9)

![Figure 9. Closed-cell (left) and open-cell (right) foam structure of polyurethane](image)

Closed-cell structures with discrete foam cells are typical of rigid foams. They are characterized by good thermal insulation properties. The reason for this comes, from the combination of a fine, closed-cell foam structure and enclosed cell gases, e.g. CO\textsubscript{2}, pentane and the long used CFC 11, which are poor heat conductors. However, when an appropriate surfactant is selected, or when extreme internal pressures are produced, then the cells can open during foaming, which can lead to foams with a significant open-cell level or fully open-cell foam. Although not desired for conventional rigid foam applications, the properties of open-cell rigid foam can be beneficial in some specific applications. (e.g. packaging) Additionally, rigid polyurethane foams are derived from highly functional starting materials, therefore, they are densely crosslinked and have high strength. The isocyanates used are generally polymeric MDI types (PMDI) with functionalities of 2.6 to 2.8. The main constituents of the polyol component are short-chain polyols with 2 to 8 hydroxyl groups. Their density determines the mechanical property level of rigid polyurethane foams. Density can be adjusted via the content of physical blowing agent and water in the PU system. Common catalysts for rigid PU foam production are tertiary amines.
and they are chosen to ensure that the foaming process starts after 5 to 50 seconds and is completed after 20 to 400 seconds. The flame retardancy of the rigid polymer foams can be considerably improved by increasing the equivalent NCO/OH ratio. As a result isocyanate trimers are formed which have very good thermal stability. However, this action leads to an increase in the brittleness if the foamed material. Consequently, flame retards are added to rigid polyurethane foams.

Flexible foams on the other hand generally have open-cell structure; i.e. during the last stage of the foaming operation, the cell walls rupture and the polymer material retracts to form a web of elastic bands. Suitable additives can promote the process of cell opening. This elastic web structure is what makes flexible polyurethane foams such excellent cushioning materials. Properties of flexible polyurethane foams can be controlled through a series of parameters. Flexibility (elongation) depends on the degree of crosslinking, which can be adjusted via the choice of starting materials. Indentation hardness (resistance of material to deformation) under compression increases with increasing NCO/OH equivalent ratio content. Content of urea linkages from the NCO/water reaction also raise the indentation hardness. The density of foam can be reduced within certain limits by increasing the water content in the polyol component. At the same time, urea content and hardness increase.

Unlike other polyurethanes, the polyaddition reaction to produce thermoplastic polyurethane elastomers (TPU) is carried out in a separate step prior to molding. Processors receive TPU as cubic, cylindrical or lens-shaped pellets, which can be molded into the required shape by injection molding as well as extrusion or blow molding. The thermoplastic processability of this material, for example the ability to repeatedly re-melt it, is possible due to the structure of TPU, which consists essentially of linear macromolecules. In order to achieve this structure, di-functional MDIs are reacted either with long-chain linear polyester polyols of adipic acid, glycol and butanediol or with polytetrahydrofuran. The properties of an elastomer depend on phase separation during the polyaddition reaction. A flexible phase (basically polyol) and a rigid phase showing good crystallization are formed from the product of MDI and butanediol. Reversible crosslinking takes place by crystallization of the rigid segments consisting of MDI and butanediol. The rigid segment content of TPU fundamentally determines its mechanical properties and particularly the hardness.
Chapter 5. Polyurethane Chemistry

Polyurethanes are in class of compounds called reaction polymers, which include epoxies, unsaturated polyesters and phenolics. The basis of polyurethane chemistry is the high reactivity of isocyanates. The reactivity of the isocyanate group can be contributed to the positive charge of the carbon atom in the cumulated double bond system of its N=C=O group. Resonance structures of an aromatic isocyanate makes it clear to understand (Fig. 10). The electron deficiency on the carbon explains the reactivity of isocyanates towards nucleophilic attack, therefore most reaction take place across the C=N bond (Structure 1). Structure 3 becomes important when if R is aromatic, in which case the negative charge on the nitrogen will be distributed throughout the benzene ring, reducing further the electron change on the central carbon of the isocyanate. This is also the reason why aromatic isocyanates such as MDI and TDI are more reactive than aliphatic isocyanates like HDI and IPDI. As a general outline, any electron-withdrawing group linked with R will increase the positive charge on carbon, thereby increasing reactivity of the isocyanate group towards nucleophilic attack. On the other hand, electron donating groups will decrease the reactive of isocyanate groups.

\[
\begin{align*}
R-N=\overset{\delta^-}{C}=O & \quad \longleftrightarrow \quad R-N=\overset{\delta^+}{C}=O \\
\overset{\delta^-}{R-N}=\overset{\delta^-}{C}=O & \quad \longleftrightarrow \quad \overset{\delta^-}{R-N}=\overset{\delta^-}{C}=O
\end{align*}
\]

\[
\begin{align*}
R=\overset{\delta^-}{N}=\overset{\delta^-}{C}=O & \quad \longleftrightarrow \quad R=\overset{\delta^-}{N}=\overset{\delta^-}{C}=O \\
\overset{\delta^-}{R-N}=\overset{\delta^-}{C}=O & \quad \longleftrightarrow \quad \overset{\delta^-}{R-N}=\overset{\delta^-}{C}=O
\end{align*}
\]

\(Ar = \text{aromatic group}\)

Figure 10. Resonance structure of the isocyanate group

Isocyanates react under mild conditions with all compounds that contain “active” hydrogen atoms. These are compounds containing –OH and –NH groups (e.g. alcohols, amines and water). Production of polyurethanes is achieved by the polyaddition reaction of a polyisocyanate with polyalcohol (polyol) in the presence of
a catalyst and other additives. Polyisocyanate is a molecule with two or more isocyanate functional groups and polyol is a molecule with two or more hydroxyl groups (Fig. 11).

![Figure 11. Polyaddition reaction: polyurethane from diisocyanate and diol](image)

When the isocyanate group (NCO) reacts with alcohols, amines, carboxylic acids and water, urethane, urea and amide linkages are formed (Fig. 12).

![Figure 12. Reaction of isocyanates and compounds containing ‘active’ hydrogen atoms](image)

The most important reaction in production of polyurethane is between isocyanate and hydroxyl groups. The reaction is exothermic and reversible and yields to urethane. Aliphatic primary alcohols are the most reactive and react much faster than secondary and tertiary alcohols due to steric reasons. Phenols also react with isocyanates but much more slower than alcohols and result in readily broken urethane groups. The reaction of isocyanates with water is accelerated by the addition of catalysts such as acids, bases (tertiary amines) and metal complexes (organo tin compounds).
The reaction of isocyanate with water is also important for the production of polyurethanes and produces primary amine and carbon dioxide. The amine will immediately react with another isocyanate to form symmetric urea. Due to the formation of carbon dioxide the isocyanate, water reaction is often used as a blowing agent. Catalysts are also used for this reaction because water tends to be very insoluble in isocyanates such as MDI and TDI.

The next important reaction is the isocyanate-amines reaction. Isocyanate reacts with primary and secondary amines to produce di- and tri-substituted urea. These conversions are exothermic, and diamines are used as chain extenders and curing agents in polyurethane manufacture.

The urethane and urea groups, which are formed, contain other “active” hydrogen atoms, which can further react with isocyanate in side reactions to form allophanates and biurets (Fig. 13). Isocyanate-biuret reaction is significantly faster than the allophonate reaction and occurs at lower temperature. In polyurethane systems, this reaction, which is reversible upon heating, is often used for crosslinking. Isocyanate-biuret and isocyanate-urethane reactions lead to branching or cross-linking of the polymer chain with significant effects on properties of the polyurethane product.

![Figure 13. Side reactions of isocyanates with urethane and urea groups](image_url)
Isocyanates also react among each other under specific conditions or if special catalysts such as trialkylphosphines are used (oligomerization reaction) (Fig. 14). In these reactions, products such as isocyanurates (trimers), uretdiones (dimers) or carbodiimides are formed. Isocyanates undergo a mild exothermic cyclo-addition reaction across two C=N bonds resulting in a four-membered ring called a dimer or uretdiones. The use of catalysts results in the formation of dimers at low temperatures, generally as an intermediate in the formation of more stable dimers. Dimer formation mainly arises with aromatic isocyanates, but the reaction is slowed down by ortho substituents. Consequently, dimer formation is more important for MDI than TDI. Also, three isocyanates can undergo a cyclisation reaction across the C=N bond resulting in a six-membered ring called trimer or isocyanurate. Trimerization reaction is exothermic and continues until all the NCO groups have reacted. Both aliphatic and aromatic isocyanates can undergo trimerization forming trimers. The reaction occurs under basic catalysts, such as alkyl metal alkoxides and carboxylic acid salts. If isocyanates react at very high temperatures, formation of carbodiimides occurs.

![Diagram of isocyanurate, uretdione, and carbodiimide](image)

**Figure 14. Oligomerization reactions of isocyanates**
These products are also industrially important:

- **Isocyanurates**, because of the thermal stability, are deliberately incorporated into the polymer structure to improve the flame retardancy of rigid PU foams or to increase the crosslink density.
- **Uretdiones**, similar to isocyanates permit heat-activated cross-linking because isocyanate is released above 160 °C.
- **Carbodiimides**, are useful as hydrolysis stabilizers and acid scavengers. The CO₂ formed in this reaction is used as a blowing agent.
5.1 Composition

Raw materials for polyurethanes consist of three components: Polyisocyanates which form the hard segments in the polyurethane polymer, polyols and additives such as blowing agents, catalysts, surfactants, chain extenders and cross-linkers which inevitably form the soft segments of the polymer.

The main sources of raw materials are petroleum, coal, salt, air and renewable natural materials. *Fig.15* shows the involvement of the polyurethane raw material chemistry in the overall complex of natural resources.

![Figure 15. The "family tree" of PU raw materials](image-url)
5.1.1 Polyisocyanates

Isocyanates with two or more functional groups are the key products required for the formation of polyurethane polymers. Quantitatively, aromatic isocyanates account for the vast majority of global diisocyanate production. Aliphatic and cycloaliphatic isocyanates are also important building blocks for polyurethane materials, but in much smaller degree. The reasons for this, is that aromatically linked isocyanate group is much more reactive than an aliphatic one. Another reason is that aromatic isocyanates are more economical than the aliphatic isocyanates. When special properties are required for a product, aliphatic isocyanates are highly recommended. Isocyanates are characterized by the percentage of NCO content and their functionality, which indicates how many NCO groups a molecule contains.

Phosgenation of amines was discovered by Hentschel in 1884 and is the process for producing isocyanates in a large scale. Chlorine circulated continuously under optimum conditions acts as the “chemical vehicle” in the process.

**Process 1**: Rock salt electrolysis: \(2\text{NaCl} + 2\text{H}_2\text{O} \rightarrow \text{el. current} \rightarrow 2\text{NaOH} + \text{H}_2 + \text{Cl}_2\)

**Process 2**: Phosgene production: \(2\text{C} + \text{O}_2 \rightarrow 2\text{CO}\)
\[2\text{CO} + 2\text{Cl}_2 \rightarrow 2\text{COCl}_2\]

**Process 3**: Phosgenation: \(\text{H}_2\text{N} - \text{R} - \text{NH}_2 + 2\text{COCl}_2 \rightarrow \text{OCN} - \text{R} - \text{NCO} + 4\text{HCl}\)

**Process 4**: Hydrochloric acid electrolysis: \(4\text{HCl} \rightarrow \text{electr. current} \rightarrow 2\text{H}_2 + 2\text{Cl}_2\)

**Process 5**: Hydrogenation of dinitro compounds: \(\text{O}_2\text{N} - \text{R} - \text{NO}_2 + 6\text{H}_2 \rightarrow \text{H}_2\text{N} - \text{R} - \text{NH}_2 + 4\text{H}_2\text{O}\)

Processes 2 and 3 are normally carried out in open-air industrial plant. The foreseeable risks of phosgene leak are protected by a staggered safety system. In case of a leak ammonia is added to the tank to detoxify the phosgene. Between processes 2 and 4, the chlorine is circulated via hydrochloric acid from process 3. If the hydrochloric acid is sold, chlorine from process 1 is supplied at a later stage. Up to two-thirds of the hydrogen required to hydrogenate nitro compounds (process 5) into amines for process 3, is evolved during electrolysis (process 1 and 4).
Phosgene-free methods for producing organic isocyanates have also appeared but never been commercialized. A method for developing TDI, consists of reductive carbonylation of nitro compounds in the presence of a monoalcohol to produce urethane compound, followed by thermal decomposition of the resulting urethane compound.

**Reductive Carbonylation:**

\[
\text{R-NO}_2 \rightarrow \text{R-NH-CO-O-R'} + 2\text{CO}_2
\]

\text{Urethane}

**Thermal Decomposition:**

\[
\text{R-NH-CO-O-R'} \rightarrow \text{R-NCO} + \text{R'-OH}
\]

Additional method for the production of MDI was also developed. This process consists of 3 steps: (1) oxidative carbonylation, (2) condensation and (3) thermal decomposition of the condensation product.

Isocyanates are manufactured as a pure or single isomer compounds such as 2,4-TDI, HDI, NDI or easily defined isomer mixtures such as TDI and pure MDI except from Polymer MDI. The reason for the majority of isocyanates is because each molecule has different characteristics and properties such as the shape of a molecule, number of isocyanate groups per molecule (functionality), colour exposure on different environments, reactivity of a molecule and that’s why each molecule has its unique application on the polyurethane production.

The most important aromatic diisocyanates are TDI and MDI. *Toluylene diisocyanate* (TDI) is derived from toluene. Nitration yields mixtures of 2,4- and 2,6-dinitrotoluene (DNT) isomers in the weight ratio of 80/20 and 65/35, depending on the method of process control adopted. TDI-80, TDI-65 and TDI-100 types are obtained after the hydrogenation (process 5) and subsequent phosgenation (process 3) *(Fig.16)*. TDI-100 is the most active. The least active TDI-“0”, i.e. the pure 2,6-isomer, is not used industrially as it is not easily available, even though its symmetry suggests interesting PU properties. Commercially available TDI’s are colorless, low-viscosity liquids at room temperature. TDI-80 is the most important diisocyanate for PU flexible foams.
On the other hand, diphenylmethane -4,4'-diisocyanate, commonly abbreviated as MDI is a colorless crystalline solid at room temperature with tendency to dimerize. The diamine MDA which is to be phosgenated by process 3 to MDI, can be obtained from nitration of benzene which yields nitrobenzene, which is then catalytically hydrogenated to aniline, which after purification is reacted with formaldehyde (Fig.17).

A wider mixture of isomers and homologues is produced by this process than by just the nitration of toluylene for obtaining MDI. The range of isomers is extended beyond the position isomerism of NCO groups on the “binuclear” products by condensates with 3, 4 and more aromatic nuclei. The diphenylmethane -4,4’-diisocyanate – the actual MDI – is distilled in part from the crude phosgenation product.
Figure 17. Synthesis of diphenylmethane-4,4'-diisocyanate

It contains small quantities of the 2,4-isomer and is predominantly used for PU elastomers. The majority though, is a mixture of binuclear and higher nuclear individuals known as *polymeric* MDI (PMDI). It has functionality of > 2 and is standard low viscosity, dark brown product. It’s the most important polyisocyanate for producing PU rigid foams. Some 2,4’–MDI–rich types are also suitable for PU flexible molded foams (See Fig.18).

Hexamethylene diamine (HDA) is the amine produced for the nylon 6,6 industry by a range of commercial process. A small proportion is phosgenated to convert the amine groups to isocyanate groups and after removal and recycling of solvent and excess phosgene the crude diisocyanate is distilled to generate pure HDI. HDI is a flexible, linear, symmetrical molecule with two primary aliphatic isocyanate groups of equal reactivity. It has the highest isocyanate content of all others and due to the high volatility of molecule most of it is converted into isocyanurate or biuret derivatives.
For a number of applications, so-called *prepolymers* are required. Prepolymers with terminal NCO groups are obtained when polyol reacts with an excess of isocyanate. Via this process, part of the polyaddition is deliberately carried out in advance under controlled conditions.

There are three important advantages associated with this procedure. Prepolymers have higher molecular weight, so they have a lower vapor pressure, which helps to improve the workplace environment. Processing can be better controlled so that properties of PU-part being produced can be adjusted easily and the reaction energy released is reduced in the processing step. Crystallization and dimerization are also avoided.

*Figure 18. MDI isomers and polymeric MDI*
5.1.2 Polyols

The predominant reaction partners of the isocyanates are polyhydroxyl compounds (polyols). The hydroxyl number (OH number, in mg KOH/g) which is inversely proportional to molecular weight characterizes these compounds. The two main classes of polyols are Polyether Polyols and Polyester Polyols. Polyols in comparison with isocyanates are normally of very low toxicity.

5.1.2.1 Polyether Polyols

Polyether polyols are the most commonly used products. They form the “backbone” of polyurethanes (e.g. polyols with molecular weight of about 500). A wide range of long- and short-chained polyether polyols with 2 to 8 OH groups per molecule can be synthesized by the alkali-catalyzed polymerization reaction between low molecular weight di- and polyfunctional “starting” alcohols (initiators) with epoxides (ethylene and/or propylene oxide). The initiators serve as reaction partners for the alkylene oxides and also engage the ether chain as it is forming. (Fig.19, 20)

The structure of the polyols and hence the processing and property profile of the polyurethane products can be controlled within wide limits by selection of the length and composition of the polyether chains and the functionality of the starter molecules.

<table>
<thead>
<tr>
<th>Functionality 2</th>
<th>Functionality 3</th>
<th>Functionality 4</th>
</tr>
</thead>
<tbody>
<tr>
<td>Propylene glycol</td>
<td>Glycerol</td>
<td>Pentaerythritol</td>
</tr>
<tr>
<td>Ethylene glycol</td>
<td>Trimethylolpropane</td>
<td>Methyl glycoside</td>
</tr>
<tr>
<td>Water</td>
<td>1,2,6-Hexanediol</td>
<td>Ethylenediamine</td>
</tr>
<tr>
<td>Methyl diethanolamine</td>
<td>Triethanolamine</td>
<td>Toluenediamine</td>
</tr>
<tr>
<td></td>
<td>Phosphoric acid</td>
<td></td>
</tr>
</tbody>
</table>

<table>
<thead>
<tr>
<th>Functionality 5</th>
<th>Functionality 6</th>
<th>Functionality 8</th>
</tr>
</thead>
<tbody>
<tr>
<td>Diethylene triamine</td>
<td>Sorbitol</td>
<td>Sucrose</td>
</tr>
</tbody>
</table>

Figure 19. Initiators for Polyether Polyols
Polyether polyols come in a wide variety of grades based on their end use, but are all constructed in a similar manner. Polyols for flexible applications use low functionality initiators such as dipropylene glycol ($f=2$) or glycerine ($f=3$). Polyols for rigid applications use high functionality initiators such as sucrose ($f=8$), sorbitol ($f=6$), toluenediamine ($f=4$), and Mannich bases ($f=4$). Propylene oxide is then added to the initiators until the desired molecular weight is achieved. Polyols extended with propylene oxide are terminated with secondary hydroxyl groups. In order to change the compatibility, rheological properties, and reactivity of a polyol, ethylene oxide is used as a co-reactant to create random or mixed block heteropolymers. Polyols capped with ethylene oxide contain a high percentage of primary hydroxyl groups, which are more reactive than secondary hydroxyl groups. Because of their high viscosity carbohydrate, initiated polyols often use glycerine or diethylene glycol as a co-initiate in order to lower the viscosity to ease handling and processing.

5.1.2.2 Polyester Polyols

The polyester polyols for urethane include aliphatic and aromatic polyesters. They are used to a much lesser degree than polyether polyols. They are more expensive to produce and much more viscous than polyethers with comparable chain lengths. On the other hand, they are far less sensitive to photo-oxidation but susceptible to hydrolysis.

*Aliphatic Polyesters* are prepared by polycondensation reaction of dibasic acids such as adipic acid, phthalic acid and sebacic acid with glycols such as ethylene glycol, propylene glycol, diethylene glycol, 1,4-butanediol and 1,6-hexanediol. These polyesters have high viscosity, low functionality and are difficult to handle but they offer physical properties not obtainable by polyether polyols. They are distinguished...
by the choice of monomer, molecular weight and degree of branching. Preparation of Polyethylene adipate is shown below:

\[(n+1) \text{HO} \xrightarrow{\text{C}_2\text{H}_4 \text{OH}} + n (\text{CH}_2)_4 (\text{COOH})_2 \xrightarrow{\text{HO}}\]

Aliphatic polyesters can also be prepared by the ring opening polymerization of lactones, for example, ε-caprolactone as shown below:

\[
\text{n} \xrightarrow{\text{O}} \text{O} \xrightarrow{\text{C}} \text{O} \xrightarrow{\text{O}} \text{C}_2\text{H}_4\text{OH}
\]

_Aromatic Polyesters_ are prepared by the trans-esterification of recycled polyethylene terephthalate (PET), which includes medical films and beverage bottles. The reclaimed polyols are dark-coloured liquids with functionality of 2. This polyol can be used in part for rigid urethane foams. Because of low compatibility of aromatic polyesters, blending it with aliphatic polyesters is recommended for PUR foams.

Polyurethanes produced from polyesters are characterized by good mechanical properties, but they have only moderate hydrolytic stability. In comparison, products based on polyether polyols are more stable to hydrolysis but more sensitive to oxidation.

_Assertion(s) of Polyether Polyols over Polyester Polyols_

- Various functionality polyols (2 to 8) are available.
- Equivalent weight can be widely changed.
- The viscosities are lower than those of polyesters.
- Production costs are cheaper than those of aliphatic polyesters
- Resulting foams are hydrolysis resistant.
Since functionality and equivalent weight of polyether polyols can be widely varied, polyether polyols are extensively used for producing various polyurethanes such as flexible, semi-flexible and rigid foams as well as elastomers, coatings, adhesives, sealants and resins.

Among the advantages polyether polyols over polyester polyols, the former polyols lower oxidation resistance than that of the latter.

### 5.1.2.3 Other Polyols

The free radical vinyl copolymerization of acrylonitrile and styrene in a conventional polyether polyol yields in the production of Graft Polyols. Polymer Polyols (Graft Polyols) contain finely dispersed acrylonitrile-grafted as well as acrylonitrile- and styrene-grafted polyether polyols. They are used to increase the load bearing properties of low density high-resiliency foam, as well as to add hardness to macromolecular foams and cast elastomers. In this process, the vinyl monomers react with polyether polyol chain (grafting). Polyurea polyols can be produced by the polyaddition reaction of an isocyanate with an amino-polyol in a conventional polyether polyol. Caster oil is glycerol ester of ricinoleic acid, which contains secondary OH groups. Some attempts were made to prepare semirigid foams, but its commercialization was not reported. Other types of polyols include polycarbonate polyol, hydantoin-containing polyol, polyolefinic polyol and its hydrogenated polyol.

**Polycarbonate Polyol**

\[ HO\left[ \begin{array}{c} R \end{array} \right] \begin{array}{c} O \end{array} \begin{array}{c} C \end{array} \begin{array}{c} O \end{array} \begin{array}{c} \text{R}_n \end{array} \begin{array}{c} OH \end{array} \]

**Dimethylhydantoin Polyols**

\[ \begin{array}{c} CH_3 \end{array} \begin{array}{c} C \end{array} \begin{array}{c} C \end{array} \begin{array}{c} O \end{array} \begin{array}{c} \text{H} \end{array} \rightarrow \text{(OC}_2\text{H}_4)_x \begin{array}{c} O \end{array} \begin{array}{c} \text{CH}_3\text{CH}_2\text{N} \end{array} \begin{array}{c} \text{N} \end{array} \begin{array}{c} \text{CH}_2\text{CH}_2 \end{array} \begin{array}{c} O \end{array} \begin{array}{c} \text{(OC}_2\text{H}_4)_y \end{array} \begin{array}{c} \text{H} \end{array} \]
5.1.3 Additives

Apart from the basic raw materials, polyisocyanate and polyol, additives are also required for producing polyurethanes. The PU manufacturer comes into direct contact with these chemicals only if he is developing his own formulations. Otherwise, the necessary additives are contained into the raw materials.

<table>
<thead>
<tr>
<th>Additives</th>
<th>Required</th>
</tr>
</thead>
<tbody>
<tr>
<td>Crosslinking agents/ chain extenders</td>
<td>frequently</td>
</tr>
<tr>
<td>Catalysts</td>
<td>always</td>
</tr>
<tr>
<td>Surfactants</td>
<td>usually</td>
</tr>
<tr>
<td>Blowing agents</td>
<td>for foams</td>
</tr>
<tr>
<td>Flame retardants</td>
<td>as necessary</td>
</tr>
<tr>
<td>Fillers</td>
<td>as necessary</td>
</tr>
<tr>
<td>Antioxidants</td>
<td>frequently</td>
</tr>
<tr>
<td>Release agents</td>
<td>for mouldings</td>
</tr>
<tr>
<td>Colorants</td>
<td>as necessary</td>
</tr>
</tbody>
</table>

5.1.3.1 Chain extenders and cross linkers

The two terms are often mistakenly used as synonyms. This is may be due to the fact that processors are more familiar with “crosslinking” than chain extension. Crosslinking agents (f=2) and chain extenders (f=3 or greater) are both low molecular weight diols or triols and diamines so the same chemical can even perform both roles. In other words the process rather than the specific chemical determines whether a diol is a crosslinking agent or a chain extender. It can be said that although a chain extender leads to a “longer” but still functional reactive intermediate product, a crosslinking agent leads to the “crosslinked” final product, which is polyurethane.

Di- and polyhydric alcohols such as butanediol, glycerol or trimethylolpropane are used as OH crosslinking agent/chain extender. (Fig.21) Aromatic diamines, whose NH$_2$ groups react much more slowly with NCO due to the steric hindrance caused by neighboring alkyl groups or Cl atoms, are used extensively as NH$_2$ crosslinking agents/chain extenders. (Fig.21)
The network density of the PU polymer can be controlled using crosslinking agents/chain extenders and its properties thereby influenced. Urethane structures are obtained with OH crosslinking agents and urea structures with NH₂ crosslinking agents. A different crosslinking principle is involved during the crosslinking of PU rubber. On one hand, the PU rubber can be crosslinked as OH prepolymer with a capped, usually uretdione or diisocyanate. On the other hand though, vulcanization with sulphur is permitted by introduction of double bonds into the prepolymer. Finally, a polyester/MDI polyurethane can also be crosslinked radically on the CH₂ groups of the MDI by using cumyl peroxide.

**OH crosslinking agents/chain extenders**

\[ \text{Butandiol-1,4} \quad \text{Glycerol} \quad \text{Trimethylolpropane} \]

**NH₂ crosslinking agents/chain extenders**

\[ 4,4'\text{-methylenebis(2-chloroaniline)} \quad \text{isobutyl 3,5-diamino-4-chlorobenzoate} \]

*Figure 21. Crosslinking agents and chain extenders*
5.1.3.2 Catalysts

Catalysts have a key role in PU production being required to maintain a balance between the reaction of the isocyanate and polyol. The combination of very complex PU chemistry and diverse processing and molding conditions make great demands of the catalyst. Its main function is to exploit the diverse reactions to create a product with the desired properties. Polyurethane catalysts can be classified into two categories, amine compounds and organo-metallic complexes. They can then be further classified as to their specificity, balance and relative efficiency. Common amine catalysts are, triethylenediamine, dimethylethanolamine (DMCHA), and dimethylethanolamine.

Tertiary amine catalysts for isocyanate-based polymers include gelling catalysts, such as tetramethylbutanediamine (TMBDA) and blowing catalysts, such as bis-(2-dimethylaminoethyl)ether and N-ethylmorpholine. For flexible urethane foam preparation, two kinds of reactions take place. The isocyanate – hydroxyl and the isocyanate – water reaction, hence two catalysts are necessary. Tin catalysts promote mainly isocyanate – hydroxyl reactions and they are considered “gelation catalysts”. In contrast, tertiary amine catalysts accelerate the isocyanate – water reaction, which generates CO$_2$ gas and they are considered as “blowing catalysts”. A good balance of gelation vs. blowing results in open-cell foams. A greater amount of blowing results in collapsed foams and a greater amount of gelation results in closed-cell foams and shrinkage.

Organo-metallic compounds based on mercury, lead, tin (dibutyltin dilaurate), bismuth (bismuth octanoate), and zinc are used as polyurethane catalysts. Mercury carboxylates, such as phenylmercuric neodeconate, are particularly effective catalysts for polyurethane elastomer, coating and sealant applications, since they are very highly selective towards the isocyanate-polyol reaction. Mercury catalysts can be used at low levels to give systems a long pot life while still giving excellent back-end cure. Lead catalysts are used in highly reactive rigid spray foam insulation applications, since they maintain their potency in low-temperature and high-humidity conditions. Due to their toxicity and the necessity to dispose of mercury and lead catalysts and catalyzed material as hazardous waste, formulators have been searching for suitable
replacements. Since the 1990s, bismuth and zinc carboxylates have been used as alternatives but have shortcomings of their own. In elastomer applications, long pot life systems do not build green strength as fast as mercury catalyzed systems. In spray foam applications, bismuth and zinc do not drive the front end fast enough in cold weather conditions and must be otherwise augmented to replace lead. Tin-catalysts have hydroxyl groups. The OH group of the tin catalyst reacts with the isocyanate group and therefore eliminating the amine odor and fogging problems faced with amine catalysts. Alkyl tin carboxylates, oxides and mercaptides oxides are used in all types of polyurethane applications. For example, dibutyltin dilaurate is a standard catalyst for polyurethane adhesives and sealants, dioctyltin mercaptide is used in microcellular elastomer applications, and dibutyltin oxide is used in polyurethane paint and coating applications. Tin mercaptides are used in formulations that contain water, as tin carboxylates are susceptible to degradation from hydrolysis.

Delayed action catalysts are used to control reactivity profiles for molded foams of flexible and rigid foams. Delayed action catalysts are known as blocked amines. Blocked catalysts are various amines partially or totally neutralized by carboxylic acids. These acids can react with isocyanate groups and the resulting primary amines react with the isocyanate groups. An example of blocked catalyst is, bis-(2-dimethylaminoethyl) ether.

5.1.3.3 Surfactants

Surfactants, for example emulsifiers, improve the miscibility of the reactants, polyisocyanate/polyol/water, which are actually “incompatible” and when combined with catalysts, contribute to a uniform PU reaction, meaning stabilizing the early stages of the reacting foam structure until sufficient polymerization has occurred to form a self-supporting polymer network. During the early stahes of foam rise, carbon dioxide diffuses into air bubbles, which act as nucleation sites. To obtain the most efficient bubble stability and prevent merging, the correct balance of foam reactivity and surfactant activity must be obtained. In most polyurethane systems, the surfactant must act within few minutes since if this balance is not optimized, the surfactant will not be able to do its job and surface film rupture and defoaming can occur. Special
Organo-silicon compounds are used as foam stabilizers and/or cell regulators during foam production. They stabilize the rising foam until it cures and also regulate the open and closed cell character and pore size of the foams. Generally, silicone surfactant copolymers are classified as hydrolysable and non-hydrolysable depending on the chemical bond between the siloxane chain and the oxyalkylene chain. In hydrolysable copolymers, the chains are linked by silicon-oxygen-carbon bonds, whilst in non-hydrolysable copolymer they are linked by silicon-carbon bonds.

### 5.1.3.4 Blowing agents

Gas generation is an essential part of plastic foam formation. In preparing polyurethane foams, two kinds of gas generation methods are used: chemical gas generation and physical gas generation, as well as combinations thereof. Chemical blowing agents are chemical compounds that react with isocyanate groups to generate carbon dioxide gas. A typical chemical blowing agent is water. Other blowing agents include enolizable organic compounds and boric acid. Physical blowing agents are liquids that have low boiling points and nonreactivity to isocyanate groups that’s why they vaporize by the exotherm of foaming reaction. Physical blowing agents include various fluorine-containing compounds suchs as C₅-hydrocarbons, azeotropes with or without halogen and liquefied CO₂.

**Chemical Blowing Agents:** The conventional gas generation reaction for flexible urethane foams is the water-isocyanate reaction:

\[
2R\text{NCO} + H_2O \rightarrow CO_2\uparrow + R\text{NH}--\text{CO}--\text{NH}--R
\]

The foaming reaction is composed of two simultaneous reactions: generation of carbon dioxide gas and formation of substituent ureas. Water has been used as a chemical blowing agent since the beginning of the urethane foam industry for both flexible and rigid foams. In mid-1995 low-density urethane foams, both flexible and rigid, were blown by the co-use of a physical blowing agent, CFC-11. However, owing to the ban of the use of CFC-11, the use of water alone as a blowing agent for foams was being developed. The use of water alone though, has the following disadvantages:
Increased use of water results in higher reaction exotherm, which is the cause of fire.

System viscosity is high, so flowability of foaming systems in the mold is bad.

In two component-rigid foam systems, mixing ratios become high, so mixing efficiency gets lower.

System costs are high because using water, consumes high amounts of costly polyisocyanates.

Most flexible foams are now produced by using water as sole blowing agent. Other chemical blowing agents include enolizable organic compounds like nitroalkane, aldoxime, nitrourea, acid amide, active methylene compounds as well as boric acid.

**Physical Blowing Agents:** They are inert liquids with low boiling points and they evaporate by exotherm of the foaming reaction. A variety of physical blowing agents exists, which include chlorofluorocarbons (CFCs), hydrochlorofluorocarbons (HCFCs), hydrofluorocarbons (HCFs), perfluorinated hydrocarbons (PFCs), hydrochlorocarbon ethers (HFEs), liquid carbon dioxide, C$_5$-hydrocarbons, halogen-containing and halogen-free azeotropes, methylene chlorine-hydrocarbon blends and blends of zero ozone depletion potential (ODP) blowing agents.

Chlorofluorocarbons (CFCs) were representative physical blowing agents in the foam industry for over 30 years. Trichloromonofluoromethane (CCl$_3$F), (CFC-11), was the ideal physical blowing agent for both flexible and rigid foams. The advantages included nonflammability, non toxicity, good compatibility with foaming ingredients, low molecular weight and moderate boiling point. It was used extensively for flexible and rigid polyurethane foams. In flexible foam production, CFC-11 reduced reaction exotherm and made possible to produce large slabstocks in low densities. CFC-11 blown rigid foams had excellent thermal insulation properties. However, because of the ODP of CFCs and HCFCs in stratosphere, they were phased out from the industries. HFCs were one of the major candidates for the third generation blowing agents. Because of high global warming potential (GWP), the use of them was restricted to some extent. The cost of HFCs also limited their applications. Some PFCs were also proposed but they were banned because of the ODP. HFCEs showed that they have better compatibility with polyols during the foaming process. Liquid CO$_2$ appeared as a blowing agent in the 80s. This blowing agent has zero ODP, low GWP and low cost. It is used to produce very low-density, flexible slabstock foams.
CO₂ is a gas at normal pressure and temperature and therefore when CO₂-containing system is dispensed from mixing head, the system immediately turns froth, without the cream time. C₅-Hydrocarbons is used as an alternative blowing agent for CFC-11 for appliance and building insulation since the 90s. Some examples include pentane, isopentane and cyclopentane. Halogen-containing azeotropes such as 2-methylbutane/1,1-dichloro-fluoromethane and CFC-11/methyl formate were investigated. Advantages of azeotropic blowing agents include better compatibility, with foaming ingredients and lower boiling points than those of comparable components. This agents have no ODP but very high GWP. Halogen-free azeotropes on the other hand, were proposed such as pentane/methyl formate, pentane/methyl acetate, cyclopentane/ethyl formate as well as isoprene/acetone. Halogen-free azeotropes have the following advantages over C₅-Hydrocarbons:

- They give lower foam density with lower thermal conductivity than the same number of moles of comparable C₅-hydrocarbon components
- They have better compatibility with polyols and result in better foam cell structures
- They can be used in traditional CDC-11 formulations
- Integral skin urethane foams, micromolecular urethane foams, polyisocyanurate foams are easily prepared by azeotrope blowing agents

### 5.1.3.5 Fire retardants

The addition of fire retardants to polyurethanes reduces the level of fire, flame and smoke combustion products when checked for combustibility test methods. There is an extensive range of products available from solids such as melamine, exfoliated graphite or aluminium trihydrate to low-viscosity liquid compounds. These products may be reactive or non-reactive, usually bromine, chlorine or phosphorus. Other products are phosphate, phosphite or phosphonate groups. The general scope is that halogen fire retardants function in the gas or vapor phase by interfering with free radical process, which is associated with combustion, whilst phosphorous retardants are thought to act in solid phase and promote formation of proactive char.
Chapter 6. Polyurethane Synthesis

During the production of polyurethanes, liquid and sometimes fused, dissolved and dispersed raw materials are chemically reacted while heat is liberated. There are two methods of reaction control, the components being allowed to react either simultaneously (“one-shot-process”) or successively in two stages (prepolymer process).

The implementation and operation of PU plant, including transportation and storage of raw materials require official approval. Safety devices also have to be provided, e.g. protective metallic baths for storage tanks and other containers, overflow preventers, venting and temperature control systems as well as personnel protection like goggles, gloves, e.t.c. Fig.22 represents a block diagram of the implementation and operation of PU. The main components A and B (polyisocyanate and polyol), are transferred from storage tanks into working containers, brought to the prescribed temperature and fed by metering units to the mixing head. From there, the reaction mix is discharged onto a substrate or into a mould where it fully reacts. The raw materials for PU elastomers, which are usually solids, they have to be melted, dewatered and degassed into the working container. In such a case, one of the additives (components C to F in Fig. 22) is a crosslinking agent/chain extender. By supplying additives separately, including gases, the PU manufacturer is able to control formulations and therefore the properties of his out-coming product. The feed positions can be on the suction side and on the delivery side of the metering pump or direct introduction into the mixing head as well.

PU plant can be regulated to extreme processing conditions, if that is necessary:

- Processing of raw materials at elevated temperatures, which are liquid at room temperature with viscosities of 5 to 20000 mPas, including fused polyester polyols.
- Metering and mixing of the raw materials in ratios of 1 : 100 to 1 : 1 for moldings.
- Adaption of metering unit output to the reactivity of the system
- Discharge techniques for continuously operating the plant and feed techniques for discontinuously operating plant.
- Processing of filler-containing components with granular, flaky or fibrous additives.

![Figure 22. Block diagram of PU system processing plant]

The development and use of suitable measuring, control, monitoring and data processing systems allow high level automation in PU plant and machinery. Sensors and control elements provide assistance by measuring and checking the following process parameters:

- Temperature of raw materials
- Volumetric and mass flow rate - stoichiometric ratio of components
- Densities of components
- Mixing times
- Operating, injection and circulation pressures
- Molding temperatures
- Gas content
So called “live shift records” (what sensors read and measure), can also be obtained from graphic on-line displays. Finally, communication via modem/telephone/ISDN allows world-wide contact between machine suppliers and customers.

Slow gear pumps running at maximum working pressures of 40 bar are used for metering high-viscosity raw materials in low-pressure machines. Mechanical stirrers carry out the mixing of components. High-pressure machines have various piston pumps for metering low-viscosity raw materials and convey the raw materials to an injection mixing head at working pressures of 100 to 300 bar. The reactants are mixed in a turbulent counterflow in the injection mixing head while utilizing their kinetic energy.

Major advantages of the high-pressure process, apart from accurate metering and maintenance of the shit weight, are the possibility of processing “fast” i.e. highly reactive systems, minimal material loss and low environmental pollution, particularly when using self-cleaning injection mixers.

With the combination of high- and low-pressure machines, the components are injected under high pressure by piston pumps into a (low-ressure) stirrer-equipped mixing chamber. This method is adopted when two or more additives are to be metered separately in addition to the two main isocyanate and polyl reactants. The closed-circuit principle applied to the raw materials is common to both the low-pressure an high-pressure techniques as the quality of the finished part is crucial.

Spraying machines can operate by the low-pressure and high-pressure principle. A suitable jet is created by the additional air introduced in the first case and by the high mixing pressure in the second pneumatic driven cylinder piston pumps and tubing up to 100m long are commonly used. The mixing head should be light and easy to handle. It is usually self-cleaning in design.
Chapter 7.  Goals of Experiment

Goals of the experiment is to get familiar with the polyurethane prepolymer and specifically the prepolymer process for the production of NCO-terminated and acrylate-terminated prepolymer. Rigid polyurethane prepolymer are used in the construction industries as thermal insulating foams. For the fact that NCO group is toxic and slowly comprehends into destroying the environment, we have to develop a prepolymer that is less harmful to the environment (ODP and GWP).

The project is to develop a PU-prepolymer which has similar NCO-content as the Desmodur product we were supplied. Also an alternative NCO/OH ratio should be investigated for the preparation an acrylate-prepolymer. After producing the corresponding acrylate-terminated prepolymer, we will try to react it with ethylene diamine in order to observe the crosslinking of the polymer and make quality control tests like measuring the viscosity and IR-Spectra of the products.

Below is a flow diagram for the production:

```
  MDI  Polyol  PU-Prepolymer  2-HEA
     |        |             |        |
     |        |             |        |
     |        |             |        |
     |        |             |        |
     PU-Prepolymer   AC-Prepolymer
```


Chapter 8. Experiment

For our research, the raw materials that we had to work with, were bought from Sigma Aldrich company. The experimental procedures together with the related data sheets were given to us by our industrial partner, which we were performing the project for.

Basic Raw Material list

<table>
<thead>
<tr>
<th>Compound</th>
<th>Description</th>
</tr>
</thead>
<tbody>
<tr>
<td>Desmodur 44M</td>
<td>Pure 4-4'-MDI, delivered in flakes, m.p 40°C, must be stored in a refrigerator to avoid dimerization</td>
</tr>
<tr>
<td>Desmodur E22</td>
<td>PU-prepolymer from MDI, polyol compound and plasticizer not published</td>
</tr>
<tr>
<td>Voranol 2000 L Voranol 1010 L</td>
<td>Polyol</td>
</tr>
<tr>
<td>Desmophen</td>
<td></td>
</tr>
<tr>
<td>2-Hydroxyethylacrylate (Fluka)</td>
<td>Acrylate, water content &lt; 0.5 %</td>
</tr>
</tbody>
</table>

8.1 Characterization of initial components

The first step of our research was to characterize the initial components and synthesis process as was recommended by our partner. The NCO-content and OH-content were determined for the initial components by the use of automatic titration. For all the titrations during the laboratory work, we used the Metrohm 672 Titroprocessor.

8.1.1 Titrations

For the titration of NCO-content, several flasks containing isocyanate and dibutylamine in chlorobenzol solution (in excess) were prepared. Afterwards, isopropyl alcohol was added to the flasks to acquire uniform mixing (dilute the solution). The titrant that was used for the determination of the NCO-content was
0.1M of hydrochloric acid (HCl) in methanol solution. First, dibutylamine alone was titrated in order to get the reference value for the rest of the titrations. During the titrations of isocyanates and dibutylamine, voltage was recorded as well.

For the titration of OH-content, several flasks as well, containing Polyol and Phthalic anhydride in piridin solution (in excess) were prepared. We also had to boil the mixture for 60 minutes at 125 °C to reassure the unifying mixing of the components. Then after boiling we added water, where the water molecules immediately reacted with anhydride groups forming an acid from which the OH-content will be derived. The titrant that was used for the determination of the OH-content was Potassium Hydroxide (KOH). Then, phthalic anhydride was titrated first in order to have a reference for the rest of the OH-content titrations.

8.2 Synthesis of PU-Prepolymer

In the second step, reactions for the preparation of NCO-terminated PU-Prepolymer were carried out. The amount of the polyol component was chosen based on the determined OH-content so that the final NCO-content should be around 8.6%, which is equivalent to the NCO-content of Desmodur E22 value given from the suppliers data sheet. Raw materials that we used for this experiments were, Voranol, that was supplied to us as flakes, Desmophen and Desmodur 44M (diphenylmethane-4,4'-diisocyanate).

**Procedure:** (as given by the industrial partner) MDI flakes are melted and feded to a vessel (or melted in the vessel) and heated up to 50 – 60 °C. fresh MDI gives a clear, colourless liquid, a slight turbidity because of beginning dimerization of MDI may be accepted. Voranol at room temperature is added stirring during approximately 30 minutes, when 5kg of prepolymer is produced. The reaction is exothermic, but the reactivity of Voranol is very low, therefore crystallization of the MDI may occur in case the content of the vessel cools down under 40 °C. the mixture is heated up to maximum 80 °C and held at this temperature for 3 hours. After 3 hours, the NCO-content should be stable. The result is a clear, colourless or slightly yellow, viscous prepolymer. At the end of the experiments, quality control tests were performed to determine the viscosity and NCO-content of the product.
We carried out three different experiments with three different NCO/OH ratios:

1. 60 grams of Desmodur 44M and 90 grams of Voranol 1010 L
2. 45 grams of Desmodur 44M and 89 grams of Voranol 2000 L
3. 47 grams of Desmodur 44M and 89 grams of Desmophen

The chemical reaction between the MDI and the polyol for the current experiment is expected to be:

Viscosity is a measure of the resistance of a fluid that is being deformed by either shear stress or extensional stress. It is commonly perceived as "thickness", or resistance to flow. Viscosity tests for our project were made by the aid of rotational viscometer. The viscometer operates by the principle of rotation of a cylinder or disc (spindle) which is submerged in the material to be analyzed, measuring the resistance of the substance at a pre-set speed. The resulting resistance or torque is the
measurement of the flow viscosity. The greater the resistance of the product to be determined, the greater the viscosity. Based on the speed and the characteristics of the spindle, the torque is calculated and a direct reading of the viscosity is provided in mPa-s (IS).

8.3 Synthesis of AC-Prepolymer

In the third step of our research, reactions for the preparation of AC-Prepolymer were carried out. Desmodur E22 as well as previously prepared NCO-terminated PU-Prepolymers from the second step of the experiments were reacted with 2-hydroxyethylacrylate (2-HEA). The acrylate amount used was chosen so that the NCO-content percentage would be equal to zero.

Procedure: (as given by the industrial partner) Desmodur E22 is fed to a vessel (with stirrer, preferably a dissolver, protected against humidity by a drying tube filled with CaCl₂) and heated to approximately 50 °C. 2-Hydroxyethylacrylate, (2-HEA), is slowly added under mixing. The reaction is exothermic and the mixture should not exceed 80 °C. The time for adding 2-HEA is about 30 minutes when 5kg of material is produced. Afterwards, the content is stirred for additional 2 hours at constant temperature of 80 °C and then stored at room temperature in a closed container. At the end of the experiments quality control tests were performed to determine the viscosity and NCO-content of the product.

Reaction: After putting the equipment in place, we started heating and stirring Desmodur E22 up to 50 °C and then begin to add 2-HEA drop-wise through the dropping funnel. Addition of 2-HEA took about 2 hours and then the mixture was left to heat and stir for another 2 hours at constant temperature of 80 °C.

The experiments carried out together with their respective contents are as follow:

1. 154 grams of Desmodur E22 and 40 grams of 2-HEA
2. 70 grams of 1st NCO-prepolymer and 16 grams of 2-HEA
3. 70 grams of 2nd NCO-prepolymer and 17 grams of 2-HEA
4. 70 grams of 3rd NCO-prepolymer and 16 grams of 2-HEA
The chemical reaction for this experiment is expected to be:

\[
\text{OCN} \quad \text{R} \quad \text{NCO} + \quad \text{CH}_2=\text{CH} \quad \text{C} \quad \text{O} \quad \text{CH}_2=\text{CH}_2=\text{OH}
\]

\[
\text{PU-Prepolymer} \quad \quad \quad \quad \quad \text{2-hydroxyethyl acrylate}
\]

\[
\begin{align*}
\text{CH}_2=\text{CH} \quad \text{C} \quad \text{O} \quad \text{CH}_2=\text{CH}_2=\text{O} \quad \text{C} \quad \text{N} \quad \text{R}_1 \quad \text{O} \quad \text{N} \quad \text{C} \quad \text{O} \quad \text{R}_2 \quad \text{O} \quad \text{C} \quad \text{N} \quad \text{R}_2 \quad \text{N} \quad \text{C} \quad \text{O} \quad \text{CH}_2=\text{CH}_2=\text{O} \quad \text{C} \quad \text{CH} \quad \text{CH}_2
\end{align*}
\]

The exact molecular structure of this product, hence the notation \(R_1\) in the schematic reaction equation, could not be achieved because Desmodur E22 is a commercial prepolymer which is used for the preparation of polyurethane foams. It doesn’t matter though, because the aim of the project was to produce such a product, which we succeed on that. \(R_2\) notation is the chemical formula of the polyol blend.
Experimental setup:

- CaCl$_2$
- Condenser (water cooling)
- Dropping funnel (2-HEA)
- Thermometer
- Stirrer
- Heater & Magnetic stirrer
8.4 Crosslinking

Preliminary tests regarding the crosslinking of the prepolymer were made. For this task we used ethylene diamine as a crosslinking agent. A reaction occurred between the acrylate based prepolymer and the diamine but not as intense as in the case of NCO-terminated prepolymer (Desmodur E22) and a primary crosslinking amine agent.

Based on the chemical characteristics of the components the crosslinking can be expected through the following reaction:

\[
\begin{align*}
\text{CH}_2=\text{CH}-\text{C}-\text{O}-\text{CH}_2-\text{CH}_2-\text{O}-\text{C}-\text{N}-\text{R}_1 \quad &\quad \text{N}-\text{C}-\text{O}-\text{R}_2-\text{O}-\text{C}-\text{N}-\text{R}_1 \quad \text{N}-\text{C}-\text{O}-\text{CH}_2-\text{CH}_2-\text{O}-\text{C}-\text{H} \equiv \text{H}_2 \\
\quad &\quad + \\
\text{H}_2\text{N} \quad \text{CH}_2-\text{CH}_2 \quad \text{NH}_2
\end{align*}
\]

Where:

\[
\text{R}_3 = \text{CH}_2-\text{CH}=\text{O}-\text{CH}_2-\text{CH}_2-\text{O}
\]
Chapter 9. Results and Discussions

9.1 Characterization of initial components

Below are the results for the characterization of initial components performed by automatic titration, which show good correlation with the related values of the data sheets we have. The tests we performed prove that titrations and characterization of the components were successful and that we will be able to carry out the required polymer preparations with good reliability. The results of titrations show that the measured and given values relationship was very good.

<table>
<thead>
<tr>
<th></th>
<th>NCO (%) (given)</th>
<th>NCO (%) (measured)</th>
<th>OH number (given)</th>
<th>OH number (measured)</th>
</tr>
</thead>
<tbody>
<tr>
<td>Desmodur E22</td>
<td>8.6</td>
<td>9.5</td>
<td></td>
<td></td>
</tr>
<tr>
<td>Desmodur 44M</td>
<td>33.9</td>
<td>35</td>
<td></td>
<td></td>
</tr>
<tr>
<td>Voranol 2000 L</td>
<td>-</td>
<td>55.2</td>
<td></td>
<td></td>
</tr>
<tr>
<td>Voranol 1010 L</td>
<td>110</td>
<td>109.3</td>
<td></td>
<td></td>
</tr>
<tr>
<td>Desmophen</td>
<td>56</td>
<td>62.2</td>
<td></td>
<td></td>
</tr>
<tr>
<td>2-hydroxyethylacrylate</td>
<td>-</td>
<td>249.7</td>
<td></td>
<td></td>
</tr>
</tbody>
</table>

9.2 Synthesis of PU-Prepolymer

As mentioned, PU-prepolymer was prepared by Desmodur 44M and three different kinds of polyl components. The experiment procedure was quite straightforward and easy to perform and only few problems with the temperature regulation appeared due to the exothermic nature of the reaction. At the end of the experiments we carried out titrations for the determination of NCO-content to see if the prepolymer we prepared has similar characteristics to the Desmodur E22. The results were very close to the desired ones and more specifically the reaction of Desmodur E44 with Voranol 1010L yielded a NCO-content of 8.45%. The reactions of Desmodur E44 with Voranol 2000L and with Desmophen yielded an 8.59% and
8.69% NCO-content respectively. We also observed that the reactions of Desmodur 44M with the two blends of Voranol (polyol) gave no color distinction (white liquids). On the other hand, reaction of Desmodur 44M with Desmophen gave out a light yellow liquid product.

Viscosity results of the PU-prepolymer we prepared showed that they are in a similar range of Desmodur E22. Specifically, one of the PU-prepolymers we prepared had a bit higher value than the specified and another one had a bit lower. So the partner we work with suggested to mix the two blends of PU-prepolymer so that we can get a more accurate viscosity result.

### 9.3 Synthesis of AC-Prepolymer

Desmodur E22 was a colorless viscous liquid and 2-HEA was a colorless liquid. At the beginning of the experiment we used a magnetic stirrer for the uniform mixing of the mixtures but little after we started adding 2-HEA the mixture became very viscous that the stirrer just stuck and didn’t turn. For this we had to change the magnetic stirrer into an electric one which at the end showed up that the mixing of the two components was uniform. The experiment was not difficult to perform but keeping the temperature to the suggested points was hard to maintain due to the fact that the reaction of Desmodur E22 and 2-HEA was exothermic by itself. At the end of the experiments, we observed some color distinctions particularly with the reactions of Desmodur E22 with 2-HEA and the first and third NCO-prepolymers prepared before with 2-HEA, which gave out a light yellow liquid mixture. Reaction of the second NCO-prepolymer with 2-HEA had no color. In addition, the quality control tests for the determination of NCO-content came up to the expected value which was 0% NCO-content.
9.4 Crosslinking

We carried out crosslinking tests with ethylene diamine as curing agent to see if the polymer can be crosslinked or not and if it is, will it achieve sufficient properties in order to be able to be blown up to form foam. The results were not that satisfactory as in the case of a polyurethane prepolymer crosslinked with a primary amine curing agent. Further investigation and tests shall be carried out in the future in order to come to a position that we can reliably say “This polymer can be successfully crosslinked and can be used as a novel acrylate-based polymer foam”.
Chapter 10. Conclusion

Polyurethane is one of the most versatile polymers in the plastic industries. It does not matter where you look, you will most probably find polyurethane.

An industrial partner had an idea about the production of an isocyanate-free polymer that could be used for insulating foam. So he proposed his idea to us and let us make a research about it. He provided us with a list of materials that we could use. The project was very interesting indeed. The aim of this project was to produce an acrylate-terminated prepolymer. Before reaching the final goal though, we had to also prepare a NCO-terminated PU-Prepolymer. We manage to prepare both of the above products with a quite good reliability. Characterization of polymers was performed by the aid of titration which also yield promising results.

Preliminary tests concerning the crosslinking of the polymers were also studied. Reaction occurred between the isocyanate-free polymer and the curing agent but not as intense as in the case of NCO-terminated prepolymer and a primary amine. The chemistry involved in the reaction of the prepolymer with 2-hydroxyethyl acrylate and the crosslinking of their product should be discussed further.
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