

# Synthesis of Biodegradable and Biocompostable Polyesters

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# **Chemical Engineering**

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"I was taught that the way of progress is neither swift nor easy."

Maria Skłodowska Curie

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# Synthesis of Biodegradable and Biocompostable Polyesters

# Abstract

The main objective of this work was to synthesize linear saturated polyester polyols by polyesterification reaction from dicarboxylic acids and diols. The process conditions were optimized by the temperature profile and also point of vacuum distillation.

During the experimental production of each polyester polyol synthesis the process, parameters were controlled. A special attention was paid to the determination of the convention procedures such as determination of acid and hydroxyl value, as well as viscosity.

Different dicarboxylic acids with a number of various glycols were used as raw materials to give distinct molecular structures with specific features.

The Properties of the products, their application and processing methods depend both on composition and structure of the polyesters and on the composition and structure of the compounds with which they react to produce final products. The scale up of the manufacture was made at laboratory scale of 1 or 2 liters production reactors. To obtain extended and higher average molecular weight diphenylmethane disocyanate (MDI) was additionally added polyester polyols.

For characterization of the product colour determination were carried out. Confirmation of a successfully conducted process of polyesterification was obtained by FTIR-ATR spectroscopy (Infrared Fourier Transform – Attenuated Total Reflectance), as well as viscosity determination.

To evaluate preliminarily the biodegradation of polyester polyols, the hydrolytic stability test performed, due well know statement that biodegradation will start with hydrolysis, and this one would require water absorption.

Keywords: polyester polyol, dimer acid, prepolymers, biodegradability.

# Síntese de Poliésteres Biodegradáveis e Biocompostable

## Resumo

O objectivo do presente trabalho consistiu na síntese de poliésteres-polióis lineares saturados através da reacção de poliesterificação de diácidos carboxílicos e dióis.

Foram utilizades como matérias-primas, diácidos carboxílicos com diferentes estruturas e dióis de modo a obterem-se poliésteres-polióis com diferentes estruturas moleculares e diferentes propriedades.

As propriedades dos produtos finais, bem como a sua aplicação e processamento dependem da composição e da estrutura dos poliésteres desenvolvidos que, por sua vez, dependem da estrutura das matérias-primas usadas.

Os poliésteres-polióis desenvolvidos foram sintetisados à escala laboratorial em reactores com 1 a 2 litros de capacidade. De modo a obterem-se poliésteres-polióis com pesos moleculares mais elevados, foram adicionados como extensores de cadeia difenilmetano diisocianato (MDI).

Efectuou-se a caracterização de determinação da cor do produto. A confirmação do processo conduzido com sucesso de poliesterificação, foi obtido por FTIR-ATR espectroscopia (Infrared Fourier - Reflectância Atenuada Total).

Para avaliação preliminar da biodegradação de polióis de poliéster foi efectuada uma avaliação de absorção de água, devido à conhecida relação de que a biodegradação começa com a hidrólise.

Palavras-chave: poliol poliéster, ácidos dímero, prepolímeros, prepolímeros

# List of Abbreviations and Symbols

[NCO]	Concentration of the functional isocyanate group given as %
η	Viscosity
ρ	Density
а	Parameter of the Mark-Houwink equation
AD	Adipic acid
AS	Succinic Acid
BD	1,4-Butanediol
DEG	Diethylene glycol
FTIR	Fourier transform infrared spectroscopy
ISOR	Isosorbide
IST	Instituto Superior Técnico
MA	Maleic anhydride
MDI	Methylene diphenyl 4,4'-diisocyanate
MPG	Monopropylene glycol
MW	Molecular weight
NPG	Neopenthyl glycol
Polyol	Polymer with OH functionality higher or equal to 2
PU	Polyurethane
TDI	Toluene 2,4-diisocyanate
THF	Tetrahydrofuran
ТМР	Trimethylopropane
V <sub>AN</sub>	Acid number (calculated by titration with O.1 N alcoholic solution of KOH)
V <sub>OH</sub>	Hydroxyl number (calculated by titration with O.5 N alcoholic solution of KOH)

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# **Chapter 1**

## 1. Introduction

### 1.1. Aim

The need for packaging can be linked to the progress of civilization and to the need to preserve perishables for longer period of time. Plastic packaging mostly being used is non biodegradable as it causes ecological imbalance and aesthetic deterioration of nature. There is, therefore, great need to develop biodegradable packaging materials which do not cause environmental pollution. Biodegradable packaging materials neither promote any waste disposal problems nor affect the trade and safety of the food product.

The main objective of this work was to develop polyester polyols with different structure and different molecular weight from dicarboxylic acids and diols with slight additional amount of triols. Those products would be potentially use in the production of polyurethanes packaging materials. For that reason, should be biodegradable and biocompostable.

As a target synthesis, polyester should possess molecular weight under 10000 g/mol and should be in a solid state at temperature equal to 20<sup>o</sup>C, this form will create future processing simple to achieve. In order to obtain more solid structure and higher molecular weight diphenylmethane diisocyanate (MDI) was additionally added.

### 1.2. Polyurethanes

Polyurethanes are versatile polymers with a wide range of properties and the broadest range of industrial applications.

Polyurethanes (PUs) are a special group of heterochain polymers. The distinguishing feature from other polymers is the presence of a carbamate group also known as urethane with the following structure:



The urethane group can be synthesized by various methods [1-2]. The basic raw material for the synthesis of polyurethanes are isocyanates, obtained for the first time in 1849 by Wurtz R. Reactions of isocyanates with compounds containing active hydrogen atoms (in particular, oligomers) leads to synthesis polymers. Bayer, in 1937, with colleagues created new chemistry and technology of polyurethanes, by discovery polyaddition reaction (Figure 1).

Polyurethanes are used in almost all fields of life and economy. Depending on the composition of raw materials and reaction conditions on the composition of the polymer can include ether groups, ester, urethane, urea, allophanate, and others.



Figure 1. Obtaining a linear polyurethane [6]

This tape of reaction is used to synthesise macromolecular compounds, by reaction of diisocyanate (or polyisocyanate which is a molecule with 2 or more isocyanate functional groups,  $R-(N=C=O)n \ge 2$ ) and an oligomeric polyol (which is molecule with 2 or more hydroxyl functional groups,  $R'-(OH)n \ge 2$ ). They are processed, both by classical methods and energy-efficient reactive injection molding. Reaction occur in the presence of catalyst, diamines, additives blocking agents. [2] Polyols used in the reaction are either polyethers or polyesters.

Classifications of polyurethanes can be divided by type of polyol used; examples are polyester polyurethane or polyether polyurethane. The type of polyol can affect the properties. Polyethers polyurethanes are more resistant to hydrolysis than polyester urethanes, while this second one have better resistance to fuel and oils.[2] Polyurethanes of these two groups also differ in glass transition temperature, typically polyether having it lower. Flexibility at low temperatures can be controlled by proper selection of the polyol chain, heat resistance of polyurethane hard blocks. Polyurethanes are noted for their abrasion resistance, hardness, and impact of the low temperature strength, resistance to cutting, resistance to weathering and fungi resistance. [3-5]

#### 1.2.1. Application

Figure 2 presents worldwide polymer market segmants in 2004 with a total of 10.6 million metric tons. Polyurethanes in this comparison represent only 5%, but the average annual growth is constantly high, around 4-6% [6]. Depending on the nature of the raw materials and modifying agents obtained polyurethanes will have very different physical properties. They can be soft, flexible or hard and stiff.



Figure 2 Worldwide market segments of plastics zoon [6]

They are used for flexible and rigid foams, elastomers, and coatings. Elastomeric PU are used as adhesive, coatings and sealants. Due to the high mechanical resistance they are used in the manufacture of transport wheels for industrial trucks carrying large loads. Coatings application is used to protect metals, concrete and wood from weather and chemical conditions. PU adhesives are known, giving high strength joints and characterized by good adhesion to metals, wood, fabric, rubber and various types of laminates. In addition, this type of plastic was applied to the processing of fabrics, leather, and pharmaceutical industries, in agriculture production of plant protection products, as rocket fuel and even in the household. Rigid foam used in the construction industry, shipbuilding and aviation as reinforcing elements and fill the various structures, such as glue, borders, doors, windows, as part of the thermal and acoustic insulation. Low-density flexible foam are used in upholstery, bedding, and automotive and truck seating. Skin substitution is field of application in which PU begin to earn

recognition. They are mostly dedicated to footwear industry as soles and for clothing. The percentage distribution of application of PUs is featured at Figure 3. [6-7]



Figure 3 Polyurethanes applications [6]

# 1.3. Prepolymers

The group of materials representing a reactive intermediate between monomeric isocyanates and polyurethane polymers are called prepolymers.[8] In the Dictionary of Tech-Sci, we can find the following explanation for prepolymer: "A reactive low molecular weight macromolecule or oligomer capable of further polymerization".

A prepolymer is the reaction product of a diisocyanates (rigid component) with an oligo-polyol (flexible component) at the molecular ratio [diisocyanate]/[OH group] lower then 2:1.[6]



Figure 4 Prepolymer formation from MDI and Polyol.

Figure 4 represents a reaction of the NCO groups of diisocyanate with one of the OH groups of polyol, reacting to the other end of the polyol with diisocyanate. The resulting prepolymer has an isocyanate group at both ends. The prepolymer is a diisocyanate itself, and it reacts like a diisocyanate but with several important differences. Compared with the original diisocyanate, the prepolymer has higher molecular weight, greater viscosity, lower isocyanate content by weight (NCO%), minor vapor pressure. Instead of a diol, a triol or higher functional polyols can also be used for the polyol in the reaction only if and the excess of diisocyanate is used. The molar ratio of diisocyanate to polyol larger than two to one is very often used. This is the so-called quasi-prepolymers.[9]

Crosslinked polyurethane can be obtained if a prepolymer derived from an oligo-triol or an oligo-polyol (possesing three or more terminal -NCO groups) enters in contact with atmospheric humidity.

Polyurethanes with high molecular weight are formed by the reaction of the prepolymer with chain extender such as 1,4 butane diol, ethylene glycol, diethylene glycol or diamine.

#### 1.3.1. Properties

Prepolymers are materials with very good chemical and mechanical resistance. They have also good adhesion and low substrate monomer content. Another advantage is their reactivity which is adaptable. Prepolymers possess a wide range of viscosities, flexibility, water resistance and storage stability. The properties of prepolymers may be modified by proper selection of polyol components (such as polyester or polyether) and the polyisocyanate component (aromatic or aliphatic), by the molar ratio of these two reactant and to the resulting formulation (catalyst, filler, plasticizer).

#### 1.3.2. Applications

Linear prepolymers are typically used in the production of sealant, expansion joint, high performance coatings and adhesives, block paving seal, concrete sealer, and wood lacquers.

### 1.4. Polyols

Polyols are polyhydroxyl compounds, the basic raw materials in the synthesis of polyurethanes alongside isocyanates. Polyols on a weight basic are approximately 2/3 of polyurethanes. Polyols are polymeric materials with long flexible chains, with a molecular weight from 200 to 12000. They contain at least two hydroxyl groups. A Polyhydroxyl compound provides flexibility, softness, and resistance to low temperatures. They are usually cheapest components of polyurethanes. [5]

Due to the chemical structure of polyols can be divided into three types:

- Polyester,
- Polyethers,
- Acrylic.

#### 1.4.1. Polyether polyols

"Polyether, any of a class of organic substances prepared by joining together or polymerizing many molecules of simpler compounds (monomers) by establishing ether links between them; polyethers, which may be either chainlike or network like in molecular structure, comprise an unusually diverse group of polymers", this description can be found in Encyclopedia Britannica. They are typically produced through an alkylene oxide polymerization process. Various polyether polyols currently used are mostly exploit to make flexible foams or thermoset elastomers.

Polyethers polyols are polymers formed from cyclic ethers, produced by ethoxylation/ propoxylation of polyhydric alcohols in the present of catalyst. [10] Considering manufacturing process polyethers are obtain by treatment of compounds containing active hydrogen (polyalcohols, polyamines, and others) alkylene such as ethylene oxide, tetrahydrofuran or a mixture of these compounds. As compounds with active hydrogen can be used: glycols, pentaerythritol, sorbitol, sucrose, phenols, amines, and others. Polyether's technology used mostly polyoxides propylene or copolymers of propylene oxide and ethylene glycols or polyols. To obtain polyethers the addition reaction of propylene oxide, ethylene

oxide, or less often at the same time both of these compounds to glycols, glycerin, sucrose, sorbitol, and amines need to be involved.[12-18]

#### 1.4.2. Polyester polyols

Polyester polyols are polyesterification products of a glycol and dicarboxylic acid or acid derivatives [15-18]. They are also known as macroglycols. The three types of polyester polyols can be distinguish by manufacture process, those produced from aliphatic acids, aromatic diacids or caprolactone with excess polyhydric alcohols. The components are mostly acidic polyesters dicarboxylic acids such as: adipic acid, succinic acid, phthalic acid and maleic anhydride or their anhydrides. Components containing hydroxyl groups are mostly ethane-, propane-, butane-, hexane-I heptanodiole, pentane-, and hexanetriol, glycerin, pentaerythritol, polyalkylene oxides and epichlorohydrin.

Polyester materials are used to make most forms of clothing like shirts, running shorts, track pants, windbreakers, and lingerie. It can also be made into curtains and draperies. [10]



Figure 5 Polyester worldwide production by segments of types (source: Tecnon OrbiChem).

#### 1.4.2.1. Properties

Polyester fabrics and fibers are extremely strong and durable. Their great advantage is resistance to most chemicals, stretching and shrinking, and wrinkles, mildew and abrasion resistant. Polyester has a hydrophobic character. It is characterized by the rapid drying. It can be used to isolate the production of hollow fibers. Is a material that retains its shape, so it is good for making outerwear for raw climate. Easily washed and dried.

#### 1.4.2.2. Market

Market polyesters polyols experienced very significant growth between 2005 and 2008. In the fourth quarter of 2008, before economic crisis affected the chemical industry, growth was the highest so far. Global demand for polyester has increased from around 1.3 million tonnes in 2005 to 1.52 million tonnes in 2008, representing an average increase of 5.4% annually in 2005-2008. The most dynamic markets can be found in China and Central and Eastern Europe. In terms of end-uses, the demand for insulation (polyurethane / polyisocyanurates) resulted in the demand for polyester foam in the most developed industrial countries in North America and Europe. [10]





### 1.5. Raw materials for the polyester polyol production

#### 1.5.1. Direct Polyesterification

The simplest way of synthesizing polyester involves heating a hydroxycarboxylic acid, or a mixture of a glycol with a dicarboxylic acid, to temperatures in the range of 150-250°C at which the polyesterification process occurs producing the polyester and water. [12] The esterification reaction, as the elementary step of the polyesterification, is an equilibrium process and therefore its progress and increase in molecular weight of the polyester is highly dependent on the efficiency of continuous elimination of water from the reaction system.

nHO-
$$\overrightarrow{C}$$
  $\overrightarrow{R}$   $\overrightarrow{C}$   $\overrightarrow{OH}$  + (n+1)HO- $\overrightarrow{R}$   $\overrightarrow{OH}$   $\overrightarrow{C}$   
HO- $\overrightarrow{R}$   $\overrightarrow{OH}$  + (n+1)HO- $\overrightarrow{R}$   $\overrightarrow{OH}$   $\overrightarrow{C}$   
HO- $\overrightarrow{R}$   $\overrightarrow{OH}$  + 2n H<sub>2</sub>O

Figure 7 Polyester polyol formation [6]

During the reaction progress, transesterification reaction also takes place, which provide a relatively high molecular weight distribution in the final polyester polyol (especially compared to polyether polyols). In the case of the formation of polyester when the reaction will consist of two or more glycols, regardless of the order addition, they will be added to the polymer chain in a statistical distribution. Nevertheless, careful monitoring of the ratio of ingredients is necessary to ensure that the final product contains a suitable hydroxyl and not acidic end groups.[11]

The esterification reaction, as the elementary step of the polyesterification, is an equilibrium process and therefore its progress and increase in molecular weight of the polyester is highly dependent on the efficiency of removing the water from the reactor. Depending on the desired degree of polymerisation different measures have to be taken. When the desired degree of polymerization is in the range 5-20 (common for polymeric plasticisers or for polyurethane precursors) the flow of a dry inert gas such as nitrogen is usual enough to remove the water from the reactor. However to obtain higher degrees of polymerization, or in cases that the removal of water is more difficult for some reason, the reaction can be carried out with a rather small amount of a boiling inert organic solvent (e.g. xylene) with azeotropic entrainment of the produced water, or, at high conversions, vacuum can be applied[12]

To obtain high conversion polymerization similar numbers of reactive groups should be present at all stages of the reaction. In the reaction between dicarboxylic acids and glycols the latter are often relatively volatile and some quantity may be lost by distillation of the glycol that can be carried in the gaseous stream out of the reactor. [12-13]

This is more relevant during the early stages of the reaction because, as the conversion increases, nearly almost all glycol molecules have reacted at one end or the other (or both) and thus no longer exist as free molecules [13]. At temperatures up to approximately 150°C the main reaction to be considered is the esterification-hydrolysis equilibrium.

In the above reaction, if the reactants fall out of balance so that the glycol is in excess (the one monomer is present in stoechiometric excess), then the equation of step-growth polymerization (the Carothers equation which gives the degree of polymerization), can be applied [14]:

$$DP = \frac{1+r}{2r(1-p)+1-r}$$
 Eq ( 1)

Where r is the stoichiometric ratio of reactants, the excess reactant is conventionally the denominator so that r < 1 and p is the extent of reaction (or conversion to polymer), defined by

$$p = \frac{(N_0 - N)}{N_0} \qquad \qquad \mathsf{Eq} \ (2)$$

where  $N_0$  is the number of molecules present initially and N is the number of unreacted molecules at time (t).

If neither monomer is in excess, then r = 1 and the equation reduces to the equimolar.

The effect of the excess reactant is to reduce the degree of polymerization for a given value of p. In the limit of complete conversion of the limiting reagent monomer,  $p \rightarrow 1$  and

$$DP = \frac{1+r}{1-r} \qquad \qquad \mathsf{Eq} \ (3)$$

Consequently, an excess of either glycol or dicarboxylic acid will have strong influence on the molecular weight of the polyester and the type of end groups. Due to the two referred aspects, an excess of glycol is usually used both to compensate the losses by distillation and to lead to hydroxyl-terminated polyesters[12].

The equilibrium constant (K) is define by equation below, where n is stoichiometric ratio or reaction:

$$K = \frac{[polyester \ polyol][water]^{2n}}{[diol]^{n+1}[dicarboxylic \ acid]^n} \qquad \qquad \text{Eq (4)}$$

In order to generate terminal hydroxyl groups an excess of glycol is currently used. The reaction takes place in uncatalysed reaction conditions (self catalysis by the acidic carboxyl groups), however, the best performances (low reaction time, low final acidity) are obtained in the presence of specific catalysts. [6] Such catalysts include sulfonic acids (e.g. *p*-toluenesulfonic acid or camphorsulfonic in 0,1-0,25% upon the total weight of reactants), antimony pentafluoride, phosphoric acid, titanium alkoxides (e.g. tetraisopropyl orthotitanate, 0,2 to 0,5% upon the total weight of reactants) or dialkyntin oxides (e.g. dibutyltin oxide, 0,2 to 0,5% upon the total weight of reactants).

Due to the water removal during reaction the typical yield is around 85 per cent. [7]

Polyester polyols are normally manufactured in a stirred batch process. The raw materials are heated in an inert atmosphere. Usually the reaction is carried out at a temperature of 150-220°C, Temperature plays an important role in the synthesis of these polyols, the water distilled off through a column at the reactor. In high temperatures reaction occurs faster which make all the process shorter and products received have high MW. In the case of low temperatures 120-140°C, the reaction is very slow (changing the acid number is negligible).[17]

Water initially distils off very rapidly, but the rate of polymerization decreases as the concentration of acid groups decreases. The removal of water can be facilitated by processing under vacuum. The presence of an inert gas, such as nitrogen or carbon dioxide, helps remove the water but also prevents discoloration (which would occur in the presence of oxygen). [10]

#### 1.5.2. Dicarboxylic acid

Dicarboxylic acids are organic compounds that contain two functional groups of carboxylic acid. Aliphatic dicarboxylic acids have a general formula HOOC-(CH2) n-COOH. We can differentiate between a huge variety of molecular forms of dicarboxylic acids, which include a simple form of straight-chain or branched carbon chains, as well as complex forms of dicarboxylic acid and alkyl chain effects such as alkylitaconates.

Table 1 Aliphatic dicarboxylic acids used for polyester polyol synthesis						
No.	Dicarboxylic acid	Formula	MW, Daltons	Acid	number,	
				mgKOH/	g	
1.	Adipic acid	HOOC(CH2)4COOH	146.14	767.78		
2.	Glutaric acid	HOOC(CH2)3COOH	132.12	849.2		
3.	Succinic acid	HOOC(CH2)2COOH	118.09	950.1		
4.	Sebacic acid	HOOC(CH2)8COOH	202.0	555.4		
5.	Azelaic acid	HOOC(CH2)7COOH	186.0	603.2		

Comparing dicarboxylic acids to monocarboxylic acids it can be noted that the properties and chemical reactivity are very similar. But in case of dicarboxylic acids second ionization of the carboxyl group occurs more difficult than the first. This is because more energy is needed to separate a positive hydrogen ion from the anion than in the neutral molecule. For the short-chain dicarboxylic acids, fatty acids can include those that are of major importance in the general metabolism and until n = 3 cannot be treated as lipids since their water solubility is very good. The simplest of these is oxalic acid, whose IUPAC name is ethanedioic acid (n = 0), n=1 is malonic acid (acid propanedioic), succinic (butanedioic acid) contains the n=2, pentanedioic acid also now as glutaric (n=3) acids. The other members of the group of lipids in natural products synthesis or have "n" value from 4 to 21 Adipic acid is the first from those with n=4 (hexanedioic acid) is a product of oxidative rancidity (lipid peroxidation). Tables 1 and 2 presents most often used dicarboxylic acids for production of polyesters.

Dicarboxylic acids are also suitable for surface preparation of organic acids for pharmaceutical and food industries. Furthermore, they are useful materials for the preparation of aromatic polyamides, adhesives, lubricants. [6]

Table 2 Aromatic dicarboxylic acids and derivatives used for polyester polyol synthesis									
No.	Dicarboxylic	Formula	MW, Daltons	Acid number					
	acids			[mg KOH/g]					
1.	Isophthalic acid (IPA)	HOOC	166.13	675.3					
2.	Phthalic anhydride		148.12	757.4					
3.	Terephthalic acid	ноос-Д-соон	166.13	675.3					

#### 1.5.3. Diols

Comparing the synthesis of polyester diol amount and acid quantity, always an excess of diol take place. This leads to higher MW estimate when the molar content is the same. This excess value is important while a mixture of glycol and water has boiling point at about 102°C which is much of nearby the boiling point of water (100°C), this resulting in some losses due simultaneous destilation.

Hydroxyl group-terminated polyesters are also very important as far as their pre-polymers in a variety of other polymers as polyester-PU copolymers, copolymers polyester polyamide. During the selection of alcohol from which diol should rise importance of properties is particularly vulnerable, those might be flexibility, crystallinity, water and heat sensitivity. [6]

Table 3 The most important diols and triols used for polyester polyol synthesis									
No.	Polyol	Formula	MW, Daltons	Hydroxyl number,					
				mg KOH/g					
DIOLS									
1.	Ethyleneglycol (EG)	HOCH2CH2OH	62.07	1807.6					
2.	Diethyleneglycol (DEG)	(HOCH2CH2)2O	106.12	1057.2					
3.	1,2 Propyleneglycol (PG)	HOCH2CH(CH3)OH	76.10	1474.3					
4.	1,4 Butanediol (BD)	HO–(CH2)4–OH	90.12	1245.0					
5.	Neopentyl glycol (NPG)	(CH3)2C(CH2OH)2	104.0	1078.8					
6.	1,6 Hexanediol (HD)	HO–(CH2)6–OH	118.18	949.3					
TRIOLS	5								
1.	Glycerol	(HOCH2)2CHOH	92.1	1827.3					
2.	Trimethylolpropane (TMP)	(HOCH2)3CCH2CH3	122	1379.5					

#### 1.5.4. Isocyanates

Isocyanates are one of the key reactive materials required to manufacture polyurethanes. Those compounds contain highly reactive isocyanate group (-N = C = O), having two cumulative double bonds.

They fulfilled a dual role, extend the polyol molecule by reactions with hydroxyl groups, resulting in polymerization, and their reaction with water releases carbon dioxide which cause the foaming of the reaction mass.

The most widely used isocyanates in case of polyurethane production are toluene diisocyanate (TDI) and diphenylmethane diisocyanate (MDI).

TDI is produced by chemically adding nitrogen groups on toluene, reacting these with hydrogen to produce a diamine, and separating the undesired isomers. This compound was used for the production of conventional flexible foams with high resilience, the production of elastomers and coatings. For security reasons, its use was not advisabled in certain conditions, which resulted to the dynamic development of MDI.[6]

MDI is commercialized in numerous forms and functionalities, the most important appearance: pure MDI, 'crude' MDI and polymeric MDI (called PAPI). The structures and of MDIs isomers general scheme for MDI production and are presented in Figure 8.



Figure 8 General scheme for MDI production

Pure MDI has two -NCO groups/mol, is commercialized mainly as 4,4' isomer. The main applications of pure are: polyurethane elastomers, microcellular elastomers and some flexible foams. A high functionality polymeric MDI is attained after the distillation of one part of pure 4,4' MDI isomer, has a high functionality, close to three -NCO groups/mol.[5,23]

'Crude' MDI and PAPI are especially used in highly crosslinked polyurethanes, such as rigid polyurethane foams.[7,23]

### **Chapter 2**

## 2. Syntesis of polyester polyol from dicarboxylic acid

### 2.1. Reactants

This work presents production of polyesters polyols by using the raw materials such as dicarboxylic acids, diols and triols with the presence of one catalyst.

### 2.2. Structure of the polyester polyols

A polymer chain usually consists of a number of repeating monomer units. The repeating monomer unit is also called repeating unit. The polyol polyesters manufactured in the present work, also consist of monomer units: dimer acid and glycol monomer units. The general formula of a polyester polyol is as shown in Figure 9.



Figure 9 Repeating monomer unit of the linear polyesters.

### 2.3. Dicarboxylic acids

The dicarboxylic acids used in production of polyester polyols are listed in table 4, whereas those used in presented work were: adipic acid, succinic acid and maleic anhydride (which is not so common for polyester polyol production).

Adipic acid is by far the most important dicarboxylic acid used for polyester polyols fabrication. It is white, crystalline, odourless powder.



Figure 10 Molecular structure of adipic acid

Figure 11 Molecular structure of succinic acid

OH

Acid which has been used in the greatest quantities than the others in the present work is succinic acid. Is acid of four carbon atoms, that can also be named butanedioic acid is colourless, cristalline solid.

The compound which has been used less often is white powder with acrid odour, maleic anhydride. Melting point of it is much lower comparing to acids listed above and reaches 52.8°C. Maleic anhydride is an important raw material used in the manufacture of phthalic-type alkyd and unsaturated polyester resins, surface coatings, lubricant additives, plasticizers and copolymers. [24-28]



Figure 12 Maleic anhydride molecular structure.

Table 4 Main properties of used dicarboxylic acids.

	Adipic Acid	Succinic Acid	Malanic Anhydride
	(AD)	(AS)	(MA)
Appearance at 25°C	white powder	solid	white crystals
Molecular Weight	146.14	118.09	98.06
			a 10
pH (of a solution)	3.2	-	2.42
Density [g/cm <sup>3</sup> ]	1.360	1.56	1.48
Melting Point/ Boiling	152.1 / 337.5	187 / 235	52.8 / 202
Point (°C)			
Acidity	4.43 / 5.41	4.2 / 5.6	-/-
Suppliers	Chimica (IT)	Chimica (IT)	Chimica (IT)

### 2.4. Glycols

Commonly used diols and triols for production polyester polyols ale listed in Tables 1 and 2. They were used in the present thesis with one exception- isosorbide which is versatile ingredients and maybe used in wide range of applications [26]. The difunctional alcohols (glycols) used in the synthesis of polyesters were 1,4-butanodiol (BD), monopropylene glycol (MPG), isosorbide (ISOR), diethyleneglycol (DEG), neopenthylglycol (NPG). Trifunctional ones were glycerol, glycerol propoxylate with different MW and trimethylopropane (TMP) (Table 5).

	BD	DEC	ISOB	MPC	NPC	Glycorol	тмр	Glycorol
	ы	DEG	ISOK	MFG	NFG	Giyceroi		Giycerol
								propoxylate
Appearance at	clear	liquid	colourless	liquid	white	liquid	colourless	liquid
25°C	liqiud		solid		solid		solid	
Functionality	2	2	2	2	2	3	3	3
Melting	20.1	-	-	-59	129.13	18	58	flash point
Point/Boiling	/	/		/	/	/	/	113
Point [°C]	235	244		188.2	208	290	160	
Molecular								(*)
Weight [g/mol]	90.1	106.	174.19	134.17	104.14	92.08	134.14	depends
		12						which was
								used
Density at 25°C	1.08	1.11	1.170	1.036	1.04	1.261	1.084	-
[g/cm <sup>3</sup> ]		8						
Supplier	CPB	CPB	Cargil	CPB	CPB	Merck	Sigma-	Sigma-
							Aldrich	Aldrich

Table 5 Main properties and suppliers of the diols and triols used

### 2.5. Catalyst



Figure 13 Titanium (IV) butoxide structure.

The direct polyesterification reaction is self-catalysed by carboxyl groups of the acid reactants. However, due to the reduction of the concentration of these groups with increasing conversion, external catalysts are often used to maintain the rate of reaction. The catalyst used in synthesis was titanium (IV) butoxide light yellow liquid with boiling point at 206<sup>o</sup>C. Product was used from Fluka (Sigma-Aldrich) whit reagent grade equal to 97%.

### 2.6. Synthesis method

#### 2.6.1. Calculations

The excess of diol have influence in final MW of polyester. Usually in industry a 5-15% excess of diol is used. In prepared work is equal to 10%.

The stoichiometric calculation can be easily understood:

$$n R(COOH)_2 + (n+1)R'(OH)_2 \rightleftharpoons HO[R'OOCRCOO]_n R'OH + 2n H2O$$
Eq(5)

$$MW polyol = n * MW acid + (n + 1) * MW diol - 2n * MW_{H_2O} \qquad Eq(6)$$

$$n = \frac{MW_{polyol} - MW_{diol}}{MW_{diol} + MW_{acid} - 2 * MW_{H_2O}}$$
 Eq (7)

Where:

MW<sub>polyol</sub> : Forecasted final molecular weight of polyol.

MW<sub>acid</sub>: Molecular weight of used diacid.

MW<sub>diol</sub>: Molecular weight of used diol.

MW<sub>H20</sub>: Molecular weight of water.

So the stoichiometric ratio is n mol of diacid for (n+1) mol of diol.

For very high MW polyols this ratio becomes almost 1:1.

Of course this is not assuming losses of diol as condensate, so we must add an additional excess by determining amount of diol in distillate, estimated by its distillate refraction index.

### 2.6.2. Experimental apparatus

The heating of the reaction media can be provide by using one electrically heating mantle. The heating equipment should be connected to PID controller, which though thermocouple control temperature of the reaction.

The condenser in position for vacuum or distillation during the whole process. Water distilled in the polyesterification reaction at the initial stage very fast, whereas in the late stage of reaction should be running under lower pressure in order to shorten time of whole process.

The polymerization reaction takes place under inert protective atmosphere of nitrogen (having less than 10 ppm oxygen) and these conditions should be obligatory also during overnights. The inert atmosphere protects against an thermo-oxidative degradation.



Figure 14 Set up equipment (top picture)

Figure15 Set up equipment part 2 (bottom picture)

Set up equipment:

- 1. Three-necked round bottom flask
- 2. Heating mantle
- 3. PID controller
- 4. Electric motor
- 5. Condenser
- 6. Erlenmeyer flask
- 7. Thermocouple
- 8. Thermometer
- 9. Stirrer
- 10. Nitrogen sparge

( nitrogen bubble meter was also used, but not included in the figures)



#### 2.6.3. Polyesterification reaction



#### Figure 15 Scheme of polyesterification process.

General information about direct polyesterification reaction were described in section 1.4.1 however, more detailed progress of the process and the conditions under which the reaction occurs are given below.

The synthesis of polyester polyols by direct polyesterification between diacids and glycols is operated under inert atmosphere (flow of nitrogen is controlled by bubbler which can be also used as a trap in case the product is forced back). At the beginning of the reaction the nitrogen flow should be 2 bubbles/second. Afterwards when most of water was distilled off speed of the bubbles should be more intensive, 4-6 bubbles/second in order to remove part of glycol excess.

The water is removed from reaction system through a distillation column. Vapor temperature of distilled water should be controlled very precise to avoid removal of water with glycols (temperature of reflux should be 105<sup>0</sup>C at maximum point).

At the beginning of reaction, the mixture should be heated up to  $160-170^{\circ}$ C, at this temperature first reflux drops should occur and then subsequently elimination of water should be rapid. Further, the set point settled down on PID controller should be augment very slowly for  $5-10^{\circ}$ C to guarantee that vapor temperature of reflux will not be too high. The temperature should be continuously raised up until reaches  $220^{\circ}$ C which is the highest possible temperature of reaction. At the temperature equal to  $220^{\circ}$ C when the reflux will stop, we can confirm that about 90% of total water is distilled.

When no further reflux of water is observed a few grams of resin (1-3g.) should be taken in order to measure the acid number ( $V_{AN}$ ) and hydroxyl number ( $V_{OH}$ ). The acid number is measure (1-2g of resin) by titration with 0.1N alcoholic solution KOH (Fluka). In parallel hydroxyl value should be also measured 2-3g of resin is needed for  $V_{OH}$  determination by titration with 0.5N alcoholic solution of KOH (Fluka).

When almost all water has been distilled from the reaction and reaction becomes very slowly, second stage of the polyesterification appears. Before second stage and after large number of water is eliminated, catalyst ought to be used. The pressure in second stage should be decrease to 400-200 Pa. In this stage speed of stirrer should be higher and flow of nitrogen ought to be faster. If all those conditions will be fulfilled reaction will run smoothly.

### 2.7. Controlled parameters

The controlling parameters of the polyesterification reaction are:

- determination of acid number (V<sub>AN</sub>)
- determination of hydroxyl number (V<sub>OH</sub>),
- determination of molecular weight (MW),
- amount of water removed,
- determination of viscosity,
- determination of colour,
- determination of density,
- Infrared Fourier Transform Attenuated Total Reflectance Spectroscopy (FITR-ATR),

- o insaturation,
- o clouding point,
- o ashes content,
- o sodium and potassium contents,
- o antioxidant content,
- o hydroxyl primaly groups content,
- o fogging index.

• appearance,

Group of parameters controlling the quality of the polyols located above at the left side are analyzed in detail in the present work. Moreover, some of controlling parameters ( $V_{AN}$ ,  $V_{OH}$ , MW, viscosity) should be calculated and checked during the whole reaction process, while rest of those should be monitored after finishing the reaction. The evolution of the polyesterification reaction is monitored by measuring the quantity of water distilled and by the determination of acid number, hydroxyl number and viscosity.

#### 2.7.1. Acid number

The acid number is expressed as the number of milligrams of potassium hydroxide required to neutralize the acidity of one gram sample. Acid number is important to correct the value of hydroxyl number, in order to obtain the real value for OH (for a good correction of the OH value, the acid number is added to the determined value of OH).

It is a measure of polyesterification from acid groups, which together with the hydroxyl groups will not react with KOH.

Acid number is a physical permanent usually used as process control during the synthesis resin. It was observed that with the progress of the reaction, reduces the amount of acid in a proper manner is becoming permanent when the reaction reaches the end. Acid number is inversely proportional to MW in the polyol chain.

Procedure of the acid number determination end with following equation:

$$V_{AN} = \frac{V_{KOH} * 0.1 * 56.1}{m}$$
 Eq (8)

where:

 $V_{AN}$  [mg KOH / g sample] is acid value of the sample,

 $V_{KOH}$  [L] is the volume of KOH solution used in the titration of the sample.

0.1 [eq/L] is the normality of the KOH solution,

56.1 [g/mol] MW of KOH,

m [g] is the weight of the sample.

#### 2.7.2. Hydroxyl number

The hydroxyl number is defined as the numerical value of quantities of hydroxyl groups available for reaction with isocyanates. The number of hydroxyl (or hydroxyl index) is expressed in milligrams of potassium hydroxide equivalent per gram of sample (mg KOH / g). The most important analytical method to determine the number of hydroxyl (OH) is the reaction of hydroxyl end groups of organic anhydrides (acetic anhydride or phthalic anhydride). Acid carboxyl groups as a result of this reaction is neutralized with equimolecular amount of potassium hydroxide. Reaction with acetic anhydride is shown in reaction. The most frequently described method for determining the hydroxyl number is the conversion with acetic anhydride in pyridine with subsequent titration of the acetic acid.



Figure 16 Shame of method describing determination of the hydroxyl number.

The method used for the determination of hydroxyl number will be consider almost the same like method of determination of acid number that is confidential. Whereas, hydroxyl value determination is based on DIN 53240-2, which is establish on catalyzed acylation of the hydroxyl group. After hydrolysis of the intermediate, the residual acetic acid is titrated in non-aqueous medium with an alcoholic solution of KOH.[6,31]

After titration, where also blank test was obligatory to carry on and fulfilled determination process we were using following equation:

$$V_{OH} = \frac{(Vol_{blank} - Vol) * 0,5 * 56.1}{m} + V_{AN}$$
 Eq (9)

Where:

 $V_{\text{OH}}$  [mg KOH / g sample] is the hydroxyl value

 $V_{AN}$  [mg KOH / g sample] is acid value of the sample, previously determined

V<sub>olblank</sub> [L] is the volume of KOH solution used in the titration of the blank

 $V_{ol}$  [L] is the volume of KOH solution used in the titration of the sample

0.5 [eq/L] is the normality of the KOH solution

56.1 [g/mol] MW of KOH

m [g] is the weight of the sample

#### 2.7.2.1. **Glycol corrections**

If hydroxyl number (V<sub>OH</sub>),calculated by titration with 0.1 N alcoholic solution of KOH is lower than the desire value, we need to add additional glycol amount, which can be estimated by following equation:

$$Glycol (extra) = \frac{(V_{OH}(real) - V_{OH}(set)) \cdot W_{mixture}}{V_{OH}(real)}$$
 Eq (10)

where:

V<sub>OH</sub>(real): Actual V of mixture,

V<sub>OH</sub>(set): Value needed,

W<sub>mixture</sub>: Actual weight of mixture in reactor (obtained by subtracting the distilled water to the total weight charged to the reactor in the beginning of the reaction).

#### 2.7.3. Molecular weight

After obtaining the hydroxyl number and the acid number determination we were able to determine molecular weight of polyester polyol using following formula:

$$MW = \frac{f_{*}56,10}{(V_{AN}+V_{OH})} Eq(1)$$

where:

MW- molecular weight,

f- functionality, the number of OH groups/mol,

V<sub>AN</sub>- mg KOH / g sample] is acid value of the sample,

V<sub>OH</sub>- mg KOH / g sample] is the hydroxyl value,

56,10- [g/mol] MW of KOH.

1)

#### 2.7.4. Functionality

Functionality is also one important characteristic of polyols and is classify as a number of hydroxyl groups/ molecule of polyols.

#### 2.7.5. Amount of water removed

Amount of water removed during the process is equal to 5% of initial weight of reactants.

The number that we can obtain via: the calculation of twice the molar mass of diacid in reactor, and then multiplying the result by the molecular mass of water.

#### 2.7.6. Viscosity

Given the fact that the viscosity increases logarithmically with molecular weight, it is clear why the monitoring of viscosity is so important in the processing of polymers (Figure 18). Determination of the viscosity is of great importance for the purposes of processing due to the fact that for flexible chain polymers is a critical molecular weight (Mc which was marked on the Figure 18) is the point at which entanglement begins, molecular weight and viscosity can be directly related to each type of polymer. [6]

Whereas, the viscosity of polyols was measured as a pure polyol, solvent free.



Figure 17 Relation between molecular weight (MW) and viscosity ( 70)

#### **ICI Cone and Plate Viscometer**

The ICI Cone and Plate Viscometer was used for determination of viscosity of the polyester polyols. It is a manual viscometer, which is still very useful in industry. It is type of rotational viscometer, where small amount of polymer (a few drops) is contained between the cone and bottom plate. The cone rotates at a constant velocity, is illustrated in Figure 19. The instrument works very fast even less than a minute. In Figure 20 used equipment is shown. It thermostatically controlled over a wide range of temperature, it posses 5 switched temperature in the range between 25-175°C, one of which is selected so that the melt viscosity comes within the viscosity range of the instrument (0-40 Poise).



Figure 18 Shame of Cone plate viscometer



Figure 19 ICI cone plate viscometer equipment used during viscosity determination

#### Procedure:

- 1. Turn on equipment for warming up (orange light will be continuously on),
- 2. Set the temperature, when the light starts to blink, this means the plate reach the settled temperature,
- 3. Put the relevant amount of product on plate, subsequently drain down reels of cone,
- 4. Press button "press to read" and read the value of the top scale (units of it is Poise),
- 5. If value of the viscosity is too high and merges the instrument too narrow, increase the temperature.
- 6. Repeat operation 3 times.

#### 2.7.7. Colour

Colour is an important indicator of product quality and in most cases important for the future use. Colours of transparent liquids have been studied visually since the early 19th century. Changes in colour can indicate contamination or impurities in the raw materials, process variations, or degradation of products over time.

Fundamentally points required color polyester polyol is a clear colour. When it is darker resin may indicate some shortcomings in the process, such as:

- inadequate flow of inert gas,
- too high or too long maintained a high reaction temperature,
- contamination with thermal degradation product or others

These variables may affect the setting time of the resin.

One dimensional scales for yellowness were created, e.g., Gardner Color Scale. The yellowness of the transparent liquid is determined by pouring the sample into a tube and comparing it to a pre determined and known standard. The standard that the sample falls closest to then becomes the value for the liquid. This procedure isn't extremely accurate due to variations of observers, illumination and to some extent the standards themselves.

#### The Gardner Colour Scale



Figure 20 Lovibond Comparator System 2000

"The Gardner Colour scale as specified in ASTM D1544 is a single number colour scale for grading light transmitting samples with colour characteristics ranging from light yellow to brownish red. It is widely used for oils, paint and chemicals, such as resins, varnishes, lacquers, drying oils, fatty acids, lecithin, sunflower oil, linseed oil. The scale is defined by the chromaticities of glass standards numbered from 1 for the lightest to 18 for the darkest." [33]



Figure 21 Scale discs colour standards: Gardner 4/30AS (with the colours 1 to 9; on the left) and the Gardner 4/30BS (with the colours 10 to 18; on the right)

The Gardner colour scale is used for polyols having a more intensive colour, of yellow to brown colour. The light colour of polyols increases their commercial value and is an indication that the product was not degraded during the process of synthesis.

Using a suitable Comparator instrument, the sample is visually matched against calibrated, colour stable glass standards in test discs.

The instrument used was the Lovibond 2000 Comparator with Daylight 2000 (Figure 22), which has an optional illumination system to guarantee correct lighting conditions for colour grading. The scale discs colour standards used were the Gardner 4/30AS (with the colours 1 to 9) and the Gardner 4/30BS (with the colours 10 to 18) (Figure 23).

#### **Principle of operation**

"The sample is poured into a 10.65 mm diameter test tube and placed in the sample hole in the comparator. The sample is viewed through a prism which brings the sample and the colour standards into adjoining fields of view. The two discs containing the colour standards are rotated by turning the control knobs on the front of the comparator until the colour of the sample falls between two standards which are 1 Gardner Colour unit apart, or until it exactly matches one of the standards. The reading given directly as Gardner Colour is then taken from the scale on the control knobs." [33]

#### 2.7.8. Density

Density is another significant parameter which is indicative of the the quality of the polyester polyol.

For measuring the density we used the pycnometer, also called as specific gravity bottle. It is a glass flask with a close-fitting ground glass stopper with a capillary hole through it (Figure 24 represent pycnometer special to measure density of liquids products, for solid ones it is looking similar). Given volume obtained by this equipment can be accurately obtain, fine hole releases a spare liquid or solid after closing a top filled pycnometer a given volume of measure by reference to appropriate working fluid, with well known density, such as water or mercury, using an analytical balance. [32]



Figure 22 Pyconometers (specific gravity bottles) empty and full

#### **Principle of operations**

- 1. Determine weight of empty dry and clean pycnometer,
- 2. Fill pycnometer with distilled water,
  - Carefully note temperature of water (water should posses the same temperature during whole measuring process),
  - To avoid expansion of the pycnometer due to the heat of the hand, pick it up by the neck with gloves,
  - During filling make sure that no air bubbles are in bulb or capillary of pycnometer, and no air space at the top of capillary,
  - Before weight the full pycnometer, the outside should be perfectly dry,
- 3. Weigh full pycnometer on analytical balance,
- 4. After measuring the weight clean and make it dry,
- 5. Insert sample in pyconometer and weight on analytical balance,
- 6. Add distilled water and determine the weight,
- 7. Perform necessary calculation.

The results of the experiment will have high precision only if the pycnometer is used at this temperature throughout the experiment.

#### 2.7.9. FTIR- ATR

Fourier Transform Infrared (FTIR) spectroscopy is a conventional infrared spectroscopy, FTIR is used to detect vibrational transitions of a molecule. In this project ATR-FTIR was used. ATR is a sample interface that enables routine analysis of solids with little to no sample preparation. Each of functional group corresponds to absorption wavelength, thus allowing identification by analysis of infrared spectroscopy. [34]

#### **Principle of operation**

The sample is sandwiched between a crystal of high refractive index and a clamp constructed of a diamond tip. The IR beam is directed through the crystal toward the sample at an angle that ensures total reflection at the interface between the crystal and the sample. The IR radiation penetrates into the sample a very small distance (a few wavelengths of light). This penetrating radiation is called an evanescent wave. During this penetration, the vibrating chemical bonds in the sample absorb some of the radiation. The attenuated reflected beam is then detected by the transducer and the resulting FID signal is processed to produce the reflectance spectrum of the sample. [35-39]

In this thesis a Thermo Scientific NicoletTM 380 FT-IR equipped with Smart Orbit diamond ATR attachment (Thermo Electron Corp., Madison, WI) was used to characterize the functional groups. The formation of the polyester polyol was confirmed by this method. A total of 128 scans of each sample from 4000 to 500 cm<sup>-1</sup> wavenumber were obtained at a resolution of 4 cm<sup>-1</sup>.

### 2.7.10. Absorption of water

According to ASTM-D570 Standard Test Method for water Absorption of Plastic methods were used. This test method covers the determination of the relative rate of absorption of water by plastics when immersed. This test method is intended to apply to the testing of all types of plastics, including cast, hot-molded, and cold-molded resinous products.

To calculate water absorption we used simple equation:

Percent Water Absorption = 
$$\frac{(\text{weight after test - weight before test})}{\text{weight before test}} \cdot 100\%$$
 Eq( 12)

Water absorption is expressed as increase in weight percent.

#### Absorption

Water absorption is used to determine the amount of water absorbed under specified conditions. Factors affecting water absorption include: type of polymer, additives used, temperature and length of exposure. The data sheds light on the performance of the materials in water or humid environments.

#### Procedure:

- Weigh samples around 1g each, therefore insert into the test tube,
- Fill test tube with 10 ml of distilled water ,
- Leave sample in test tube for 15 days in constant condition (temperature, humidity, aces of air),
- Weigh sample after appointed time (after being drained from the excess of water with a dry cloth),
- A visual analysis of the samples before and after the test should be recorded to report the changes.

#### Hydrolysis resistance

For hydrolysis to occur, water as liquid or vapor must be present. The reaction is markedly accelerated by elevated temperatures. In the hydrolysis reaction, water molecules break up the resin molecules, leaving an organic acid of varying acidity depending on the particular resin and a mixture of molecules of water, alcohols, and glycols. After a period of time, only the heavier alcohols and the glycol will remain.

Polyesters undergo hydrolysis, a water molecule attacks the bond between the central carbon atom and the adjacent single-bonded oxygen atom. The water molecule dissociates into a hydrogen atom and an OH pair. The OH pair takes the place of the original singlebonded oxygen while the hydrogen joins the O-R to become H-O-R. The C = O pair is referred to as a carbonyl.

#### Procedure:

- Weigh samples around 1g each (2 samples of each formulation), therefore insert into the test tube,
- Fill test tube with 10 ml of distilled water ,
- Insert test tubes into oil bath at constant temperature of 95°C, controlled by thermometer,
- Remove samples from bath after 2h and then after 5h,
- Weight sample after overnight cooling the samples (after being drained from the excess of water with a dry cloth),
- A visual analysis of the samples before and after the test should be recorded to report the changes.

# 2.8. Chain extenders, cross linking agents and addition of MDI

Polyurethanes based on polyols are known for excellent hydrophobicity, hydrolytic and chemical resistance, electrical insulation properties, and low-temperature flexibility [1-3]. Incorporating chain extenders, such as diols of low molecular weight, in the gum stock formulas enhances the elastomeric properties of the resulting polyurethanes, because the small diols react with diisocyanates and form hard domains to serve as the physical crosslink for the polyurethane systems. Traditionally, 1, 4-butanediol is one of the most important chain extenders used in commercial polyurethane elastomers based on polyether or polyester polyols.

Cross-linking agents and chain-extending agents are low molecular weight polyfunctional compounds, reactive with isocyanates and are also known as curing agents. The chain extender reacts with isocyanate to form a polyurethane or polyurea segment in the polyurethane polymer. Isocyanate through reaction transform the chain extender effectively into a thermo-reversible cross linker. [6]

In case to obtain chain extension of the polyester polyols addition of isocyanates MDI was needed.

Appropriate amount of MDI we could calculate the following ratio:

	1 mol of MDI -		250g/mol (molar mass of MDI)
	2 moles of polyester polyol	-	MW of polyester polyol
Relation 1:2			
	Mass of sample of polyester polyol	-	2xMW of polyester polyol
	Х	-	250g
Relation 2:3			
	Mass of sample of polyester polyol	-	3xMW of polyester polyol
	Х	-	2x250g
Relation 3:4			
	Mass of sample of polyester polyol	-	4xMW of polyester polyol
	Х	-	3x250g

#### **Prepolymer Procedure:**

To a four-necked reactor with previously measured weight of polyester polyol with PID controller set at 75°C, constant stirring and under nitrogen atmosphere, MDI was added. Amount of isocyanates was calculated previously by procedure above. MDI addition was conducted very slowly in order not to lead to a possible form of gel formation. Reaction was held during 1.5h.

At first decrease of the torque number can be notice, this condition is caused by the concentration isocyanates. Bubbles presents on the surface and in the center of the sample testify about the appropriate reaction process. After sometime, the increase of the torque number be observed. This point is crucial and high vigilance should be care here. To avoid problem of removal prepolymer from the reactor, it should be conducted just before total merged of it, to store in prepared container.

The sample should be further aged at least two weeks at room temperature to ensure complete before the testing of physical and mechanical properties will be performed.

### **Chapter 3**

# 3. Experimental results and discussion

These experiments studied mainly the effects of: reaction time, amount of catalyst, reaction temperature and the type of reactants and its ratio in the synthesis of polyesters.

### 3.1. Formulations

Percentage ratio moles of dicarboxylic acids, diols and triols used to each formulation is shown in Table 6. Formulations were divided into five separate sub-groups in which we can note some dependency, such as, for example, for the synthesis were used identical dicarboxylic acids in the same ratio and alike diols, synthesis are differ among themselves in a group from content of triol (eg. group A).

However, it is needed to highlight again that amount of glycols in each reaction was with 10% of excess to make sure that most of the carboxylic acid groups will reacted.

### 3.2. Acid number, hydroxyl number and Molecular Weight

These three parameters were very strictly controlled during the whole synthesis process. Hydroxyl and acid numbers are indirectly proportional to polyesters molecular weight (mention the equation number). Through duration of the polycondensation reaction, the acid and the hydroxyl values decreased until the desired values are obtained. For acid value calculated by titration with O.1 N alcoholic solution of KOH less than five units (mg KOH/g polyol) was desire for OH value enough to achieve high MW. Table 7 represents the final acid and hydroxyl values obtained for each of fifteen synthesis.

Numb	per of		ACIDS				DIOLS			TRIOLS			
formu	lation	AD	AS	MA	BD	DEG	ISOR	MPG	NPG	Glycerol	ТМР	Glycerol propoxylate	Density
1.	А	0.3	0.7		0.5	0.5							1.230658
2.	roup	0.3	0.7		0.5	0.5				0.15			1.1860146
3.	Ū	0.3	0.7		0.5	0.5				0.3			1.203021
4.	В	0.5	0.5		0.43		0.43				0.14		1.182876
5.	roup	0.5	0.5		0.86						0.14		1.121958
6.	Ū	0.5	0.5					0.86			0.14		1.14604
7.	U	0.5	0.5		0.43		0.43			0.14			1.198763
8.	dno	0.5	0.5		0.43		0.43						-
9.	Ū	0.5	0.5		0.43		0.43					0.14 (1500MW)	1.17325
10.	D	0.8		0.2	0.9							0.1(1500MW)	1.012181
11.	dno	0.6	0.2	0.2	0.9							0.1 (1000MW)	1.169559
12	Gr	0.1	0.9		0.9							0.1 (3600MW)	1.050047
13.	ш	0.1	0.9			0.5			0.5				1.144722
14.	roup	0.1	0.9			1						0.1 (3600MW)	1.024691
15.	Ċ	0.1	0.9			1						0.1 (1000MW)	1.238791

Table 6 Formulations of prepared synthesis (where units mole%), division into groups with density determination (where units are grams per cubic meter).

### 3.3. Colour

If considering the colour parameter in the case of the most commercially attractive products, then the lighter ones should be on the first place with low MW. Although, darker colours are still acceptable for production point of view and for certain applications. Taking this in account the purpose of this work was to obtain polyester with high molecular weight and in a solid state, which also will be easy to undergo through treatment process. Unfortunately, during the synthesis process correlation between the duration of the process and its color was not found. Dark colour of samples might be explained by the thermal decomposition of the diols, although maximum temperature is higher than this performed during synthesis.

Colour determinations of the synthesis products are presented in Table 7. The colour of the polyester polyol was exactly between two colors from the Gardner colour scale (example 10-11), but was closer to one of the colours (11'-12 in this case, colour was a colour between 11 and 12, but more like 11), and therefore had to differentiate between signs. As it can be notice not all of the samples were assigned a colour value, the reason for this situation was their state of aggregation, which made determination impossible.

### 3.4. Density

To obtain the best imaging of results for the density determination, the synthesis of polyester polyols were divided into five groups (Table 6 presents each group divided by colour line from another). In each of the group there are some dependences and similarities between reactants. Of course this summary is not entirely accurate, since the synthesis obtained do not possess the same values of MW, but it shows the way as the choice reactants affects the final density of synthesis polyesters polyols.

The first group (Group A, above red line) is a group in which dicarboxylic acids were used in the same proportion, diols are the same and the same precentage values are identical, the only differences between the syntheses are triols. The highest density in this group is obtained without adding any triol to the reaction. Whereas only considering synthesis with glycerol added, we can observe that if we will use glycerol with superior amount, density will be greater also. Increase glycerol amount will increase the density.

The second group is a collection of synthesis with the same dicarboxylic acids with equal proportion and with identical TMP amount; the only variation is the type of diol (in case of those reactions BD, ISOR and MPG were used). The greatest density value was obtained when in the reaction is located BD without others diols.

it was difficult to assess The group C because the density determination of one reaction was impossible, and therefore using only two results we can assume that presents of glycerol peroxylate (MW=1500) did not influence on density of reaction in the same way as glycerol.

The most difficult to define is group fourth, in this group dicarboxylic acids in each synthesis possess different molar percentage values and triols used (glycerol propoxylate) have dissimilar MW. The highest density was obtain from three dicarboxylic acids used in synthesis.

The last group is collection of synthesis in which DEG, NPG and glycerol propoxylate with different MW were used. Far the most density value was received during the last synthesis, with DEG and glycerol propoxylate.

Table 7 The final results of acid value and hydroxyl value determination, number of days reaction occurred, colour of product and amount of water distilled during process

Numberof formulation (sinthesis	Capacity of	V <sub>AN</sub> [mg KOH/g	V <sub>он</sub> [mg KOH/g	MW	n⁰ of days	Colour	Reflux of water	Appearance
grade)	reaktor [l]	polyol]	polyol]	[g/mol]	(approx.)	[Gardner]	[ml]	
1. (AD+AS+BD+DEG)	2	4.93	16.15	5322.73	9	11'-12	244	Solid state
2. (AD+AS+BD+DEG+glycerol)	1	3.48	25.50	3871.45	7	11-12'	108	Solid state
3. (AD+AS+BD+DEG+glycerol)	1	3.64	29.09	3428.72	8	12	101	very viscous liquid
4. (AD+AS+BD+ISOR+TMP)	1	7.87	84.29	1217.44	1	•	106	gel
5. (AD+AS+BD+TMP)	1	6.91	86.15	1205.60	1		21.8	gel
6. (AD+AS+MPG+TMP)	2	4.9	67.76	1544.17	11	11'-12	205	viscous liquid
7. (AD+AS+BD+ISOR+glycerol)	1	2.46	115.24	953.23	5	13'-14	86	viscous liqiud
8. (AD+AS+BD+ISOR)	1	1.77	104.92	1051.63	1	•	45	gel
9. (AD+AS+BD+ISOR+glycerol perop)	1	4.45	17.92	5015.29	5	•	114.5	very viscous liqiud
10. (AD+MA+BD+glycerol prop)	2	5.96	59.13	1723.60	8	17'-18	78.5	solid
11. (AD+AS+MA+BD+glycerol prop)	1	167.99	-	-	4	8	128	viscous liqiud
12. (AD+AS+BD+glycerol prop)	2	5.26	50.24	2021.64	9	14-15	178	solid
13. (AD+AS+DEG+NPG)	2	3.82	6.77	10596.44	12	17-18'	216	solid
14. (AD+AS+DEG+glycerol prop)	1	5.63	51.29	1971.04	10	14	114	very viscous liquid
15. (AD+AS+DEG+glycerol prop)	1	5.87	28.34	3279.62	9	13	123	viscous liquid

### 3.5. Acid number versus Molecular weight

Relation between the acid number and MW of polyester polyols was described in Figures 24 and 25. However, for all the synthesized products the profiles of AN value against MW are very similar. For this reason, these figures are shown in appendix (Appendix A).



Figure 23 V<sub>AN</sub> profile against MW for sample No.10



Figure 24 V<sub>AN</sub> profile against MW for sample No.7

As it shown in the graphs during the reactions acid value decrease while the evolution of the MW (calculated from the  $V_{AN}$  and  $V_{OH}$  values) is defined as increasing. As it was mention before (in section 3.2) the desire was to obtain the acid value calculated by titration with O.1 N alcoholic solution of KOH equal less than five units (mg KOH/g polyol). If the first requisite was required and hydroxyl value determination was respectable, molecular weight achieved become very high and thus the MW is inversely proportional to these numbers.

### 3.6. Viscosity versus acid number

Relation between the viscosity and the acid number of the polyester polyol was described in Figures 26 and 27. The determination of viscosity was obtain in the temperature range between 25-175<sup>o</sup>C. However, to attain better visible results of relation graphs were made only in the case of one selected temperature. Figures of this correlation are also shown in appendix (Appendix A).



Figure 25 V<sub>AN</sub> profile against viscosity for sample No.2

The knowledge of profiles of variation between viscosity and acid value gives opportunity to find correspondence among them. As it is shown in graphs when acid value decrease then the viscosity is greater.



Figure 26 V<sub>AN</sub> profile against viscosity for sample No.7

### 3.7. FTIR-ATR

Polyester polyols formation was confirmed by FTIR-ATR. Spectra of samples with high MW and also the most solid state are presented below and in Appendix section of this thesis. All five group has at least one representative. Each sample posses two spectra, one is the spectrum of polyester polyol (A) blue colour), and the second one is spectrum of polyester polyol with MDI chain extender (B)green colour). Between polyesters polyols based on the same pair dicarboxylic acid/diol, no significance change was observed.

In order to evaluate the structural differences between polyester polyols and polyester polyols with MDI, the spectrums of elements are compared. It can be notice that the more relevant peaks presents in each one of the spectra showed, occurs for the same wavelengths.

Each functional group corresponds to range of absorption wavelengths, thus allowing it's identification by analysis of the infrared spectrum. The stretching vibrations of typical organic molecules tend to fall within district regions of infrared spectrum, as shown below:

- 3700 2500 cm-1: X-H stretching (X = C, N, O, S),
- 2300 2000 cm-1: C ≡X stretching (X = C or N),
- 1900 1500 cm-1: C=X stretching (X = C, N, O),
- 1300 800 cm-1: C-X stretching (X = C, N, O). [41]

Most organic molecules own single bond that is why the region below 1500 cm<sup>-1</sup> can become relatively multifaceted and is often referred to call as finger print region.

Starting identification of spectrum from the left side it can be notice that in the region 3500-3100cm<sup>-1</sup> stretching band of OH can be finding (Figure 28). The bands are broadened and sometimes may pass unnoticed (Figure 29), it may happen because of low intensity comparing to other peaks. It was expected that the presence of polyester polyol terminal OH group will be confirmed through FTIR-ART spectrum. However, the purpose of this determination was not quantitative, the fact that for all polyester polyols which were studied it is observed low intensively OH peak, can be explain by the reality that the ratio between the terminal hydroxyl groups and the other group which are parts of polyester polyol chain is rather significant. Beyond doubt OH vibration might be also treated as proof of the successful esterification process.



Figure 27 Transmission ATR-FTIR of Sample No.1

The peaks corresponding to the C-H stretching (on spectrums respectively 2930 and 2850 cm<sup>-1</sup>), are not significant, but easy to noticed.

The sharp intense band located at around 1700 cm<sup>-1</sup>, which corresponds to the saturated carboxylic acids. In case of both samples presented on Figure 28 and Figure 29 it can be observed that free carbonyl group is in the same position 1724 cm<sup>-1</sup> and 1726 cm<sup>-1</sup> respectively. It should be emphasized that the presence of the mentioned peak testified can be confirmation of accomplished the

esterification process. However in case of samples where MDI was added, according to the literature the free carbonyl group should appear at 1690 cm<sup>-1</sup>, that corresponds to urea, but in performed determination it was not found.

At lower wavenumber, significant peaks which are presented around 1140cm<sup>-1</sup> (1135 and 1147cm<sup>-1</sup> respectively) may be attributed of C-O linkage.



Figure 28 Transmission ATr-FTIR of Sample No. 6

### 3.8. Resistance hydrolysis and water absorption

The first requirement for hydrolysis is water absorption. After hydrolysis, molecules have some mobility and also occupy a greater volume than the polyester molecules from which they came. The result is internal pressure. The pressure, along with the natural mobility of the molecules, elevated temperature accelerates the hydrolysis reaction. Delaminating and blistering are possible if polyester has poor resistance to hydrolysis.

In order to assess the impact on resistance to hydrolysis, short at temperature 95<sup>o</sup>C during 2 and 5 hours and long at temperature 24<sup>o</sup>C for 15 days water absorption were conducted on several samples, those with the highest MW and most solid state, results are listed in Table 8.

Considering long time (15 days) water absorption the polyester with the highest percentage gain of weight and this one with the lower can be easy marked (sample no. 2 and sample no.12 respectively).

Number of formulation		Short time water (temp. 95 <sup>0</sup> C)	Long time water absorption (temp. 24 <sup>0</sup> C)		
		2 hours	5 hours	15 days	
1.	+MDI	9.78	6.612	5.32	
2.	+MDI	13.88	18.8	12.16	
6.	+MDI	3.9	7.58	2.26	
12.		3.08	7.58	0.69	
13.	+MDI	6.01	4.4	3.53	

Table 8 Weight gain of the samples after short and long time water absorption test

The first remark to make after the analysis of Figure 30 is that one prepolymer polyol sample has clearly the highest value of water absorption (sample 2, the same one as in case of long time water absorption). But it need to be mention that this sample during the test melt slightly and hence change its previous shape.

For two samples (sample No 1 and sample No 13) the most significant weight increase happened during first two hours of immersion. Those samples also possess the highest MW from those that were determined during the test. This is entirely reasonable since through immersion in 95<sup>o</sup>C water two phenomena may take place. First one is water absorption with successive swelling and weight increase. The second one is hydrolysis of chemical bonds with subsequent loss of small molecules to the water and weight decrease. The polyester polyols are hydrophobic and thus more hydrolysis-resistant. Very relevant is acid value of the polyester, the lowest acid value yielding the more stable polyurethane. The lower the water solubility of the diacid or diol used to make a polyester, the greater the resistance to hydrolysis.

The hydrolysis resistance could be also evaluated by the visual aspect and the texture of polyurethanes samples after absorption test. However the most important is the weight loss or gain.

Samples discussed above, those with the highest MW (sample No 1 and sample No 13) had maintained their shape and consistency, although they become wider. Whereas, sample No 2 had clearly lost it mechanical resistance as it even could not retain the original shape for the test trial. Samples No 6 and No12 keep up their shapes although they become slightly softer then at the beginning of the test.



Figure 29 Short time water absorption to define hydrolysis resistance

### **Chapter 4**

### 4. Conclusions

The experimental part of this work involved synthesis of saturated polyester polyols with dimer acids, which can be used as building blocks for the polyester macromolecular structure. Different molecular structure were achieved, however main goal of this thesis was to obtain saturated polyester polyols with high molecular weight. Target has been attained fully only once. However, strong and stiff polyester polyols with low acid value and fairly low hydroxyl value and high viscosity were obtained. Hardness of products was obtained by the use of an chain extender which also increase the performance at elevated temperatures. The role of chain extenders is very important in the enhancement of certain polyurethane properties; together with MDI (Section 2.2.5.) they increase the hard segment content.

Confirmation of successfully conducted process of polyesterification was confirmed via FTIR-ATR spectroscopy. All spectra which have been obtained show satisfactory results. On the other hand in case of samples with MDI free carbonyl group corresponds to urea group was not found. Nevertheless, additionally transmission test should be performed to confirm fully structure of product.

Biodegradable behavior is last feature of the important characteristics that the present work intends to prove. The use of dimer acids in the polyester backbone structure is a way of improving the hydrolysis resistance of such prepolymers because dimeracid-based polyesters contain a higher content of methylene groups per repeating ester unit than usual which confers them a highly hydrophobic character to the polyester backbone.

### 4.1. Future perspective

As for the future recommendations, the supplementary work with obtained products should be done focus on the biodegradability test. Water absorption and hydrolysis resistance is just first indication on polyesters polyols chain extended by MDI have biodegradability properties. Advance work in this area need to be performed.

Moreover, new synthesis formulation should be performed to gain broader understanding on the strategies to obtain higher molecular weight.

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# Appendix A



FigureA 1  $V_{AN}$  profile against MW for sample No.2



FigureA 2 V<sub>AN</sub> profile against MW for sample No.3



FigureA 3 V<sub>AN</sub> profile against MW for sample No.1



FigureA 4 V<sub>AN</sub> profile against viscosity for sample No.1



FigureA 5 V<sub>AN</sub> profile against viscosity for sample No.3



FigureA 6 V<sub>AN</sub> profile against viscosity for sample No.11



FigureA 7 Transmission ATR-FTIR of Sample No. 7



FigureA 8 Transmission ATR-FTIR of Sample No. 9



FigureA 9 Transmission ATR-FTIR of Sample No. 12



FigureA 10 Transmission ATR-FTIR of Sample No.13