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Study of the production of polyesters for polyurethanes at pilot plant scale

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“I have not failed. I've just found 10,000 ways that won't work.”

Thomas A. Edison (1847-1931)

To all friends, colleagues and family.

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I would like to thank my supervisors, Professor João Fernando Gomes and João Carlos Bordado, whose expertise, understanding, and patience, added considerably to my MSc graduating experience.

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This work would also not have been possible without the support of my colleagues, giving me attention for the importance of this study of production of polyesters for polyurethanes at pilot plant scale.

Production process of saturated polyester polyols for flexible polyurethane foams

ABSTRACT

In the present work during an internship in ICTPOL (IST), we tried to develop a relationship between all the works done. Understanding variables that affect production of unsaturated polyester polyols based on dimer fatty acids Unidyme®14 and Unidyme®18 with ethylene glycol and 1,4-butane diol that were synthesized via the polycondensation reaction mechanism. We studied a fast way to determine molecular weight, which usually takes a lot of time and that is not very economical and ecological.

Among the experimental controlled parameters for each polyol synthesis a special attention was paid to these products viscosity, color, molecular weight, acid and hydroxyl value parameters of extremely commercial importance.

The Unidyme®14 dimer fatty acid, having a dimer acid percentage of 94%, induces the polyols based on them to be products of relatively commercial relevance. As for the Unidyme® 18 dimmer fatty acid, its dimer percentage is 81,8%. Unidyme®18 its based polyols commercial interest is specially relevant not only when a lower cost is a relevant factor, but also when its trimmer content is important to confer non-crystallinity properties to the final end product.

Additionally, flexible polyurethane foams were developed from the 1250 and 2000 molecular weight polyester polyol and tested regarding oil absorption capacity.

Keywords: polyester polyol, dimer fatty acid, Unidyme® 14, Unidyme® 18, flexible polyurethane foam, renewable sources.

Processo de produção de polióis poliésteres saturados baseados em ácidos gordos diméricos para produção de poliuretanos flexíveis

RESUMO

No presente trabalho durante o estágio no ICTPOL(IST) foram sintetizados alguns polióis poliéster saturados a partir dos ácidos gordos diméricos Unidyme®14 e Unidyme ®18 da Arizona Chemicals e dois dióis, etileno glicol e 1,4-butanodiol, através do mecanismo reaccional de policondensação. Foram estudadas as variáveis que afectam a produção dos poliésteres-poliois baseados nestes, tais como a viscosidade, cor, peso molecular e o valor ácido e hidróxido, todos com especial interesse comercial para especificação do produto final.

Foi estudado um método mais rápido para determinação aproximada do peso molecular de um determinado poliol, que habitualmente tem tempos elevados de análise e não é muito económico e ecológico

O ácido gordo dimérico Unidyme®14, tendo na sua constituição uma percentagem de dímero de 94%, e o Unidyme®18, com uma percentagem de dímero de 82% leva a que os produtos derivados tenham valor comercial elevado para produção de polióis difuncionais.

O interesse comercial deste polióis é baseado no facto de estes poderem produzir produtos de elevado valor comercial e serem derivados de fontes renováveis.

Posteriormente, foi testado o uso de alguns destes poliésteres na produção de espumas flexíveis de poliuretanos para tendo como base os polióis de massa molecular 1250 e 2000, e testadas quanto à capacidade de absorção de vários tipos de óleos.

Palavras-chave: poliol poliéster, ácido gordo dimérico, Unidyme®14, Unidyme®18, espuma flexível de poliuretano, produtos biológicos recicláveis.

List of Abbreviations and Symbols

[NCO]	Concentration of the functional isocyanate group given as %
V_H	Acid number (mg KOH / g polyol)
V_{OH}	Hydroxyl number (mg KOH / g polyol)
AZC	Arizona Chemicals
BD	1,4-Butanediol
CPB	Companhia Petroquímica do Barreiro
dPa.s	Deci Pascal second (viscosity unit; 1dPa.s = 100 cp = 1E-01 Pa.s)
DABCO	1,4-diazabicyclo[2.2.2]octane
DIN	German Institute for Standardization
DBTL	Dibutyltin dilaureate
DOP	Dioctyl Phthalate
EG	Ethyleneglycol
FTIR	Fourier transform infrared spectroscopy
ISOR	Isosorbide
ICTPOL	Instituto de ciência e tecnologia de polímeros
IST	Instituto superior técnico
mPa.s	Mili Pascal second (1mPa.s = 1 cp = 1E-03 Pa.s = 1E-02 P)
MDI	Methylene diphenyl 4,4'-diisocyanate
MW	Molecular weight
NCO	Isocyanate group
PID	Proportional-integral-derivative (controller)
PET	Polyethylene terephthalate
Polyol	Polymer with functionality higher or equal to 2
PU	Polyurethane
THF	Tetrahydrofuran
U14	AZC dimer acid (94% in mass)
U18	AZC dimer acid (81.8% in mass)

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1. Introduction

1.1 Polyesters

1.1.1 History and uses

Polyesters are one of the most important classes of polymers in use today. In their simplest form, polyesters are produced by the polycondensation reaction of a glycol with a difunctional carboxylic acid.

Hundreds of polyesters exist due to combinations of dialcohols and diacids, although only about a dozen are of commercial significance [1].

The first attempt to make an alkyd or polyester resin is attributed to the Swedish Chemist Jons Jacob Berzelius who, in 1847, reacted tartaric acid with glycerol to obtain a resinous mass [2].

During many years many materials were laboratory synthesised, but only in 1941-1942 the first commercially produced unsaturated polyester appeared from Pittsburgh Plate Glass Company [2], although some report that the true synthesis of aliphatic polyesters previously began in 1930s by Carothers at DuPont in the USA [1].

The dimer acid based polymers are reported to be useful in both rigid and flexible foam formulations. They are useful in surface coating applications and they find a wide variety of applications for hot melt adhesives, films, lubricants and so forth. The major applications for the dimer acid based polyester films so far is in food packaging materials and shrink labels [3].

The world production capacity is nowadays 3.5 million tonnes and a growth rate of 4% per year is forecasted [4].

In Europe, production of polyesters in primary forms has been relatively constant for last 6 years (see figure 2).

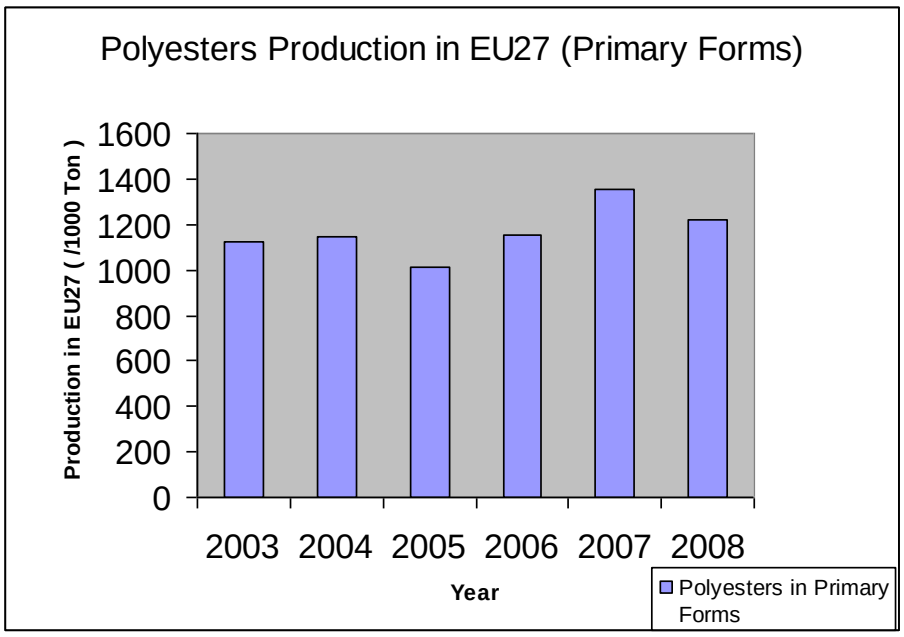


Figure 1: European production of polyesters in primary forms (Font: EuroStat).

1.1.2 Raw materials and synthesis

Polyols are polymeric materials with molecular weight between 200 and 12000 and OH functionality of two or more. They can be solid, but they are often liquid at room temperature. The three main types of polyols are polyether, polyester and acrylic [3].

The typical reaction scheme has an equimolar ratio, as follows:

$$n\ R(OH)_2 + n\ R´(COOH)_2 \rightleftarrows HO[ROOCR´COO]_nH + (2n-1)\ H_2O \quad (1.1)$$

But for polyurethane flexible foams where acid value must be low, an excess of diol must be used, so that polyester have the minimum of carboxylic terminations.

$$(n+1)\ R(OH)_2 + n\ R´(COOH)_2 \rightleftarrows HO[ROOCR´COO]_nROH + 2n\ H_2O \quad (1.2)$$

With an equilibrium constant K, defined as follows:

$$K = \frac{[polyester\ polyol][water]^{2n}}{[diol]^{n+1}[diacid]^{n}} \quad (1.3)$$

Therefore, it is influenced by the presence of water in the equilibrium with the reactants and the polymer. The removal of water in the later part of the reaction process is essential for the development of the required molecular weight (MW). During polyesterification resins normally lose between 5 and 12% of initial weight as condensate, depending on the final MW [1].

Due to the equilibrium of the esterification reaction, all polyesters are to some extent degradable in presence of water (by cleavage of the ester bonds). However, the strong hydrophobic character of the aromatic polyesters repels water from the proximity of the ester bonds. Therefore only aliphatic polyesters will degrade over observable time scale [5]. Actually, aliphatic polyesters belong to the group of the most used biodegradable polymers [6].

Some critical factors during the reaction are the reaction temperature, the agitation, the quality and flow of inert gas used.

The presence of an inert gas, such as nitrogen or carbon dioxide, not only prevents oxidation, but it also helps to remove the water formed during the polycondensation reaction. Usually, the sparge rate of the inert gas is increased at the final stages of the polyesterification to assist to the removal of the residual water. Although, the removal of water can be facilitated by using a reduced pressure[2].

Usually, the reaction is carried out at temperatures in the range of 190-200ºC for the synthesis of low MW polyesters, while a temperature above 200-220 ºC is maintained to guarantee the polyester has higher MW.

The temperature plays an important role in these polyols synthesis. While at 120- 140ºC the reaction is extremely slow (the change in the acid number is negligible), at 160, 180, 200ºC the velocity constants for the uncatalyzed polyesterification increase [3].

1.1.2.1 Diols

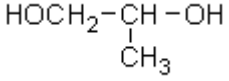
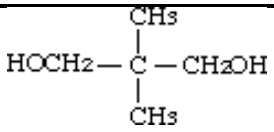
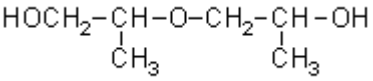
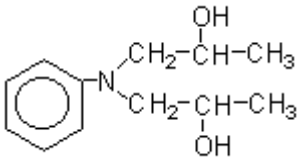
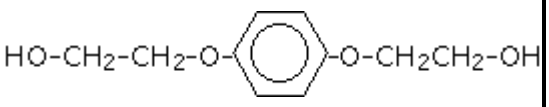
An excess of diol over dimer acid is always used. Due to its vapor pressure at working temperature some will be lost as condensate.

The molar ratio of monomers not only determines the MW but it also controls the nature of the end group of the polyester [7, 8].

The hydroxyl- group- terminated polyesters are further important from the point of view of their applications as pre-polymers for various other polymers as polyester-PUs copolymers, polyesterpolyamide copolymers.

Flexibility, crystallinity, water and heat sensibility are properties which are particularly affected by the choice of alcohol [9].

Table 1: Most common bifunctional diols used for polyol production.

Compound	Structure	MW
ethylene glycol	HOCH2-CH2OH	62
di-ethylene glycol	HOCH2-CH2-O-CH2CH2OH	106
propylene glycol		76
neopentyl glycol		104
di-propylene glycol		134
1,4 butane-diol	HOCH2-CH2-CH2-CH2OH	90
2-methyl-1,3-propylene-diol	HOCH2-CH(CH3)-CH2OH	90
N-N'-bis-(2 hydroxy-propylaniline) (DHPA)		221
1,4-di-(2-hydroxyethyl) hydroquinone (HQEE)		198

Ethylene glycol (EG) is the simplest glycol having a symmetrical structure, and is also widely used in industry for making polyester resins [10] EG is often used because of its reduced cost, whereas diethylene glycol (DEG) produces a more flexible polymer that can resist cracking when impacted [2].

Another diol is not commonly used, but as it comes from renewable sources and it was used in present work is isosorbide (ISOR) which is produced from sorbitol. Its structure is represented in figure 2.

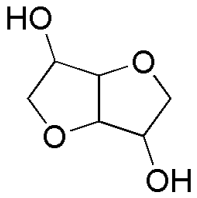


Figure 2: Structure of isosorbide

1.1.2.2 Diacids

We will focus on polyesters based on Unidyme®14 and Unidyme®18 dimer acids.

Dimer acids are commercial products resulting from clay-catalysed, high temperature polymerization of unsaturated fatty acids, usually oil fatty acids [11, 12]. The products have been commercially available since the 1950´s [13].

One type of naturally occurring fatty acids used to produce these dimer acids are palmitic , oleic and linoleic acids, available from tall oil fatty acids (TOFA), a by-product of wood industry [14].

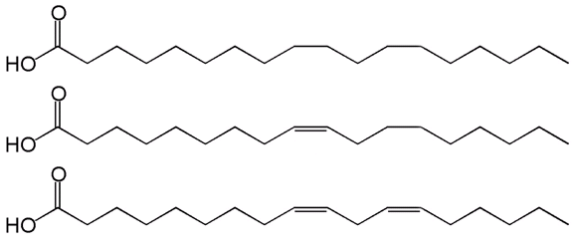


Figure 3: Structure of palmitic, oleic and linoleic acids.

Under the appropriate conditions, one molecule of unsaturated fatty acid reacts with another to form a dicarboxylic acid with double the original molecular weight with following typical structure (figure 4).

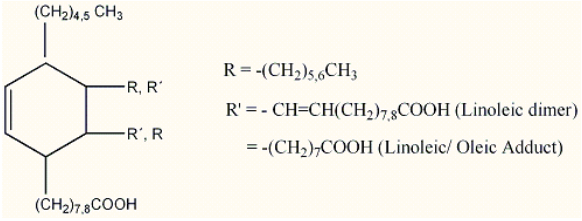


Figure 4: General structure of dimer acid.

Trimers of the original fatty acid can also be formed, making a mixture of monomers, dimers and trimer acids, which need to be distilled to increase concentration of dimer species. Even so, the final product still has some mixture content of monomers and trimers, but the product is sold as "dimer acids".

Between 2000 and 2010, the production of fatty acids is expected to rise from 3.05 to 4.00 million tonnes worldwide [11].

These dimers are chosen because they are from renewable sources, and oleochemical-based polymers that uses vegetable fats and oils enables the synthesis of competitive products that are both consumer and environmentally-friendly [15, 16].

In these dimer acids more than one hydrocarbon isomer is present, which decreases their crystallinity. They do not crystallize and contribute to flexibility in polymers derived from them [3, 17]. Their average molecular weight is 560 g/mol [3].

The main purpose of using dimer acids as components in the formulation of polymers, beside that they come from renewable sources, is to impart special characteristics to the final product such as elasticity, flexibility, high impact strength, hydrolytic stability, hydrophobicity and lower glass transition temperatures [15].

The next table presents some properties of some of these compounds, produced by Arizona Chemicals:

Table 2: Properties of some Unidyme® Products. (Font: Arizona Chemicals).

	Typical Properties						
	% Monomer	% Dimer	% Trimer	Color Gardner	Acid Value	Viscosity (cSt 25° C)	Saponification Number
UNIDYME® 10	0.1	99	0.9	1.8	197	6,450	201
UNIDYME® 14	0.2	94	5	5	196	7,250	201
UNIDYME® 18	1.7	82	17	6	195	8,900	200
UNIDYME® 22	2	81	17	7	195	8,900	199
UNIDYME® 35	3	80	18	10	193	9,400	200
UNIDYME® M15	10	75	15	7-	189	5,410	197
UNIDYME® 40	0.5	64.5	35	11-13	185	25,000	200
UNIDYME® 60	0.5	44.5	55	14	192	40,000	201

For the linear polyesters that we intend to obtain, the most important component is dimer acid content which has functionality of two and can make long chain polymers.

The range of applications for dimer acids has been growing. In 1987 [18] the main uses for dimer acids were polyamides, polyesters, curing component for epoxy resins, lubricants, plasticizers and pesticides. Nowadays, the applications mentioned in the technical leaflets of two major players in the dimer acid market [19] are polyamides, polyesters, corrosion inhibitors, rheology modifiers, additives for fuel and lubricant, polyamide and epoxy resins curing agents, intermediates for personal care, surfactants, polyurethane polymers, ink resins, surface coatings, paper chemicals and fatty alcohols.

Another important and growing application of dimer acids in the polymer field is the production of dimer based polyesters that can be used in further reactions to produce polyurethanes or polycarbonates [20-23].

1.1.3 Actual scenario

Many recent studies are trying to use only renewable sources for raw materials used in polyester production.

Some examples include the use of monoglycerides prepared from rubber seed oil [24], potato starch and natural oils by a transesterification reaction [25], Oleic acid (1) from "new sunflower," linoleic acid (2) from soybean, linolenic acid (3) from linseed, erucic acid (4) from rape seed, and ricinoleic acid (5) from castor oil [26-29] and even soybean oil [30].

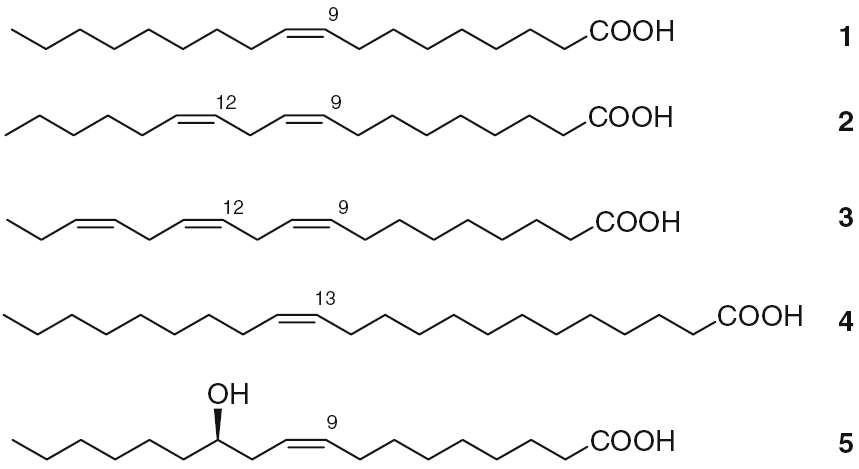


Figure 5: Some structures of bio available fatty acids.

Succinic acid is also predicted to be one of the future platform chemicals that can be derived from renewable resources [31], and other simple acids that can be used are malic acids and citric acid [32].

Polyesters produced from renewable resources and susceptible to hydrolysis under the industrial composting conditions offer ecological advantages as compared to thermoplastics polymers and elastomers produced from fossil carbon sources [33].

1.2 Polyurethanes

1.2.1 History and uses

Polyurethanes are among one of most important class of specialty polymers. Although the reaction between isocyanate and hydroxyl compounds was identified in the 19th century [34]. The basis of the polyurethane industry was started with the discovery by Otto Bayer and co-workers in 1937 [35, 36] of the polyaddition reaction.

Since then the polyurethanes have found many different applications and the polyurethanes market has been growing uninterruptedly [37].

Polyurethanes (PU) are polymers containing urethane linkages (–NHCOO–) in the main polymer chain.

Polyurethanes (PU) have developed as a unique class of materials and have found use in a wide variety of applications [35, 36].

They can be classified in the following major groups: flexible foams, rigid foams, elastomers, fibers, molding compositions, surface coatings and adhesives.

Polyester polyols used in the foams are based on industrial waste streams of polyester and depolymerized PET from scrap bottles. Flexible foam is based on a flexible aliphatic polyester polyol (such as adipic polyester resin) and rigid foam is prepared from aromatic polyester polyol, e.g. depolymerized PET [30].

The main raw materials used for preparing PU are polyisocyanates, polyols, diamines, catalysts, additives, and blocking agents. Polyols are either polyethers or polyesters.

By controlling variables such as the functionality, chemical composition, and the MW of the different reactants, a wide class of materials with significantly varying properties can be obtained. This flexibility has led PU to find use as synthetic polymers in foams, elastomers, coatings, sealants, and adhesive based products. Some of the applications of PU lie in the automotive, furniture, construction, thermal insulation, and

footwear industries. The 2000 urethanes market was estimated to be of the order of 8.2 million tonnes worldwide (Figure 6) [4].

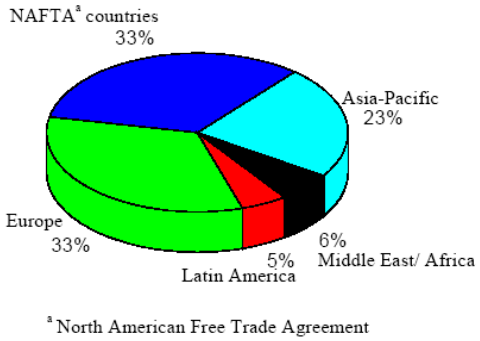


Figure 6: Worldwide Consumption of PU.

Flexible foams are one of major sectors of the PU industries, which occupy the sixth position among all plastics sold. These foams provide a combination of versatility, light weight, durability, and ease of fabrication at a reasonable cost [38].

1.2.2 Raw materials and synthesis

Urethane functional groups are based in isocyanate and alcohol reaction:

$$R^1\text{-}N{=}C{=}O + R^2\text{-}O\text{-}H \longrightarrow R^1\text{-}\overset{H}{N}\text{-}\overset{O}{\overset{\|}{C}}\text{-}O\text{-}R^2 \qquad (1.4)$$

The use of bifunctional isocyanates and diols will produce the so called polyurethanes.

The first commercial production of flexible PU foams, based on the reaction between an aromatic isocyanate and a polyester polyol, was carried out in 1954.

However, these foams were unable to withstand the severe humidity and temperature conditions in which they were used, and thus foams based on polyether polyols were developed. This second generation foams provided better durability as well as comfort. A major advancement in PU technology was the introduction of the 'one-shot' system using new catalysts and silicone-based surfactants. In the one-shot process; the isocyanate, polyol, water, and other ingredients are rapidly and intensively mixed and immediately poured to carry out the foaming. Since then, advances in

flexible PU foam technology have been numerous, all targeted to provide the customer with enhanced performance properties, while trying to improve processability, increase production rates, and lower costs. The more than five-decade-old technology of PU foams might have been expected to reach a mature growth by now (Figure 7).

However, formulations based on newer and more sophisticated applications continue to develop, thus demanding a better understanding of the structure-property correlations.

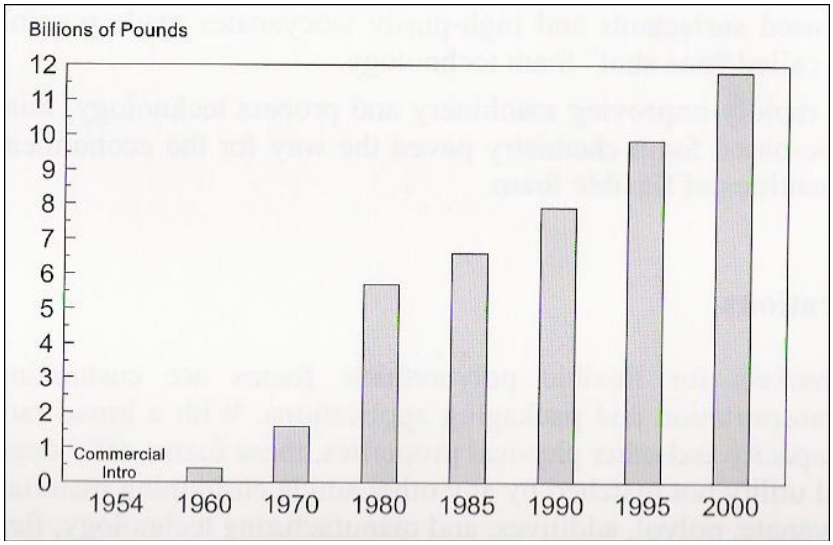


Figure 7: Global market growth for flexible PU foams [38],

1.2.2.1 Isocyanates

The polyurethane industry is mostly based on isocyanate chemistry. The functional group of isocyanates, -NCO, is capable of undergoing several different types of chemical reactions and is highly reactive toward proton-bearing nucleophiles such as alcohols, water, amines and urethanes [39].

The isocyanate, which provides the NCO groups that are essential to the PU production reaction, is quite important to the final physical and chemical properties of the foam.

Although there are many isocyanates available in the market, most all of the PUs are based only on two of them. These are toluene diisocyanate (TDI), and the diphenylmethane diisocyanate (MDI) and its derivatives. The first is used mainly in the production of low-density foams, but its use under certain working conditions was not advisable for safety issues, giving therefore rise to the development of MDI.

The MDI used in PU production is a dark colored liquid, less hazardous than TDI due to its lower vapor pressure at normal temperatures [40]. Despite this, MDI is still a very reactive and toxic reagent. MDI is prepared from aniline, formaldehyde, and phosgene according to the following general reaction scheme:

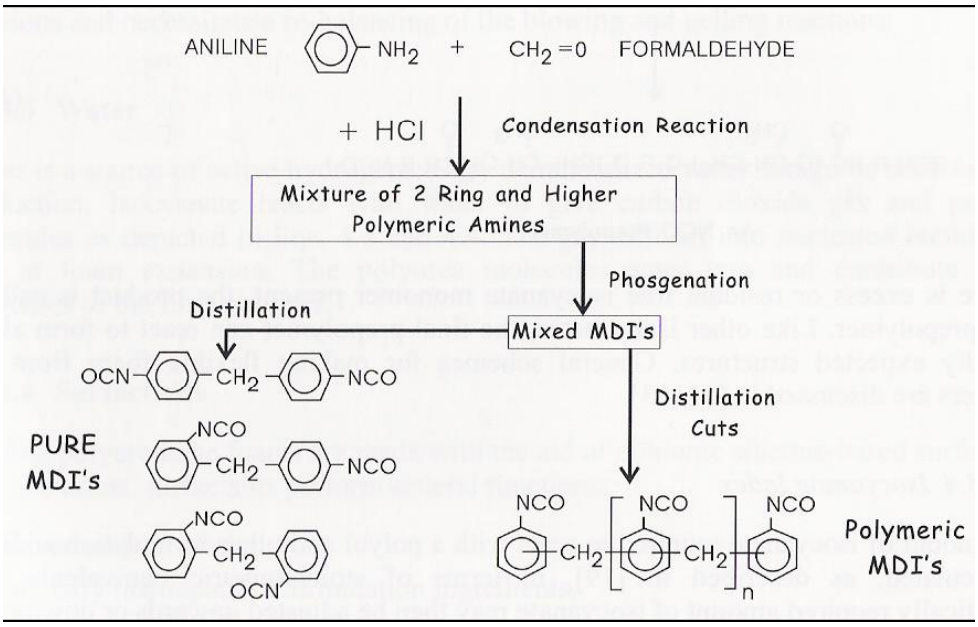


Figure 8: General scheme for MDI production [38]

Isocyanate index.

The equivalent weight is the amount of reactive functional groups on the polymer chain. For an isocyanate, the reactive group is -N=C=O (NCO) its concentration is measured by weight percent NCO [41]. And its equivalent weight:

$$Isocyanate\ equivalent\ weight = \frac{4,2}{\%NCO}\ g/eq \qquad (1.5)$$

For a polyol, the reactive group is -O-H (OH). OH concentration is measured by the hydroxyl value (mg KOH/g sample). The equivalent weight is as follows:

$$Hydroxyl\ equivalent\ weight = \frac{56,100}{V_{OH}}\ \text{g/eq} \qquad (1.6)$$

When reacting an isocyanate with one or more polyols to form a PU, one NCO group reacts with one OH group. When the number of NCO groups equals the number

of OH groups the stoichiometric NCO/OH ratio is 1.0. This ratio is commonly referred to as the index (or %). The amount of MDI required to react with a given polyol blend is calculated from the desired index (often 1.0 - 1.05), the MDI equivalent weight (MDI eq. wt.), and the weight fractions (pbw) and equivalent weights of the polyols and any water present in the blend, as stated below [41]:

$$\text{Total weight of MDI required} = (\text{index})(\text{MDI eq. wt.})\left(\frac{\text{pbw polyol A}}{\text{eq. wt. polyol A}}+\frac{\text{pbw polyol B}}{\text{eq. wt. polyol B}}+\cdots\cdots+\frac{\text{pbw polyol N}}{\text{eq. wt. polyol N}}+\frac{\text{pbw } H_2O}{\text{eq. wt. } H_2O}\right) \quad (1.7)$$

1.2.2.2 Polyester polyols

Polyesters can be designed to have hydroxyl groups and their chain, so they can thus be used in polyurethane synthesis. The use of aliphatic polyesters with high MW has been extremely important for the development of new PU because their incorporation in such structure means the integration of flexible segments between rigid aromatic isocyanate segments [5].

Polyesters have been largely replaced by polyethers in most of foam areas as well in sealant applications. However they are still used extensively for the production of elastomers, coatings and spandex fibers [37, 39, 40, 42, 43].

1.2.3. Flexible Polyurethane foams and its chemistry

The electronic structure of the isocyanate group allows the following resonance structures to contribute to the hybrid:

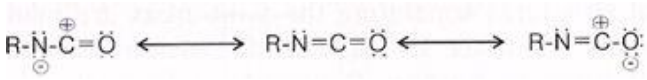


Figure 9: Resonance structures of the isocyanate group [38].

The electronic density increases from the carbon to the nitrogen and from the nitrogen to the oxygen. In the chemistry of the isocyanate group dozen of reactions are known, but the ones of most interest to foam chemistry are shown in the Figure 10 [38]:

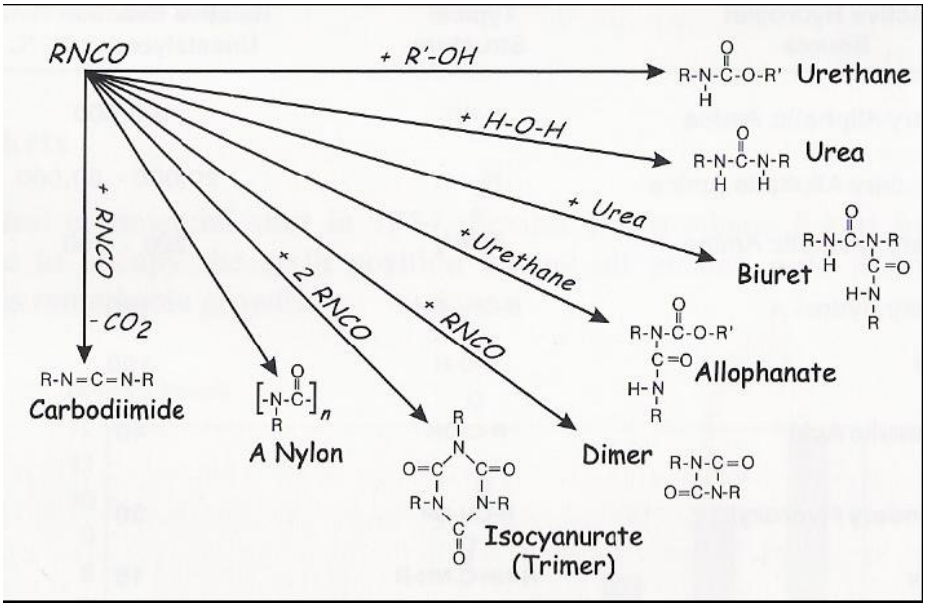


Figure 10: Major isocyanate reactions[38].

The flexible PU foams are manufactured by the controlled expansion of a gas during the polymerization process. They are designed to be open-celled, i.e., at the completion of foam expansion, the cells open and form a structure composed of interconnected polymer struts, which allow the free movement of a gas within the foam cells. The successful production of a cellular urethane is highly dependent on the relative rates of the two important competing reactions, that of isocyanate with water and isocyanate with polyol (figure 10).

The first of these is the primary blowing reaction, producing carbon dioxide and ultimately urea structures within the foam. The second reaction produces the urethane linkages which constitute the bulk elastomeric structure. They are often referred to as the "blowing" and "gel" reactions respectively [44].

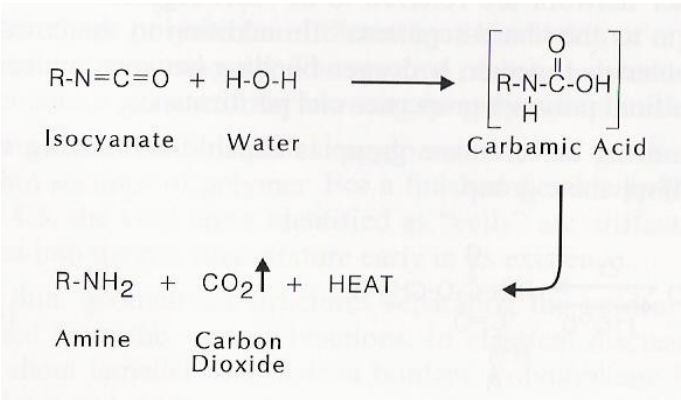


Figure 11: The "blowing" reaction [38].

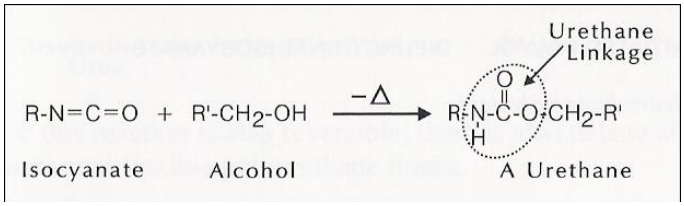


Figure 12: The gel reaction.

The chemical reactions involved generate the foaming mass as well as the heat necessary to cure the resulting foam. During these reactions the initially closed cell structure is converted to an open cell structure.

- Water

Water is a source of active hydrogen. Only demineralised water should be used for foam production. Isocyanate reacts with water to give carbon dioxide gas and polyurea molecules as depicted in Figure 11.

The gas diffuses into nucleated bubbles and is the key factor for the foam expansion. The polyurea molecules enter into and contribute to the properties of the final polymer.

- Surfactants

Surfactants act as emulsifiers and foam stabilizers in the foam manufacturing process. They contain both hydrophobic and hydrophilic groups, enabling them to retain an affinity for both water and organic phases and thus remaining at the interface. Surfactants also help to control the size of the foam cells by stabilizing the gas bubbles formed during the nucleation and reduce stress-concentrations in the thinning cell walls. Most common surfactants used are silicone or silicone-based surfactants.

- Catalysts

The manufacture of flexible PU foam is made with the aid of at least one catalyst. From all the investigated compounds, the amines and the organometallics show to be the most useful. The organometallic catalysts are virtually all tin based and promote the gel reaction (Figure 12) almost exclusively. The most popular organometallic catalysts are dibutyltin dilaurate (DBTL) and stannous octoate.

Unlike the tins, the amines catalyze both the blow and the gel reactions to a significant degree, and thus afford controllability not possible with a tin catalyst. The

amine catalysts most often employed are triethylene diamine (DABCO), bis (2-dimethylaminoethyl) ether, and other such amines. The type and concentration of amine catalyst(s) can be selected to satisfy process requirements such as cream times, rise profiles, gel times, and even cure of the outer surface skin [45].

The Figure 13 shows the effect on cell-openness of varying the concentration of the catalysts.

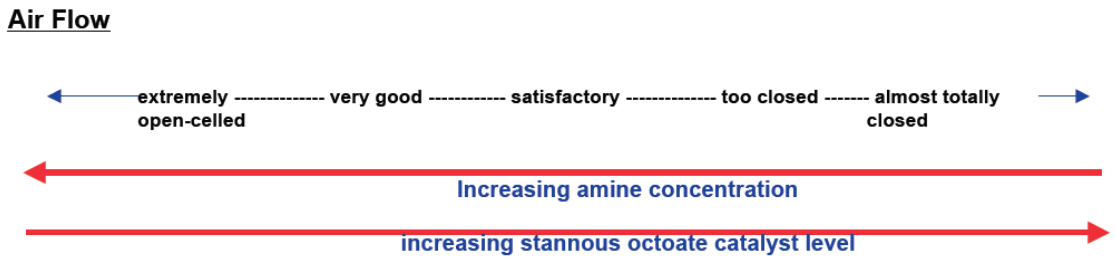


Figure 13: Catalyst variation effect on cell-openness[46].

In mixing step several different ingredients, some of which are incompatible with one another are combined. The silicone surfactant, soluble in the PU intermediates, functions as an emulsifier promoting efficient mixing. Good emulsification of the reacting mixture contributes to superior flowability, and also improves blowing agent utilization, resulting in lower foam densities. Figure 14 represents the several phases of foam formation [47].

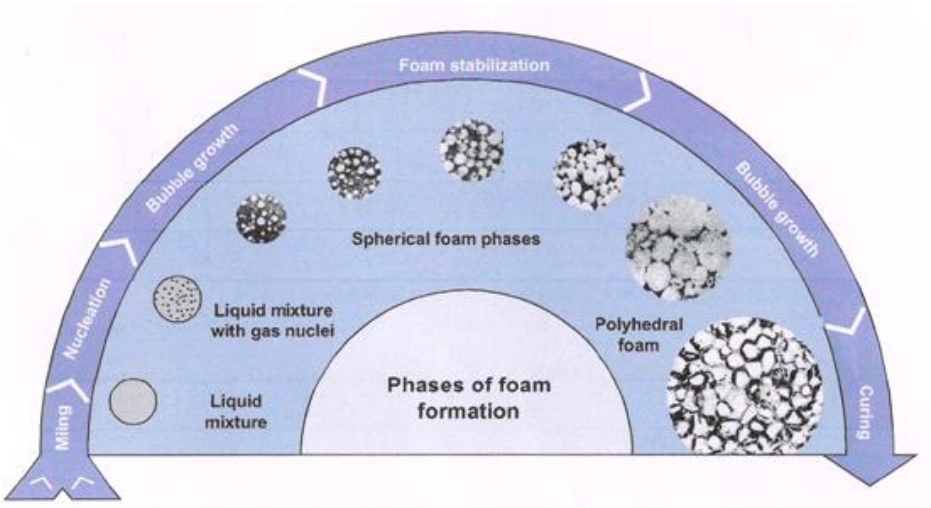


Figure 14: Phases of foam formation [48].

In nucleation step bubbles of air are introduced during the mixing process of the foam ingredients. In the absence of any surfactant the volume of air introduced is very small. This results in foam with finer, more uniform cells. The mixing and nucleation take around 10 seconds.

After that bubble growth starts, where diffusion of newly formed gas into existing bubbles, simultaneously with the heat of reaction vaporizes the liquid blowing agent. At this point, the dissolved gas begins to come out of the solution.

There is also expansion of gas in the bubbles due to heat of reaction.

After bubbles are formed in the developing foam system, these bubbles must be stabilized until the cell structures attain structural integrity through polymerization. The surfactant must operate to make the liquid draw toward the thinned area, and restore the original thickness of the cell wall (Figure 15). The surfactant functions to stabilize or reduce surface tension gradients (thinning in the cell walls) by allowing the surface layer to diffuse from areas of lower to those of higher surface tension, thus restoring the film to its original thickness [37, 47, 49].

The bubble growth and bubble stabilization takes around 20 seconds [48].

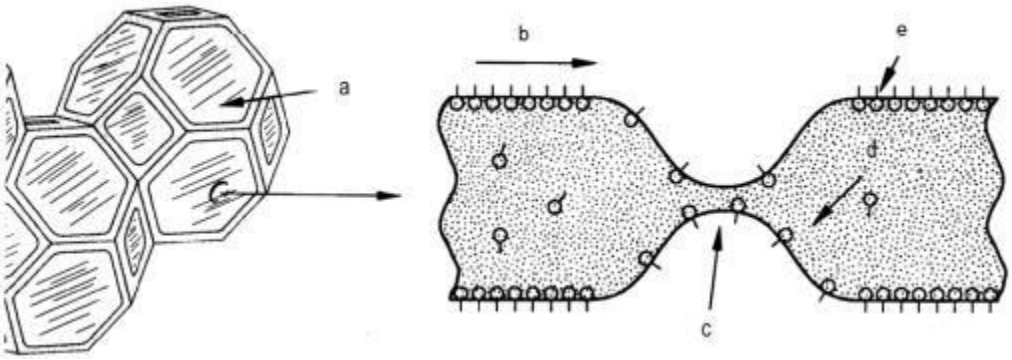


Figure 15: Thinning in a cell window, a) intact cell window; b) surface transport; c) thin area with rupture danger; d) bulk transport; e) surfactant molecules.

Water absorption for polyurethanes is a critical factor in applications where this kind of material is exposed to a wet environment either continuously or periodically.

Higher hydrophobicity is of special importance for polyester backbones to prevent the ingress of water molecules and resulting hydrolysis [50]. Therefore, low water absorption or good hydrophobicity is a prerequisite for polyurethanes to be hydrolysis-resistant [51].

1.2.4. Polyurethane foams for oil absorption and current scene.

The cleaning of the sea or river water after an oil spill has always been of major importance when these accidents happen. There are already some solutions that act as oil absorption materials but the majority is either a complex system or the material they are made of, is not easily biodegradable.

The objective is to present a novel type of polyurethane foam whose structure is specially designed for oil absorption, taking advantage of the high hydrophobicity and oleophilicity of dimer acids based polyesters [52].

Currently many studies in the polyurethane industry involve biodegrability for ecological purposes. Some prepared from castor oil and glycerol [53], some using sugar alditols as a source of hydroxyl function [54, 55], starch based [56] or isosorbide , a diol derivate of sorbitol [57].

Also studies have also been made about biodegradability of novel polyurethanes in seawater [58].

2. Synthesis of polyester polyols from dimmer fatty acids

2.1 Raw Materials

The main raw materials used for the production of the polyester polyols were a dimer fatty acid and one or more glycols.

2.1.1. Fatty Acids

The fatty acids used to produce the polyester polyols in the present work were the Unidyme®14, Unidyme®18 and Tall Oil Fatty Acids (TOFA) from AZC (Arizona Chemicals). These are essentially dimer acids: for the Unidyme®14, the percentage of dimer is 94% and for the Unidyme®18, this percentage is 81.8% (it has still in its composition 16.5% of trimer, what is convenient in terms of flexibility for the foams produced with this dimer fatty acid as raw material). Moreover, in terms of cost, the Unidyme®18 products are less expensive than the Unidyme®14 product because it is less pure. Tall Oil Fatty acids are monofunctional fatty acids which are used to produce dimer acids.

2.1.2 Glycols

The glycols with functionality 2 used in the present work were the 1,2-Ethylene glycol (EG) and 1,4-Butanediol (BD). The chemical structure of these polyols as well as their MW is also shown in the Table 1. We have also used other diol, not commonly used in polyesters which is ISOR.

All the glycols used were provided by Companhia Petroquímica do Barreiro (CPB), except ISOR that was offered by Cargill.

Glycol Corrections:

If V_{OH} lowers from the set value (so it means that MW is already higher than the projected one), we must add additional glycol mass, which can be estimated by following equation:

$$Glycol\ (extra) = \frac{(V_{OH}(real) - V_{OH}(set)) * W_{mixture}}{V_{OH}(real)} \qquad (2.1)$$

V_{OH}(real): Actual V_{OH} of mixture.

V_{OH}(set): Value needed

$W_{mixture}$: 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);

where:

$$V_{OH} = \frac{f*56100}{MW(Glycol)} \quad (2.2)$$

f: Functionality of the glycol (number of OH groups per molecule);

MW(*Glycol*): Molecular weight of the glycol (g/mol).

After an additional amount of glycol has been added, the reaction mixture should be heated to 220ºC for at least 30 minutes to make sure that the glycol has been properly mixed and reacted with the polyester.

2.2 Structure

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, as shown in Figure 16.

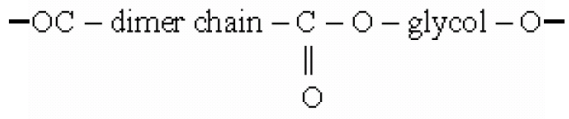


Figure 16: Repeating monomer unit of the manufactured polyesters.

The MW of this repeating unit is the sum of the MW of dimer and glycol minus two times the MW of water, so with ethylene glycol it would be:

572 (dimer) + 62 (EG) – 36 (water) = 598 g/mol.

The number of these repeating units is also called degree of polymerization.

2.3 Synthesis method

2.3.1 Calculations

The excess of diol have influence in final MW of poltester. Usually in industry a 5-15% excess of diol is used.

The stoichiometric calculation can be easily understood:

$$n\,R(COOH)_2 + (n+1)R'(OH)_2 \;\rightleftarrows\; HO\left[R'OOCRCOO\right]_n R'OH + 2n\,H_2O \quad (2.3)$$

$$MWpolyol = n * MWacid + (n+1) * MWdiol - 2n * MW_{H2O} \quad (2.4)$$

$$n = \frac{MW_{polyol} - MW_{diol}}{MW_{diol} + MW_{acid} - 2 * MW_{H2O}} \quad (2.5)$$

MW_{polyol} : Pretended final molecular weight of polyol.

MW_{acid}: Molecular weight of used diacid.

MW_{diol}: Molecular weight of used diol.

MW_{H20}: 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 ration 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.

2.3.2 Experimental apparatus

At ICTPOL:

The experimental setup used in ICTPOL is shown in Figure 17.

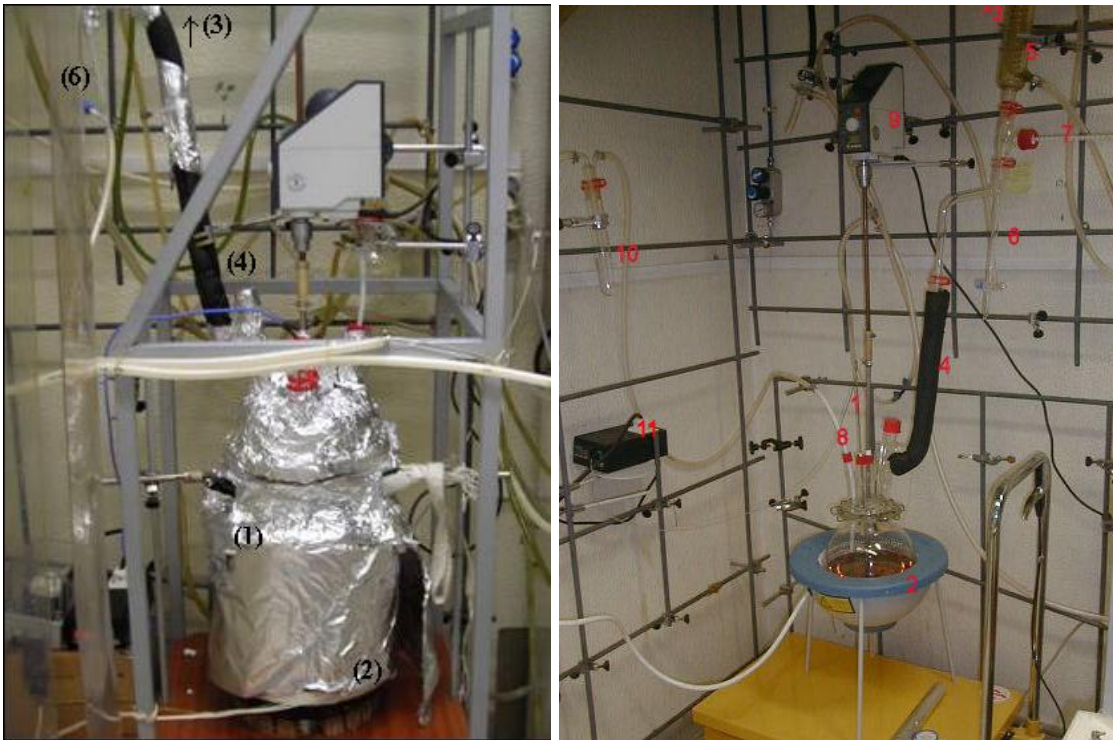


Figure 17: The experimental setup. 20L pilot reactor (left) and 4L reactor (right).

Legend:

(1) Thermocouple.

(2) Heating mantle.

(3) Pressure Equilibrium.

(4) Vigreux column.

(5) Condenser.

(6) Dean-Stark apparatus (removal of formed water).

(7) Thermometer (to measure the vapor temperature).

(8) Nitrogen sparge.

(9) Stirrer.

(10) Nitrogen bubble meter.

(11) PID controller.

The heating was be provided by an electrical heating mantle or a hot oil bath.

A Vigreux column was be used, followed by a Dean-Stark apparatus.

In a later stage of the reaction should run under reduced pressure, applied in the end part of the condenser.

The reaction is carried out in an inert nitrogen atmosphere which should pass through a bubbler which will act not only as a bubble counter but also as a trap (in the case the resin is forced back).

A thermocouple should be used to control the reaction temperature, which is connected to a PID controller and this one to the electrical heating mantle or to the bath.

During overnight nitrogen atmosphere should be also on.

When acid number (V_H)and hydroxyl number (V_{OH}) reach the specifications the heating is turned off, and polyol is removed through bottom valve when reaction mixture is at 60ºC (for viscosity reasons and also for not damaging containers). Depending on quantity of batch, they were stored in 1L or 5L containers.

At CPB:

A general view of pilot reactor at Companhia Petroquímica do Barreiro (CPB), is presented in figure 18. The basic configuration is not much different of reactor at ICTPOL. The main differences are the type of stirrer (which works with steam) , there is a nitrogen flow meter instead of a bubble meter and reactor is heated with steam.

Figure 18: Pilot reactor at CPB. General view.

Legend:

(1) Thermocouple.

(2) Heating

(3) Vigreux column.

(5) Condenser.

(5) Dean-Stark apparatus (removal of formed water).

(6) Thermometer (to measure the vapor temperature).

(7) Steam Working Stirrer.

2.3.3 The polycondensation reaction

At the beginning of the reaction the nitrogen flow does not need to be very high (about 2 bubbles/second), as water come out easily as it is formed in higher quantities in the beginning of the reaction (as predicted from the reaction equilibrium). The stirrer should be started at the same time or 3-4 minutes after heating and should continue throughout the synthesis process.

Some of these diacids have extremely high viscosity at room temperature, and sometimes a small pre-heat should be done so that stirrer do not exceeds its maximum power.

At first, the set point in PID controller for the temperature of the reaction mixture should be around 180ºC. At 170-180ºC the reflux will start and the temperature of the vapor should be controlled in by using a thermometer placed between the end of the Vigreux column and the beginning of the Dean-Stark. The temperature here should be around 105ºC (maximum).

As soon as temperature lowers from this point, the temperature of the reaction mixture in the PID set point should be set to 190ºC.

This procedure of checking the vapor temperature and increasing the set point of the controller by 10ºC each time the temperature falls lower than 105ºC should continue until the temperature set in the PID controller is 220ºC. When no further reflux of water is observed, a few grams of resin (1-2 g) should be taken in order to measure the acid number (V_H) by titration with 0,1N alcoholic solution of KOH. When the acid number is lower than 3.0 mg KOH/g, the nitrogen flow should be increased to 4-6 bubbles/second to remove part of the glycol in excess. Vacuum can be applied to speed

up the process. The acid number should be measured again and the synthesis is finished when V_H is lower than 1.0 mg KOH/g and V_{OH} is required.

In parallel with the acid value (V_H) analysis, hydroxyl value (V_{OH}) should be also measured (starting this measurement when the V_H is lower than 1.0 mg KOH/g). For this 2-3g of resin should be taken and the V_{OH} is determined by titration with 0.5N alcoholic solution of KOH. If the V_{OH} number is lower than the desired one, a glycol correction should be done (see 2.1.2 in Glycols corrections).

After most of the water has been distilled the reaction becomes very slow.

The total time cycle of the polyesterification reaction in this second phase can be reduced in 3 different ways:

- The flow of nitrogen can be increased with careful monitoring of glycol loss;
- The speed of the stirrer can be increased;
- Reduced pressure can be applied with special care to prevent foam rising.

2.4 Controlled parameters

The industrially used parameters to control the quality of the polyols are:

- Appearance
- Color
- Hydroxyl Number (V_H)
- Acid Number (V_{OH})
- Humidity Contents
- MW Distribution
- Insaturation
- Viscosity
- Antioxidant contents
- Hydroxyl primary groups contents (%)
- Density

In the present work the analyzed parameters were the color, the hydroxyl number, acid number, viscosity, and refraction index.

Moreover, during the reaction, these control procedures were used to keep track of its progress [9, 10].

- Amount of water removed: one mole of water is removed for every glycol-acid linkage;

- Acid and hydroxyl number (V_H and V_{OH}, respectively): a measure of un-reacted acid groups and/or the hydroxyl number; and is therefore related to the average MW.

These are the tests most frequently used in industry to follow and terminate the condensation reaction

2.4.1 Acid Number (V_H)

Acid number is defined as the number of milligrams of potassium hydroxide (KOH) required for neutralizing the acid in 1 gram of resin (mg of KOH/ g of polyol).

The used indicator was phenolphthalein.

This is a direct measure of the degree of polyesterification, since acid groups which have react to form ester groups will not react with KOH.

Acid number is the physical constant most frequently used as a process control during the synthesis of a resin. It is observed that as the reaction proceeds, the acid number decreases in a regular manner becoming constant as the reaction reaches toward completion. The acid number is inversely proportional to the MW of a polyol chain.

Procedure:

- Take about 1g of polyester into the Erlenmeyer.
- The solubilization of polyester should be done with 50 ml of Xylene/Ethanol (2:1) mixture.
- Add 2 drops of indicator (phenolphthalein alcoholic solution).
- In buret, a KOH solution (0,1N in ethanol from Riedel) is placed.
- After titration we use following equation for determining $V_{H.}$

$$V_H = \frac{V_{KOH} * 0{,}1 * 56.1}{m} \qquad (2.6)$$

V_H [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

2.4.2 Hydroxyl Number

Hydroxyl is an important functional group and knowledge of its content is required in many intermediate and end-use products such as polyols, resins, lacquer raw materials and fats (petroleum industry). The hydroxyl number is defined as the mg of KOH equivalent to the hydroxyl content of 1 g of sample.

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 released, however, this method suffers from the following drawbacks:

- The sample must be boiled under reflux for 1 h (a long reaction time, laborious and expensive sample handling).
- The method cannot be automated.
- Small hydroxyl numbers cannot be determined exactly
- Pyridine has to be used, which is both toxic and foul-smelling

The method used for our determinations is based in DIN 53240-2**.** It is based on the catalyzed acylation of the hydroxyl group. After hydrolysis of the intermediate, the remaining acetic acid is titrated in a non-aqueous medium with alcoholic KOH solution.

Hydroxyl number determination (Based on Method DIN 53240-2):

- Take about 2-3 g of polyester into the Erlenmeyer.
- Solubilization of sample with 50 ml of THF (Riedel)
- Add 10 ml of acetic anhydride solution (12.5 % in THF) to the flask.
- Add 10 ml of catalyst solution (1% DMAP in THF).
- After 10 min add 2 ml distilled water.
- Wait 30 min stirring regularly.
- Add 5 drops of indicator (thymolphtalein solution in THF).
- Titration is started with a KOH solution (0.5N in ethanol from Riedel).
- A blank must be also made.
- After titration we use following equation for determining $V_{OH.}$

$$V_{OH} = \frac{(Vol_{blank} - Vol) * 0{,}5 * 56.1}{m} + V_H \qquad (2.7)$$

V_{OH} [mg KOH / g sample] is the hydroxyl value
V_H [mg KOH / g sample] is acid value of the sample, previously determined
Vol_{blank} [L] is the volume of KOH solution used in the titration of the blank
Vol [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

For a specific reaction at industrial scale and where successive batches of the same product are needed, it is possible to overcome these titrations almost until the end of reaction to save reagents and time.

In our work we have calibrate a curve of viscosity versus MW for a specific polyol.

Even so, a titration in the end of the reaction is needed, with a valid ASTM or DIN method to confirm correct MW given by viscometer method.

The average MW of a polyol, after having AN (acid number) and OH (hydroxyl number) expressed in mg KOH/ g of polyol, can be calculated in the following way:

$$MW = \frac{f * 56100}{(AN + OH)} \qquad (2.8)$$

A study for determination of approximate MW by viscosimetry was made for U18 - EG (with ICI Cone & Plate Viscometer described in 2.4.5.2). With graph produced is it possible to estimate MW of polyols, produced in the same operational conditions.

Some considerations about this method so that it has reproducibility.

- Method is for a specific polyol.
- The excess of diol at beginning of the synthesis of the polyol must be the same as the one in study, as this will have influence in mixture viscosity.
- PID must be set to work at same temperature or temperature cycles.

- Viscosity tests must be made a short time after taking out the sample, as they can absorb moisture that also changes its properties. Usually it decreases with time (long term), as water can produce hydrolysis of part of the polymeric chain.

These are some conditions that must apply so this method gives an approximated MW. Changing some of previous conditions will change the mixture properties and thus an incorrect MW prevision.

2.4.3 Amount of distillate removed

The maximum expected amount of water that is formed during the polycondensation reaction is twice the molar quantity of diacid in reactor (as this one is the limiting reagent).

Usually this loss of water corresponds to 5% of total mass inserted into reactor.

2.4.4 Refraction index of distilled

For control purposes of any glycol loss that may happen we can measure refraction index of distillate.

Table 3: Refraction index of water and used diols.

Component	Refraction Index
Water	η_{20}= 1,3330
EG	η_{20}= 1,4385
BD	η_{20}= 1,4460

If the distillate has a very different refraction index of water we can use a linear regression and estimate glycol content in it, adding fresh amount of glycol to reactor.

We used an industrial refractometer, usually used for continuous systems, but it is also used for one time measures. This device is from Schmidt and Haensch, GmbH. Operation: Remove top cap and place a drop into round glass area. Close again and a digital display will give refraction index value and actual temperature.

Figure 19: Refractometer.

2.4.5 Viscosity of polyester polyol

Viscosity of a resin is a direct indication of the degree of polyesterification and MW which has been obtained. With a given resin formulation a plot of acid number versus viscosity will follow a similar pattern during the condensation reaction, provided all reaction variables are held as constant as possible.

The viscosity of the synthesized polyols was measured as pure polyol, without any solvent.

2.4.5.1 HAAKE Viscotester 2 Plus

The viscosity measurements were carried out according to the ISO 3219:1993, at 25 ± 1ºC, using a HAAKE Viscotester 2 Plus, from Thermo Electron Corporation. This is a rotation viscometer with a digital display (Figure 20).

Figure 20: Haake Viscotester 2.

- Measurement

The needle rotates with a constant speed when it is immerse on the liquid to test. The resistance offered by the liquid is measured and the binary value is processed. The measured viscosity is shown in the digital display of the viscometer.

- Measurement scale

The HAAKE Viscotester 2 Plus has three measurement scales (Table 4), depending on the range of viscosities to measure. The presented viscosity values are presented in dPa.s and are based on calibration comparative measurements done with standards of known viscosity.

Table 4: HAAKE Viscotester 2 Plus measurement scales.

Digital display	Measurement scale	Needle number
R3	0.3 – 13 dPa.s	3
R1	3 – 150 dPa.s	1
R2	100 – 4000 dPa.s	2

Procedure:

1) Place the measurement needle R2 on the viscometer and place this last one in its stand;
2) Plunge the needle R2 in the measurement glass which contains the polyol; the surface of the polyol sample must be in the middle of the two dashes marked in the needle;
3) Switch the viscometer on, select the measurement scale for the used needle and measure;
4) Read the viscosity in the digital display of the viscometer;
5) Repeat this procedure three times for each polyol and take the average value of the three readings.

2.4.5.2 - ICI Cone & Plate Viscometer.

This is a type viscometer with manual reading, but still very useful in industry.

The amount of product needed for analysis is very insignificant (only one drop), compared with previous viscometer where amount should be at least 100-150 ml.

If calibrated for a specific polyol it can give an idea of MW at a specific time without needing to measure hydroxyl value which take a lot of time (usually 40 min.) and wastes many reagents that need proper disposal.

Procedure:

1) Set temperature which test will be made. Available temperatures are 25, 50, 75, 100, 150 and 175ºC.
2) At beginning, orange light is continuously on. When the light starts blinking, this means the plate is already at set temperature.
3) Put one drop of product to analyze on the plate and place the top part of viscometer down, using lever in the right side.
4) Pressing button “press to read” and read value in top scale in Poise.
5) Repeat last step 3 times.

Figure 21: ICI Cone & Plate Viscometer.

2.4.6 Color

Color acts as an important indicator of product quality, oxidation level and processing performance throughout the industry. Specifically color is used:

- As an early indication of degradation or adverse growing conditions experienced by raw materials.
- As an indicator of the quality of raw material which may influence the color of finished product.
- To determine the suitability of a product for a particular purpose and therefore its price.
- As a guide to the condition of used product.

The color of a polyol may be even more significant when it is desirable to produce pale yellow resins. Dark color may indicate insufficient flow of inert gas, too high reaction temperature or impurities, particularly iron. These variables can influence the setting time of the resin [10].

-Gardner Color Scale

The Gardner Color scale as specified in ASTM D 1544 is a single number color scale for grading light transmitting samples with color characteristics ranging from light yellow to brownish red. It is widely used for oils, paint and chemicals and 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.

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

The instrument used was the Lovibond 2000 Comparator with Daylight 2000 (Figure 20), which has an optional illumination system to guarantee correct lighting conditions for color grading. The scale discs color standards used were the Gardner 4/30AS (with the colors 1 to 9) and the Gardner 4/30BS (with the colors 10 to 18).

Figure 22: Lovibond Comparator System 2000.

Figure 23: Scale discs color standards: Gardner 4/30AS (with the colors 1 to 9; on the left) and the Gardner 4/30BS (with the colors 10 to 18; on the right).

- 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 color standards into adjoining fields of view. The two discs containing the color standards are rotated by turning the control knobs on the front of the comparator until the color of the sample falls between two standards which are 1 Gardner Color unit apart, or until it exactly matches one of the standards. The reading given directly as Gardner Color is then taken from the scale on the control knobs.

- Technical Specification

Measuring principle: Visual comparison with colored glass standards
Mode: Transmittance
Viewing system: Prismatic with integral blue filter for light standardization
Light source: Tungsten halogen lamp, 12 Volt, 20 Watt.

2.4.7 FTIR (ATR)

Fourier transform infrared spectroscopy (FTIR) was used to confirm molecular structural groups of dimer acid and polyester polyol. FTIR (ATR mode) was performed in Nexus equipment from *Thermo-Nicolet* using a Smart MIRacle ^{TM} ATR (Attenuated Total Reflection) accessory, from Pike Technologies, with a ZnSe single reflection ATR heated plate. The experiment was conducted with a resolution of 4 cm^{-1}, 128 scans, and measured in the range of 4000-600 cm^{-1}.

2.5 Experimental Results

2.5.1 Acid and Hydroxyl number

Figure 24 presents the typical behavior of the curves of acid number, hydroxyl number and MW over time for a produced polyol. The MW is calculated from the V_H and V_{OH}. Straight horizontal line represents desired final V_{OH} value.

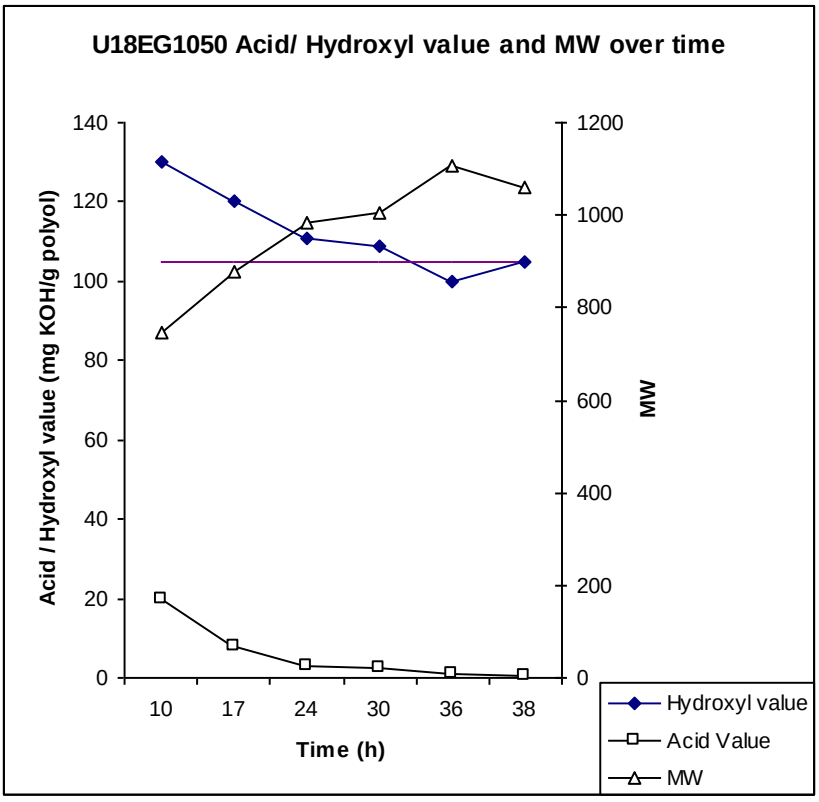


Figure 24: U18EG1050 controlled medium values of V_H, V_{OH} and MW over time.

If we control hydroxyl and acid values regularly, glycols corrections are not so common. Hydroxyl and acid values are indirectly proportional to polyol MW.

In the graph of the Figure 24 one can observe a time during the reaction in which a small glycol correction had to be made at 36h, asV_{OH} was already lower than desired one which was V_{OH}=105. Tendencies of V_H and V_{OH} over time and MW over time are very similar for all types of produced polyols (see Annex 7.1).

On the other hand, the final achieved V_H and V_{OH} numbers provides medium MW of polyols which is very important for commercial purposes (table 7).

In Table 5 it is presented the diols and diacids for each polyol.

Most of synthesized products (U18EG2000 and U14EG2000 batches) were sent to Arizona Chemicals for analysis and for new products development.

Table 5: Diols and diacids used in each formulation.

Number	Grade	Reaction Code	Reactor	U18	U14	EG	BD	ISOR
1	U18EG1050	ICTPOL1	4L	×		×		
2	U18EG1250(1)	ICTPOL2	20L	×		×		
3	U18EG2000(1)	ICTPOL3	20L	×		×		
4	U18EG2000(2)	ICTPOL4	20L	×		×		
5	U18BD2000(1)	ICTPOL5	20L	×			×	
6	U18BD2000(2)	ICTPOL6	20L	×			×	
7	U18EG1250(2)	CPB	20L	×		×		
8	U14EG2000(1)	ICTPOL7	20L		×	×		
9	U14EG2000(2)	ICTPOL8	20L		×	×		
10	U14EG2000(3)	ICTPOL9	20L		×	×		
11	U18ISOR800	ICTPOL10	4L	×				×

We obtained the following specifications (V_H,V_{OH} and MW for each produced polyol):

Table 6: Final specifications obtained for synthesized polyols and approximate number of days to complete synthesis.

Number	Grade	V_H	V_{OH}	MW	Approximate days
1	U18EG1050	0.7	106	1051	5
2	U18EG1250(1)	0.6	94	1186	6
3	U18EG2000(1)	1.2	58	1895	6
4	U18EG2000(2)	0.9	53	2081	7
5	U18BD2000(1)	0.7	60	1848	8
6	U18BD2000(2)	0.8	54	2047	7
7	U18EG1250(2)	0.3	103	1083	5
8	U14EG2000(1)	0.6	53	2093	5
9	U14EG2000(2)	0.9	54	2043	6
10	U14EG2000(3)	0.8	56	1975	6
11	U18ISOR800	N/A	N/A	N/A	4

2.5.2. Formulation

In Table 7 it is presented the quantities and ratio used in each formulation.

Table 7: Amount of diacid and diol in each formulation and its ratio.

Number	Grade	Diacid(g)	Diol (g)	Total	Racio diol/diacid
1	U18EG1050	2504	576	3080	2.10
2	U18EG1250(1)	13250	2910	16160	2.00
3	U18EG2000(1)	14070	2311	16381	1.50
4	U18EG2000(2)	13996	2300	16296	1.50
5	U18BD2000(1)	14231	3281	17512	1.45
6	U18BD2000(2)	13895	3203	17098	1.45
7	U18EG1250(2)	13293	2918	16211	2.00
8	U14EG2000(1)	13145	2060	15205	1.43
9	U14EG2000(2)	13675	2140	15815	1.43
10	U14EG2000(3)	13655	2135	15790	1.43
11	U18ISOR800	2025	1044	3069	2.00

2.5.3 Distillate mass, ratio and refraction index

Table 8: Distillate mass and its ratio regarding initial batch mass.

	Grade	Total in batch (g)	Distillate Mass (g)	% Distilled
1	U18EG1050	3080	182	5.9
2	U18EG1250(1)	16160	1276	7.9
3	U18EG2000(1)	16381	1010	6.2
4	U18EG2000(2)	16296	997	6.1
5	U18BD2000(1)	17512	1044	6.0
6	U18BD2000(2)	17098	987	5.8
7	U18EG1250(2)	16211	1370	8.5
8	U14EG2000(1)	15205	965	6.3
9	U14EG2000(2)	15815	997	6.3
10	U14EG2000(3)	15790	1023	6.5
11	U18ISOR800	3069	95	3.1

At final stage of distillation, the refraction index of distillate was measured, so that any amount of diol in it can be understood. If too much diol was removed we can correct diol level in reactor if MW is too high.

Table 9: Distillate refraction index and diol content.

	Grade	η_{20} of distillate	η_{20} diol	Estimated diol %
1	U18EG1050	1.3458	1.4385	16.3
2	U18EG1250(1)	1.3576	1.4385	25.7
3	U18EG2000(1)	1.3481	1.4385	8.9
4	U18EG2000(2)	1.3444	1.4385	10.8
5	U18BD2000(1)	1.3390	1.4460	11.0
6	U18BD2000(2)	1.3397	1.4460	9.8
7	U18EG1250	a)	1.4385	-
8	U14EG2000(1)	1.3476	1.4385	13.8
9	U14EG2000(2)	1.3453	1.4385	11.6
10	U14EG2000(3)	1.3425	1.4385	9.0
11	U18ISOR800	1.3341	b)	Low

a) Not measured
b) Isosorbide have very high boiling point and it is a solid at room temperature

2.5.4 Viscosity *vs* temperature for several MW of U18EG polyol.

With this study of viscosity at several temperatures and different polyol MW (U18EG), it was possible to produce a set of curves (figure 25).

The viscometer used was an ICI Cone Plate viscometer (section 2.4.5.2) which has specific temperature readings (25, 50, 75, 100, 150, and 175 ºC).

With these curves, it is possible to estimate the status of a synthesis (MW) of U18EG polyol when same initial operational conditions are set.

By taking a sample of the reaction mixture and measuring its viscosity at 25, 50, 75 and 100ºC a new curve is produced that can be compared with the ones in the graph. By analysing the relative position of this new curve to the others in the graph it is possible to estimate its MW.

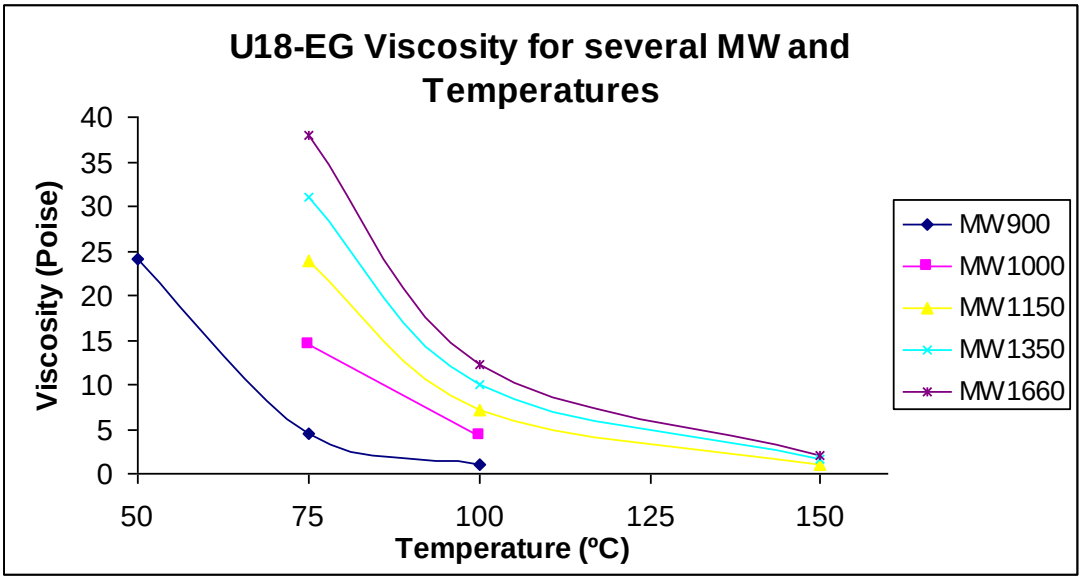


Figure 25: Viscosity of U18EG polyester for several MW and temperatures.
Initial operational conditions: Diol/diacid ratio = 2, PID set point temperature = 220ºC.

2.5.5. FTIR

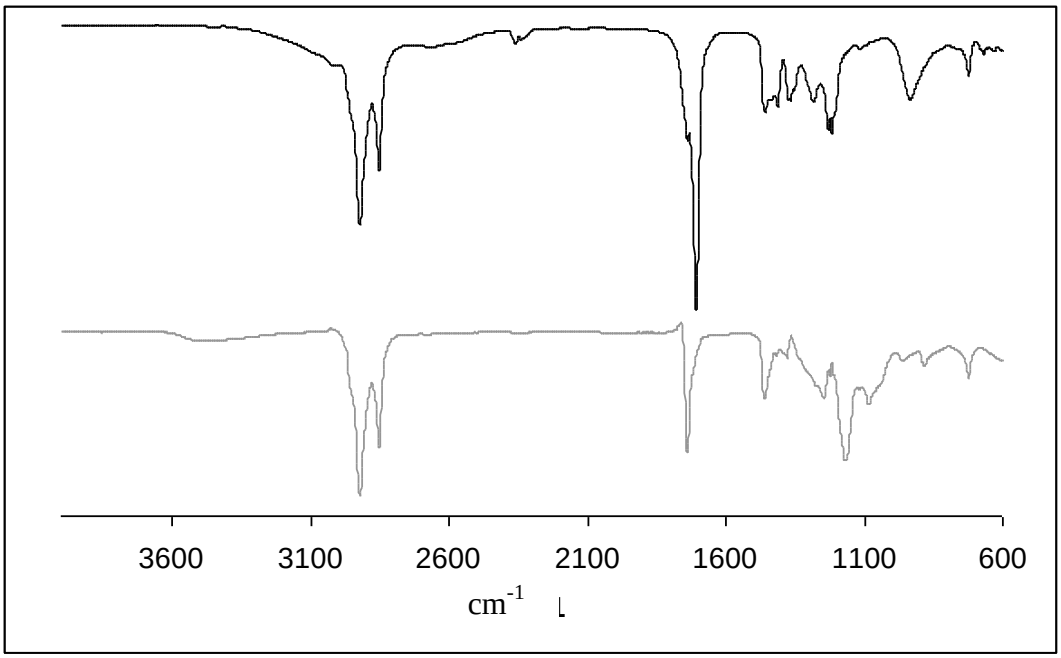


Figure 26: FTIR analysis of diacid U18 (top) and polyester polyol U18EG1250 (bottom).

Although the objective of the present analysis is not quantitative, the fact of hydroxyl band has low intensity-peak, can be explained by the fact that the ratio between the terminal hydroxyl group and other groups is far low. The peaks corresponding to the C-H stretch (2921 and 2851 cm^{-1}) are much more intense as their presence in the long polyester chain is significant.

The peak at 1741 cm^{-1} corresponds to the carbonyl of the ester group, while the carbonyl of the free acid (U18) has the value of 1708 cm^{-1}.

The peak corresponding to the bending of the C-H bonds, at 1459 cm^{-1}, is also rather intense. At 1172cm^{-1}, there is the energy absorption of C-O bond, also very significant since we are dealing with polyesters that can be compared with 1230 cm^{-1} same bond for the free acid.

2.5.6 Color Results

The results obtained from ICTPOL for the color and approximate reaction time of the synthesized products are presented in Table 8.

Table 10: Color results for the synthesized products.

Number	Grade Code	Approximate days	Color (Gardner)
1	U18EG1050	5	6
2	U18EG1250(1)	6	7
3	U18EG2000(1)	6	8
4	U18EG2000(2)	7	9
5	U18BD2000(1)	8	8
6	U18BD2000(2)	7	8
7	U18EG1250(2)	5	6
8	U14EG2000(1)	5	8
9	U14EG2000(2)	6	9
10	U14EG2000(3)	6	9
11	U18ISOR800	4	>18

2.5.7. Viscosity at 25 ºC for polyols produced (by the method described in 2.4.5.1).

Table 11: Viscosity of polyols at 25 ºC

	Grade	Viscosity at 25 ºC (Poise)
1	U18EG1050	55
2	U18EG1250	88
3	U18EG2000(1)	286
4	U18EG2000(2)	266
5	U18BD2000(1)	321
6	U18BD2000(2)	299
7	U18EG1250	67
8	U14EG2000(1)	181
9	U14EG2000(2)	180
10	U14EG2000(3)	186
11	U14ISOR800	N/A

N/A: Not applicable as it produced a dark mass

2.6 Discussion

Dimer acid polyesters were synthesized based on EG and BD.

The syntheses based on the different raw materials followed similar evolutions, (annex 7.1) taking longer reaction times when higher MW was to be attained (table 6).

During the polycondensation reaction, the acid value and the hydroxyl value decreased until the desired values were obtained (less than 1 mg KOH/ g polyol for V_H and enough V_{OH} number to achieve the desired MW);

An attempt to make a polyol not only with the diacid from renewable sources, but also with a renewable source diol (ISOR) was also made, since EG and BD we used before are still petrochemical derived.

The working conditions for this reaction were the same as EG and BD, but unfortunately we obtained a dark brown mass which is not suitable for any commercial use.

The diol content is always an important variable to have in mind. In most formulations a 10% diol excess was used regarding the stoichiometric amount needed to produce polyol of a specific MW, so there is still a comfortable margin to some loss as distillate. For instance, vapor Pressure of EG is still 15mmHg at 100 ºC and 28mmHg at 110ºC.

It is observable that diol the amount in distillate is not so negligible, usually about in 8-12% range. In calculations of production of U18EG1250 (in ICTPOL and CPB), some wrong calculations lead to the use of much more EG than needed, and that can be seen in EG content of distillate of U18EG1250 which was 25.7%. Unfortunately it was not possible to measure the refraction index of the distillate for the same reaction at CPB, but the amount of distillate was far more than predictable (if it was only water) due to the same wrong calculations.

Thus it is always advisable to decrease glycol excess to lowest possible, so its loss and consequently the end cost of the final product (time and raw products) is minimized.

The produced set of curves of Viscosity *vs* temperature for several MW of polyol U18EG (section 2.5.4), revealed interesting data for industrial purposes, as they enable control of the evolution of the polyester molecular weight by analysis of a single drop of the reaction mixture in a cone and plate viscometer (section 2.4.5.2). When

inserting the sample viscosity data (for the referred temperatures) in the graph we can have an estimation of MW. This will save lots of time and products in titrations.

Concerning the color parameter, the most commercially attractive products are the lighter ones (low MW). Taking this into account, better results were achieved for the products whose synthesis times were lower. As diacids are unsaturated they are temperature sensitive. However, even the darker products obtained are still acceptable from a commercial point of view.

3. Production of Flexible Polyurethane Foams from polyester polyols based on U18

3.1 Formulation

In the Table 10 it is shown the typical formulation for the flexible PU foam produced.

Table 12: General formulation for flexible PU foams.

Product	Mass (g)
Polyol	100
Water	0 – 6
Silicon surfactant	0 - 2.5
Amine catalyst	0 – 1
Tin catalyst	0 – 0.5
Isocyanate	Determined by polyol type and quantity of water used.
Plasticizer	10% of total mass

In the present work, all formulated foams the polyols used were based on the dimer acid Unidyme®18, not only for cost reasons, but also because its 18% content on trimer increase flexibility of the foams. The polyols used for foam production were the U18EG1250, U18DB2000 and U18EG2000 produced at ICTPOL.

The two samples of MDI crude were provided by Dow and their NCO levels (determined by titration) were 29.9 and 31.5%.

The silicon surfactant (Tegostab B1048) was obtained from Degussa.

The amine catalyst was DABCO-33LV (DABCO 33% solution in propylene glycol) and the plasticizer was dioctilphthalate (DOP), both provided by CPB. The tin catalyst was DBTL was obtained from Aldrich.

3.2 Preparation procedure

The reaction vessel was charged with 100 parts (weight) of the polyol, 4-6 parts of water, 0-1 parts of DABCO, 0-0.5 parts of DBTL, 0-2.5 parts of the silicon surfactant and 10% (w/w) of DOP, considering total mass of previous components. This mixture was stirred during 30s at 1.500 rpm.

Then the required parts of crude MDI, enough to a MDI index of around 105 - 110 %, were added and the whole mixture was stirred during 20s, until we notice some heat development. Around 2 hours later the foam was demoulded.

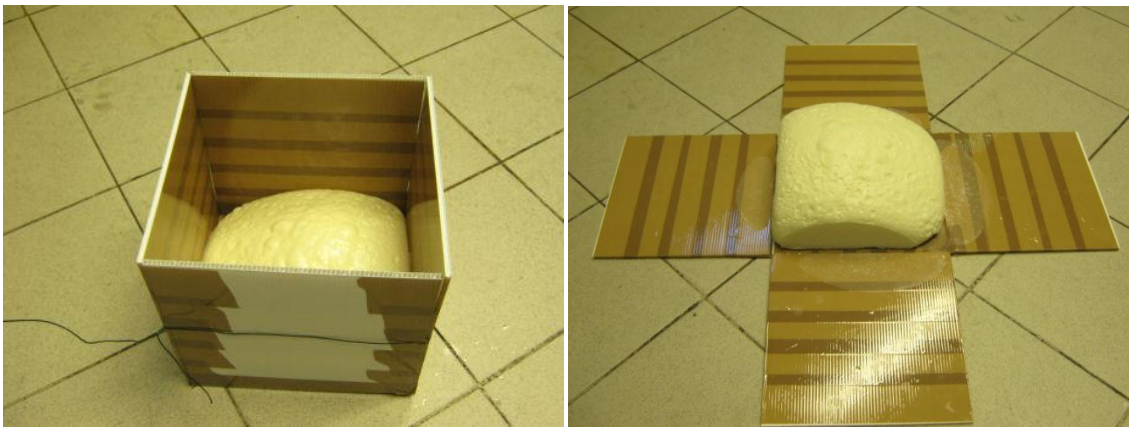


Figure 27: Foam Rising (left) and demoulding (right).

3.3. Equipment and methods

The equipment used in the evaluation consisted of the following:

- One box made of five plastic parts (20×20cm each) glued together (volume = 7.6l).
- Balance (Sartorius; model: GP 3202; precision of ± 0.01 g; maximum weight: 3200 g);
- Analytical Balance (Metler Toledo ClassicPlus AB204-S, min precision of ± 0.001g; maximum weight: 220g).
- Mechanical stirrer (Heidolph; model: RZR 2051);

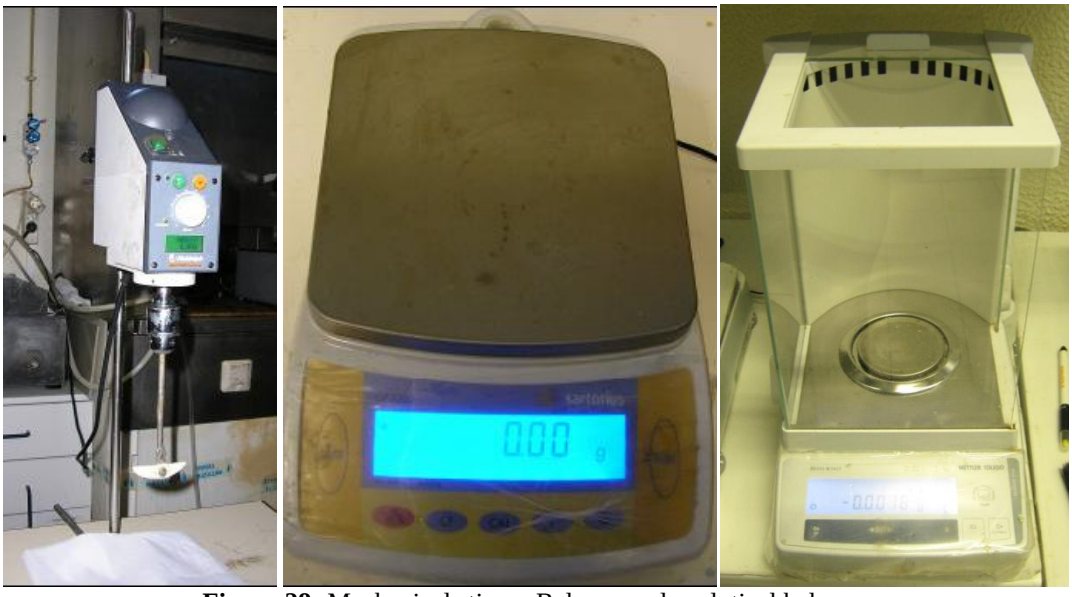


Figure 28: Mechanical stirrer; Balance and analytical balance

Band saw (Plus moder BS-8) was used for cutting foam in smaller pieces, and a digital caliper (pro-max) for measuring size for volume calculations.

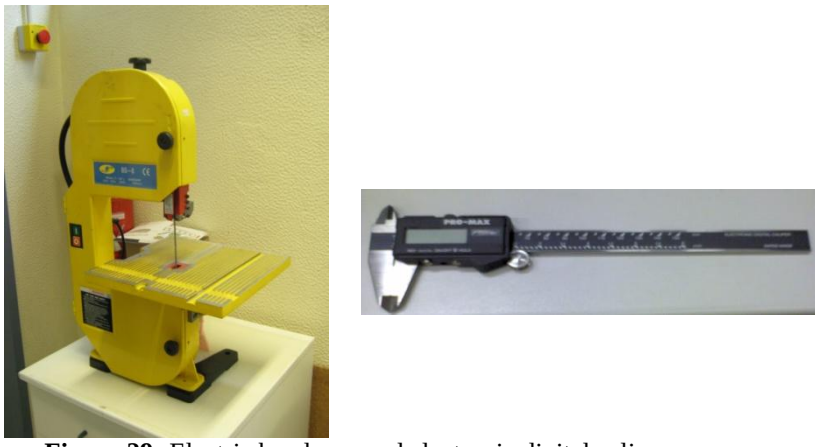


Figure 29: Electric band saw and electronic digital caliper pro-max.

3.3.1 Determination of %NCO (for MDI crude)

The procedure used for the free NCO content was based on ASTM D2572.

This method is based on the ability of the isocyanate group to react readily and equitably with di-n-butylamine. A sample of approximately 2-4 g was weighted into a 250 ml Erlenmeyer and dissolved in 100ml of acetone and 20ml of a solution of di-n-butylamine in toluene (130g of di-n-butylamine in 1L solution). The Erlenmeyer containing the sample solution was then placed on the magnetic stirring plate for 10 min. After this period, 2-3 drops of a bromophenol blue indicator solution (0,5g in 100ml of isopropanol) were added and the sample titrated with a solution of HCl 1N (titrisol blister HCl 1N from Merck in 1L aqueous solution), until the solution color turned into yellow.

The whole process was repeated for a blank solution. The free NCO content of the sample was then calculated using the following equation:

$$\%NCO_{free} = \frac{(V_b - V_s) * N * 42}{m} * 100 \qquad (3.1)$$

$\%NCO_{free}$ is the free NCO content of the sample

V_b [L] is the volume of HCL solution used in the titration of the blank

V_s [L] is the volume of HCL solution used in the titration of the sample

N [eq/L] is the normality of the HCL solution

42 [g/eq] is the equivalent weight of the NCO group

m [g] is the weight of the sample

3.3.2 Determination of the specific gravity

The specific gravity of polyurethane foams is a very important parameter both for research and for scale-up and industrial purposes.

The procedure used to determine the specific gravity of the synthesized polyurethane foams consisted of five very simple steps:

1. Using a cylindrical sharp metallic cutter (diameter = 4.5 cm, height = 5 cm), 3 cylindrical pieces were cut from the central part of the foam.
2. The diameter of each foam cylinder was measured 5 times and the average calculated.
3. The height of each foam cylinder was measured 5 times and the average calculated.
4. The weight of each sample was determined using an analytical scale.
5. The foam specific gravity was calculated, in kg/m^3, using the results obtained in steps 2, 3 and 4.

3.3.3 Determination of the oil absorption

To evaluate the performance of the produced polyurethane foams as oil absorbent material, a simple procedure for determining the oil absorption of polyurethane foams was developed.

The procedure used comprised the following steps:

1. Four small cubes of polyurethane foam were cut, each one with an approximate volume of 1-1.5 cm^3.
2. The cubes were then crushed in a foam crusher in order to open all the cells that may have been closed.
3. The foam cubes were weighed all together.
4. A mixture of water and mineral oil (oil in an amount sufficient to cover the entire surface of the water) was prepared in a 25 cm wide transparent cup.
5. The foam cubes were put in contact with the mixture oil/water and the chronometer started and the final mixture was gently mixed with a glass stirrer.
6. From t= 20 s to t = 5 min, the mixture was stirred with time intervals of approximately 1 min.
7. Then the mixture was left for 6 min without any stirring, after which the foam cubes were taken out from the oil/water mixture. The excess of oil was drained and the cubes were weighed.

8. The quantity of absorbed oil (in kg) by m^3 of foam was calculated (this assumes that mostly oil is absorbed).

3.4 Experimental Results

3.4.1 Production

Several initial formulations were tested, some with the available Crude MDI with a NCO content of 29,86%, then with a fresh acquired one, with NCO content of 31,5%

Table 13: Formulations for flexible polyurethane foams.

Foam	**1**	**2**	**3**	**4**	**5**	**6**	**7**	**8**	**9**
Polyol (g)	90	90	90	90	90	90	90	90	90
Polyol Type	a)	a)	a)	a)	a)	a)	a)	b)	c)
Water (g)	6.21	6.65	7.1	7.1	6.21	6.21	6.21	6.21	6.1
Tegostab® B1048 (g)	0.9	0.9	0.9	0.9	0.9	0.9	0.9	0.9	0.9
DBTL (g)	0.09	0.09	0.09	0.18	0.09	0.09	0.09	0.09	0.09
DOP (g)	22.3	22.4	22.5	22.5	22.9	23.5	22.3	17.2	17.2
Crude MDI (g)	123	123	123	123	129	135	123	75	75
DABCO33LV (g)	0.55	0.55	0.55	0.55	0.55	0.55	0.55	0.55	0.55
Crude %NCO	29.9	29.9	29.9	29.9	29.9	29.9	31.5	31.5	31.5
NCO factor	1.05	1.05	1.05	1.05	1.10	1.15	1.05	1.05	1.05
Shrunk	YES	YES	YES	YES	YES	YES	NO	NO	NO

a)U18EG1250 b)U18EG2000 c)U18BD2000

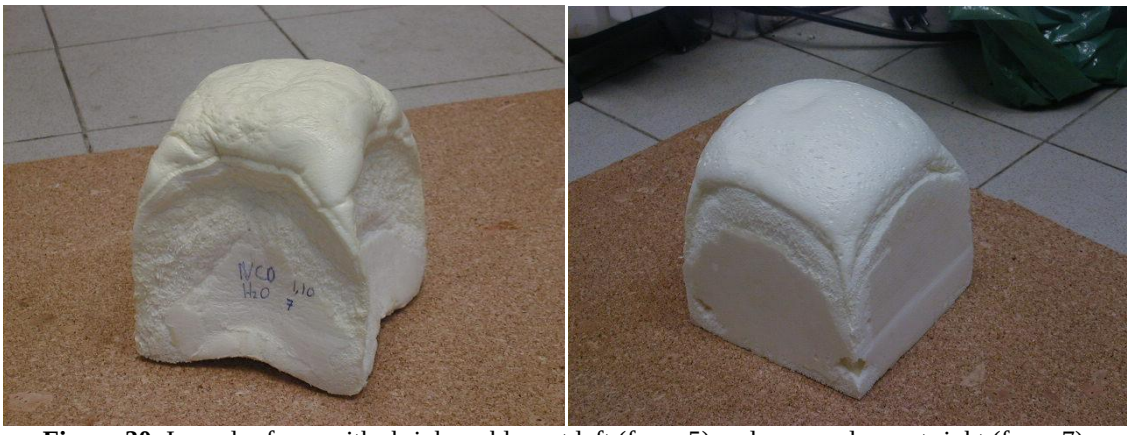


Figure 30: Irregular foam with shrink problem at left (foam 5) and a normal one at right (foam 7).

In section 7.2 the aspects of foams 1 to 6 (with shrinkage problems) is shown.

3.4.2 Oil absorption properties

The capacity of foams based on polyols derived from dimer acids to absorb oleochemicals was tested. Initial foam was cut into small cubes, 1-2 cm^3 each.

Figure 31: Foam cubes for tests of oil absorption.

Figure 32: Foam oil absorption steps: a) Initial aspect of crude oil in water. b) Foam starts to absorb oil. c) Final aspect. d) Final aspect after crude oil absorption and foam removal.

Even if the foam is previously immersed in water it does not loose all its oil absorption properties. The specific gravity of tested organic oleochemicals was measured with a pycnometer (table 14) and absorption data for three types of foams (table 15).

Table 14: Specific gravity of analysed oleochemicals

Type	**Specific gravity (Kg/m^3)**
Crude Oil (BP)	849
Biodiesel (IST)	888
Mineral oil (Midas car workshop)	883
Diesel (Galp)	830
Gasoline (Galp – 95 type)	738

Table 15: Oil absorption of some foams.

Oil Absorption Data (Kg oil/m^{3}foam)			
Type	**Foam U18EG1250**	**Foam U18EG2000**	**Foam U18BD2000**
Crude Oil (BP)	755	640	625
Biodiesel (IST)	745	620	605
Mineral oil (Midas car workshop)	675	538	520
Diesel (Galp)	765	638	602
Gasoline (Galp - 95 type)	768	620	595

3.4.3. Foam specific gravity

The specific gravity determined by the volume of the external geometrical shape and the mass of the sample is often designated apparent density, bearing in mind that it does not measure the specific gravity of the polymeric matrix of the foam. The apparent densities for the studied foams were calculated by measuring volume and weight.

Cubic shaped samples of the synthesized foams were cut with a sharp cylindrical metallic cutter. The dimensions of the foam (diameter and height) were determined with a electronic digital caliper pro-max (from Fowler; model: S225; precision: 0.01 mm) and the mass was determined by weighting in the analytical balance in Figure 25. The volume for each cylinder was then calculated

Table 16: Medium specific gravity of foams produced with different polyols.

Foam with	**Mass (g)**	**Volume (cm^3)**	**Specific gravity (Kg/m^3)**
U18EG1250	2.1372	79.48	26.89
U18EG2000	2.7589	78.38	35.20
U18DB2000	3.0698	80.11	40.32

3.5 Discussion

The used formulations were based in the synthesized polyols to produce a material with high oil absorption capacity, suitable for example on catastrophic situations such as major crude oil spills (e.g. Mexico Gulf oil spill by BP).

Dimer acid based polyesters are capable of conferring high hydrophobicity, which is essential for preventive operations when the foam may be in contact with water before getting into contact with any oil.

Initial used formulations in this study were given by Dr. Cristina Correia [52] who in her study, found the optimal formulation for oil absorption foams which are the ones with low MW polyols, based in U18 and EG, even so, U14 derived foams also provided a good performance, although its higher price makes it less attractive.

Initial formulations gave shrunken foam (annex 7.2). That happened because of low component quality (MDI crude), having 29.9% of NCO content.

After getting new crude with a 31.5% of NCO, no more shrinkage problems were noticeable. That happened as MDI crude has tendency to polymerize in higher molecular weight isocyanates, decreasing its NCO value significantly.

Regarding oil absorption of studied foams (the one that did not shrunk), it is noticeable that ones with lowest specific gravity have higher oils absorption properties.

Oil absorption was high for foam derived from U18EG1250, meeting almost the specific gravity of pure oleochemical.

When comparing same MW polyols derived from different diols (U18EG2000 and U18BD2000) it is noticeable that EG polyols give better performance.

4. Conclusions

In pilot plant scales, properties like viscosity and the amount distilled are some of most important factors for determination of the status of reaction.

It is possible with proper calibrations to overcome titrations at some point only by viscosimetry to save time and materials. It is possible to track diol loss as distillate with refractometer, if it were possible to connect it for constant data acquisition of refractive index of distillate it would be possible to optimize the whole process.

The production process was studied without any catalysts and the scale-up was performed for 20 L production reactor for some polyesters that were tested for polyurethanes foams.

The main used raw materials for synthesis of the unsaturated polyester polyol production were dimer fatty acids, derived from tall oil (a by-product of paper industry).

Dimer acids can be used as a building block for polyester polyol synthesis and different molecular structures can be achieved, to impart certain features to the final application, since the polyester polyol is an intermediary product, used as a raw material for polyurethane production. Some examples are polyols, based on U18 and U14 dimer acids that are suitable for making flexible foams for oil absorption with an extra advantage that they come from renewable sources.

Regarding these dimer acid based polyols synthesis there is already a paper and an internal information sheet that have been included in section 7.3 of the annexes.

The use of isosorbide as a diol font has failed for the same conditions that were applied for other diols. Some different conditions must apply so that is possible to produce polyesters based on isosorbide and dimer acids.

Polyurethane foams for oil absorption were produced to take advantage of the high hydrophobicity and oleophilicity that dimer acids impart to the final polyurethanes.

Some formulations were tested and their performance evaluated in terms of oil absorption. One of the foams produced has the ability to absorb 755 Kg of crude oil for cubic meter of foam, when it has a specific gravity of 849Kg/m^3. These are very promising results, as it can be used to help in the control of oil spills in aquatic environments. Other further tests should be done, depending on the final application of the aimed foams.

5. Further perspectives and future trends

New possibilities for synthesizing polyesters for polyurethanes and unsaturated polyester resins are open, building new structures with some characteristics so far difficult to impart.

The viscosity which is an important variable and the most problematic to measure in polyesters synthesis is an area where some study must be made, so that we can predict MW and MW distribution at a given moment of the production.

With the incorporation of dimer acid based polyester polyols in polyurethanes, the weight percentage on the final product that comes from renewable resources increases significantly when compared to the traditionally used raw materials.

Another good advance would be to incorporate in these polyester polyols not only the dimer acids but also diols from renewable resources as EG and BD are still coming from petrochemicals. Some candidates would be isosorbide or monoglycerides if the needed functionality is two.

Regarding other diacids, there is already a company producing succinic acid through biotechnological sources, so dimer acids are not alone in this run.

Some work must be done to find a 100 % renewable polyester (both diacid and diol) with useful properties for many different applications.

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7. Annexes

7.1 Profiles of V_H, V_{OH} and MW over time for different types of produced polyols (horizontal line represents the needed V_{OH}).

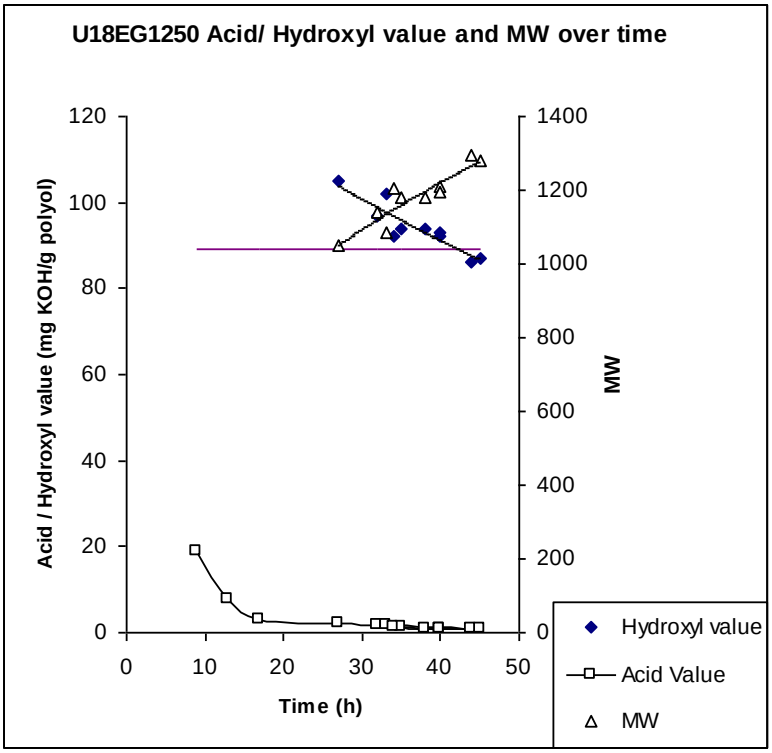

Figure A1: Profiles of V_H,V_{OH} and MW during synthesis of U18EG1250(ICTPOL)

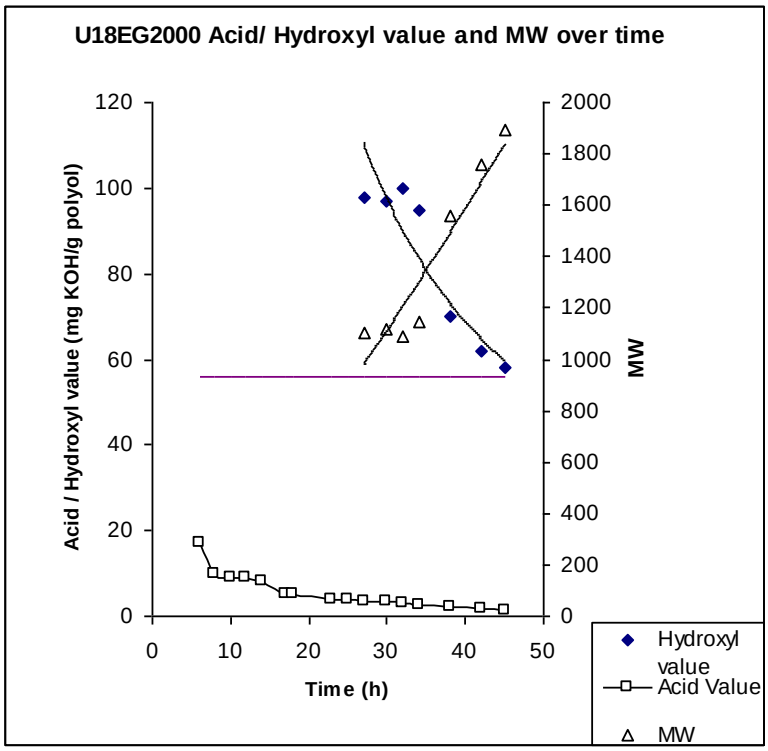

Figure A2: Profiles of V_H,V_{OH} and MW during synthesis of U18EG2000(1)

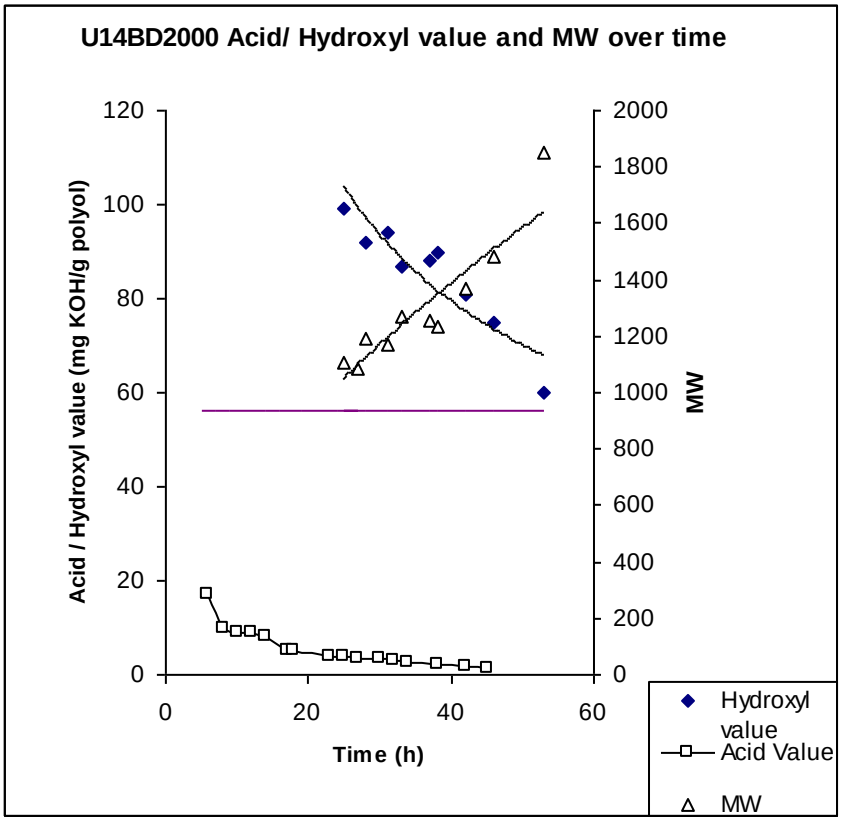

Figure A3: Profiles of V_H,V_{OH} and MW during synthesis of U14BD2000(1)

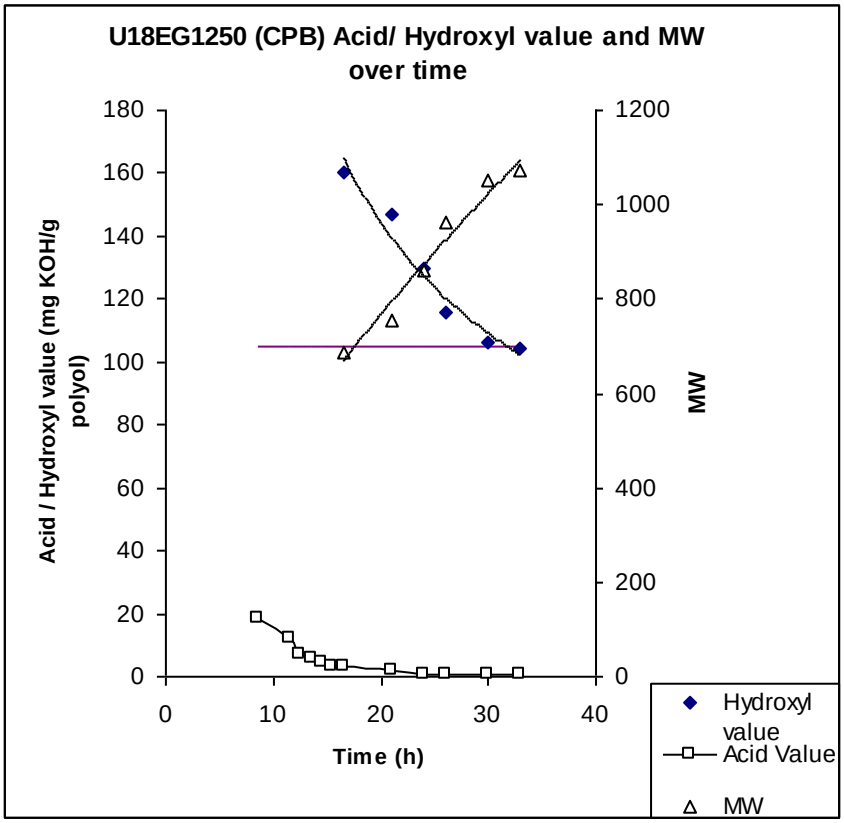

Figure A4: Profiles of V_H,V_{OH} and MW during synthesis of U18EG1250 at CPB.

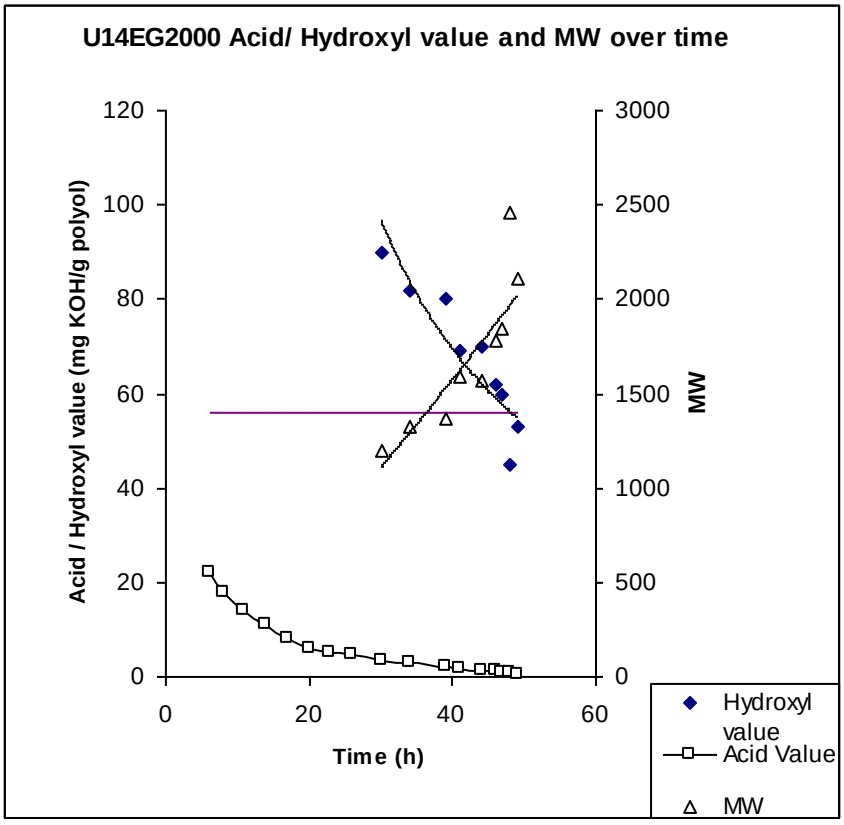

Figure A5: Profiles of V_H,V_{OH} and MW during synthesis of U14EG2000(1).

7.2. Foam aspect (Foam 1 to 6).

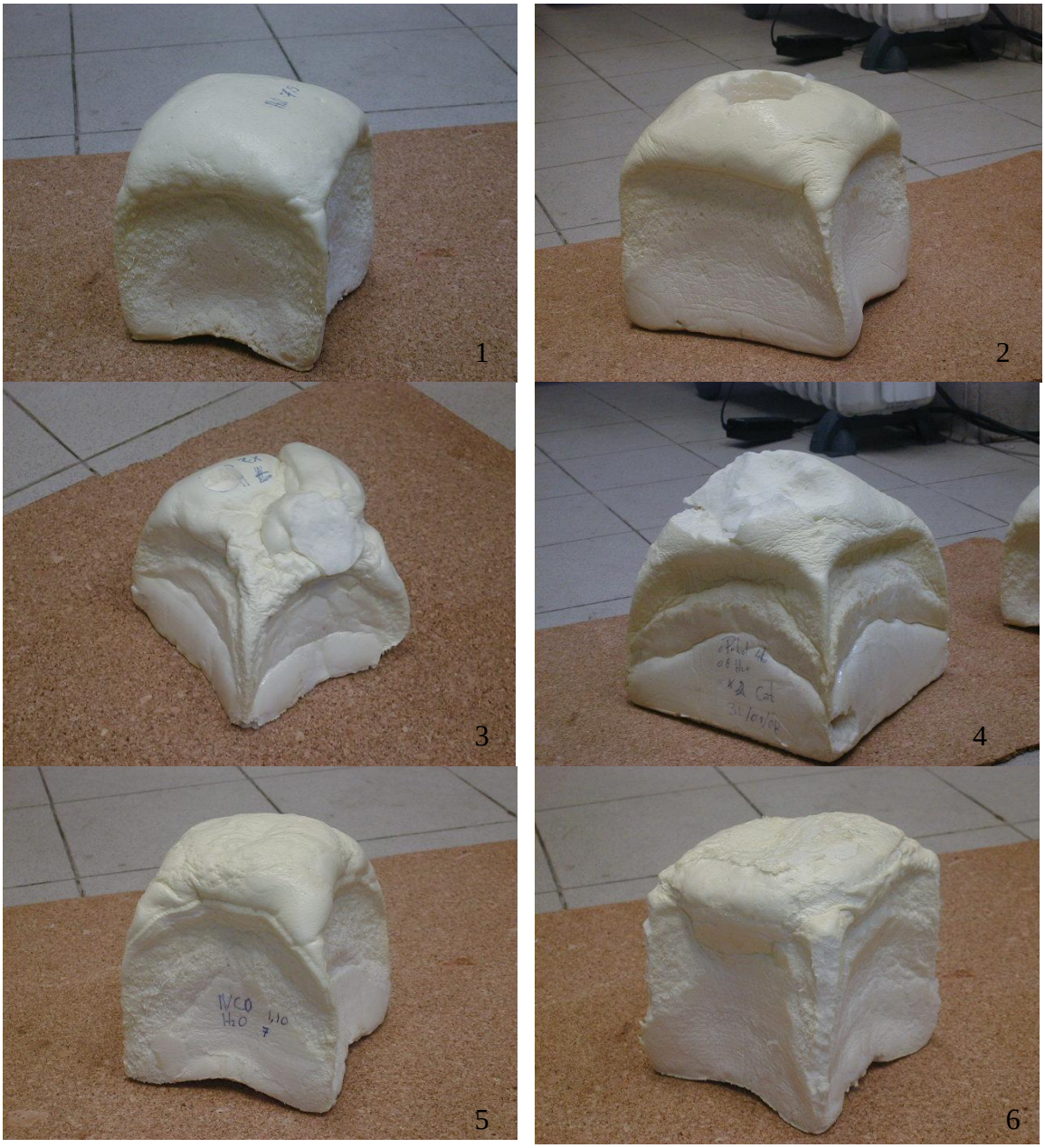

Figure A6: Foams 1 to 6 with shrinkage problems. Foam 1: 7% water, Foam 2: 7,5 % water, Foam3: 8,0% water Foam4 : Double catalyst content, Foam 5: NCO index of 1.10 Foam 6: NCO of index 1.15.

7.3. Papers and information sheet

Overview of Current R.&D. Activities on Reactive Polymers and Catalysis of Polymerization Reactions

João Bordado, João Gomes, Susete Fernandes, Inês Raposeiro, Helena Mota, Tiago Fonseca, Sandro Matos, Helena Domingos, Humberto Ferreira, José Oliveira, Fernando Ramôa Ribeiro.

IBB-Institute for Biotechnology and Bioengineering, Centre for Biological and Chemical Engineering, Instituto Superior Técnico, Av. Rovisco Pais, 1049-001 Lisboa.

Reactive Polymers are very seldom found amongst Commodities and are the only class of polymers with a recognized high potential for grow due to their large scope of different applications. Both the synthesis of oligomers and reactive prepolymers as well as the further reaction of those to form the final macromolecular structure requires a careful control of the reaction kinetics, by the use of specific catalysts as well as a detailed knowledge of the involved reaction mechanism. Novel Functional Polyesters are designed, synthesized and later on formulated and compounded by one experienced compounder (CABOPOL). Within the scope of a QREN funded Project the monomers and the backbone structures are selected to impart biodegradability, as well as biocompostability since foreseen application is their use as main component for packaging film. Process development and preliminary scale-up of the production process is included in the scope of the Project. Amongst the techniques used in Surgery, the surgical adhesives are recognized as one area of larger growing potential. Within the scope of a FCT funded project, Polymer backbones are designed and tested for intrinsic biocompatibility and bioabsorbility by the metabolic processes of the living cell tissues. Functional groups with selectivity for chemical adhesion to proteins are then attached to the structure. Within the scope of the cooperation between IBB and the Institute for Science and Technology of Polymers (ICTPOL), new polymeric structures with elastomeric properties are synthesized from bio produced Polyhydroxialcanoates, to be applied in formulated bitumen asphalt and in binders for cork stoppers. [1]

Reference

[1] J. Bordado *et al.*, New Reactive Binders, PCT Patent applied (2008)

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Reactive Polymers
Catalysis of Polymerization Reactions

João Moura Bordado, Susete Fernandes, Helena Mota, Tânia Fernandes, Inês Raposeiro and Rui Lopes

Master Students: Tiago Fonseca, Sandro Matos, José Oliveira, Barbara Valdés

General Objectives

One of the main goals is to develop scientific basis, technological knowledge and intellectual property ground in order to design and synthesize new reactive polymers, primarily by using renewable resources, as well as, the design and manufacture of new polymers using developed reactor systems. The knowhow acquired is aimed to provide qualified and useful collaboration with the industry.

Mission and Scope of Activities

To contribute to the well recognized scientific prestige of IBB and IST in the Chemical and Biological Engineering field.

To stimulate young scientists and engineers for the field of industrially applied research, contributing to the success of their research activities, and latter on for their successful integration in the Industry.

Main Research Areas:

a) Catalysis and Mechanisms of Polymerization Reactions; b) New Functional Polymers. c) New polymer films with controlled permeability. for energy production (Salinity power process).

Progress

A start review of the progress in each of the working lines is presented together with the forecast actions. The projects were mainly funded by FCT and QREN/Adl.

♦ Surgical suturing and stapling have been so far the most common clinically procedures to fasten soft body tissues together; however numerous disadvantages have been reported. Generally, biodegradable urethane-based prepolymers containing free isocyanate groups have excellent physical properties in addition with blood and tissue compatibility which sustained their use as biomaterials. The aim of this work was to develop urethane-based polymers containing free isocyanate groups capable of reacting with the amino groups present in living tissues and several new polymers were obtained and characterized.

The *in vitro* cell culture experiments performed in some formulated polymers shown that 3T3 mouse fibroblast cells could adhere to the surface of the polymer and proliferate over time with low toxic response.

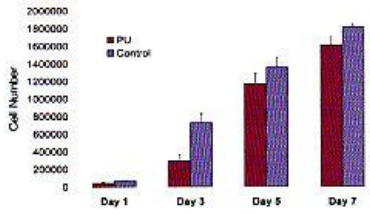


Figure 1. 3T3 fibroblast cell growth on polyurethane (PU) surface and tissue culture polystyrene (used as a control) over a period of 7 days. Values represent means + standard deviation.

The cell adhesion to the polymer surface was also observed by SEM micrographs. Despite this good results, the intense used of catalysts proved to be essential due to undesired polymer curing times. Catalysts with low water affinity will be tested, with further improvement of the prepolymer structure.

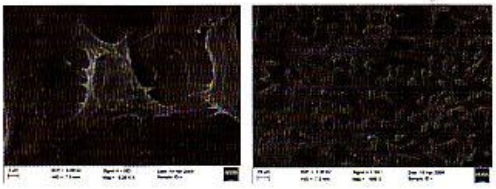
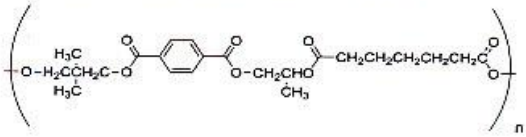


Figure 2. SEM micrographs of 3T3 fibroblast cells after 3 days in culture on polymer film.

♦ The development of new polyester structures



with biodegradable segments and biocompatibility has started and samples with new structures were already supplied to the industrial partner for mechanical testing.

Figure 3. Pilot reactor used in polyester synthesis.

♦ In the scope of a QREN project in cooperation with the company Multirecolha (Multirecolha-Recolha de Resíduos Industriais para Reciclagem, Lda) the study of the used vegetable oil is being performed. The separation of this components, which have a deep influence on viscosity, limiting their used as fuel raw material, as well the separation of other non-desirable components, will be implemented at Multirecolha, after a carefully scale-up.

♦ Isocyanate terminated prepolymers are replacing all the other polymers that in the past were used for the production of cork agglomerates and specially in the field of technical stoppers, class in which the stoppers for champagne are included. The qualification and certification for food contact have been performed for many years by laboratories in France, Germany and more recently in United States of America.

In cooperation with company Fabrires-Produtos Químicos, S.A. and with National Institute for Health (INS), within the scope of a QREN project, new polymers are being developed utilizing renewable raw materials and the aggregated samples will be interactively extracted and qualified by INS.

♦ New surface active agents based on renewable raw material were successful synthesized and samples delivered to Protec & Gamble (Germany) and CIBA (UK). Comparative tests were performed against other surface active agents and the performance was considered outstanding ("better than ariel"). New surfactants with higher HLB are bieng synthesised in order to cover a larger range of technical requirements.

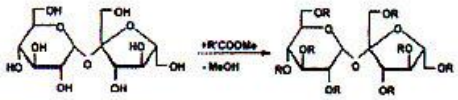


Figure 4. Simplified reaction mechanism of surface active agents based on renewable source.

♦ New methodologies for the synthesis of *C*-glycosylflavonoids employing rare-earth metals based catalysts have been investigated under the main theme of catalysis. These compounds are widespread in nature and are embodied of a great biological significance. Bioactivities such as anxioloitic, anti-diabetic, Anti-hypercholesterolemic, anti-oxidant among others are presented by those polyphenolic derivatives. The studies conducted over the last year involved the optimization of the one pot synthesis promoted by lanthanides triflates as an alternative to the classical methodologies. A coupling reaction followed-up by a *in situ* rearrangement, commonly known as Fries-type rearrangement, leaded exclusively to the aimed molecules. Different reaction conditions such as solvent mixtures, temperatures, and reaction time were tested. The desired compounds were synthesized and characterized by NMR experiments.

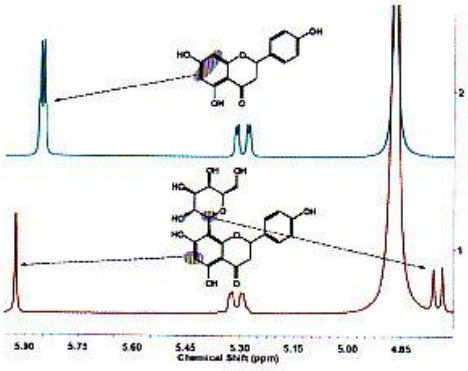


Figure 5. Comparison between 1H-NMR spectra obtained for the synthesized 8-C-Glucosylnaringenin and naringenin.

Ultrasounds were also applied in order to shorten the reaction time and to enhance the catalyst performance. The results encourage us to continue to develop this methodology in order to access those compounds in a very simple and easy way.