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Natural Resource Sustainability through Bio-based Polymers Development

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ABSTRACT

Polyurethane foam is the mostly studied of polyurethane materials, it is widely used for several applications such as automotive, insulation, furniture and packaging. Polyols currently used in the production on polyurethane foams are petrochemical derived products. As the price of crude oil escalated, the price of polyurethane reactants steadily increased and the interest for natural resources as source for polyols grew up. In this work was presented a synthetic pathway to valorise lignin wastes to make a product that was more environmental friendly and economically viable than the polyurethanes produced by current synthetic processes.

The usage of lignin with suitable chain extenders, as a potential replacement to petroleum polyols, in the production of flexible foam polyurethanes, was investigated. Advantages of lignin is that it is a renewable resource, cheap and easily available and it is a waste material from the wood and pulp industries. Two different kind of lignin were employed, one from kraft and one from soda process, also the soda lignin was subjected to chemical modification process to improve its reactivity. In the attempt to produce flexible foams two kind of chain extender were used in combination with liquefied lignin: polypropilenglycol triol and castor oil. The samples were produced with the "one shot" technique and the only blowing agent used was water. Characterization results indicated that samples with liquefied lignin and PPG triol had a low T_g soft phase clearly separated from the hard segment phase, samples with liquefied lignin and castor oil had phase mixed morphology. The amount of lignin that was possible to introduce in the network varied from 6 to 13% and considering also the renewable origin of the castor oil the renewable content in these samples was more than 45%.

The kind of lignin did not influenced greatly the structure and properties of the produced foams, modified lignin was easily dissolved in the liquefying agents and the characterizations of the foams produced with this material showed an intense phase mixing between liquefied lignin and chain extenders (in particular with castor oil). The cell structure as well as physico-mechanical and thermal properties were characterized to compare with commercial analogues. It was investigated that liquefied lignin foams had high content of open cell, density, physico-mechanical and thermal properties were comparable with foams made with commercial petroleum based polyols. The properties of these foams was modulated introducing flexible chains in the macromolecular structure that can reduce the glass transition temperature of the materials and generate foams with higher flexibility.

Keywords: Lignin, Natural polyols, Biobased polyurethanes, Mechanical properties, Thermal properties, Flexible foams.

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1. Introduction

1.1. Overview

Energy consumption has increased steadily over the last century as the world population has grown and more countries have become more industrialized. Crude oil has been the major resource to meet the increased energy demand, so the consequences of inadequate oil availability could be severe. Therefore there is a great interest in exploring alternative energy and material sources; the synthesis of polymeric materials, using renewable resources, has been a subject of research in last decades. Both agriculture and industry will benefit from the use of any materials from renewable resources.

Polyurethanes are a broad class of polymers with the urethane bond as a common element. One of the most important commercial polyurethane products is the foam. Polyurethane foams are commonly classified as either flexible, semi-rigid, or rigid, depending on their mechanical performances and core densities. The applications of these foams are highly dependent on the cellular structure of the resulting foam.

The main field of polyurethane application is the furniture industry, around 30% of the total polyurethanes produced worldwide is used for the production of mattresses from flexible slabstock foams. Automotive manufacture is the second important application for flexible and semiflexible polyurethanes (seat cushioning, bumpers, sound insulation, etc.). Rigid polyurethane foams are used in thermal insulation of buildings and refrigerators, cold stores, pipe insulation, refrigerated transport, thermal insulation in chemical and food industries. The polyurethane elastomers are used for shoe soles, footwear, athletic shoes, pump and pipe linings, industrial tyres, microcellular elastomers, etc. Polyurethane adhesives, sealants, coatings and fibres represent another group of polyurethanes with specific applications.

Flexible polyurethane foam, the key player in this thesis, is a very versatile material, this kind of polyurethane is a block copolymer that owes its elastic properties to the phase separation of so-called "hard blocks" and "soft blocks". Hard blocks are rigid structures that are physically cross-linked and give the polymer its firmness; soft blocks are stretchable chains that give the polymer its elasticity. By adapting the composition and the ratio of the hard and the soft blocks, polyurethane can be customized to its application and as for most polymers, further tailoring of the material properties can occur through additives.

Polyurethanes are prepared from the polyol component and isocyanates. At this moment it is realistic to produce only the polyol from renewable resources for foam applications. Although aliphatic diisocyanates from dimerized fatty acids are commercial (Petrovic, 2008), they do not have sufficient reactivity for application in foams, but they could be used for coatings and other urethane applications. Thus, isocyanates for foams must be aromatic. On the other hand, vegetable oil polyols have an excellent chance to compete with petrochemical polyols. The importance of the development of polymeric materials using renewable sources rises from the concern about raw material processing and the development of alternative synthesis routes less hazardous to the environment. The goals are to reduce demand for non-renewable fossil fuels and to cut production of carbon dioxide "greenhouse gas" to lower global warming. From the point of view of the polyurethane industry, the use of polyols produced with a closed carbon cycle, seems to be attractive also, especially if we consider the low cost of these residues.

1.2. Organization of thesis

The attention was focused on flexible foams because replacing petroleum polyols using polyols from renewable resources can have a deep impact on polyurethane industry. In addition no success has been reported yet on flexible foams synthesized from lignin derived polyols. A briefly introduction to renewable resources and polyurethanes is given in the first chapter.

An updated state of the art on these subjects is presented in the second chapter, giving more insight into the basics and relevant areas regarding the production of polyurethane based on renewable resources and the characterization and usage of lignin. Also the current status of research in this field and the most interesting researches are introduced and analyzed.

The materials used, the production process and the characterization methods are presented in chapter 3, the emphasis of this part of the thesis lies on the lignin liquefaction process to produce suitable intermediates for flexible polyurethane production.

The experimental results and their discussion are presented in chapter 4. Because different lignins in different amounts and different chain extenders were used to produce polyurethane foams, comparative method was used to uncover the role that liquefied lignin and chain extenders played in changing foams mechanical and thermal properties.

in Chapter 5 a summary of the research is presented with some insight on future developments.

2. Literature review

2.1. *Introduction*

In ages of increasing emission of greenhouse gases it is obvious that the utilization of renewable raw materials, where and when is possible, is a necessary step towards a sustainable development. By the late 19th century, the tanning of leather, papermaking, the conditioning and dyeing of natural fibres, the vulcanization of natural rubber, the use of drying oils in inks, paints, the use of starch and natural resins as adhesives, the chemical modification of cellulose to prepare the first thermoplastic polymers, and the processing of woods for different uses, had reached a high degree of technological application.

However, the relative importance of macromolecular materials based on renewable resources suffered then a gradual setback first with the rapid development of coal-based chemistry starting from that period and later with the petrochemical revolution of the 20th century. Although certain sectors, like papermaking and the use of drying oils, remained unchallenged; others, like the production of tires and cellulose esters, lost their market supremacy, and still others, like the utilization of natural resins, were relegated to a minimal industrial role. Within a few decades, polymers prepared from fossil resources spread into the world, with huge quantities of plastics, elastomers, fibres, adhesives, paints, and packaging materials.

The essential reasons why this state is going to a change are extremely well-known, fossil resources, particularly petrol and natural gas, are likely to start decreasing within one or two generations, the price of petrol is rising and there are no indications that it will return to a small fraction of its present value, the sense of urgency related to sustainability has finally reached awareness of governments and industries, and the concept of a biomass refinery is rapidly becoming a reality, with efficient realizations being implemented throughout the world (Gandini, 2008).

In particular renewable raw materials can perennially provide a basis for daily life products and avoid further contribution to greenhouse effects, furthermore the utilization of renewable raw materials, taking advantage of the synthetic potential of nature can meet the other principles of the green chemistry, such as built-in design for degradation or an expected lower toxicity of the resulting products. Some of the most widely applied renewable raw materials in the chemical industry for non-fuel applications include plant oils, polysaccharides (cellulose and starch mainly).

2.2. *Polyurethanes*

Polyurethanes usually are defined as polymers which contain urethane group in the main polymer chain. The commercial development of polyurethanes officially started in 1937 when Dr. Otto Bayer synthesised the first polyurethane, by the reaction of a diisocyanate with a polyester having two terminal hydroxyl groups. Bayer invented a new method for the synthesis of macromolecular compounds: the polyaddition reaction, which is a special case of polycondensation, in which the reaction product is exclusively the polymer. In the classical polycondensation reactions, the products are: the polycondensation polymer and a low molecular weight compound (water, alcohols, etc.). The fact that in the polyaddition reactions the product is only the polymer is of great technological importance, especially for the purity and the morphology of the resulting macromolecular compound.

After the war growing interest on polyurethane was established, the German chemical industry quickly recovered from the effect of the war and Bayer developed elastomers and flexible foams and shortly after his company developed machines for continuous production of the foams broadening the market and lowering the price.

In the slightly more than 65 years of the existence of polyurethanes, the growth of the polyurethanes was constant and the prediction for the future is very optimistic due to the new markets opened in Eastern Europe, Asia and South America. The increase of polyurethane consumption between 2000-2010 is shown in Figure 2.1.

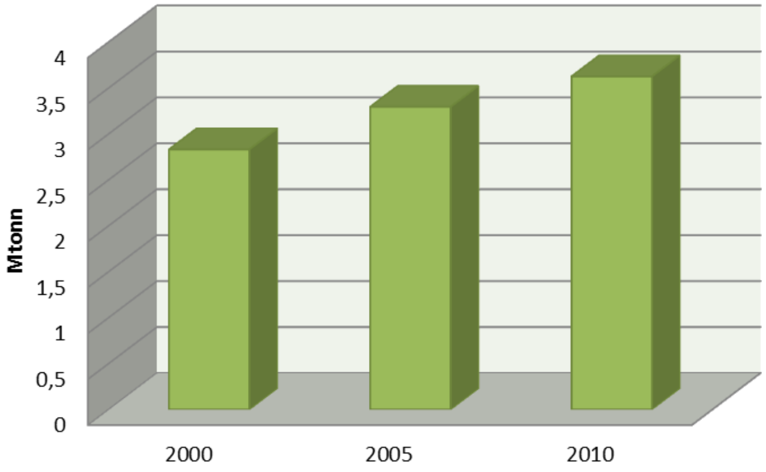


Figure 2-1 Growth of polyurethane consumption (Ionescu, 2005).

Polyurethanes represent only 5% of the worldwide polymer consumption (Figure 2-2 shows around 10.6 million metric tonnes in 2004), but the dynamics of their growth is constantly high.

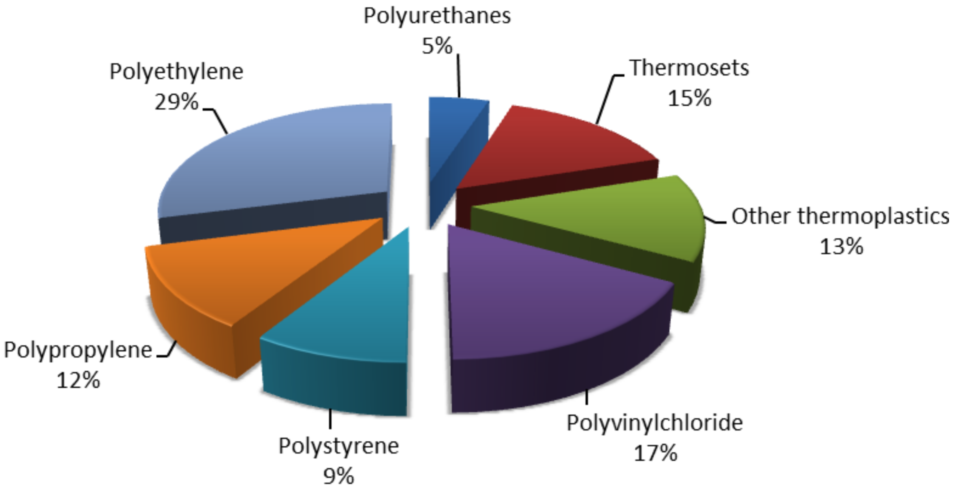


Figure 2-2 Polyurethanes and world production of plastics.

The main field of polyurethane application is the furniture industry, around 30% of the total polyurethanes produced worldwide is used for the production of mattresses from flexible slabstock foams. Automotive manufacture is the second important application for flexible and semiflexible polyurethanes. The polyurethane elastomers are used for shoe soles, footwear, athletic shoes, pump and pipe linings, industrial tyres, microcellular elastomers, etc. Light but highly abrasion-resistant polyurethanes are perfect for hardwearing shoe soles, with excellent long-term mechanical properties. Polyurethane soles are practical and keep water out, while in no way limiting design potential. Polyurethane adhesives, sealants, coatings and fibres represent another group of polyurethanes with specific applications. Polyurethane's adhesive properties can also exploited in the manufacture of high-performance composite wood products. As shown in Figure 2-3., flexible polyurethane foams can be used in applications such as seating, cushioning, carpet underlayment, fabric backing, insulation, and packaging.

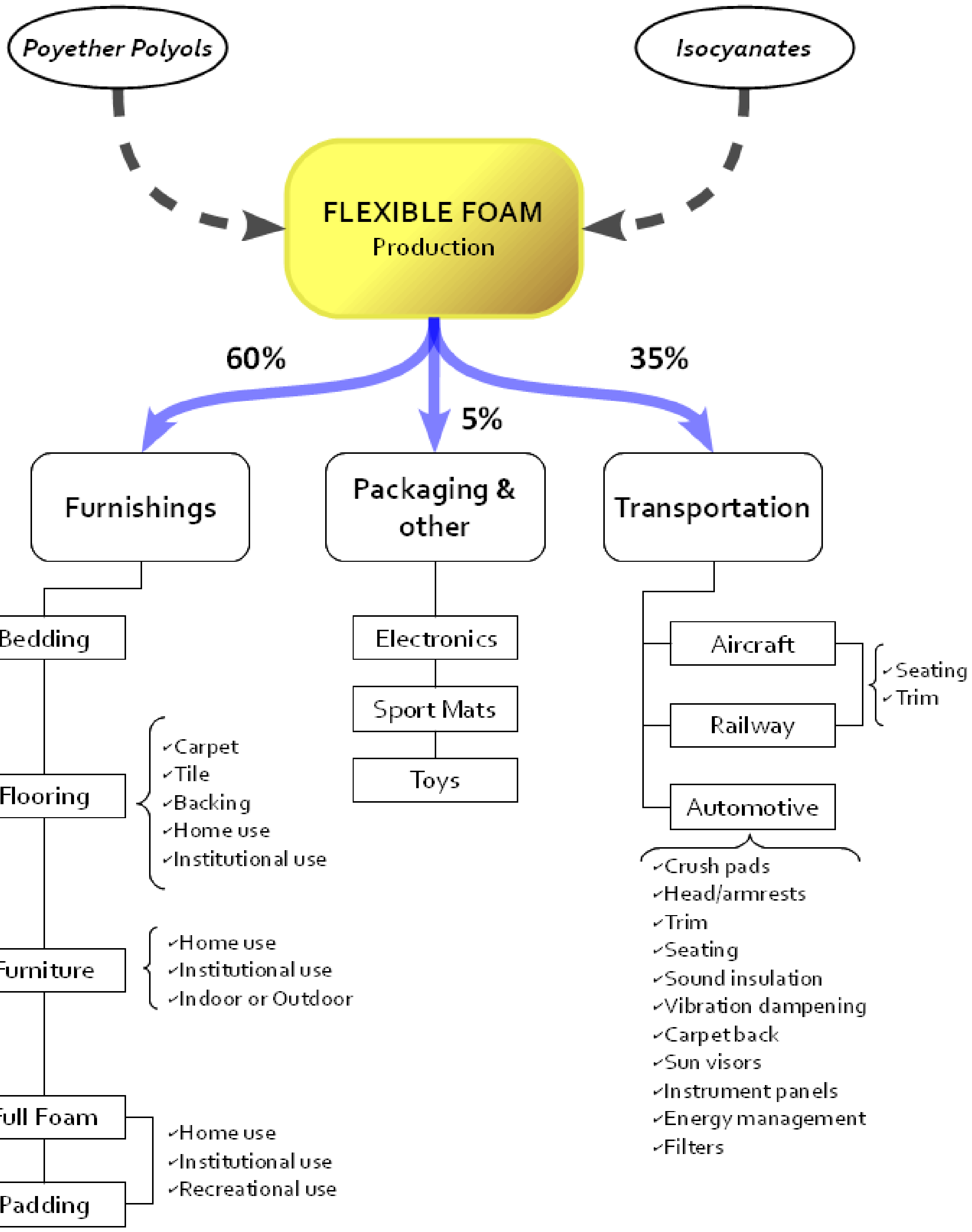


Figure 2-3 Application of flexible polyurethane foam technology.

Rigid polyurethane foams are used in thermal insulation of buildings and refrigerators, cold stores, pipe insulation, refrigerated transport, thermal insulation in chemical and food industries. In transportation, the lightweight nature of polyurethanes, combined with their versatility, strength and durability, makes them ideal for use in car seating, as coatings for car frames, in the bodies of vehicles to regulate noise and heat, and even in airbags. Their greatest benefit in terms of energy efficiency is that their use in cars and trucks leads to a reduction in vehicle weight, and therefore greater fuel economy.

The main applications of polyurethanes are presented in Figure 2-4.

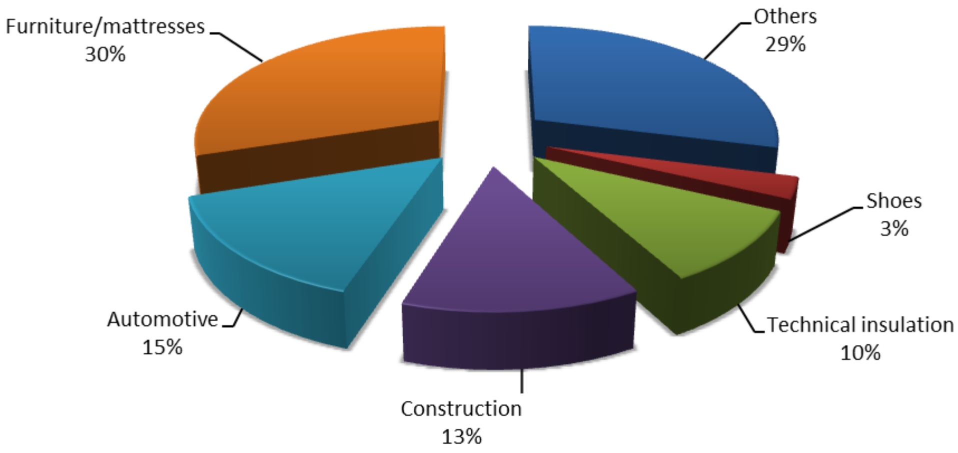


Figure 2-4 The main application fields of polyurethanes.

Polyurethanes are an extremely versatile group of polymers, Figure 2-5 illustrates the broad range of polyurethanes, with reference to density and stiffness., they can present, from very soft to very hard structures. It is well known that a foam is a composite solid-gas material. The continuous phase is the polyurethane polymer and the discontinuous phase is the gas phase.

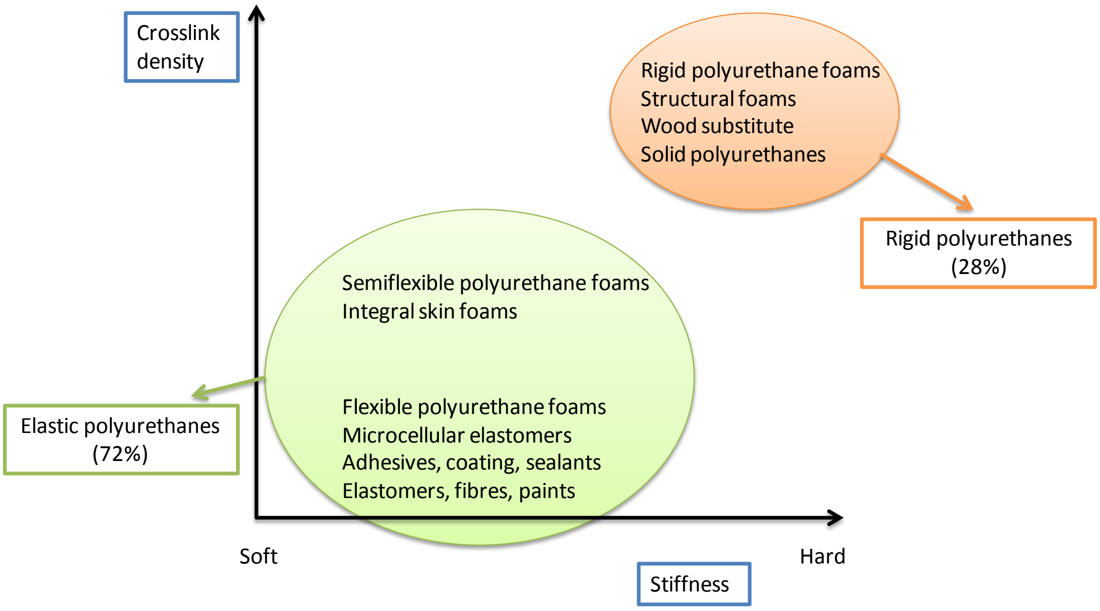
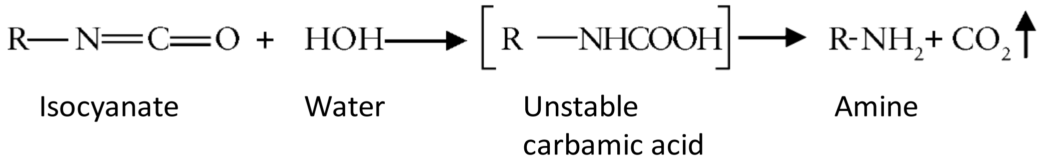


Figure 2-5 Classification of polyurethanes as function of crosslink density and stiffness.

2.2.1. Basic chemistry of flexible polyurethanes

Flexible foams have relatively low load bearing properties but high recovery properties when compared to semi-rigid and rigid foams. In addition, flexible polyurethane foams could range widely in terms of softness or firmness, resilience, density and others; and flexible foams could also be utilized in various applications including furniture, packaging, automotive and etc.

In the production of flexible polyurethane foams there are two main reactions: the blow reaction and the gelation reaction. If the gelation (cross-linking) reaction occurs too quickly, a close celled foam may result. If the blow (gas-producing) reaction occurs too quickly, the cells may open before the polymer has enough strength to maintain the cellular structure, resulting in collapse of the foam. These two reactions must kept in proper balance in order to obtain the desired product. The reaction between isocyanates and water leads to production of gaseous carbon dioxide and an urea group. This reaction is a very convenient source of a gas necessary to generate the cellular structure of polyurethane foams. The first step of blowing reaction is shown in Figure 2-6.

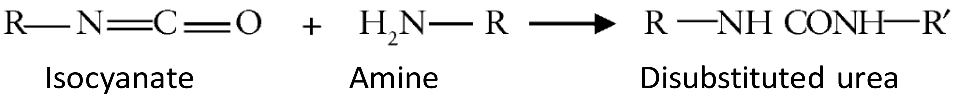


$$R{-}N{=}C{=}O + HOH \longrightarrow [R{-}NHCOOH] \longrightarrow R\text{-}NH_2 + CO_2\uparrow$$

Figure 2-6 Reaction between water and isocyanate.

It is evident that one mole of water reacts with two -NCO groups, which is very important in order to calculate the correct quantity of isocyanate needed for polyurethane formulations. Water is considered, in polyurethane foam manufacture, as a chemical blowing agent, because the gas generation is a consequence of a chemical reaction.

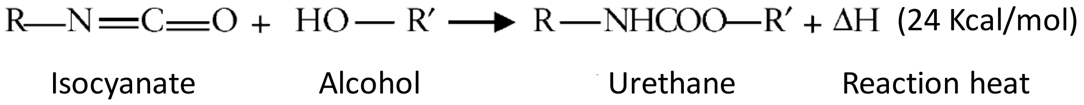
As shown in Figure 2-7, the amine reacts very quickly with other isocyanate molecules and generates a symmetrical disubstituted urea. The hard urea domains are organized into loose hydrogen-bonded structures which increases the modulus. This step is responsible for the cell expanding until no further rise in volume is possible.



$$R{-}N{=}C{=}O + H_2N{-}R \longrightarrow R{-}NH\,CONH{-}R'$$

Figure 2-7 Reaction between isocyanate and amine.

The reaction of an alcohol functionality with an isocyanate group, as shown in Figure 2-8, is the most important reaction involved in polyurethane synthesis, it is an exothermic reaction and leads, to production of urethanes.



$$R{-}N{=}C{=}O + HO{-}R' \longrightarrow R{-}NHCOO{-}R' + \Delta H \text{ (24 Kcal/mol)}$$

Figure 2-8 Reaction between isocyanate and alcohol.

The isocyanate group shows a very high reactivity that can be explained by the following resonance structure (Figure 2-9). Electron density is higher at the oxygen atom, while the carbon atom has the lowest electron density. As an immediate consequence, the carbon atom has a positive charge, the oxygen atom a negative one and the nitrogen atom an intermediate negative charge.

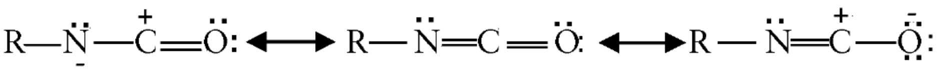


Figure 2-9 Resonance structure of isocyanate.

Isocyanate can therefore react with hydrogen active compounds like urethane groups (may be considered hydrogen active compounds, due to the hydrogen atom linked to the nitrogen atom) to form an allophanate (Figure 2-10), in order to promote the allophanate formation higher temperatures are necessary: greater than 110°C. It is important to mention that the allophanate formation is a reversible reaction however, this side reaction has not been shown to actually occur in typical foam production (Herrington and Hock, 1998). and it is generally not favourable under the catalytic conditions used for flexible foam production.

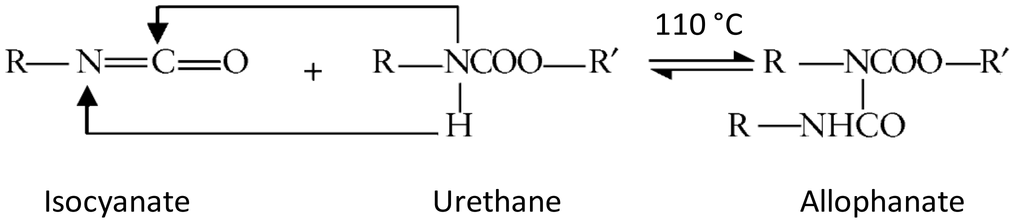


Figure 2-10 Reaction between isocyanate and urethane leading to allophanate.

Similarly to the allophanate formation, the -NH groups of urea react with isocyanates, to generate a biuret (Figure 2-11), also similarly to the allophanate formation, the reaction between urea and isocyanates is an equilibrium reaction and needs temperatures higher than 110 °C. Formation of allophanates and biurets in polyurethane chemistry, especially when an excess of isocyanate is used, is in fact a supplementary source of crosslinking.

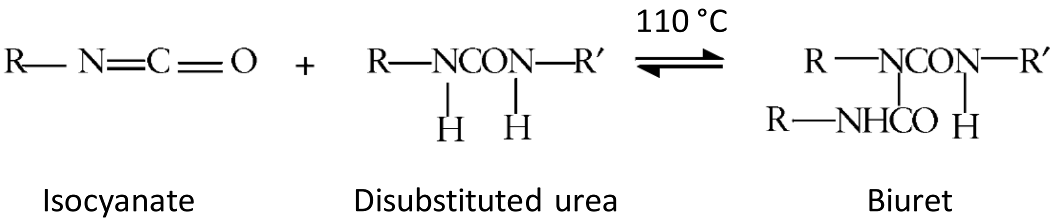


Figure 2-11 Reaction between isocyanate and disubstituted urea leading to biuret.

The reactivity of isocyanates toward carboxylic acids is much lower than the one with amines, alcohols and water. The final product is an amide and gaseous carbon dioxide.

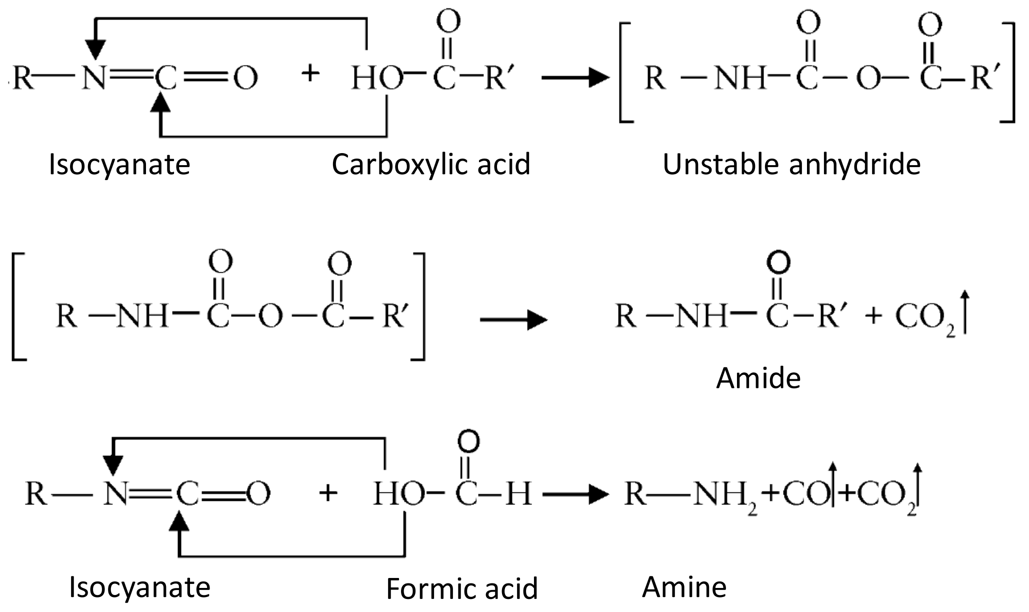


Figure 2-12 Reaction between isocyanate and carboxylic acid.

A special case is the reaction of an isocyanate group with formic acid (Figure 2-12). One mole of formic acid generates two moles of gases: one mole of carbon dioxide and one mole of carbon monoxide. Formic acid is considered, like water, to be a reactive blowing agent.

All the amines are much more reactive than the hydroxyl compounds, the relative order being as shown in Figure 2-13.

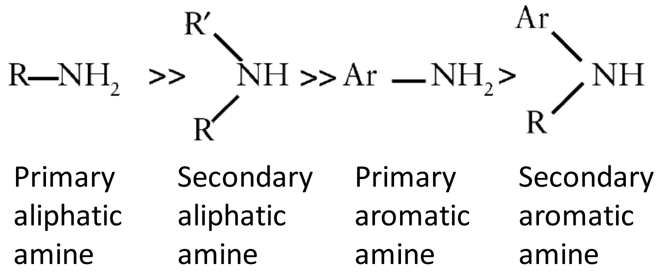


Figure 2-13 Relative reaction rates of isocyanates against amine.

Primary hydroxyl groups are more reactive than secondary hydroxyl groups and much more reactive than tertiary or phenolic hydroxyl groups (Figure 2-14).

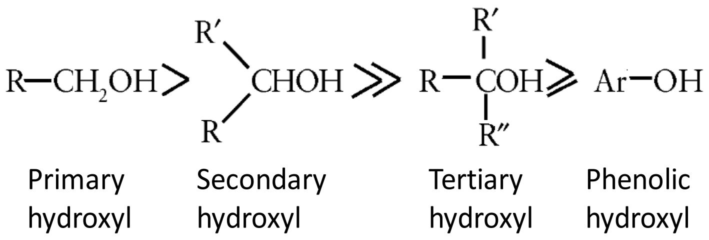


Figure 2-14 Relative reaction rates of isocyanates against hydroxyl.

The relative rates of reaction of the isocyanate component with other foam reactants at 25 °C under uncatalyzed conditions are provided in Tab. 2-1. These can serve as a guideline to make appropriate catalyst adjustments to achieve a suitable balance of the two reaction schemes.

Tab. 2-1 The relative reactivities of isocyanates against different hydrogen active compounds (Herrington, 2004).

Hydrogen active compound	**Relative reaction rate (non-catalysed, 25 °C)**
Primary aliphatic amine	2500
Secondary aliphatic amine	500÷1250
Primary aromatic amine	5÷7.5
Primary hydroxyl	2.5
Water	2.5
Carboxylic acid	1
Secondary hydroxyl	0.75
Urea	0.3735
Tertiary hydroxyl	0.0125
Phenolic hydroxyl	0.0025÷0.0125
Urethane	0.0025

A combination of both the foam gas bubbles, or cells, and the polymer phase morphology contributes to the final properties of flexible foams.

The cellular structure can be described as a collection of tetrakaidecahedral shaped cells, influences foam mechanical properties via a number of parameters, the foam modulus is most influenced by foam density, typically described by a power law relationship (Gibson and Asby, 1997). At the microstructural level, polymer phase morphology varies at different length scales (Figure 2-15).

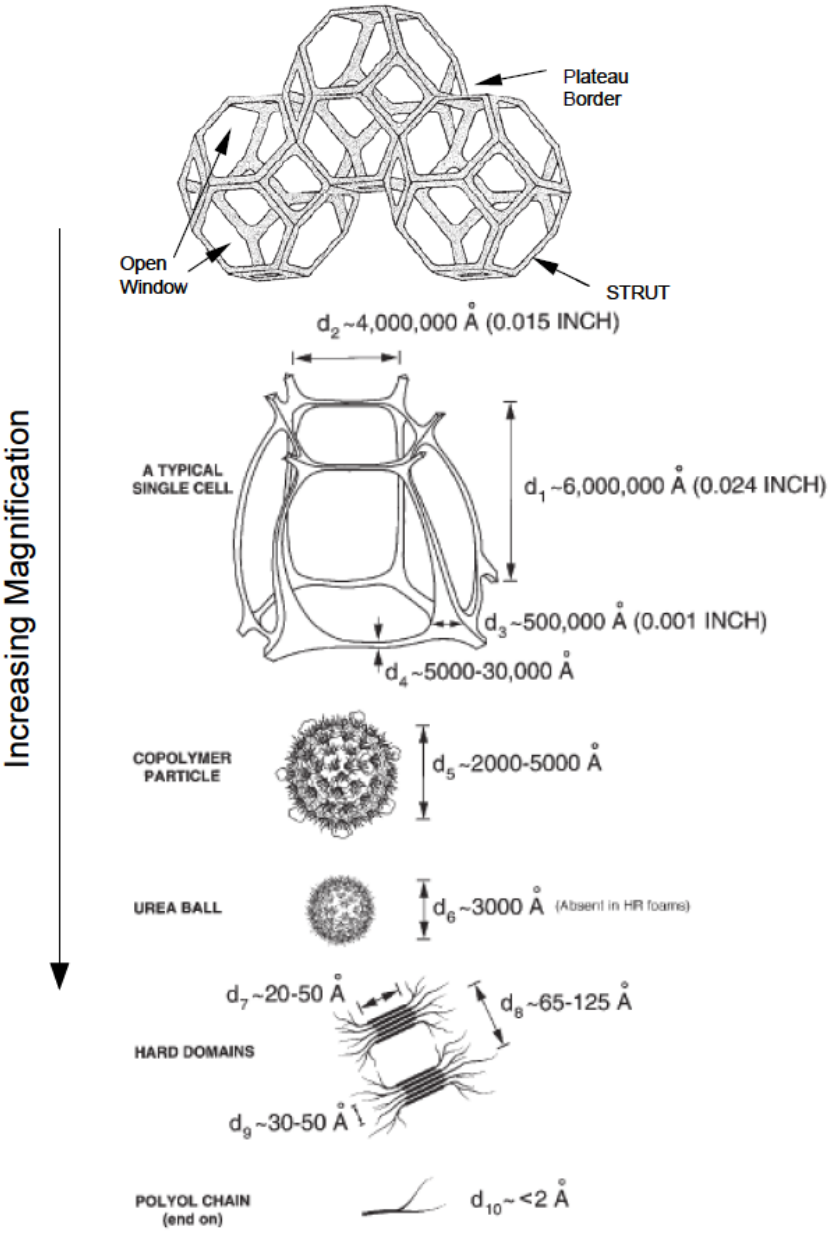


Figure 2-15 Flexible foam morphology at different length scales (Herrington, 2004).

Both blowing and gelling reactions compete for isocyanates in the foaming mixture. The kinetically faster reaction, water-isocyanate reaction, quickly forms polyurea segments and releases CO_2 gas to expand the mixture. The hydroxyl-isocyanate reaction, gradually polymerizes isocyanates and polyols building up molecular weight. At a critical conversion, the entire system crosses the thermodynamic boundary of a miscible system, and phase separation occurs (Macosko, 1989; Ryan et al., 1991). The resulting polymer is a segmented block copolymer with domains that are rich in either polyurea segments or polyol segments (Cooper and Tobolsky, 1966). Within a polyurea-rich hard domain, further association of the segments can also occur through hydrogen bonding (Paik-Sung and Schneider, 1975; Coleman et al, 1986). A simple illustration of this phase-separated morphology is shown in Figure 2-16.

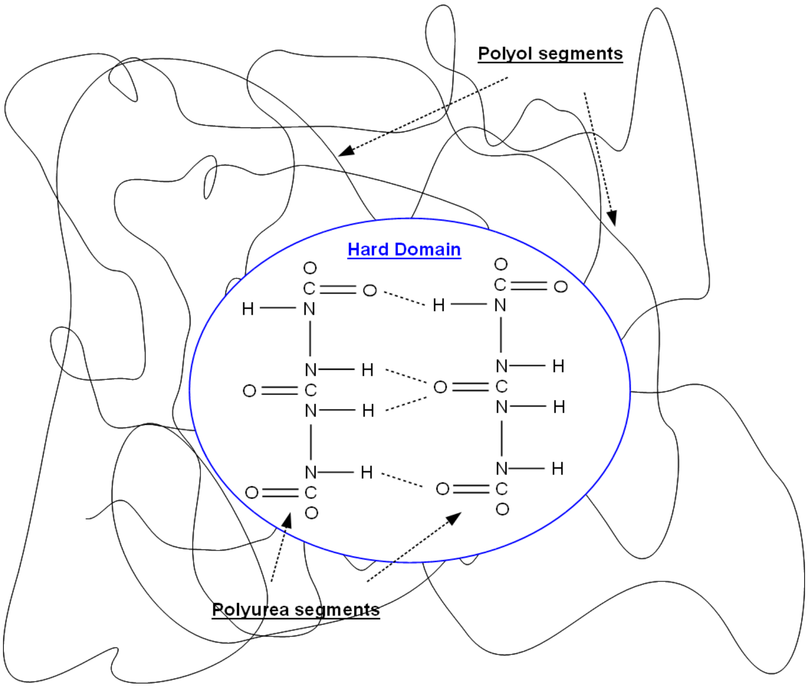


Figure 2-16 Phase separated morphology of polyurethanes flexible foams. Dashed lines indicate hydrogen bonding within a hard domain.

The polyol-rich domains, also called soft domains, have a low glass transition temperature (T_g) that usually is between –50 °C to –70 °C. The low T_g domains give polyurethane flexible foam its visco-elastic properties and allow energy absorption and dissipation. The polyurea-rich hard domains, have a much higher T_g, in comparison, generally above 100 °C. The high T_g hard domains provide polyurethane flexible foam with its modulus and thermal stability. These hard domains are not, generally, covalently bound together but derive their cohesive strength from physical associations. However, since most hard segments will eventually be bound into the polyol phase via the gelation reaction, it is considered that the properties of these polymers depend on a network of covalent and a physical cross-links. The presence of hard domains in segmented polyurethanes is very important to the mechanical properties. In segmented polyurethanes, hard domains act as physical crosslinks, playing a role similar to chemical crosslinks in vulcanizates and imparting the material's elastomeric behaviour. Since hard domains also occupy significant volume and are stiffer than soft domains, they also function as effective nano-scale fillers and make the material behaviour similar to that of a composite (Petrovic and Ferguson, 1991).

2.2.2. Polyols

The polyol flexible segments impart flexibility to polyurethanes and are responsible to their high elongation at break, low temperature resistance and low T_g. The best strength properties of polyurethane are achieved by using polyols of symmetrical structure. Polyols are polyhydroxyl compounds, polyether polyols and polyester polyols are two major kinds of polyols consumed in the global polyols market. Therefore, although about ninety percent of polyols utilized today are polyether polyols because they are cheap, easy to handle, and are more resistant to hydrolysis than polyesters. There are made by the addition of alkylene oxides, usually propylene oxide, onto alcohols or amines which are usually called starters or initiators. The addition polymerization of propylene oxide occurs with either anionic (basic) and cationic (acidic) catalysis although commercial polyols production is usually by base catalysis. Polyethers based on propylene oxide thus contain predominantly secondary hydroxyl end groups. Secondary hydroxyl end groups may have inconveniently low reactivity. The primary hydroxyl content may be increased by the separate reaction of the polyoxypropylene polyols with ethylene oxide to form a block copolymer. By this means the primary hydroxyl end group content may be varied from about 5% to over 80% of the total hydroxyl end groups as shown in Figure 2-16. The reaction is carried out at ca. 100 °C. Water removal is an important step. Since the monomers and polyether polyols are easily oxidized, air is excluded from the manufacturing process. When the polymerization is complete, antioxidants are added to prevent the oxidation of the polyether (Woods, 1990).

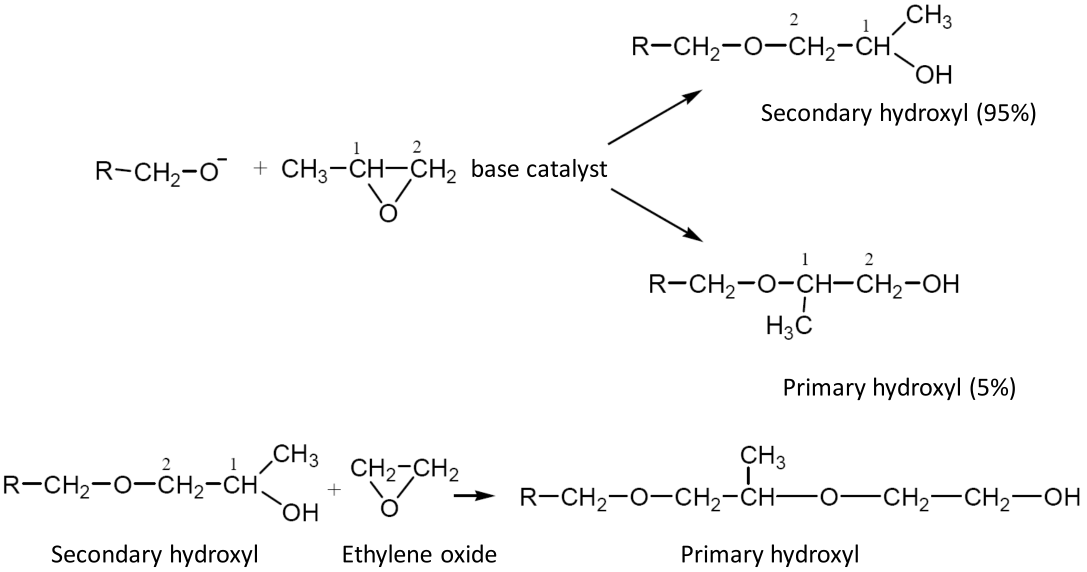
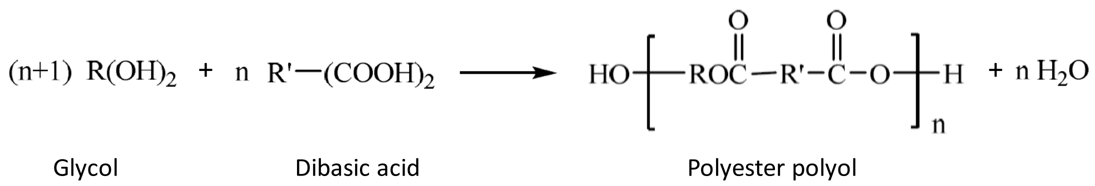


Figure 2-17 Synthesis of polyether polyol.

Saturated polyesters with terminal hydroxyl-groups are used to make both flexible and rigid polyurethane polymers. Polyester polyols tend to be more expensive than polyether polyols and they are usually more viscous and therefore more difficult to handle. They also yield polyurethane polymers which are more easily hydrolyzed. Consequently they are only used to make polyurethanes for demanding applications where the particular physical properties obtainable from polyester are important. Polyesters are also less easily oxidized and resist to higher temperatures than polyethers. Polyester polyols are formed by direct esterification in a condensation reaction (Figure 2-18). The reaction is a reversible equilibrium reaction driven by continuous water removal. As the reaction proceeds, transesterification occurs to form the polymer backbone and culminating in a relatively wide molecular weight distribution in the final products. The control over the ratio of the ingredients used is also necessary in order to obtain products with the required hydroxyl end group instead of an acid end group.

Conventionally, polyester polyols are prepared from polyhydric alcohols such as ethylene glycol, diethylene glycol and butylene glycol reacted with polyfunctional organic acids, such as adipic acid or phthalic acid.



$$(n+1)\ R(OH)_2 + n\ R'{-}(COOH)_2 \longrightarrow HO{-}\left[RO\overset{\overset{O}{\|}}{C}{-}R'{-}\overset{\overset{O}{\|}}{C}{-}O \right]_n{-}H + n\,H_2O$$

Figure 2-18 Synthesis of polyester polyol.

Two important properties of polyols play a dominant role in properties of the final product, polyurethane polymers. These properties are functionality and equivalent weight. The functionality of polyols can be defined as the average number of functional groups reacting to isocyanate per molecule of polyols. The equivalent weight of polyols can be defined as follows:

$$Equivalent\ weight = \frac{Molecular\ weight\ of\ polyols}{Functionality\ of\ polyols} = \frac{56100}{Hydroxyl\ number}$$

The hydroxyl number (mgKOH/g) is milligrams of potassium hydroxide equivalent to the hydroxyl groups found in one gram of polyols.

The molecular weight of the oligo-polyols used in polyurethane synthesis varies between 300-10000 daltons, in the region of low molecular weight polymers (oligomers), the number of hydroxyl groups/molecule of oligo-polyol (the oligo-polyol functionality) being generally in the range of 2-8 OH groups/mol. A polyol of low functionality, having around 2-3 hydroxyl groups/mol and with a high molecular weight of 2000-10000 daltons, leads to an elastic polyurethane and on the contrary, a low molecular weight oligo-polyol of 300-1000 daltons, with a high functionality of around 3-8 hydroxyl groups/mol leads to a rigid crosslinked polyurethane. A polyol of high molecular weight (3000-6500 daltons) and of low functionality, of around 2-3 hydroxyl groups/mol, if reacted with a diisocyanate, leads to a low crosslinked, flexible polyurethane structure. Petrović and coworkers (Petrović et al., 2002) studied the effect of NCO/OH molar ratio on properties of polyurethane based from soy polyol that was derivative of the soy triglyceride of molecular weight 874 g mol^{-1} and functionality 3.6. It was found that the casting polyurethane with a high NCO/OH ratio displayed a rigid and brittle nature, but the cast resin with a low ratio became more and more flexible. For thermal analysis, T_g of the cast polyurethane decreased when the NCO/OH molar ratio was decreased from 64 °C for the NCO/OH ratio of 1.05 to below 0 °C for the NCO/OH ratio of 0.4. Tensile strength decreased but elongation increased with decreasing molar ratio of NCO/OH. The highest flexural modulus and lowest impact resistance are obtained from the cast resin with an NCO/OH ratio of 1.05.

2.2.3. Isocyanates

Isocyanates are mainly constituents of hard segments of polyurethanes. With increasing symmetry of the isocyanate, the following properties increase: the ability of the polyurethane to crystallize, microphase separation, modulus of elasticity, tensile strength, hardness. From isocyanates of a more regular structure and with an aromatic backbone structure, improvement of the strength of polyurethane is obtained.

Methylene diphenyl diisocyanate (MDI) and toluene diisocyanate (TDI) are two major kinds of isocyanates consumed in the global isocyanate market. TDI is usually obtained as a mixture of 2,4- and 2,6- TDI isomers.

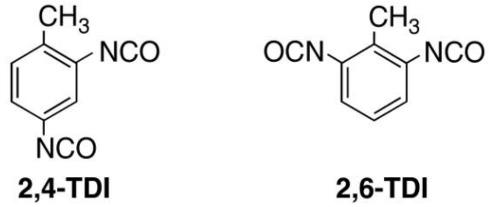


Figure 2-19 Structures of TDI isomers.

The two isomers differ in two ways. Firstly the reactivity of the ortho position in the 2,4 isomer is approximately 12% of the reactivity of the para position due to the steric hindrance caused by the methyl group. However, when the reaction temperature approaches 100 °C, steric hindrance effects are overcome and both the positions react at nearly the same rate. The second way in which the two isomers differ is that the 2,6 isomer is symmetric as compared to the 2,4 isomer and therefore is expected to form hard segments with better packing characteristics.

There are also a few types of MDI available in the market such as 4, 4-, 2, 4-, 2, 2- and polymeric MDI, a liquid mixture containing monomeric MDI isomers and oligoisocyanates, that is used in high resiliency, semiflexible, and microcellular foams as shown in Figure 2-20. Pure MDI is the most widely used, and it is obtained by distilling the mixed product. Blends of MDI and TDI are also frequently utilized. A benefit of these products is that using polymeric MDI and TDI endcapped polyol reduces the vapour hazard of the isocyanate component.

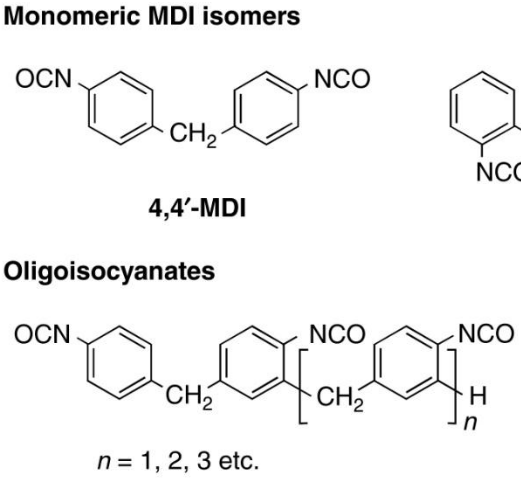


Figure 2-20 Chemical structures of MDI species, oligoisocyanates are products having 3, 4, 5 etc. rings, as indicated in the above example of an oligoisocyanate series.

Many publications studied the effect of the isocyanate structure on the polyurethane properties. Dounis and coworkers have discussed the effect of TDI index on the morphology and physical properties of flexible slabstock polyurethane foams, increasing the index increased the level of covalent crosslinking (Dounis and Wilkes, 1997). Lee and Tsai (Lee and Tsai, 2000) studied the effect of types of diisocyanates on properties of polyurethane material with hard segment content of 40% by bulk polymerization of a poly(tetramethylene ether) glycol and 1,4-butanediol and various diisocyanates (MDI, TDI, IPDI, HMDI and HDI). The data from DSC and DMA showed that the thermal transitions are influenced significantly by the diisocyanates structure. In the segmented polyurethane materials with aliphatic hard segment, the polyether soft segment is immiscible with the hard segment. However, in the segmented polyurethane materials with aromatic hard segment, the soft segment is partially miscible with the hard segment. Javni and coworkers (Javni et al., 2003) studied the influence of different isocyanates on the properties of soy based polyurethanes. They indicated that the properties of the soy based polyurethanes strongly depend on crosslinking density and structure of isocyanates. Aromatic triisocyanates impart the highest density, modulus and tensile strength but the lowest elongation at break, swell in toluene and impact resistance. Aliphatic triisocyanates and diisocyanates give rubbery materials with the highest elongation at break, the highest swelling and the lowest tensile strength. Polyurethanes with aromatic and cyclodiisocyanates showed values between those of the two previous groups.

2.2.4. Water

In polyurethane production, water is added to react with the isocyanate. This reaction ultimately produces polyurea, carbon dioxide and heat. This carbon dioxide diffuses to existing gas bubbles in the polyol and so expands the mixture into a foam. Control of the amount of air contained in the polyol raw material is one way that manufacturers control the number of nucleation sites in the reacting mixture. These initially small bubbles quickly grow through either gaining gas from the diffusing carbon dioxide or by coalescing with other bubbles. Increasing the water content influences both the cell structure and the solid-state morphology of the foam. Higher water contents typically result in foams with lower density due to the increased blow reaction. Also, since the hard segment content is increased on reacting more water with the isocyanate, this increases the stiffness of the foam.

2.2.5. Catalysts

Because flexible polyurethane foams are the product of two competing reactions, a proper balance is required between the two reaction rates to obtain a good open-celled morphology of the desired apparent density. Various combinations of catalysts are used in order to establish an optimum balance between the chain propagation reaction (isocyanate with hydroxyl) and the blowing reaction (isocyanate with water). The polymer formation rate and gas formation rate must be balanced so that the gas is entrapped efficiently in the gelling polymer and the cell-walls develop sufficient strength to maintain their structure without collapse or shrinkage. Catalysts are also important for assuring completeness of reaction in the finished foam. The most commonly used type of catalyst are the tertiary amines, they are compounds which contain a nitrogen atom having three substituent groups and a free pair of electrons (Figure 2-21). These catalysts are generally thought of as blowing catalysts but they do provide some enhancement of the gelation reaction. The extra electron pair on the nitrogen atom provides a strong nucleophile which is capable of attacking the carbon of the isocyanate group. Steric hindrance and electronic effects of the substituent groups are the two main tools used to adjust the relative catalytic activity in the various tertiary amines. Besides the electronic effects discussed above, the role of a catalyst is also determined by other physical and chemical properties. For instance, catalysts which have low boiling points, are readily volatized in the exothermic reactions taking place and are lost from the reacting mixture. Once they volatilize, it leads to a decrease in the catalytic effect. Other catalysts, which contain hydroxyl groups, such as dimethylaminoethanol, chemically react with the growing polymer chain, and thus are no longer able to find their way to a reaction site. In some foam systems, combinations of amines are used to balance the gelation and blow reactions.

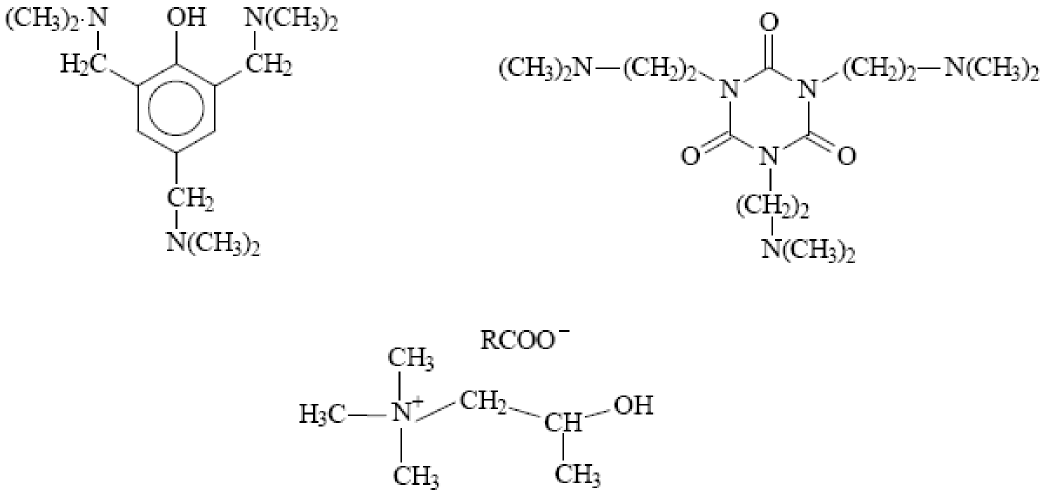


Figure 2-21 Tertiary reactive amines (Kirk-Othmer, 2002).

The gelation reaction is also promoted through the use of organometallic catalysts, of which the tin based catalysts are the most popular. These compounds behave as Lewis acids and are generally thought to associate with the basic sites of the isocyanate and polyol groups. One common hypothesis is that this interaction enhances the Lewis acidic nature of the carbon in the isocyanate group, making it more reactive towards the oxygen of the polyol hydroxyl functionality. Another hypothesis suggests that the organometallic compound actually complexes with the strongest Lewis bases in the system—the tertiary amines. This new complex is postulated to associate with a polyol molecule forming a tin alkoxide and promoting its reaction with isocyanate groups (Burkhart et al., 1984). This reaction generates a urethane linkage and regenerates the catalytic complex. It is important to point out that the use of these catalysts varies widely according to desired performance in a specific manufacturing processes, even after careful literature reviews and pilot scale testing, the exact amount of catalyst used must often be tuned to each system once applied to production scale.

2.2.6. Surfactants

Almost all flexible polyurethane foams are made with the aid of nonionic, silicone-based surfactants. In broad terms, surfactants perform several functions. They:

- Lower surface tension
- Emulsify incompatible formulation ingredients
- Promote nucleation of bubbles during mixing
- Stabilize the rising foam by reducing stress concentrations in thinning cell-walls
- Counteract the defoaming effect of any solids added to or formed; e.g., precipitated polyurea structures, during the foam reaction

Among these functions, stabilization of the cell-walls is the most important. By doing this, the surfactant prevents the coalescence of rapidly growing cells until those cells have attained sufficient strength through polymerization to become self-supporting. Without this effect, continuing cell coalescence would lead to total foam collapse. Surfactants also help to control the precise timing and the degree of cell-opening.

Within each foam formulation, a minimum level of surfactant is needed to produce commercially acceptable foam.

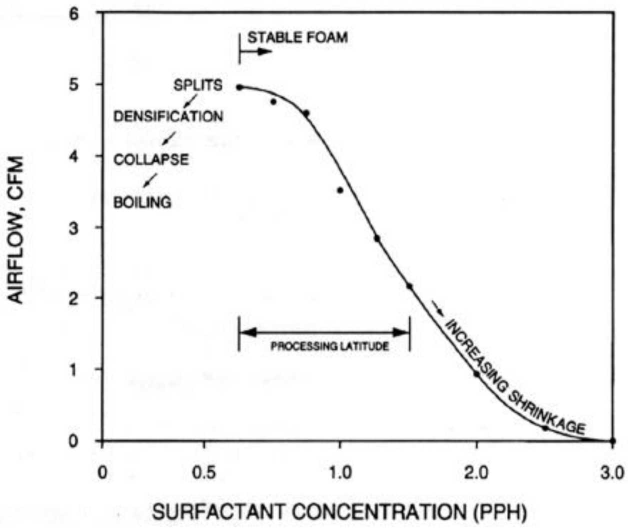


Figure 2-22 Effect of concentration for a typical silicone surfactant on airflow.

The processing window for surfactants is generally in the range of 0.5-2.5 parts per hundred polyol (pphp), and the actual quantity of surfactant added is dependent on the type of surfactant used as well as on the other constituents of the foam formulation. In the absence of a surfactant, a foaming system will normally experience catastrophic coalescence and exhibit the event known as boiling. With addition of a small amount of surfactant, stable yet imperfect foams can be produced. With increasing surfactant concentration, a foam system will show improved stability and cell-size control. At optimum concentrations, stable open-cell foams may be produced. At higher surfactant levels the cell-windows become overstabilized and the resulting foams are tighter with diminished physical properties. Today the majority of flexible foams are made from a class of surfactants identified as polysiloxane-polyoxyalkylene copolymers. The siloxane block is known to lower the bulk surface tension whereas the polyoxyalkylene promotes the solubilization of the surfactant into the polyol and aids in emulsification of the foaming components. Also, the polyoxyalkylene part is tailored according to the type of foam application. This is done by varying the percentage and arrangement of ethylene oxide units and propylene oxide units which make up the polyoxyalkylene. By doing so, desired levels of affinity of surfactant for water, and solubility of surfactant in the foam polyol, can be achieved.

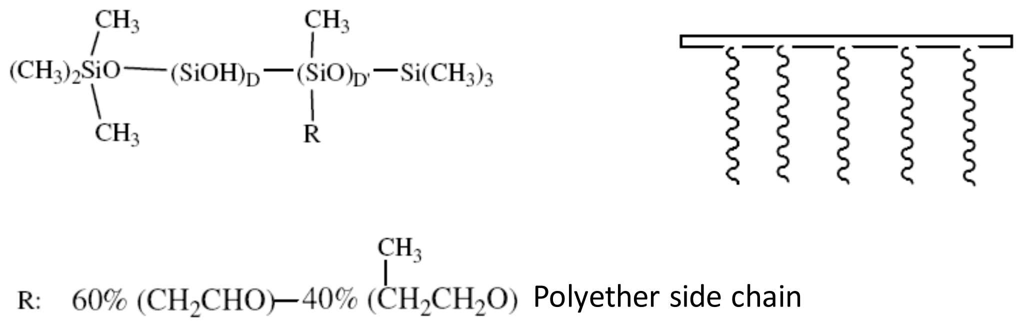


Figure 2-23 Structure of a standard silicone surfactant.

Zhang and co-workers (Zhang et al, 1999) studied the effects of silicone surfactant in flexible polyurethane foams, investigating the phenomena related to the bubble formation and stabilization. Cell window stabilization is one of the most important phenomenon. As the volume fraction of the gas bubbles exceeds 74%, the spherical bubbles will distort into multisided polyhedrals and cell windows with Gibbs Plateau borders are formed (Figure 2-

24). Due to capillary pressure, pressure inside the plateau borders is lower than that in the cell windows. This pressure difference will cause liquid in the cell window to drain into the struts. Without adding silicone surfactant, this drainage rate will be very fast so that film rupture and bubble coalescence occur rapidly, when silicone surfactant is added the cell window drainage rate is slower. During the initial stages of foam formation, at the liquid-liquid interface, surfactants have been shown to promote the interfacial mixing of the water and the polyol. At the latter stages, when urea hard segments are generated, the surfactant has been shown to stabilize the precipitating urea phase (Snow et al., 2005).

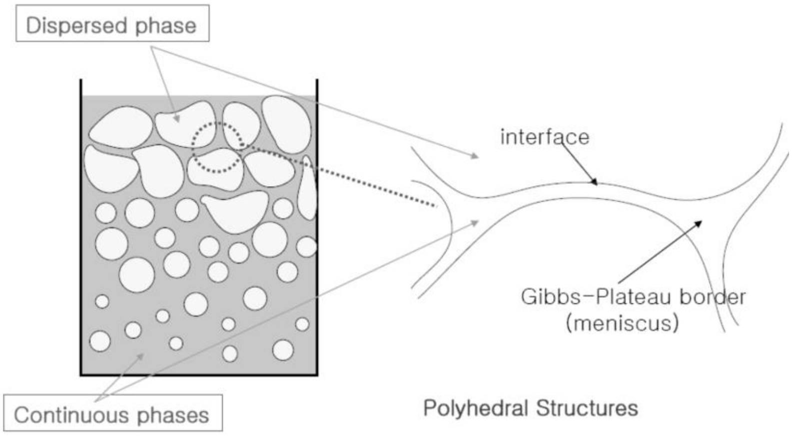


Figure 2-24 A generalized foam system (Kim and Kim, 1997).

2.2.7. Foaming process

Fourier transform infrared spectroscopy (FTIR) has been extensively used to study the foaming reactions. In general, there is agreement amongst different workers that the water-isocyanate reaction takes place sooner and faster as compared to the polyol-isocyanate reaction. This is supported by a growing urea carbonyl absorption at ca. 1715 cm^{-1} early in the reaction which is observed to shift to ca. 1640 cm^{-1} once half the foam rise height is reached. This suggests that a stage is reached when the polyurea being formed is no longer soluble in the foaming mixture and phase separation takes place. Some researcher observed that the urea formation takes place within the first 5 min of the foaming process. The urethane formation, however was not significant in the first 5-10 min, but was found to increase at a steady rate for the next 30 min (Bailey and Critchfield, 1981). The phase separation of the urea, therefore, was responsible to give the foam its structural integrity. It has also been observed that cell rupture took place just after the urea precipitation. For this reason, it has been suggested that the precipitation of the urea destabilizes the foam mix and aids in cell opening (Rossmy et al., 1981).

Different techniques were used to try and identify the event of cell-opening. The simplest method to do so is by visual observation of blow-off which is marked by a swift cessation of the foam expansion and a release of the gas under pressure. Miller and Schmidt used a porosimeter to measure bulk permeability of the foam, and identified cell-opening with a rapid increase in foam permeability (Miller and Schmidt, 1983). In a more recent work, a parallel plate rheometer was used to study cell opening. It was observed that the normal force exerted by the expanding foam mixture on the rheometer plates was a function of the rate of foam expansion, and the foam modulus. This work suggested that the visually observed blow-off of the foam coincided with a sudden drop in the normal force which marked the cell opening event (Neff and Macosko, 1996) .

2.3. Polyurethanes from vegetable oils

Polyurethanes are known for their versatility, but one of the problems related to the production of polyurethanes nowadays is their dependence on petroleum derivative products. As the oil crisis and global warming deepens, the study of polyurethanes based on renewable resources has re-emerged. Usually, both isocyanate and polyol are petroleum based. Due to uncertainty about the future cost of petroleum, as well as the desire to move toward more environmentally friendly feedstocks, many recent efforts have focused on replacing all or part of the conventional petroleum-based polyols with those made from vegetable oils. Combined with isocyanates, vegetable oil-based polyols produce polyurethanes that can compete in many ways with polyurethanes derived from petrochemical polyols. Since 60s, a wide range of vegetable oils have been considered for the preparation of polyurethane; the most important oils are highly unsaturated oils, where, by using various chemical reactions, the double bonds are transformed into hydroxyl groups including, sunflower, palm, rapeseed, but mainly castor and soybean oils.

Several researches are focused on polyurethanes based on vegetable oils (Petrović, 2008; Narine et al., 2007a; Das et al., 2008), depending on the reactant and process methods polyurethane polymer can be an elastomer, foam or plastic with a wide range of applications such as automotive seating, furniture, packaging and medical devices.

Tab. 2-2 Average annual worldwide production of 17 commodity oils, for 2001-2005 period.

Oil	**Average annual production (million tons)**	**Main producer**
Soybean	26.52	US
Palm	23.53	Malaysia
Rapeseed/canola	15.29	Europe
Sunflower	10.77	Europe
Tallow	8.24	US
Lard	6.75	China
Butterfait	6.26	Europe
Groundnut	5.03	China
Cottonseed	4.49	China
Coconut	3.74	Philippines
Palm kernel	2.95	Malaysia
Olive	2.52	Europe
Corn	2.30	US
Fish	1.13	Peru
Linseed	0.83	Europe
Sesame	0.76	China
Castor	0.56	India
Total	**121.67**	

Natural oil polyols all have similar sources and applications, but the materials themselves can be quite different, depending on how they are made. Usually they are clear liquids, ranging from colorless to medium yellow. Their viscosity is also variable and is usually a function of the molecular weight and the average number of hydroxyl groups per molecule (higher molecular weight and higher hydroxyl content both giving higher viscosity).

Vegetal oils can be extracted from different species, as summarized in Tab. 2-2, which gives the average annual worldwide production of the 17 most important commodity oils. The major growth in the vegetable oil production is presently related to palm and rapeseed/canola oil (Belgacem and Gandini, 2008) .

As a general rule, the chemical composition of oils arises from the esterification of glycerol with three fatty acid molecules. A given oil is always made up of a mixture of triglycerides bearing different fatty acid residues. The chain length of these fatty acids can vary from 14 to 22 carbons and contain 0–5 double bonds situated at different positions along the chain and in conjugated or unconjugated sequences.

Vegetable oil polyols have to satisfy some structural requirements in order to compete with petrochemical polyols, such as the right functionality, molecular weight, and OH number. Functionality of most flexible polyols is around 3 and molecular weights between 3000 and 6000 (OH numbers≈56-28 mgKOH/g, respectively). Higher OH numbers usually increase the cost of the formulation due to a higher isocyanate consumption. Vegetable oils have molecular weights below 1000 and cannot be easily transformed into triols of the given molecular weights. Besides, hydroxyl groups are usually introduced at the positions of double bonds, they are not terminal as in petrochemical polyols. When the OH groups are from oleic acid, they are located on the 9th or 10th carbon while the rest of the fatty acid chain of 9 or 8 carbons is left as a side group (dangling chain). This means that the real network chain is considerably shorter than if OH groups were located on the 18th carbon.

Recently, a variety of epoxidized plant oils (canola, midoleic sunflower, soybean, linseed, sunflower and corn) were used to prepare polyols, these polyols were polymerized with MDI revealing that canola, corn, soybean, and sunflower based polyols gave polyurethane resins of similar cross-linking density (and thus similar T_g) values as well as mechanical properties despite the different distributions of fatty acids. Higher crosslinking densities and higher mechanical properties were obtained from linseed oil derived polyols, whereas midoleic oil gave softer polyurethanes characterized by lower T_g and lower level of strength but higher elongation at break. The observed properties of the polyurethanes could be correlated to the different hydroxyl values of the used polyols (resulting in different cross-linking densities of the polyurethane networks) and were less dependent on the position of functional groups in the fatty acids of the polyols (Meier et al, 2007).

The exploitation of plant oils and derivatives, as practically unlimited resources, has recently attracted great interest in polyurethane technology. Undecylenic and oleic acids, two of the most valuable renewable building blocks from plant oils, were used to prepare a variety of diols and polyols. The recently emerged thiol-ene click chemistry (the addition of thiols to double bonds) of fatty acids obtained from plant oils is a promising entry to the easy and rapid preparation of new fatty acid-derived diols and polyols (Lligadas et al, 2010). Click chemistry concept, introduced by some researcher in 2001, describes chemistry tailored to generate substances quickly and reliably by joining small units together (Kolb et al, 2001). All the synthesized hydroxyl-containing monomers can be used in the preparation of linear thermoplastic and crosslinked polyurethanes systems, depending on its functionality.

Rigid polyurethanes can be prepared using soy polyols via the oxirane ring opening reaction of epoxidized soybean oil with methanol (Guo et al., 1999), to increase OH number to obtain necessary ridigity. This kind of foams have properties comparable to the one produced by petroleum-based polyols and even a better thermal and thermo-oxidative stability due to the lack of ether linkages in soy based foams which are apparently less stable towards thermal degradation than hydrocarbon and ester linkages present in the soy polyol.

In a recent work, conventional petroleum based polyols were substituted with increasing amounts of soy based polyols (Das et al., 2009). The soy polyol were functionalized in three step process, oxidation with formation of peracetic acid that reacts with triglyceride double bonds to form an epoxide and ring opening to form hydroxyl and acetate groups by acid catalysis. Flexible foam samples contained an amount of soy polyol ranging from 0 to 30%, this affected the properties and morphology, all the samples were microphase separated and an increase of soy polyol brought to an higher number of closed cell and broadening of T_g peak from DMA analysis, but still the samples showed respectable properties compared to the petroleum only based foams.

The transformation of an unsaturated triglyceride in a polyol was made by the generation of hydroxyl groups by using various reactions of double bonds. The most important way to transform an unsaturated vegetable oil into a polyol is the epoxydation of double bonds, followed by the various reactions of the resulting epoxidic ring which are transformed by hydroxyl groups. Some studies (Tu et al., 2009) reported however that the epoxidized soybean oil can directly participate in the polyurethane foaming reaction without opening the oxirane ring first. The resulting polyurethanes showed an increase in the hard segment, compared to control foam made with a commercial petroleum-based polyether polyol, because soybean oil has higher hydroxyl number and shorter polymer chains that caused stiffer foams.

A unique vegetable oil is castor oil, extracted from the seeds of the plant *Ricinus communis*, which is a triglyceride of ricinoleic acid. The idealised structure of castor oil is shown in Figure 2.25, castor oil, as sole polyol, leads to semi-flexible to semi-rigid polyurethane foams.

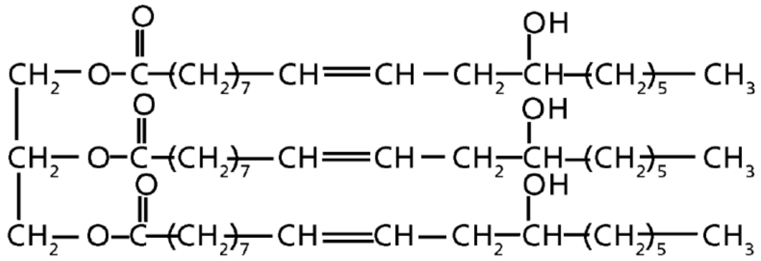


Figure 2-25 The structure of castor oil.

Concerning the direct utilisation in rigid polyurethane foams, castor oil has some major disadvantages: low functionality, and low hydroxyl number and secondary hydroxyl groups leads to a low reactivity. By mixing castor oil with polyols such as glycerol (for example 75% castor oil and 25% glycerol) a higher hydroxyl number polyol mixture is obtained, which leads to rigid PU foams with good physico-mechanical properties (Baser and Khakhar, 1993). Unlike other processed natural oil polyols, unprocessed castor oil containing hydroxyls naturally, has been experimented as a potential polyol for elastomer synthesis. The addition of castor oil was shown to lower the Young's modulus and improve elongation properties. Although both castor oil and processed oil polyols are considered as natural oil polyols, their resulting elastomers differ in mechanical properties (Yeganeh and Mehdizadeh, 2004).

A recent study (Corcuera et al., 2010) has the purpose to synthesize bio-based elastomeric polyurethanes derived from castor oil on the soft segment structure and an aliphatic diisocyanate. The polyol is derived from castor oil and it is been modified by alkoxylation with ethylene and propylene oxide in basic conditions, the polyurethanes were prepared using a two-step polymerization procedure in a flask fluxed with nitrogen. Higher amount of hard segment promotes higher hardness, tensile modulus and tensile strength and lower strain as measured by mechanical tests.

Interesting comparison between three natural oil (canola, soybean and castor oil) used as raw materials is found in literature (Narine et al., 2007), the chemical diversity of the starting materials allowed the evaluation of the effect of dangling chain on the properties of the foams. The reactivity of soybean oil-derived polyols and of unrefined crude castor oil were found to be lower than that of the canola based polyol as shown by their processing parameters (cream, rising and gel times) and FTIR. Canola-polyurethane foam demonstrated better compressive properties than soybean polyurethane foam but less than castor-polyurethane foam. Due to the hydrophobic nature of the triacylglycerols, the predominant component in vegetable oils, the produced polymers have some excellent chemical and physical properties such as enhanced hydrolytic and thermal stability (Zlatanic et al., 2002).

Zlanatic et. al. surveyed a range of natural oil polyols and their elastomers and concluded mechanical properties are largely dependent upon the crosslinking density and functionality of the polyol, and less influenced by the position of the hydroxyls (Zlatanic et al., 2004).

2.4. Lignin

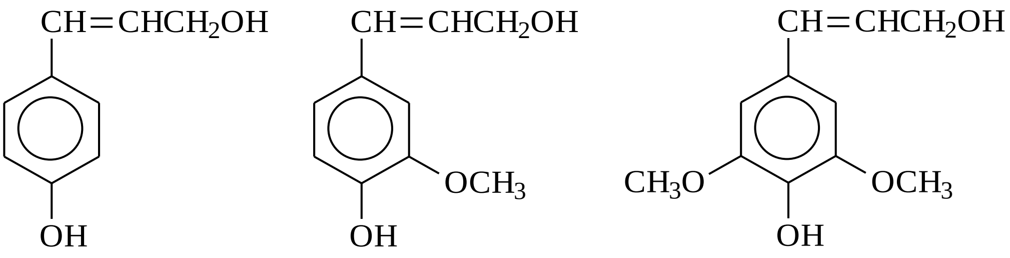
2.4.1. Introduction

Lignocellulosic biomass is composed mainly of three chemicals: cellulose, lignin, and hemicellulose. The proportions of the three components vary with the type of biomass. Traditionally, the aim of separating the wood components has been associated with papermaking, in which delignification isolates the cellulose fibres. Predominantly two types of wood – hardwood and softwood – are used in paper industry. In this context, the dissolved lignin has been utilized as fuel, which provides not only the energy required by the process, but also a convenient way of recovering its inorganic catalysts.

Softwoods are used more frequently because of their relatively long fibre length. Softwoods are species in which the seed is exposed and which are evolutionary older and therefore simpler in structure than the hardwoods which have their seeds enclosed. Typical biomass contains 40% to 60% cellulose, 20% to 40% hemicellulose, and 10% to 25% lignin. The biomass constituents can be separated and then converted into useful chemicals. The pulp can be used for either paper or cellulose derivatives. The lignin can be converted to valuable products such as carbon fibre and adhesives (Xiao et al., 2001).

The content of lignin in wood varies according to the nature of the wood and is around 19-30%, the highest content being in coniferous wood (27-30%). It is a complex aromatic polymer, highly branched and irregular compared with the repetition of identical glycoside units found in linear cellulose, lignin appears to function both as a strengthening agent in the composite wood structure and also as a component which assist in the resistance of the woods towards attack by micro-organisms and decay.

All lignin appears to be polymers of 4-hydroxycinnamyl alcohol (p-coumaryl alcohol) or its 3- and/or 3,5-metoxylated derivatives, respectively coniferyl and sinapyl alcohol (Figure 2-26), having a molecular weight of around 3000-7000 daltons, around 10-20 hydroxyl groups/mol, an hydroxyl number of around 1000-1500 mgKOH/g and a methoxy group content of 13-14%.



p-Coumaryl alcohol Coniferyl alcohol Synapil alcohol

Figure 2-26 The three monomer repeat units of lignin.

The contribution of each of these three monomers (Figure 2-26) to the lignin macromolecule differs depending on the source of the lignin. Softwood lignin is based only on coniferyl alcohol, whereas hardwood lignin is a mixed polymer based on both coniferyl and sinapyl alcohols.

Structural studies of lignin have proved to be extremely difficult and have been complicated by the fact that there are many bond types in the polymer and the numerous techniques available for delignification provide oligomeric or polymeric fragments with very variable chemical and topological features. It follows that, when a specific lignin is employed to test its viability, one can run into a number of difficulties related to complex irregular structures, but also into problems connected with the irreproducibility of results if the source material (and therefore its specific structure) is changed. Some idealised structures of lignin are presented in Figures 2-27 and 2-28.

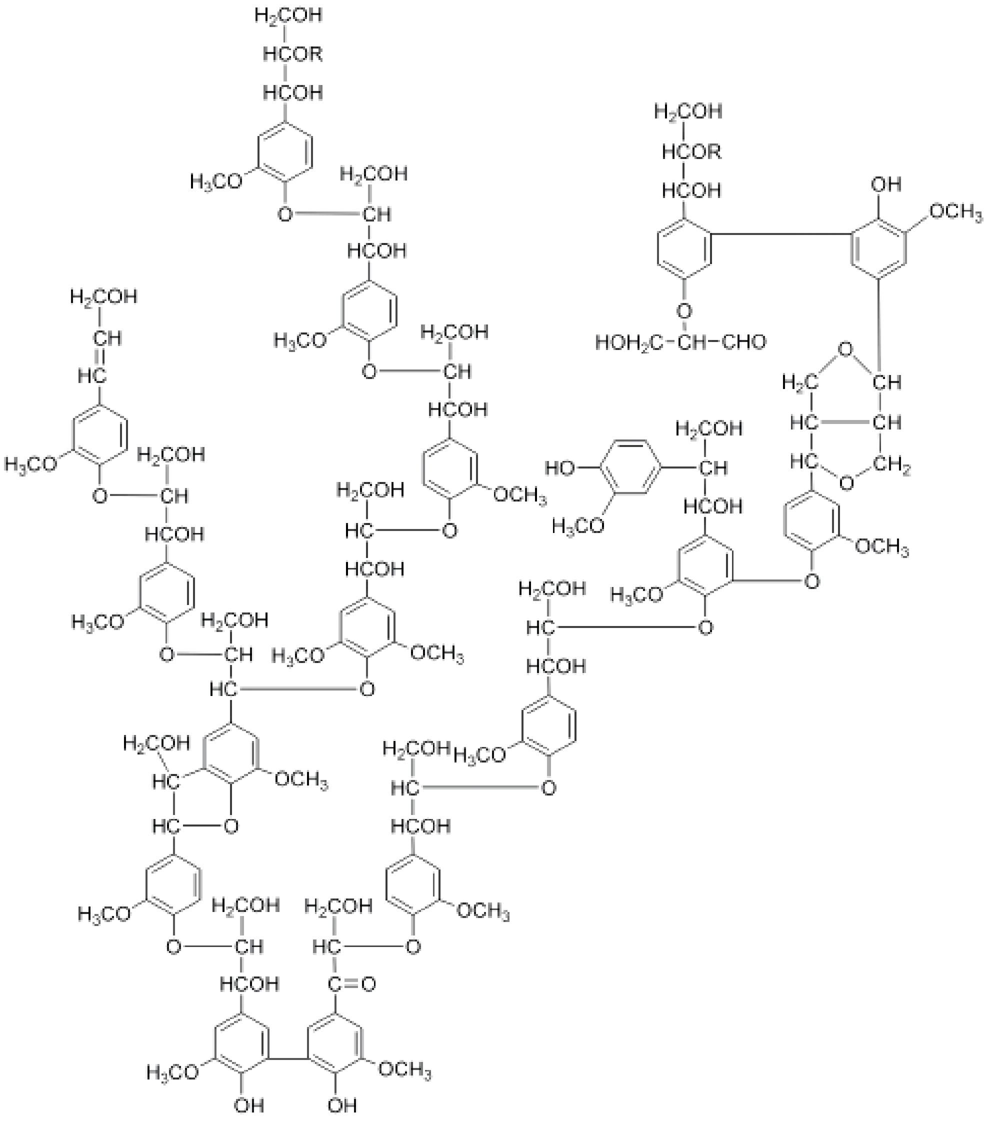


Figure 2-27 Pine lignin structure (Ullmann's, 2002).

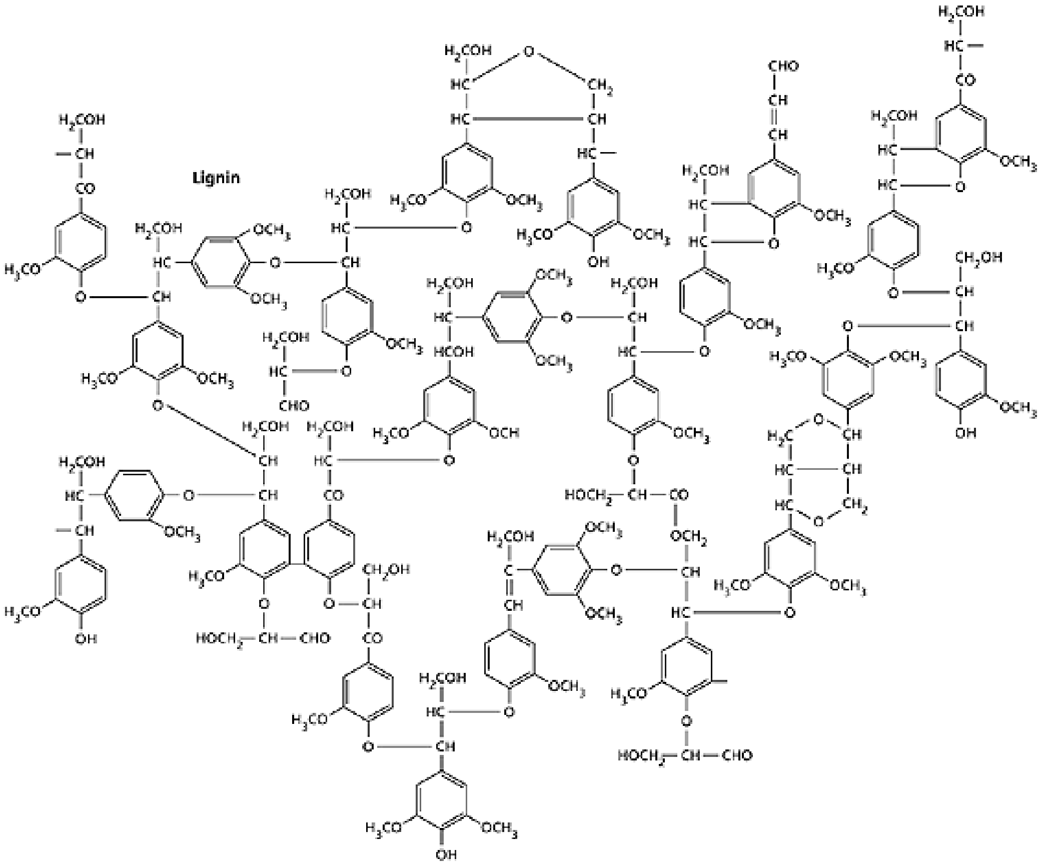


Figure 2-28 Fagus lignin structure (Ullmann's, 2002).

Lignin cannot be isolated from plant cells without degradation related to the kind of process used for delignification. Monomeric units are connected by carbon-carbon bonds with high stability and difficult to break and ether bonds which are the main breaking point of the molecule during degradation process. Important delignification reaction include the cleavage of phenolic linkages, cleavage of non-phenolic linkages, and removal of residual lignin fractions, either by cleavage of carbon–carbon linkages or by carbohydrate degradation, releasing lignin-carbohydrate fractions, which are mainly oxidised into aliphatic carboxylic acids (Sun et al., 2000). The lignin isolated by known methods (physical, chemical or enzymatic treatments) is a mixture of degraded or solubilized lignin, but to enhance the industrial use of lignins, there is need for a continuous supply of lignin products with constant quality as related to purity, chemical composition, and functional properties (Boeriu et al., 2004). Lignin is mainly isolated from wood pulping and papermaking operation where is used as fuel and only a small amount of lignin (1-2%) is separated and employed in other kind of products (Lora and Glasser, 2002). Given its unattractive structure, the interest in lignin as a possible source of macromolecular materials does not arise from the desire to isolate it and valorise it, but simply from the fact that its fragments are available in enormous quantities, even if in different molecular weights and specific structures.

Additionally, novel papermaking technologies, like the organosolv processes and biomass refinery approaches, like steam explosion, provide lignin fragments without the need of their use as a source of energy and with more accessible structures, in terms of lower molecular weights and higher solubility. Therefore, lignin macromonomers represent today a particularly promising source of novel materials based on renewable resources.

Several attempts are made to show how lignin can be integrated into materials industry processes and to highlight that lignin can be used as a novel and appropriate, renewable feedstock, rather than as a replacement for synthetic phenols, and to overcome the idea that lignin is a waste material or a low value by-product of pulping used as a fuel to fire the pulping boilers (Stewart, 2008). The use of lignin fragments as such, or after suitable chemical modifications, as macromonomers has also been extensively investigated through the usage of both their phenolic and aliphatic hydroxyl groups to prepare polyesters and polyurethanes (Belgacem et al, 2008), but none of these polymers have reached a sizable commercial stage, despite their interesting properties.

Lignin used as raw material for manufacture of polyurethanes could represent a superior utilisation of a waste, because lignin is a waste product of the wood and cellulose industry. Lignin has the advantage of low cost, aromaticity and of course is a renewable resource, but its disadvantages are: the issue of ensuring raw materials with reproducible characteristics from one batch to another, the presence of impurities and a the very dark colour it imparts to the blends.

2.4.2. Kraft lignin

The kraft process is the most dominant pulping process, but the recovery of kraft lignin for chemical uses is still not practiced commonly. Worldwide only one company is currently recovering kraft lignin for chemical uses. In the kraft process, the fibrous feedstock is digested with a mixture of sodium hydroxide and sodium sulphide at about 170 °C. During the digestion several reactions take place, including cleavage of lignin-carbohydrate linkages, depolymerisation of the lignin, its reaction with hydrosulphide ion and its recondensation.

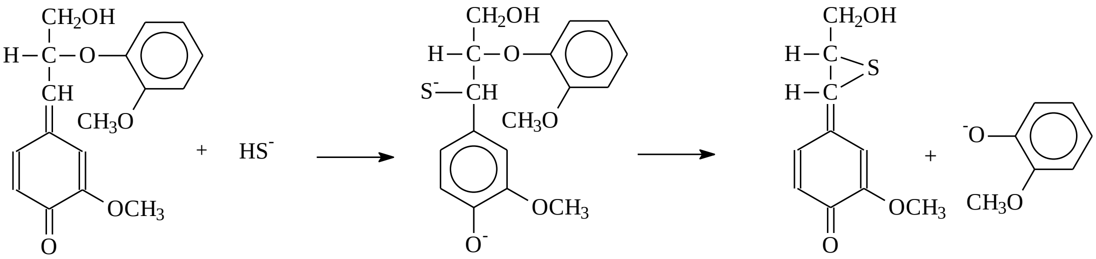


Figure 2-29 Main reaction scheme for the formation of kraft lignin.

Most current commercial application for kraft lignin involve its chemical derivatives, rather than the lignin as such (Figure 2-30). The most used kraft lignin derivatives are water-soluble sulphonated products, which are used as surfactants. Since the starting lignin material is low in sugars and ash, the resulting sulphonated lignin has high purity and may be used in high value-added applications. The introduction of sulphonate groups into kraft lignin is normally accomplished by sulphomethylation. As a result, a methanesulphonate group is introduced at the lignin aromatic ring. Other important derivatives of kraft lignin are lignin amine derivatives.

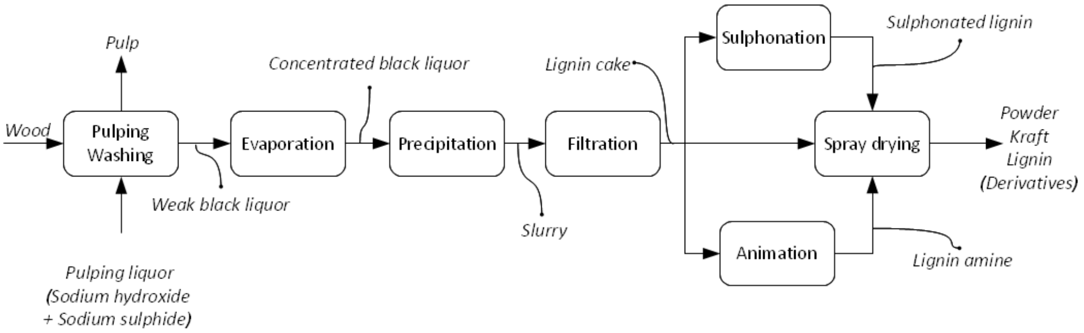


Figure 2-30 Diagram for production of kraft lignins and its derivatives.

Industrial unmodified kraft lignins (such as Indulin AT produced by MeadWestvaco) are characterized by a relatively high degree of purity. Kraft lignins contain 1.5–3.0% sulphur, some of it organically bound and some as elemental sulphur (Gellerstedt and Lindfors, 1984). For softwood kraft lignin, the sulphur content appears to be higher in low molecular weight fractions (Morck et al., 1986). The total hydroxyl content of industrial kraft lignin has been reported at 1.2–1.27 groups per C9 unit, of which 56–60% are phenolic. Industrial kraft lignin exhibits a glass transition temperature at around 140 °C. The main applications for kraft lignin derivatives are as dispersants and emulsifiers. MeadWestvaco in the US is the only industrial producer of kraft lignin and derivatives for chemical use worldwide. The company produces mostly low sugar content sulphomethylated lignins from wood at various degrees of sulphonation and molecular weights. Most products are provided in powder form and are used all over the world. The production capacity of the company has been previously reported at 35000 ton per year (dry basis) (MeadWestvaco web site).

2.4.3. Soda lignin

Soda pulping has traditionally been used for non-wood fibres, such as straw, sugarcane bagasse, flax, etc. Soda pulping is also used to produce high yield hardwood pulps that are employed to make packaging papers and boards. Non-wood fibre soda pulp mills are normally small in capacity, since the feedstock often is not produced constantly all year around. In the soda pulping process the fibrous feedstock is digested with an aqueous solution of sodium hydroxide (Figure 2-31). Since non-wood fibres have a relatively open and more accessible structure and low lignin content, the pulping temperature can be 160 °C or lower. There are some similarities between soda pulping and the kraft process and reactions such as cleavage of lignin–carbohydrate linkages and depolymerisation of the lignin and its recondensation take place.

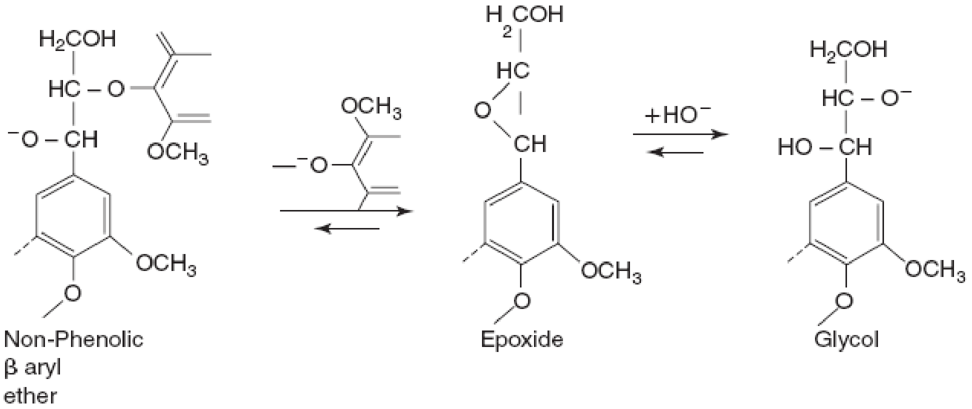


Figure 2-31 Main reaction scheme for the formation of soda lignin.

The recovery of soda lignin is based on acid precipitation and adjustment of other process variables. An example of a process used industrially to recover non-wood lignins from soda black liquors is the Lignin Precipitation System (LPS). In this case the pH of the black liquor is reduced, usually with a mineral acid, to form a lignin slurry, which is filtered, the lignin cake obtained is washed and dried to generate a high purity lignin powder (Abächerli and Doppenberg, 2001). Among the commercially available lignins, soda lignins are unique in the sense that they are sulphur-free, and therefore can be considered as being closer to lignins as they exist in nature. Currently available industrial soda lignins are mostly obtained from non-wood plants, while commercial kraft lignins are obtained from woods. Soda lignins flow when heated and their glass transition temperatures have been reported in the range of 158–185 °C. GreenValue SA is the main producer of high purity sulphur-free soda lignins. This group has two production facilities, including the largest sulphur-free lignin factory in the world, which is located in Asia. Total capacity is in excess of 10000 ton per year on a dry basis. The group produces lignins derived from non-wood plant sources, such as flax, wheat straw and other grasses (ALM India Pvt. Ltd website).

2.5. Lignin based polyurethanes

The interest to use lignin as raw material for polyurethane production dates back to the past few decades and has led to some research works where various type of materials have been produced using different chemical systems. The valorisation of lignin is motivated by environmental concerns and the constant rise of petroleum prices; these tendencies conjugated with the policies and guidelines that encourage sustainability, and development of solution to replace petroleum based materials, are promoting lignin use. Lignin based polyurethanes can be very versatile, the usage of lignin do not restrict the field of application of these materials, in fact several researches are based on films, elastomers, rigid and flexible foams.

Among the various research on lignin based polyurethanes, the work of Prof. Glasser group's was indeed very innovative. The materials prepared and reported in that systematic series of studies were made with unmodified and modified lignins. The reasons for the modifications were attributed to the modest accessibility of the lignin hydroxyl groups for their reaction with isocyanate (Wu and Glasser, 1984).

It was reported (Thring et al.,1997) that some polyurethane films prepared from Alcell® lignin and MDI by solution casting were very brittle and immediately cracked or shattered upon removal from a glass plate coated with a dry teflon spray. Rials and Glasser also found that lignin-based, solution cast polyurethane films, prepared from non-derivatized lignin and isocyanate alone, without the incorporation of a soft segment, have been considered unsuitable for tensile testing because of their brittleness (Rials and Glasser, 1986). This can be attributed to the aromatic nature of the hard segments of lignin and MDI and also to the crosslinked construction on the final product. In an effort to improve this behaviour and provide for a wider range of thermal and mechanical properties, it is therefore necessary to introduce soft segment such as polyethylene glycol (PEG) into the network. Once connected between hard segments which connect each other through crosslinking, PEG would give the network some degree of mobility and absorb more energy under stress because of its long flexible chain. The major cornmercially used soft segment component is glycol, such as polypropylene glycol (PPG), polyethylene glycol (PEG) and polytetramethylene ether glycol (PTMEG, PTHF) (Reimann et al., 1990). In both studies, Reimann and Thring, it was found that the increase of PEG content caused more significant changes in these properties than the effect of PEG molecular weight.

Several papers dealt with the conversion of lignin into polyurethanes (Hirose et al., 1998; Kelley et al., 1989). Two alternative approaches became apparent, and these dealt with the use as polyol component of solutions of (low molecular-weight) lignin fractions in aliphatic glycols and of hydroxyalkylated lignin derivatives. The characterization of these materials showed that the lignin had participated chemically to the construction of the network through some of its OH groups.

Two research groups have been involved more recently in the synthesis and characterization of polyurethanes based on unmodified lignins. In both approaches, the idea aimed at enhancing the lignins reactivity consisted in using a diol as third monomer, preferably capable of dissolving the lignin.

Prof. Gandini contribution to this field started with a study of polyurethane foams prepared from kraft lignin and hexamethylene isocyanate (HDI) in the presence of an oligo(caprolactone) macrodiol (Cheradame et al., 1989). As to rigid foams, it was found that polyurethanes prepared with oxypropylated glycerol, ethylene glycol and kraft lignin, and HDI had good dimensional stability, thermal and mechanical properties comparable to those of equivalent industrial materials. Subsequent studies (Gandini et al, 2002) based upon the use of Alcell® lignin whose reactivity was considerably higher than kraft lignin because of the reduction of steric crowding around the hydroxyl groups. Before carrying out the polymer syntheses, various model reactions were studied with the aim of establishing comparative reactivity criteria related to both the difference between phenolic and aliphatic OH groups and the role of steric hindrance around each type. Thus, various lignin models, as well as a model monoisocyanate, were employed together with the actual monomers, Alcell® lignin, an oligoether monoisocyanate and the corresponding diisocyanate. FTIR and NMR spectroscopy were used to study these reactivity features and the conclusion was that, although differences existed in terms of the nature of the OH group and its steric availability, all the reactions went to completion. This work was then extended to oxygen-organosolv lignins isolated from spent liquors after delignification of aspen and spruce in different acidic water/organic solvent media (Evtugin et al. 1998). It was found that the nature of the organic solvent used for the organosolv pulping had an influence on the reactivity of the isolated lignin towards the diisocyanate because of the variation in the amount of alcoholic groups caused by reactions with solvent molecules during the delignification

The investigation carried out in Prof. Hatakeyama's laboratory considered various unmodified lignins including Kraft, organosolv and sulphonate varieties which were dissolved into oligoether diols before mixing the solution with a multi-functional aromatic isocyanate. The strategy for improving the reactivity of the lignin OH groups consisted in using the macrodiol as both the solvent for lignin and a comonomer (Hatakeyama, 2002). The aim was to reduce the stiffness of the networks by introducing flexible oligoether sequences as spacers among the rigid aromatic domains formed by the condensation of lignin macromolecules with the isocyanate. All the materials prepared in this study in the form of sheets or foams were characterized in terms of thermal transitions and decomposition, as well as mechanical properties. Semirigid polyurethane foams, developed for housing insulation, were prepared using lignin molasses polyethylene glycol polyols. By changing the mixing ratio of lignin polyol and molasses polyol, apparent density was controlled. It was found that mechanical properties depended directly on apparent density, by TGA it was confirmed that foams were thermally stable up around 300 °C (Hatakeyama et al, 2008).

A recent report (Borges da Silvia et al, 2009) was based on integrated process that included reaction and separation steps for producing vanillin and lignin-based polyurethanes from kraft lignin. In this work some studies were conducted using a three-component system, lignin, 4,4-methylene-diphenylene isocyanate (MDI) and a linear polycaprolactone (PCL) of different average-molecular weights. PCL, a biodegradable polyester, was introduced in the formulation to impart flexibility to final products and enable polymerization in bulk. Samples were characterized and the obtained results, using FTIR-ATR monitoring and swelling studies, pointed out for effective lignin incorporation into final three-dimensional polyurethane networks (Cateto et al, 2008).

A very interesting research was based on the use of biopitch as precursor of polyurethanes (Araújo et al., 2005). Biopitch is a renewable source of polyol obtained from eucalyptus tar distillation, is similar to lignin, however lignin is a macromolecular network while biopitch shows the same chemical groups despite having smaller molecular mass and thermoplastic behaviour. The higher the biopitch content, the higher the thermal stability and the lower the density of the flexible foams, behaviours similar to those of lignin based polyurethanes. Biopitch was used also in combination with castor oil (Melo and Pasa, 2004) in polyurethanes production. Biopitch, castor oil, and MDI system produced polyurethanes with excellent surface finishing and good compatibility among the reagents. Biopitch increased the crosslinking and the carbonaceous residue of the PU produced, but decreased its thermal stability. Eucalyptus tar pitch contributed significantly to the formation of rigid segments due to its three-dimensional and aromatic macromolecular structure, and to the increase in heterogeneity and the reduction of its elastomeric behaviour.

Not only academic research, but a considerable number of patents, covering a wide range of lignin-based application field was produced. Kurple (Kurple, 2000) patented a process to produce lignin based polyols, these polyols were used to produce rigid polyurethane foams with increased resistance to moisture and flame compared to the commercial polyurethane foams because lignin act as flame retardant. Also using the lignin molecule in the polyol portion of the system the amount of isocyanate can be reduced 40% or more and still produced rigid foams, reducing the amount of toxic gases that are derived from the isocyanate portion of the system. Another interesting patent is based on the usage of isocyanates with cellulose, hemicellulose, and lignin in the preparation of polyurethanes (Hirose et al.,1989). The polyurethane of this invention contained a hard segment derived from one polyhydroxy compound selected from cellulose and lignocellulose and showed excellent mechanical and thermal characteristics and was very economical in cost. The polyurethane properties was easily modified varying the proportion of the hard segment and the soft segment derived from the polyol.

Prof. Glasser's work was not limited to academic research but he was author of a several patents based on production of lignin-based polyurethanes, modification and preparation of suitable prepolymers from lignin. In "Method of producing prepolymers from hydroxyalkyl lignin derivatives" (Glasser et al, 1992) it was reported a method of producing prepolymeric materials from lignin (kraft, organosolv, steam exploded lignin) that was hydroxaylkyl modified, so the lignin became substantially non phenolic and solvent soluble and/or liquid and then it was able to react with material which yield prepolymers to obtain a polymer. In a previous patent (Glasser et al, 1977) a polyol intermediate from lignin was produced by reacting lignin with maleic anhydride copolymers, which are then reacted with an oxyalkylating medium with or without prior hydrolysis to form the polyol intermediates. The polyester-ether intermediates react with an isocyanate medium having an isocyanate with at least two NCO groups per molecule to produce polyurethane products with or without simultaneous foaming.

Usage of lignin is an interesting topic even for the industries, a single component foam that can be used in building sector, for example to fill the cavities caused by building methods and the fixing of windows and doors, is developed in a patent assigned to Elastogran® (Reese, 1998). Owing to its low reactivity the direct processing of solid lignin as hydroxyl-containing natural material to give polyurethanes presents difficulties. Lignin solution are usually highly viscous and not readily miscible with organic polyisocyanate. The foams of this patent was prepared using an alkoxylated lignin based polyol and organic isocyanate, the advantage of using lignin in single component foam was that the final product showed good dimensional stability and higher expansion shrinkage resistance compared to the commercial products.

Despite the complexity of the structure and the high aromatic content that make lignin suitable for rigid foams production, the aim of this work is to demonstrate that lignin can be suitable also to produce a flexible foam.

3. Experimental

This chapter presents detailed information on synthesis of polyurethane polymers included in this study. In addition, the characterization techniques and sample preparation method are presented.

3.1. Materials

3.1.1. Lignin

The lignin selected in this study were two different kind:

- Indulin® AT, provided by MeadWestvaco Corporation, was a kraft pine lignin, free of hemicelluloses, characterized by a relatively high degree of purity.
- Protobind™ 1000, provided by GreenValue SA, was soda pulping lignin, this lignin derived from non-wood plant sources, such as flax, wheat straw and other grasses.

Soda lignins are significantly different from lignosulphonates, as they are low molecular weight, insoluble in water, and obtained with low levels of sugar and ash contaminants. They have more in common with kraft lignins, resembling them in molecular weight and hydrophobicity. Among the commercially available lignins, soda lignins are unique in the sense that they are sulphur-free, and therefore can be considered as being closer to lignins as they exist in nature. Another important difference for current commercial products has to do with their genetic origin, which impacts functional groups. Currently available industrial soda lignins are mostly obtained from non-wood plants, while commercial kraft lignins are obtained from woods. In nature, non-wood lignins have structural differences compared to wood lignins. In addition to guaiacyl and syringyl moieties, non-woods have significant amounts of p-hydroxyl groups. In Tab. 3-1 are reported some of the principal characteristic of these lignins.

Tab. 3-1 Principal characteristic of lignins.

		Indulin® AT	**Protobind™ 1000**
Moisture %		5	~ 2
Ash % (on dry basis)		3	< 2
pH		6.5 (15% aqueous suspension, 25°C)	~ 4 (10% aqueous suspension)
Lignin content %		97	
Softening point			~ 190°C
Sintering point		188°C	~ 200°C
Solubility in	**Water (acid or neutral)**		Nil
	Aqueous alkali	99.95 (warm 5% aqueous NaOH)	Very high
	Phenol		Very high
	Furfuryl Alcohol		High
	Benzene	Nil	
	Hexane	Nil	
	Methyl ethyl ketone	Partial	
	Methyl alcohol	Partial	
	Ethylene glycol	Complete	
	Dioxane	Complete	

Hydroxypropylation is a widely accepted method to improve the functionality of biomasses, Protobind 1000 was used because Indulin AT is a kraft lignin and several studies proved that it is not the ideal choice for the process because of the high molecular weight coupled with a significant steric hindrance around his OH groups. The process was performed in aqueous alkali at room temperature at moderate pH (only the phenolic OH groups are ionized) and produced a well-soluble lignin derivative of lower T_g compared to the pure lignin. These chain extension reaction did not produce any increase in the OH functionality of the starting substrate, since their role was to transport this group as chain ends of the inserted polyether segment.

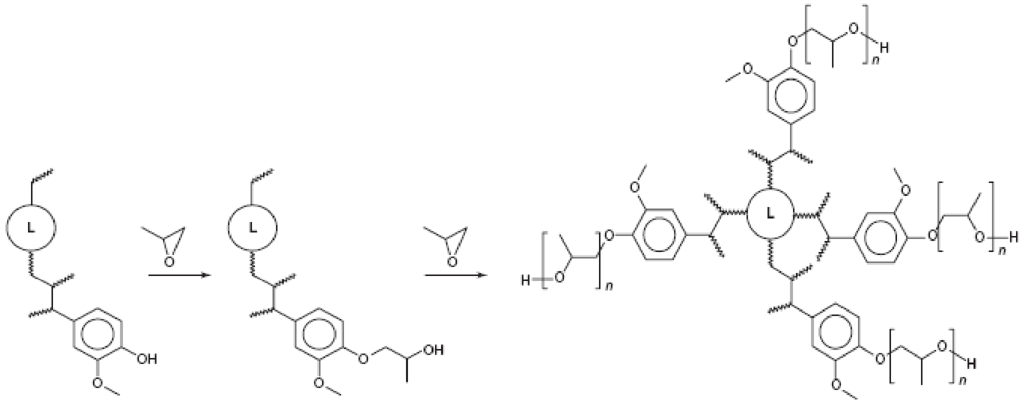


Figure 3-1 Hydroxypropilation process.

3.1.2. Polyols

The polyols used as chain extenders for the production of flexible foams required a high functionality and low molecular weight or, in equivalent terms, a low OH value. The polyols chosen for this research were:

- Polypropylene glycol triol (PPG triol) purchased from Sigma Chemicals and used as received.
- Castor oil purchased from Sigma Chemicals and used as received.

Polypropylene glycol triol is a polyether obtained from the polymerization of propylene oxide, the polyol has an average functionality of about 3 and a high molecular weight, as shown in Tab. 3-3, which gives considerable flexibility to the polymer chain.

Castor oil is a compound derived from natural sources and it is obtained by esterification of glycerol with various fatty acids. The composition of the mixture can be related to the percentage of fatty acids involved in esterification, as shown in Tab. 3-2.

Tab. 3-2 Composition of fatty acids in castor oil (Ogunniyi, 2006).

Acid	%
Ricinoleic acid	85 ÷ 95
Oleic acid	6 ÷ 2
Linoleic acid	5 ÷ 1
Linolenic acid	5 ÷ 1
Staeric acid	1 ÷ 0.5
Palmitic acid	1 ÷ 0.5
Dihydroxystearic acid	0.5 ÷ 0.3
Others	0.5 ÷ 0.2

The main fatty acid of castor oil has a molecular weight of 298.5 g/mol, so the oil has an average molecular weight is slightly less than 1000 g/mol. The functionality of castor oil is 2.7.

The selected polyols, may be appropriate to obtain a flexible foam, however, are not suitable solvents to liquefy the lignin, on the basis of various articles found in the literature in which the liquefaction of lignocellulosic materials (Kržan et al., 2005; Hassan and Shukruy, 2008; Wang and Chen, 2007; Alma and Basturk, 2003) and the dissolution of lignin (Asano and Hatakeyama, 2003; Goncalves and Schuchardt, 2002) was studied, so in this work, polyethylene glycol with a molecular weight of 400 g/mol and glycerol were used as solvents (Lin et al., 1997, Jin et al., 2011), their characteristics are shown in Tab. 3-3.

Tab. 3-3 Chemical properties of polyols used for polyurethane production.

	Molecular weight (g/mol)	Functionality	OH value (mgKOH/g)
PPG triol	~ 4800	~ 2.6	35
Castor oil	< 1000	< 3	~ 160
PEG#400	380÷420	2	280.5
Glycerol	92	3	1829

3.1.3. Polyisocyanate

ISO 116/1, a polymeric diphenylmethane diisocyanate (MDI) had 25.7% part by weight of NCO content, it was provided by ELASTOGRAN. Isocyanate in excess of that needed to react with the OH groups on the polyols reacted with distilled water to form CO_2, which acted as the only foam blowing agent.

3.1.4. Catalysts and additives

As already mentioned before, the catalysts can be divided into gelling catalysts and blowing catalysts, these two reactions must kept in proper balance in order to obtain the desired product. The catalysts used were kindly provided by Air Products and belong to two different series: classic catalysts and new generation catalysts (NE), low emission of amine.

The classic catalysts consisted of non-reactive amines that can be released from the foams, once is produced, were DABCO 33LV (gelling) and DABCO BL11 (blowing), and their composition is shown in Tab. 3-4.

The series of catalysts NE comprised: DABCO NE1070 (gelling) and DABCO NE300 (blowing), this series of catalysts can reduce emissions because the molecules that act as catalysts can chemically bind themselves to the polyurethane matrix.

To ensure uniformity of structure and enhance the cells opening DABCO DC2525 was used, it was a silicone surfactant made from 70% by weight of polysiloxane.

Tab. 3-4 Catalysts composition.

Type	**Composition**
DABCO 33LV	triethylenediamine (67% by weight) dipropylene glycol (33% by weight)
DABCO BL11	bis(dimethilamminoethil)ether (70% by weight) dipropylene glycol (30% by weight)
DABCO NE1070	dimethylaminopropyl urea, 3- (30 - 70% by weight)
DABCO NE300	N-[2-[2(dimethylamino)ethoxy]ethyl]-N-methyl-1,3-propanediamine (90% by weight)

3.2. Methods

3.2.1. Hydroxyl value calculation

There are several methods to determine the content of hydroxyl groups of the reagents, the ASTM D 2849-69 provides the esterification of polyol with an excess of acetic anhydride or phthalic anhydride, hydrolysis of unreacted anhydride with the formation of a dicarboxylic acid and titration of the resulting solution with sodium hydroxide. The procedure requires long time for esterification but, in the literature similar methods are reported in which the reaction time is drastically reduced by using imidazole as a esterification catalyst (Kurimoto et al., 2001; Hassan and Shukruy, 2008).

The OH value determination was carried out for different solutions in which the lignin was dissolved. The hydroxyl numbers of liquefied lignin was determined as follows: a mixture of 1 g liquefied lignin and 25 ml of a phthalation reagent was heated for 20 min at 110 °C. This was followed by addition of 50 ml of pure 1,4-dioxane and 25 ml of distilled water, and the mixture was titrated with a 1M sodium hydroxide solution to the equivalence point using a pH meter. The phthalation reagent consisted of a mixture of 150 g phthalic anhydride, 24.2 g imidazol and 1000 g dioxane. The hydroxyl number in mgKOH/g of sample was calculated by the following equation:

$$Hydroxyl\ number = \frac{(B - A) \cdot N \cdot 56.1}{W}$$

Where:

- A is the volume of the sodium hydroxide solution required for titration of liquefied lignin sample (ml).
- B is the volume of blank solution (ml).
- N is the normality of the sodium hydroxide solution.
- W is the weight of liquefied lignin (g).

This method is not very accurate but it is proved to be quite simple and a fast way to get a good estimation of the OH groups in the liquefied lignin.

3.2.2. Polyurethanes production

The dissolution of lignin, previously dried for 24 hours in an oven with air circulation at a temperature of 80 °C, was the first task performed.

Samples of the lignin, at predetermined weight ratio, placed in glass flasks were subjected to the microwave treatment in a microwave oven just after the addition of liquefying polyols (glycerol and PEG#400). Parameters such as heat power (from 200 to 400 W) and the duration of heating, between 5-15 min, were varied. The liquefied lignin was rich in polyols, which can be directly used as feedstock for making polymers without further separation or purification.

The mixture obtained from the liquefaction of lignin was not suitable for the production of flexible polyurethanes for the excessive viscosity and a very high OH value.

It was therefore necessary to add an additional compound capable of reducing the viscosity of the solution and increasing the flexibility of the structure, reducing the T_g of the final material, so we used some polyols (castor oil or polypropilenglycol triol) with lower OH value, as chain extenders.

The solution obtained by mixing and dissolving the lignin and the chain extender can be used as a reagent (Figure 3-2), after determining the concentration of hydroxyl groups. The foams were produced in plastic containers (85x85x55 mm).

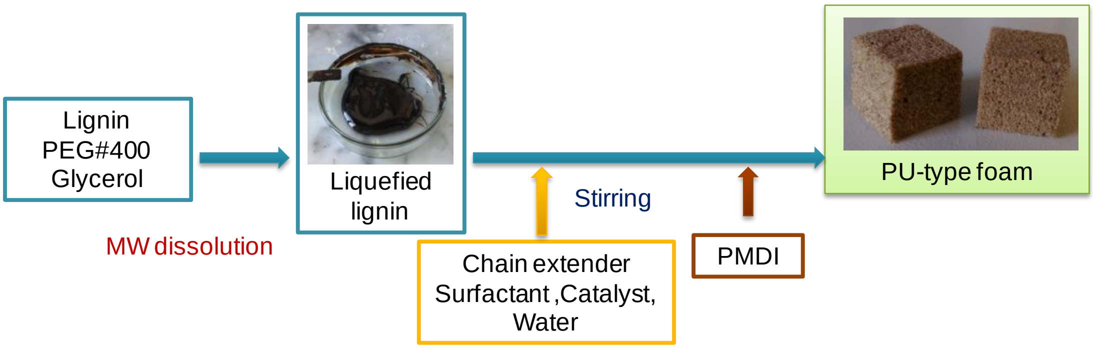


Figure 3-2 Process of polyurethane production

One of the most used techniques to obtain polyurethanes is the one-shot technique, which consists of a very efficient mixing, in one step only, of all the raw materials involved in polyurethane fabrication: isocyanate, oligo-polyol, chain extenders or crosslinkers, silicon emulsifiers, blowing agents, catalysts.

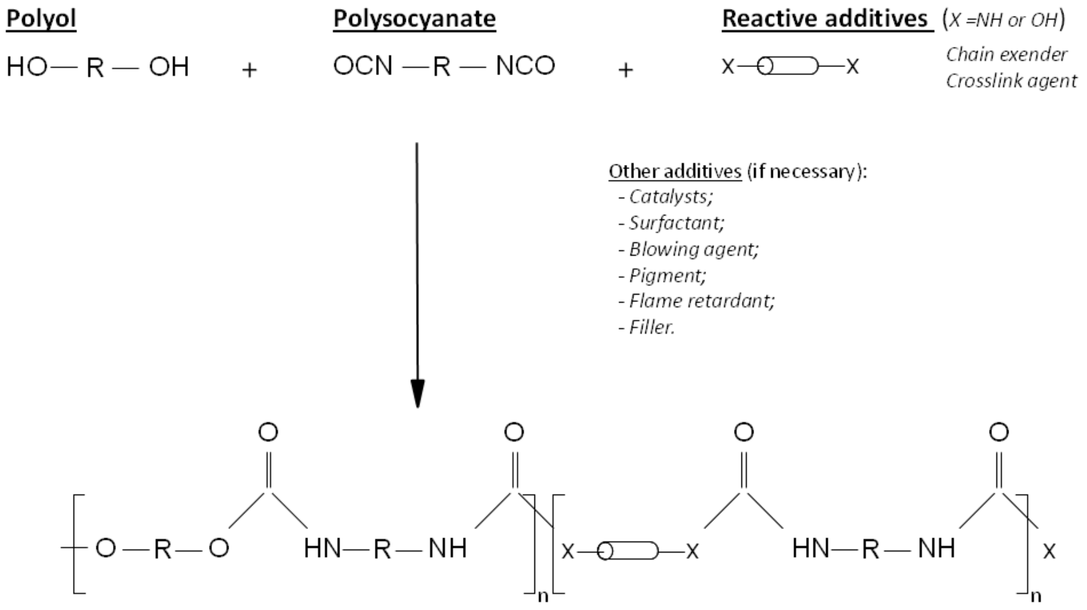


Figure 3-3 Synthesis of polyurethanes by "one shot" technique.

The key to the one shot technique is extremely efficient mixing, in a very short time (Figure 3-3). At this initial stage, the reactions between isocyanates and active hydrogen compounds are insignificant and the reaction mixture is liquid. In order to simplify the procedure of using too many components, a masterbatch, that is a mixture of the components that do not react with each other, (e.g., oligo-polyol, water, chain extender, catalysts, etc.), is made before foaming. Then it is possible to use only two components: one is the polyolic component (called component A or formulated polyol, containing a mixture of all raw materials except for the isocyanate, in the proportions needed) and the second component is the isocyanate (called component B or isocyanate component). The polyurethane that results is a consequence of the very efficient contact between the isocyanate component and the polyolic component. When the entrapped air bubbles in the reacting mixture grow large enough to scatter visible light, a visible coloration change, known as creaming is observed. The point where the majority of the cells open is accompanied by a sigh-back of the foam, since at this time, gas can move freely through the foam cells, and this lets the foam assume its final height. A common method to determine the reaction rate of polyurethane foam formation is to monitor the cream time, the gel time and the rise time. The cream time is defined as the time for the polyol and the isocyanate to transition from a clear colour to a creamy colour (liquefied lignin has a very dark colour, but it was possible to recognize a change in colour when cream time was reached), the gel time is the time it takes for an infinite network to be formed, and the rise time is the time needed for the foam to fully expand.

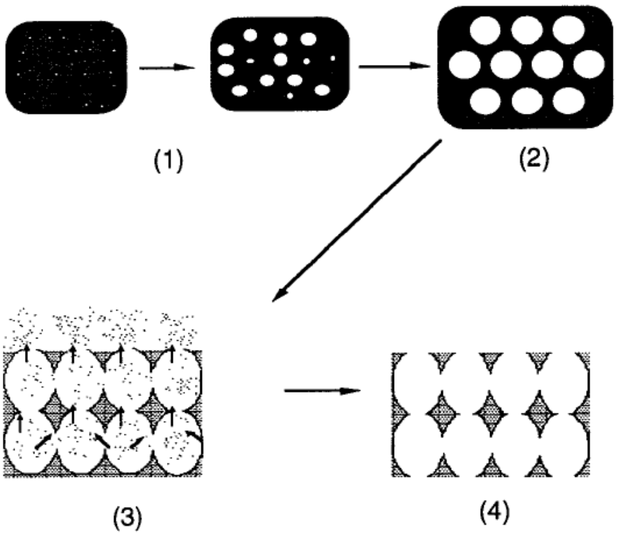


Figure 3-4 Different stages during the foaming process. The four regions of the process are: (1) Bubble generation and growth, (2) packing of the bubble network and cell window stabilization, (3) polymer stiffening and cell opening, and (4) final curing (Kim and Kim, 1999).

After mixing, the foaming mixture was deposited into an open container and be allowed to rise freely (free-rise process). The foaming mixture was also be deposited into a mold that is then closed thus forcing the foam to take on the shape of the mold (controlled-rise process). In the case of close molded systems, the density is controlled by the mass of polyurethane mixture in the mold since the volume is fixed. Consequently the physical properties of these foams can differ from the properties of free rise foams. The buns of foam produced from this process are then placed in a storage area for a period of at least forty-eight hours to complete the curing. The samples for mechanical testing were trimmed to 20x20x20 mm and 30x30x30 mm using a band saw.

3.2.3. Thermal characterization

Thermal methods of analysis of polymers are important because these techniques can provide information about the thermal stability of polymers, their lifetime or shelf-life under particular conditions, phases and phase changes occurring in polymers, and information on the effect of incorporating additives in polymers.

Differential scanning calorimetry (DSC) (Q200, TA Instruments) was used to determine the soft domain T_g. An amount of 6 mg of foam was loaded into an aluminium pan and sealed hermetically. The sample was first heated at 10 °C/min from -150 °C to 220 °C and equilibrated for 2 minutes before cooling down to –150 °C. The second temperature ramp heated the samples up to 220 °C at 10 °C/min and was used to determine the T_g. The samples of pure lignin were subjected to the same cycles.

Thermogravimetric analyzer (TGA) is an analytical technique which uses heat to drive reactions and physical changes in materials. TGA provides a quantitative measurement of mass change in the polymer or material associated with a transition or thermal degradation under a controlled air or inert atmosphere such as nitrogen. TGA can directly record the change in mass due to decomposition, or oxidation of a polymer with time and temperature while the material is subjected to a controlled temperature program. Because mass is a fundamental attribute of a material, any mass change is more likely to be associated with a chemical change, which may, in turn, reflect a composition. The sample is placed in a furnace while being suspended from one arm of a precise balance. The change in sample weight is recorded while the sample is either maintained isothermally at a temperature of interest or subjected to a programmed heating. The thermogravimetric analysis (TGA) measurements were carried out following the ASTM standard procedure D3850-94. The apparatus used was a Rheometric Scientific instrument and the experiments were performed under a nitrogen gas atmosphere. The samples were ground into a fine powder prior to measurement. The samples were heated from room temperature to 900 °C at a rate of 10 °C/min under nitrogen atmosphere.

3.2.4. Characterization of mechanical properties

The mechanical properties of polyurethanes are strongly influenced by the microphase separated morphology which results from an incompatibility between soft flexible aliphatic polyether (or polyester) segments alternating with the commonly utilized aromatic, isocyanate-based hard segments. The hard segments which are formed from the reaction of an isocyanate moiety with a reagent containing amine or alcohol groups, react with the soft segments forming urethane linkages. Dynamic mechanical analysis (DMTA) (Gabo Eplexor 100 N) was used to investigate the mechanical properties of foams over a large temperature range. Foams were cut into 20x20x20 mm cube and tested under compression mode between two 25 mm diameter serrated parallel plates. Storage modulus (E′) and tan δ were recorded at a frequency of 1 Hz over the temperature range from –150 to 120 °C. The temperature ramp rate was controlled at 2 °C/min. DMTA was also used to determine the soft domain T_g. Unlike melting temperature, which is a thermodynamic property of a solid material, T_g is a dynamic property for amorphous polymer and it related to relaxation behaviour of local chain segments. As a results T_g depends on the following factors affecting the mobility of the chain segments: crosslinking density in the network structure, aromaticity (weight fraction of aromatic structure in the polymer matrix), plasticizer concentration and so on. Glass transition induced a large change in rheological properties: sudden drop in storage modulus (E′), a small peak in loss modulus (E″), and a sharp peak of loss tangent (tan δ). Although all these three features can be used to locate T_g, the peak of tan δ was used in this study because it was easy to identify with less error than using the other two parameters.

Based on the ASTM procedure D 3574-05, the density and the 50% compression force deflection (CFDV) of flexible polyurethane foams were measured. The ASTM procedure D 3574-05 describes the standard test methods for flexible cellular materials including slab, bonded, and moulded urethane foams. The density of a material indicates the amount of mass in the unit of volume in the case of cellular materials two types of density can be distinguished: the one on the solid phase and density which refers to the two-phase structure.

The actual size of the samples were determined using a calliper and weighted with a scale. The sample size was 30mmx30mmx30mm. The result of dividing between weight (M) and volume (V) of the specimens was the density in the unit of kg/m^3 as shown below:

$$Density = \frac{M}{V}$$

The compression force deflection test was performed using a Instron 1185 equipment according the following procedure:

- Preflex the specimen twice, 75 to 80% of its original thickness at 240 mm/min.
- Rest for 6 min.
- Bring the compression foot into contact with specimen and determine the thickness after applying a contact load of 140 Pa.
- Compress the specimen 50% of this thickness at 50 mm/min and observe the final load after 60 sec.

Three specimens per sample were tested and each sample was tested at room temperature. The compressive strength was obtained from the average value of three specimens and was reported in unit of megapascal (MPa) as written in equation below:

$$Compressive\ strenght = \frac{F}{A}$$

- F is the final force at 50% compression of thickness of the specimen (N) after 60s.
- A is the cross section area of specimen (mm^2).

The typical compression load-strain behaviour of the flexible foams is shown in Figure 3-5 where the loading curve is shown. As can be seen, the curve can be divided into three deformation regions as has been well described by Gibson and Ashby: the linear bending region, the elastic buckling region, and the densification region. The first region is representative of elastic bending of the cell struts followed by a buckling of the cell struts where the strain increases with small changes in load. Eventually, at high strains, the cells collapse sufficiently that the opposing cell walls touch (or their broken fragments pack together) and further deformation compresses the cell wall material itself. This gives the final, steeply rising portion of the stress strain curve labelled densification.

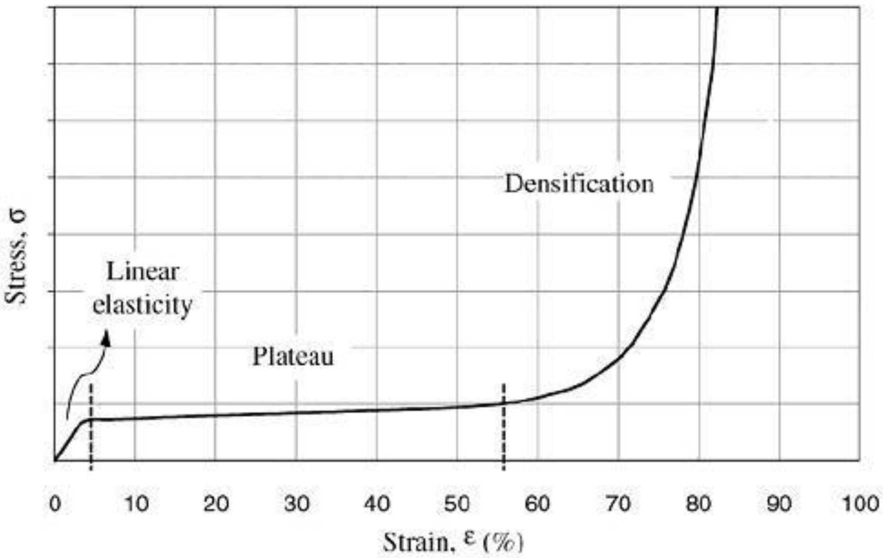


Figure 3-5 Typical stress-strain curve of compression test of flexible foams.

3.2.5. Spectroscopic analysis

An interesting research (Cole et al., 1987) was based on the determination of residual isocyanate in flexible polyurethane foam using attenuated total reflection (ATR)-Fourier Transform Infra-Red spectroscopy (FTIR) method. Foams with varying isocyanate index were made and the residual isocyanate as a function of time was measured. The unreacted isocyanate groups in the foams were measured through the NCO stretching band at 2270 cm^{-1}. By using this method, Cole managed to conclude that foams aged under humid condition showed decrease of isocyanate concentration faster than foams aged under dry condition. However, residual isocyanates were found to remain in foams even after a long period of time.

A Thermo Scientific Nicolet^{TM} 380 FT-IR was used to characterize the functional groups in the flexible polyurethane foams. The flexible polyurethane foams were grounded first and then placed into a 105°C oven for 4 h to remove water that might have been absorbed.

A total of 128 scans of each sample from 4000 to 400 cm^{-1} wavenumber were obtained at a resolution of 2 cm^{-1}. Before each series of absorbance spectrum, a background spectrum was recorded. Functional groups, particularly hydrogen bonded and free urethane carbonyl groups were followed to investigate hydrogen bonding within urethane domains. Some important peaks assigned to NCO, C=O (hydrogen bonded or free).

In Tab. 3-5 are listed the frequencies of functional groups of lignins while Tab.3-6 summarizes the wavenumbers most significant for polyurethanes.

Tab. 3-5 Frequencies of functional groups of lignins.

Group	Wavenumbers (cm^{-1})
Unconjugated ketone and unconjugated carbonyl stretching	1706
Carbonyl stretching conjugated with aromatic rings	1636
Aromatic skeleton vibrations	1598, 1511
C-H deformations and aromatic ring vibrations	1464
Aromatic skeleton vibrations	1425
breathing with C-O stretching	1334, 1270, 1225
Syringyl units	1334
Guaiacyl units	1270
Aromatic C-H in-plain deformation for syringyl type	1129
Aromatic skeleton vibrations	1033
Aromatic C-H in-plain deformation for guaiacyl type	895
Aromatic C-H out of bending	840

Tab. 3-6 Frequencies of functional groups of polyurethanes.

Group		Wavenumbers (cm^{-1})
Hydroxyl	(O-H)	3650 ÷ 2400
Ketone	(C=O)	3500 ÷ 3400, 1780 ÷ 1660
Ammine	Primary (N-H)	3550 ÷ 3250
	Secondary (N-H)	3450 ÷ 3310
Isocyanate	(-N=C=O)	2275 ÷ 2230
Ether	Cyclic	1300 ÷ 800
	Non cyclic	1300 ÷ 1000
Ammine	(C-N)	1380 ÷ 1000
Hydroxyl	Primary(C-O)	1075 ÷ 1000
	Secondary(C-O)	1150 ÷ 1030
	Tertiary (C-O)	1170 ÷ 1100
	Phenol (C-O)	1230 ÷ 1140

3.2.6. Analysis of morphology

The properties of flexible polyurethane foams are a strong function of its cellular structure, SEM has been used to study the detailed features of cellular structure. A Jeol JSM5600LV was used to study the microstructure of the PU foams. The foams were fractured by hand before analysis and gold sputtered before they were scanned in the free rise direction. The layer of gold was coated to the samples using a Edwards Sputter Coater prior to investigation to ensure a sufficient contrast image. The microscope was operated at 15 kV and images were taken at magnifications of 50x, 80x and 150x. The images were taken parallel to the blow direction, usually the foam cells appear more spherical when viewed parallel to the blow direction instead in an orthogonal direction the cells appear more elliptical or elongated.

4. Results and discussions

4.1. *Raw materials*

Lignins

The TGA curves showed in Figure 4.1 were obtained at a heating rate of 10 °C/min, from room temperature to 600 °C, under nitrogen atmosphere.

For Indulin AT lignin a two step thermal degradation was observed. Weight losses and characteristic temperatures determined from the maximum of the derived curve were analyzed.

Degradation of Indulin AT started at a temperature slightly above 150 °C and its decomposition temperature was 410 °C while the lignin Protobind 1000 had a gradual decomposition from 120 °C and the derived curve showed three minima, at 285, 410 and 840 °C, related to different composition of the starting material.

At 1000 °C the residue was greater for lignin Indulin AT, about 45%, than Protobind 1000, less than 30%, the difference may be associated with a higher aromatic structure of the first material.

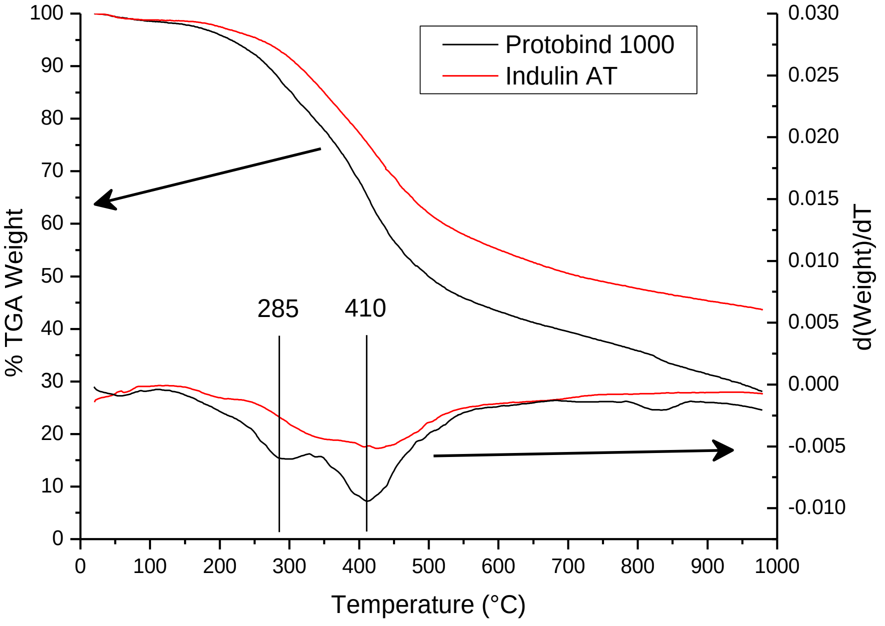
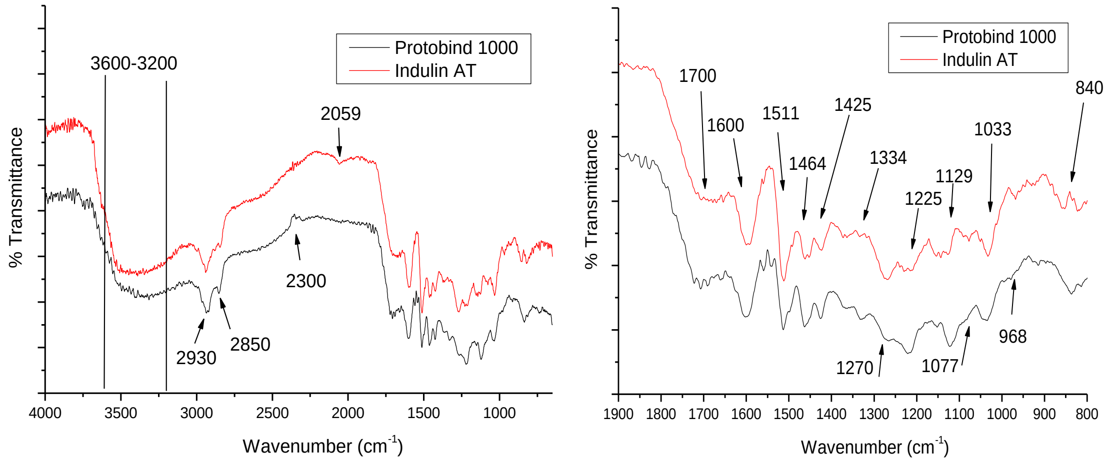


Figure 4-1 TGA curves of lignins.

The two materials were also characterized by FT-IR analysis (Figure 4-2), as expected many absorption peaks are generated by the different type of bonds present in this kind of materials.



(a) (b)

Figure 4-2 FT-IR spectra of lignins: (a) FT-IR spectrum from 4000 to 600 cm-1; (b) Typical peaks of carbonyl vibration zone.

The spectra of the two materials were similar and examining the individual peaks the following observations can be made:

- a very broad peak from 3600 to 3200 cm^{-1} indicated different types of hydroxyl groups (aromatic and aliphatic).
- at frequencies slightly lower than 3000 cm^{-1} two peaks associated to methyl, aliphatic or aromatic, and olefins and methoxyl groups were observed.
- at wave numbers less than 1700 cm^{-1} all the characteristic peaks of lignocellulosic materials were reported, the detail of spectra interpretation and band assignment were provided in Tab. 3-5 in the previous chapter.

Lignin Indulin AT, also showed a peak at a frequency slightly above 2000 cm^{-1} related to alkenyl conjugate or carbonyl conjugated alkenes.

Polyols

Figure 4-3 shows the FT-IR spectra of the polyols used for lignin liquefaction and the production of foams.

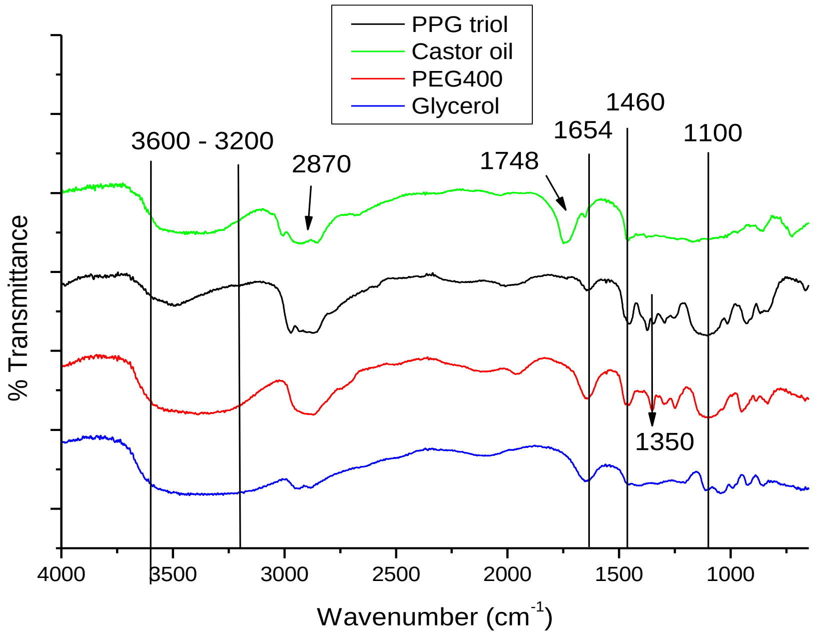


Figure 4-3 FT-IR spectra of polyols.

All the polyols examined showed typical OH groups absorption bands at wavenumbers ranging from 3200 to 3650 cm^{-1}, the bands next to 2900 cm^{-1} and at 1650 cm^{-1}, represented stretching of CC single bonds. In the spectra of glycerol, PEG#400 and PPG triol was easily identifiable the peak typical of primary and secondary OH (1000 to 1150 cm^{-1}), which was absent in the spectrum of castor oil. The two polyols also had an absorption peak at 1300 cm^{-1}, due to the ether bond. The spectrum of castor oil was characterized by the absorption of a characteristic triglyceride ester carbonyl, found at 1740 cm^{-1} (Corcuera et al., 2010).

Isocyanate

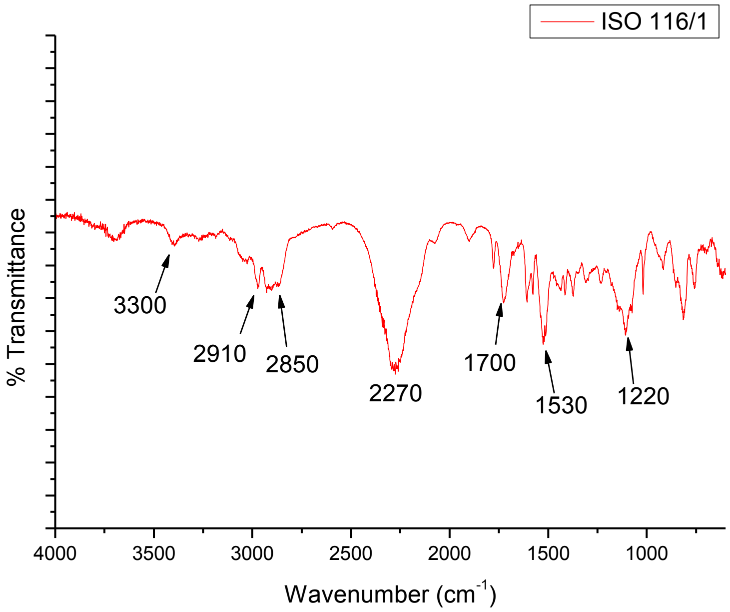


Figure 4-4 FT-IR spectrum of isocyanate.

In Figure 4-4 is shown the spectrum of isocyanate Elastogran ISO 116/1, at 2910 cm^{-1} was shown the absorption of methyl bound to two aromatic rings (Ar-CH2-Ar').

The absorption bands typical of aromatic isocyanates were detectable at 2270 (-NCO) and 1530 cm^{-1} (-NH) while those generated by aromatic urethanes can be found at 3300, 1700 and 1220 cm^{-1}, the peak at 1700 cm^{-1} was generated by the carbonyl group.

The presence of diphenyl methyl group (2910 cm^{-1}) indicated that it was a urethane prepolymer; the peak at 2850 cm^{-1} was related to the presence of aliphatic chains in the isocyanate.

4.2. Lignin dissolution

The production of polyurethane foams requires reagents with low viscosity, the best solution to reach a high amount of lignin in final material, it would be the dissolution of lignin directly with reagents suitable to obtain flexible foams, but experimentally it was observed the insolubility of lignin in the chain extenders selected so the dissolution was carried out using as solvent a mixture of glycerol and PEG#400.
Optimization of liquefaction is aimed at reducing the amount of solvents used, and still having a mixture with moderate viscosity and capable to mix with chain extenders.

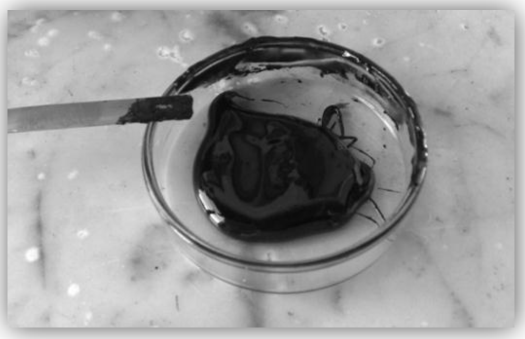


Figure 4-5 Liquefied lignin.

The first trials of the dissolution process were carried out using an excess of solvent in order to evaluate the solubility of lignin, subsequently were used different ratios between the reagents (Tab. 4-1) trying to raise as much as possible the amount of lignin in the final products.

Tab. 4-1 Reagent ratio used for lignin dissolution.

Foam series	**Lignin**	**Glycerol**	**PEG#400**
(PPG-CO)A-B	1	0.4	2
(PPG) C-G	1	0.2	1.5
(CO) C-D	1	0.2	1

The most important parameter for the production of polyurethanes containing lignin was the hydroxyl value of liquefied lignin, the solutions were titrated with the procedure described in the previous chapter and the results were summarized in Tab. 4-2.

Tab. 4-2 OH values of liquefied lignin calculated with titration.

Lignin	Lignin/Glycerol/PEG400	OH value (mmol/g)
Indulin AT	1/0.4/2	6.61
Protobind 1000	1/0.4/2	6.85
Protobind 1000 HPL	1/0.4/2	6.85
Indulin AT	1/0.2/1	6.53
Protobind 1000	1/0.2/1	6.65
Protobind 1000 HPL	1/0.2/1	6.65
Indulin AT	1/0.2/1.5	6.45

An approximate value of this parameter can be calculated using the weighted average OH value of the individual reagents in the literature was available the OH value lignin of Indulin AT that is 6.89 mmol/g (Borges da Silva et al. 2009). The results obtained for the dissolutions using the weighted average values are shown in Tab. 4-3.

Tab. 4-3 OH values of liquefied lignin calculated with weighted average.

Lignin	Lignin/Glycerol/PEG#400	OH value (mmol/g)
Indulin AT	1/0.4/2	8.79
Indulin AT	1/0.2/1.5	8.36
Indulin AT	1/0.2/1	7.74

The experimental OH value was lower than the one calculated with the weighted average, the difference can be attributed to the presence of acid groups in lignin, that influenced the necessary volume of titrating agent, and to the partial reactivity of hydroxyl in the mixture towards phthalic anhydride.

4.3. Foams production

The polyol used as a reagent for the foam production was obtained by mixing the liquefied lignin with chain extenders, increasing the amount of chain extenders reduced the OH value of the starting reagent (higher flexibility of the foam), but at the same time there was a reduction of the amount of lignin in the final material. Weight ratios between liquefied lignin and chain extenders ranging from 1:1.4 to 1:0.8 were used and it was noted that lowering the amount of solvent for the liquefaction led to a worse miscibility of the liquefied lignin with the chain extender, this behaviour was evident especially when castor oil was used.

The "one shot" production technique was used. The liquefaction of lignin can be achieved also using only PEG#400 as solvent, but experimentally it was noted that when catalysts were added to the mixture there was the formation of aggregates and the viscosity greatly increased. It is possible that, when the catalyst was added, a reaction between acid groups of lignin with hydroxyls of the other reagents occurred, generating molecules with high molecular weight, but when glycerol was used also as reagent for liquefaction, the mixture maintained low viscosity so it is possible that glycerol reacted with lignin, preventing the formation of macromolecules.

The amount of isocyanate required for the reaction is calculated using the following equation:

$$\%\frac{NCO}{OH} = \frac{M_{NCO}W_{NCO}}{\sum M_{OH}W_{OH} + \sum M_{Ad}W_{Ad} + (2/18)W_{H_2O}}$$

Where:

- M_{NCO} is isocyanate group number contained in one gram of isocyanate.
- W_{NCO} is the weight of isocyanate (g).
- M_{OH} is hydroxyls group number contained in one gram of polyol (liquefied lignin and chain extender).
- W_{OH} is the weight of polyol (g).
- M_{Ad} is hydroxyls group number contained in one gram of additives (catalysts and surfactant).
- W_{Ad} is the weight of additives (g).
- W_{H_2O} is the weight of water (g).

The calculation was made using the OH value determined by titration.

4.4. Reference polyurethanes

For better investigations of the thermomechanical behaviour of the samples, two control samples were prepared with only the chain extender as polyol (PPG triol and castor oil).

Figure 4.13 showed the DSC analysis of the reference samples. A transition at -90 ° C common to both foams can be seen, the broad glass transition around 20 °C for the reference sample made with castor oil and the glass transition around -50 °C for the PPG triol.

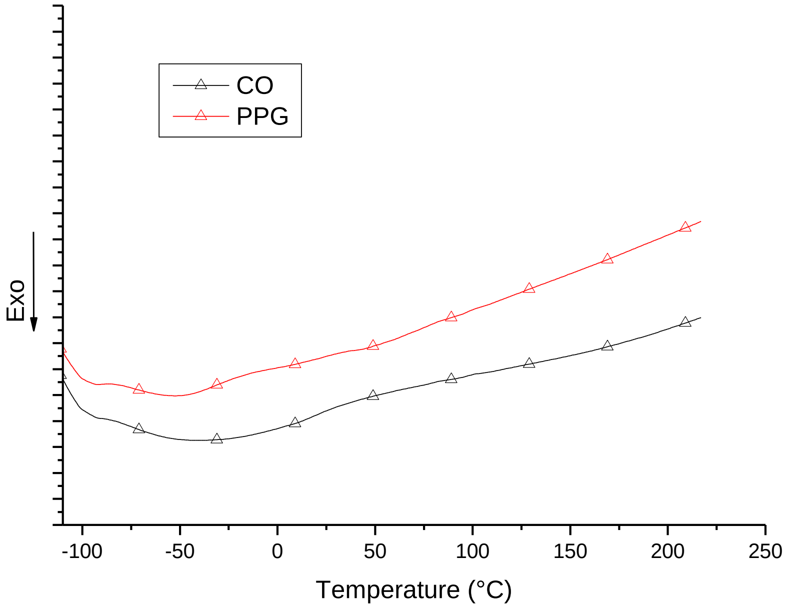


Figure 4-6 DSC results of reference samples.

Sample with PPG triol showed the typical trend of standard flexible foams with a drop in E' at approximately -50 °C, the soft domain T_g, and a plateau, typical of crosslinked polymers like flexible foams. Sample with castor oil had a broader distribution of peak that is generally considered as an indication on network homogeneity and the peak height is related to the relative elasticity of the sample, so a broad peak suggest a lesser degree of uniformity and less phase separation.

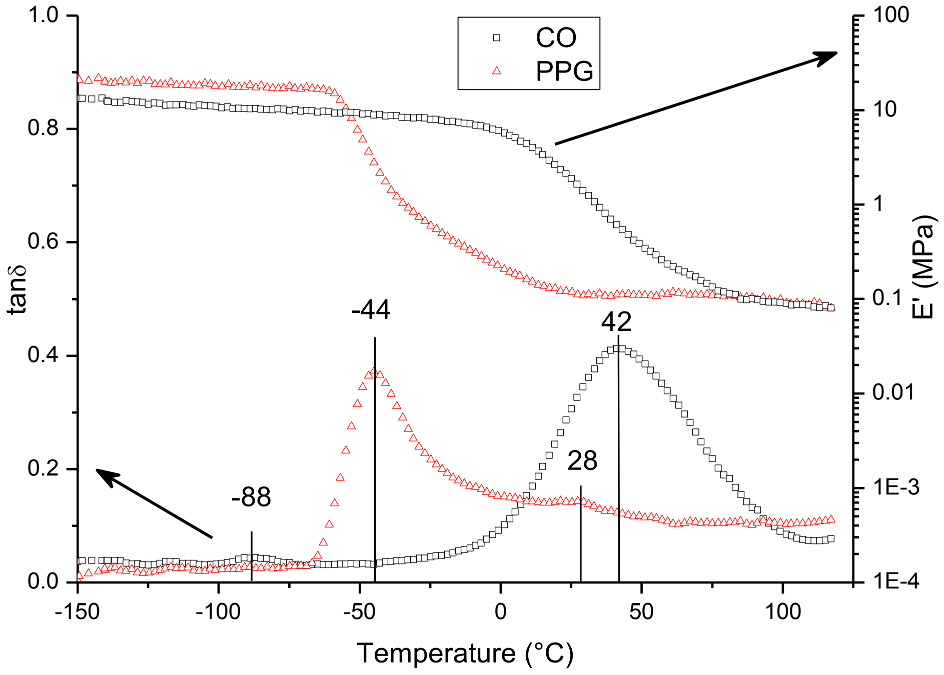


Figure 4-7 DMTA results of reference samples showing tan δ and E' as function of temperature.

4.5. Polyurethanes with Indulin AT

In Tab. 4-4 are listed the series of flexible foams produced using Indulin AT lignin, the kind of chain extender and catalysts, the ratio NCO/OH and the amount of lignin. The value in brackets for the samples with castor oil was referred to the renewable amount of reagents in this foams considering the contribution of castor oil too.

Tab. 4-4 List of foams produced with Indulin AT.

Sample	Chain extender	Lignin/Chain extender ratio	NCO/OH	Catalysts	% Lignin
I-PPG-A	PPG triol	1.45	0.88	Classic	6.7
I-PPG-B	PPG triol	1.45	0.82	NE	6.7
I-CO-A	Castor oil	1.45	0.80	Classic	6 (40.3)
I-CO-B	Castor oil	1.45	0.78	NE	6.3 (42.7)
I-PPG-C	PPG triol	1.4	0.80	Classic	10
I-PPG-D	PPG triol	1	0.68	Classic	11.9
I-PPG-E	PPG triol	0.8	0.63	Classic	13.35
I-PPG-F	PPG triol	1.4	0.76	NE	10
I-PPG-G	PPG triol	1	0.66	NE	11.78
I-CO-C	Castor oil	1	0.70	Classic	11.69 (43.4)
I-CO-D	Castor oil	1	0.65	NE	12.11 (45.5)

Tables 4-5 and 4-6 give the formulation used to prepare the foam samples. The amount of each component was in grams, all ingredients, except MDI, were weighted into a plastic cup and mixed for 1 minute. At the end of the mixing period, pre-measured isocyanate was added to the cup and the mixing continued for additional 20 seconds. Three samples for each formulation were prepared, sample 1 was free rise and samples 2-3 were controlled rise samples. The foams were allowed to cure for 48 hours before testing. Samples I-PPG-A-B and I-CO-A-B were prepared using liquefaction ratio of lignin/glycerol/PEG400 of 1/0.4/2, samples I-PPG-C-F were prepared using liquefaction ratio of lignin/glycerol/PEG400 of 1/0.2/1 and samples I-CO-C-D were prepared using liquefaction ratio of lignin/glycerol/PEG400 of 1/0.2/1.5.

Tab. 4-5 Foam formulations used in sample synthesis with PPG triol as chain extender, all formulations are in grams.

	I-PPG-A	I-PPG-B	I-PPG-C	I-PPG-D	I-PPG-E	I-PPG-F	I-PPG-G
Liquefied lignin	14.20	11.40	10	10	10	10	10
PPG triol	20.80	16.60	14	10	7.6	14	10
Water	0.6	0.7	0.66	0.66	0.66	0.65	0.65
Gelling catalyst	0.53	0.9	0.36	0.34	0.31	0.63	0.6
Blowing catalyst	0.53	0.35	0.35	0.31	0.31	0.2	0.22
Surfactant	0.35	0.56	0.26	0.21	0.17	0.21	0.2
Isocyanate	25	23	20	16.8	15	20	16.9

Tab. 4-6 Foam formulations used in sample synthesis with castor oil as chain extender, all formulations are in grams.

	I-CO-A	I-CO-B	I-CO-C	I-CO-D
Liquefied lignin	17	17	23	23
Castor oil	27.5	27.5	23.5	23.5
Water	0.81	0.5	0.32	0.34
Gelling catalyst	0.67	1.24	0.41	0.74
Blowing catalyst	0.67	0.25	0.26	0.16
Surfactant	0.45	0.66	0.29	0.3
Isocyanate	36.8	32	25.1	22.3

Kinetics of the foam formation is followed by the cream time and gel time. The cream time corresponds to the start of bubble rise and hence color of the mixture becomes light brown from very dark brown due to the introduction of bubbles. The gel time was the starting point when the stable spatial shape was formed by the reaction of forming urethane and urea linkage and the crosslinking reaction.

Samples with classic catalysts showed reaction times slightly lower than samples with NE catalysts, this is due to the higher reactivity of the classic catalysts, but the final products showed no significant differences regardless the catalysts employed for their production.

Tab. 4-7 Reactivity of foams produced with Indulin AT.

Sample	Cream time (s)	Rise time (s)
I-PPG-A	15	15
I-PPG-B	20	45
I-CO-A	30	45
I-CO-B	60	130
I-PPG-C	25	40
I-PPG-D	25	45
I-PPG-E	30	50
I-PPG-F	45	120
I-PPG-G	50	135
I-CO-C	40	90
I-CO-D	80	150

4.5.1. FT-IR spectroscopy

The FT-IR results of polyurethanes with Indulin AT are shown in Figures 4-6/4-8. The samples for FT-IR measurement were taken from the centre of foam buns, grinded and dried at 105 °C for 2 hours to ensure no water was adsorbed on the foam. The spectrum confirmed qualitatively the presence of urethane linkages.

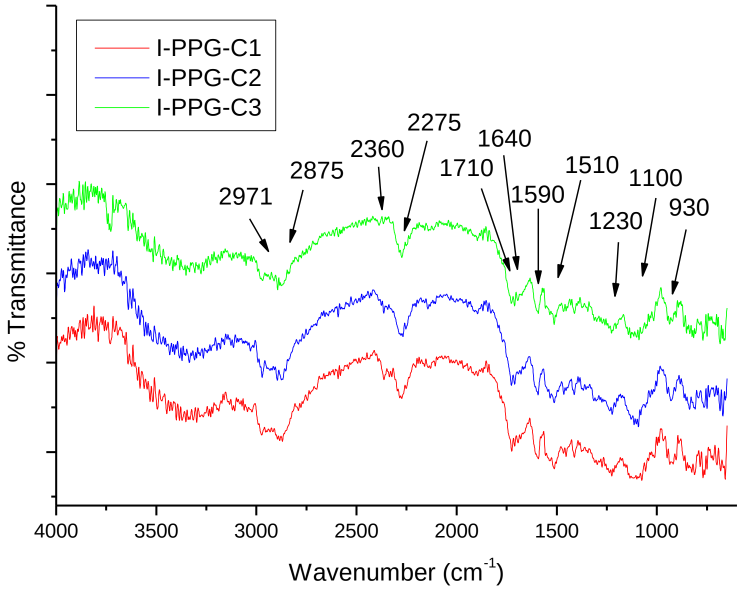


Figure 4-8 Typical FT-IR spectra for samples produced with Indulin AT and PPG triol as chain extender with different degree of expansion.

The characteristic -NH stretching vibrational region (3200-3500 cm^{-1}) and the characteristic -CO vibrational region (1700-1730) are well represented. FT-IR spectra for sample I-PPG-C were shown in Figure 4-8, as can be seen the degree of expansion did not change the typical peaks of the foams.

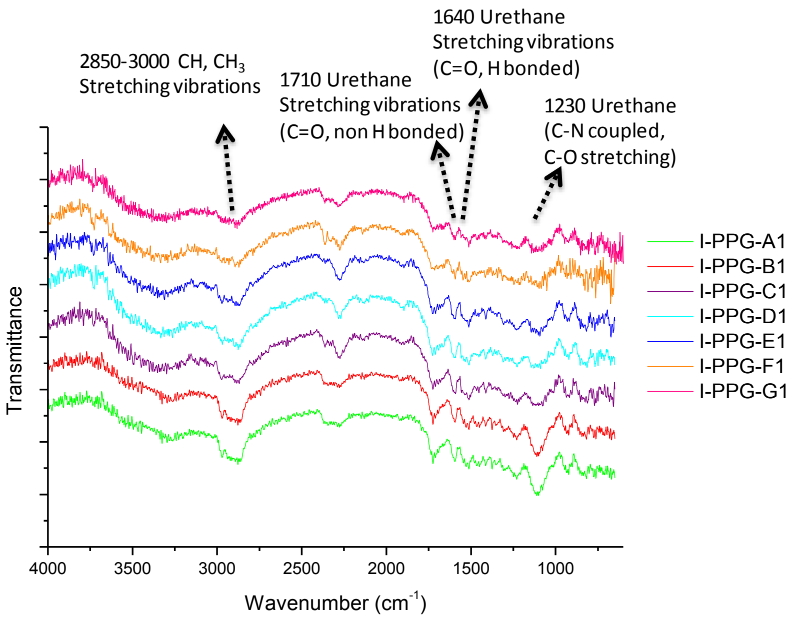


Figure 4-9 General FT-IR spectra for all the samples produced with Indulin AT and PPG triol as chain extender.

From Figure 4.9 it can be seen that the characteristics bonds in the material were the same even with varying the composition, only some small differences between samples can be found on the intensity of some absorption peaks. The unreacted isocyanate (-NCO group) was shown by a peak centred at 2275 cm^{-1}, even if the NCO/OH ratio was less than one there can be a small amount of unreacted isocyanate due to steric hindrance of lignin structure, the different ratio between the intensity of absorption peaks at 1710 and 1640 cm^{-1} was an index of phase separation in the material. The peak at 1640 cm^{-1}, in fact, was typical of bidentate urea that interacted through hydrogen bonds with the surrounding molecules and the peak at 1710 cm^{-1} indicated the presence of free urea. Hydrogen-bonded ureas, including both monodentate and bidentate, were indication of hard domain ordering.

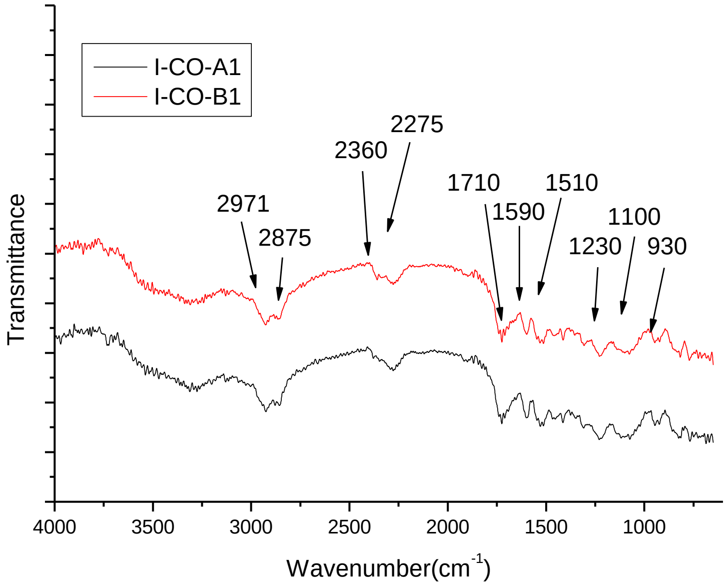


Figure 4-10 General FT-IR spectra for the samples produced with Indulin AT and castor oil as chain extender.

The FT-IR spectra of the foams produced with castor oil were shown in Figure 4-10 were similar to those obtained from samples containing PPG triol but they were characterized by the decrease of absorption peak at 1640 cm^{-1} (associated with the H-bonded carbonyl in ordered hard domains) that is an index of less phase separation of this samples (Choi et al., 2009) compared to the samples obtained with PPG triol.

4.5.2. Thermogravimetric analysis (TGA)

The thermodegradation stages of vegetable oil based polyurethane network have been commonly studied through TGA (Javni et al., 2000) and it was demonstrated that these polyurethanes usually shows two or three degradation phases. Fig. 4-11 showed the TGA of I-PPG-A sample in all three different expansions.

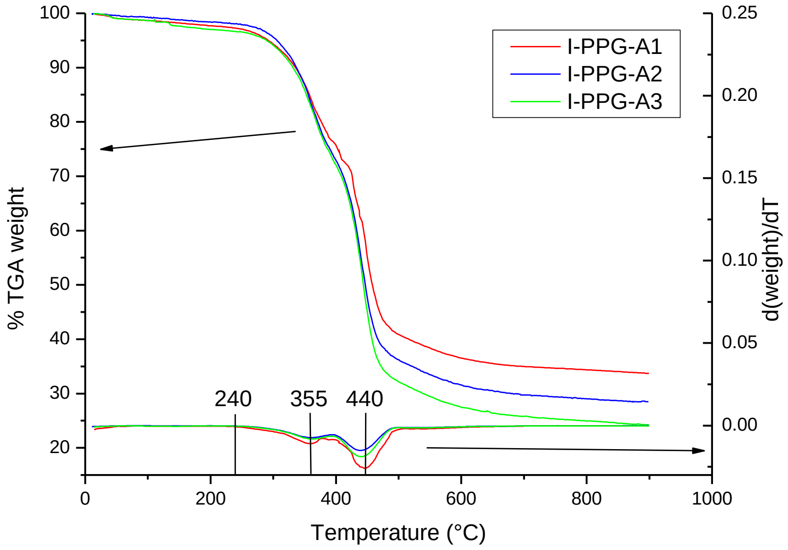
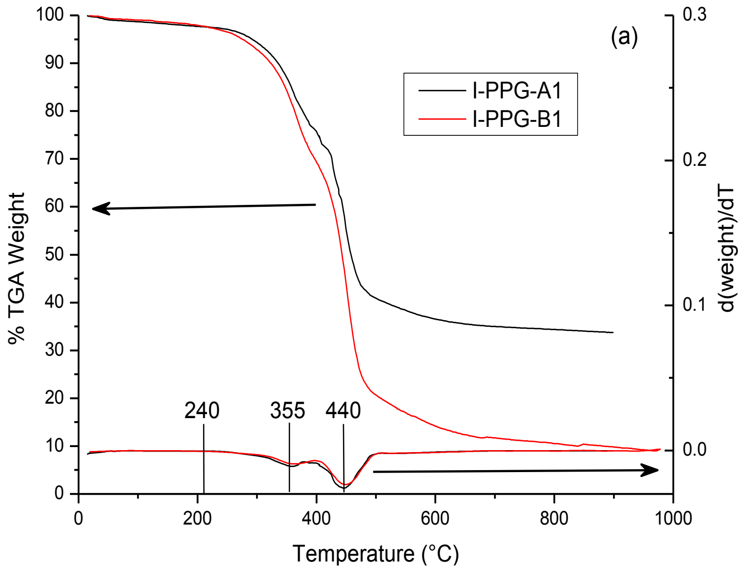


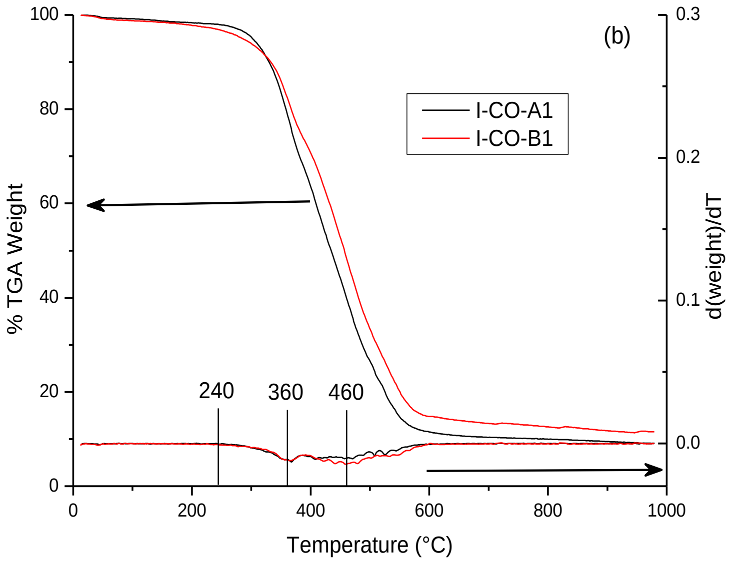
Figure 4-11 Typical TGA curves for samples produced with Indulin AT and PPG triol as chain extender with different degree of expansion.

For the sample I-PPG-A the decomposition took place around 250 °C and two degradation phases were shown. This first degradation step was associated with the first 25% of the weight loss, and the last two steps with the remaining 75%. Urethane bonds were known to dissociate and re-associate simultaneously from around 160 °C, this degradation became irreversible from around 200 °C, depending on the nature of the polymer. Thus, it was assumed that urethane bonds degradation took place in the first degradation stage. The two degradation temperatures (355 and 440 °C) were associated with the presence of two phases within the material, probably the first event is related to soft segments and the second to the thermal degradation of hard segments in which the lignin is inserted, as reported in the literature (Hablot et al. 2008).

The residue at 1000 °C was less than 40% and was higher for the free rise foam, this can be caused by a difficult heat transfer in the sample, caused by a very regular and uniform cell structure (Araujo et al. 2005). The comparison between foams of different compositions was carried out on free rise samples, as shown in Figure 4-12.



(a)



(b)

Figure 4-12 TGA curves for free rise samples produced with Indulin AT and (a) PPG triol (b) castor oil as chain extender.

All of the foams obtained by Indulin AT showed the beginning of degradation at 240 °C, indicating that the same degradation mechanism can occur independent of the nature of the reagents, and two degradation phases. The second step may correspond to the castor oil degradation, the soft polyurethane segment, in good agreement with literature data (Kumar and Siddaramaiah, 2007). Finally, the third degradation stage occurred in the same range of temperature, with a temperature comprised between 420 and 480 °C, depending on the polyurethane nature. This should correspond to the degradation of advanced fragments produced after the second stage. In the samples of foams made using castor oil, however, the distinction between the two degradation was less pronounced that can anticipate an intense mixing of the two phases. In castor oil foams the residue at 1000 °C is less than 20% and can be explained with better heat transfer within the sample.

4.5.3. Differential scanning calorimetry (DSC)

The calorimetric analysis was carried out on samples taken from the central area of the foams. For a well phase separated foams the soft domains must share similar properties as their polyols, which makes the T_g and indication of the degree of phase separation. The glass transition for the samples with PPG triol and liquefied lignin was around -65 °C that is similar with its pure polyol, this led a good phase separation in this samples. Heating curve also showed two transitions above room temperature: one at 70 °C and one at 150 °C that can be related to lignin.

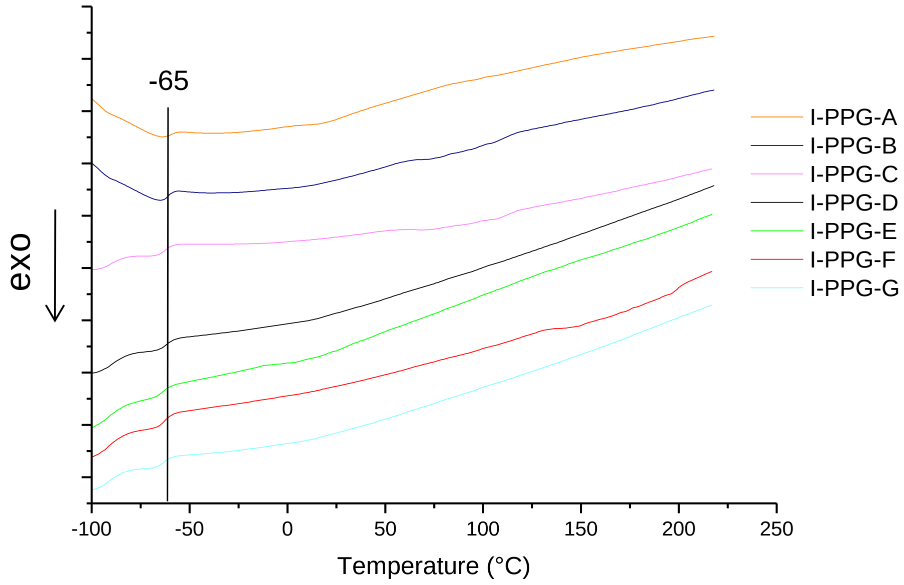


Figure 4-13 DSC traces of samples with Indulin AT and PPG triol as chain extender. The curves were shifted vertically to avoid overlapping of curves.

The samples with castor oil showed significant shift of their foam T_g (around 0 °C), from the pure polyol (-60 °C), this could led to high T_g of the soft domains and morphologically an increase in phase mixing also result in a broader T_g. This shift of glass transition range can be attributed to the restriction of chain mobility resulted from the locking of the chains in polyurethane foams due to an increase in chemical crosslinking density and in an increase in the melting temperature of the hard segments. This must be due to the disruptions of H-bonds of long range ordering and microcrystalline hard segments and the re-ordering of hard segments into short range ordering domains by the incorporation of castor oil.

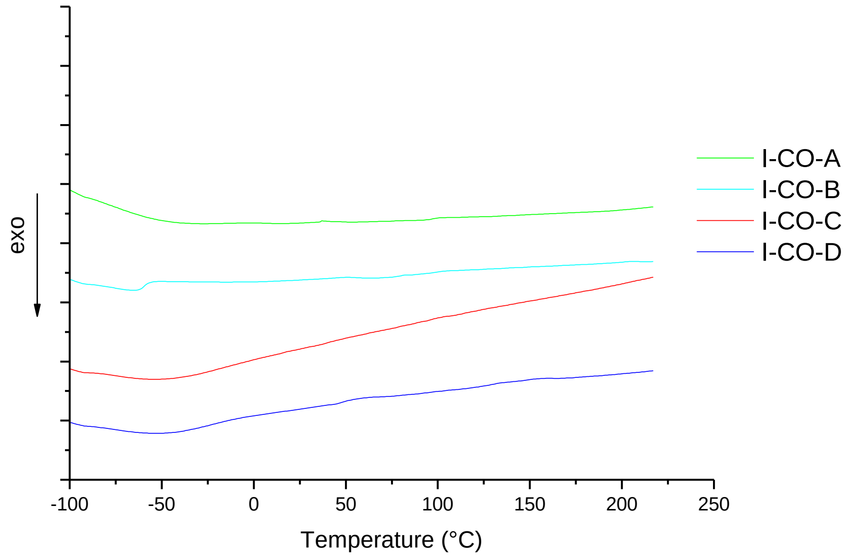


Figure 4-14 DSC traces of samples with Indulin AT and castor oil as chain extender. The curves were shifted vertically to avoid overlapping of curves.

4.5.4. Dynamic mechanical thermal analysis (DMTA)

A direct approach to study the thermal and mechanical properties of the polymer phases is via DMTA. Figure 4-15 showed the modulus profile and tan δ of samples with Indulin AT, PPG triol as chain extender and standard catalyst with different degree of expansion, Figure 4-16 shows the modulus profile and tan δ of samples with Indulin AT, PPG triol as chain extender and NE catalyst with different degree of expansion.

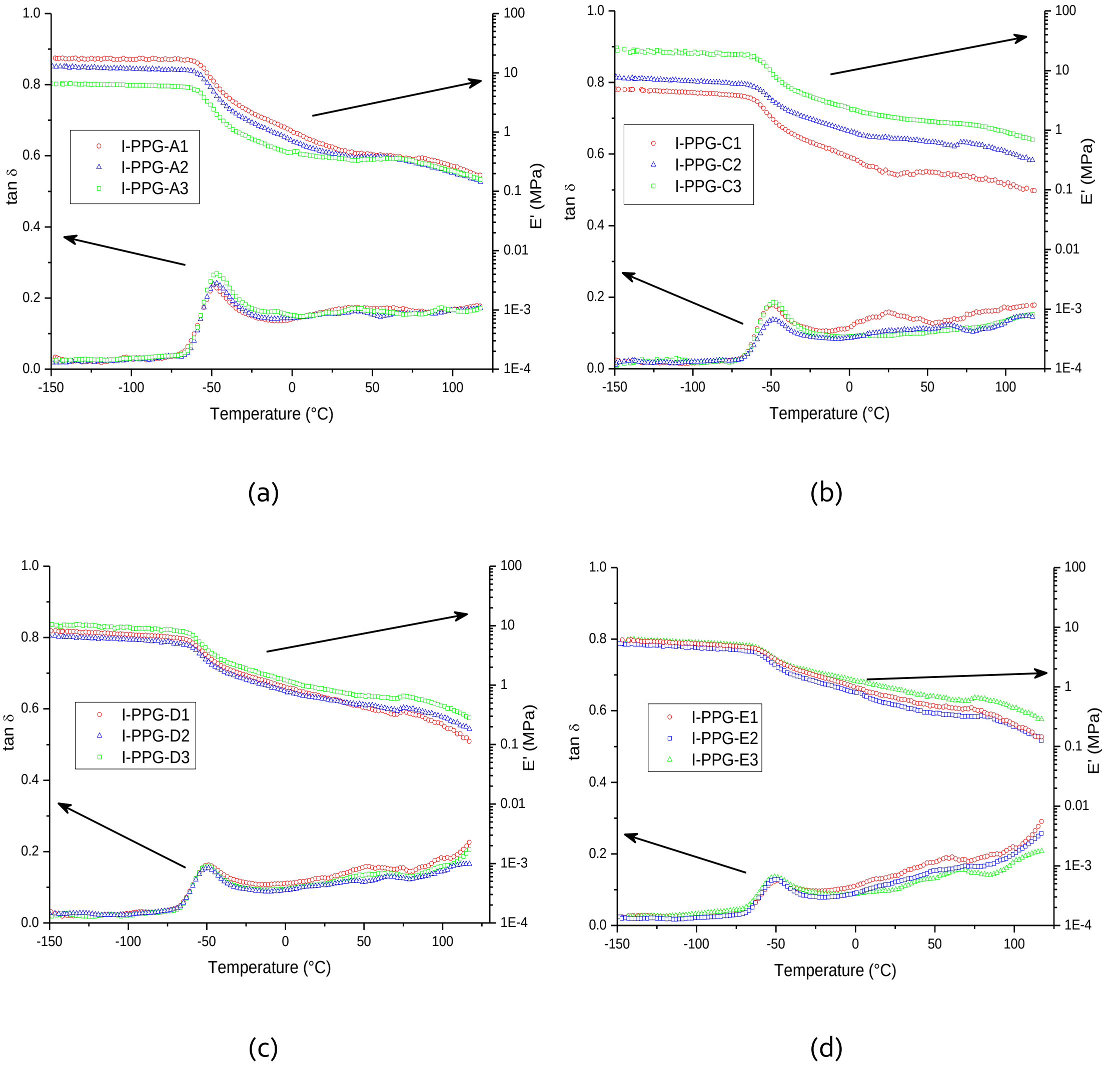
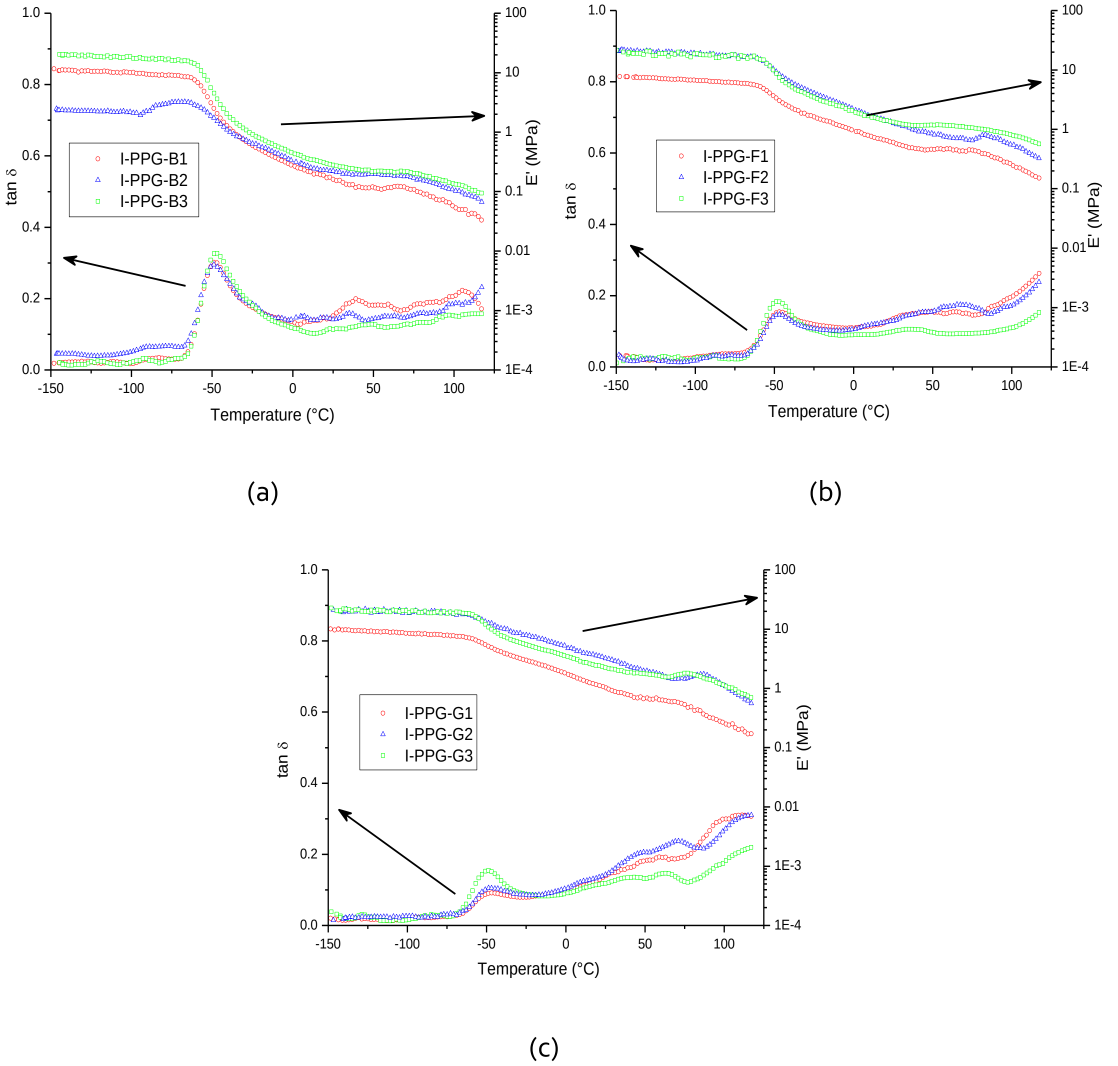


Figure 4-15 DMTA results of samples with Indulin AT, PPG triol as chain extender and standard catalyst with different degree of expansion. (a) samples with 6.7% of lignin, (b) samples with 10% of lignin, (c) samples with 11.9% of lignin, (d) samples with 13.35% of lignin.

At low temperatures, foams behaved like a solid showing high values of E′, as temperature went through T_g a dramatic increase in molecular motion caused E′ to decrease and reached a plateau. Two different transition were shown, one related to the flexible domain and one to the hard domain, both domains had a distinct T_g and mechanical stiffness. The tan δ curves of all foams exhibited peaks at the same temperature, the soft phase in all foams were PPG triol based with a T_g of -50 °C. The value of T_g was higher than the one calculated with DSC, this may due to differences in heating rate (2 °C/min by DMTA versus 10 °C/min by DSC) and in the fact that DMTA measurements were transitional peaks, DSC was a non mechanical measurement and transitional behaviour was determined from the onset temperatures.

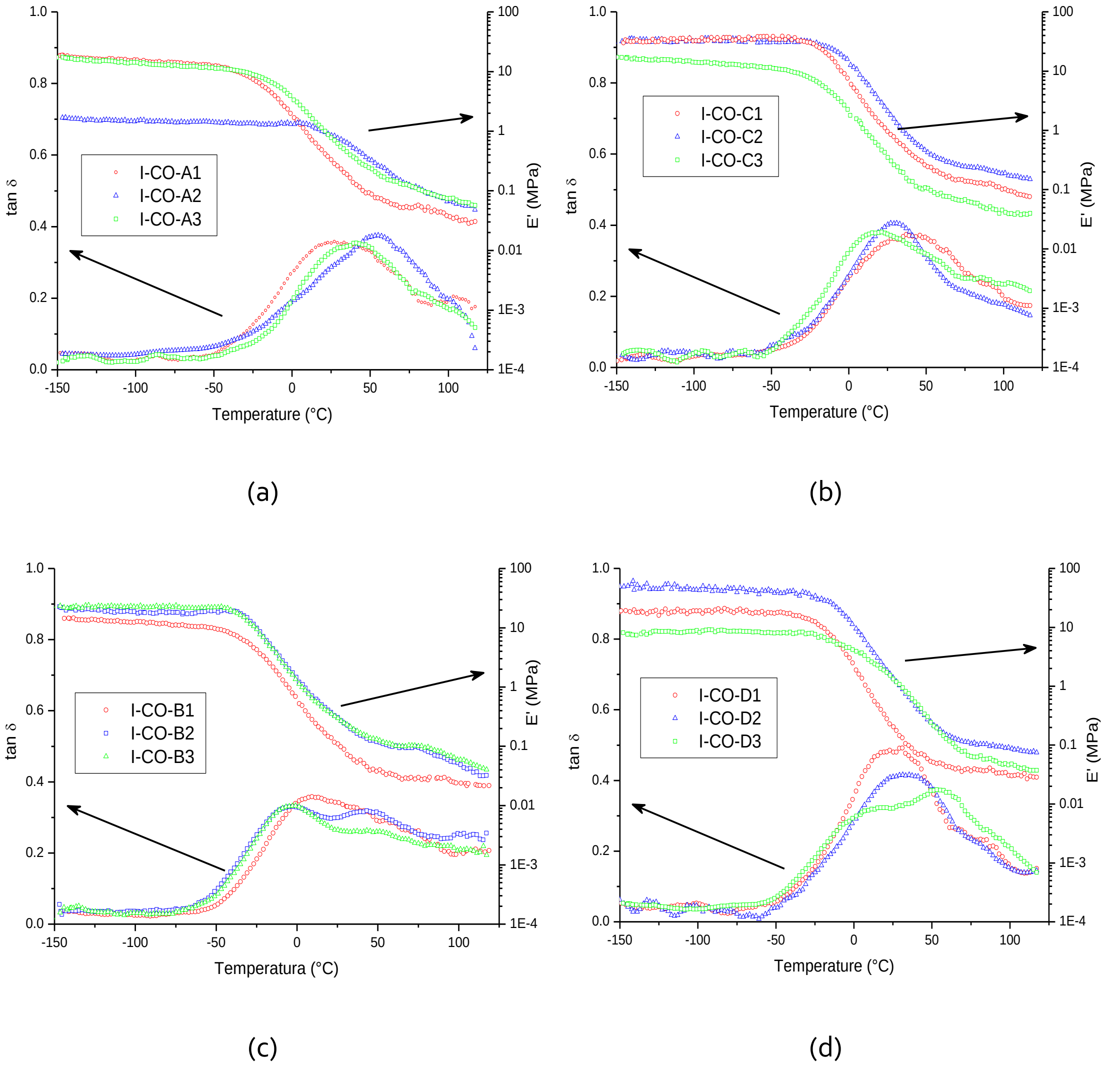


(a) (b)

(c)

Figure 4-16 DMTA results of samples with Indulin AT, PPG triol as chain extender and NE catalyst with different degree of expansion. (a) samples with 6.7% of lignin, (b) samples with 10% of lignin, (c) samples with 11.78% of lignin.

Soft phase T_g of all PPG foams determined from tan δ peak remained the same as the control, however the tan δ peak heights were significantly reduced. The smaller peaks indicated that a large part of the soft segment was mixed with a higher T_g component (lignin polyol), in fact the peak height decreased when lignin content increased. The observed increase in modulus, for samples with higher amount of lignin, could be explained by a higher concentration of hard segments due to the aromatic structure of lignin. Same behaviour could be observed for samples produced with classic catalysts and with NE catalysts.



(a) (b)

(c) (d)

Figure 4-17 DMTA results of samples with Indulin AT, castor oil as chain extender with different degree of expansion. (a) samples with 6 % of lignin and standard catalysts, (b) samples with 11.69% of lignin and standard catalysts, (c) samples with 6.4% of lignin and NE catalysts, (d) samples with 12.11% of lignin and NE catalysts.

In the samples with castor oil as chain extender (Figure 4-17), the foam showed several transitions, the transition at temperatures close to 50 °C was also in the reference sample. The peak of foams with castor oil and liquefied lignin had a broad shape, different from the foam with PPG triol and this could be explained by a wider distribution of crosslinking density and a lower homogeneity of the structure of the foam, as can be seen from SEM images shown in next paragraph. For these samples the intensity of the tan δ peak was similar to the reference sample and the modulus at temperatures above the transition is slightly lower. The storage modulus E' dropped first gradually then exhibited a relatively small drop around -90 °C and another large drop around 0 °C during the transition from glassy to the rubbery states. The first small drop was attributed to the β-transition and the second to the glass transition. The β-transition may be related to the rotation (Petrović et al., 2005) or movement of the dangling chains of castor oil fatty acids (Danch et al. 2005). From Figure 4-17 it was clear that the T_g decreased as the amount of castor oil increased and that the intensity of the peak decreases with increasing NCO/OH ratio; peaks of lesser intensity were then related to less flexible foams.

4.5.5. Density

Table 4-7 showed the density of the samples prepared with Indulin AT and chain extenders. In the samples with PPG triol the density decreased as the amount of lignin was increased and samples with standard catalysts showed lower density than the samples with NE catalysts. Samples with castor oil as chain extender showed higher density probably due to a less regular structure. Series 1 was produced in free rise expansion, the other series were controlled rise expansion.

Tab. 4-8 Density of foams prepared with Indulin AT.

Sample	**Apparent density (Kg/m^3)**		
	1	**2**	**3**
I-PPG-A	82.5	106.4	154
I-PPG-B	121.3	133.9	156.1
I-CO-A	120.6	133.3	154.7
I-CO-B	146.1	203	215.8
I-PPG-C	55.4	61.8	98.2
I-PPG-D	58.9	59.4	64.8
I-PPG-E	64.6	67.4	70
I-PPG-F	74.7	84	102.3
I-PPG-G	72.7	92.8	109
I-CO-C	140.3	182	184.3
I-CO-D	142.7	147.1	187.7

4.5.6. Compression force deflection test

This test measured the force necessary to produce a 50% compression over the entire top surface area of the foam specimen. The compression force deflection value increased linearly as the apparent density increased for the samples with PPG triol, castor oil foams had higher density compared to PPG foam but in this case density and compression force deflection value cannot be directly correlated because the structure of the foam was less regular, thinner cell walls and larger foam cells cause to the compressive strength to decrease even if the density is higher than the samples with PPG triol (Figures 4-18 and 4-19).

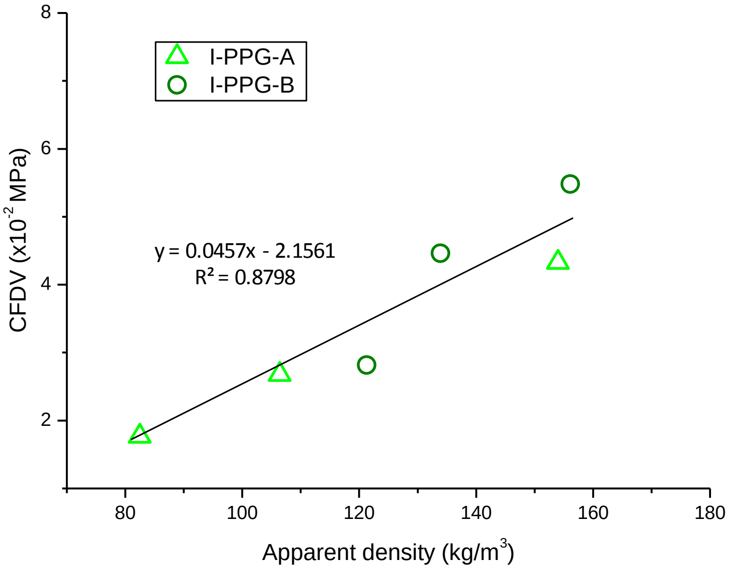


Figure 4-18 Compression force deflection value for samples with Indulin AT and glycerol/PEG400 ratio 1/0.4/2 and PPG triol as chain extender.

When loading is compressive the plateau is associated with collapse of the cells, by elastic buckling in elastomeric foams. When the cells have almost completely collapsed opposing cell walls touch and further strain compresses the solid itself giving the rapid region of rapidly increasing stress. Increasing the relative density of the foam increases modulus, raises the plateau stress and reduces the strain at which densification starts.

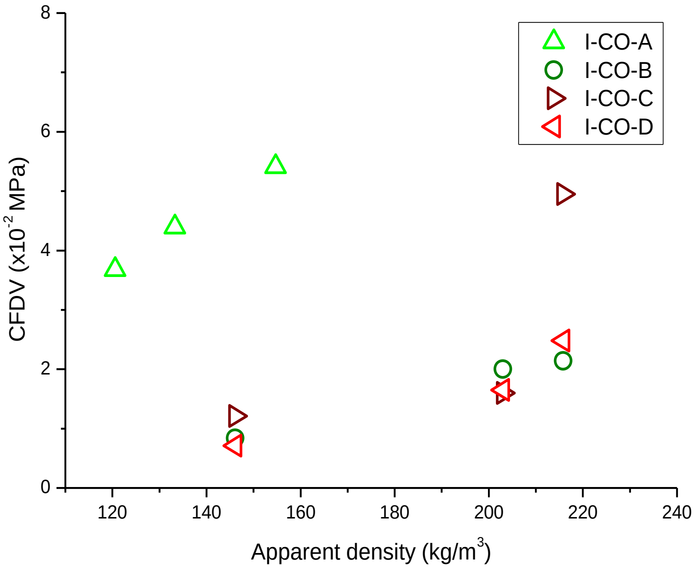


Figure 4-19 Compression force deflection value for samples with Indulin AT and glycerol/PEG400 ratio 1/0.4/2 andcastor oil as chain extender.

The measurement of foam's ability to recover after compression was also observed. All the samples, with PPG triol as chain extender, after the preflex load and recover time of 6 min showed a small decrease in thickness, around 2% of initial thickness. The samples with castor oil had around 6% loss in thickness after the test was performed. This is an indication of better ability to recover after compression with PPG triol as chain extender.

In Figure 4-20 are shown the results for the samples with higher content of lignin, prepared with lignin/glycerol/PEG400 ratio of 1/0.2/1, strength is proportional to density and is related to the amount of lignin that because of its aromatic rings lead to an increase in chain stiffness. A higher compression force deflection indicated that the foam was firmer resulting from either a higher crosslinking density or a higher foam density or both. Such physical interaction also contribute to a slightly reduced flexibility of foams, which is a direct consequence of an increased elasticity modulus as can be seen from DMTA analysis.

The compression force deflection values of the samples varied from 0.02 to 0.07 MPa that is currently in the range of compressive strength in the industrial standard. Therefore, the lignin based polyurethane foams still could be regarded as a kind of materials in industrial rank.

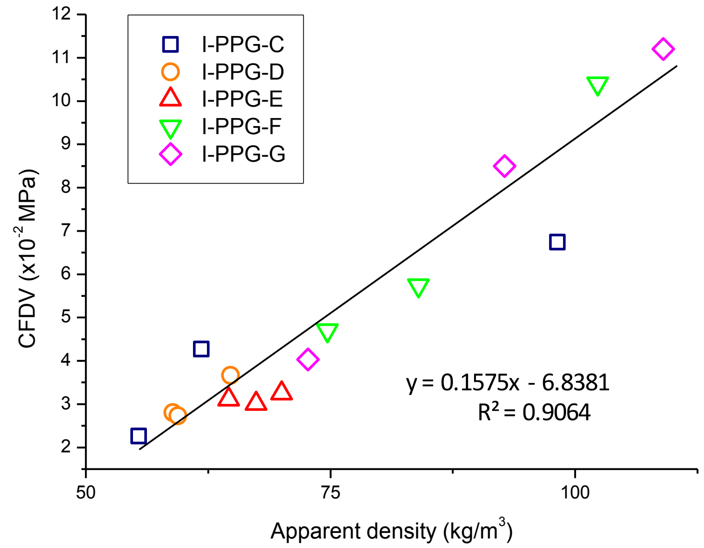
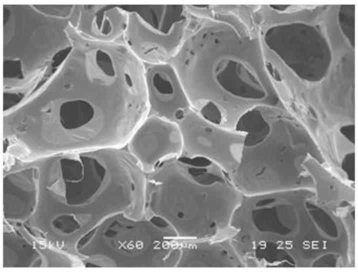
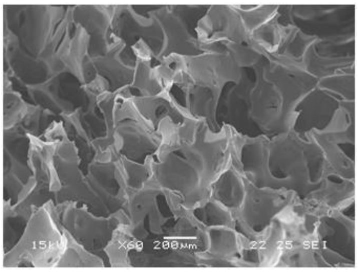
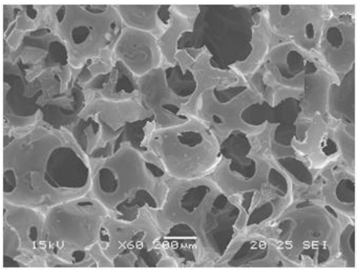
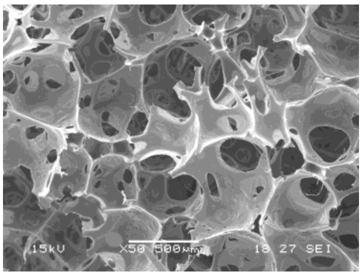
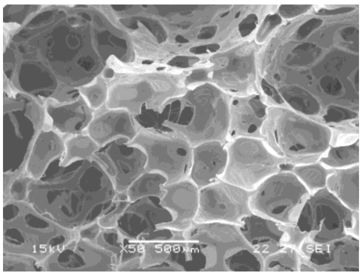
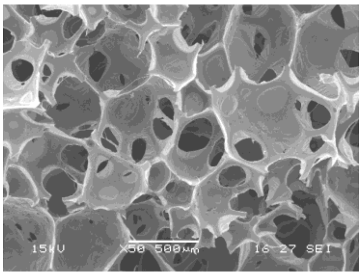


Figure 4-20 Compression force deflection value for samples with Indulin AT, PPG triol as chain extender and glycerol/PEG400 ratio 1/0.2/1.

4.5.7. Morphology (SEM)

Tab. 4-8 showed SEM images of foams produced with PPG triol as chain extender. Tab. 4-9 showed micrographs of foams produced with castor oil as chain extender.

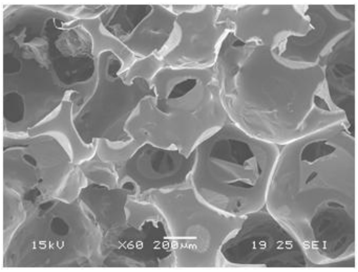
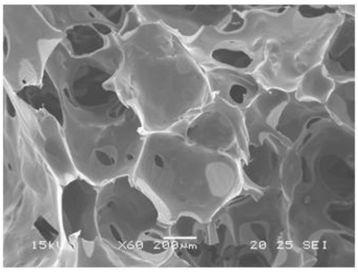
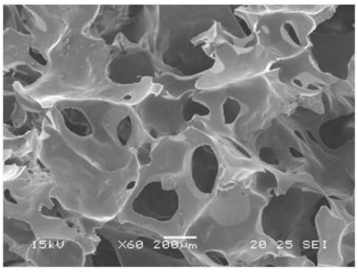
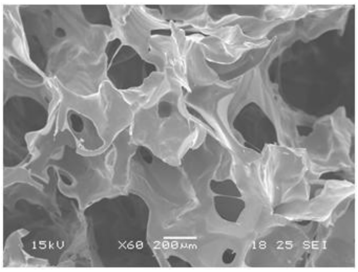
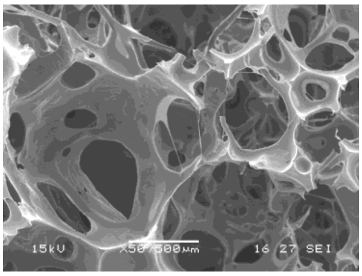
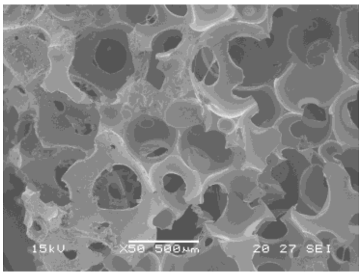
Tab. 4-9 SEM images of samples with Indulin AT and PPG triol as chain extender.

I-PPG-A1	**I-PPG-A2**	**I-PPG-A3**
		
I-PPG-D1	**I-PPG-D2**	**I-PPG-D3**
		

The cells shape of the foam was polyhedral and show preferential orientation associated with the polyurethane rise direction. Performance of flexible foam requires high open cell content. The important parameters that affect mechanical properties of foams are cell strut thickness and length. The hypothesis of open cell structure is confirmed by the morphological analysis performed by scanning electron microscope.

Samples produced in the free expansion had slightly larger cells than those produced in controlled rise, and in the controlled rise samples some of the intercellular membranes are not completely broken. As can be seen, the foam designed to be an open-celled structure has very few closed cells. Cell walls are thinner for the samples with PPG triol and the shape of the cells is more regular compared to the samples with castor oil as chain extender.

Tab. 4-10 SEM images of samples with Indulin AT and castor oil as chain extender.

I-CO-A1	**I-CO-A2**	**I-CO-A3**
		
I-CO-B1	**I-CO-C1**	**I-CO-D1**
		

Samples with castor oil as chain extender in general showed less regular structure, the cell shape was bigger than samples with PPG triol and a larger number of untouched intercellular membranes can be found. In these samples probably the blow-off was not optimal, that indicated that some of the CO_2 released in the blow reaction was not able escape the foam bun.

4.6. Polyurethanes with Protobind 1000

In Tab. 4-11 were listed the series of flexible foams produced using Protobind 1000 lignin, the kind of chain extender and catalysts, the ratio NCO/OH and the amount of lignin. The value in brackets for the samples with castor oil was referred to the renewable amount of reagents in this foams considering the contribution of castor oil too.

Tab. 4-11 List of foams produced with Protobind 1000.

Sample	Chain extender	Lignin/Chain extender ratio	NCO/OH	Catalysts	% Lignin
P-PPG-A	PPG triol	1.45	0.82	Classic	6.7
P-PPG-B	PPG triol	1.45	0.77	NE	6.7
P-CO-A	Castor oil	1.45	0.75	Classic	6 (40.3)
P-CO-B	Castor oil	1.45	0.72	NE	6.3 (42.7)
P-PPG-C	PPG triol	1.4	0.8	Classic	10
P-PPG-D	PPG triol	1	0.69	Classic	11.9
P-PPG-E	PPG triol	0.8	0.63	Classic	13.35
P-PPG-F	PPG triol	1.4	0.81	NE	10
P-PPG-G	PPG triol	1	0.70	NE	11.78

In Tab. 4-12 and 4-13 were listed the formulations used for the production of the flexible foams using PPG triol and castor oil as chain extenders. The procedure used for making the foams was the same of the samples with Indulin AT lignin. Three samples for each formulation were prepared, sample 1 was free rise and samples 2-3 were controlled rise samples. All the ingredients except the MDI were weighted in a polypropylene cup and mixed for 1 minute, at the end of the mixing period, MDI was added and the mixing continued for another 20 seconds. The foams were allowed to cure for 48 hours before testing. Samples P-PPG-A-B and P-CO-A-B were prepared using liquefaction ratio of lignin/glycerol/PEG400 of 1/0.4/2, samples P-PPG-C-F were prepared using liquefaction ratio of lignin/glycerol/PEG400 of 1/0.2/1.

Tab. 4-12 Foam formulations used in sample synthesis with Protobind 1000 and PPG triol as chain extender, all formulations are in grams.

	P-PPG-A	P-PPG-B	P-PPG-C	P-PPG-D	P-PPG-E	P-PPG-F	P-PPG-G
Liquefied lignin	14.20	11.40	10	10	10	10	10
PPG triol	20.80	16.60	14	10	7.6	14	10
Water	0.6	0.7	0.66	0.66	0.66	0.65	0.65
Gelling catalyst	0.53	0.9	0.36	0.34	0.31	0.63	0.6
Blowing catalyst	0.53	0.35	0.35	0.31	0.31	0.2	0.22
Surfactant	0.35	0.56	0.26	0.21	0.17	0.21	0.2
Isocyanate	25	23	20	16.8	15	20	16.9

Tab. 4-13 Foam formulations used in sample synthesis with Protobind 1000 and castor oil as chain extender, all formulations are in grams.

	P-CO-A	P-CO-B
Liquefied lignin	17	17
Castor oil	27.5	27.5
Water	0.81	0.5
Gelling catalyst	0.67	1.24
Blowing catalyst	0.67	0.25
Surfactant	0.45	0.66
Isocyanate	36.8	32

Kinetics of the foam formation was followed by the cream time and gel time. The cream time corresponds to the start of bubble rise and the colour of the mixture becomes light brown from very dark brown due to the introduction of bubbles. The gel time was the starting point when the stable spatial shape was formed by the reaction of forming urethane and urea linkage and the crosslinking reaction.

Samples with classic catalysts showed characteristic reaction times slightly lower than samples with NE catalysts, this is due to the higher reactivity of the classic catalysts, but the final products showed no significant differences regardless the catalysts employed for their production.

Tab. 4-14 Reactivity of the foams produced with Protobind 1000.

Sample	Cream time (s)	Rise time (s)
P-PPG-A	10	15
P-PPG-B	20	40
P-CO-A	30	45
P-CO-B	70	190
P-PPG-C	30	80
P-PPG-D	50	170
P-PPG-E	40	180
P-PPG-F	40	150
P-PPG-G	50	180

4.6.1. FT-IR spectroscopy

The samples for FT-IR measurement were taken from the centre of foam buns, grinded and dried at 105 °C for 2 hours to ensure no water was adsorbed on the foam. Figure 4-21 showed the spectra for all the samples produced with Protobind lignin and PPG triol as chain extender.

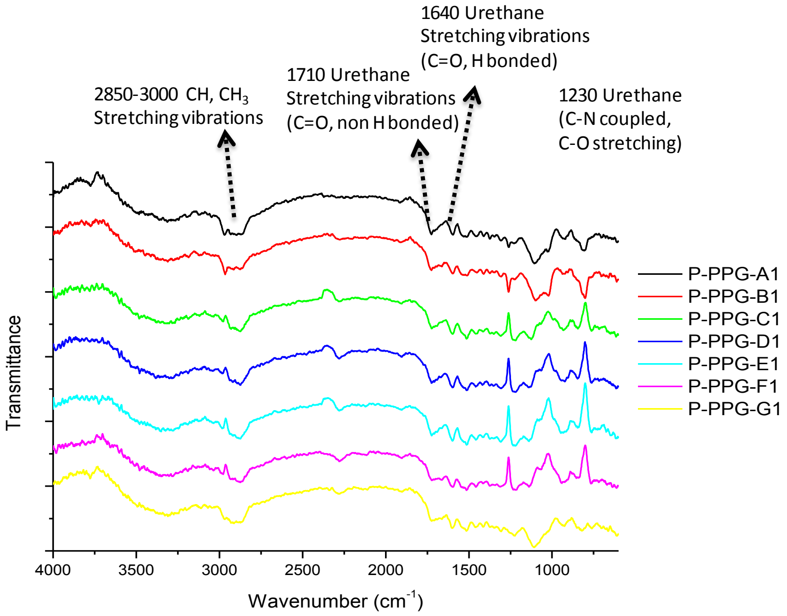


Figure 4-21 General FT-IR spectra for all the samples produced with Protobind 1000 and PPG triol as chain extender.

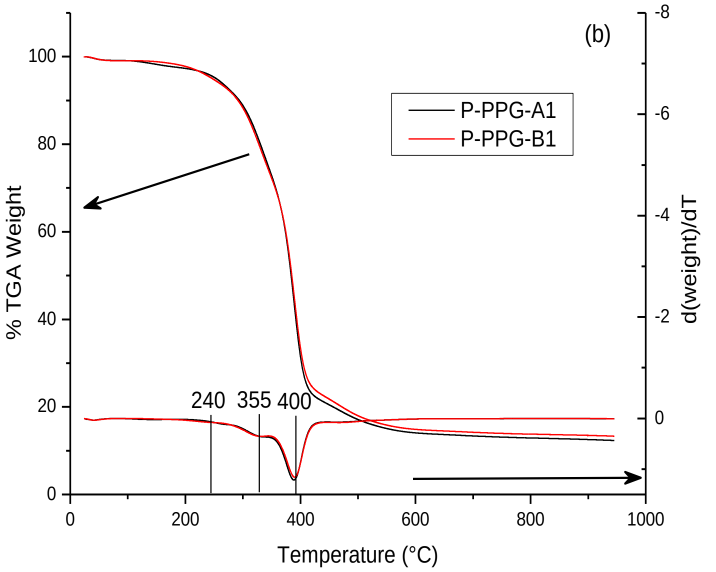
Compared to the samples produced with Indulin lignin (Figure 4-8) the amount of NCO unreacted (peak at 2270 cm^{-1}) was lower probably due to the simpler structure and less steric hindrance of this soda lignin.

The FT-IR spectrum confirmed qualitatively the presence of urethane linkages. The characteristic -NH stretching vibrational region (3200-3500 cm^{-1}) and the characteristic -CO vibrational region (1700-1730 cm^{-1}) were well represented. The bands in the region below 1600 cm^{-1} represented the fingerprints of the polyurethanes. The -NH stretching region showed two distinct bands. The bands centred at 3444 cm^{-1} corresponds to the free -NH region (3441-3446 cm^{-1}) and the band centred at 3329 corresponds to the bonded -NH region (3324-3329 cm^{-1}). There were also two stretching regions attributed to the -CO group. The band centred at 1710 cm^{-1} corresponded to the free carbonyl group (1710-1733 cm^{-1}) while the band centred at 1640 corresponded to the H-bonded carbonyl group (1640-1700 cm^{-1}) (Tsai et al. 1998; Goddard and Cooper, 1995). These results indicated that the polyurethane matrices undergo physical bonding.

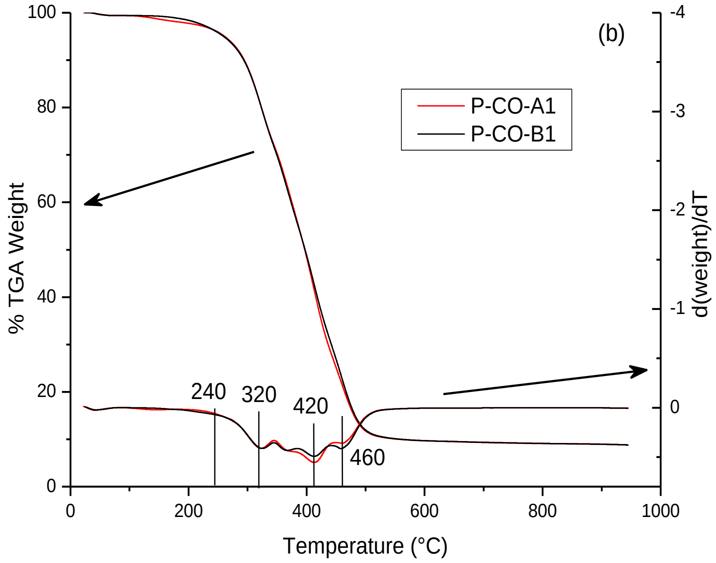
4.6.2. Thermogravimetric analysis (TGA)

Thermogravimetric analysis were carried out in nitrogen as observed in Figure 4-22. Samples with PPG triol as chain extender presented a residual carbon yield around 15% at temperature above 500 °C. This effect could be explained by the difficult heat transfer in cellular materials. If the open cell volume is high and the cellular structure is regular the heat transfer is hindered and pyrolysis is less effective. This behaviour was not so evident in polyurethanes with castor oil, whose carbon residues were less than 10% and cellular structure was less regular.

It is important to point out that all lignin based foams, with PPG triol as chain extender, presented similar characteristic temperatures. Urethane bonds degradation takes place in the first degradation stage at temperature around 250 °C, degradation temperatures of 355 °C was associated to soft segments and the second that starts at 400 °C to the thermal degradation of hard segments in which the lignin was inserted.



(a)



(b)

Figure 4-22 TGA curves for free rise samples produced with Protobind 1000 and (a) PPG triol (b) castor oil as chain extender.

Samples with castor oil as chain extender showed three degradation step, the second step at 320 °C might correspond to the castor oil degradation, the soft polyurethane segment and the third degradation stage occurred in the same range of temperature, with a temperature comprised between 420 and 480 °C, depending on the polyurethane nature. This should correspond to the degradation of advanced fragments produced after the second stage. Several degradation steps were related to the mixed morphology of the samples prepared with castor oil.

4.6.3. Differential scanning calorimetry (DSC)

It was observed from the DSC scans (Figure 4-23) that the breadth and position of the T_g remained relatively constant for all the samples examined. This implied that the mobility of the soft phase in all the samples remained relatively unchanged. Further support of this observation was gained via DMTA by which the temperature position of the tan δ peak, as well as its breadth, were also noted to be very similar for all the samples tested. The T_g determined for polyurethane foams based only on PPG triol is around -60 °C, and for that added with lignin this value approaches -65 °C. The insignificant variation in T_g with the increase in lignin content indicated that this material was a multiphase system. DSC traces showed no endothermic peaks that could be assigned to any melting of the hard segment, this means no cristallinity for these samples.

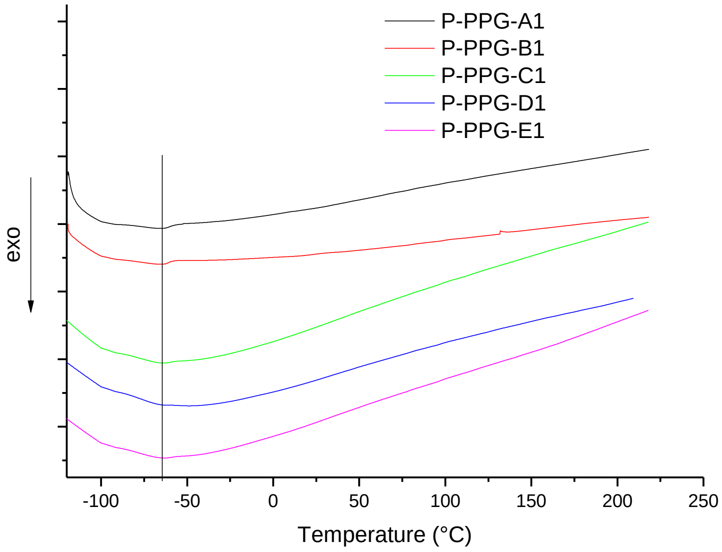


Figure 4-23 DSC traces of samples with Protobind 1000 and PPG triol as chain extender. The curves were shifted vertically to avoid overlapping of curves.

From the DSC traces it was noted that in general PPG triol based networks were more flexible than castor oil networks, in fact PPG triol based networks showed lower T_g. It was also important to underline that higher T_g in segmented polyurethane based on polyol with dangling chains when compared to the segmented polyurethane based on linear polyol have been reported in the literature (Coll Ferrer et al., 2008).

The T_g determined for polyurethane foams based on castor oil and liquefied lignin was very broad and could be located around 0 °C .

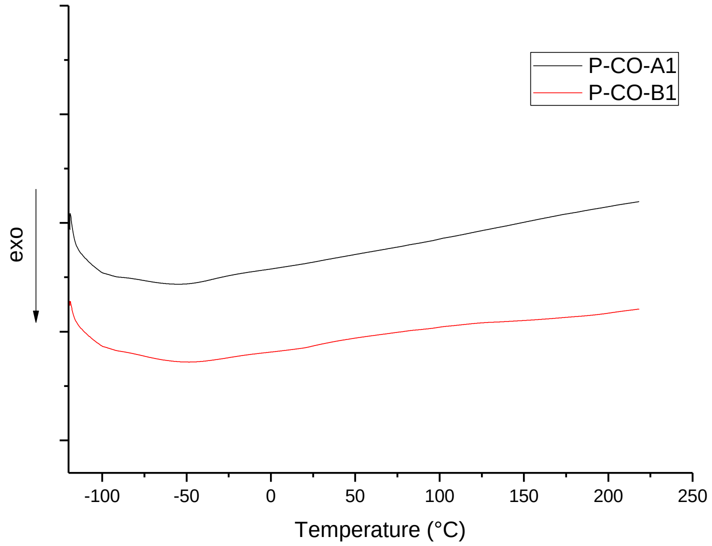
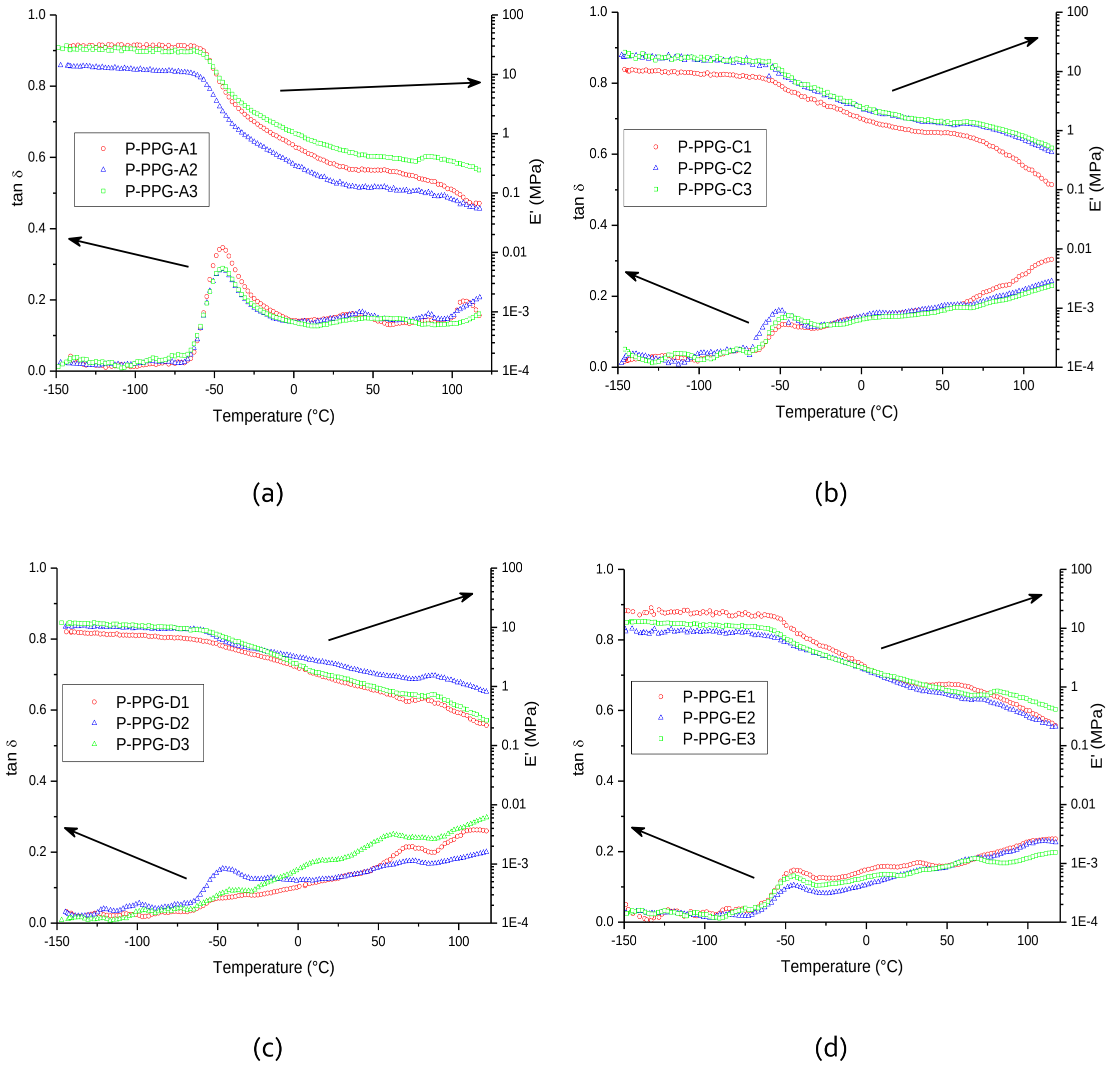


Figure 4-24 DSC traces of samples with Protobind 1000 and castor oil as chain extender. The curves were shifted vertically to avoid overlapping of curves.

4.6.4. Dynamic mechanical thermal analysis (DMTA)

Figure 4-25 displayed the storage modulus and mechanical tan δ as a function of the temperature for the samples with different amount of Protobind 1000, PPG triol as chain extender and standard catalyst with different degree of expansion. The precise T_g locations for the polyurethane materials were determined from the DMTA tan δ peaks. This value was higher than the value obtained by DSC, due to the effect of frequency. The increase in amount of lignin produced an increase in hard segment content that was accompanied by a substantial decrease in the loss factor (tan δ) intensity as can be seen in Figure 4-25. As the hard segment was increased, the number of physical crosslinks that was available to restrict the soft segment chain mobility also increased and hence the tan δ intensity, which characterized the damping behaviour, successively decreased. For the materials with 10% or more of lignin the intensity was almost one half the intensity of P-PPG-A series, indicating a greatly reduced damping behaviour. The storage modulus of polyurethanes was almost constant until T_g was reached, then decreased slowly with increasing temperature, followed by a steady increase in rubbery state. The slightly increase in modulus was found in almost all samples and was attributed to the retraction of chains to the equilibrium position from the stretched state, fixed during the cross-linking reaction. However, these polyurethanes did not display the large volume relaxation at T_g observed with castor oil based polyurethanes.

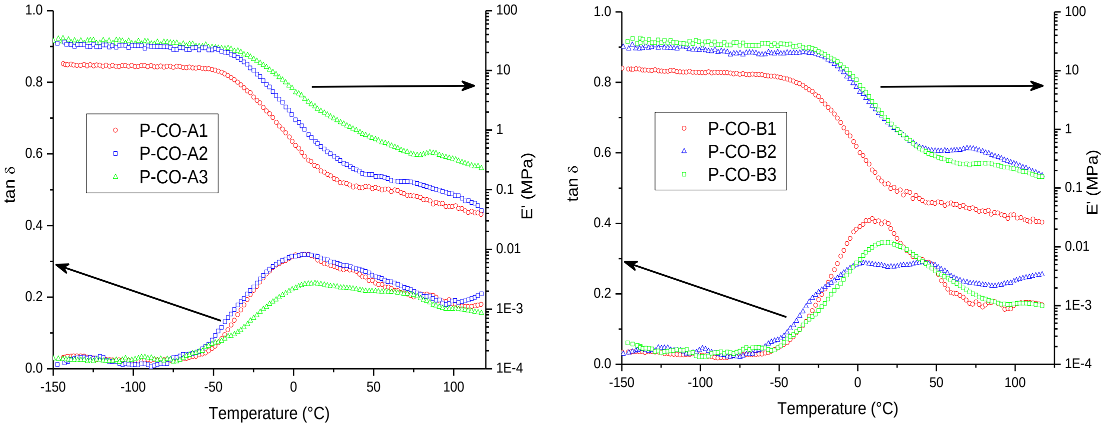


(a) (b)

(c) (d)

Figure 4-25 DMTA results of samples with Protobind 1000, PPG triol as chain extender and standard catalyst with different degree of expansion. (a) samples with 6.7% of lignin, (b) samples with 10% of lignin, (c) samples with 11.9% of lignin, (d) samples with 13.35% of lignin.

Samples with castor oil as chain extender were reported in Figure 4-26, these materials exhibited multiple relaxation peaks associated with the T_g in the -25 °C and 50 °C range. Usually the more intense and dominant peak related to the relaxation of the soft segment rich phase and the weaker shoulder presumably relates to the soft segment phase mixed regions (Kojio et al., 2007). When samples displayed a single broad tan δ peak this appeared to be a result of merging of the multiple soft segment relaxation peaks. This is likely due to a change in morphology as a result of the greater phase mixing of castor oil and liquefied lignin material.



(a) (b)

Figure 4-26 DMTA results of samples with Protobind 1000, castor oil as chain extender with different degree of expansion. (a) samples with 6 % of lignin and standard catalysts, (b) samples with 6.4% of lignin and NE catalysts.

4.6.5. Density

Table 4-15 showed the density of the samples prepared with Protobind 1000 and chain extenders. In the samples with PPG triol the density decreased as the amount of lignin was increased and in general samples with NE catalysts showed lower density than the samples with standard catalysts. Samples with castor oil as chain extender showed higher density probably due to a less regular structure. Series 1 was produced in free rise expansion, the other series are controlled rise expansion.

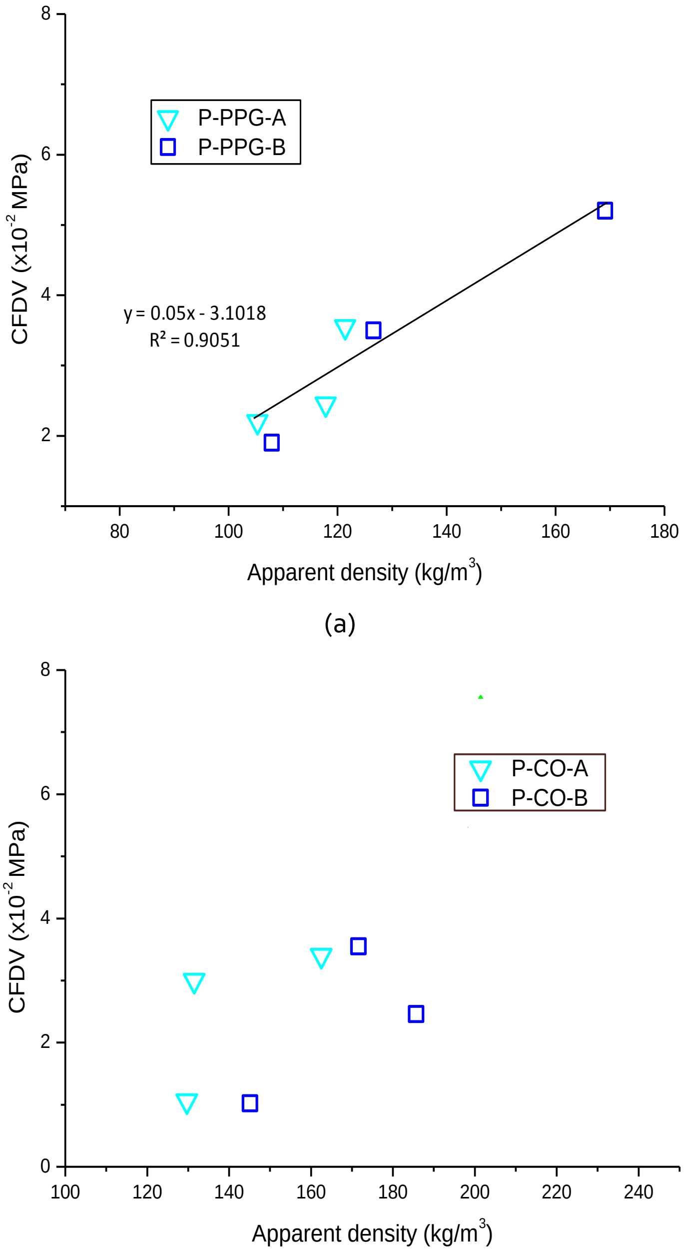
Tab. 4-15 Density of foams prepared with Protobind 1000.

Sample	Apparent density (Kg/m^3)		
	1	2	3
P-PPG-A	117.8	105.3	121.4
P-PPG-B	107.9	169.1	126.6
P-CO-A	129.7	131.5	162.5
P-CO-B	145.1	185.7	171.6
P-PPG-C	87.1	79.4	111
P-PPG-D	80	88.6	118.7
P-PPG-E	83.7	100	105
P-PPG-F	69.8	95.1	115
P-PPG-G	81.9	91	110

4.6.6. Compression force deflection test

One fundamental property of polyurethane foam is the tendency to undergo non-recoverable deformation under a defined compressive load. Compression force is so important that many individual manufacturers and end users have established specific tests and criteria to qualify the acceptability of specific foam samples. Fundamentally, compression value has been shown to result from stress-induced deformation of the polyurethane co-continuous hard phase, decomposition of the urethane bond, and hard segment slippage through the co-continuous soft phase. The force is a measure of flexibility of the foam, in general, this value increased from free rise sample to compressed ones. Since it has been shown that the physical properties vary depending on the loading direction, all foams were loaded parallel to the rise direction for consistency.

The compression force deflection value increased linearly as the apparent density increased for the samples with PPG triol, castor oil foams have higher density compared to PPG foam but in this case density and compression force deflection value can hardly correlated because the structure of the foam is less regular, thinner cell walls and larger foam cells cause to the compressive strength to decrease even if the density is higher than the samples with PPG triol.



(a)

(b)

Figure 4-27 Compression force deflection value for samples with Protobind 1000 and glycerol/PEG400 ratio 1/0.4/2. (a) samples with PPG triol as chain extender, (b) samples with castor oil as chain extender.

In Figure 4-28 were reported the results for samples produced with glycerol/PEG400 ratio 1/0.2/1, this samples with increased amount of lignin showed compression force deflection values similar to samples with lower amount, this samples maintained a high flexibility and a regular cellular structure. Samples produced in controlled rise showed higher values of compression strength. Compression force deflection values are in a range from 0.02 to 0.07

MPa which is similar to the commercially available polyurethane foams derived from petroleum. All the samples, with PPG triol as chain extender, after the preflex load and recover time of 6 min showed a small decrease in thickness, around 2% of initial thickness. These results obtained by mechanical measurements indicated that the polyurethane foams derived from lignin can be used for practical purposes.

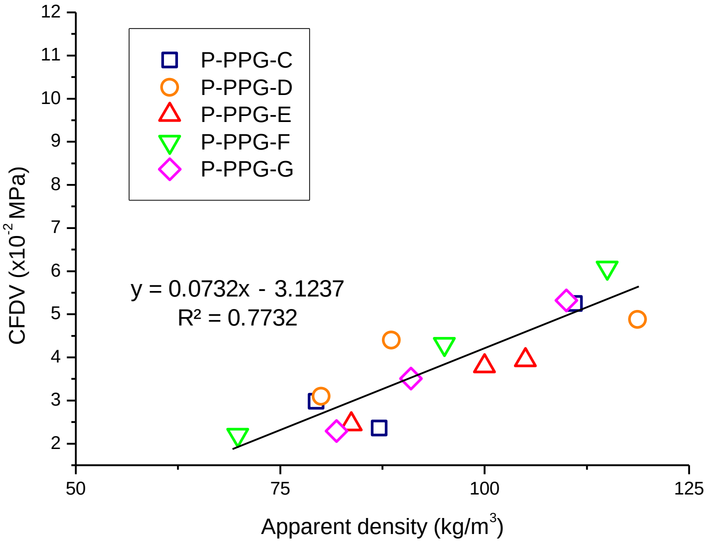


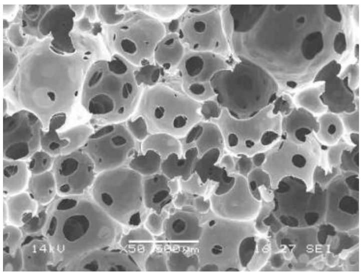
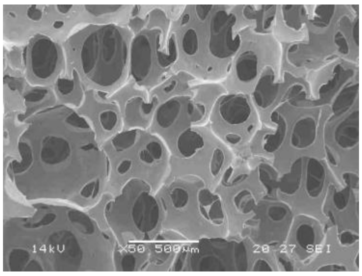
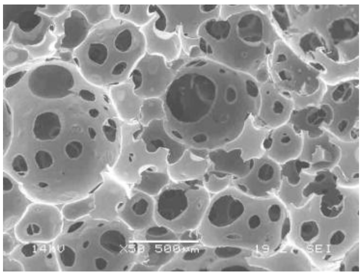
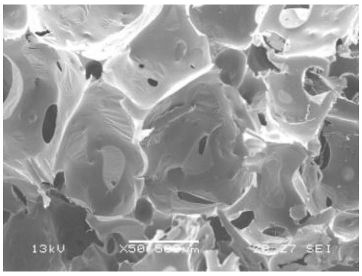
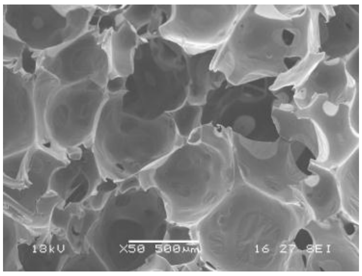
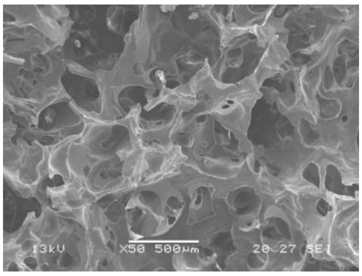
Figure 4-28 Compression force deflection value for samples with Protobind 1000, PPG triol as chain extender and glycerol/PEG400 ratio 1/0.2/1.

From the applicative point of view, adding up to 13% of lignin impart to the polyurethane flexible foam strength, slightly lowering the elasticity. The use of polyurethane polymers to prepare different lignin-polymer system could be a good way of given a better use and add value to lignin wastes.

4.6.7. Morphology (SEM)

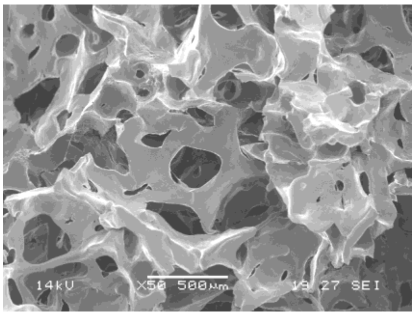
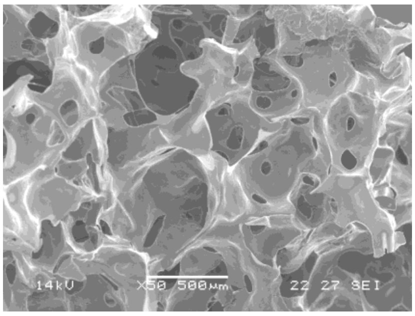
The cellular morphology of the flexible polyurethane foams was characterized by SEM, typical macrostructures of the foams are shown in Tab. 4-16 and 4-17. These foams were found to consist of a three dimensional array of struts. The cells shape of the foam was polyhedral and show preferential orientation associated with the polyurethane rise direction. Results showed that though the cell size and strut size were similar for all the foams with PPG triol, slightly bigger cells were found on the free rise samples. The number of closed cells was found to be greater in series with higher amount of lignin and lower amount of chain extender, and the cellular structure showed less regularity compared with samples with lower amount of lignin.

Tab. 4-16 SEM images of samples with Protobind 1000 and PPG triol as chain extender.

P-PPG-A1	**P-PPG-A2**	**P-PPG-A3**
		
P-PPG-C1	**P-PPG-F1**	**P-PPG-G1**
		

Previous studies have shown that the precipitation of the urea phase and the formation of the urea aggregates can be directly related to the cell-opening event in flexible PU foams (Rossmy et al, 1981). In fact, one of the mechanisms which led to cell-opening was thought to be the formation of urea aggregates where the aggregates acted as particulates and led to cell-opening. Foams with higher amount of lignin displayed more closed cellular material due to the slowing down of the blow reaction which leads to a poor blow-off, and probably to less formation of urea aggregates.

Tab. 4-17 SEM images of samples with Protobind 1000 and castor oil as chain extender.

P-CO-A1	**P-CO-B1**
	

For the studied liquefied Protobind 1000 and castor oil foams, cells with large size and very coarse with thickest walls are often detected thus contributing to less homogeneous structure. This heterogeneity can justify the reason why compressive modulus is lower even if apparent density is higher compared to the more regular samples produced with PPG triol. All the materials studied showed a homogenous structure without evidence of macroscopic phase separation.

4.7. Polyurethanes with hydroxypropylated Protobind 1000

4.7.1. Hydroxypropylation process

The process to obtain hydroxypropylated Protobind 1000 was described in previous chapter, the extent of hydroxypropylation was assessed by FT-IR spectroscopy as shown in Figure 4-28 and its corresponding plasticizing effect from glass transition temperature measurements by DSC (Figure 4-30). The T_g of hydroxypropylated lignin is about 20 °C lower than the T_g of unmodified lignin.

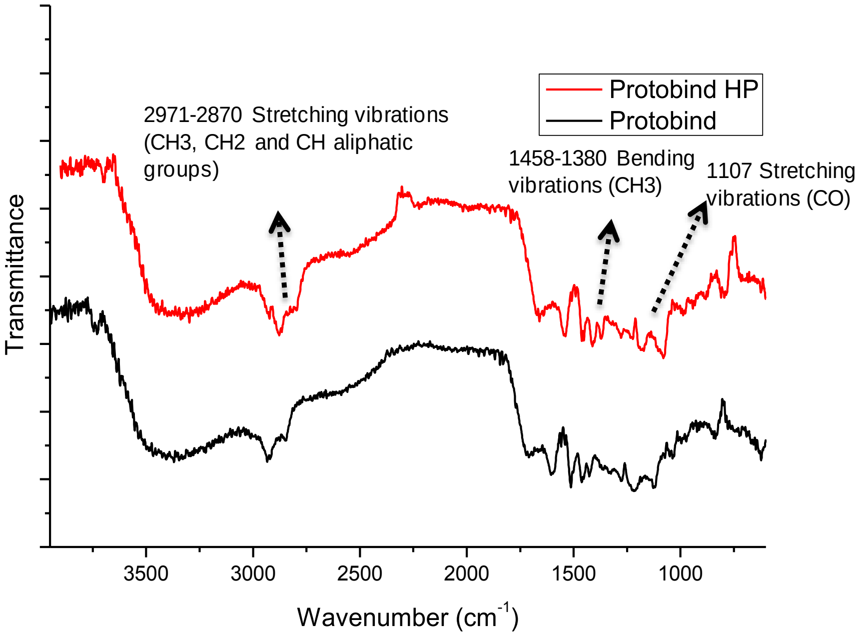


Figure 4-29 FT-IR of unmodified and hydroxypropylated Protobind 1000.

Figure 4-29 was taken as examples to show the FTIR spectra of Protobind lignin, before and after its chain extension with propylene oxide monomer. Several features indicated the occurrence of propylene oxide grafting on lignin: (Nadji et al. 2005; Cateto et al., 2009):

- increase in the bands at 2971–2870, 1458 and 1373 cm^{-1} attributed to stretching of -CH3, -CH2 and -CH aliphatic groups.
- reduction in the intensity of the carbonyl peak at 1714 cm^{-1}.
- increase in the band at 1107 cm^{-1} associated with the presence of stretching vibration of -CO moieties.

The presence of these peaks indicates that the branching reaction between lignin macromolecules and propylene oxide units had indeed occurred.

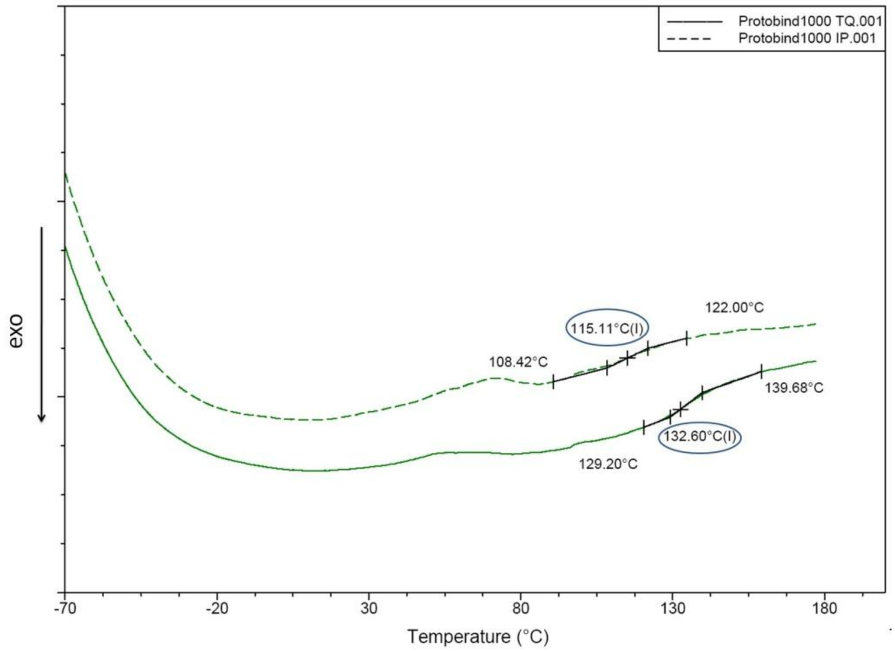


Figure 4-30 DSC of unmodified and hydroxypropylated Protobind 1000.

After the process the lignin was washed with distilled water until the pH reached 6, centrifuged and dried in oven at 50 °C, grinded and then used like the unmodified lignins for the microwave driven liquefaction process with glycerol and PEG#400. The OH value of this lignin is almost the same of the unmodified Protobind 1000 because chain extension reaction do not produce any increase in the OH functionality of the starting substrate, since their role is only to transport this group as chain ends of the inserted polyether segment. Samples produced with hydroxypropylated lignin showed a more uniform structure and colour compared to the samples with unmodified lignin that sometimes presented small dark spots of liquefied lignin due to the difficult mixing because of high viscosity when the chain extender was in lower amount.

In table 4-18 are listed the series of flexible foams produced using hydroxypropylated Protobind 1000 lignin, the kind of chain extender and catalysts, the ratio NCO/OH and the amount of lignin.

Tab. 4-18 List of foams produced with hydroxypropylated Protobind 1000.

Sample	Chain extender	Lignin/Chain extender ratio	NCO/OH	Catalysts	% Lignin
HP-PPG-A	PPG triol	1.45	0.82	Classic	6.7
HP-PPG-B	PPG triol	1.45	0.77	NE	6.7
HP-CO-A	Castor oil	1.45	0.75	Classic	6 (40.3)
HP-CO-B	Castor oil	1.45	0.72	NE	6.3 (42.7)
HP-PPG-C	PPG triol	1.4	0.8	Classic	10
HP-PPG-D	PPG triol	1	0.69	Classic	11.9
HP-PPG-E	PPG triol	0.8	0.63	Classic	13.35
HP-PPG-F	PPG triol	1.4	0.81	NE	10
HP-PPG-G	PPG triol	1	0.70	NE	11.78

In Tab. 4-19 and 4-20 were listed the formulations used for the production of the flexible foams using PPG triol and castor oil as chain extenders. The procedure used for making the foams was the same of the samples with unmodified lignin. Three samples for each formulation were prepared, sample 1 was free rise and samples 2-3 were controlled rise samples. All the ingredients except the MDI were weighted in a polypropylene cup and mixed for 1 minute, at the end of the mixing period, MDI was added and the mixing continued for another 20 seconds. The foams were allowed to cure for 48 hours before testing. Samples HP-PPG-A-B and HP-CO-A-B were prepared using liquefaction ratio of lignin/glycerol/PEG400 of 1/0.4/2, samples HP-PPG-C-F were prepared using liquefaction ratio of lignin/glycerol/PEG400 of 1/0.2/1.

Tab. 4-19 Foam formulations used in sample synthesis with hydroxypropylated Protobind 1000 and PPG triol as chain extender, all formulations are in grams.

	HP-PPG-A	HP-PPG-B	HP-PPG-C	HP-PPG-D	HP-PPG-E	HP-PPG-F	HP-PPG-G
Liquefied lignin	14.20	11.40	10	10	10	10	10
PPG triol	20.80	16.60	14	10	7.6	14	10
Water	0.6	0.7	0.66	0.66	0.66	0.65	0.65
Gelling catalyst	0.53	0.9	0.36	0.34	0.31	0.63	0.6
Blowing catalyst	0.53	0.35	0.35	0.31	0.31	0.2	0.22
Surfactant	0.35	0.56	0.26	0.21	0.17	0.21	0.2
Isocyanate	25	23	20	16.8	15	20	16.9

Tab. 4-20 Foam formulations used in sample synthesis with hydroxypropylated Protobind 1000 and castor oil as chain extender, all formulations are in grams.

	P-CO-A	P-CO-B
Liquefied lignin	17	17
Castor oil	27.5	27.5
Water	0.81	0.5
Gelling catalyst	0.67	1.24
Blowing catalyst	0.67	0.25
Surfactant	0.45	0.66
Isocyanate	36.8	32

Kinetics of the foam formation was followed by the cream time and gel time. The cream time corresponds to the start of bubble rise and hence color of the mixture becomes light brown from very dark brown due to the introduction of bubbles. The gel time was the starting point when the stable spatial shape was formed by the reaction of forming urethane and urea linkage and the crosslinking reaction.

Samples with classic catalysts showed reaction times slightly lower than samples with NE catalysts, this is due to the higher reactivity of the classic catalysts, but the final products showed no significant differences regardless the catalysts employed for their production.

Tab. 4-21 Reactivity of foams produced with hydroxypropylated Protobind 1000.

Sample	Cream time (s)	Rise time (s)
HP-PPG-A	10	10
HP-PPG-B	20	50
HP-CO-A	25	40
HP-CO-B	60	120
HP-PPG-C	25	40
HP-PPG-D	30	50
HP-PPG-E	30	60
HP-PPG-F	40	110
HP-PPG-G	50	150

4.7.2. FT-IR spectroscopy

The FT-IR spectra of the polyurethanes made with hydroxypropylated lignin, PPG triol and castor oil as chain extenders were shown in Figure 4-31 and 4-32. FT-IR gives useful qualitative information about the molecular structure of the polyurethanes. A strong 3340 cm^{-1} band characteristic of -NH group and a band characteristic of the -CO group centred around 1700 cm^{-1} were present in all the FT-IR spectra demonstrating the formation of urethane linkages in all the samples. The -NCO absorption band centred at 2270 cm^{-1} was less intense compared to the foams produced using lignins without modification, this means that the -OH groups of liquefied lignin were easily available for the reaction with isocyanate after the hydroxypropilation process.

The band centred around 1700 cm^{-1} for polyurethanes based on PPG triol split into two branched peaks, indicating the presence of hydrogen bonded urethane carbonyl groups (Yu et al., 1999). The reaction between liquefied lignin and PPG triol -OH groups and diisocyanate -NCO groups was related to the disappearance of the broad absorption near 3418 cm^{-1}, due to -OH axial stretching vibration, and the appearance of a narrow absorption in 3344 cm-1, related to the -NH axial stretching vibration.

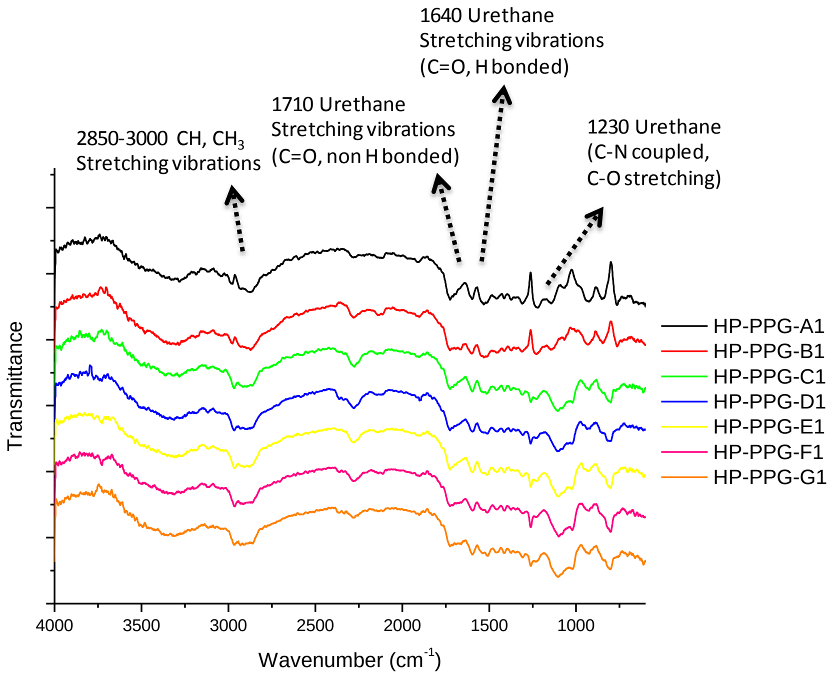


Figure 4-31 General FT-IR spectra for all the samples produced with hydroxypropylated Protobind 1000 and PPG triol as chain extender.

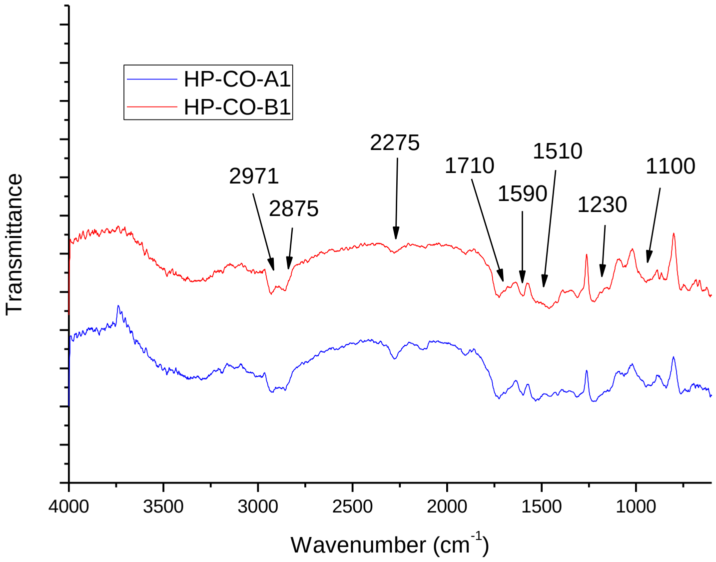
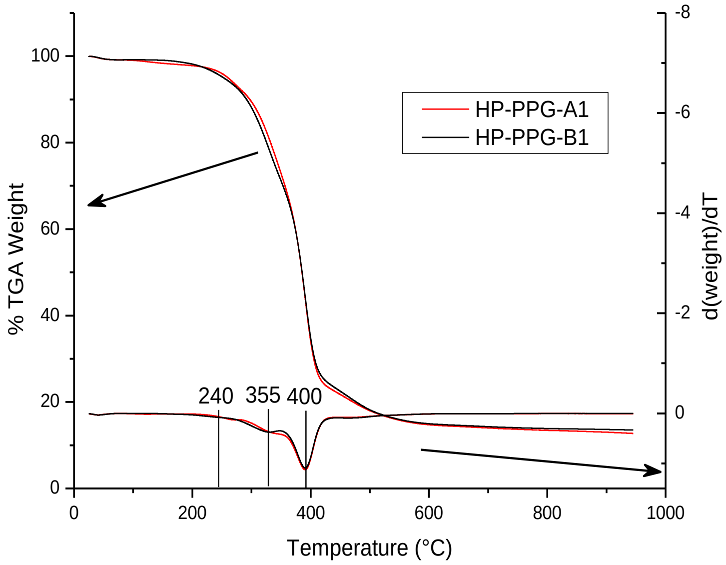


Figure 4-32 General FT-IR spectra for all the samples produced with hydroxypropylated Protobind 1000 and castor oil triol as chain extender.

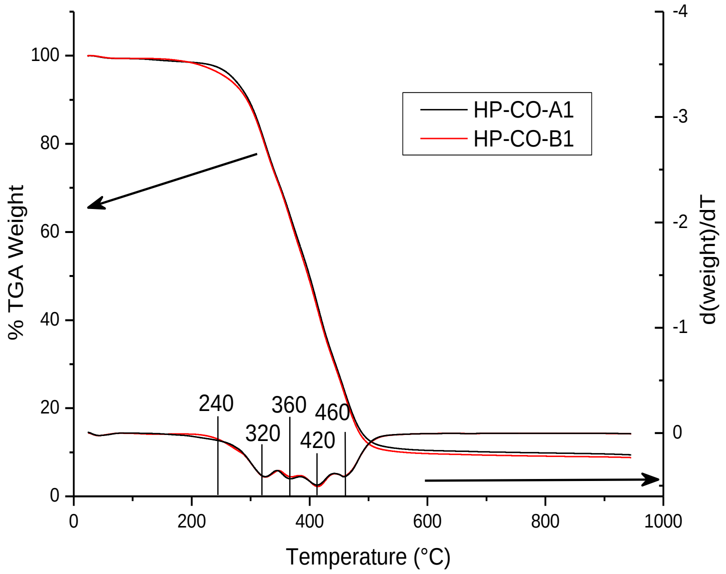
Also, for polyurethanes based on castor oil and liquefied lignin (Figure 4-32) a shoulder appeared for the band centred at 1710 cm^{-1} indicating some hydrogen bonded urethane carbonyl. In case of the polyurethane based on castor oil the intensity of the absorption band at 3300 cm^{-1} was smaller. This was due to a steric hindrance effect caused by the large amount of dangling chains generated by the usage of castor oil, which blocked the formation of hydrogen bonds (Narine et al., 2007b). The -CN axial stretching vibration in 1530 and 1230 cm^{-1} also is a typical polyurethane absorption band.

4.7.3. Thermogravimetric analysis (TGA)

Dynamic TGA curves in nitrogen for hydroxypropylated Protobind 1000, PPG triol and castor oil are shown in Figure 4-33. The thermal degradation of polyurethanes occurred as a result of a multitude of physical and chemical phenomena and it was not dominated by a single process. The stability of polyurethanes was related to the hard segment nature, soft segment and chain extender structures. The polyurethanes with PPG triol as chain extender showed two step degradation. Derivative TGA curves of the same polymers revealed actually two main degradation processes. The first step was associated with the first 20% of the weight loss at the temperature of 350 °C, and the second with the 80% remaining at the temperature of 400 °C. The shapes of the weight loss curves of all polyurethanes are almost identical, and overall differences in thermal stability appeared to be small, suggesting that degradation started at the urethane bonds. Urethanes were known to be relatively thermally unstable materials. Decomposition of the urethane bonds starts at about 150-200 °C and the main degradation product is carbon dioxide. For the samples with castor oil as chain extender the degradation started at 240 °C and several degradation step could be seen, related to the structure of the polyol and the presence of dangling chains.



(a)



(b)

Figure 4-33 TGA curves for free rise samples produced with hydroxypropylated Protobind 1000 and (a) PPG triol (b) castor oil as chain extender.

4.7.4. Differential scanning calorimetry (DSC)

The DSC curves were obtained in a second scan (Figure 4-34 and 4-35) and showed slight changes in T_g observed for polyurethanes with lignin addiction, compared to the reference samples. For the samples with PPG triol the T_g of the soft segment can be used as an indicator of the relative purity of the soft domain. In this case T_g did not showed great variations with lignin addiction respect to the reference sample and this denoted that a relative small amount of hard segment was mixed in the soft domains. No melting endotherm appeared in the first or second scans for any polyurethane based on lignin, which indicated the absence of cristallinity in these materials. T_g under room temperature referred to the soft segments present in polyurethanes and were attributed to PPG triol. Other transitions above room temperature could be related to the hard segments into which the lignin was inserted. In Figure 4-34 were reported the DSC traces for samples with hydroxypropylated Protobind 1000 and castor oil as chain extender, the curves exhibited a broadening of the T_g with a noticeable shift with higher temperature suggesting a greater phase mixing. In the traces is it possible to find shoulders at ~150 °C which are associated with the phase mixed hard segment.

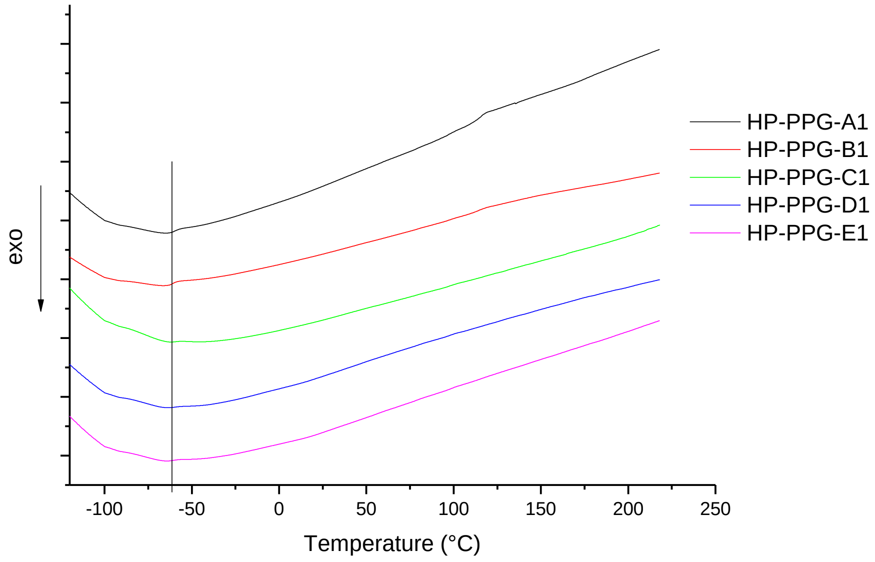


Figure 4-34 DSC traces of samples with hydroxypropylated Protobind 1000 and PPG triol as chain extender. The curves were shifted vertically to avoid overlapping of curves.

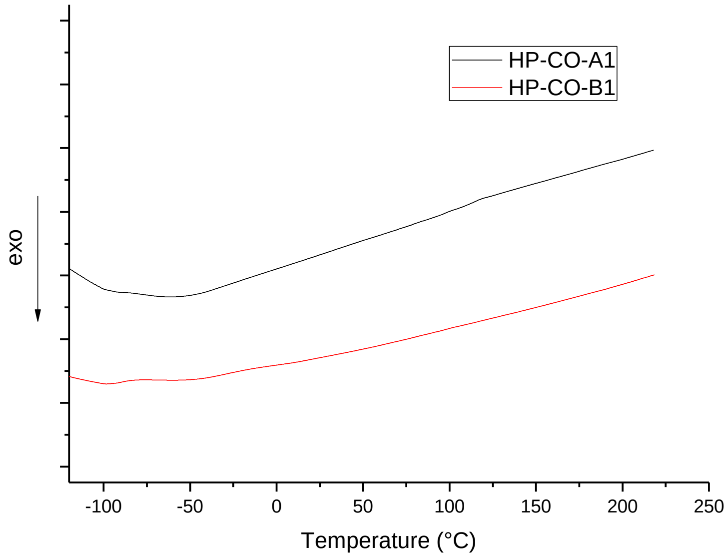
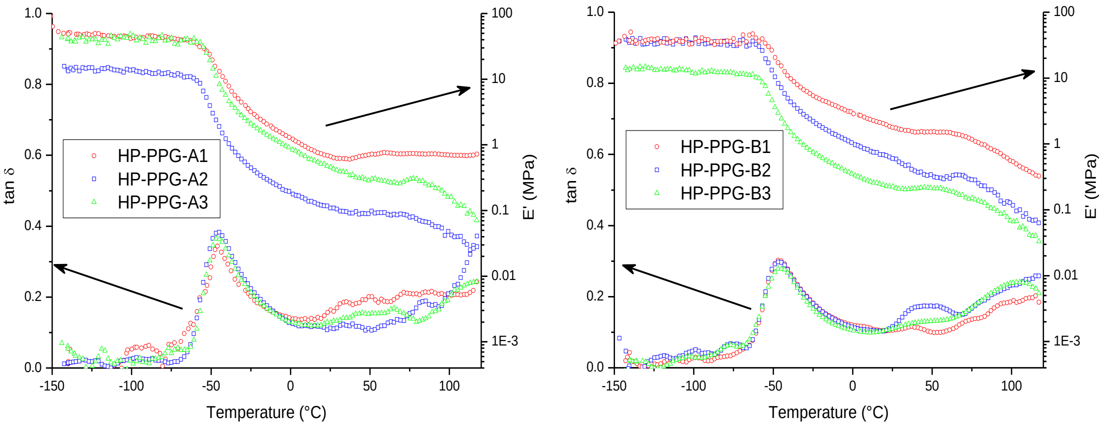


Figure 4-35 DSC traces of samples with hydroxypropylated Protobind 1000 and castor oil as chain extender. The curves were shifted vertically to avoid overlapping of curves.

4.7.5. Dynamic mechanical thermal analysis (DMTA)

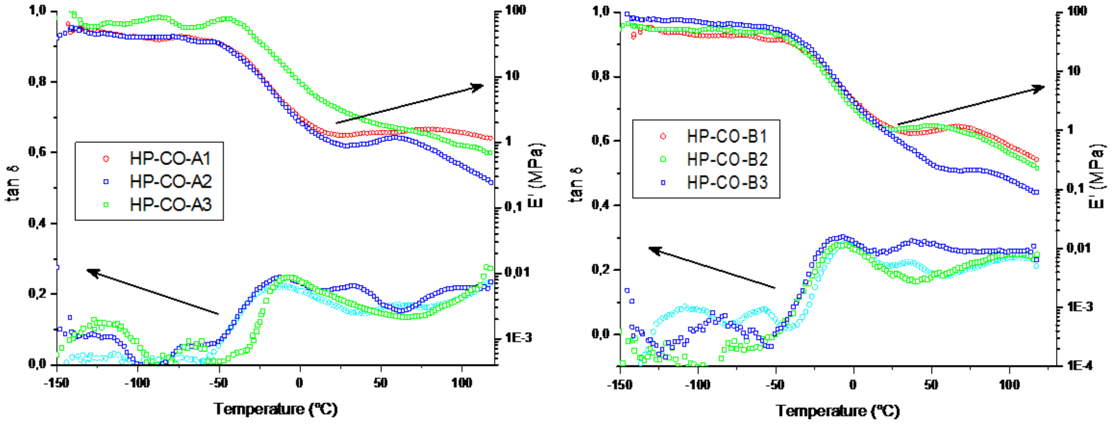
The materials produced were found to have some similar physical properties as well as some important differences. DMTA analysis provided initial insight into the several features of these series with PPG triol as chain extender (Figure 4-36). At temperature below -60 °C, all the samples behaved like a glassy solids with storage modulus values in excess of 50 MPa. As the samples were heated, the soft segment phase of each went through a glass transition at ca. -50 °C. Accordingly E′ distinctly decreased as the sample passed through T_g. Each sample maintained approximately a constant value until it softened beyond the sensitivity of the DMTA at temperatures in the range of 130 °C. Thus, the service window for these materials, as defined by the E′ plateau between the soft segment T_g and the hard segment softening point, is quite broad (-20 °C to 130 °C). The relatively high modulus of the material in this region is one indication of a microphase separated structure. The upper temperature limit of the plateau is attributed in part to the bidentate hydrogen bonding between urea linkages on adjacent hard segment.



(a) (b)

Figure 4-36 DMTA results of samples with hydroxypropylated Protobind 1000 and PPG triol as chain extender with different degree of expansion. (a) samples with 6.7% of lignin and standard catalysts, (b) samples with 6.7% of lignin and NE catalysts.

A low temperature process was observed around -100 °C: its magnitude increased for the samples with castor oil as chain extender, probably was related to the segmental motion of the dangling chains. This transition was associated with the segmental relaxation of a second (mixed) soft phase (Hernandez et al., 2008) due to the increased compatibility with hydroxypropylated lignin and castor oil (Figure 4-37). A second process was observed at higher temperature, around 0 °C for the samples with castor oil. This process broadened and decreased slightly in magnitude in the case of castor oil. The degree of expansion did not influence the height of the peaks. Compared to the samples with unmodified Protobind this DMTA traces showed higher number of secondary processes probably related to the increased compatibility between modified lignin and chain extenders, especially castor oil, and motion effects of the dangling chains.



(a) (b)

Figure 4-37 DMTA results of samples with hydroxypropylated Protobind 1000 and castor oil as chain extender with different degree of expansion. (a) samples with 6.7% of lignin and standard catalysts, (b) samples with 6.7% of lignin and NE catalysts.

A higher T_g value was an indication of the increase in chain connectivity. It raised the stiffness of the matrix and thus reduced the loss modulus. This was observable by the tan δ curves where the ratio of the loss modulus to the storage modulus was shown. The polyurethane samples experienced a general trend where tan δ peak intensity decreased as the crosslinking density and the amount of lignin increased.

4.7.6. Density

Tab. 4-22 showed the density of the samples prepared with hydroxypropylated Protobind 1000 and chain extenders. In the samples with PPG triol the density decreased as the amount of lignin was increased and samples with standard catalysts showed slightly lower density than the samples with NE catalysts. Samples with castor oil as chain extender showed higher density probably due to a less regular structure. Series 1 was produced in free rise expansion, the other series were controlled rise expansion.

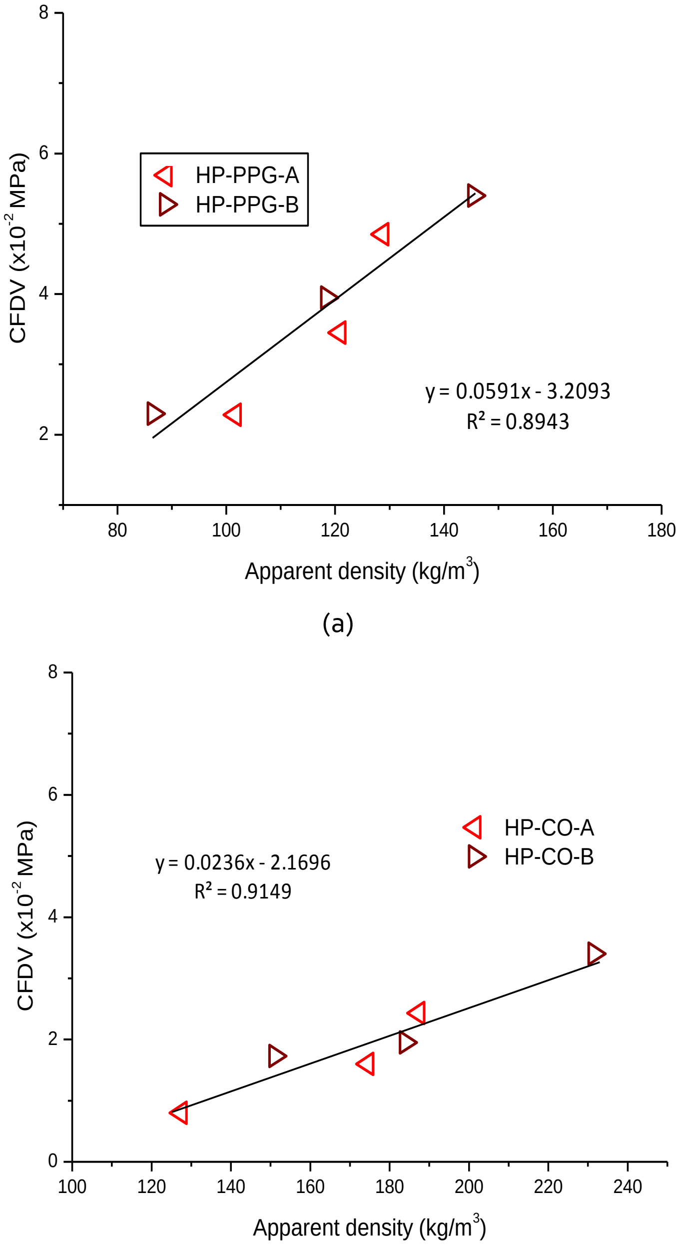
Tab. 4-22 Density of foams prepared with hydroxypropylated Protobind 1000.

Sample	**Apparent density (Kg/m^3)**		
	1	**2**	**3**
HP-PPG-A	101.6	120.8	128.7
HP-PPG-B	86.6	118.5	145.5
HP-CO-A	127.4	174.4	187.3
HP-CO-B	151.1	184	231.6
HP-PPG-C	72.1	92.1	107.8
HP-PPG-D	76.6	94.9	105.4
HP-PPG-E	78.8	92.1	94.6
HP-PPG-F	77.5	98	112.8
HP-PPG-G	85.9	91.6	101

4.7.7. Compression force deflection test

Since it has been shown that the physical properties vary depending on the loading direction, all foams were loaded parallel to the rise direction for consistency. In the case of hydroxypropylated Protobind 1000 it was possible to find a trend for the samples produced with castor oil, this did not happened for the samples with unmodified lignins, probably the increased compatibility between modified lignin and castor oil contributed to create a more homogeneous structure in which the compression force deflection value could be directly related to the apparent density of the materials as already happened for samples with unmodified lignins and PPG triol as chain extender.

Compression force deflection values are in a range from 0.02 to 0.07 MPa which is similar to the commercially available polyurethane foams derived from petroleum. All the samples, with PPG triol as chain extender, after the preflex load and recover time of 6 min showed a small decrease in thickness, around 2% of initial thickness. These results obtained by mechanical measurements indicate that the polyurethane foams derived from lignin can be used for practical purposes.



(a)

(b)

Figure 4-38 Compression force deflection value for samples with hydroxypropylated Protobind 1000 and glycerol/PEG400 ratio 1/0.4/2. (a) samples with PPG triol as chain extender, (b) samples with castor oil as chain extender.

It is known that the strength of open cell foam is greater than that of a closed cell material which had his wall fractured, because the broken walls are unable to contribute any reinforcement to support stress when the network is under load. The compressive strength of PPG triol foams were the highest mainly because it had the lowest closed cell content and a regular structure. The lower compressive strength of castor oil foams was also the results of plasticizing effect of the dangling chains combined with a smaller amount of hard segment cell size and cell wall thickness. The plasticizer weakened the network under load and lowered the compressive strength. It is clear that the variation of the chain extender structure and the crosslinking nature affected the compressive properties of the crosslinked polyurethane materials. In segmented polyurethanes, the mechanical properties were generally accredited to a pseudo-crosslinking effect resulting from the hard segment aggregation. The hard segment domain generally exhibits a different degree of ordered structure, which was considered to be able to reinforce the hard segment domain added a crosslinking effect deriving from the usage of PPG triol of castor oil.

Higher lignin content lowered the apparent density but the strength of the foams remained almost the same of the sample with lower amount of lignin (Figure 4-38). The highest recovery after the cycle of loading and unloading was shown by the samples with PPG triol as chain extender and lower amount of lignin, this may be due to the fine structure nature of the foam cells of these samples.

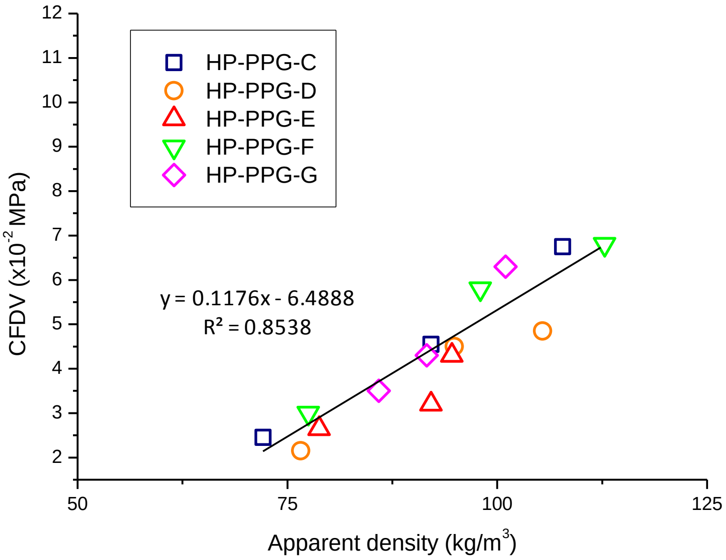
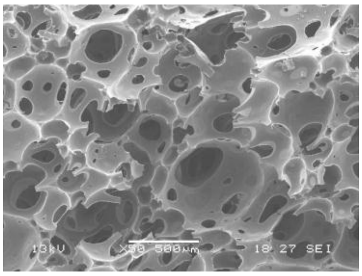
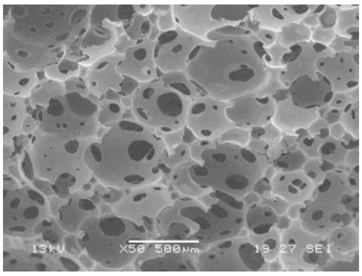
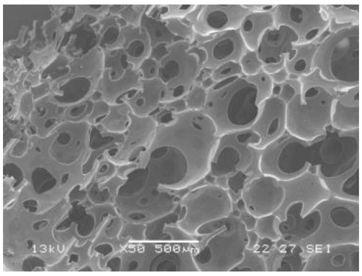
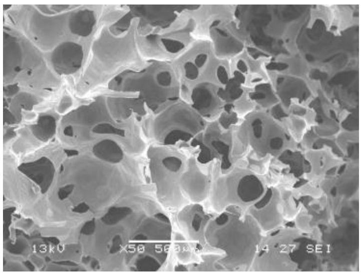
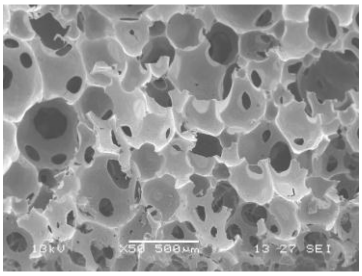
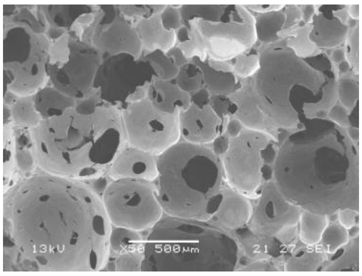


Figure 4-39 Compression force deflection value for samples with hydroxypropylated Protobind 1000, PPG triol as chain extender and glycerol/PEG400 ratio 1/0.2/1.

4.7.8. Morphology (SEM)

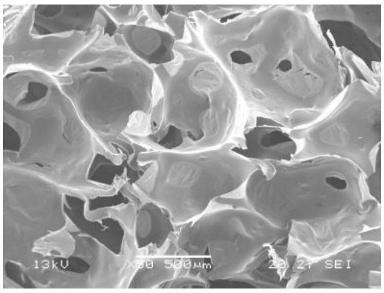
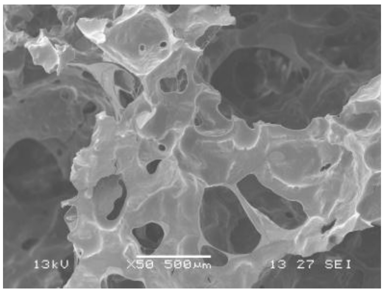
Tab. 4-23 showed the SEM images of hydroxypropylated Protobind 1000 and PPG triol based polyurethanes with different degree of expansion. All PPG triol and liquefied lignin foams exhibit anisotropic cellular structures, as expected, where the cells appear more elongated along the blow direction. This anisotropy in cellular structure and its importance with respect to mechanical behavior has been reported in previous studies (Moreland et al., 1994a,b). Results showed that though the cell size and struts were similar for all the foams produced with PPG triol, the number of closed cells was found to be slightly greater in series B with NE catalysts, which may be attributed to the slowest rate of reaction and consequently CO_2 production found with the NE catalyst that can interfere with the opening of the cells. It can be observed from these images that the size of the cells, cell size distribution, and strut thickness were comparable for all the foams investigated. It was noted from Tab. 4-23 that foam with PPG triol as chain extender possessed a fair number of open cells.

Tab. 4-23 SEM images of samples with hydroxypropylated Protobind 1000 and PPG triol as chain extender.

HP-PPG-A1	**HP-PPG-A2**	**HP-PPG-A3**
		
HP-PPG-B1	**HP-PPG-B2**	**HP-PPG-B3**
		

Samples with hydroxypropylated Protobind 1000 and castor oil are shown in Tab. 4-24, even if the cells were not regular as the samples with PPG triol, the structure was more regular compared to the other samples made with castor oil and unmodified lignins, the cells are less coarse even if a higher amount of closed cells could be seen. The cell morphology was found to be in general disordered consisting of a variety of cell shapes. It was also shown by John and co-workers (John et al., 2002) that samples containing more synthetic polyol (with primary OH groups) had more organized cell shapes than the foam samples with vegetable polyols.

Tab. 4-24 SEM images of samples with hydroxypropylated Protobind 1000 and castor oil as chain extender.

HP-CO-A1	**HP-CO-B1**
	

4.8. Economic aspects

As already seen, based on different formulations, polyurethanes cover a wide range of stiffness, hardness and density. The application can be categorized in the three broad aspects :

- Flexible foams that are widely used in automotive seating, sofas and mattresses to provide confortablness. It is by far the biggest application of polyurethanes.
- Rigid foams that are used for insulation and various other applications in construction and refrigeration.
- Coatings, adhesives, sealants and elastomers (CASE market).

With regard to current application area for polyurethanes, it should be noted that by combining different raw materials such as polyols, isocyanate and additives, it is possible to obtain numerous varieties of foam products, as well as various of other materials. The substitution of the petrochemical-sourced raw material, in a polyurethane, with bio-based product has to meet all processability and in-use requirements. As an example of how public perception can influence the substitution and market acceptance of the product, consumers often associate bio-based with biodegradable. This is generally not the case of polyurethanes, although some biomass-sourced components (plant-derived polyols containing carboxyl groups) result in more easily biodegraded products. This may lead to the false impression that a polyurethane with a bio-based component can be less durable than a pure petrochemical-derived equivalent.

Basically, flexible polyurethane foam is made with two main ingredients: polyols and isocyanates., usually a two-thirds polyol and one-third isocyanates is a good rule when discussing the overall polyurethane flexible foam recipe. Historically these components chemicals were made form petroleum-based materials. In this work we started by replacing up to 6% of petroleum-based polyol with our lignin-based formulations. Then we worked to increase the amount of lignin in the foam formulation. reaching a formulation with between 13% and 45% of bio-based foam, taking into account that the final product has to present always a high degree of flexibility.

A rough estimation of the amount of lignin that can be used for this products can be made; if the product contains 13% lignin on a weight/weight basis and the total production of flexible polyurethane amounts to about 1,000 tonnes per year, which is equivalent to a yearly consumption of 130 tonnes of lignin.

Understanding that, isocyanates and other synthetic ingredients will make up at least one-third of all flexible polyurethane foam regardless of how much bio-based material is used in the polyol. Yet, every step taken to replace petroleum-based materials with new carbon renewable materials is a step forward in this world of finite petroleum resources. It is important to focus on the positive aspects to make advancements increasing the ratio of bio-based materials used in the polyols.

Today, the market for bio-based polyurethanes is small and premium applications are being targeted. In the future, there will be the potential for bio-based flexible foam product to enter other markets including agriculture, transportation and housewares As new applications for polyurethanes are still emerging with the substitution of other materials and performance improvements are being achieved in automotive seating, furniture, and footwear it may be concluded that there is also some potential for bio-based polyurethane to substitute other materials (Sherman, 2007).

The market price for petrochemical PURs is in the range of € 2.60 – 2.90 per kg for ester-types and € 3.65 - €3.85 for ether types (Plasticnews, 2011). At the moment lignin is mainly used to .produce process heat by combustion or in animal feeds although around 1 million tonnes of lignin polymers are traded as chemicals. It is normal to expect that lignin bio-based polyurethane product could be commercially viable, even at a higher price than its petrochemical-based equivalent. However, this is actually possible in niche markets where environmental or other credentials of the bio-based product justify the price differential. It is expected that in these markets, the price of bio-based polyurethanes could be higher than conventional equivalents due both to the smaller scale of production and the high cost associated with using the renewable feedstock. Sales will thus be dependent on proactive consumer choice for the bio-based product.

5. Conclusions

In this study was investigated the usage of lignin as a potential partial replacement to petroleum polyols in the production of flexible foam polyurethanes. In an early attempt two different kind of lignin were employed, one from kraft and one from soda process. Subsequently the soda lignin was subjected to an hydroxypropylation process to make the OH group easily accessible for the reaction with isocyanate. All the lignins were liquefied using an innovative microwave process which is less time and energy consuming compared to the traditional liquefaction process. Through this work liquefied lignin, with suitable chain extenders, was shown to be potential replacement to petroleum polyols for the production of flexible polyurethane foams. To increase the content of liquefied lignin in foam formulation, and ultimately achieving the goal of making still flexible foam with liquefied lignin, lowering the T_g of polyol phase was determined to be the most important issue. In the attempt to produce flexible foams two kind of chain extender were used in combination with liquefied lignin: polypropilenglycol triol and castor oil. The samples were produced with the "one shot" technique and the only blowing agent used was water. All samples were produced with a ratio NCO/OH less than one, because it is well known that it significantly reduces the degree of crosslinking, resulting in higher flexibility of the material. Samples were produced in free and controlled rise expansion. Characterization results indicated that samples with liquefied lignin and PPG triol had a low T_g soft phase clearly separated from the hard segment phase, samples with liquefied lignin and castor oil had phase mixed morphology as shown from the FT-IR, DSC and DMTA analysis. The amount of lignin that was possible to introduce in the network varied from 6 to 13% and considering the renewable origin of the castor oil it is possible to state that in these samples the renewable content is more than 45%.

The kind of lignin did not influenced greatly the structure and properties of the produced foams, hydroxypropylated lignin was easily dissolved in the liquefying agents and the characterizations of the foams produced with this material showed an intense phase mixing between liquefied lignin and chain extenders (in particular with castor oil), higher than the unmodified lignins as can be seen from the FT-IR, DSC and DMTA analysis.

The increase in amount of lignin produced an increase in hard segment content that was accompanied by a substantial decrease in the loss factor (tan δ) intensity as can be seen from DMTA analysis.

For all the kind of liquefied lignins, PPG triol was proven to be an effective chain extender, samples are homogeneous with good cellular structure, and high open cell volume, the density of these samples ranged between 50-150 kg/m^3 a value that is comparable with industrial synthetic foams. The general cellular structure of the foams was evaluated using SEM, samples with liquefied lignins and PPG triol showed a regular structure with high amount of open cells that led to a compression force deflection values comparable to industrial foams and high recovery of the samples after the compression test cycle.

Samples with liquefied lignin and castor oil had phase mixed morphology and high T_g which was believed to be the factor giving rise to rigidity in those kind of foams, these samples showed a density between 160-230 kg/m^3 that was comparable with foams made with renewable resources, like palm or soy oil. From SEM analysis these samples showed a less regular structure with coarse cells and thicker cell walls, the structure of the foams directly affected the compression force deflection values that were lower than samples produced with liquefied lignin and PPG triol. Also lowest compressive strength of liquefied lignin and castor oil foams was the results of plasticizing effect of the dangling chains combined with a smaller amount of hard segment. The plasticizer weakened the network under load and lowered the compressive strength. An improvement in the structure of samples produced with castor oil was found when hydroxypropylated lignin was used, an increased compatibility between modified lignin and castor oil contributed to create a more homogeneous structure as can be seen from micrographs of these samples.

Calorimetric and thermogravimetric analyses proved that liquefied lignin participated in the chemical reaction, influencing the glass transitions and the thermal stability of the materials. The thermal decomposition mechanism followed the same behaviour for all polyurethanes. Because of the segmented structure observed for the synthesized polyurethanes, the degradation process occurred mainly in two or three events which consisted in the hard segment or soft segment degradation. It is important to notice that all polyurethanes produced showed a thermal stability comparable to that of synthesized from petroleum polyols.

The properties of these foams could be modulated, in a future work, by the individuation of more efficient chain extenders, which introducing flexible chains in the macromolecular structure, can reduce the glass transition temperature of the materials and generate foams with higher flexibility. It is demonstrated that controlling the phase mixing will be a key to improve the material performances in various fields of application. Vegetable oils offers a variety of new structures in polyols, resulting in polyurethanes with new properties suitable for a range of applications, then it is possible to guess an increase in the use of renewable resources in the polyurethane field.

It is normal to expect that lignin bio-based polyurethane product could be commercially viable, even at a higher price than its petrochemical-based equivalent. However, this will be actually possible in niche markets where environmental or other credentials of the bio-based product justify the price differential.

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