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Lise Maisonneuve, Guillaume Chollet, Etienne Grau, Henri Cramail. Vegetable oils: a source of polyols for polyurethane materials. OCL Oilseeds and fats crops and lipids, 2016, 23 (5), D508 (10 p.). 10.1051/ocl/2016031 . hal-01373161

HAL Id: hal-01373161

<https://hal.science/hal-01373161>

Submitted on 27 Nov 2019

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Vegetable Oils: a source of polyols for polyurethane materials

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Résumé

Cet article fait un état de l'art de la synthèse de polyuréthanes issus des huiles végétales par la voie alcool/isocyanate. De nombreux efforts ont été réalisés pour remplacer les ressources pétrolières. Parmi les ressources renouvelables, les huiles végétales représentent de nombreux avantages liés à leur disponibilité et aux nombreuses possibilités de modification chimique qu'elles offrent. Dans cet article, les principales huiles, leur composition, et les principaux précurseurs commercialisés issus des huiles végétales sont d'abord présentés. Concernant les PUs issus des huiles végétales, les travaux portent d'une part sur des réseaux tridimensionnels directement à partir des triglycérides et, d'autre part, sur des PUs thermoplastiques à partir des acides gras et de leurs dérivés. Les méthodes d'introduction de fonctions alcool et isocyanate sur les triglycérides et acides gras sont présentées puis la synthèse de PUs thermoplastiques par la voie alcool/isocyanate est discutée de façon détaillée.

Abstract

This manuscript is dedicated to the literature on vegetable oil-based polyurethanes *via* the isocyanate/alcohol route. A lot of efforts have been made to replace petroleum-based resources. Among renewable resources, vegetable oils present various advantages going from their availability to the large range of possible chemical modifications they permit. Firstly, the vegetable oil chemical composition and the main commercially available vegetable oil precursors are exposed. Concerning vegetable oils-based polyurethanes, research groups first focused on cross-linked systems directly from triglycerides then on thermoplastic ones from fatty acids or fatty acid methyl esters. This manuscript focuses on thermoplastic PUs and underlines the literature about the introduction of hydroxyl groups and isocyanate functions onto triglycerides and fatty acid derivatives. Besides, in a view to the isocyanate/alcohol approach, vegetable oil-based thermoplastic PUs and corresponding diols and diisocyanates are described in details.

Mots clés : polyuréthanes, bio-sourcé, huiles végétales, acide gras, diol, di-isocyanate.

Keywords: polyurethanes, bio-based, vegetable oils, fatty acid, diol, di-isocyanate.

Introduction

Various renewable resources (cellulose, hemicellulose, starch, lignin, natural oils, chitosan, etc.) have gathered a lot of attention as potential substitute for fossil resources in the polymer field. Three ways have been studied to obtain renewable polymers. The first and second are respectively the fermentation of the biomass and the chemical degradation and transformation of natural polymers. The third route, which is followed in this manuscript, consists in using the biomass obtained from Nature with or without chemical transformation.

Why choosing vegetable oils as renewable resources? Vegetable oils are among the most promising renewable resources thanks to various advantages. Indeed, vegetable oils present different chemical structures and various reactive sites that can be straightforward chemically modified into a large range of tailor-made monomers with variable functionalities. Moreover, the latter are available and annually renewable, regenerated by photosynthesis year after year. The inherent biodegradability of vegetable oils is also an attractive characteristic in the growing environmental concerns context.

One question, which returns continuously, is the competition with the feed and food industry. The scientist's opinions are split on this question. On one hand, some support that conventional crops is only a part of the solution and underline the serious competition between the production of food and feed, with the bio-based products (chemicals and polymers) and the transportation biofuels (bioethanol and biodiesel). They recommend the use of agricultural wastes and the development of both new crops grown on marginal land, and fast-growing vegetative biomass such as grass, wood, etc. [Gallezot 2007a] On the other hand, it has been shown that biomass can be produced in a sufficient volume for industrial utilization without compromising the food supply for the increasing global population. [Schäfer 2011] Besides, the needs of raw materials for bio-based products will always be very modest compared to the food and feed requirements. [Gandini 2008] Indeed, the bio-based and biodegradable plastics rely on only 0.006% of the global agricultural area of 5 billion ha in 2011, and is predicted to be 0.022% in 2016.[Bioplastics] To replace fossil resources in polymer science, different strategies need to be studied at the same time such as the use of wastes (agricultural and others), the use of inedible resources, the improvement of biomass growing and the use of various renewable resources (vegetable oils but also others) to satisfy the requirement of sustainability and to get the expected performances.

Another key issue up to date is the high cost involved in processing renewable resources into chemicals compared with their synthesis from fossil resources. The difference is that processes from fossil resources have been continuously improved during more than one century resulting in a very high degree of technical and cost optimization, whereas methods to obtain chemicals from biomass are comparatively in their infancy. Therefore, wide research

and development efforts in biotechnology, chemistry and engineering are required to reduce processing cost by valorizing co-products and by-products and optimizing the inputs (feedstock supply, water management) and outputs (energy and product recovery, treatment of waste).[Gallezot 2007a] The life cycle analysis of the synthesized product is also a crucial tool to take into account in order to validate whether the use of biomass in such or such application is relevant or not.

In the last decades, numerous studies and reviews have emerged using fats and oils for the polymer field. [Schneider 2000, Meier 2011, Schubert 2007, Metzger 2009, Larock 2010, Cramail 2013a, Mecking 2016]

Vegetable oils: general data

The main constituents of vegetable oils are triglycerides, which are the esterification product of glycerol with three fatty acids. The fatty acids account for 95% of the total weight of triglycerides. Each vegetable oil contains different triglycerides with various fatty acid chains. Fatty acids and fatty acid methyl esters can be recovered and purified from vegetable oil respectively by saponification and transesterification with methanol. [Vargas 1998] The common fatty acids that can be obtained vary from 14 to 20 carbons in length, with 0 to 3 double bonds per fatty acid. Soybean and sunflower oils, for instance, consist of largely linoleic acid (C18:2) and oleic acid (C18:1). The fatty acid structure and the compositions of few common oils are given in Figure 1.

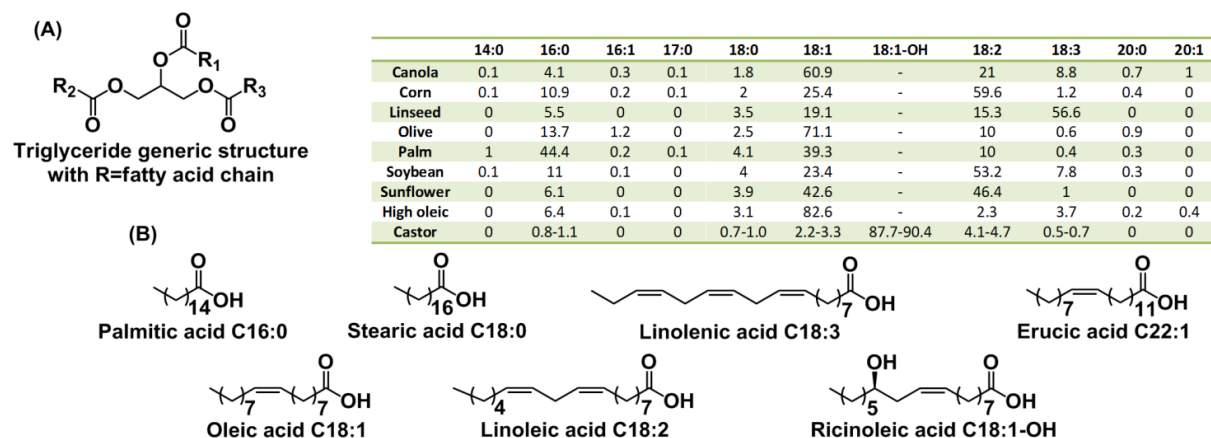


Figure 1- (A) General triglyceride structure and the proportion of the different fatty acid chains in vegetable oils.

(B) Common fatty acids found in vegetable oils. (In C_x:_y, the x=chain carbon atoms and y=number of C-C double bonds. [Meier 2011, Meier 2010]

The fatty acid composition in vegetable oils varies depending on the plant, the crop, the season, the growing conditions, the year and the location of crops. [Cádiz 2013] The annual world supply and distribution of the major vegetable oils in 2015/16 amounted to 179 Million tons (Mt). On the Figure 2, the variation of the world supply and distribution of the major vegetable oils, as well as the compared proportion of each vegetable oil are represented.

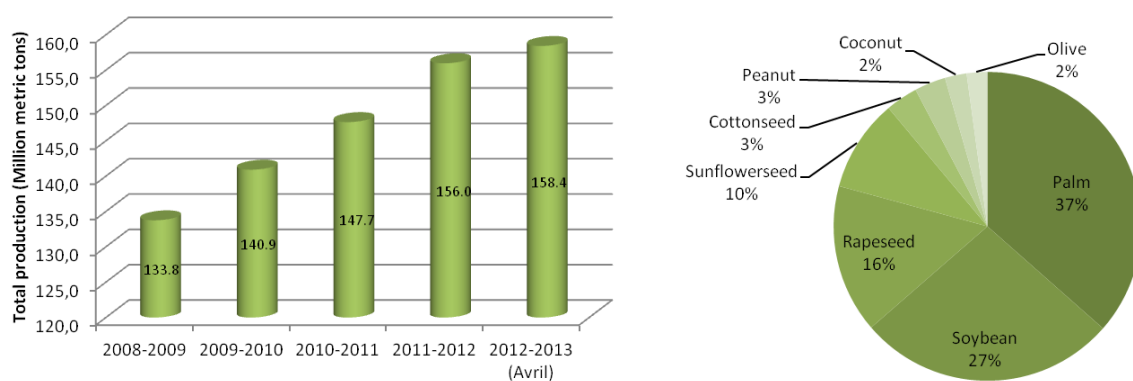


Figure 2- World supply and distribution of the major vegetable oils and their proportions in 2011-2012. [FAS]

The Table 1 summarizes the composition of the average production of the fourth more produced vegetable oil in European country and in France.

Table 1 Fatty acid production in Mt per year of the four most produced vegetable oil

Oils	Production in Europe (Mt) ^{a, b}
Sunflower	2.7 ^d (0.5) ^c
Rapeseed	9 (1.8) ^c
Soybean	2.3 (0.1) ^c
Linseed	0.2 (0.02) ^c

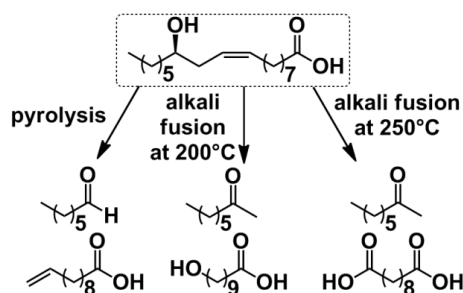
^a Average over the 2010-2014 period, ^b FEDIOL source ^c Production in France within the same period, ^d Including Very High Oleic Sunflower Oil

Reactive sites and common derivatives from vegetable oils

Two main approaches are followed to synthesize polymers from vegetable oils. The first way is the direct use of triglycerides taking advantages of the naturally occurring functional groups or after chemical modifications, to end up with cross-linked materials. The second route is the use of purified fatty acids or fatty acid methyl esters to design well-defined thermoplastic polymers and to better control the relationship between the chemical structures of the monomers and the final polymer properties. The reactive sites in triglycerides and fatty acids available for chemical modifications are the carbon-carbon double bonds, the allylic carbons, the ester groups, the alpha carbons to the ester group and, in some cases, the hydroxyl and epoxide moieties.

Castor oil is a unique vegetable oil because it is non-edible, owing to the presence of ricine in it, which is a toxic protein. Moreover, it contains up to 90% of ricinoleic acid, a mono-unsaturated fatty acid with 18 carbons bearing, natively, a hydroxyl function. Other

advantages that can be noticed is that the plant itself requires relatively less fertilizers, pesticides, water and maintenance than most other cultivated crops.[CastorOil] Those properties make castor oil a veritable interesting renewable precursor for chemical and polymer syntheses. Castor oil is extracted from the seeds of the castor bean plant *Ricinus communis* (*Euphorbiaceae*), which grows in tropical and subtropical areas.[Stevens 2009] Several platform molecules, widely used in polymer industry (giving access to PA-11 for example), can be derived from castor oil: the methyl 10-undecenoate [Stevens 2009, Ogunniyi 2006, Vasishtha 1989] and the sebacic acid [Meier 2010, Demirel 2008], as can be illustrated in Scheme 1.



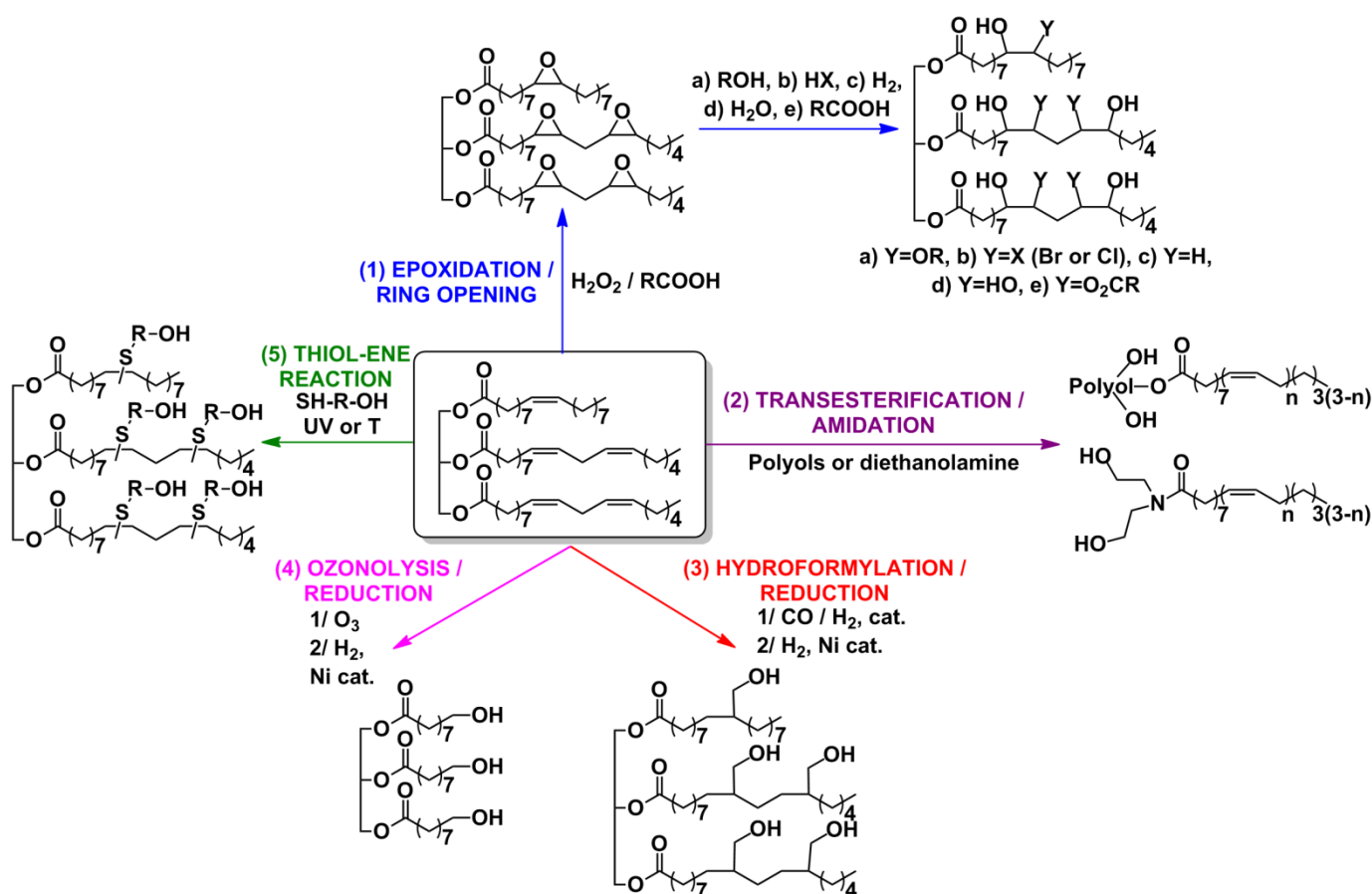
Scheme 1- Castor oil as a platform precursor. [Meier 2010]

In addition to fatty acids, glycerol is also a valuable biomolecule; the main utilization of glycerol is the production of glycerol esters, used as emulsifiers, surfactants and lubricants. Besides, among the various chemicals that can be obtained from glycerol, some of them, which are interesting for PUs preparation, can be listed: the 1,3-propanediol and the glycerol carbonate. [Gallezot 2007b, Morales 2009] In terms of added value provided, glycerol and glycerol carbonate take part of the top 30 chemicals for the chemical industry.[Peterson 2004]

Derivatization of fatty acid derivatives to thermoplastic PUs *via* the alcohol/isocyanate route

Industrially a broad range of polyols is available whereas only few diisocyanates are commonly prepared from petrochemical resources. This wide range of polyols brings PUs a plethora of different properties, making them suitable in many fields of applications. [Dormish 2013] A lot of efforts have been done to develop alternatives from vegetable oils. The synthesis of polyols and corresponding PU networks from vegetable oils has been already well reviewed in the literature. [Meier 2011, Cramail 2013a, Boutevin 2012a, Larock 2011] Castor oil is an exception in vegetable oils with its naturally occurring hydroxyl groups and thus was studied in priority in PU synthesis. [Meier 2010, Ogunniyi 2006] Different methods (Scheme 2) have been followed such as (1) epoxidation / ring opening of the epoxide, (2) transesterification or amidation, (3) hydroformylation / reduction, (4) ozonolysis / reduction

and (5) thiol-ene addition. Nowadays, the commercialization of vegetable oils-based polyols and corresponding PUs is growing.



Scheme 2- Commonly used strategies to introduce OH groups into triglycerides and thus prepare polyols. [Larock 2011, Mouloungui 2013]

Vegetable oil-based polyisocyanates have been studied to a much lesser extent compared to vegetable oil-based polyols. Two strategies have been followed to bring isocyanate groups onto the double bond of the triglycerides; they both use the very expensive silver isocyanate salt AgNCO , prepared from NaOCN , and AgNO_3 . The silver counter ion in AgNCO ensures that the isocyanate reacts on the nitrogen end, and not on the oxygen end of the group. [Küsefoğlu 2008, Küsefoğlu 2010]

A remarkable large series of papers and reviews investigated the functionalization of triglycerides to get interesting multifunctional PU precursors. The main problem encountered in such cases is the heterogeneity of the monomers due to the distribution of double bonds per triglyceride. This has a negative effect on the mechanical properties and the correlation between the final polymer properties and the monomer structures is more complicated. In light of this, the following part covers the advances made in the synthesis of vegetable oil-

based well-defined difunctional PU precursors, collecting the literature data of the different synthetic routes used.

Table 2- Raw material, trade names and major producers of vegetable oil-based polyols and PUs in 2009. [Patel 2009]

Bio-based raw material	Product type	Trade name	PU applications	Company	Capacity p.a.
Soybean oil	Polyol	BiOH TM	Flexible foams	Cargill	~10 kt ^c
	Polyol	Renuva TM	Flexible foams and CASE ^a	Dow	n/a
	Polyol	SoyOyl [®]	Flexible and rigid foams, PUR spray foam, elastomers	Urethane Soy System	23-34 kt
	Polyol PU	Agrol [®] Bio-based [®]	CASE, moulded foams	Bio-based Technologies	n/a
	PU	Baydur [®] SOVERMOL [®]	Rigid and flexible foams ^b	BASF	n/a
Castor oil	Polyol	Lupranol [®] BALANCE	Rigid foams /mattresses	BASF	n/a
	Polyol	POLYCIN [®]	Coating	Vertellus	n/a
	Polyol PU		Flexible and rigid foams	Mitsui Chemicals	8kt
Rapeseed oil	Polyol		Rigid foams / refrigerator insulation	IFS Chemicals	~ 1kt ^d
Sunflower oil	PU	RUBEX NAWARO [®]	Flexible foams / mattresses	Metzeler Schaum	n/a
Palm oil	Polyol	Edenor [®] , Emersol [®] , Emery [®]	Foams, coatings, adhesives	Emery Oleo-Chemicals	n/a
Vegetable oil	Polyol	RADIA [®]	Flexible and rigid foams	OLEON – Avril Group	n/a
	Polyol	PRIPLAST TM	Coatings, adhesives	CRODA	n/a

^a CASE: Coatings, Adhesives, Sealants and Elastomers; ^b For Bayer's flexible PU foams, SoyOyl polyols from Urethane Soy System are used; ^{c,d} Estimation; ^e Projected data for the next 2-4 years by the company.

Fatty acid-based diols

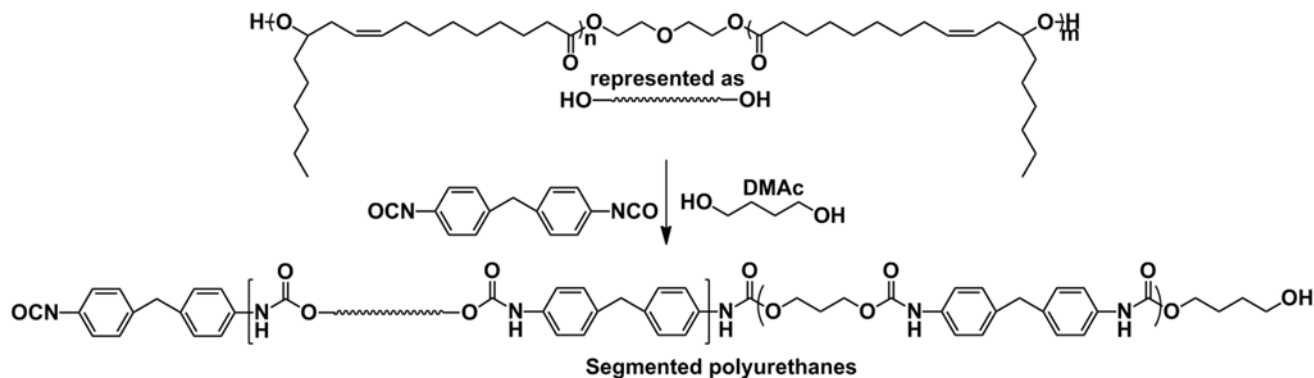
Diols containing ether and ester functions

Segmented thermoplastic elastomer PUs or TPUs are commonly used for their excellent properties, such as good transparency, tunable stiffness, good wear resistance, excellent biocompatibility, etc. These properties are obtained thanks to the alternating of soft and hard

segments in the structure of the polymer. Soft segments are usually flexible low glass transition polyether or polyester chains with molar masses between 1 and 4 kg.mol⁻¹, and can be easily obtained from fatty acid derivatives. Hard domains are usually crystalline with high melting points. For polyether diol obtained from vegetable oil, only one example of TPUs was reported from vegetable oil derivatives.[Metzger 2006] This polyether diol containing ester pendant groups was obtained by the acid-catalyzed ROP of epoxidized methyl oleate and partial reduction with lithium aluminum hydride (LiAlH₄). Polyols with various hydroxyl functionality degrees were obtained depending on the conversion of the reduction step and PUs were synthesized with methylene di-isocyanate (MDI). The TPU obtained with the polyether diol (f=2) presents a low glass transition temperature of -15°C and an interesting degradation temperature at 5wt% loss of 307°C.

Synthesis of polyester diols, diols containing ester and/or amide linkages, dimer diols, linear saturated or unsaturated diols and diols containing thio-ether linkages are widely reported using fatty acids or fatty acid methyl esters as starting materials. The synthesis of diols containing ester group have been much more widely explored due to the initial presence of ester or acid function in vegetable oil derivatives. Few research groups have prepared low Tg polyester diols from vegetable oil derivatives to use them in TPE-Us. The fatty acid-based polyester diols were synthesized either by transesterification of methyl ricinoleate with diethylene glycol as an initiator or by transesterification of diesters with diols in excess.

Petrovic and coll. have used a poly(ricinoleic acid) diol of 2580 g.mol⁻¹ as soft segment to prepare a series of TPE-Us by reacting MDI and 1,4-butanediol with various soft segment weight concentrations ranging from 40% to 70%.[Wilkes 2008] (Scheme 3) The TPE-Us obtained display a microphase separation and two glass transition temperatures at around -50°C and 100°C. Melting points in the range 170°C to 220°C were observed depending on the soft segment content. The mechanical and thermal features of these bio-based PUs suggest that they could be used in conventional TPE-Us applications. A co-continuous morphology with domains around 15 nm was obtained in the case of the TPE-Us with 50% of soft segment weight concentrations. However, in the sample of TPE-Us with 70% of soft segment weight concentrations, dispersed hard domains were observed in the soft matrix. The biodegradation of these TPUs has been investigated by respirometry.[Klamczynski 2010] These TPE-Us with poly(ricinoleic acid) as soft segments have been found to exhibit faster degradation rates than the corresponding petrochemical poly(ester urethane)s, even if this rate is relatively slow. The authors observed that TPE-Us with a co-continuous morphology demonstrated a slightly slower biodegradation than those with dispersed hard domains in the soft phase.



Scheme 3- Thermoplastic elastomer polyurethane prepared from poly(ricinoleic acid). [Wilkes 2008]

Using the same methodology, a hydroxytelechelic α,ω -OH polyester was prepared by transesterification of methyl 12-hydroxy stearate with 1,6-hexanediol catalyzed by titanium isopropoxide. [Petrovic 2010] This precursor of 1552 g.mol^{-1} was used in segmented PU with MDI and 1,4-butanediol with 50% and 70% of soft segment content. Glass transition temperatures of -40°C and 100°C were obtained for the soft segments and hard segments respectively. Besides, T_m of -18°C to -14°C and 175°C to 180°C were observed for the soft segments and hard segments respectively.

Polyester diols (pre-polymer) have been synthesized by transesterification of diesters with diols in excess. Using this strategy, Koning and coll. have prepared partially fatty acid-based aliphatic polyester diols from dimethyl sebacate using TBD as a catalyst.[Koning 2011] Moreover, Corcuera and coll. have used similar polyester diols from dimethyl sebacate with molar mass from 1320 g.mol^{-1} to 3500 g.mol^{-1} to prepare TPE-Us with HMDI and 1,3-propanediol as chain extender. The TPE-Us obtained by a two-step bulk polymerization without catalyst exhibited a molar mass in the range of 52.1 kg.mol^{-1} to $138.9 \text{ kg.mol}^{-1}$. The authors have studied the effect of the soft segment molar mass on the morphology and the final properties.[Corcuera 2012] A decrease in the polyester diol molar mass leads to a better phase mixing between hard and soft domains, giving higher T_g for the soft segments than the one for the prepolymer. The same approach has also been used to synthesize polyester diols from azelaic acid and 1,9-nonanediol using titanium (IV) butoxide, with molar masses ranging from 500 to 1500 g.mol^{-1} . The effect of the polyester diol have then been studied in aliphatic thermoplastic poly(ester urethane)s with fatty acid based HPMDI (1,7-heptamethylene diisocyanate). [Narine 2012] The use of polyester diols with various lengths into the TPUs enabled to control the crystalline morphology, the chain dynamics and eventually the strength of the polymer. The crystal structure and the physical properties are directly linked to the polyester chain length and can be explained by the interplay between

polyester dipole-dipole intermolecular forces, as well as by the Van der Waals and hydrogen bonding attractive interactions.

Another effective strategy to polyester diols was developed by Cádiz.[Cádiz 2010] These telechelic macrodiols with a molar mass of $3.1 \text{ kg}\cdot\text{mol}^{-1}$ have been synthesized through two one-pot thiol-ene reactions; first a step-growth polymerization using 3,6-dioxa-1,8-octanedithiol and then an end-group post-polymerization modification with 2-mercaptoethanol. Then TPE-Us have been prepared with MDI and 1,4-butanediol. A low T_g and T_m at -45°C and -9°C respectively were observed, which correlate well with the thermal properties of the polyester diol precursor. The phase separated morphology has been confirmed by the hard segment transitions: a second T_g at 55°C and a broad melting endotherm at 190°C .

An alternative to synthesize TPE-Us with a fatty acid-based diol as soft segment, is to use the CRODA polyester diol synthesized by transesterification between dimerized fatty acids (obtained by Diels-Alder reaction) and an excess of linear diol. Averous and coll. have synthesized bio-based TPE-Us from this diol of $3 \text{ kg}\cdot\text{mol}^{-1}$ having dangling alkyl chains, MDI and 1,4-butanediol, with several hard segment contents from 10% to 40%. [Jiménez 2012, Averous 2012] Molar masses of $14.7 \text{ kg}\cdot\text{mol}^{-1}$ to $38.0 \text{ kg}\cdot\text{mol}^{-1}$ with dispersity from 2.17 to 5.52 have been reached. Only one glass transition temperature at -47.0°C was noticed for the PU with 10% of hard segments. Otherwise two glass transition temperatures were obtained; one for the soft segments (-51.3°C to -47.8°C) and one for the hard segments (118.1°C to 122.8°C). Melting points around 200°C are observed for PUs with hard segment content of 30% and 40%. By selecting the appropriate hard segment concentration, different thermo-mechanical properties were achieved and could fulfill some industrial requirements in diverse fields. [Jiménez 2012, Averous 2012] To obtain well-defined monomers, several research groups have synthesized bis-unsaturated compounds with one or two ester functions from methyl oleate and methyl undecenoate or from the corresponding acid derivatives. Afterwards, the hydroxyl moieties were introduced on the double bonds by thiol-ene reaction or ring-opening of the epoxide. By using the thiol-ene addition method, asymmetric ester diols have been prepared from oleic and undecenoic acids by esterification with allyl alcohol and thiol-ene reaction with 2-mercaptoethanol [Cádiz 2011] (see Figure 3). Polymerizations with MDI and using tin(II) 2-ethylhexanoate as catalyst, have led to TPUs with molar masses from 50 to $70 \text{ kg}\cdot\text{mol}^{-1}$ and dispersity in the range 1.6-1.9. Amorphous ($T_g=8^\circ\text{C}$ to 20°C) to semi-crystalline PUs ($T_m=124^\circ\text{C}$) were obtained depending on the fatty derivative used. These TPUs revealed both good thermal and mechanical properties as well as no cytotoxic response, which make them possible candidates for biomedical purposes.

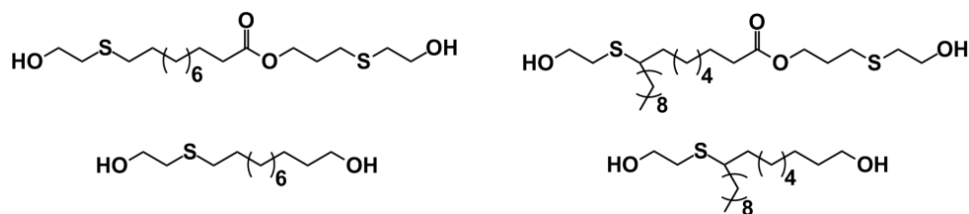


Figure 3- Examples of diols synthesized from undecenoic and oleic acids.[Cádiz 2011]

Boutevin and coll. have used a similar strategy to prepare symmetrical diester diols by transesterification of methyl oleate with ethylene glycol followed by a grafting of 2-mercaptoethanol onto the double bonds using thiol-ene click chemistry.[Boutevin 2012b] The diester diols appeared not pure enough to synthesize TPUs. Finally, PU networks with interesting thermal properties were obtained by step-growth polyaddition with MDI.

To further explore the potential of such diester diols, Cramail and coll. have synthesized a plethora of diester diols by transesterification of methyl oleate or methyl undecenoate with various central diol blocks followed by either thiol-ene reaction with 2-mercaptoethanol, or ring opening of epoxidized double bonds.[Cramail 2012a] Diols containing ether linkages were also synthesized in this work. These diester diols have been polymerized with IPDI in the presence of dibutyl tin dilaurate (DBTDL) as a catalyst. The behavior of the PUs was correlated to the purity and to the chemical structure of the starting ester-containing diols. As expected, the reactivity of primary diols obtained by thiol-ene reaction was found to be higher than the one of secondary diols synthesized by ring-opening of the epoxide, yielding higher molar mass TPU up to $35 \text{ kg}\cdot\text{mol}^{-1}$. The rheological properties were also impacted by the monomer structure and the purity. Glass transitions below room temperature were observed due to the pendant alkyl chains along the PU backbone.

Cramail and coll. also prepared sugar-based fatty ester polyols by selective transesterification of epoxidized methyl or ethyl oleate with unprotected methyl α -D-glucopyranoside and sucrose respectively, followed by hydrolysis of the epoxide moiety.[Cramail 2012b] The polyols were then used in PU synthesis with IPDI. The authors noticed that the reactivity of the hydroxyl functions attached to the sugar and to the fatty ester chain moieties respectively could be discriminated with respect to the solvent used, enabling the synthesis of either linear or cross-linked PUs.

Finally, polyesterdiols, obtained after transesterification of methyl ricinoleate in presence of an excess of butanediol or propanediol, have been reported for the synthesis of PU latexes via a miniemulsion process. [Cramail 2015] Stable latexes were obtained with IPDI with solid content up to 40% wt, with particles size around 100 nm.

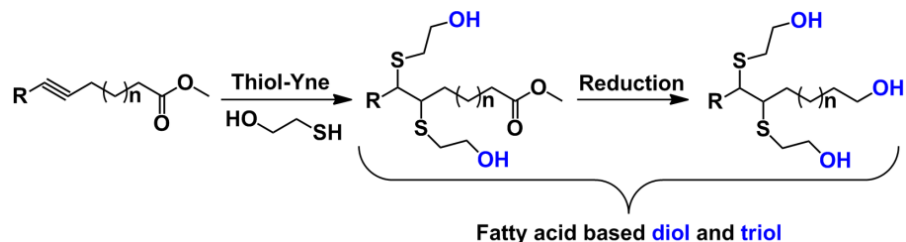
Saturated and Unsaturated diols

By taking advantage of the prominent metathesis reaction, Narine and coll. have synthesized 1,18-octadec-9-endiol, a long chain diol from oleic acid, by self-metathesis followed by reduction to the diol (Y=58%). [Narine 2010a] Alternatively, a saturated shorter terminal diol, 1,9-nonanediol, has been synthesized from oleic acid with a purity of 99% (Y=72%). These diols were reacted with different di-isocyanates namely HMDI and the fatty acid-based HPMDI to give TPUs. The properties of such aliphatic TPUs will be described in the fatty acid-based diisocyanate section.

Cationic dimerization of oleic and linoleic acids could also be done to synthesize saturated diols with pendant chains. This complex reaction is realized at high temperature with homogeneous catalysts such as ionic salts of alkali metals, or heterogeneous catalysts such as clays (montmorillonite or bentonite) or aluminosilicates. The synthesized diacids are reduced to yield fatty acid-based diols. This methodology was initially introduced, in the 1950s, by General Mills Chemicals and Emery (became Cognis Corp. acquired by BASF). [US 2793219, US 2955121] These fatty acid dimer diols are commercially available and used in TPUs providing biocompatibility, high hydrophobicity, mechanical elasticity and chemical stability properties. [Hill 2000]

Diols containing thio-ether linkages

Using efficient functionalization techniques such as thiol-ene and thiol-yne reactions, fatty acid-based diols containing thioether linkages have been synthesized. Diols by thiol-ene reaction of methyl oleate and methyl undecenoate with 2-mercaptoethanol followed by reduction of the ester group using LiAlH_4 have been reported. [Cádiz 2011] Afterwards TPUs having molar masses from 40 to 80 $\text{kg}\cdot\text{mol}^{-1}$ and dispersities in the range 2.1-2.2 were done with MDI. Only semi-crystalline PUs were obtained with glass transition temperature from 28°C to 56°C and melting temperatures around 110°C. No cytotoxic response was observed for these TPUs suitable in the medical field. In a significant contribution, the same group demonstrated the use of thiol-yne reaction for the synthesis of polyols and in particular diols for PUs. [Cadiz 2012] These diols were synthesized in two steps, the first being an alkyne derivatization of fatty acids by bromation and dehydrobromation of the double bond and the second being a thiol-yne addition with 2-mercaptoethanol (Scheme 4). Such TPUs obtained with MDI as comonomer were amorphous ($T_g=15$ to 20°C). Based on the analyses of biocompatibility, in terms of cell attachment of an osteoblastic cell line, the authors have suggested using such PUs as polymeric scaffolds for tissue engineering. Although the literature above proved the contribution of research groups to the synthesis of fatty acid-based diols to TPUs, a lack of papers on fatty acid-based diisocyanates can be noticed.



Scheme 4- Use of the thiol-yne reaction to prepare diol and triol. [Cadiz 2012]

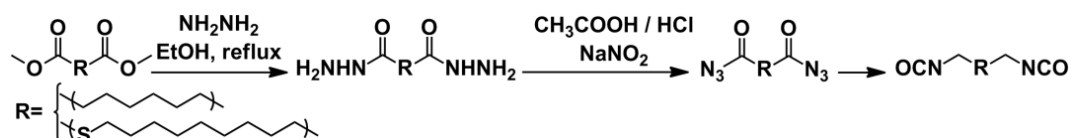
Fatty acid-based di-isocyanates

Vegetable oil-based diisocyanates have been studied in a much lesser extent perhaps as a consequence of the inherent aliphatic structure of the isocyanate that could be prepared and their lower reactivity compared to aromatic ones, as well as due to the intrinsic toxicity of isocyanates. Indeed the most commonly di-isocyanates used industrially are aromatic namely MDI and TDI due to their high reactivity required to produce foams. Thus, the uses of aliphatic diisocyanates are limited to coatings in which the absence of unsaturation is profitable. In industry, isocyanates are synthesized from primary amines by phosgenation. As primary amines are not easily introduced into vegetable oils, other strategies have been developed on vegetable oils and their derivatives.

Isocyanates can be synthesized by taking the advantage of the Curtius, Hoffman and Lossen rearrangements, which involve nitrene intermediates. In an effort to access fatty acid-based di-isocyanates, Narine and coll. used the Curtius rearrangement to prepare oleic acid-based linear diisocyanates, both saturated and unsaturated. [Narine 2009, Narine 2010b] Two linear diacids were first synthesized by methods reported earlier in this chapter, then converted to acyl azides by the reaction with sodium azide and, upon heating, had decomposed to isocyanates. The fatty acid-based HPMDI was used to prepare TPUs and compared with HMDI.[Narine 2010a] The odd number of methylene groups in HPMDI-based TPUs affected the thermo-mechanical properties, because the crystal structure was less ordered and the strength of the hydrogen bonding was weaker. Indeed lower T_g and T_m were obtained for HPMDI-based TPUs than for HMDI-based TPUs. Still the authors claim that HPMDI-based TPUs exhibit comparable properties that HMDI-based TPUs within acceptable tolerances considering the impacts on physical properties.

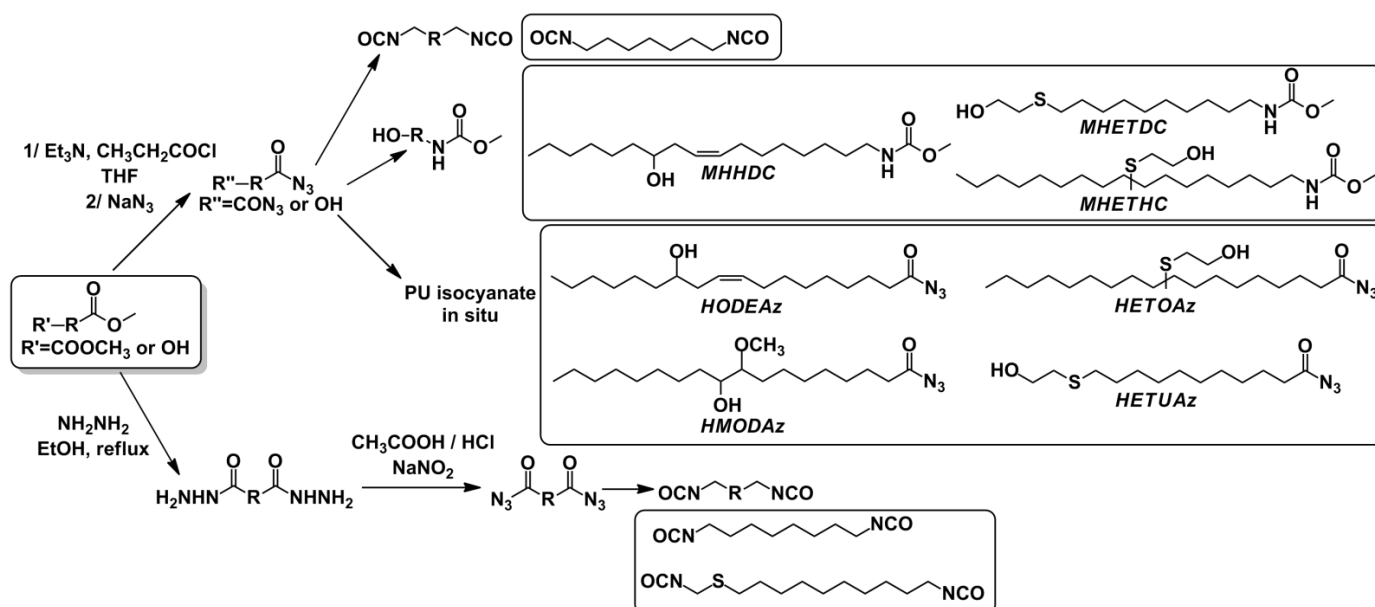
Our group reported the synthesis of fatty acid-based diisocyanates using the Curtius rearrangement through acyl hydrazide fatty acid-based derivatives without the use of harmful sodium azide (Scheme 5). [Cramail 2013b] Diesters were first synthesized and then reacted with hydrazine hydrate to form diacyl hydrazides in quantitative yields. Afterwards, these diacyl hydrazides were converted into diacyl azides then into diisocyanates *via* the Curtius rearrangement. A series of partially and fully vegetable oil-based TPUs were synthesized and

a large range of thermo-mechanical properties were achieved. Relatively good thermal behaviors were observed with decomposition temperatures at 5 wt% loss from 230°C to 280°C. For some PUs, a close resemblance to HDPE was obtained in terms of solubility and thermal transitions with melting points close to 145°C.



Scheme 5- Fatty acid-based diisocyanates using hydrazine hydrate. [Cramail 2013b]

In the Scheme 6, the different routes to isocyanates or equivalents are summarized.



Scheme 6- Summary of the different routes to fatty acid based-isocyanates or equivalents via the Curtius rearrangement.

Conclusion

Vegetable oils represent an interesting substitute to fossil resources. This manuscript highlights the tremendous research efforts that have been made and are still currently made on the synthesis of fatty acid-based polyurethanes following the isocyanate / alcohol route with a focus on thermoplastic PUs. In most cases, the use of vegetable oil derivatives in thermoplastic polyurethanes leads to the preparation of low glass transition temperature materials due to the inherent aliphatic structure and the presence of dangling alkyl chains.

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