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Discipline : Chimie des matériaux

Présentée par :

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Elaboration et caractérisation de nouvelles architectures macromoléculaires à base de lignine - Applications dans le domaine du bâtiment

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« Le succès c'est d'aller d'échecs en échecs
sans perdre son enthousiasme »

Winston Churchill

Trois années se sont écoulées, une véritable aventure pour moi, jalonnée de difficultés bien sûr mais également de rencontres inoubliables. Je tiens donc en premier lieu à remercier et exprimer ma profonde gratitude à tous ceux, qui de près ou de loin, m'ont permis d'avancer et de ne jamais renoncer en gardant le sourire et l'enthousiasme.

Les travaux présentés dans cette thèse de doctorat ont fait l'objet d'une convention CIFRE entre la société SOPREMA et l'Institut de Chimie et Procédés pour l'Energie, l'Environnement et la Santé (ICPEES). J'aimerais tout d'abord remercier vivement le Pr. Avérous qui m'a permis de réaliser cette thèse dont le sujet me tenait à cœur. Il a su trouver les mots pour me pousser à me dépasser , ses conseils et ses critiques m'ont aidée à mener à bien ce travail.

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Cette thèse de doctorat a été rédigée en utilisant pour chaque chapitre le format habituellement adopté pour la rédaction d'article scientifique paraissant dans des revues à comité de lecture. L'indulgence du lecteur est ainsi sollicitée pour les répétitions et redites nécessairement inhérente à la forme de rédaction choisie.

Le présent mémoire de thèse a ainsi partiellement été rédigé en langue anglaise, conformément à l'autorisation délivrée par le Professeur Jean-Pierre Bucher, professeur des universités à l'Institut de Physique et Chimie des Matériaux de Strasbourg et directeur de l'Ecole Doctorale de Physique et Chimie-Physique.

Communications liées à l'étude

Publications

Les résultats présentés dans cette thèse font l'objet de trois articles et d'une revue bibliographique.

- ***Article publié***

- S. Laurichesse, L. Avérous. Synthesis, thermal properties, rheological and mechanical behaviors of lignins-grafted-poly(ε-caprolactone), *Polymer*, **2013**, 54, (15), 3882-3890.

- ***Articles en cours de publication***

- S. Laurichesse, L. Avérous. Chemical modification of lignins: towards biobased polymers, *soumis dans Progress in Polymer Science (juin 2013).*

- S. Laurichesse, C. Huillet, P. Pichon, L. Avérous. Original polyols based on organosolv lignin and fatty acids: new bio-based building blocks for polyurethanes synthesis, *soumis ultérieurement dans Green Chemistry.*

- S. Laurichesse, C. Ilan, L. Avérous. Novel segmented polyurethanes based on oxypropylated soda lignins: toward high performance materials, *soumis dans Green Chemistry (Septembre 2013).*

Conférences

- S. Laurichesse, L. Avérous. New challenges for lignins: towards the synthesis of biobased polymeric materials. Woodchem 2011, 1-3 décembre **2011**, Strasbourg (France) – *Communication par poster.*

- S. Laurichesse, L, Avérous. New challenges for lignins: towards the synthesis of biobased polymeric materials. São Carlos Advanced School on Materials Science & Engineering (SanCAS-MSE), 25-31 mars **2012**, São Carlos (Brésil) – *Communication par poster.*

- S. Laurichesse, L. Avérous. Valorisation de la lignine: vers l'élaboration de nouveaux matériaux polymères. Journée de rencontres Bioplastiques – Les Bioplastiques : polymères biosourcés et/ou biodégradables, 23 et 24 mai **2012**, Strasbourg (France) – *Communication par poster.*

- S. Laurichesse, L. Avérous. Valorisation de la lignine: vers l'élaboration de nouveaux matériaux polymères. Journée d'Etude des Polymères (JEPO 40), 30 septembre au 5 octobre **2012**, Anduze (France) – *Communication orale.*

- S. Laurichesse, L. Avérous. Original polyol based on organosolv lignin: towards polyurethane synthesis. Woodchem 2013, 26-27 Septembre **2013**, Nancy (France) - *Communication par poster.*

- S. Laurichesse, L. Avérous. Chemical modifications of lignin: Towards polymer synthesis. BIOPOL 2013, 1-3 Octobre **2013**, Rome (Italie) - *Communication par poster.*

- A. Arbenz, S. Laurichesse, L. Avérous. Oxypropylation: Efficient polymerization process to obtain new biobased polyols for the development of innovative macromolecular architecture. BIOPOL 2013, 1-3 Octobre **2013**, Rome (Italie) - *Communication par poster.*

Liste des abréviations

AFM	Microscopie à force atomique
ATG / TGA	Analyse thermogravimétrique, i.e. courbe de perte de masse
BTX	Benzène Toluène et les Xylènes
C	Catalyseur
CES / SEC	Chromatographie à exclusion stérique
CL	Caprolactone
$CDCl_3$	Chloroforme deutéré
DCM	Dichlorométhane
DMSO	Dimethylsulfoxide
DMTA	Analyse thermo-mécanique dynamique
DBTDL	Dilaurate de dibutylétain
DP_n	Degré de polymerisation
DSC	Calorimétrie différentielle à balayage
E (MPa)	Module d'Young
E' (Pa)	Module de conservation (DMTA)
E'' (Pa)	Module de perte (DMTA)
EL	Lignine estérifiée par l'acide oléique (Esterified lignin)
ELO	Lignine estérifiée-époxydée (Epoxy Lignin Oleate)
f	Fonctionnalité
FT-IR (ATR)	Spectroscopie infrarouge à transformée de Fourier – Réflexion totale atténuée
G' (Pa)	Module de conservation (ARES)
G'' (Pa)	Module de perte (ARES)
H	Homopolymer
I_{OH}	Indice d'hydroxyle
Ip / PDI	Indice de molécularité / Polydispersity Index
k ($kg.mol^{-1}.min^{-1}$)	Constante de vitesse
KOH	Hydroxyde de Potassium
L (SL- OL- KL)	Lignine (Lignine soda – lignine organosolve – lignine Kraft)
LOAP	Polyol à base de lignine estérifiée par l'acide oléique (Lignin-Oleic Acid Polyol)
LPU	Polyuréthane à base de lignine modifiée acide gras
M_n ($g.mol^{-1}$)	Masse molaire moyenne en nombre

M_w (g.mol^{-1})	Masse molaire moyenne en poids
MEB / SEM	Microscopie électronique à balayage / Scanning electron microscopy
OC	Chlorure d'acide oléique (Oleoyl Chloride)
OL	Lignine oxypropylée (Oxypropylated lignin)
OLPU	Polyuréthane à base de lignine oxypropylée
P_{max} (Bar)	Pression maximale
P_x	Prepolymère polyuréthane synthétisé avec du PPO de masse molaire X (g.mol^{-1})
PCL	Poly(Caprolactone)
PEO	Poly(oxyde) d'éthylène / Poly(ethylene) oxide
PF	Phenol Formaldehyde
PMMA	Poly(méthacrylate) de méthyle
PO	Oxyde de propylène
PPO	Poly(propylène) oxyde / Polypropylene glycol
PU	Polyuréthane
PVC	Polychlorure de vinyle
RMN / NMR	Résonnance magnétique nucléaire / Nuclear Magnetic Resonance
R (J.mol^{-1}.K^{-1})	Constante des gaz parfaits
RI	Indice de réfraction
RPUF	Mousse rigide polyuréthane
SAXS	Diffusion des rayons X aux petits angles / Small-Angle X-ray Scattering
$Sn(Oct)_2$	Octanoate d'étain
T (°C ou K)	Température
T_α (°C)	Température de transition (DMTA)
T_c (°C)	Température de cristallisation (DSC)
T_{dmax} (°C)	Température de dégradation maximale
T_f / T_m (°C)	Température de fusion (DSC)
T_g (°C)	Température de transition vitreuse (DSC)
$T_{g\,SS}$ (°C)	Température de transition vitreuse des segments souples (soft segment)

$T_{g\,HS}$ / $T_{g\,SR}$ (°C)	Température de transition vitreuse des segments rigides (hard segment)
T_{max} (°C)	Température maximale
$T_{x\%}$ (°C)	Température à laquelle la perte de masse est égale à x% de la masse initiale
Tan δ	Angle de perte (DMTA et rhéologie)
TEA	Triéthylamine ou N,N-diéthyléthanamine
TEM	Microscopie électronique en transmission
THF	Tetrahydrofurane
UV	UltraViolet
V (mL)	Volume
WAX	Diffraction des rayons X aux grands angles- Wide Angle X-Ray
wt (%)	Pourcentage massique
X_c (%)	Taux de cristallinité
δ (ppm)	Déplacement chimique (RMN)
ΔH_c ($J.g^{-1}$)	Enthalpie de cristallisation
ΔH_f / ΔH_m ($J.g^{-1}$)	Enthalpie de fusion
ΔH_f^0 / ΔH_m^0 ($J.g^{-1}$)	Enthalpie de fusion du polymère 100% cristallin
ν_e	Densité de réticulation
ε (%)	Allongement à la rupture
σ (Pa)	Contrainte

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Introduction

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Introduction générale

Encouragée par la quête perpétuelle de matériaux toujours plus innovants et performants, le XX^{ème} siècle a vu le développement massif des polymères synthétiques. Face à cet essor, l'utilisation de produits chimiques issus des ressources fossiles (pétrole, gaz…) s'est considérablement accrue. Actuellement, la consommation mondiale de pétrole est évaluée à 3,5 milliards de tonnes par an, avec une forte empreinte carbone qui se traduit par l'émission d'une dizaine de milliards de tonnes de CO_2 dans notre atmosphère. Toutefois, l'épuisement inévitable des réserves pétrolières, les problèmes de réchauffement climatique (Global Warming) et la mise en place de politiques environnementales strictes (Grenelle de l'environnement…) ont conduit à l'émergence de nouvelles alternatives. Elles visent à promouvoir la production de nouveaux produits chimiques et le développement d'une chimie plus respectueuse de l'environnement.

Dans un contexte économique difficile, impacté à la fois par (i) les variations et l'envolée des prix du pétrole et de ces dérivés, et (ii) la raréfaction de certaines fractions/coupes issues des raffineries (exemple : les bitumes), les enjeux actuels de l'industrie chimique deviennent cruciaux pour son avenir. Il s'agit à long terme de trouver, pérenniser et sécuriser de nouvelles ressources de substitution. Cependant, l'élaboration de nouveaux matériaux ou produits chimiques devra se faire avec un bilan écologique positif et en respectant les équilibres sociétaux actuels.

La démarche de substitution de produits pétro-sourcés par des matières renouvelables repose sur l'un des douze principes de la chimie verte. De nouvelles approches, autres que celles proposées par la chimie « classique », par exemple l'association chimie-biochimie (bioproduction) sur de nouveaux sites de production, ont permis de générer de nouvelles architectures chimiques.

Les industriels se sont donc peu à peu orientés vers de nouvelles sources de matières premières issues de la biomasse. Cette dernière est une source de carbone renouvelable abondante qui comprend les cultures et les résidus agricoles (paille, bagasse, etc.), le bois, la biomasse aquatique (macro et micro-algues) ainsi que les déchets organiques et animaux (boues d'épuration, lisiers, etc.). Parmi les recherches menées pour remplacer les intermédiaires issus de ressources fossiles, l'utilisation de la biomasse et notamment la biomasse lignocellulosique (bois et plantes annuelles) suscite un grand intérêt de par son abondance et sa disponibilité. Cette utilisation est d'autant plus intéressante qu'elle n'entre pas en compétition directe avec un usage alimentaire contrairement à l'amidon ou aux huiles végétales par exemple. Avec près de 4 à 5 milliards de tonnes de production au niveau

mondial par an, cette biomasse représente un potentiel exceptionnel d'innovations qu'il reste encore à exploiter.

Dans ce contexte favorable et passionnant, nous nous sommes donc attachés à la valorisation de la lignine, un polymère naturel issu de la biomasse lignocellulosique. La matière organique qui structure les végétaux est pour l'essentiel constituée de trois parties distinctes : la cellulose, les hémicelluloses et la lignine. Après la cellulose, la lignine est le deuxième biopolymère le plus abondant sur Terre. Constituant principal de la paroi cellulaire des végétaux, la lignine peut représenter jusqu'à 40% du poids sec de la biomasse lignocellulosique selon la ressource botanique. Elle confère la résistance mécanique et apporte aux tissus lignifiés une certaine hydrophobie. L'extraction de la lignine du végétal peut s'effectuer par divers procédés thermochimiques, chimiques et même biochimiques. La technique la plus communément utilisée est le procédé Kraft, procédé lié à l'industrie papetière et dans lequel la lignine est essentiellement utilisée comme ressource énergétique de par son fort pouvoir calorifique. Considérée comme résidu ou co-produit de l'industrie papetière, la lignine est très peu valorisée pour des applications industrielles, seulement 2 % sont utilisés, principalement comme sources d'additifs (anti-oxydant, anti UV…) pour les industries de l'agroalimentaire, la plasturgie, les peintures etc. Toutefois, la lignine est aussi valorisée pour la production industrielle de vanilline et de DMSO.

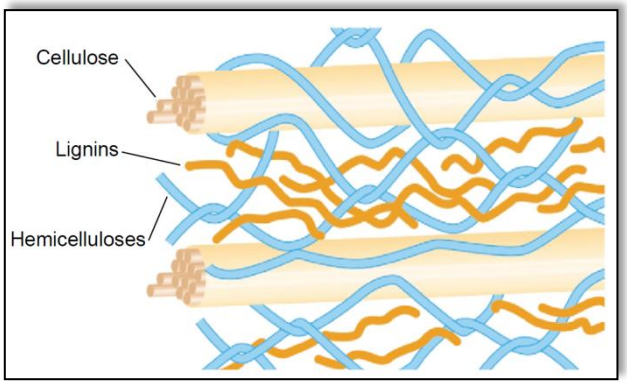

Figure Int- 1. Représentation schématique de la structure de la paroi végétale secondaire. Outre la présence de cellulose, lignine et hémicellulose, d'autres constituants sont présents en moindres quantités tels que les protéines ou des composés phénoliques de faibles masses molaires[1].

Depuis quelques années de nouvelles productions de lignines techniques se développent dans des bioraffineries spécifiques. Au sein de ces entités, la biomasse est fractionnée par divers procédés basés sur des traitements chimiques, biochimiques et physiques afin de la convertir notamment en produits de hautes valeurs ajoutées tels que les carburants ou les produits chimiques par exemple. Dans cette optique de valorisation de la biomasse, de nombreuses recherches ont été menées afin d'améliorer les procédés d'extraction et de fractionnement pour proposer des structures chimiques de plus en plus « raffinées », capables de s'intégrer dans l'élaboration de matériaux polymères.

Dans une approche d'ingénierie macromoléculaire contrôlée, la lignine, de par son caractère hydrophobe et sa structure condensée aromatique, est apparue comme un synthon potentiel pour l'élaboration de nouveaux matériaux polymères. En effet, rares sont les synthons issus de la biomasse qui portent des noyaux aromatiques. De plus, d'un point de vue industriel, certaines lignines dites « techniques », sont disponibles commercialement en grande quantité, ce qui permet d'envisager l'exploitation industrielle de ce polymère naturel avec une finalité de matériaux polymères originaux pour un grand nombre d'applications.

Le présent projet de thèse mené en étroite collaboration entre l'Institut de Chimie et Procédés pour l'Energie, l'Environnement et la Santé (**ICPEES** – UMR (CNRS) 7515), au sein du groupe de recherche *BioTeam,* et la société **SOPREMA** (**So**ciété des **Pr**oduits d'**E**tanchéité « **Ma**mmouth ») repose sur le développement d' « éco-membranes » d'étanchéité à partir de biomasse et plus particulièrement de lignine. Dans un contexte d'éco-conception et de développement durable, l'objectif premier de ce travail est de trouver une alternative aux matériaux à base de bitume et autres produits issus de ressources fossiles.

Ce travail doctoral fait partie intégrante d'un projet ISI financé par l'organisme Oséo sur 5 ans réunissant un consortium de 6 partenaires industriels et académiques dont la coordination est assurée par la Société SOPREMA. Ce projet ambitieux de 20 millions d'Euros vise à améliorer significativement l'analyse du cycle de vie (ACV) des produits d'étanchéité et de couvertures développés par la société SOPREMA à travers la conception de matériaux durables (sous garantie décennale) issus de matières renouvelables ou recyclées, dans une approche de haute qualité environnementale (HQE). Les travaux de thèse s'inscrivent dans ce programme de recherche. Le but est de développer des éco-matériaux performants, durables et à coût compétitif pour se substituer aux produits actuellement utilisés.

L'enjeu global de ce travail est donc de valoriser la lignine en l'intégrant dans la structure chimique de nouveaux polymères lesquels devant répondre à un cahier des charges industriel très précis (donné en annexe de ce mémoire). Une des premières difficultés à surmonter dans ce projet a consisté à sélectionner des gisements adéquats de lignine et à développer une chimie spécifique permettant une modification chimique de ce macromère. Des contraintes particulières ont orienté certains choix, par exemple la nécessité de scaling-up vers une production industrielle à grande échelle en respectant des critères économiques. Il s'agit de faire de ce macromère très abondant une alternative réaliste aux monomères traditionnels et synthons issus du pétrole. La recherche dans le domaine de la modification chimique des lignines, bien qu'abondante et mondialement active, n'a à ce jour pas encore été totalement convertie en une solution économiquement viable pour élaborer de nouveaux matériaux bio-sourcés, en dépassant à la fois les verrous technologiques et scientifiques actuels.

Un état de l'art scientifique et technique (***Chapitre I***) rend tout d'abord compte des différentes modifications chimiques effectuées sur la lignine en vue de l'intégrer dans la structure chimique de nouveaux matériaux polymères. Cette partie est essentiellement présentée sous forme d'un article de synthèse bibliographie (review) intitulé «Chemical modification of lignins: towards biobased polymers» et soumis dans *Progress in Polymer Science*. De manière générale, cette revue bibliographique a permis de mettre en avant plusieurs points : (i) La lignine présente une très grande variabilité structurale de par sa nature, son origine mais aussi son mode d'extraction, (ii) il est par ailleurs difficile d'envisager l'introduction de cette dernière en quantité importante dans des matrices polymères sans une modification chimique préalable, (iii) la lignine est généralement considérée comme un macropolyol avec des fonctions hydroxyles plus ou moins accessibles sur lesquelles on peut effectuer une fonctionnalisation. Cette modification chimique de la lignine a pour objectif d'augmenter l'accessibilité, et par conséquent la réactivité des fonctions hydroxyles de la lignine, en offrant aussi la possibilité de la solubiliser dans des solvants organiques usuels et donc de rendre plus facile son introduction dans des organisations macromoléculaires. Par ailleurs, la très grande diversité des lignines nous a conduits à privilégier dans un premier temps les lignines techniques dites « sans soufre », reconnues pour être plus appropriées à la modification chimique. Toutefois, dans un contexte industriel futur et dans la perspective d'une potentielle application industrielle, la question de l'utilisation de lignines Kraft (lignines « avec soufre ») sera abordée.

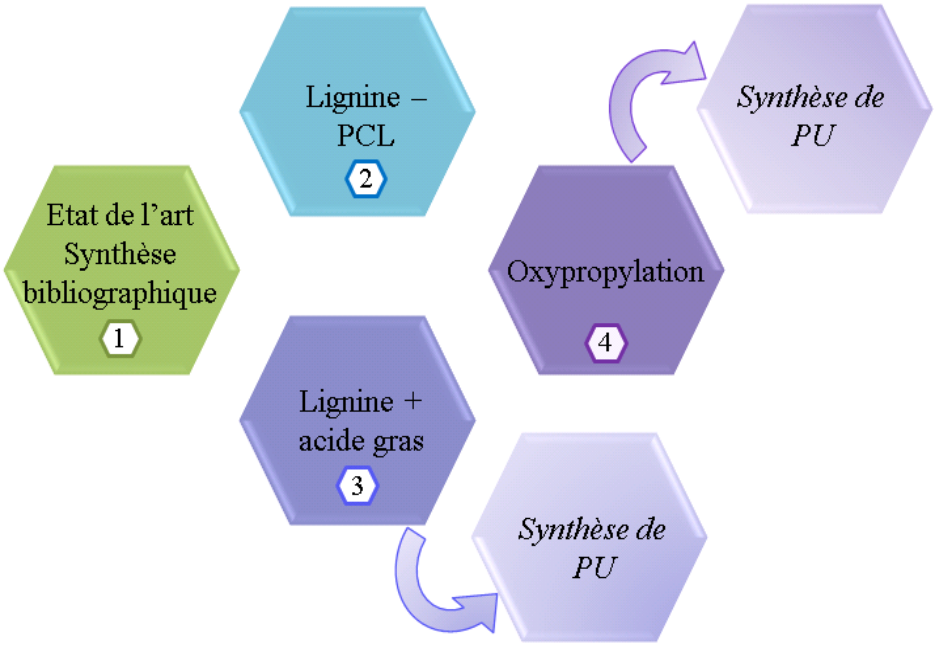

Figure Int- 2. Organisation du manuscrit.

Cet état de l'art associé à des essais préliminaires innovants nous a permis de sélectionner trois voies de synthèse (Figure Int-2) pour l'obtention de nouveaux intermédiaires réactifs à base de lignine. Rapidement dans cette étude, nous avons été amenés à développer des polymères du type polyuréthane à partir des synthons élaborés. La fonctionnalisation de la lignine nous a conduits à l'élaboration de nouveaux macropolyols avec des architectures contrôlées de type étoile dont la lignine est le « corps » et les segments greffées jouent le rôle de ramifications. Le partenaire industriel, l'entreprise SOPREMA, bénéficie d'une grande expertise dans le domaine des polyuréthanes. En effet, ces polymères sont appréciés pour leurs propriétés dans les matrices bitumineuses des revêtements d'étanchéité. On retrouve notamment les polyuréthanes thermoplastiques (TPU- norme NE ISO 18067) qui sont obtenus par réaction entre des polyisocyanates, des polyols (polyéther ou polyester généralement) et des diols de faibles masses moléculaires jouant le rôle d'extendeurs de chaines. Les propriétés des TPU dépendent de la structure des différents composés rentrant dans la formulation du polymère. Ces polymères présentent certaines particularités relativement intéressantes pour des applications dans le secteur du bâtiment et de la construction notamment en termes d'abrasion, de tenue mécanique, et de résistance à la pliure et la déchirure. Dans le cadre de ce projet de thèse, nous nous sommes donc attachés à l'élaboration de polymères de type polyuréthane à partir des macropolyols chimiquement modifiées. L'originalité de ce projet repose sur la structure en étoile des lignines modifiées obtenues, et sur leur intégration en tant

que polyol dans des matrices polyuréthanes. Les modifications chimiques développées dans le projet de thèse ont donc donné lieu à la synthèse de nouvelles architectures polyuréthanes.

Dans un premier temps, nous avons étudié la réaction de polymérisation entre la lignine et l'ε-caprolactone conduisant ainsi à la formation d'une lignine fonctionnalisée appelée Lignine-poly(caprolactone) (LPCL) (***Chapitre II***). Cette partie a fait l'objet d'une publication intitulée « Synthesis, thermal properties, rheological and mechanical behaviors of lignins-grafted-poly(ε-caprolactone) », publiée dans *Polymer* en 2013 [2]. Les polymères synthétisés sont bio-sourcés jusqu'à 48% et ont pu être facilement mis en œuvre. Certains d'entre eux ont montré la formation de réseaux amorphes et flexibles due à la présence d'interactions intermoléculaires entre les chaines de PCL greffées et la lignine. La relation entre la longueur des chaines de polymères greffées sur la lignine et les propriétés finales obtenues est discutée et s'appuie sur des analyses rhéologiques et IR.

En s'inspirant de travaux réalisés sur l'hydrophobation du bois, de la cellulose et du papier à partir de chlorure d'acide gras, et afin de conférer des propriétés hydrophobes à notre polyol de base, la lignine a tout d'abord été modifiée avec un monoacide gras insaturé (***Chapitre III***). Cette partie à fait l'objet d'une publication intitulée « Original polyol based on organosolv lignin and fatty acids: new bio-based building blocks for polyurethane synthesis », soumise ultérieurement dans *Green Chemistry*. L'étude de l'estérification de la lignine par un dérivé d'acide est détaillée ainsi que la modification consécutive de l'insaturation présente sur la chaine alkyle greffée.

De la même façon, nous avons étudié la réaction d'oxypropylation de la lignine par réaction avec l'oxyde de propylène en condition de catalyse basique. L'étude de cette réaction et des propriétés chimiques des produits en résultant est présentée dans le ***Chapitre IV*** sous la forme d'une publication intitulée « Novel segmented polyurethanes based on oxypropylated lignins: toward high performance materials.», soumise dans *Green Chemistry*. Cette réaction a en effet été largement étudiée dans la littérature mais toujours dans la perspective de réaliser des mousses rigides de PU. L'approche de cette étude est donc différente et se positionne comme un moyen de concevoir un macropolyol à façon aux propriétés modulables.

En adéquation avec l'approche visant à développer des matrices polyuréthanes, les macropolyols synthétisés dans les Chapitres III et IV ont chacun été intégrés dans des matrices PU. On retrouvera ainsi au sein de chaque chapitre la description des différentes formulations développées. L'introduction de prépolymères isocyanate a contribué à

l'amélioration des propriétés de souplesse des matériaux. L'influence du ratio molaire NCO:OH, ainsi que la masse molaire des prépolymères a par ailleurs été étudiée. L'utilisation de méthodes de caractérisation thermo-mécaniques et rhéologiques a permis de déterminer les structures et organisations des différents polymères. L'existence d'une séparation de phase entre segments souples et rigides a été mise en évidence. La participation de chacun des composants dans les deux phases est également discutée.

L'objectif de cette thèse était double. Il s'agissait de développer des matériaux pour le domaine industriel de l'étanchéité et du bâtiment, tout en préservant une approche scientifique de qualité avec une bonne compréhension des mécanismes d'élaboration des systèmes synthétisés et des structures correspondantes. Le développement de nouvelles architectures moléculaires à base de lignine a permis d'apporter une expertise supplémentaire au laboratoire et à l'équipe *BioTeam* quant à l'utilisation de la lignine pour des applications matériaux mais aussi de proposer des solutions innovantes et viables pour la synthèse de nouveaux polyuréthanes fonctionnels.

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Chapitre I.

Modification chimique de la lignine : vers l'élaboration de nouveaux polymères biosourcés - Etat de l'art

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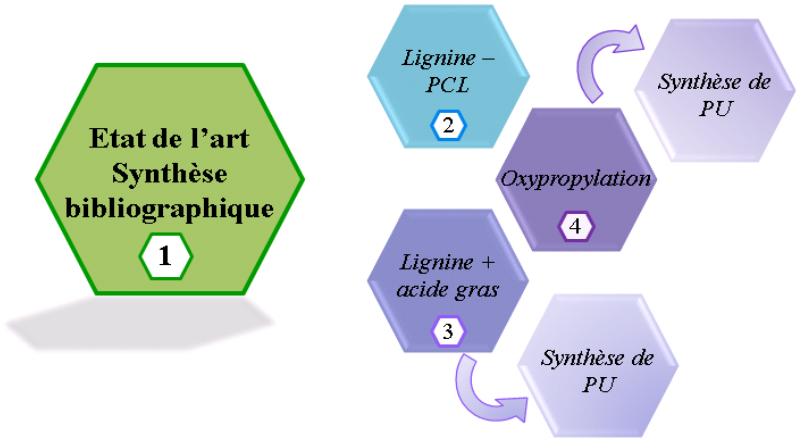

Introduction

Le travail de synthèse bibliographique présenté dans ce chapitre est composé de deux parties distinctes. La première partie se présente sous la forme d'une publication intitulée "Chemical modification of lignins: towards biobased polymers" et soumise dans le journal *Progress in Polymer Science*. Cette dernière est consacrée aux multiples modifications effectuées sur la lignine en vue de la fractionner ou encore de la fonctionnaliser. Cette publication vise, dans un premier temps, à présenter de façon synthétique les points marquants dans la récente histoire des découvertes scientifiques concernant la lignine. Les divers modes d'extraction et les propriétés correspondantes des différentes lignines techniques sont ainsi abordés de façon détaillée. Dans un second temps, ce papier fait état de l'art de l'ensemble des voies de modification de la lignine. Pour cela, nous avons choisi de les présenter en trois parties distinctes, chacune faisant l'objet d'un développement plus précis mettant en avant les résultats issus de travaux récents pertinents. Ainsi, la valorisation de la lignine peut suivre trois stratégies principales :

(1) Fractionner la lignine par différentes techniques visant à la fragmenter en molécules de plus faibles masses moléculaires (synthons ou « building-blocks » pour la chimie).
(2) Introduire de nouveaux sites réactionnels tels que des fonctions amines ou méthoxy en vue de la faire réagir chimiquement ultérieurement.
(3) Fonctionnaliser la lignine par l'intermédiaire des fonctions hydroxyles existantes.

Chacune de ces voies présente un potentiel intéressant pour transformer la lignine en une matière première de plus forte valeur ajoutée. Dans le contexte de notre étude, nous nous sommes finalement concentrés sur l'utilisation de ces modifications pour intégrer la lignine dans des synthèses de polymères. Les propriétés et performances finales des polymères obtenus et leurs applications potentielles sont également discutées.

L'utilisation de la lignine en tant que synthon ou précurseur dans la synthèse de polymères constitue un axe majeur de recherche. Parmi les polymères développés, les polyuréthanes (PU) ont retenu notre attention et font l'objet de la seconde partie de cette synthèse bibliographique. La compréhension de la synthèse des PU, en relation avec leurs morphologies finales et propriétés correspondantes, doit nous permettre de mieux appréhender les stratégies de synthèse développées dans la suite de ce manuscrit.

* * *

I. Modification chimique de la lignine – Etat de l'art

Chemical modification of lignins: Towards biobased polymers

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Progress in Polymer Science – Article soumis

Abstract

Lignins are now considered as the main aromatic renewable resource. They represent an excellent alternative feedstock for the elaboration of chemicals and polymers. Lignin is a highly abundant biopolymeric material that constitutes with cellulose one of the major components in structural cell walls of higher vascular plants. Large quantities of lignin are yearly available from numerous pulping processes such as paper and biorefinery industries. Lignin extraction from lignocellulosic biomass (wood, annual plant) represents actually the key point to its large use for industrial applications. One of the major problems still remains is its unclearly defined structure and its versatility according to the origin, separation and fragmentation processes, which mainly limits its utilization. While currently often used as a filler or additive, lignin is rarely exploited as a raw material for chemical production. However, it may be an excellent candidate for chemical modifications and reactions due to its highly functional character (i.e., rich in phenolic and aliphatic hydroxyl groups) for the development of new biobased materials. Chemical modification of lignin has driven numerous efforts and researches with significant studies during the last decades.

After an overview with some generalities concerning the main extraction techniques, the structure and the properties of lignins, this review describes in details the different chemical modifications of lignins. They have been classified into three main groups: (1) lignin fragmentation into phenolic or other aromatic compounds for fine chemistry, (2) synthesis of new chemical active sites to impart new reactivity to lignin, and (3) functionalization of hydroxyl groups to enhance their reactivity. In that frame, the potential applications of lignin as precursor for the elaboration of original macromolecular architecture and the development

of new building blocks are discussed. Finally, the major achievement and remaining challenges for lignin modifications and its uses as a macromer for polymer synthesis are also mentioned with emphasis on the most promising and relevant applications.

Keywords

Lignin, Biopolymer, Biomass, Pyrolysis, Polyurethane foams, Epoxy resins.

1. Introduction

The petrochemical boom of the second half of the last century has marked the strong development of the production of synthetic polymers. The availability of a growing number of monomers from fossil resources has supplanted during a period of time the use of biobased chemicals and their corresponding polymers. For different reasons, mainly economic, modest investments were devoted for a long time to the development of renewable resources in chemistry. Nevertheless, the increasing use of fossil fuel associated with the lack of availability of some petrol fractions and an increasing awareness concerning the human impacts on the environment have led recently to a renew strong interest in the use of sustainable resources for energy and material [1]. This growing interest about another green and sustainable chemistry has also contributed to call attention to biomass and specifically on lignocellulosic feedstock that is considered as a promising, renewable and vast resource for chemicals. Lignocellulosic biomass is mainly composed of carbohydrate polymers (cellulose and hemicellulose), and aromatic polymers (lignin and tannin). After cellulose, lignin is the second most abundant polymer from biomass and the main based on aromatic units. It can be isolated from wood, annual plants such as wheat straw or agricultural residues (sugar cane bagasse) by different extraction processes. The research investigated on lignin chemistry is not recent. Several progresses concerning lignin characterization at the mid-nineteenth century have contributed to the actual development of new materials based on renewable resources. The improving of technologies associated with papermaking, wood processing and textile has also contributed to the actual development of these polymers from biomass [2] that could be integrated in biorefineries [3, 4] to produce a large range of outputs such as materials, power, chemicals and fuel. The following paper presents an overview of the major breakthrough in lignin valorization by mainly development of biorefinery industries and new processes to convert this biomacromolecule into value-added products.

The objective of this review is to provide overview and background information about lignin valorization from its extraction by several processes to its thermal conversion or chemical modification. Beyond the presentation of the different chemical investigations performed on lignin, a special stress will be laid on potential applications for production of chemicals and polymers.

2. Lignin chemistry

2.1 Historical outline

A period of about 170 years has passed since the French chemist, Anselme Payen (1795-1871) treated wood with nitric acid and caustic soda, removing two different products from the wood [5]. He called the first one "cellulose" and the other material with higher carbon content was considered as an *incrusting material*, in which the fiber-forming cellulose was imbedded. The Payen's "incrustation theory" [6] marks the beginning of the history of what latter was named "lignin", a word derived from the Latin *lignum*, meaning wood [7, 8]. At that time, the nature of this abundant material was very unclear for the researchers, and its chemical structure remained a mystery for a long time. The aromatic nature of lignin was highlighted by the work of Bente (1868), and as late as 1890, Benedikt and Bamberger found that lignified material, unlike the cellulose, contained methoxyl groups [9]. The first main understanding in lignin chemistry is in major part due to the work of Peter Klason (1848-1937), who has devoted a great interest to lignin chemistry and its characterization. Based on experimental evidence but also with his intuition, he postulated that lignin was build up from coniferyl alcohol [10]. Many of his procedures were valuable in lignin research, and his method is still largely used [11, 12].

Freudenberg also well contributed to the field of lignin chemistry. With his co-workers, he investigated various methods for isolating lignin from the wood and characterizing it by careful analytical methods. On the basis of this work, he stated in 1928 that lignin is an amorphous and apparently unordered material, with a kind of structural order based on connected blocks consisting on phenylpropane units [13]. However, this principle was not as simple and clear as he had previously postulated for cellulose [14]. Based on the result of oxidative dehydrogenation procedures of lignin, he suggested that the main connecting systems would be both ether linkages, preferentially alkyl-aryl ether linkages, and carbon-carbon linkages [15]. Moreover, lignin structural formula has encouraged several investigations for its elucidation. Thus, Adler proposed in 1961 the first formulae containing 12 phenylpropanoïc units connected by C-C and C-O bonds while Freudenberg established a more complex structure based on 18 units in 1965 for spruce lignin [16]. Based on NMR studies, lignin polymer structural models have been then published by Ludwig [17] and Nimz [18] for softwood and beech lignins respectively. The increasing interest on lignin during the last few years is also revealed by the considerable amount of books, reviews, publications and patents,

covering a wide range of topics and applications fields [5, 12, 19]. These works aimed to define the structure and reactivity of lignin. Some of them have also considered their valorization to produce polymers [20, 21]. It is also worth to mention the pioneering contributions of Glasser and Sarkanen who have greatly participated on the knowledge of lignin's structure and have published a great number of works on lignin valorization [22-27].

2.2 Chemical structure

As it has already been mentioned, lignocellulosic biomass is a composite of biopolymers with intertwined cellulose (35-83% dry weight basis), hemicellulose (0-30% dry weight basis), lignin (1-43% dry weight basis) and some other compounds (xylose, arabinose, tannin, etc.)[28]. Lignin plays a major role in woody plant, adding strength and structuration to the cell walls, controlling fluid flow and protecting against biochemical stresses by inhibiting enzymatic degradation of others components [29]. Its chemical structure consists of phenylpropane units, originating from three aromatic alcohol precursors (monolignols), *p*-coumaryl, coniferyl and sinapyl alcohols [30]. The phenolic substructures that originate from these monolignols are called *p*-hydroxyphenyl (**H**, from coumaryl alcohol), guaiacyl (**G**, from coniferyl alcohol) and syringyl (**S**, from sinapyl alcohol) moieties (Figure I-1).

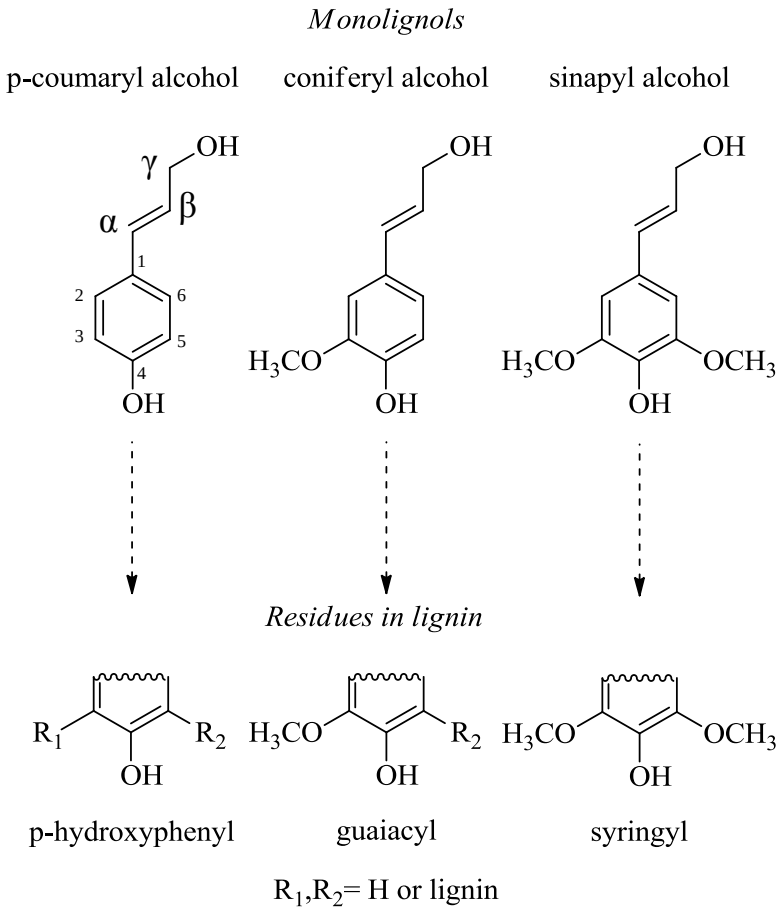


Figure I-1. The three main precursors of lignin (monolignols) and their corresponding structures in lignin polymers.

During the biological lignification process, the monolignols units are linked together via radical coupling reactions [13, 31] to form a complex three-dimensional molecular architecture that contains a great variety of bonds with typically around 50% β-O-4 ether linkages [30, 32, 33]. The main characteristic linkages in a section of softwood lignin are depicted in Figure I-2. Lignin composition and content are influenced by the type of species and also by the environment. Hardwood lignins consist principally of **G** and **S** units and traces of **H** units [34], whereas softwood lignins are mostly composed of **G** units with low levels of **H** units. Lignins from grasses -monocots- incorporate **G** and **S** units at comparable levels and more **H** units than dicots [29]. Based on the first full lignin structure proposed by Adler in 1977 [10], lignin is recognized as a highly branched polymer with a variety of functional groups: aliphatic and phenolic hydroxyls, carboxylic, carbonyl and methoxyl groups. Its chemical structure has been thoroughly investigated by various chemical and spectroscopic methods, which are well described in numerous books and publications [27, 28, 35-37]. The abundance of the chemical sites offers different possibilities for chemical modification and suggests that lignin could play a

central role as a new chemical feedstock, particularly in the formation of supramolecular architecture and aromatic chemicals.

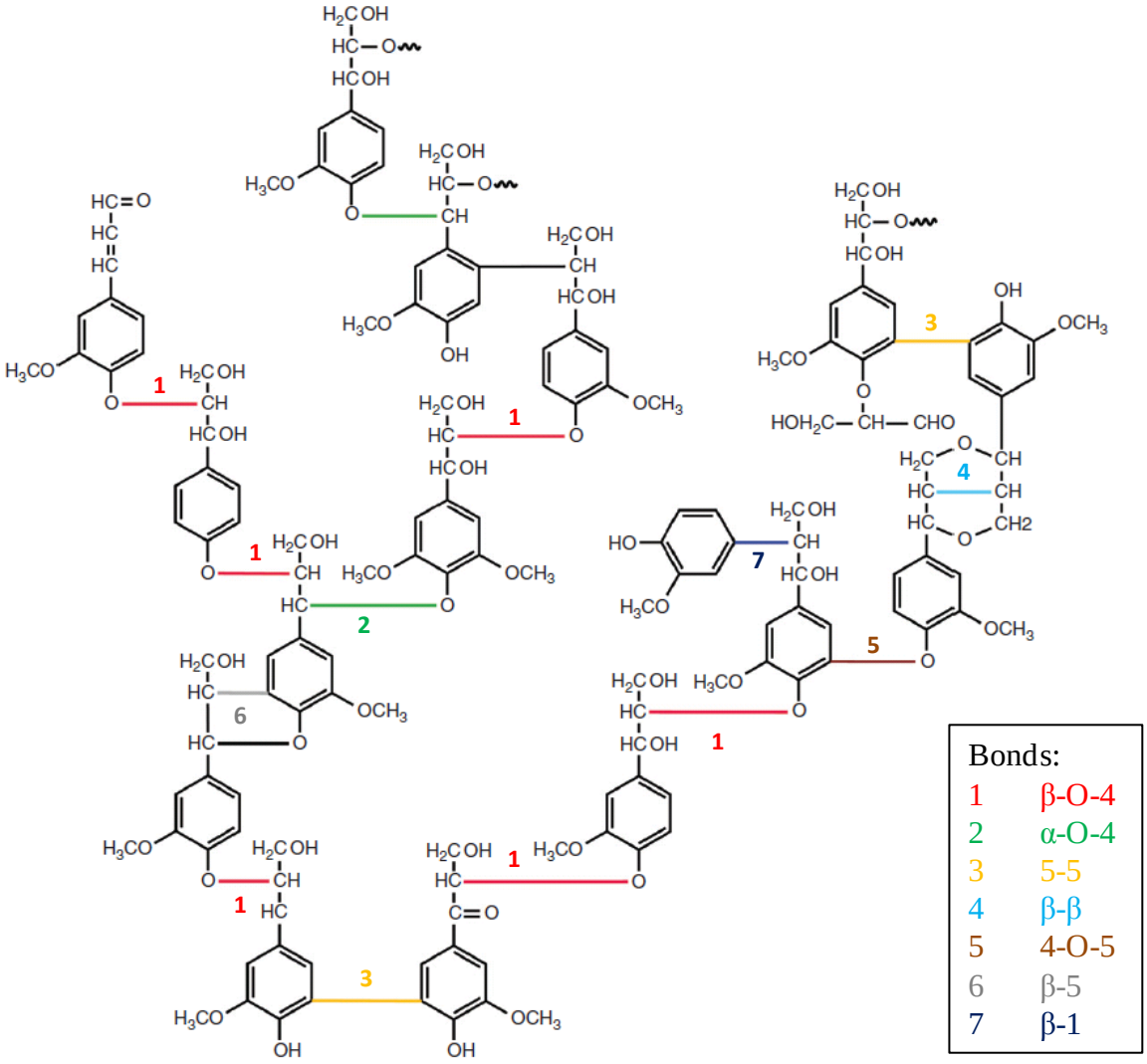


Figure I- 2. Main linkages in a softwood lignin [38].

2.3 Physical properties

Lignin may be defined as an amorphous polymer which behave as a thermoplastic material, undergoing a glass transition (T_g) at temperature which vary widely depending on the method of isolation, sorbed water, molecular weight and thermal history [8]. Thus, only two local mode relaxations are expected to be found in the lignin, i.e. T_g and decomposition temperature (T_d).

T_g is usually determined by differential scanning calorimetry (DSC) but other techniques such as dilatometry, viscoelastic measurements and temperature dependency of wide angle X-ray (WAXS) have been reported. The T_g of isolated lignin samples are often difficult to determine due to the heterogeneity of the lignin structure and its broad molecular weight distribution. WAXS results revealed the wide distribution of inter-molecular distance whereas IR spectra of lignin at different temperatures shown that around T_g, intermolecular hydrogen bonding is broken and molecular motions are enhanced [39]. T_g shifts to higher temperatures with increasing average molar masses. As already discussed, since T_g is a relaxation phenomenon, it is markedly affected by the thermal history of the corresponding samples [40]. Goring (1963) had first reported the T_g of different lignins, which can varies from 127-277°C [41]. Later, other authors founds that T_g varies from 90-150°C depending mainly on plant species and extraction procedures [42].

The molecular motion of isolated lignin has also been investigated in the presence of water. So far, lignin is hydrophobic *in planta* and its numerous hydroxyl sites involve the hydrogen bonds with water molecules. Bouajila et al. (2006) [43] studied the mechanism of lignin plasticization in presence of small amount of water and its effect on T_g. The molecular mobility of water molecules is affected by lignin molecule resulting in a decreasing of the T_g, water being a plasticizer of lignin [44]. Furthermore, modifying inter and intramolecular hydrogen bondings by chemical modification of hydroxyl groups, usually by esterification or alkylation, resulted in glass transitions which are more easily detected [24]. This is typically accompanied by an increase in the solubility of the lignin and its ability to undergo melt flow, both characteristics desirable in polymer processing and blending.

Thermal decomposition of the lignins is another important topic and a considerable number of studies have been devoted to this field [28, 45-47]. Lignin degradation is a complex process including competitive and/or consecutive reaction steps due to its hindered structure. Lignin thermally decomposes over a broad temperature range, because e.g., the various oxygen-based functional groups have different thermal stability with scissions occurring at different temperatures. The decomposition of the lignin structure starts at relatively low temperatures, i.e. 150-275 °C [48]. It is though that the first step of decomposition is due to the dehydration from the hydroxyl groups located to the benzyl group. Between 150 and 300°C, the cleavage of α- and β-aryl-alkyl-ether linkages takes place. Around 300°C, aliphatic side chains start splitting off from the aromatic ring while the carbon-carbon cleavage between lignin structural units occurs at 370-400°C. Finally, the complete rearrangement of the backbone at

higher temperatures (500-700°C) leads to 30-50 wt% char and to the release of volatile products (CO, CO_2, CH_4, H_2) [49].

3. Isolation of lignin from wood

3.1 Concept of biorefinery

The objective of chemical pulping processes is to remove enough lignin to separate cellulosic fibers one from another to produce a suitable pulp for the manufacture of paper and other related products [15]. Until recently, lignin has been considered for a long time as a waste from pulp and paper industry that constitutes only the fuel to power paper mills. During kraft pulping process, the resulting black liquor (containing between 35 and 45% of lignin) [50] is concentrated with an evaporator train and then fired into a recovery boiler for the production of steam, electricity and inorganic chemical for internal mill use. However, with the increase of pulp production, a large excess of lignin was produced. Therefore, several studies were conducted for value addition to lignin via its conversion into various chemicals.

Currently, lignin represents 30% of all non-fossil organic carbon on Earth. Its availability exceeds 300 billion tons [51], increasing annually by around 20 billion tons. The pulp and paper industry estimated that 50 million tons of lignin were extracted in 2010, but only 2% has been commercialized for the formulation of dispersants, adhesives, and surfactants or as antioxidants in plastics and rubbers. In this way, the challenge is then to explore the potential of this renewable resource, producing valuable functional molecules for chemistry.

At that time, the concept of biorefinery can be defined as “an integral unit that can convert biomass into bio-based products including food, feed, chemical and/or materials, and bio-energy such as biofuels and power” [52]. The aim of this emerging concept is to use e.g., lignocellulosic biomass by separating their main constituents with e.g., a valorization of cellulose, lignins, hemicelluloses and xylose. In that frame, pulp mills can be considered as fully integrated biorefinery which converts wood into (i) cellulose to make paper, (ii) high value co-products such as lignin, and (iii) hemicellulose, without degrading their functionality (Figure I-3). This concept of biorefinery falls within an approach of green chemistry avoiding the production of waste low value-products and recycling solvents used to extract all the components of biomass feedstock [53]. Considering this concept, it should be stated that lignin

cannot be anymore considered as a waste, it is now a raw material with a huge potential for the synthesis of value-added products.

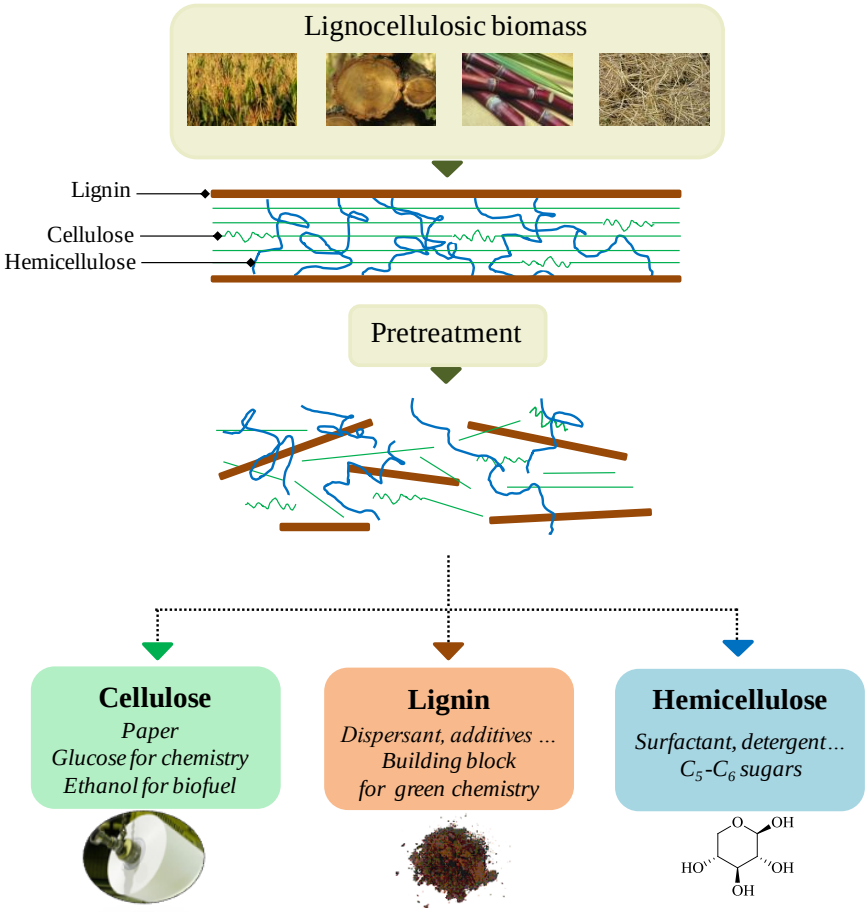


Figure I- 3. Schematic concept of biorefinery based on lignocellulosic biomass.

3.2 Extraction processes and their resulting technical lignins

Lignin is extracted from the other lignocellulosic parts by physical and/or chemical and biochemical treatments. The botanical source, but also the pulping process (delignification) and extraction procedures highly influence the final lignin structure, purity and corresponding properties [54]. Common pulping processes are based on the cleavage of ester and ether linkages, then the resulted technical lignins differ considerably from the *in planta* lignin. In this part, we will focus on the different extraction processes that are used to recover these lignins, which are commercially available. Figure I-4 shows the classification into two main categories, sulfur and sulfur-free processes, respectively. A special attention will be paid on the chemical structure differences (Table I-1), which can affect the lignin reactivity e.g., for further chemical modifications.

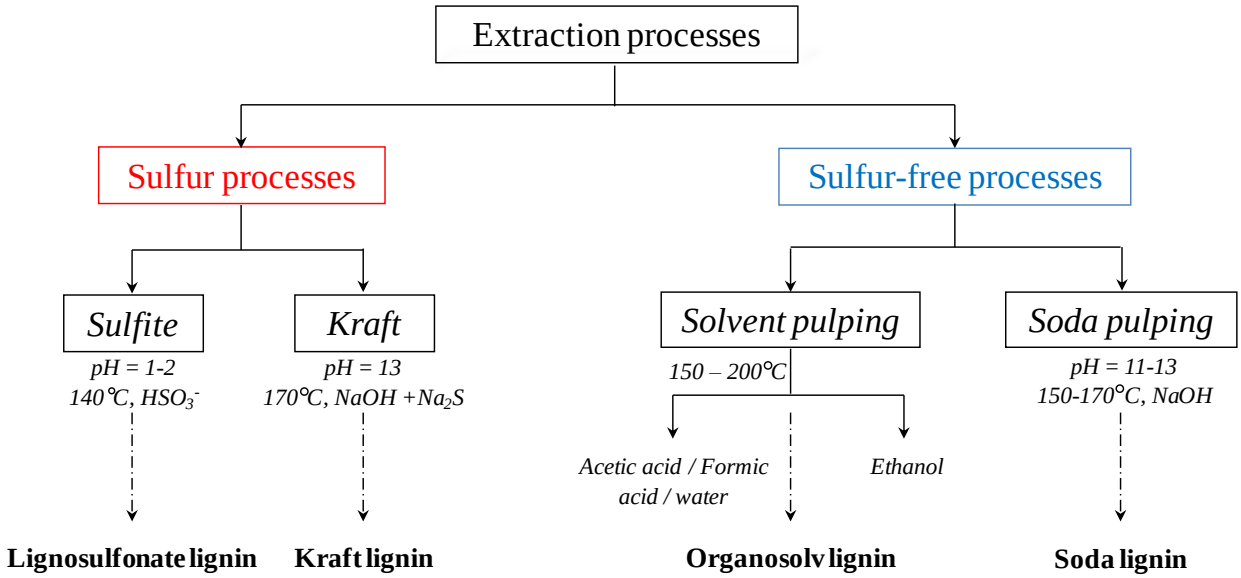


Figure I- 4. Different extraction processes to separate lignin from lignocellulosic biomass and the corresponding productions of technical lignins.

3.2.1 Sulfur lignins

Sulfur lignins include Kraft and lignosulfonates lignins, which are primarily produced by pulp and paper industries and mainly correspond to the lignin extraction from the cellulose. Kraft process uses a mixture of chemicals composed by sodium hydroxide (NaOH) and sodium sulfide (Na_2S), whereas the sulfite process is based on a cooking with an aqueous sulfur dioxide (SO_2) and a base – calcium, sodium, magnesium or ammonium. The two kinds of black liquor generated are then acidified to recover both lignins.

Considering the high sulfur environment used for Kraft lignin extraction, it is quite surprising that the residual sulfur content is so low, typically less than 1-2%. Moreover, it contains a high amount of condensed structures and a high level of phenolic hydroxyl groups, due to extensive cleavage of β-aryl bonds during cooking. The number-average molar mass (M_n) of Kraft lignin is generally low, between 1000 and 3000 $g.mol^{-1}$ [55, 56]. In order to improve the traditional process of Kraft pulping, several studies have investigated the lignin removal process to extract it more efficiently from black liquor [57, 58]. The new Lignoboost process has been developed by Innventia (Sweden) and largely patented with numerous applications [59, 60], that are now owned by Metso Company (Finland) [61, 62]. Considering the biorefinery concept, this process represents an excellent enhancement to Kraft pulping process by using lignin as a chemical product or as fuel for lime kiln in paper mills.

Lignosulfonates contain a considerable amount of sulfur in the form of sulfonate groups present on the aliphatic side chains. Lignosulfonates are water-soluble. They have a higher average molar mass than Kraft lignin with a broad polydispersity index, around 6 to 8 [63]. They take advantages from these properties and represent the technical lignins which are the most exploited for several industrial applications such as e.g., binders, dispersing agent, surfactant, adhesives and cement additives. However, they are generally contaminated by the cations used during pulp production and recovery. Their reactivity depends to some extent on the cation nature. Calcium and ammonium-based products exhibit the lowest and the highest reactivity, respectively, while sodium and magnesium-based lignosulfonates show a medium reactivity [64].

3.2.2 Sulfur-free lignin

Sulfur-free lignins are an emerging class of lignin products which have a low macromolecular size, after the fractionation steps. The structure of these lignins is close to those of the native lignins. They show interesting properties that can make them as an attractive source of low-molar mass phenol or aromatic compounds. Sulfur-free lignins can be divided into two main categories, lignins from solvent pulping (organosolv lignin) and from alkaline pulping (soda lignin) (Figure I-4).

Organosolv lignins are generally the most pure, with the highest quality [65, 66]. They show high solubility in organic solvents and practically insoluble in water, since they are very hydrophobic. They are recovered from the solvent by precipitation, which typically involves adjusting different parameters such as concentration, pH, and temperature [54]. The most common organosolv processes are based on ethanol/water pulping (Lignol© - Canada) and pulping with acetic acid, containing a small amount of mineral acid such as hydrochloric or sulfuric acid (Acetosolv) [67, 68]. In addition, another extraction based on a mixture of formic acid, acetic acid and water was developed by CIMV Company (France). The lignin produced was called Biolignin© and was supposed to be linear and have low molecular weight according to some published works [69-71].

Soda based cooking methods are mainly obtained from annual plants such as straw, flax, bagasse, and, to some extent, hardwoods. Lignin extraction is based on hydrolytic cleavage of the native lignin but it results in a relatively chemically unmodified lignin compared to the others lignin types. A famous example of this approach has been developed by Granit SA Company (Green Value SA - Switzerland) with a specific method for the precipitation of

lignin from black liquor, by adjusting pH value with mineral acids. This method is specially adapted from paper factories in the production of cellulose from annual plants or agricultural residual substances. Soda lignin can present also high silicate and nitrogen contents due to its extraction procedure [72-75].

Lignin type	Sulfur-lignins		Sulfur-free lignins	
	Kraft	Lignosulfonate	Soda	Organosolv
Aspect				
Raw materials	Softwood Hardwood	Softwood Hardwood	Annual plants	Softwood Hardwood Annual plants
Solubility	Alkali Organic solvents	Water	Alkali	Wide range of organic solvents
Number-average molar mass (M_n – g.mol^{-1})	1000 - 3000	15 000 - 50 000	800 - 3000	500 - 5000
Polydispersity	2.5 - 3.5	6 – 8	2.5 - 3.5	1.5- 2.5
T_g (°C)	140-150	130	140	90-110

Table I- 1. Properties of technical lignins.

Efficient breakdown and conversion of lignocellulosic material to chemicals and fuels remain one of the biggest obstacle currently holding back the development of successful biomass-based biorefineries that can compete with traditional fossil-based refineries [53].
Successful introduction of lignin in the production of new biobased materials is highly dependent on its structure and purity. Process extraction represents actually the key point to use lignin in industrial applications. However, despite these limitations, the huge amount of available lignin has driven numerous efforts and researches to develop its uses for industrial applications. Moreover, the absence of sulfur in lignin makes them more suitable for chemical modification. Hence, numerous researches have been investigated to develop sulfur-free extraction process to isolate lignin from biomass and to obtain chemicals that can be valorized for several applications.

4. Chemical modification

4.1 General background

The huge potential of lignin gives several opportunities to take advantage from its versatility for multiple applications. Main uses of lignin have been classified into two different groups, (i) without chemical modification, lignin is directly incorporated into matrix to give some new or improved properties, (ii) with chemical modification to carry out a large range of chemicals, building blocks and polymers.

Lignin has been subjected to a vast array of reactions for both fundamental and applied studies. However, this section has been restricted to the identification and discussion of relevant works in terms of the chemical exploitation of lignin as a source of chemicals and monomers for polymerization purpose. As presented in Figure I-5 and for a better understanding, the chemical modification of lignin can be classified into three main categories:

(1) Fragmentation or lignin depolymerization to use lignin as a carbon source or to cleave lignin structure into aromatic macromers.

(2) Modification by creating new chemical active sites.

(3) Chemical modification of hydroxyl groups.

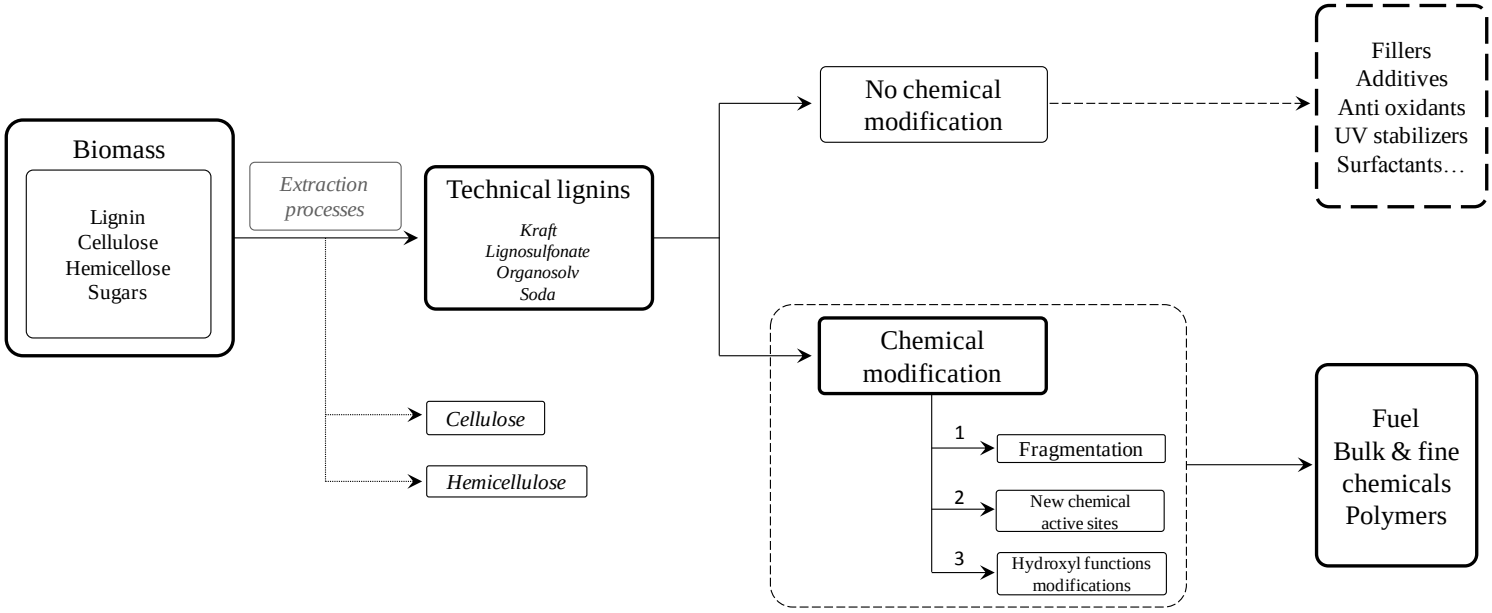


Figure I- 5. Global scheme of the uses of lignin with or without chemical modifications.

As previously mentioned, due to its hindered phenol structure, lignin can be directly used with elastomers or polyolefins as antioxidant [76-78], ultraviolet light stabilizer [79] and possibly also as a flame retardant [80]. Several studies have investigated the incorporation of lignin into polymeric matrix such as industrial thermoplastics (polyesters, polyamides, polycaprolactone and polyhydroxybutyrate) to reduce the costs of polymer production [81-83]. Lignin can also be utilized for other purposed where polyelectrolyte or surface active properties are required or where the tendency for self-condensation reaction is requested [84, 85]. For example, lignosulfonates provide plasticity and better flowability to some polymers giving also to the final material higher compressive strength, durability and better uniformity [86, 87]. Although lignin presents potential direct applications in polymer industry, it can only be incorporated in small amount, taking into account its thermal degradation and mechanical properties. At that time, the modification of lignin seems to be the best way to use this renewable product as a starting material for polymer and chemical synthesis.

4.2 Fragmentation of lignin

Lignins have been found to be an appropriate raw material for producing low molar mass compounds like vanillin, simple and hydroxylated aromatics, quinines, aldehydes, aliphatic acids and many others chemical compounds [88, 89]. The recognition that lignin can be degraded into phenolic materials has stimulated almost 60 years of research. A great number of thermochemical conversion methods have been proposed to depolymerize lignin [90]. Among them, base-catalyzed depolymerization, pyrolysis, gasification and Lewis acid-catalyzed solvolysis have received a considerable amount of attention during the last decades [48, 91-95]. At the beginning, lignin fragmentation has had two objectives: (i) the elucidation of the composition and structure of lignin, and (ii) the production of useful materials from waste lignin. Recently, with the upcoming focus on biorefineries, lignin fragmentation has gained new interest as a chemical resource, since the fossil feedstock is becoming more and more insecure and expensive [96].

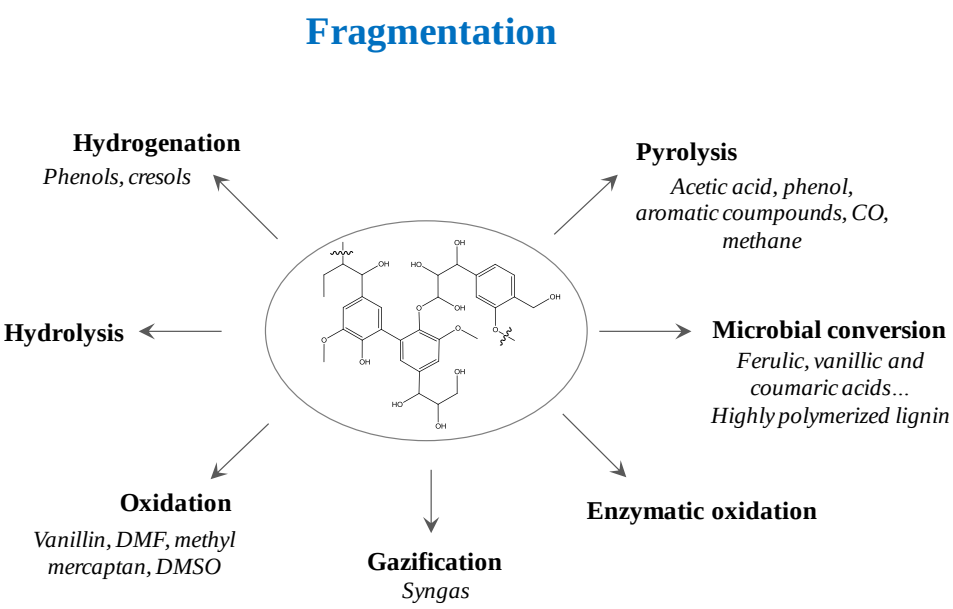


Figure I- 6. Summary of main processes for lignin fragmentation.

Thermochemical, biochemical and chemical conversions have also been developed to produce high value compounds (Figure I-6). Various types of lignins (alkali, sulfite and kraft) from both softwood and hardwood have been subjected to these processes. Figures I-7 and I-8 give a brief overview of the processing temperature and the composition of the products resulting from these fragmentation methods.

4.2.1 Pyrolysis

Lignin pyrolysis has been studied for almost 100 years with the focus on two main aspects: (i) understanding biopolymer aromatic structure and (ii) breaking lignin down into aromatic components or repeat units. Lignin pyrolysis is based on thermochemical decomposition by heating biomass at around 500°C without oxygen. Lignin starts to decompose at 280-500°C by the cleavage of ether and carbon-carbon linkages. This degradation generates liquids (pyrolysis oil), solids and gaseous fractions (CO, CO_2, CH_4, etc.), in various proportions, depending on reactions parameters [89, 92, 97]. The liquid product resulting from lignin pyrolysis is composed by 20% of aqueous compounds (methanol, acetic acid, acetone and water) and 15% of tar (condensation of hot volatiles giving mainly phenolic compounds). The gaseous fraction represents around 10% in weight of the starting material and contains CH_4, ethane and CO [98].

Pyrolysis can be divided into two different categories: *conventional* (also named slow pyrolysis) and *flash pyrolysis*. In conventional slow pyrolysis, lignin is heated to around 500°C with a slower heating rate compared to the flash pyrolysis. The vapor residence time varies from 5 to 30 min. Thus, the components in the vapor phase continue to react with each other, as the solid char and any liquid are being formed. Pyrolysis can be used to produce predominantly a liquid (named "bio-oil") if flash pyrolysis is used, enabling the conversion of lignin to bio-crude with an efficiency of up to 80%. This process produces 60-75 wt % of liquid bio-oil, 15-25 wt % of solid char, and 10-20 wt % of noncondensable gases. Thanks to this method, no waste is generated, the bio-oil and solid char can each be used as a fuel and the gas can be recycled back into the process. Moreover, the process has the advantage of enabling short residence times (less than 2 s) and giving bio-oil by cooling rapidly vapors and aerosols.

In the past 20 years, *flash pyrolysis* techniques have been developed for the conversion of whole plant biomass into bio-oil using mainly continuous or batch fluidized-bed reactors from laboratory to demonstration scale.

However due to the complex structure of lignin, pyrolysis leaves significant amounts of residue and the corresponding bio-oil are rich in oxygen-containing compounds. Co-pyrolysis of lignin (or biomass) with polyolefins was considered as an opportunity to enhance the liquid production and to decrease the oxygen content of the pyrolysis oils [99]. In a recent publication, researchers have shown that co-pyrolysis of soda lignin with synthetic polymers, and particularly with materials having phenol-type structures (e.g., PS and PC) increase the interactions between both components and lead to higher amount of pyrolysis oil, mainly based on phenol compounds.

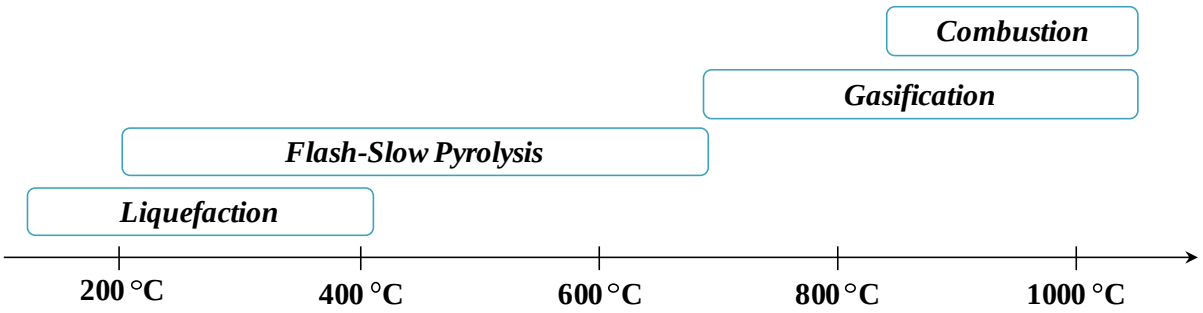


Figure I- 7. Processing temperatures used for lignin fragmentation.

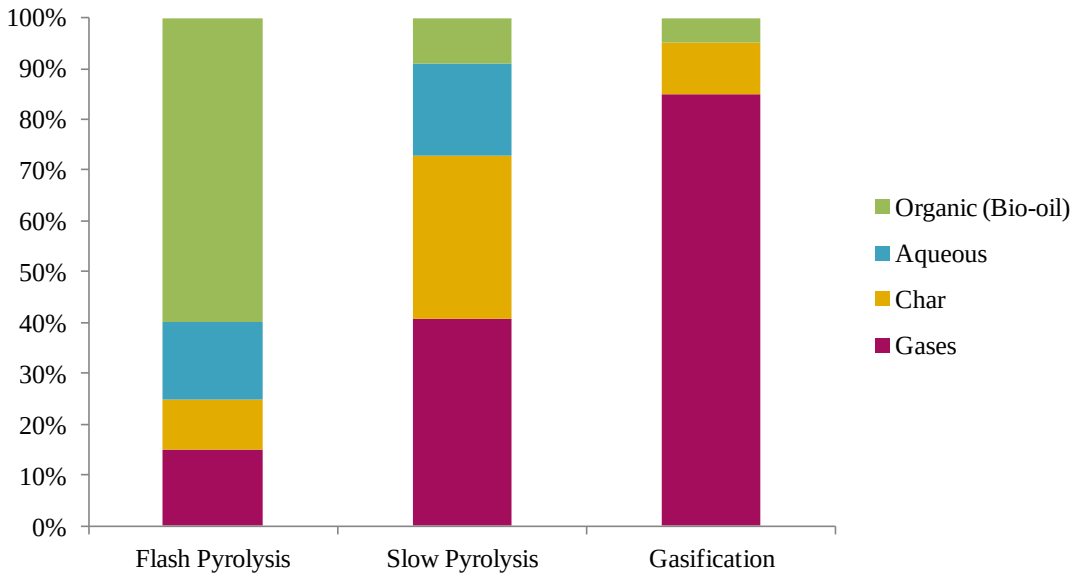


Figure I- 8. Global composition of the resulting products from the thermochemical conversion of the lignin.

4.2.2 Gasification

Gasification transforms biomass by partial oxidation at high temperatures, typically in the range 800-900°C, into combustible gas mixture mainly O_2 and CO with a low caloric value (about 4-6 $MJ.Nm^{-3}$). Gases formed during gasification can be used for several applications. The most common is to use it as fuel for gas engine and gas turbine, but gasification can offer a lot of possibilities and mainly the production of synthetic gases (*syngas*), based on a mix of CO with H_2 [91]. This syngas can be a basic source for the production of new chemicals and polymers by chemical pathways or by biochemistry (bioproduction) [100]. For example, Choi et al. (2010) have recently showed the feasibility of bioproduction of polyhydroxyalkanoates by fermentation with a carbon source based on fermentation of gasified biomass [101].

4.2.3 Oxidation

Lignin oxidation is one way to obtain phenolic derivatives. Nitrobenzene, some metallic oxides, air and oxygen are the most used oxidants that preserve the lignin aromatic rings and gives aldehydes (vanillin and syringic) and acids (vanillic and syringic acids) whose yield depend on the oxidant, with or without catalysts (Copper (II) and Cobalt (II)) [102, 103]. Among all of the existing oxidants, nitrobenzene is theoretically considered to be the aromatic compound with the highest yield, from lignin. Various lignocellulosic materials including neat

lignins have been oxidized studying the most favorable conditions (temperature, reaction time, air pressure) to obtain fractions with high added-value compounds. Among all of the products that can be produced by lignin oxidation, vanillin (4-hydroxy-3methoxybenzaldehyde) constitute the most well-know and valuable product. Vanillin is mainly used as a flavor and as a chemical feedstock in the pharmaceutical industry [104]. The first hints that it might be possible to produce vanillin from lignin-containing wastes has been published in 1875, of a vanillin-type smell in spent acid sulfite pulping liquor [105]. This opportunity was developed, and for a long time vanillin was exclusively produced by oxidation of lignosulfonates. However, the oxidation of lignin into vanillin is still complex; the yield of vanillin varied somewhat with the source of liquor and with the degree of lignin sulfonation [106]. Recently, an interesting work has been developed by Tarabanko et al. (2013) to separate efficiently vanillin and syringaldehyde, two structurally and very similar compounds that are produced from lignin oxidation. They demonstrate the possibility to separate both compounds by a one-stage crystallization with a high yield (90%) and purity over 98% [107]. Beyond the production of vanillin, mainly used by food-processing industry, lignin oxidation can provide several polyfunctionnal monomeric compounds and fine chemical products for chemical industry (Figure I-9). They represent attractive bio-based monomers that can be successfully incorporated into polymeric materials. For example, recent contributions were devoted to the development of resins, composites and polymers with vanillin and vanillic acid [108-110]. Mialon et al. synthesized a renewable polyethylene terephthalate mimic with vanillin and acetic acid anhydride with similar properties than conventional [111]. New healthy prepolymers (without bisphenol A and epichloridrin) were also designed by chemo-enzymatic epoxidation of vanillic acid in the presence of hydrogen peroxide and caprylic acid [112].

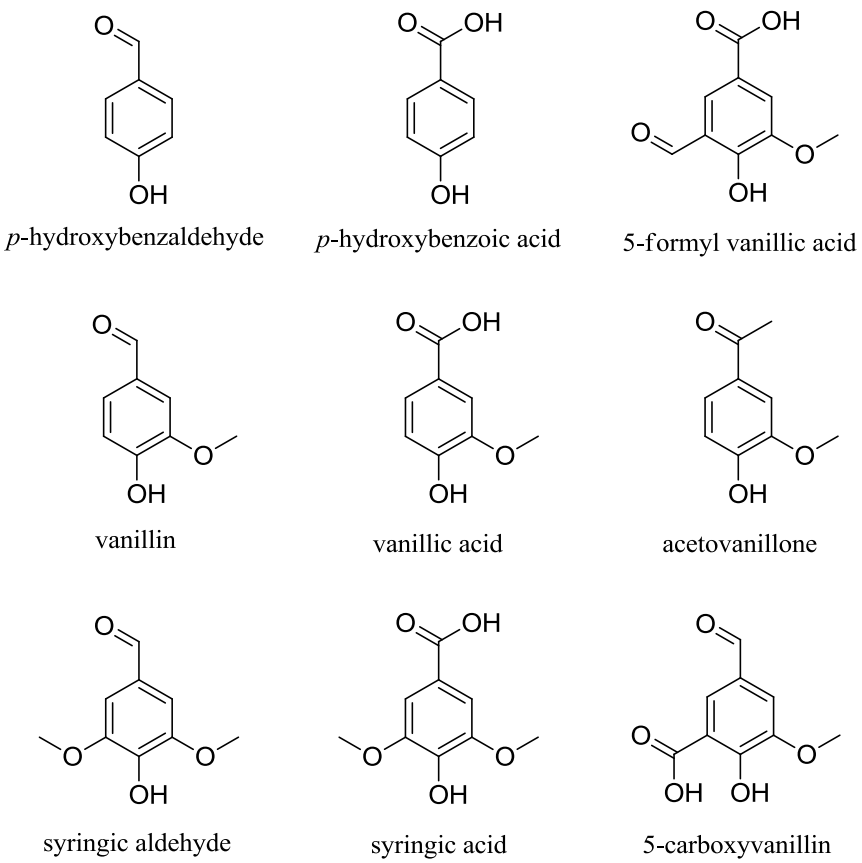


Figure I- 9. Aromatic compounds formed during lignin oxidation.

4.2.4 Liquefaction

Liquefaction of biomass consists in its thermochemical conversion with different liquefying agents and catalysts. In relation to the others methods of biomass fragmentation, liquefaction involves solvolysis and depolymerization simultaneously [113]. The concept of liquefaction is to fully convert solid biomass to liquid products, which are rich in hydroxyl groups. The resulting liquefied products can be a potential feedstock for preparation of polyesters, polyurethanes, and epoxy-resins [114, 115]. Two liquefaction processes have been developed: (i) noncatalyzed liquefaction at an elevated temperature (250-500°C) under high pressure and (ii) an acid-catalyzed liquefaction, with a selected solvent system and a catalyst. The biomass can be liquefied under atmospheric pressure at moderate temperature (120-180°C). Several studies in lignocellulosic biomass liquefaction have been investigated using different liquefying agents such as phenol and polyhydric alcohols (ethylene glycol, glycerol) and acid catalysts (chloride, sulfuric and phosphoric acids) [116-118]. Mechanisms involved during lignocelluloses liquefaction are complex and are still not fully understood. Through

this method wood components (lignin, cellulose and hemicellulose) are decomposed into small and potentially self-condensed molecules but there are also some residues that are not soluble in solvent [119]. Zhang et al. (2011) have studied the liquefied wood residues with a liquefaction solvent based on a system of glycerol/ethylene glycol (EG). This study showed that wood liquefaction process takes place in a two-step route. Firstly, the rapid liquefaction is due to the removal of lignin, hemicellulose and amorphous part of cellulose and then the decrease of residue compounds occurs. Parameters such as the yield of catalyst, reaction temperature and the solvent ratio play an important role in the composition of the liquefied product, mostly the content of acid-insoluble lignin. Nevertheless, some applications with liquefied wood and/or lignin have been tested for Phenol Formaldehyde (PF) resins giving good mechanical and thermal properties [115].

4.2.5 Enzymatic oxidation

In-planta lignin is linked to both hemicelluloses and cellulose and acts as a barrier to any solutions or enzymes to prevent the penetration of lignocellulolytic enzymes into the lignocellulosic structure. Not surprisingly, concerning the degradation resistance, lignin is the strongest component among the different lignocellulosic macromolecules. Although lignin resists attacks by most microorganisms, basidiomycetes white-rot fungi, are able to degrade lignin efficiently [120, 121].

Current methods for bioethanol production are based on physico-chemical pre-treatments, to remove lignin and hemicellulose and to access to the cellulose content of the vegetal biomass. Hence, there is interest in biological methods for lignin breakdown, which might be used for second generation biofuel production thereby increasing the bioavailability of cellulose, whilst requiring less energy input for pre-treatment. In this case, lignin degradation would release valuable aromatic chemicals with low molar masses and adds value to biofuel production, to generate fine chemicals. Lignin can be slowly degraded by white-rot fungi such as *Phanerochaete chrysosporium*, which produce an extracellular lignin peroxidase (LiP) enzyme to start the degradation process. Lignin degradation by enzyme is based on an oxidative process [122]. Other fungal strains can produce lignolytic enzymes such as manganese peroxidase (MnP) and laccase enzymes that are also active in lignin breakdown [123, 124]. However, in spite of a great deal of work on fungal lignin breakdown, all of them have been carried out in order to improve the cellulose extraction of wood but not to use lignin as a potential source of aromatic compounds. The main applications of enzymatic oxidation are

biopulping and biobleaching, which consist in a Solid State Fermentation (SSF) process, where wood-chips are treated with white-rot fungi to improve the delignification process [98, 123].

4.2.6 Outlook

Complete lignin depolymerization or fragmentation is an energy-negative process aimed at undoing what nature has done during biosynthesis. That is why, a lot of researches have been investigated to enhance the use and add value to the lignin, without modifying its intrinsic structure. As already mentioned, lignin can be considered as a macropolyol. The reactive hydroxyl sites can react with chemical compounds to give new chemical reactive sites based on carboxylic or amine groups, for example.

4.3 Synthesis of new chemical active sites

Chemically, lignin has a variety of functional groups, namely hydroxyl, methoxyl, carbonyl and carboxyl groups. Higher end uses of lignin have not previously been achieved because of its structure complexity. To improve upon this limitation, lignin can be modified to increase the range of their applications. Different types of modification have been proposed with objectives to increase its chemical reactivity, reduce the brittleness of lignin-derived polymers, increase its solubility in organic solvents, and improve the ease of processing the lignin. These modifications consist in increasing the reactivity of hydroxyl groups or changing the nature of chemical active sites, but it is always in view of synthesizing new efficient and more reactive macromonomers. On the basis of the previously described lignin structure, its reactivity is based by its particular structure with both specific functional groups - mainly *hydroxyl* groups - and specific position (mainly *ortho* position) of aromatic ring. So far, different chemical modifications pathways have been investigated to introduce new chemical active sites in the lignin chemical structure. Several modifications such as nitration, amination, alkylation/dealkylation, carboxylation, and halogenation (Figure I-10) have been investigated but less extensively than reactions involving hydroxyl groups. These latter are separately presented.

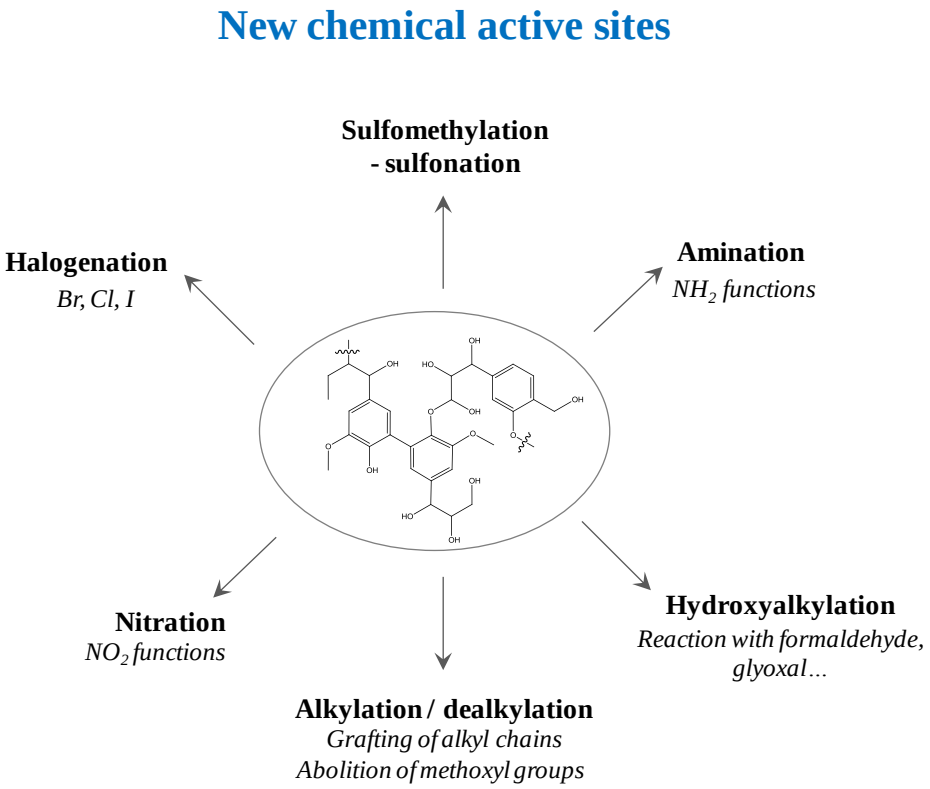


Figure I- 10. Summary of the main types of reaction for the synthesis of new chemical active sites on lignin.

4.3.1 Alkylation/dealkylation

Among the different examples based on alkylation and/or dealkylation, demethylation is the most well-known since demethylated lignins represent a byproduct of DMSO production. DMSO is a polar aprotic solvent, which plays an important role in the synthesis and processing of polymers. The corresponding synthesis starts with the reaction between lignin and molten sulfur in alkaline media. Two methyl groups are transferred from lignin to sulfur to yield DMS which is further oxidized with nitrogen dioxide to obtain DMSO (see Figure I-11). Currently, Gaylord Chemical Company (US) is the leader company to manufacture DMSO from lignin. Among various studies performed on this modification consisting on removing methyl groups from lignin, we have to mention the original work conducted by Liu and Li (2006) [125]. They have developed a new water resistant wood adhesive based on demethylated lignin and polyethylenimine. The combination of these two components was able to serve a formaldehyde-free wood adhesive, which is a very well-known lignin application [125].

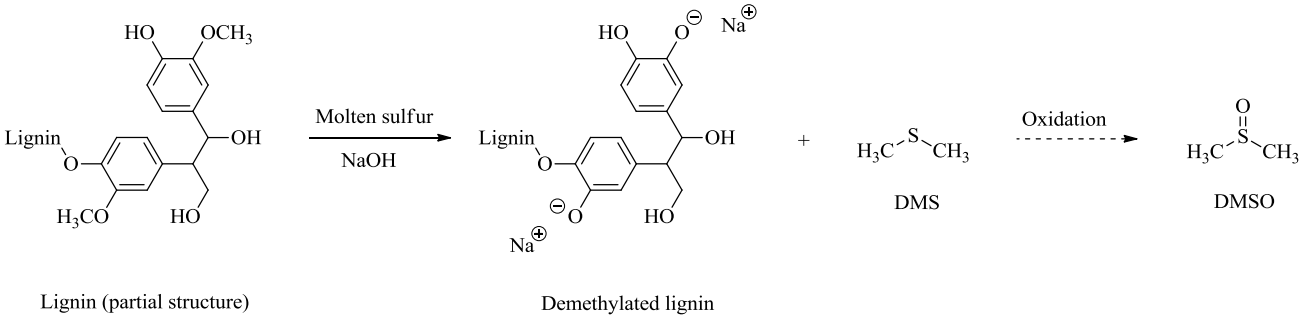


Figure I- 11. Chemical modifications occurring during the DMSO production from lignin.

4.3.2 Hydroxalkylation

The number of publications and patents pending on lignin as a substitute or extender for phenolic wood adhesives during the last decades is rather impressive [64]. The substitution of non-renewable phenol by biobased chemicals in the synthesis of phenol-formaldehyde (PF) resins and other adhesives represent some strong developments. Some similarities on chemical structure and their reactivities with formaldehyde have generated new routes for the production of wood adhesives based on lignins. The lignin-formaldehyde reaction chemistry has been described in details in the literature [126]. There are two different pathways to synthesize lignin-phenol-formaldehyde (LPF) resins. Firstly, crude lignin can react with formaldehyde. However, the condensation reaction with lignin and with PF resins is rather limited. The second pathway consists of lignin modification with demethylation, phenolation and methylolation [127] reaction processes to enhance lignin's reactivity. Methylolation consists in the reaction of lignin with formaldehyde in an alkaline medium to introduce methylol groups at C_5 position of guaiacyl units, at side chains reactions α to a carbonyl group and on the β carbon of α-β double bonds conjugated to free phenol units. However, undesirable side reactions can occur, including the well-known Canizzaro reaction in which formaldehyde reacts with itself, and the Tollens reaction where the lignin side chains are substituted by aliphatic methylol groups [128].

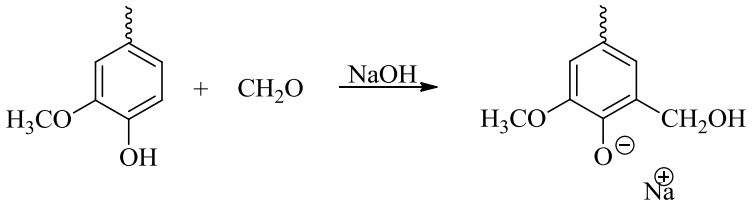


Figure I- 12. Reaction scheme of lignin and formaldehyde with basic catalyst.

By varying the reaction time and temperature, catalyst type, and the formaldehyde/lignin ratio, different adhesives systems with specific properties have been produced. Recently, hydroxymethylated lignin has been used to substitute 40 wt% phenol in PF resin synthesis, giving a formulated adhesive with low free formaldehyde content and with a satisfactory bonding strength [129]. While lignin integration into phenolic resin has utilized formaldehyde chemistry, the use of other aldehydes including glyoxal [130-134], furfural [135] and more recently glutaraldehyde [136] have also been described. For example, glyoxal represents an interesting alternative to formaldehyde; it is a non-toxic and non-volatile dialdehyde [134] that can be obtained from natural resources such as the oxidation of lipids or as a by-product of biological processes [137]. Recently, Cheng et al. (2012) have achieved to demonstrate that low molar mass biocrude oil produced from the hydrothermal liquefaction of sawdust could replace phenol up to 75% in the synthesis of Methylolated Bio-Oil-Phenol Formaldehyde (MBPF) resol resins [138]. These promising results on the valorization of lignin and other biorefinery coproducts have been also investigated to modify PF resins by copolymerization. The ethanol biorefinery residue (ER) was found to be one of the best residues for the modification of PF resin. 50% of phenol could be replaced by ER without decrease of the properties of adhesives and plywood [139].

4.3.3 Amination

Amination of lignin is mainly based on Mannich reaction with amine and formaldehyde [140]. In some recent studies, lignin amination is often carried out in presence of diethylamine and formaldehyde under various reactions conditions [141]. The Mannich reaction occurs between a carbon with high electron density and an immonium ion formed from formaldehyde and an amine. Then, an aminoethyl group can be introduced at the *ortho* position of a phenolic hydroxyl group. To elucidate the chemical reactivity of lignin toward a Mannich reaction, 1-guaiacyl-1-*p* hydroxyphenylethane was chosen to represent a simple phenolized lignin model compound. Four compounds have been isolated from this reaction. Mannich reaction of a model compound of lignin is represented in Figure I-13. The Mannich reaction products were used for two different applications: (i) preparation of a cationic surfactant with a high surface activity, larger than that of lignosulfonate (a commercial surfactant from lignin) and (ii) preparation of a composite to improve interfacial mechanical performance of PVC/wood-flour composites by increasing interfacial bonding of polymer matrix and the aminated lignin. When the wood-flour was treated by 2 wt% of lignin amine, tensile and impact strengths of the composite achieved a maximum value. Furthermore, lignin

amine treatment has significantly reduced the water absorption of the composite [142]. Another interesting amination of lignin was also investigated in the synthesis of polyurethane foams (PUF). In this case, lignin-aminated polyol was prepared from lignin with diethanolamine and formaldehyde by the Mannich reaction. It was found that the new lignin-polyol based on lignin amination can react with diphenylmethane diisocyanates (MDI-50) and glycol (PEG) in the presence of water as a blowing agent to synthesize PUF. Crosslinking kinetics reactions were studied [143]. Recently, the way of using enzymes (precisely laccases) has been studied to mediate the coupling of long alkyl chains onto lignin compounds [144]. Two long chains alkylamines (docecylamine and dihexylamine) have been successfully grafted onto lignin model compounds by this method to increase the hydrophobicity of lignocellulosic material. In a context of improving wood hydrophobicity, enzymatic processes have shown interesting results increasing in 54 and 84% hydrophobicity of lignin, considering the two alkylamines, respectively.

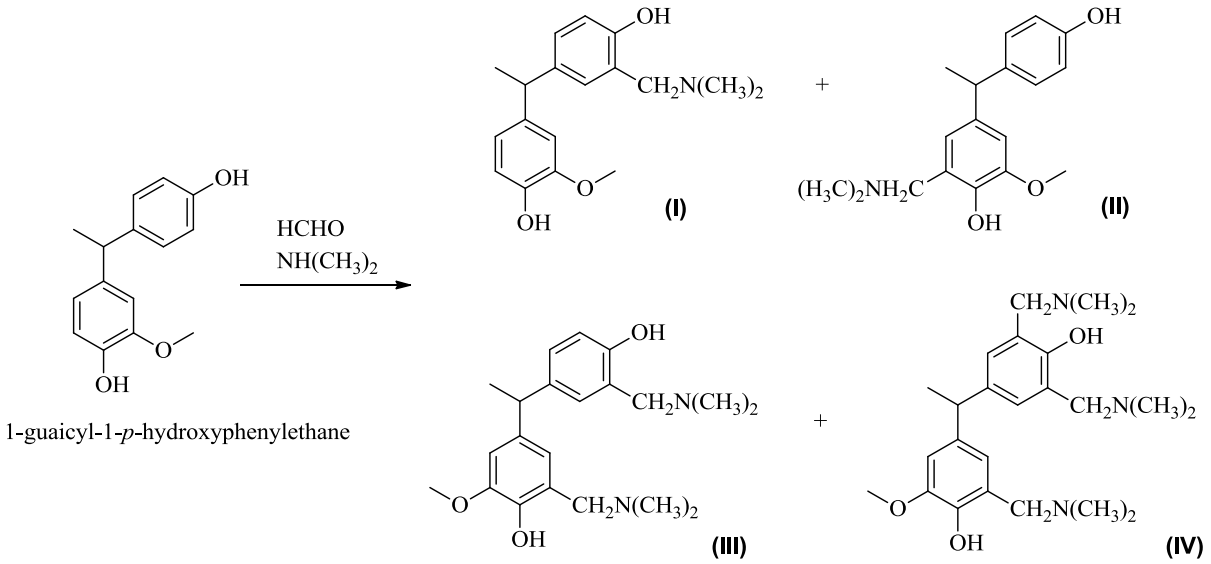


Figure I- 13. Adapted representation of Mannich reaction of a simple phenolized sulfuric acid lignin compound with formaldehyde and dimethylamine [141].

4.3.4 Nitration

Nitration is another reaction that can be carried out on lignin. It is typically run in nonaqueous solvents with nitrating agents such as nitric acid with acetic anhydride, nitric acid in concentrated acetic acid and fuming sulfuric acid. The resulting product is a reddish-brown amorphous powder with nitrogen content around 6 - 7 % estimated by elemental analysis [145].

Recently, nitrolignin has been investigated for the synthesis of graft interpenetrating polymer networks (IPN) from polyurethane. Results showed that a relatively great network structure like a star by grafting with multi-PU networks (with different NCO:OH molar ratios) was formed based on nitrolignin (NL) molecule [146, 147].

4.4 Functionalization of hydroxyl groups

Lignins have phenolic hydroxyl groups and aliphatic hydroxyl groups at C-α and C-γ positions on the side chain. Phenolic hydroxyl groups are the most reactive functional groups and can significantly affect the chemical reactivity of the material. This type of modification - affecting hydroxyl groups - results in the formation of lignin polyol derivatives, which in turn improves the solubility of the lignin. After modification, the majority of phenolic hydroxyl groups are converted into aliphatic hydroxyl units (Figure I-14). Thus, more reactive hydroxyl groups become readily available. In fact, a good strategy frequently used in several studies is the reaction of lignin with bi-functionnal compounds which allows having a reaction with one reactive site and another free reactive one that can be involved e.g., in polymerization reaction.

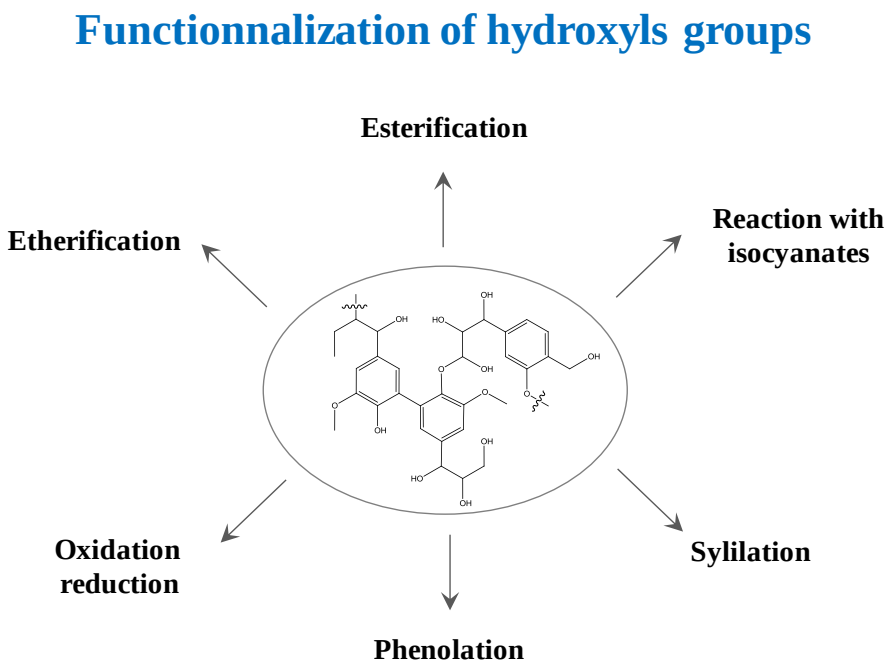


Figure I- 14. Summary of the chemical reactions for the functionalization of lignin hydroxyl groups.

4.4.1 Esterification

Among all of the reactions involving hydroxyl groups of lignin, esterification is probably the easiest to carry out considering the reaction parameters and reactants used. There are three types of reagents that can allow performing this type of reaction: acids compounds, acid anhydrides and chloride acids. The two latest are the most reactives. Table I-2 shows a summary of some representative studies with the highlight on the compounds used for lignin esterification. We can notice that most of the chemical compounds used are bi-functional which results in lignin-based polyester networks. Thus, it is a current practice to incorporate co-macromonomers such as poly(ethylene) glycol (PEG) [148], bearing complementary chemical functions, yielding esters groups and playing also the role of co-solvent. By varying the molar mass and the co-monomer content, modulation of properties of the resulting lignin-based polyesters can be obtained. Besides, triethylamine (TEA) is often used in esterification reactions and can selectively modify phenolic alcohols in presence of aliphatic alcohols. It has been shown that it can be potentially achieved to yield phenol modified-lignin [149]. However, often time both aliphatic and phenolic hydroxyl groups take part in esterification reactions.

As can be observed in Table I-2, the major part of applications based on esterified lignins is dedicated to the synthesis of polyesters, epoxy resins and elastomeric materials. Lignin derivatives and products applications from lignin are more specifically developed in section *4.5*.

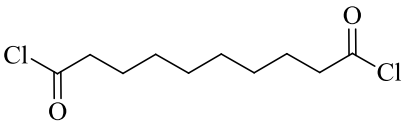
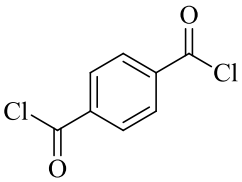
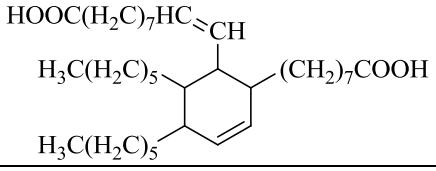
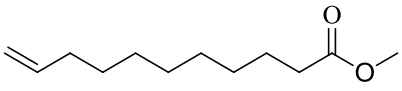
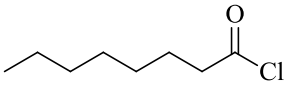
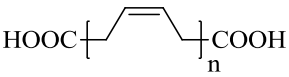
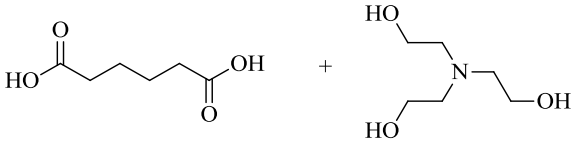
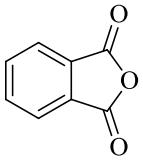
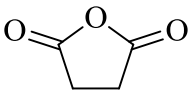
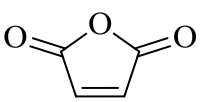
Reagents	Chemical formula	Ref	References and synthesis details	Applications
Sebacoyl chloride (SC)		1	*Solvent*: DMAc *Catalyst*: TEA 110°C – 22h	Polyester synthesis
Terephtaloyl chloride (TC)		150	*Solvent*: DMAc *Catalyst*: TEA 0°C – 1h	
		151	*Co-monomer*: PEG 300,600, 1500 $g.mol^{-1}$ 120-130°C -9h	
Dimer acid		152	*Solvent:* 1,4 Dioxane *Catalyst:* CER Reflux – 5h	Precursor for epoxy resins synthesis
Fatty acids and fatty acid chlorides		153	*Transesterification reaction* *Ester*: methyl 10-undecenoate *Catalyst*: TBD 80°C -8h	ADMET, thiol-ene addition, and polycondensation reaction
		154, 155	Acid: Octanoylchloride 130°C - 4h	Compounds with thermoplastics behaviors
$PBD(COOH)_2$		156	Kraft lignin modified with formaldehyde *Solvent*: 1,4 dioxane *Catalyst*: KOH 100°C - 24h	Lignin-based thermoplastic
HBPEA Highly branched poly(ester-amine)		157, 158	*Solvent*: THF *Catalyst*: TEA 100°C under vacuum - 4h to 20h	Polyesters amine Elastomeric materials
Phthalic anhydride		159	*Solvent*: Pyridine 120°C -3h	Compatibilizer in Low Density Polyethylene
Succinic / Maleic anhydride		160, 161	*Solvent*: basic aqueous media 28°C – 1 to 12h	Increase thermal stability of lignin
		162, 163	*Solvent*: 1,4 dioxane *Catalyst*:1 methyl-imidazole 70°C -12h	Preparation of lignopolyols

Table I- 2. Summary of some representative systems in the field of lignin esterification.

CER: Acid cation exchange resin
ADMET: Acylic Diene Metathesis
TBD: Triazabicyclodecene
DMAc: Dimethylacetamide

4.4.2 Phenolation

Phenolation (or phenolysis) consists in treating lignin with phenol in an acidic medium to lead to the condensation of phenol with the lignin aromatic rings and side chains [12]. This reaction is the most common modification for lignosulfonate, to increase the content of phenolic hydroxyl groups and thus to improve lignin reactivity as a phenol substitute [164]. The resulting material can then react readily with formaldehyde because of the phenolics with free *ortho* and *para* units. This chemical modification is most often used in the synthesis of PF resins where lignin is previously modified by phenol to react with formaldehyde in the same way than with the methylolation reaction that has been previously described. Modified lignin can also be added as a cross-linking material.

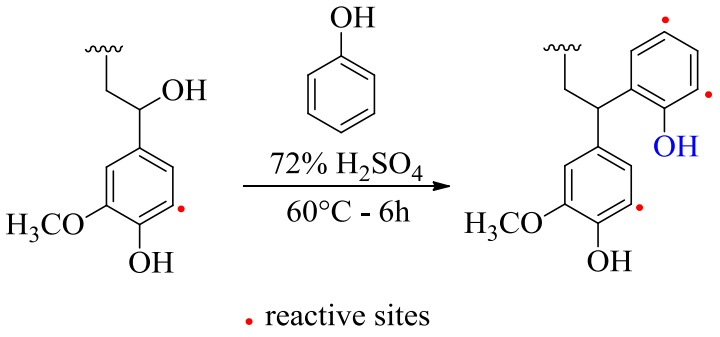


Figure I- 15. Phenolysis reaction and potential reactive sites of phenolized lignin.

A relevant study of phenolation of lignin can be mentioned [165]. This work deals with the phenolation of lignin with cardanol, a natural alkyl phenol from cashew nut shell liquid. The results demonstrate that the use of cardanol to modify lignin for the preparation of polyurethane films can improve some properties of the lignin-based polyurethanes. Moreover, it has been reported that the increase of cardanol content used in Cardanol-Lignin improves the flexibility as well as the tensile strength and the glass transition temperature of the polyurethane films.

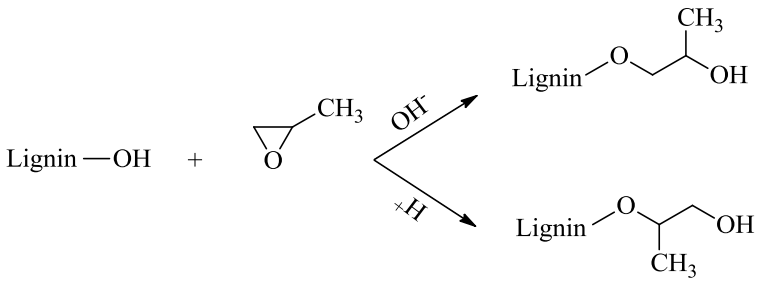
4.4.3 Etherification

Among chemical modification reactions attempted on lignin is its reaction with alkylene oxide, especially with propylene oxide (PO), named in this case "oxypropylation" that is the most well-known [166, 167]. This reaction has been extensively studied by different research groups in the world and remains one of the most attractive etherification alternatives to modify lignins, giving new macropolyols [21, 104]. In fact, the reaction allows transforming a solid and insoluble product -lignin- into a highly soluble polyol, in several common organic solvents. This reaction has been investigated extensively on different biopolymers and biobased materials bearing hydroxyl groups such as chitosan [168], cork [169, 170], pine bark, corn starch [171], sugar beet pulp [172-174] and sugar cane bagasse. This pathway has brought several polyols derived from different biomass-residue that can be potentially used for the production of novel polymeric materials such as e.g., polyurethanes foams [175]. The case of lignin has received considerable attention, Glasser and co-workers being pioneers in 1980s to investigate this type of reaction for the formulation of polyurethanes and epoxy resins [176].

The mechanism involved during oxypropylation is based on the reaction of oxianions generated from the OH groups of lignin in the presence of the basic catalyst with PO. Usually, KOH is used to catalyze oxyalkyalation with hydroxyl groups. Nevertheless, original catalysts have also been studied such as polyphosphazenium, aluminum tetraphenyl porphine, cesium hydroxide and various tertiary amines giving also excellent reactivity of lignin [177].

Through a "grafting from" approach controlled by an anionic ring opening polymerization, the phenolic hydroxyl groups are extended with poly(propylene) glycol chains leading to a long branched polyether with hydroxyl groups at the end. The modification only affects phenolic hydroxyl groups of lignin, oxypropylation being a selective reaction [163, 166]. Various techniques using quantitative methods such as ^{31}P NMR spectroscopy has been performed to highlight this selectivity towards hydroxyl groups [178-180]. However, the oxypropylation reaction is always accompanied by the occurrence of secondary reactions namely, Propylene Oxide (PO) homopolymerisation and isomerisation. The reaction is frequently carried out in bulk and the resulting polyol is a mixture of oxypropylated lignin and poly(propylene) oxide oligomers. Typically, studies related to the synthesis of lignin oxypropylation are conducted in view of polyurethane and/or polyesters synthesis. The resulting homopolymer plays an important role in the ensuing reactivity of polyol mixture with isocyanate and/or carboxylic acid, but also in the mechanical properties of the final polymeric material. The oxypropylation parameters such as temperature (80 to 200°C), type of lignin (organosolv, soda, kraft), nature

and amount of catalyst (1-10% wt %), lignin/PO ratio were varied in order to study their influence on the composition of the resulting polyol mixture. Some studies from Gandini and Belgacem have shown that the content of homopolymer decreased with the increase of lignin/PO ratio whereas catalyst content did not impact significantly this phenomenon [181, 182]. Therefore, organosolv and soda lignins reacted considerably faster than kraft lignins. Molecular weight but also the nature of hydroxyl groups in lignin have then a small influence in lignin reactivity with PO [175]. Among the numerous works dealing with etherification of lignin with alkylene oxides, the main application of the new lignin-based polyol is the synthesis of rigid polyurethane foams (RPUF). Oxypropylation was proved to be a straightforward process yielding polyol with interesting properties for the production of RPUF [183]. The resulting polymers presented good thermal properties and dimensional stability, even after ageing. The absence of the addition of any other polyol or chain extender in the formulations has to be mentioned [181, 184]. Nowadays, this reaction is an encouraging way to valorize lignin in an abundant renewable industrial by-product. In fact, oxypropylated lignin could be introduced in thermoplastics syntheses such as polyol or co-polyol to synthesize new polyester or polyurethane, for example.



Secondary reactions: homopolymerisation (i) and transfer reaction with PO monomer (ii)

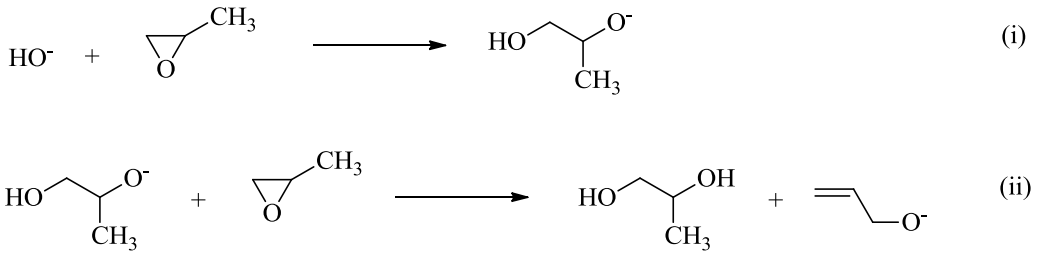


Figure I- 16. Schematic representation of oxypropylation reaction performed using basic or acid catalyst, with the potential side reactions that can occurred.

4.4.4 Urethanisation

Another reaction involving hydroxyl groups is the reaction with isocyanate groups, it means RNC=O active sites. Upon treatment with an alcohol, an isocyanate forms an urethane linkage during an exothermic reaction [177]. The polyurethane (PU) versatility offers the potential of preparing a wide range of products such as low temperature elastomers, high tensile adhesives, flexible or rigid foams depending on their applications. In a global context, factors such as price and availability of raw materials for polyurethanes syntheses contribute to create pressure on the uses of fossil-based products. Many industrials suppliers of chemicals are therefore looking for biobased alternatives of these chemical compounds. A very insistent attention was paid for many years to the use of renewable polyols in the polyurethane synthesis. Lignin can be considered as an aromatic macropolyol and its chemical modification can also convert it in a polyol precursor in the PU synthesis. In order to overcome intrinsic properties of lignin; such as polydisperse molar masses and hyperbranched structure, the reaction of lignin with isocyanate is always supporting by its chemical modification with alkilene oxide, for example [185] or by its mixing with other polyol compounds such as Poly(ethylene glycol) (PEG) or others diols [104, 186]. We can divide lignin based polyurethane synthesis into two main categories: (1) the one step reaction by mixing lignin, diisocyanate with another diol co-monomer, or (2) a two-step reaction procedure with first the synthesis of an isocyanate-based prepolymer and then the polymerization reaction between lignin and this prepolymer, as a polyol chain extender.

Briefly, in the first approach, lignin is used directly without further chemical modification in combination with different polyols. In such a multicomponent system, lignin and the diisocyanate play the role of “hard segment” whereas the diol constitutes the main soft segment in the architecture of the lignin-based polyurethane. The segregation hard-soft segments give a specific nano/micro-organization to control the final global properties. Among different studied systems, we can mentioned the use of PEG with different average molar mass, varying from 400 to 2000 $g.mol^{-1}$ [187-189] and Poly(caprolactone)-PCL- diol (400-750-1000 $g.mol^{-1}$) [190]. 4,4’ Diphenylmethane diisocyanate (4,4’ MDI) is used as isocyanate. Resulting materials from the first synthetic route were described as three-dimensional networks whose lignin acts as a crosslinking agent. Thring et al [188] describe the macromolecular architecture of the polyurethane as a network consisting in relatively large and stiff islands, each comprising many branch points (i.e., chemical bonds), held together by a soft and pliable matrix. In each study, authors pointed out the fact that the molar mass of the

diols affects considerably the properties of the ensuing material by influencing the crosslink density of the synthesized network.

In the second approach, close to industrial production, a two-step process is used. First, the synthesis of isocyanate prepolymer is carried out using diisocyanate (MDI or 2,4-diisocyanato-1-methyl-benzene-TDI) with another shorter polyol, as chain extender. This method has been recently reviewed [191]. Two relevant studies investigated respectively by the groups of Sarkar and Huang have to be mentioned [192, 193]. In the first one, they synthesized a prepolymer with Hydroxyl Terminated PolyButadiene (HTPB) and 2,4 TDI [192, 193] with three molar ratios of NCO:OH (1.5, 2 and 2.5). Lignin is then reacted with the prepolymer with a lignin content reaching 15wt%. These experiments give flexible polyurethanes with good mechanical properties (Figure I-17). However, the best results are obtained with only 3 wt.% of lignin. In the second study [146], a prepolymer was synthesized in the presence of castor oil and TDI with an NCO:OH molar ratio of 2.0. Then, three solutions with PU prepolymer, nitrolignin and butanediol (BDO) were mixed and stirred together with different NCO:OH molar ratios (from 0.73 to 2.0) and a constant amount of lignin (2.8 wt.%) to obtain a series of graft IPN.

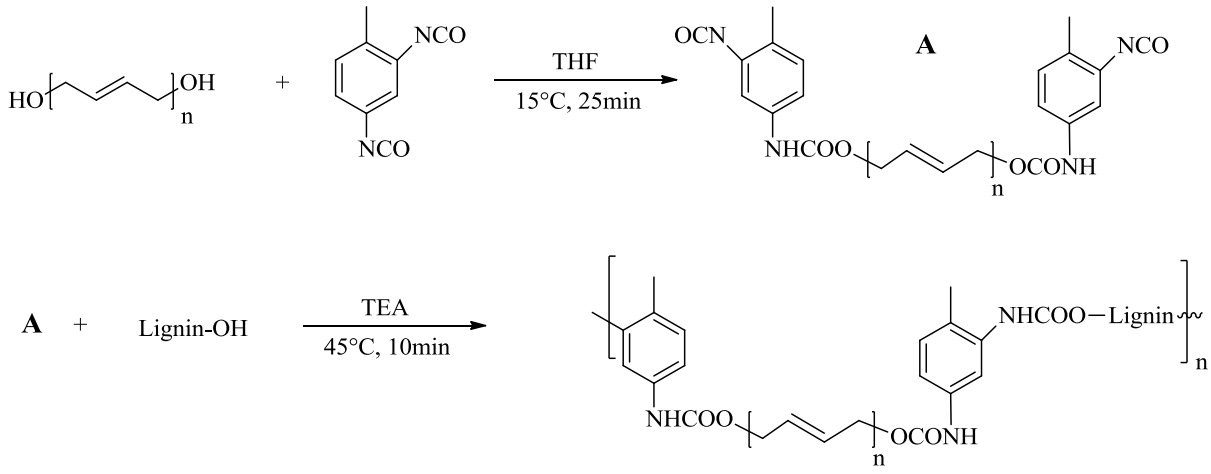


Figure I- 17. Reaction scheme for synthesis of HTPB polyurethane and lignin-HTPB copolyurethane.

4.5 Toward lignin based polymers and materials

4.5.1 Lignin as a viable route for polymers syntheses

As previously discussed, due to the aromatic structure of lignins, most of the materials based on the simple addition or incorporation of lignin is too brittle. Accordingly, lignin should be chemically modified and synthesized with other polymers to be suitable for getting materials with advanced properties such as polyurethane and polyester polymers [194]. Through the functionalization of its hydroxyl groups, lignin becomes a good candidate as a building block unit for polymer synthesis to elaborate innovative macromolecular architectures [38]. The elaboration of numerous polymers by using lignin degradation products such as e.g., polyhydroxystyrene derivatives, polyethers and polyesters [195, 196] must be mentioned.

Several attempts have been made to integrate lignin into industrial processes to highlight its use as a renewable feedstock for replacement of synthetic phenols in binders and in epoxy or phenol-formaldehyde resins formulations, for example [197]. Literature reports several methods to synthesize lignin-based epoxy resins. They have been applied for polyesters and phenolic resins applications, following different strategies[198] such as (i) blending lignin with epoxy resins [199], (ii) modifying lignin by epoxidation reaction, usually with epichloridrin [200] or (iii) modifying lignin by chemical reactions to improve its reactivity before the epoxidation step. Among all of the work dedicated to lignin-based epoxy resins synthesis, we have to mention the relevant work of Ismail et al. (2010) [201]. Sodium sulfate lignin and glycerol were modified with anhydride to formed ester-carboxylic acid derivatives, and used to crosslink glycerol diglycidyl ether and ethylene glycol diglycidyl ether to obtain the bio-based epoxy resins with adhesives applications. The main application of those types of resins is the use as binders in replacement of PF resin in particleboard and plywood. Lignin-based epoxy resins show particularly high thermal stability and allow widen the range for applications based on lignin epoxy resins.

The synthesis of PUs has also been extensively investigated to explore high-value applications of lignin e.g., as a polyol (as previously mentioned, section *4.4.3* and *4.4.4*). In this way, thermoplastics [202], rigid and flexible foams [203, 204] but also elastomers [205] were performed with advanced properties. In their review, Hatakeyama and Hatakeyama (2010) [20] emphasize that lignin chemical pre-modification increases the cost of the resulting PUs and reduce their competitive advantage compared to materials derived from fossil resources. According these authors, the use of lignin without further modification could be thus preferable. However, recent studies circumvent this problem by using lignin directly with

suitable macrodiols (PEG, DEG, TEG and glycerol) as co-monomer and co-solvent to reduce the number of chemical steps and also the cost of polymer processing [203]. According to this approach and with the use of polyisocyanate in the presence of surfactant, plasticizer, DBTDL and water (foaming agent), lignin-based rigid polyurethane foams were synthesized from Kraft, lignosulfonates, and hydrolysis lignins (Figure I-18).

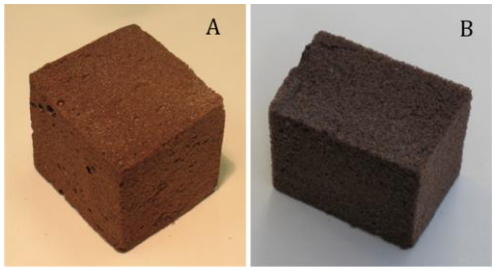


Figure I- 18. Example of rigid polyurethane foams made with lignin. A: PU foam based on 50% of organosolv lignin; B: PU foam based on 50% hardwood kraft lignin [204].

Polyurethane rigid foams have been also successfully obtained from oxypropylated lignin [181, 182, 190] (Section *4.4.3*).

Cazacu et al. (2013) have presented a good overview on lignin application perspectives for materials [37]. They highlight that integration of lignins in multi-component materials have been encouraged the last 10 years by their wide accessibility, low price and performances such as low density, high hardness, good thermal properties, chemical, friction and humidity resistance. However, until now, none of polymers developed at academic level have reached a sizable industrial scale.

4.5.2 ATRP - A useful method to develop lignin-based functional material

The use of lignin as a macroinitiator in atom transfer radical polymerization (ATRP) has been studied for the first time by the group of Kadla (2010)[206, 207]. The resulting graft copolymers displayed thermoresponsive properties due to the N- isopropylacrylamide (NIPAM) polymers grafted from Kraft lignin. This method provided good results to graft copolymers with well-defined structures onto lignin. In addition, this polymerization procedure has been successfully used to prepare polymers with various complex macromolecular architectures such as branched structure or linear chains with controlled dimension and dispersity [208]. This new approach offers several advantages including the

possibility to modulate molecular weight of grafted chains but also the number of grafts per macroinitiator. By designing new lignin-based-macroinitiators, it can be possible to polymerize them with different monomers in a controlled free radical system. 2-Bromoisobutyryl bromide (BiBB) is commonly used as an initiator for ATRP syntheses, and can be easily attached to lignin by esterification reaction with its phenolic and aliphatic hydroxyl groups in presence of catalyst, generally TEA is used. By varying ratios between BiBB, catalyst and hydroxyl groups of lignin, it was possible to modulate the number of bromine initiator sites per lignin molecule. A recent study succeed in synthesis of rosin polymer-grafted lignin composites by "grafting from" ATRP that showed interesting hydrophobic and high resistance water properties (around 90° of contact angle, less than 1.0 wt% of water uptake) [209] (see Figure I-19).

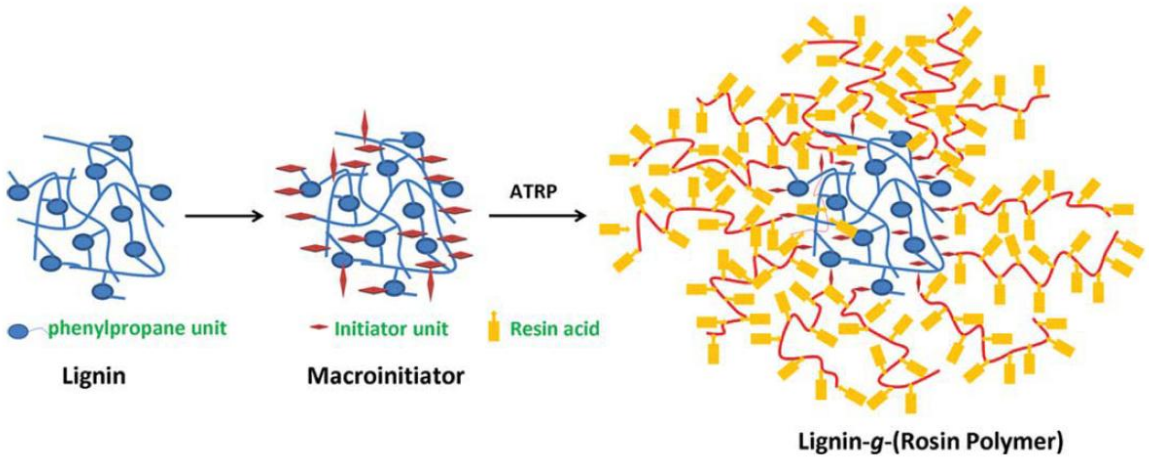


Figure I- 19. General scheme of lignin macroinitiator synthesis and rosin polymer-grafted lignin composites [209].

4.5.3 High performance material made with lignin: carbon fibers.

Carbon fibers (CF) for high performance composites materials are one of the most important advanced engineering products produced today [210]. CF possess unique combination of properties that make them suitable for a wide range of applications (sports equipment, marine products, construction, aircraft and also automotive industry). CF are lightweight, have high strength, flexibility and fatigue resistance resulting from the orientation of the fiber during the production process. Currently, the precursor raw materials used for CF production are polyacrylonitrile (PAN) and to a lesser extent, coal or petroleum derived pitch and regenerated cellulose. The CF manufacturing process involves *melt* or *wet-spinning* (according to the raw material), *oxidative stabilization* at 200–300°C and *carbonization* under

an inert atmosphere at 1000-2000°C, (in some cases, graphitization at 2000–3000°C), which is then followed by surface treatment and sizing [211].

Almost 80% of commercial CF is predicated on using PAN as the starting raw material, but its expensive cost has thus limited application to high performance material. For more than 40 years, a large activity in research and patents has shown a wide interest for lignin-based CF, which takes advantages to be readily available at relative competitive prices. The first CF made with lignosulfonate lignin, using poly(vinyl alcohol) as a plasticizer has been manufactured and developed by Nippon Kayuka Company under the name of Kayacarbon during 1967-1973 period. Various type of lignin have ever been studied for the production of low-cost CF. Kadla and co-workers [210] have studied the use of Kraft lignin without chemical modification. They have developed a specific method to remove impurities such as carbohydrates or inorganic compounds from lignin and decrease the hydroxyl content by condensing the lignin. Fiber spinning was then facilitated by the addition of the poly(ethylene oxide) PEO (3 to 5%) to lignin. This work constitutes actually a reference in this scientific area because they reported the first lignin-based CF made with a commercially available Kraft lignin. The use of pyrolitic lignin has also been studied highlighting that under precise conditions parameters, mechanical properties for CF were similar to those obtained with Kraft or Alcell (organosolv) lignins [212].

Nordström [213] et al. (Innventia) have developed a new softening agent for melt spinning softwood Kraft lignin based on ultra-filtrated black liquor. They achieved to obtain CF of very good quality solid carbon fibers. In parallel, they also developed a method to stabilize lignin CF using special oxidative conditions. These new improvements in lignin-based CF present a great potential to reduce time and cost production and to use lignin in larger scale applications. However, the need to purify lignin to make it suitable for melt spinning and carbon fiber production increases the cost of lignin based CF. The production of “low cost” carbon fibers still remains a challenge, lignin being low cost raw material compare to PAN with mechanical properties suitable for CF commercial grade [214, 215]. The development of lignin based high performance material will results in real benefits in the contexts of increased energy efficiency and reduced environmental production.

4.5.4 Toward commercialized lignin-based polymers

Recently, a new lignin-based thermoplastic polymer has been commercially developed under the trade name Arboform® (latin: arbor – the tree) by Tecnaro (Germany) [216]. This new thermoplastic material is made from specific types of lignin with natural fibers from wood, flax, hemp, sisal or other fibrous plants and natural additives (such as wax), which can be processed on injection molding machine at raised temperatures. The others advantages for this lignin-based thermoplastic include very low swelling and very high transverse tensile strength. The first produced Arboform® has been on the market since November 2000, and there are diverse applications e.g., in automotive sectors, children's toys, furniture, castings for watches, designer loudspeakers, degradable golf tees and even coffins…One of determinant barriers to the development of this material it is his price which start at 2.5 € per kilogram whereas conventional thermoplastic cost is 1-2 € per kilogram. However, the increasing demand of biobased polymers and the high performance of these new thermoplastic polymers give promising results to pursue research efforts in lignin valorization.

5. Conclusion

Over 70 million tons of lignin are produced annually in the world and around 95% are burnt. The remaining 5% is actually used for commercial applications including additives, dispersants, binders or surfactants. Observing the great number of studies performed on lignin, new technologies for extracting and processing it, lignin receive greater attention as the aromatic compounds (C_6 …) from oil exploitation are now more rare, and more costly. In this way, the emerging concept of biorefinery aimed to regard lignin as a high value added product that can compete with non-renewable aromatic compounds. In recent years, this renew interest on lignin has stimulate a great number of researches for the development of an economically viable lignin valorization route in view of production of chemicals and biobased polymers. For example, its depolymerization into phenol and BTX provides wide varieties of fine and bulk chemicals. Among all of modifications performed on lignin, some valuable successes have emerged with the industrial elaboration of vanillin, DMSO and lignin-based polyol for the synthesis of polymer giving high performance materials. However, the intrinsic properties of lignin, the variability of the resource, polydisperse molar masses and

hyperbranched structures have hindered the development of lignins materials revealing that the use of high-purity lignin is also an important issue for its valorization. However, it has to be highlighted that lignin's isolation, purification and drying require costly investments that add up to its price as a raw material. Lignin sales value vary from low grade to high grade lignin from about 50 to 1200 €/ton, knowing that the more well-defined is lignin, the more suitable it is for chemical modification, lignin becoming then a high value product...

The employment of lignin by chemistry and polymer industries represents an important field of research with major issues in term of scientific, economical and also environmental point of views and it seems to be justified that lignin will become a promising renewable aromatic resource in subsequent years.

Acknowledgments

We are grateful for Alsace Region, Oséo and ANRT for their financial supports.

Cette étude bibliographique met en évidence les différents travaux et principaux axes de recherche suivis autour de la modification chimique de la lignine. Les premiers développements principalement dédiés à la caractérisation et l'élucidation de la structure des lignines, ont permis de développer de nombreuses techniques visant à fractionner, modifier ou fonctionnaliser la lignine. La plupart de ces recherches, en étroite relation avec l'industrie papetière ou encore les biotechnologies a participé à l'élargissement de nos connaissances sur cette matière biosourcée et a contribué à sa valorisation, notamment pour la synthèse de divers polymères fonctionnels, avec des architectures macromoléculaires particulières.

II. Présentation générale des Polyuréthanes

La première synthèse de polyuréthane a été réalisée par le Dr. Otto Bayer en 1937. Cette découverte a permis d'ouvrir la voie à l'élaboration de nouvelles structures macromoléculaires aux propriétés multiples et modulables issues de la réaction entre un polyol et un diisocyanate. La chimie des polyuréthanes repose donc sur une technologie débutée il y a 75 ans et qui s'est développée très rapidement. Elle couvre actuellement une large gamme d'applications: élastomères, thermoplastiques, mousses, mastic, adhésifs, fibres et autres thermodurs…[177] Les matériaux polyuréthanes occupent ainsi une place de choix dans l'industrie des matières plastiques et se placent au sixième rang des polymères les plus utilisés. En 2010, la production mondiale de PU atteignait 10 Mt. La grande diversité des PU est conférée à la fois par leurs organisations mais aussi par leurs natures chimiques différentes qui permettent de moduler les propriétés physiques et chimiques. Les principaux avantages des PU résident ainsi dans une grande résistance à la rayure et l'abrasion, mais aussi dans le cas des TPU par exemple, dans une forte élasticité et une souplesse, accompagnée d'une résistance à la rupture et au déchirement qui en font un matériau de choix dans le domaine des revêtements.

Les deux principaux réactifs intervenant dans la réaction de polyaddition sont généralement issus de ressources fossiles. Néanmoins, dans le contexte économique et environnemental actuel, industriels et chercheurs se sont rapidement intéressés à la substitution d'une partie de ces réactifs par des produits bio-sourcés, issues de ressources renouvelables. Ces derniers présentent de nombreux avantages et peuvent, dans certains cas, être compétitifs même en termes de prix. C'est le cas par exemple de certains polyols utilisés dans la production de mousse PU, notamment pour l'industrie automobile ou l'isolation de bâtiments.

1. La chimie des polyuréthanes

Comme nous l'avons évoqué précédemment, les matrices polyuréthanes présentent une grande diversité de structures et de propriétés entre les thermodurs et les thermoplastiques, voire les élastomères, par l'intermédiaire d'une chimie modulable pour l'élaboration de diverses structures finales.

1.1 Mécanisme réactionnel entre un alcool et un isocyanate

La fonction uréthane est obtenue par réaction entre un alcool et un isocyanate. La réaction de polymérisation correspondante est une réaction de polyaddition (Figure I-20).

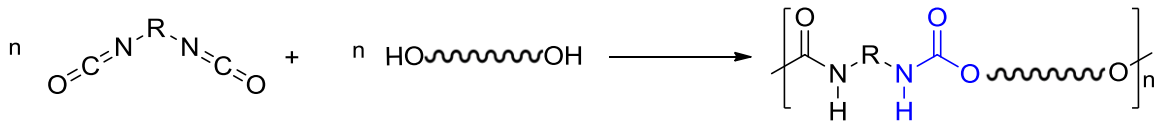


Figure I- 20. Schéma de la formation d'un polyuréthane.

Les isocyanates sont caractérisés par une réactivité importante et modulable liée à un fort caractère électrophile de l'atome de carbone, ce qui rend le groupe fonctionnel particulièrement réactif vis-à-vis d'agents nucléophiles[217]. Les isocyanates utilisés dans la synthèse de PU sont généralement bi-fonctionnels, ils peuvent être soit de nature aromatique soit de nature aliphatique. Les structures des principaux diisocyanates sont représentées sur la Figure I-21.

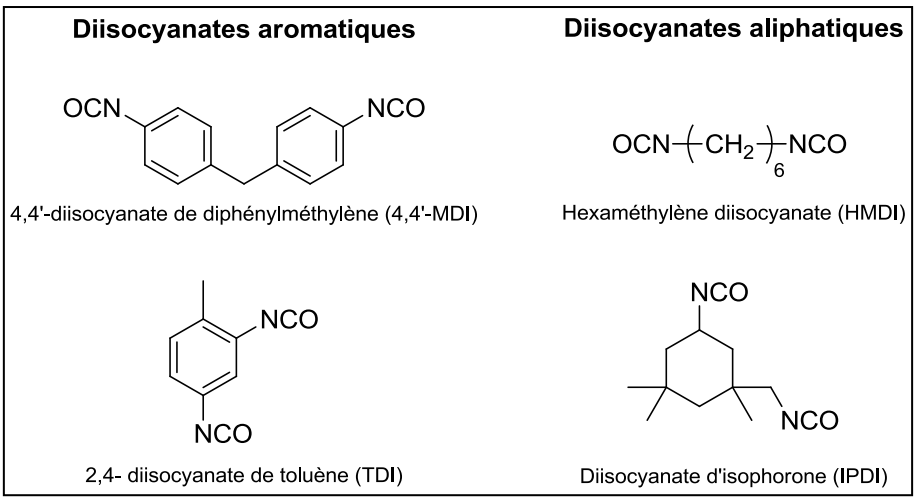


Figure I- 21. Structures des diisocyanates fréquemment utilisés.

La nature du substituant du groupe isocyanate influe également sur la réactivité de cette fonction. Ainsi, l'encombrement stérique autour de la fonction NCO peut affecter fortement la réactivité du composé. Par ailleurs, les isocyanates aromatiques sont plus réactifs que les isocyanates aliphatiques. En effet, la réactivité du groupement NCO augmente lorsqu'il y a conjugaison avec une double liaison du groupe qui le porte. Enfin, lors de la réaction d'un

diisocyanate avec un alcool, la réactivité de la fonction isocyanate restante peut être modifiée et devient souvent inférieure à celle de la première fonction ayant réagi. On pourra ainsi parfois observer une limitation de l'allongement des chaines lors de la synthèse des PU mais également une augmentation de la proportion d'isocyanate libre dues à cette baisse de réactivité.

La réaction alcool-isocyanate peut-être catalysée par un acide ou une base de Lewis générant la formation d'un complexe de coordination intermédiaire entre le catalyseur, l'alcool et l'isocyanate. En tant qu'acide de Lewis, les composés organométalliques et plus précisément les sels d'étain sont souvent utilisés. On peut par exemple citer le dilaurate de dibutylétain (DBTDL - Figure I-22) qui est un sel d'étain fréquemment utilisé pour ce type de réaction.

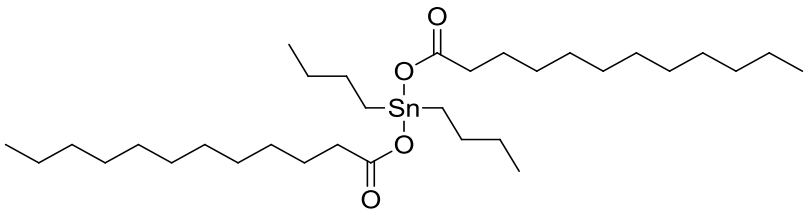


Figure I- 22. Structure du dilaurate de dibutylétain (DBTDL).

L'utilisation d'amines tertiaires est également possible, activant ainsi la fonction alcool en rendant le proton plus labile et donc plus réactif. Toutefois, il est à noter que ce type de catalyseur active non seulement la réaction entre l'isocyanate et l'alcool mais favorise aussi les réactions secondaires pouvant intervenir dans le système réactionnel.

1.2 Réactions secondaires

La réactivité importante des isocyanates est aussi à l'origine de nombreuses réactions secondaires pouvant intervenir lors de la réaction de polymérisation.

- En présence d'eau, les isocyanates forment des amines qui s'accompagnent d'un dégagement de CO_2. L'amine ainsi formée peut réagir avec d'autres fonctions isocyanates pour donner des groupements urée (Figure I-23). La formation d'urée est parfois recherchée dans les systèmes PU car elle confère généralement d'excellentes résistances chimiques et thermiques aux matériaux. L'utilisation de diamines comme allongeurs de chaines conduit alors à la formation de polyuréthanes-urées (PUU). La plupart des PUU

étudiés dans la littérature sont des élastomères et présentent une plasticité réduite par rapport aux PU [218].

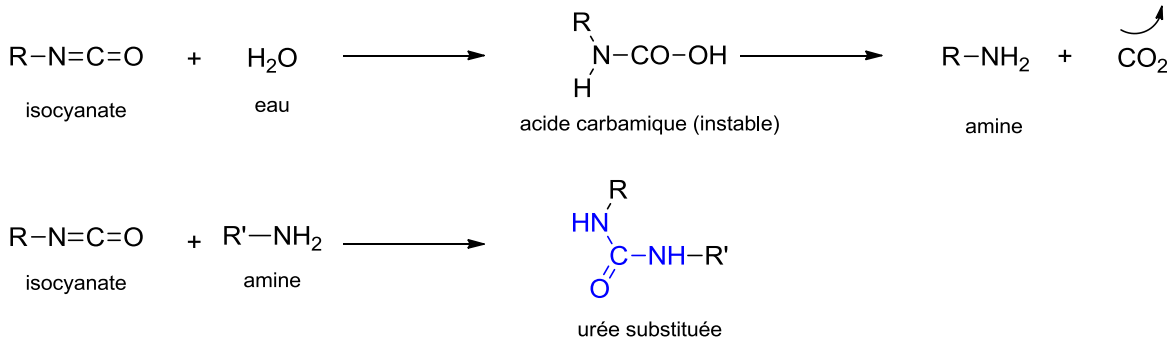


Figure I- 23. Réaction de la fonction isocyanate en présence d'eau.

- A température élevée (100-140°C), les isocyanates peuvent réagir avec les groupements uréthane ou urée pour former des liaisons allophanates ou des biurets respectivement[219]. Dans le cadre de la synthèse de PU linéaires, ces réactions secondaires peuvent engendrer la formation de ramifications sur les chaînes linéaires en croissance (Figure I-24).

- Enfin, la présence de catalyseur ou encore l'utilisation de températures extrêmes peuvent entrainer la formation de dimères, trimères voire de polymères d'isocyanates[220]. Ces réactions peuvent ainsi participer à la réticulation partielle du matériau.

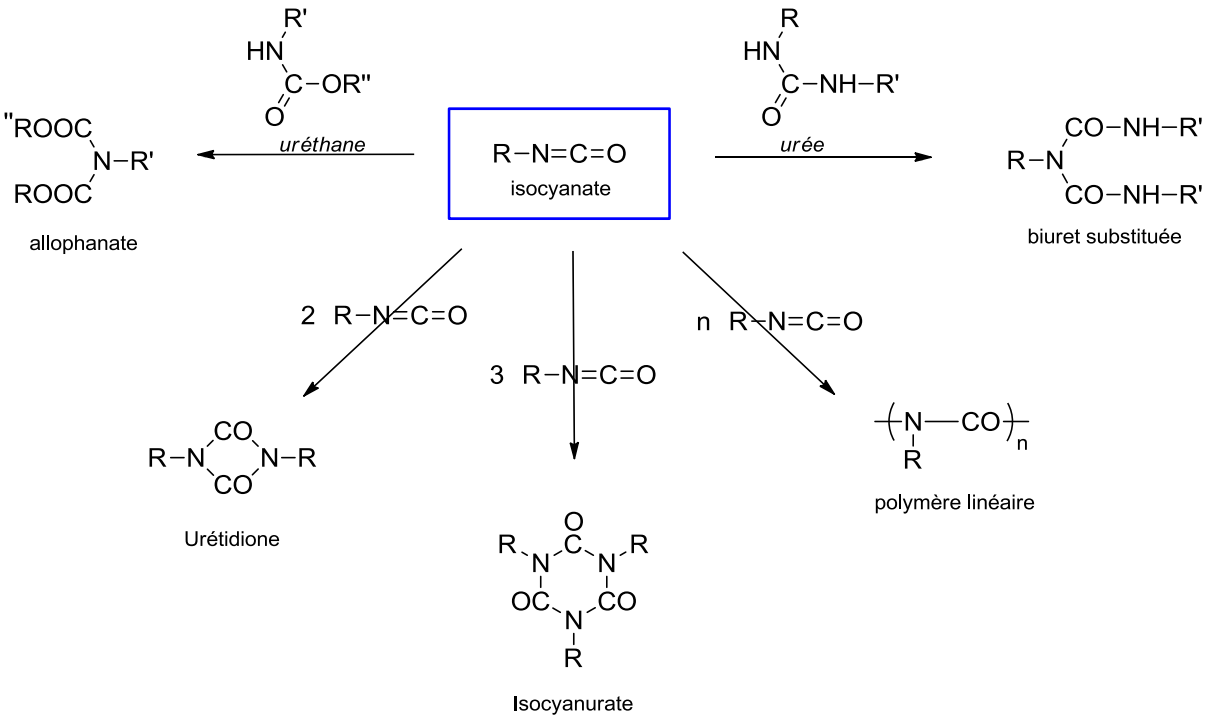


Figure I- 24. Ensemble des réactions secondaires pouvant s'effectuer avec les isocyanates en conditions de synthèse particulières.

Par ailleurs, il est important de signaler que la réaction alcool-isocyanate est réversible à haute température[221, 222]. Les liaisons uréthanes se dissocient alors pour reformer les fonctions alcool et isocyanate. Cette liaison peut toutefois se reformer lors du refroidissement tout en gardant à l'esprit la formation possible d'allophanate résultant de la réaction d'isocyanates libres avec les fonctions uréthanes. La dégradation thermique des PU est donc un paramètre qui doit être pris en compte pour toute étude de ce type de matériau.

2. Procédés de synthèse

Les procédés de synthèse des PU se distinguent principalement par les séquences d'ajout des réactifs. On parlera ainsi de procédé en une ou deux étapes.

2.1 Le procédé en deux étapes

La plupart des synthèses de polyuréthanes fait intervenir un procédé en deux étapes avec l'utilisation d'un prépolymère intermédiaire[223]. Ce prépolymère est tout d'abord synthétisé en mettant en présence un excès de diisocyanate et un macrodiol. Il est alors constitué de chaînes de polyols reliées les unes aux autres par des liaisons uréthanes et peut-être caractérisé par son taux de NCO correspondant au pourcentage de fonctions NCO libre dans le système[224].

La seconde étape de ce procédé consiste à synthétiser le polymère final. Les fonctions isocyanates restantes en bout de chaînes du prépolymère vont réagir avec un allongeur de chaînes (composé hydroxylé de faible masse molaire, généralement un diol court du type 1,4 butanediol) pour terminer la réaction et finalement obtenir un PU linéaire (Figure I-25). Les PU ainsi obtenus sont constitués par l'alternance de chaînes flexibles (appelées *segments souples* - SS) constituées principalement de macrodiol, et de blocs rigides (appelés *segments rigides* - SR) formés par la réaction du diisocyanate avec l'allongeur de chaînes. La figure I-25 détaille les différentes étapes du procédé [225].

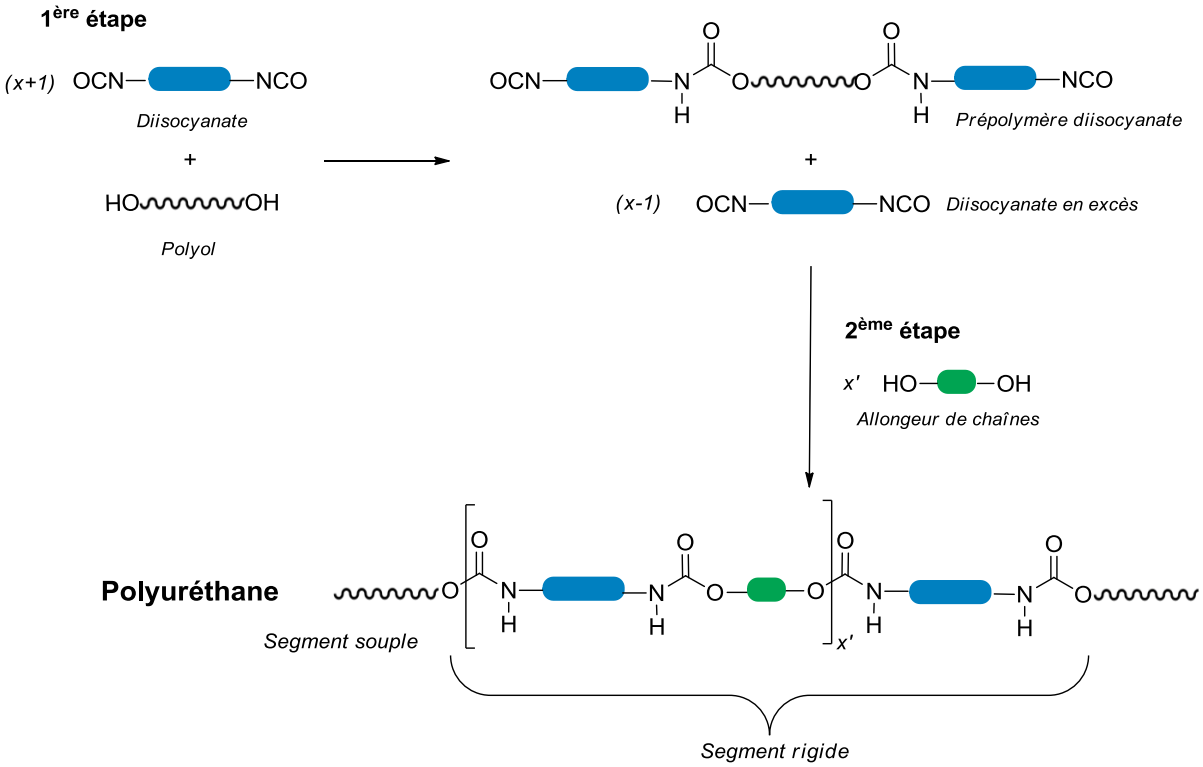


Figure I- 25. Schéma du procédé en deux étapes avec synthèse d'un prépolymère intermédiaire pour l'élaboration de polyuréthanes.

2.2 Le procédé en une étape

Dans les conditions industrielles, on retrouvera également le procédé en une étape consistant à mélanger directement l'ensemble des réactifs ; le macrodiol, l'allongeur de chaîne, le diisocyanate et le catalyseur éventuellement. En revanche, ce procédé ne permet pas un contrôle précis de la structure finale du PU mais convient particulièrement pour la synthèse de réseaux thermodurcissables ou encore de mousses.

Dans le cadre de notre étude nous nous sommes concentrés sur le procédé de synthèse en deux étapes qui permet un contrôle privilégié de la croissance des chaines de PU, mais aussi favorise la séparation de phase (voir Partie *1.4 Le cas particulier des polyuréthanes segmentés*) [226].

3. Morphologies des polyuréthanes

La très grande variété des structures chimiques d'isocyanates mais aussi de polyols permet d'accéder à une multitude d'architectures macromoléculaires de PU avec un éventail de propriétés très large. Nous allons brièvement décrire les principales morphologies que l'on peut retrouver pour les matrices PU. Enfin, nous décrirons de façon plus détaillée les polyuréthanes élastomères thermoplastiques segmentés linéaires ou TPU.

- Les polyuréthanes linéaires sont obtenus par réaction de polyaddition entre des monomères (alcool et isocyanate) de fonctionnalité 2 (Figure I-26). L'utilisation de monomères aliphatiques de masse molaire élevée génèrera la formation de chaines de polymères à structure linéaire caractérisées par une température de transition vitreuse (T_g) relativement faible. En revanche, l'utilisation de diols de faible masse molaire ou de diisocyanates aromatiques permettra de former des chaines linéaires moins flexibles avec une T_g plus élevée.

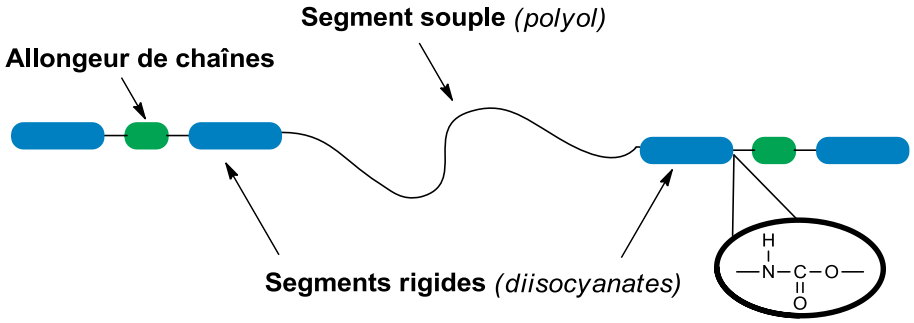


Figure I- 26. Structure d'une séquence dans un polyuréthane linéaire.

- La synthèse de réseaux thermodurcissables est obtenue avec au moins un monomère de fonctionnalité supérieure à 2. L'utilisation de monomères polyfonctionnels entraine ainsi la formation de réseau tridimensionnel, hyperbranché avec une température de transition vitreuse élevée pouvant aller jusqu'à 130°C.
- Enfin, les PU segmentés linéaires ou *TPU* sont des copolymères à blocs de type $(AB)_n$, dans lequel les blocs A et B, de nature chimique différente sont liés de façon covalente. En ce qui concerne les TPU, les blocs A et B représentent respectivement les segments souples (*SS*) et les segments rigides polaires (*SR*).

4. Le cas particulier des Polyuréthanes segmentés

Les propriétés particulières des TPU reposent sur leurs capacités à s'organiser à l'échelle macro/nanoscopique. Ce phénomène appelé « micro séparation de phase » résulte de l'immiscibilité thermodynamique entre les chaines de segments souples et les segments rigides du système, associée à l'existence de liaisons covalentes qui empêchent toute séparation macroscopique. Cette microséparation de phase entraine la formation d'un système biphasique où les segments rigides sont souvent regroupés en micro-domaines, dispersés dans une matrice de segments souples majoritairement constituée par le macrodiol (Figure I-27). Généralement, le segment rigide est caractérisé par les groupements uréthane et par les diols à chaînes courtes (allongeur de chaînes), non miscibles dans la matrice des segments souples et assurant la stabilité dimensionnelle du matériau.

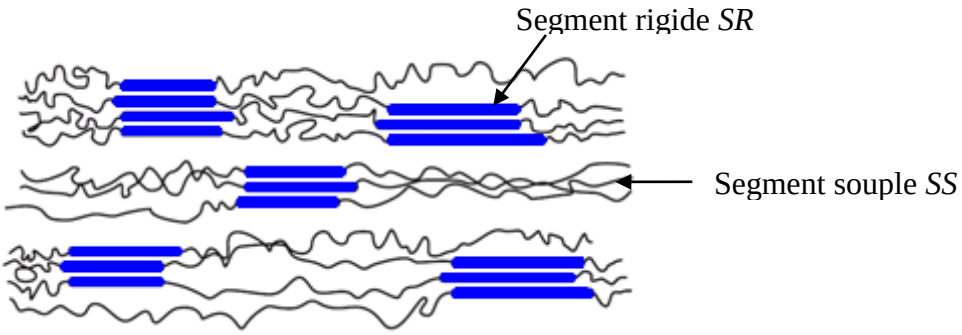


Figure I- 27. Représentation schématique de la séparation de phase dans une matrice polyuréthane[227].

Les propriétés finales de ces matériaux seront donc non seulement liées à la nature chimique des composants mais également au degré de séparation des phases entre domaines souples et rigides. La qualité de cette séparation de phase peut être reliée à différents facteurs. Par exemple, la formation de liaisons hydrogène entre les fonctions éther/ester des segments souples et les domaines rigides limitent la séparation de phase. Les polyesters contenant par ailleurs plus de fonctions polaires, sont davantage susceptibles de former des liaisons hydrogène accentuant ainsi cette structuration[228]. La masse molaire des segments souples est également un facteur important dans la structuration des TPU. Pour une même quantité de segment rigide, l'augmentation de la masse molaire du segment souple accentuera la séparation de phase dans la matrice[218]. Dans le cas des PUU, la diamine est utilisée comme allongeur de chaines pour la formation des segments rigides.

Afin de faciliter la mise en évidence et l'étude de cette ségrégation de phases, différentes techniques peuvent être utilisées telles que l'analyse calorimétrique différentielle à balayage (DSC), l'analyse mécanique dynamique (DMA), la rhéologie, la diffusion des rayons X aux petits angles (SAXS), la microscopie à force atomique (AFM)[227] et la microscopie électronique à balayage ou en transmission (MEB[229] et TEM).

5. Utilisation de la lignine pour l'élaboration de PU

La première partie de ce chapitre (*Review*) nous a permis de recenser les nombreuses ressources bibliographiques concernant l'utilisation de la lignine pour l'élaboration de polymères. Une littérature abondante est ainsi consacrée à la synthèse de PU à partir de lignine et les stratégies de synthèse peuvent se séparer en 2 voies distinctes. En effet, la lignine présente une réactivité réduite vis-à-vis des groupements isocyanates, en raison des fonctions hydroxyles peu accessibles, c'est pourquoi elle est généralement modifiée en vue de la synthèse de polymères. Toutefois, certaines études principalement consacrées à l'élaboration de matériaux PU par méthode de « solvent casting » utilisent la lignine dans des systèmes tri-composants faisant intervenir directement la lignine non modifiée avec un diisocyanate et un co-monomère, généralement un diol de type poly(éthylène) glycol (PEG) ou poly(propylène) oxyde (PPO) de différentes masses molaires. On peut notamment citer les travaux de Thring et al. qui ont synthétisé des PU flexibles mais relativement fragiles à partir de lignine organosolve (Alcell ®)[188, 189]. Des études antérieures menées par Rials et Glasser[230] avaient également démontré le comportement cassant et très fragile de polyuréthanes préparés

par la même méthode et synthétisés avec un mélange de lignine et de MDI. La nature aromatique de la lignine et du diioscyanate ainsi que la structure très réticulée en résultant, expliquent ces comportements mécaniques. L'introduction de segments souples dans de telles formulations s'était alors révélée indispensable afin d'améliorer les propriétés physico-chimiques et mécaniques des matériaux.

La deuxième voie d'obtention de PU à partir de lignine nécessite une modification chimique préalable de celle-ci. Cette modification a pour objectif d'améliorer la réactivité de la lignine vis-à-vis des isocyanates, en rendant les fonctions hydroxyles plus accessibles et disponibles. La technique de déméthylation permet par exemple d'intégrer de nouveaux groupes hydroxyles phénoliques, plus réactifs, dans la structure. Les travaux récents de Chung et al. concernent le prétraitement de la lignine par un acide de Lewis (HBr + TBHDPB) permettant de déméthyler la lignine et d'obtenir une augmentation de ces fonctions hydroxyles d'environ 28%. Ce prétraitement suivi d'une réaction avec le TDI et enfin l'ajout d'un PEF en tant que segment souple a permis la synthèse de PU. Les matériaux ainsi obtenus se sont révélés plus performants que les PU synthétisés avec une lignine non modifiée. L'augmentation de la densité de réticulation des réseaux formés a permis d'améliorer les propriétés mécaniques.

Les nombreux travaux concernant l'élaboration de mousses rigides PU (Rigid Polyurethane Foams - RPUF) doivent également être signalés. Il s'agit de l'application la plus développée permettant de valoriser la lignine. L'élaboration de ces mousses est toujours consécutive à une réaction d'oxypropylation mettant en jeu de l'oxyde de propylène qui polymérise par ouverture de cycle à partir des fonctions hydroxyles de la lignine, formant alors des chaines de PPO greffées. Les polyols polyethers ainsi obtenus présentent des indices d'hydroxyles (concentration OH) élevés et peuvent donc être intégrés dans la formulation des mousses en réagissant avec les isocyanates, en présence de surfactant, d'agent gonflant et de catalyseur. Les mousses alors synthétisées présentent des cellules fermées et possèdent de très bonnes propriétés par rapport à des mousses PU classiques (Figure I-28).

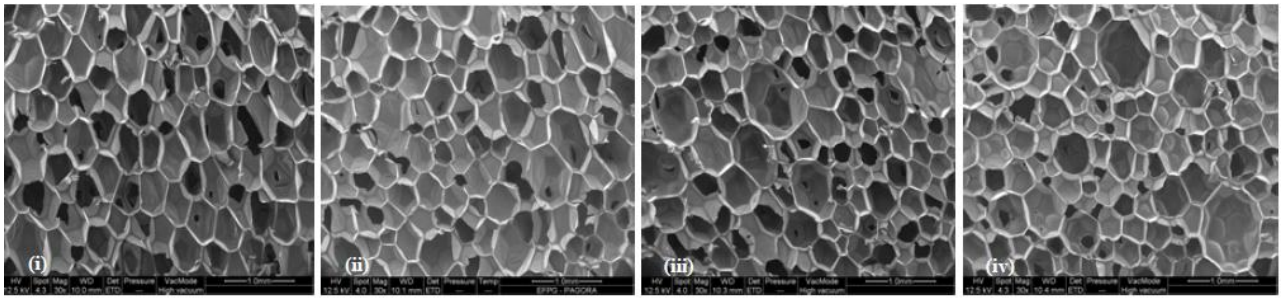


Figure I- 28. Images MEB obtenues pour des mousses PU contenant respectivement (i) 25%, (ii) 50%, (iii) 75% et (iv) 100% de polyols à base de lignine organosolve (Alcell ®)[231].

Les mousses présentent des tailles de cellules pouvant varier de 0,48 à 0,67 mm pour les celles synthétisées avec 100% de lignine en tant que polyol. Toutefois, la grande hétérogénéité dans la taille des cellules limite leurs utilisations en terme de conductivité thermique.

Nadji et al. ont également montré l'excellente tenue au vieillissement des mousses PU développées à partir de lignine organosolve et soda (Figure I-29). Les mousses présentent des T_g aux alentours de 60°C avec des propriétés semblables à celles obtenues avec des polyols commerciaux (stabilité dimensionnelle, isolation thermique…)

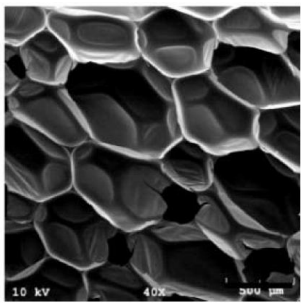


Figure I- 29. Photographie d'une mousse polyuréthane synthétisée à partir de lignine organosolve oxypropylée[232].

Les polyols synthétisés à partir de lignine permettent d'obtenir des PU fortement bio-sourcés. L'étude de ces structures chimiques dans la littérature a mis en évidence l'influence de plusieurs paramètres tels que la nature de l'isocyanate, le ratio NCO:OH et la réticulation sur les propriétés des PU. Ces propriétés extrêmement variables entre les matériaux permettent ainsi d'expliquer l'infinité des domaines d'applications de cette classe de polymères. Par ailleurs, la fonctionnalité moyenne des réactifs, l'écartement entre les fonctions isocyanates et la présence de fonctions structurantes au sein des polyols sont autant de paramètres sur lesquels on peut agir lors de la synthèse des PU afin d'en ajuster les propriétés finales. Notre étude se positionne dans cette optique pour chaque synthèse de PU. La caractérisation de la structure du macropolyol développé à base de lignine et son influence sur les propriétés finales des matériaux seront étudiées et discutées.

* * *

Conclusion

Cette étude bibliographique réalisée en préambule de nos travaux de recherche a dressé un état de l'art sur la lignine et sa valorisation pour l'élaboration de polymères et de polyuréthanes notamment. Ce travail a ainsi contribué à l'élaboration de voies de fonctionnalisation et de synthèse originales qui seront développées dans les Chapitres II à IV de ce manuscrit.

Ceci nous a conduits à l'étude de trois systèmes différents et relativement novateurs de modification chimique pour la synthèse de nouveaux matériaux polymères d'étanchéité, tout en respectant le cahier des charges de la société SOPREMA. Compte-tenu de la faible réactivité des fonctions hydroxyles de la lignine, la modification chimique de ces dernières est indispensable pour son utilisation dans des systèmes réactifs.

L'objectif principal qui a dirigé l'ensemble de ce travail doctoral est axé sur l'amélioration de l'accessibilité et donc de la réactivité des fonctions hydroxyles de la lignine. La lignine ainsi modifiée constitue alors un synthon aromatique de base pour l'élaboration de nouvelles architectures macromoléculaires et ceci au travers de différentes approches:

- *Lignine et ε-caprolactone* : greffage par une technique de polymérisation par ouverture de cycle de chaine de poly(caprolactone)- PCL- sur les hydroxyles de la lignine. Etudes des paramètres réactionnels et des propriétés des matériaux obtenus.
- *Lignine et acide oléique* : estérification de la lignine par un procédé de chimie verte et fonctionnalisation des insaturations en vue de développer une nouvelle architecture de macropolyol. Elaboration de nouveaux matériaux PU.
- *Lignine et oxyde de propylène :* Hydroxyalkylation de la lignine en présence d'oxyde de propylène, greffage de chaine de poly(propylène) oxyde sur les hydroxyles phénoliques de la lignine. Modulation des propriétés des polyols obtenus pour l'élaboration de PU.

Enfin, il est intéressant de noter que nous avons privilégié, lorsque cela était possible, des procédés de modifications chimiques exempts de solvant et/ou de catalyseur, en utilisant un minimum de réactifs, parfois bio-sourcés, et au moyen d'un procédé simple, c'est-à-dire en limitant le nombre d'étapes de purification, en accord avec les douze principes de la chimie verte, exposés par Anastas et Warner[233].

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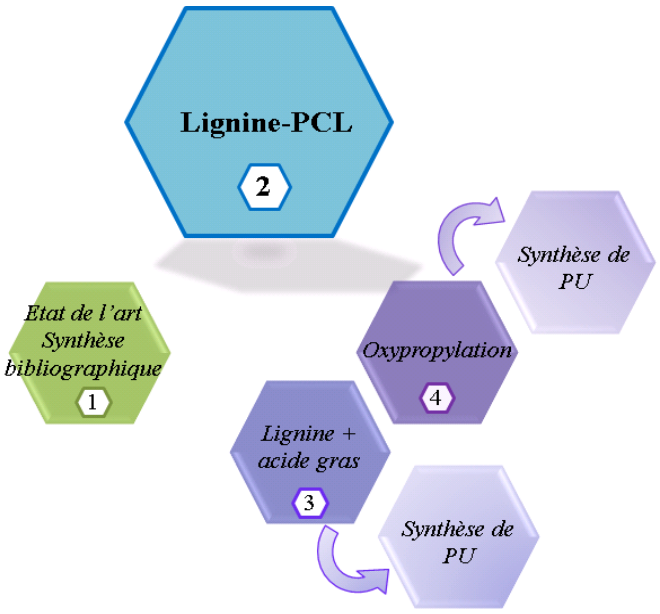
Chapitre II.

Réaction de polymérisation par ouverture de cycle – greffage de poly(caprolactone) PCL



Introduction

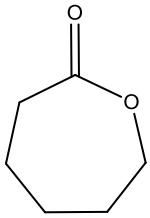
Suite à l'étude bibliographique présentée dans le Chapitre I de ce manuscrit, les réactions d'estérification et d'éthérification sont apparues comme des voies intéressantes pour les modifications chimiques des fonctions hydroxyles de la lignine. Aussi, la polymérisation par ouverture de cycle ou ROP (Ring-Opening Polymerization) a été envisagée car elle présente plusieurs avantages vis-à-vis des différentes contraintes imposées par la lignine. En effet, outre les propriétés intrinsèques de la lignine (poudre solide non fusible) qui en limitent son utilisation, ce type de polymérisation offre la possibilité de greffer directement sur la lignine, en une seule étape, de longues chaines de polymères. Cette méthode de polymérisation, largement développée et maîtrisée, permet d'accéder à un synthon (macromère) fonctionnalisé. Par ailleurs, la synthèse de polyesters par ROP est largement étudiée depuis de nombreuses années dans notre laboratoire, notamment pour la synthèse de polymères tels que le poly(ε-caprolactone) (PCL).

Pour ce travail, la polymérisation par ouverture de cycle nous a donc permis de greffer des chaines de PCL à partir d'ε-caprolactone. Dans ce chapitre, seule la synthèse et la caractérisation des composés lignine greffée PCL seront présentées. Dans un premier temps, les caractéristiques de la polymérisation par ouverture de cycle et plus précisément pour la synthèse de polyesters vont être présentées avant d'exposer les travaux réalisés dans le cadre du présent projet de doctorat.

* * *

I. Polymérisation par ouverture de cycle

La polymérisation d'hétérocycles s'effectue suivant différents mécanismes, relatifs à la nature du monomère, de l'amorceur, et peut ainsi conduire à de nombreux produits dont certains ont trouvé des applications industrielles importantes : le poly(caprolactame), le polyamide 6-6, ou le poly(oxyde d'éthylène) par exemple. Plus spécifiquement, la polymérisation par ouverture de cycles oxygénés tels que les lactones, permet d'obtenir des polyesters aux propriétés intéressantes et représente une excellente alternative à la polycondensation. La polymérisation par ouverture de cycle donne lieu à la synthèse de polymères de masses moléculaires élevées avec un indice de polydispersité relativement faible. Basée sur un équilibre de polymérisation-dépolymérisation, ce procédé de polymérisation, dans le cas des esters cycliques (lactones) peut s'accompagner de réactions secondaires de type transestérification conduisant à une cyclisation. Dans le cas présent, nous nous sommes intéressés prioritairement à l'ε-caprolactone, ester cyclique de la famille des lactones pour fonctionnaliser la lignine.



Formule brute	$C_6H_{10}O_2$
Masse molaire	114,14 $g.mol^{-1}$
Densité	1,030 $g.mL^{-1}$
Température de fusion	-1°C
Température d'ébullition	253°C

Figure II- 1. Structure et caractéristique de l' ε-caprolactone.

Plus spécifiquement, la polymérisation par ouverture de cycle peut être amorcée par différentes voies, i.e cationique (acides de Brönsted ou acides de Lewis), anionique (carboxylate ou alcoolate de métaux alcalins) ou par coordination-insertion avec des mécanismes associés différents et propres à chacune de ces voies. Divers travaux ont montré que l'utilisation d'amorceurs ioniques ne permet pas une bonne maîtrise de la réaction, entrainant notamment des réactions secondaires de transestérifications inter et intramoléculaires. Ainsi, des métaux tels que l'aluminium, l'étain, le germanium et des métaux de transition, plus électronégatifs que les métaux alcalins utilisés en polymérisation anionique, ont été utilisés pour amorcer la réaction par mécanisme de coordination-insertion. L'utilisation spécifique de ce type de catalyseur assure un meilleur contrôle des masses

molaires. Toutefois, dans ces conditions, la vitesse de polymérisation est diminuée. Le mécanisme mis en jeu est le suivant (Figure II-2): le monomère se coordonne à l'amorceur par sa fonction carbonyle puis il y a insertion du monomère dans la liaison métal-oxygène et l'ouverture de cycle se fait par la liaison O-acyle. La réaction est terminée par une hydrolyse acide de la liaison O-métal, ce qui conduit à une extrémité hydroxyle.

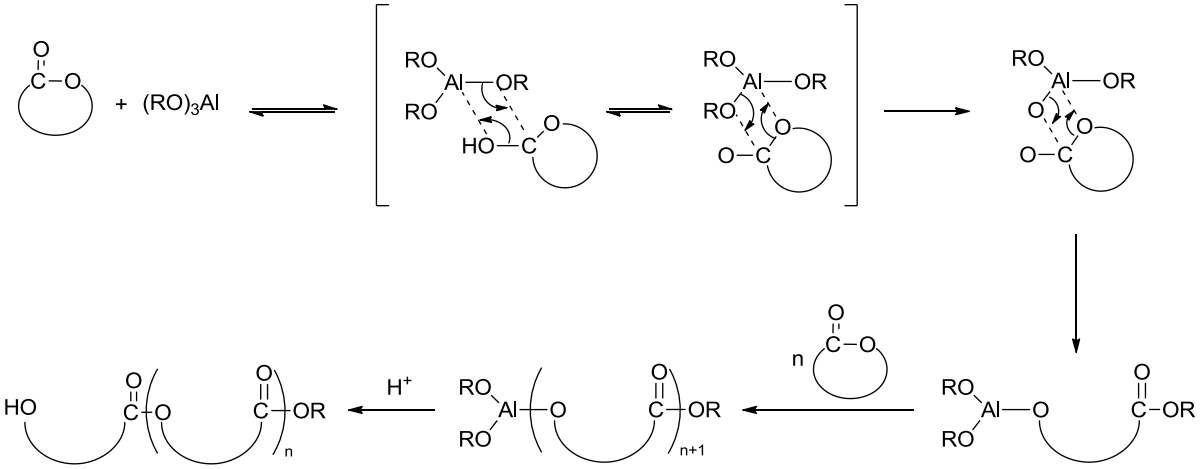


Figure II- 2. Mécanisme de polymérisation des lactones amorcé par $Al(OR)_3$ - mécanisme de coordination-insertion**.**

Parmi les nombreux alcoolates de métaux utilisés, notre choix s'est porté sur des catalyseurs à base d'étain tel que le bis(2-éthylhexanoate) d'étain (ou octanoate d'étain) $Sn(Oct)_2$. Il s'agit de l'amorceur le plus couramment utilisé pour la préparation de divers polyesters aliphatiques et copolyesters. C'est un catalyseur très efficace, facile à préparer et soluble dans la plupart des solvants organiques. Les temps de polymérisation classiques avec ce type d'amorceur vont de quelques minutes à plusieurs heures, pour des réactions se faisant généralement en masse à 140-180°C. Il donne lieu à une polymérisation contrôlée du PCL avec des masses molaires élevées (10^5 à 10^6 $g.mol^{-1}$) en présence d'un alcool ou d'une amine.

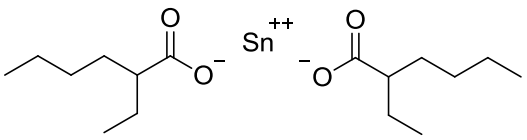


Figure II- 3. Structure de l'octanoate d'étain.

Le PCL est un polymère semi-cristallin avec un degré de cristallinité pouvant atteindre 69%. Il se solubilise très facilement dans des solvants tels que le chloroforme, le dichlorométhane ou le benzène mais reste insoluble dans les alcools, les éthers de pétrole ou l'eau. Il s'agit par ailleurs d'un matériau résistant et flexible dont la température de transition vitreuse (T_g) est bien inférieure à la température ambiante. La gamme d'application du PCL est très vaste et offre des propriétés intéressantes modulables. De nombreuses études ont été menées afin de synthétiser et modifier ce polymère pour obtenir un éventail plus large de propriétés et ainsi satisfaire de nouvelles applications.

II. Le système lignine – ε-caprolactone

Dans le cadre de notre étude, nous nous sommes donc intéressés à la polymérisation de PCL à partir de lignine. L'ouverture du cycle d'ε-CL est générée par la présence des hydroxyles de la lignine (qui servent alors d'amorceur) et l'utilisation d'un catalyseur permet d'accélérer la réaction. La chaine de PCL se greffe donc sur la lignine et croit directement sur celle-ci ; comme présenté sur la figure II-4.

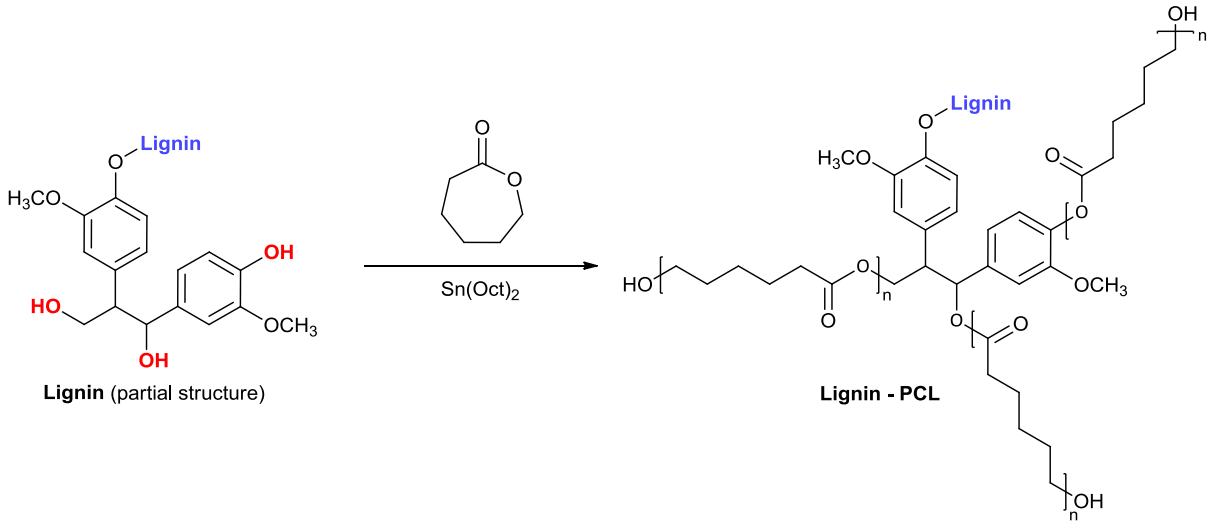


Figure II- 4. Schéma récapitulatif de la réaction de greffage de la PCL sur la lignine.

Les travaux réalisés sur ce système lignine - ε-caprolactone sont présentés sous la forme d'une publication intitulée "Synthesis, thermal properties, rheological and mechanical behaviors of lignins-*grafted*-poly(ε-caprolactone)" publiée dans *Polymer* (2013). Plusieurs expériences ont été réalisées afin de mieux comprendre la réaction mais également dans l'objectif d'optimiser les paramètres réactionnels. Ainsi, le temps de polymérisation, la quantité de catalyseur (rapport amorceur/catalyseur) mais aussi le degré de polymérisation ont été les paramètres principaux étudiés et mis en évidence des caractéristiques différentes suivant les systèmes polymères obtenus. Pour les matériaux ayant des propriétés mécaniques intéressantes, une étude particulière et approfondie a été menée afin d'établir plus précisément les relations « structure-propriétés » de ces produits.

* * *

Synthesis, thermal properties, rheological and mechanical behaviors of lignins-*grafted*-poly(ε-caprolactone)

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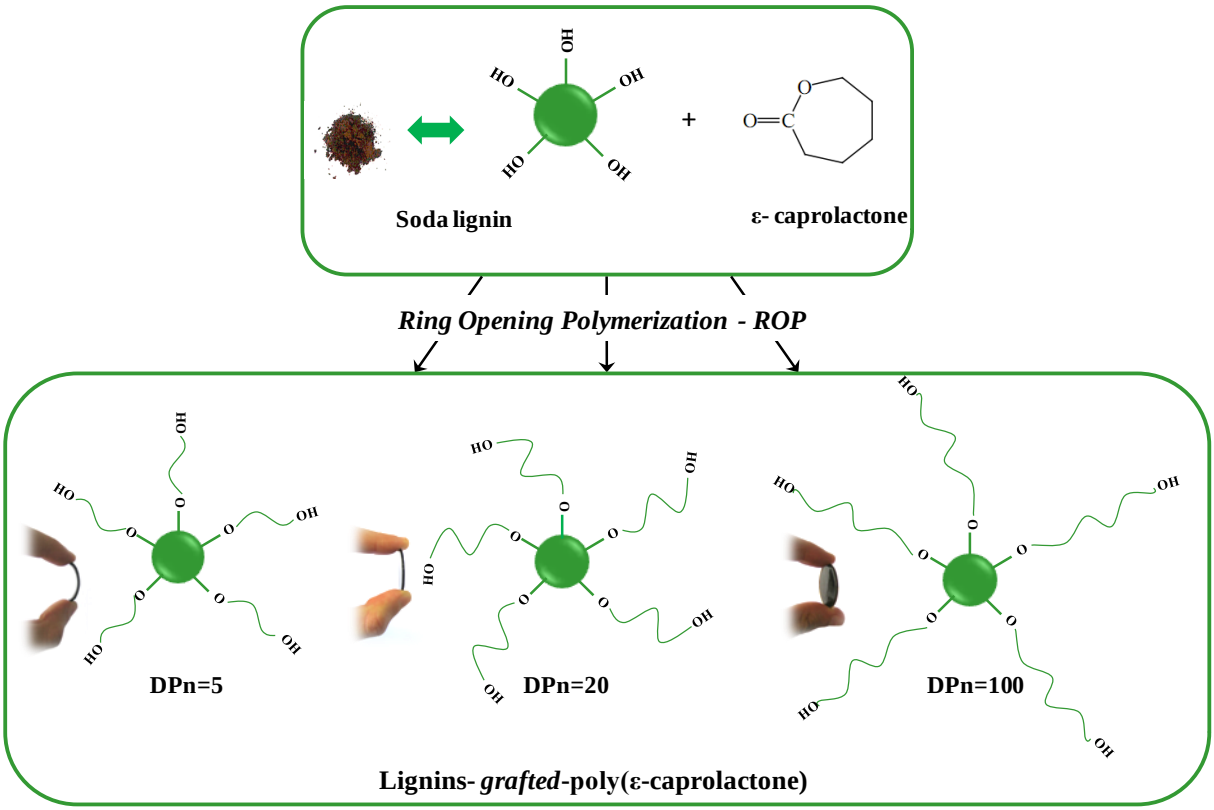


Highlights

- Syntheses of different lignin-grafted polycaprolactone were successfully achieved.
- Variation on the density and length of the grafted PCL chains induces strong influences on thermal, mechanical and rheological properties of the final biobased copolymers.
- Elastomeric properties were obtained at low caprolactone/OH molar ratio.
- Catalyst content and reaction time must be strictly controlled to obtain elastomeric polymers.
- These grafted architectures should be used as building blocks for polymer synthesis.

Abstract

Original macromolecular architectures based on lignin, a promising biobased building block or macromer, have been elaborated and analyzed. Different soda lignins-*grafted*-poly(ε-caprolactone) were synthesized by ROP of ε-caprolactone (CL) initiated by the hydroxyl groups (OH) brought by the lignins, and catalyzed by stannous octanoate. The influence of polycaprolactone (PCL) grafted chains onto lignin was investigated with a large range of CL/OH molar ratios, from 5 to 100. Based on analyses carried out by FT-IR and DSC, it was found that PCL chain organization was controlled by both intermolecular bonding and chain length. A semi-crystalline structure was observed for samples with a CL/OH ratio from 10 to 100 $mol.mol^{-1}$ which implicated the formation of a well arranged structure between PCL chains grafted around lignin. However, specific behavior has been observed at a CL/OH ratio equal to 5 due to the absence of crystallinity and specific intermolecular bonding. Mechanical tensile tests and rheological analyses were performed additionally to highlight the remarkable elastomer-like behavior of this new lignin-based material.

Key Words:

Lignin / Poly(ε-caprolactone)/ structures-properties/ rheological properties/ ROP

1. Introduction

During the last decades, there has been a growing interest in materials from the biomass, which are synthesized with biobased building blocks, or based on biopolymers i.e., polymers formed by living organisms [1]. Replacing petroleum based raw materials with renewable resources constitutes a major concern in terms of economic and environmental viewpoints [2].

Lignin is the second most abundant biopolymer after cellulose and one of the main components in plants materials. It is an amorphous and highly branched polyphenolic macromolecule. Besides, it is an important by-product of e.g., paper and biofuel productions. Due to its numerous chemical active sites, such as the hydroxyl groups (aliphatic and phenolic); lignin is considered as a macropolyol and could be expected to be an ideal alternative to chemical feedstock. Furthermore, it is a largely-available by-product which is not in direct competition with the food production such as vegetable oil or starch, for example. However, depending on the botanical origin and the separation process [3], the chemical structure of lignin differs considerably, with variations in molecular weight, in solubility and differing in architecture and amount of functional groups.

Lignin is extracted from lignocellulosic materials by different industrial and well-known processes, which can be divided into two main categories: sulfur and sulfur-free processes [4]. These two routes produce well-defined lignins, which are commercially and largely available. The first category includes Kraft and Lignosulfonates lignins, which are mainly produced by pulp and paper industries in huge quantities. Almost of these lignins are burned and used to generate energy and chemicals. The second category, the sulfur-free lignins, such as organosolv and soda lignins are extracted from annual crops like flax, straws, bagasse, and, to some extent, hardwoods and softwoods [5]. These latter as new renewable raw materials are interesting by integrating ecological and economic advantages and are considered as high value-added products [6]. Furthermore, these lignins are closer to that of *in-planta* lignins in comparison with Kraft lignins and Lignosulfonates. According to Wörmeyer et al. [7], the soda process demonstrates the best suitability for the production of lignin products for polymer applications by producing the lignin product of the highest quality.

The nowadays trend to use more and more green and biobased materials has promoted an increasing use of lignin in various applications, both as a biopolymer or as a building block. For instance, many attempts have been made to associate lignins with others polymers for the formulation of dispersants, adhesives, and surfactants or as antioxidants in plastics and

rubbers [8-10]. Studies on lignin-based blends have been reported and the effects of the structures on the miscibility and the corresponding properties have been largely investigated [11-14]. Lignin presented a good miscibility with PEO and PET whereas PVA and PP-lignin blends appeared immiscible. The association with biodegradable aliphatic polymers such as polycaprolactone (PCL) has attracted much attention because of the biotic degradation of the corresponding blends. For example, it has been reported that within a lignin content of 25%, the corresponding materials showed good mechanical properties because of the interactions with PCL [15]. Considering the absence of a softening temperature for lignin, it cannot be directly processed as a conventional polymer. Hence, chemical modifications are mandatory to develop thermoplastics and advanced materials, lignin being a potential building block or macromer. Chemistry based on more or less fractionated lignin can be developed to synthesize innovative macromolecules presenting distinctive architectures. Organosolv lignins were modified by esterification reaction giving alkylated lignin with propyl, butyl or pentyl groups and formed homogeneous blends with PCL. Crystallization studies have shown that the miscibility between modified lignin and the polyester was improved as the length of alkyl chains increased [16].

Different studies were also pursued in order to modify raw biobased materials such as lignin by using the "grafting-to" or "grafting-from" approaches. For instance, ε-caprolactone can be used to chemically modify lignin. For the "grafting-from" technique [17], the polymer chains of PCL are grown directly from the hydroxyl groups of lignin whereas in the case of the "grafting to", PCL chains are synthesized at first and are only grafted afterwards. In the last decades, some studies have been focused on the grafting of PCL on lignin by using both approaches. Multiphase block copolymers presenting lignin and PCL blocks were originally developed by De Oliveira et al. [18]. More recently, lignin was modified with propylene oxide to produce multifunctional polymeric segments and then copolymerized with PCL. This two-step method was used to enhance the reactivity of lignin by the chain extension. Another pathway has been developed using a diisocyanate with various PCL homopolymers, to produce several polyurethanes [19]. In this field, the recent study of Korish et al. [20, 21] can be also mentioned. They presented the synthesis of graft copolymers based on the formation of arylboronate esters linkages between the 1,3-diols of lignin and boron end-functionalized caprolactone. This original approach can be foreseen for the development of new lignin-based thermoplastics.

The aim of this study was to synthesize original macromolecular structures by Ring-Opening Polymerization (ROP) of ε-caprolactone (CL) onto lignin. In the present study, we chose to work with a sulfur-free lignin provided from a soda extraction process to carry out the polymerization reactions. The structural modifications were performed on the hydroxyl functions of lignin, which was previously characterized by different techniques. To evaluate the impact of the graft lengths on the thermal and mechanical properties of lignin-based materials, five grafted PCL chains were prepared. The amount of CL was varied from 5 to 100 mol per OH groups of lignin. A specific investigation using a CL/OH ratio of 5 has also been carried out to provide a better understanding on the organization of the grafted chains in the material. This study aims to contribute to the knowledge of the relationships between structure and properties of the synthesized materials in order to propose a putative structure of these macromolecular systems. Furthermore, a perspective of this work was to enhance the reactivity of lignin's hydroxyl functions to prepare a macropolyol with functional sites as a macromolecular platform which could easily react by polycondensation or polyaddition to synthesize different innovative polymers.

2. Experimental

2.1 Materials

Alcaline soda lignin (Protobind 1000) was purchased from Green Value SA (Switzerland). Soda lignin (SL) is a sulfur-free lignin obtained after extraction and fractionation from annual plants (wheat straw) with a final molecular weight of around 1000 $g.mol^{-1}$. The lignin was used as received without further purification. ε-caprolactone (CL) and stannous octanoate ($SnOct_2$) were obtained from Sigma Aldrich and used as received without any purification.

2.2 Sample preparation

Soda Lignin-based PCL (SLPCL) polymers were synthesized. CL has been used as the monomer for ROP, lignin being the macro-initiator through its hydroxyl groups.

The ratio of monomer to initiating groups determines the theoretical degree of polymerization (DP) of the polymer chains. The amount of CL was varied from 5 to 100 mol per OH groups of lignin. Different CL/OH ratios were used (CL/OH ($mol.mol^{-1}$) = 5, 10, 20, 50, 100) to graft

lignin with different equivalent lengths of PCL chain. Polymerization reactions were carried out at 130°C in dry toluene (CL/OH=5) or in bulk (CL/OH=10, 20, 50 and 100) using stannous octanoate ($SnOct_2$) as catalyst [22]. $SnOct_2$ has been selected after some preliminary tests with different catalytic systems. In the literature, $SnOct_2$ is the most often used initiator for the elaboration of grafts, block copolymers, and multibranched products. This catalyst is particularly efficient with monomers such as compound with hydroxyl groups, cyclic esters like lactides or CL [23]. The grafting reaction proceeded from 14 to 62 hours under anhydrous conditions, to avoid homopolymerization reactions. The corresponding polymer was isolated by precipitation into cold methanol to remove unreacted CL, filtered and dried under vacuum. SLPCL sheets with a thickness of 1mm were prepared by compression-molding at 80-100°C under 150 bars. The designation for the synthesized samples is S X $_{Y/Z,}$ where X is the CL/OH ratio ($mol.mol^{-1}$), Y the OH/catalyst ratio ($mol.mol^{-1}$) and Z the reaction time (h).
To fully assess the grafting of PCL chains onto lignin versus the synthesis of PCL free chains, some blank experiments were carried out synthesizing PCL macromolecules without lignin. The same reaction parameters than SLPCL polymers were used, the resulting synthesized homopolymers will be designed by B X $_{Y/Z}$, with X as the ratio of the corresponding synthesis with lignin. The homopolymers have also been fully characterized using the same techniques than for SLPCL samples.

2.3 General characterizations techniques

NMR spectra were recorded at 300 MHz on a Bruker UltraShield 300, using $CDCl_3$ as solvent. The molecular weights of the PCL chains grafted onto lignin and homopolymers were estimated from the NMR spectra by calculating the ratio of the signals at 4.02 ppm (-CH_2O- PCL repeating unit) and 3.6 ppm (-CH_2OH- PCL graft end groups).

The number-average molar mass (M_n) and the polydispersity index (PDI) of the resulting samples were determined by Size Exclusion Chromatography (SEC), using Shimadzu apparatus equipped with a pre-column PLGel 5µ, two PLGel 5µ Mixed-C 300 mm columns and one PL 100 Å 300 mm column. Refractive index (RI) and ultra-violet (UV) detectors were used. Chloroform ($CHCl_3$) was used as the eluent at a flow rate of 1 $mL.min^{-1}$. The apparatus was calibrated with linear polystyrene standard from 580 to 1,650,000 $g.mol^{-1}$.

Fourier Transformed Infra-Red spectroscopy working in Attenuated Total Reflectance Mode (FTIR-ATR) was used to detect specific changes in hydroxyl and carbonyl vibrations

which provide direct evidence of reaction between lignin and PCL and specific interactions between components. A Nicolet 380 FT-IR spectrometer was used to record FT-IR spectra.

DSC was performed using a TA DSC Q 200 under air flow. Sample mass was 2-5 mg. The samples were heated until 200°C with a heating rate of 10°C.min^{-1} (first heating scan), then cooled to -80°C at 10°C.min^{-1} and finally re-heated to 200°C at a heating rate of 10°C.min^{-1} (second heating scan). The glass transition (T_g) and the melting (T_m) temperatures were determined as midpoints of the change in slop of the baseline and the maximum of melting temperature peak, respectively. These values were determined on the second heating scan in order to erase the previous thermal history of the samples during the first scan. Cristallinity was calculated according to the Equation (1), where ΔH_f is the measured heat of fusion for the sample, and ΔH_f^* is the heat of fusion for 100% crystalline PCL i.e., 136 J.g^{-1} [24].

$$X_c\ (\%) = (\Delta H_f / \Delta H_f^*) \times 100 \qquad (1)$$

For experiments conducted with modulated DSC, samples are first stabilized at 10°C, with a modulation of ± 1.5°C each 80 seconds and then heated with a heating rate of 1°C.min^{-1} until 190°C.

TGA measurements were conducted under air (flow rate = 25 mL.min^{-1}) using a Hi-Res TGA 2950 apparatus from TA Instruments. The samples (3-5 mg placed in an aluminum pan) were heated up to 750°C at 10°C.min^{-1}. The characteristic degradation temperatures are the temperatures at the maximum of the derivative thermogram (DTG) curve (T_{dmax}) and at which the sample weight equals 98% and 2% of the initial one ($T_{98\%}$ and $T_{2\%}$, respectively).

Dynamic rheological analyses of SLPCL and neat PCL were performed by using a strain-controlled rheometer (ARES, Rheometric Scientific) with parallel-plate geometry. The oscillatory measurements were performed on 25 mm diameter disks with 1 mm thickness. The following tests have been conducted: (i) dynamic strain sweep to estimate the viscoelastic region of the samples, (ii) isothermal dynamic frequency sweep test from 100 to 0.1 rad.s^{-1} at a temperature of 80°C. Changes in the viscous and elastic modulus were registered.

Uniaxial tensile tests were carried out with an Instron tensile testing machine (model 4204, USA, load cell: 10 kN), at 25°C and at a rate of 20 mm.min^{-1}, using dumbbell specimens type H2 (ISO-527) (dimensions: 25 X 4 X 1 mm^3). For each formulation at least five samples were tested.

2.4 Specific techniques for lignin characterization

Methoxyl groups characterization

The methoxyl content of lignin was measured using a modification of a suggested TAPPI method T 209 su-72 "Methoxyl Content of Pulp and Wood" [25]. The principle of this method is based on the reaction of the methoxyl group with hydroiodic acid to generate methyl iodide. The organic iodide is then oxidized by bromine to form iodic acid, which is determined by the titration of iodine after reduction by KI.

Total hydroxyl groups (phenolic and aliphatic) characterization

Acetylation is frequently performed on lignin to improve its solubility in common solvents to carry out different analyses such as ^{1}H NMR. 1 g of air dry lignin was acetylated with 20 mL of acetic anhydride/pyridine (1:1, v:v) at room temperature for 24 hours in a 50 mL round-bottomed flask. After 24 hours, 5 mL of methanol were added to quench the remaining acetic anhydride and 40 mL of dichloromethane. The solution was then washed with chloride acid solution (2M), the organic layer was washed a second time with a saturated sodium bicarbonate solution and finally with deionized water. The dichloromethane solution was dried with anhydrous sodium sulfate and the product was evaporated at reduced pressure to dryness. Acetylated lignin was then dried under vacuum at 35°C for one night. NMR spectra of 10 mg acetylated lignin samples dissolved in 0.5 mL of $CDCl_3$ were recorded.

Proton signals were integrated from the baseline and referred to the integrated signal of the methoxyl protons (δ = 3.7 ppm) for proton quantification of aliphatic and phenolic hydroxyls. Aromatic and aliphatic acetates gave signals, at 2.3 and 2.0 ppm, respectively. These peaks are related to aliphatic and phenolic hydroxyl groups present in lignin before acetylation [26, 27].

3. Results and discussion

3.1 Lignin characterization

The main characteristics of the lignins depend on the botanical source and on the intensity of the delignification process, which govern e.g., whether it has enough free phenolic hydroxyl groups and whether the *ortho* and *para* positions of the phenyl rings are blocked by methoxyl groups or aliphatic side chains [3, 28]. These chemical data constitute a key point in this work since these hydroxyls functions will be functionalized. Several analytical methods were used to analyze and determine main functional groups [6, 29]. Total and phenolic hydroxyl contents were quantified according different techniques including chemical titration and ^{1}H NMR based on acetylated lignin and molecular weight by Size Exclusion Chromatography (SEC) in chloroform [28, 30, 31].

It is well known that the T_g of lignin is comprised between 90 and 160°C, depending on the lignin origin, the molecular weight and the corresponding extraction process [32]. T_g of SL (143°C) used in this study was carefully determined by modulated DSC. Results for soda lignin characterization were summarized in Table II-1, these values were found to be in the same range as that of others reported data from the literature [33] and also, in good correlation with values given by the lignin supplier. Among these results, it can be noticed that the PDI of soda lignin is low in comparison with Kraft or Lignosulfonate lignin [33], which allow assessing that this type of lignin presents a lower polydispersity and a more defined structure. This last point must be considered as a great advantage for future chemical modifications.

Moisture content (%)		3.56
SEC analysis	M_n *(g.mol^{-1})*	1120
	M_w *(g.mol^{-1})*	4380
	M_w/M_n	3.9
^{1}H NMR analysis	Total OH *(mmol.g^{-1})*	4.61
	OH phenolic *(mmol.g^{-1})*	1.67
	OH aliphatic *(mmol.g^{-1})*	2.94
	Average hydroxyl groups/ mol of lignin	5.17
Tappi method	Methoxy content *(mmol.g^{-1})*	3.25
DSC analysis	T_g (°C) *crude lignin*	143
	T_g (°C) *acetylated lignin*	117

Table II-1. Analysis results of Soda lignin.

3.2 Synthesis and characterization of different SLPCL systems

The branched lignin based polycaprolactone system has been previously described as a star-like copolymer with a lignin's core and PCL arm segments [34]. This architecture may show a high variety of designs with different types of lignin and PCL arm lengths. In this study, the length of the chain extensions brings the main modulations to the final macromolecular architecture. A total of 9 different SLPCL were synthesized (Table II-2). On this basis, it is possible to distinguish 5 different types of architecture, based on the variations of the CL chain lengths. The influence of the amount of catalyst has also been studied. The SLPCL polymers and their corresponding blanks were synthesized with $SnOct_2$ at two different OH/catalyst ratios ($mol.mol^{-1}$), 150 and 30, respectively. Table II-2 shows the main parameters used to carry out the syntheses of different SLPCL systems.

3.2.1 Structural analyses

Whereas the grafting of PCL chains onto lignin is confirmed by SEC analysis, the conversion of the monomer and the arm lengths is estimated by ^1H NMR. These results indicate that it is possible to control the average arm length of PCL grafted onto lignin through the CL/OH ratio and the amount of catalyst. The grafting is also confirmed by SEC analysis with both detectors (RI and UV). These 2 detectors allowed checking and controlling the grafting of PCL chains onto lignin. Neat PCL can only be detected with RI detector whereas lignin is detected with both detectors. If a sample presents one sole signal using RI and UV detectors, that it means that PCL chains are grafted onto lignin. On the contrary, if there are 2 different signals on RI chromatogram and only one with UV chromatogram, it can be concluded that PCL free side chains have been synthesized. To illustrate these comments, SEC chromatograms in Figure II-5 show the grafting of PCL chains onto lignin for $S5_{150/17}$ and $S50_{150/48}$ and their corresponding blanks $B5_{150/17}$ and $B50_{150/48}$. In the case of blank syntheses, we can see that PCL homopolymers are not detected by the UV detector whereas for the corresponding syntheses with lignin, a signal is clearly detected. These results are well correlated with what we were expected, confirming that PCL is grafted onto lignin. Furthermore $S50_{150/48}$ shows a visible shoulder on the signal detected with RI and only one by using UV detector attesting that PCL chains are grafted onto lignin, but some PCL free chains are also synthesized.

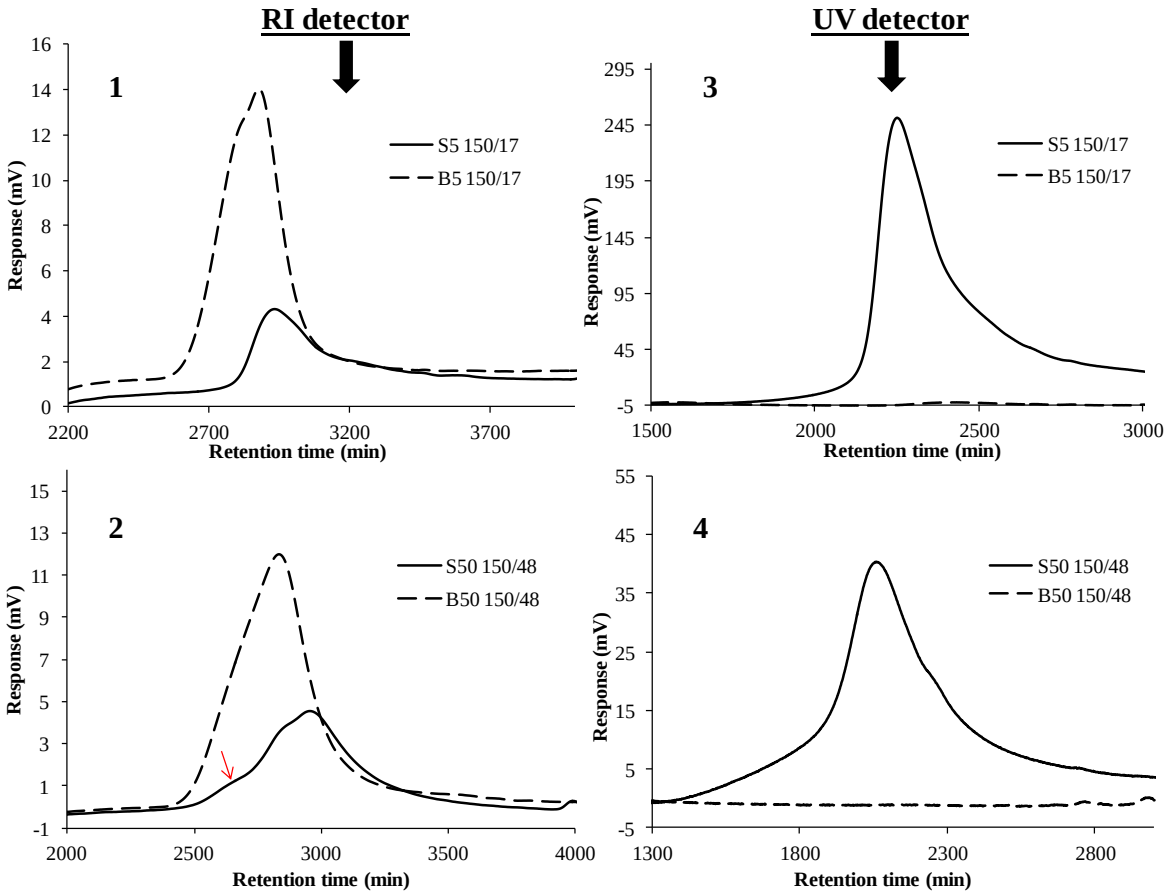


Figure II- 5. SEC chromatograms with RI (1 and 2) and UV (3 and 4) detectors for samples synthesized with CL/OH ratio of 5 and 50 and their corresponding blank syntheses.

For a better understanding, only the results obtained with UV detector are shown in Table II-2. They correspond to the exact molar mass of lignin grafted PCL excluding the molar mass of free homopolymer chains of PCL that could be synthesized by side reactions.

At this point, based on ^{1}H NMR and SEC results, it is possible to show that PCL chains are linked to the lignin. To go deeply into the details concerning the analysis of this reactive system, we can follow and analyze the influence of both parameters i.e., CL/OH and OH/catalyst ratios. For CL/OH ratio equal to 5 and 10, it seems to be possible to control the average arm length of PCL grafted onto lignin avoiding the formation of PCL free chains. SEC results confirmed the grafting of PCL onto lignin by an increase of lignin molecular weight, without the formation of PCL free chains. In the case of higher CL/OH ratio, from 20 to 100, it is impossible to avoid homopolymer synthesis as a side reaction; higher catalyst content increases this phenomenon. The architecture and PCL chains organization around

lignin were further investigated by various methods (IR, rheology…) to have a better understanding on this polymerization system.

	Reaction parameters					SEC results using UV detector		
Samples	CL/OH ratio (mol.mol^{-1})	OH/catalyst ratio (mol.mol^{-1})	Reaction time (h)	Average arm length	wt.% of lignin	M_n (10^3 g.mol^{-1})	PDI	Free PCL chains
S5 $_{150/17}$	5	150	17	7.0	48	2.2	6.1	No
S5 $_{30/17}$		30	17	5.5	46	4.5	3.1	No
B5 $_{150/17}$		150	17	127	-	-	-	-
S10 $_{150/20}$	10	150	20	20	18	4.7	23.6	No
S10 $_{30/20}$		30	20	16.7	17	5.0	23.8	No
S20 $_{150/27}$	20	150	27	15.0	-	3.9	10.3	Yes
S20 $_{30/27}$		30	27	25.0	10	7.0	26.0	Yes
S50 $_{150/48}$	50	150	48	24.4	6	5.1	41.9	Yes
S50 $_{30/48}$		30	48	44.0	2	6.1	41.9	Yes
B50 $_{150/17}$		150	48	149	-	-	-	-
S100 $_{30/48}$	100	30	48	63.3	3	41.0	4.0	Yes

Table II- 2. Main parameters of SLPCL and blank syntheses with corresponding NMR and SEC results.

FT-IR is a very efficient technique to investigate specific inter and intramolecular interactions. This method has been already used to qualitatively study interactions, which can occur between PCL and lignin [11, 35]. PCL and lignin have both functional groups which are able to interact between them through hydrogen-bonding, such as carbonyl groups for PCL, and hydroxyl groups (phenolic and aliphatic) for lignin. Figure II-6 shows the FT-IR spectra of the SLPCL samples, the inset figures corresponding to the spectra of the hydroxyl-stretching region (3000-3700 cm^{-1}) and the carbonyl stretching region (1680-1760 cm^{-1}). In the spectra of lignin, the band near 3360 cm^{-1} is linked to the hydroxyl groups of the lignin. OH stretching and the band from 1735 to 1715 cm^{-1} are due to the acetyl groups of the lignin molecule [36]. In the spectrum of neat PCL, the band of hydroxyl group is not as strong as lignin one and can be attributed to the low concentration of hydroxyl chain-ends groups of PCL. With the increasing of PCL grafts onto SLPCL (for high CL/OH ratio), the intensity of hydroxyl functions stretching band decreased. This decrease is linked to the increase of the average arm length of PCL, which induce lower hydroxyl content. For the case of CL/OH ratio of 5, it was found that the peak position of O-H stretching band shifts from 3357 to 3342

cm^{-1}. This shift to higher frequency is probably due to the formation of intermolecular hydrogen bonding, between PCL and lignin.

The carbonyl absorption of PCL at 1724 cm^{-1} is the most significant peak on IR spectrum. It has been previously reported that the IR carbonyl absorption of polyester including PCL shows a shift due to the formation of strong intermolecular hydrogen bond with the phenol hydroxyl groups [37, 38]. As shown in Figure II-6, an obvious change in the shape and position of the carbonyl peak can be shown only at a CL/OH ratio of 5. These latter results allowed concluding that at this ratio, there are possible interactions between carbonyl and hydroxyl groups. For higher content of lignin and short PCL grafts, interactions between hydroxyl and carbonyl groups are facilitated conferring special properties to the resulting polymers. In order to examine this phenomenon more carefully, we studied and analyzed in details the reaction with a CL/OH ratio of 5 in the last section of this paper.

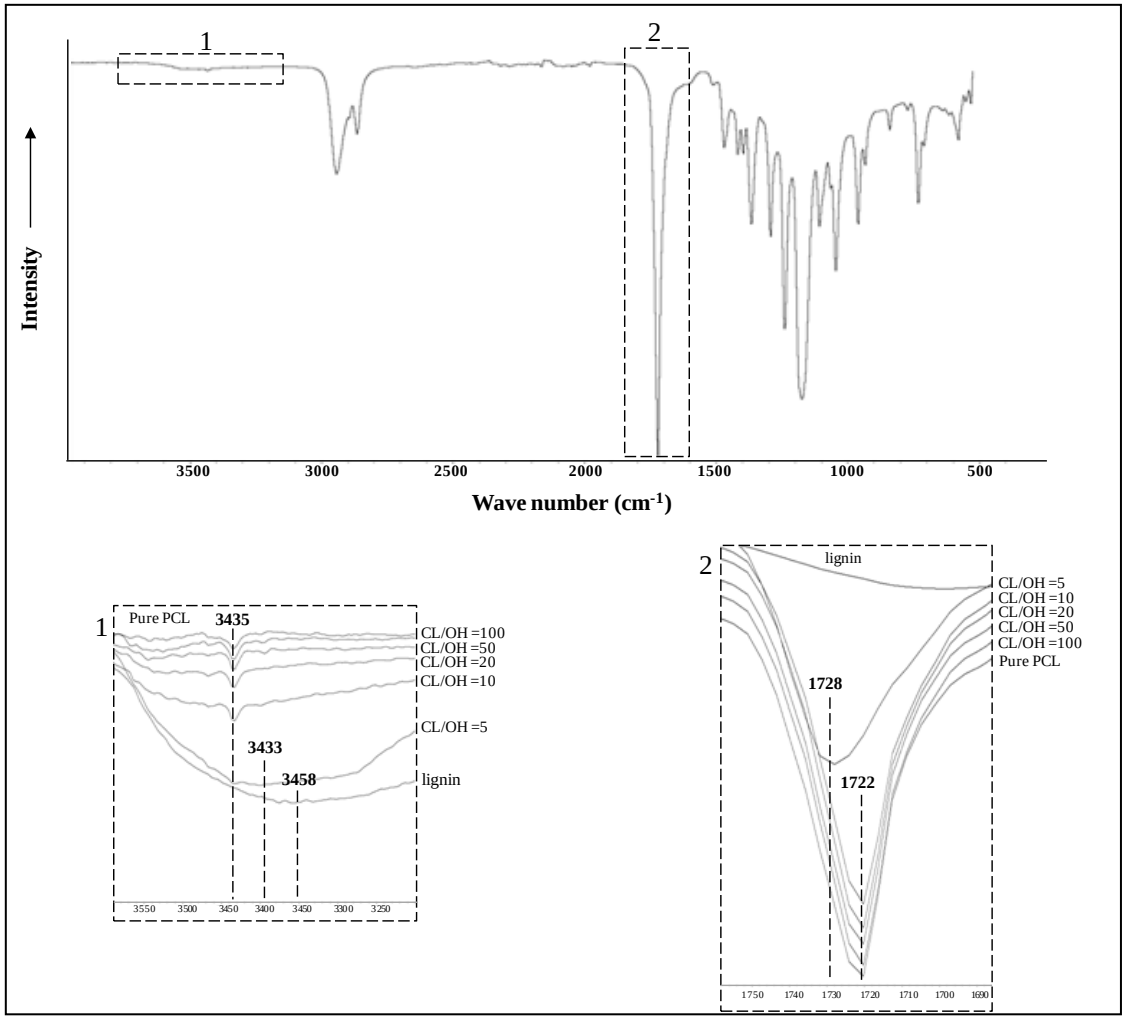


Figure II- 6. FT-IR spectra of the SLPCL samples. Insets show the OH stretching (3100-3700 cm^{-1}) and C=O stretching (1680-1760 cm^{-1}) regions.

3.2.2 Thermal and mechanical analyses

The SLPCL polymers were analyzed by differential scanning calorimetry (DSC) and thermal gravimetric analysis (TGA). The corresponding results are summarized in Tables II-3 and II-4, respectively. It is has been largely reported that DSC thermogram of PCL presents two main thermal events at around -62 and 56°C [39], which can be attributed to the glass transition and the melting temperature, respectively. However, it is not possible to detect a clear T_g transition for lignin [40]. Nevertheless, DSC analysis can provide useful information with regards to the chains mobility of the synthesized materials. Figure II-7 shows the DSC curves of samples synthesized with different CL/OH ratios, and with an OH/catalyst ratio of 30 mol.mol^{-1}. T_g of SLPCL samples can only be detected when the CL/OH ratio is 5 mol.mol^{-1}. It was not found any detectable T_g for samples with higher ratios. The T_g of the PCL chains detected for the CL/OH ratio of 5 shows an obvious shift from -62°C (neat PCL) to -30°C (SLPCL). Furthermore, for S10, S20, S50 and S100 series, melting and crystallization temperatures (T_m and T_c respectively) have been observed. The melting point temperatures of these samples tend to 55°C, which is close to the T_m of neat PCL (60°C). Table II-3 shows in details the main data derived from DSC measurements. These DSC results suggest that there is distinct difference in terms of thermal behavior between the various synthesized products. In fact, for samples with a CL/OH ratio from 10 to 100 mol.mol^{-1}, the crystallization of PCL segments reveals a crystalline organization for the SLPCL polymers. When PCL chains are grafted onto lignin, with different CL/OH ratios, the cristallinity contents of the resulting polymers reach a maximum of 50%. This crystalline organization can indicate that PCL chain mobility is reduced by increasing the CL/OH ratio i.e., the length of PCL grafts [17]. In fact, when the length of PCL molecular chains exceeds 15 units of CL, i.e. around 10% of cristallinity, the mobility of SLPCL tends to decrease significantly. From a macroscopic point of view, samples with CL/OH ratios ranging from 10 to 100 were brittle whereas those with CL/OH=5 were soft, flexible and amorphous. These first results suggest that the grafted PCL chains can induce different and specific thermal and mechanical behaviors. At that time, it is clear that the molecular motion of the main chain is restricted when PCL long chain molecules are grafted onto lignin.

Samples	CL/OH ratio (mol.mol^{-1})	DSC results				
		T_g (°C)	T_c (°C)	T_m (°C)	X_c (%)[a]	X_c (%)[b]
S5 $_{150/17}$	5	-40	-	-	-	0
S5 $_{30/17}$		-30	-	-	-	0
B5 $_{150/17}$		N.V	31	57	49.7	49.7
S10 $_{150/20}$	10	-	26	48	39.1	47.7
S10 $_{30/20}$		-	28	50	10.1	12.2
S20 $_{150/27}$	20	-	26	50	35.4	-
S20 $_{30/27}$		-	30	52	40.1	44.5
S50 $_{150/48}$	50	-	33	53	49.2	52.3
S50 $_{30/48}$		-	35	55	41.2	42.9
B50 $_{150/17}$		-	36	57	44.1	44.1
S100 $_{30/48}$	100	-	37	53	49.8	51.3

Table II- 3. Thermal properties of SLPCL and blank samples.

[a]: compared to neat PCL
[b]: compared to synthesized material
N.V: Not Visible

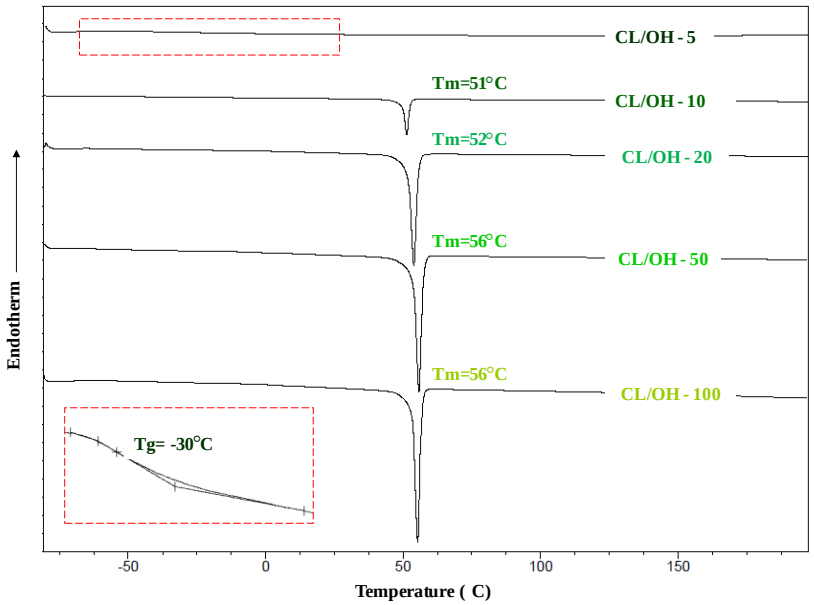


Figure II- 7. DSC curves showing the effect of chain lengths on the thermal properties.

TGA was used to investigate the influence of CL/OH on the thermal stability of the resulting synthesized polymers. In general, the neat PCL presents a two-stage degradation mechanism. The first degradation step generates water, CO_2 and carboxylic acid as evolved products. Then, the pyrolysis step generates chain cleavages and depolymerization [41]. Figure II-8 shows that the thermal stability of SLPCL samples is improved compared to neat PCL. For instance, at 400°C, the weight loss of neat PCL is about 75% and that of SLPCL samples with CL/OH ratio of 20 is only about 68%. Moreover, the sample with higher content of lignin (CL/OH=5) has less weight loss. Above 400°C, we can suppose that the residue is mainly due to the lignin. From samples S10 to S100, with a high PCL content, the maximal degradation temperature is closed to neat PCL. However, for S5 sample, the onset temperature of degradation is higher compared to neat lignin. In this case, the grafting of PCL onto lignin has a stabilizing effect and shows a higher thermal resistance compared to neat PCL [38]. For the case with CL/OH ratio of 5, it can be noticed that $T_{98\%}$ is the same that for neat PCL and $T_{2\%}$ is quite similar than those of Soda lignin. The thermal degradation of the system with the lowest PCL content does not modify significantly the degradation of the lignin counterpart. In major case, the SLPCL polymers synthesized in this study display thermal decomposition profiles dominated by PCL-like data. The only exception is the S5 series.

Samples	**$T_{98\%}$ (°C)**	**T_{dmax} (°C)**	**$T_{2\%}$ (°C)**
S5 $_{30/17}$	224	527	544
S10 $_{30/20}$	251	394	N.D.
S20 $_{30/27}$	257	394	N.D.
S50 $_{30/48}$	225	375	565
S100 $_{30/48}$	265	388	455
PCL	224	390	466
SL (Soda lignin)	148	517	562

Table II- 4. Main degradation temperatures for the different SLPCL samples.

N.D.: Not Determined

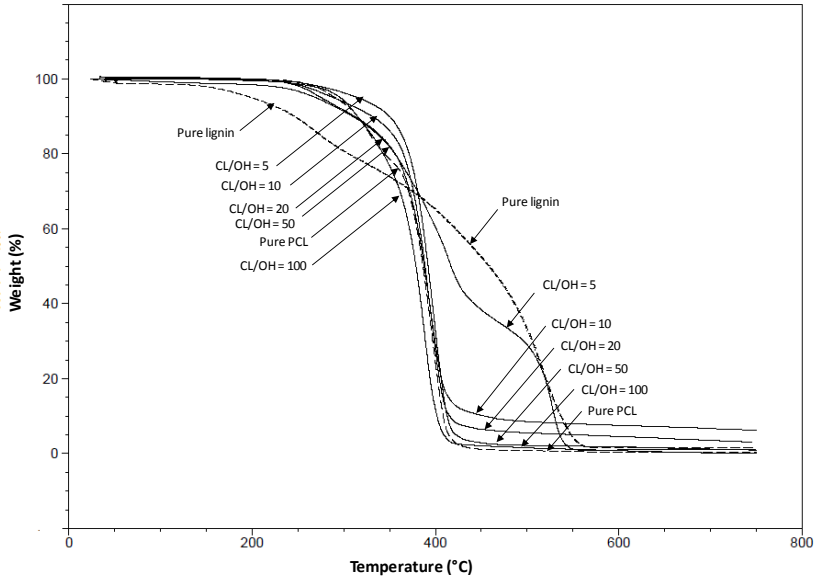


Figure II- 8. TG curves of SLCPL and neat Soda lignin and PCL samples.

Rheological analyses provided complementary information about the macromolecular architecture of the lignin-grafted PCL. Figure II-9 shows the results of isothermal dynamic frequency tests at 80°C. For a CL/OH ratio of 5, it can be noticed that the elastic (or solid-like) modulus (G') is greater than the loss (or fluid-like) modulus at all frequencies. This behavior is usually related to an elastomeric amorphous and highly cross-linked polymer. On the contrary, for the other samples synthesized with CL/OH ratios higher than 5, G'' is always greater than G' at all frequencies, which is usually the behavior of conventional thermoplastic polymers. The storage and the loss modulus of SLPCL samples are linked to the amount of lignin. For instance, G' and G'' increased when the CL/OH ratio decreased. Furthermore, additional rheological tests were performed with blank syntheses compounds B5 $_{150/17}$ and B50 $_{150/17}$, respectively, to study the influence of PCL grafts onto lignin compared to PCL homopolymers. Figure II-10 depicts clearly the thermoplastic properties of neat PCL, elastic and loss modulus decrease with frequency. In the present case, the grafting of PCL short chains onto lignin showed a clear rheological effect, compared to the corresponding blank. The covalents bonds between PCL chains and lignin seem to confer an elastomeric-like behavior to S5 product, whereas PCL chains synthesized in the same conditions presented thermoplastic behavior. For S50 and B50 samples the difference is not as important as S5 series, however, the elastic modulus for lignin grafted PCL decreased less than the corresponding homopolymer. This behavior suggests that PCL grafted onto lignin reinforces the properties of neat PCL.

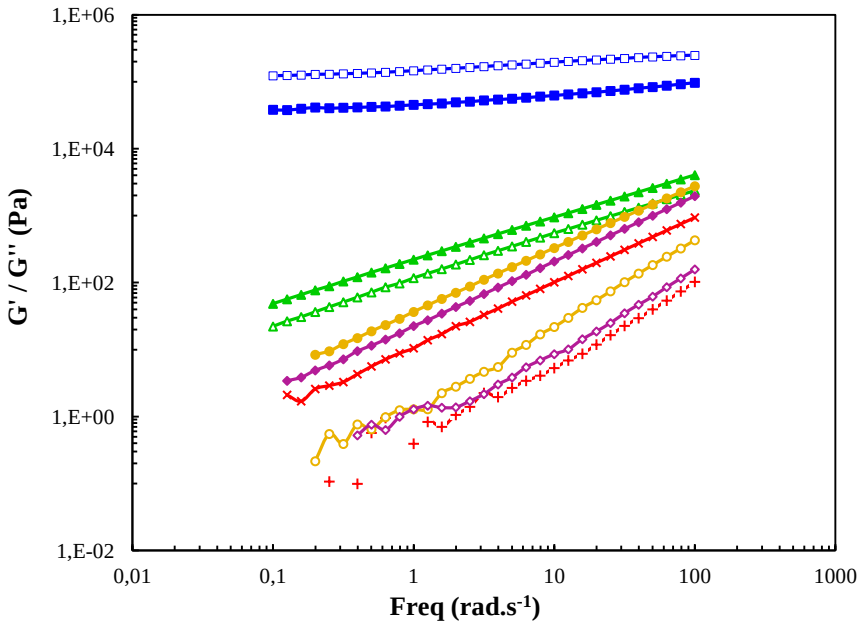


Figure II- 9. Isothermal dynamic frequency tests of SLPCL samples with different CL/OH ratios, at 80°C.

S5: G'(□) - G''(■); S50: G'(◊) - G''(♦);
S10: G'(Δ) - G''(▲); S100: G'(X) - G''(+)
S20: G'(○) - G''(●);

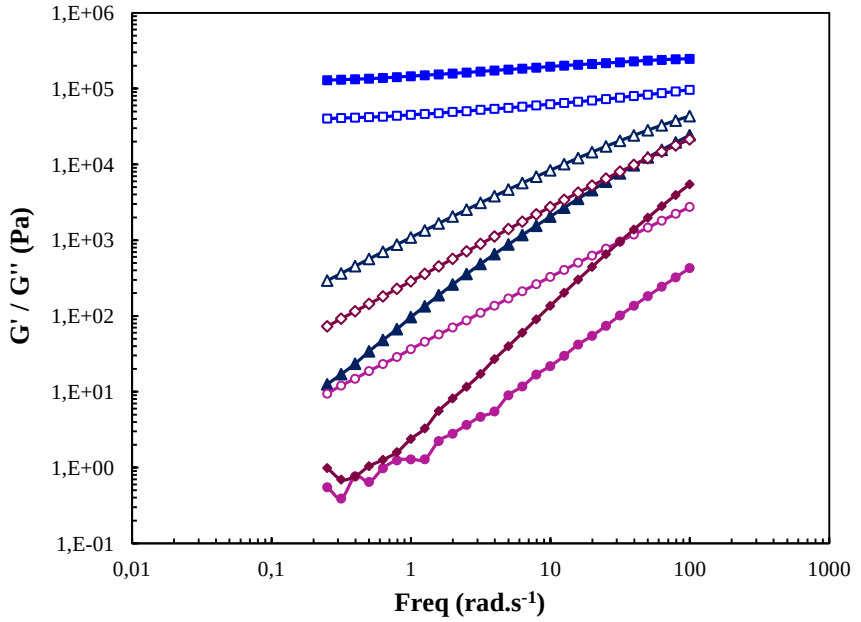


Figure II-10. Isothermal dynamic frequency tests of SLPCL samples with different CL/OH ratios of 5 and 50 and their corresponding blank syntheses (neat PCL), at 80°C.

S5: G'(□) - G''(■); S50: G'(○) - G''(●);
B5: G'(Δ) - G''(▲); B50: G'(◊) - G''(♦);

Based on the analyses that have been carried out onto lignin based materials, it should be emphasized that SLPCL polymers synthesized in this study can be classified into two main categories. When PCL grafted chains are short and relatively mobile (T_g around -42°C), they cannot be integrated in a crystalline organization based on the PCL arms. For higher CL/OH molar ratios, PCL grafts are associated to form a crystalline structure around lignin molecule. These results have to be compared to those previously published from blends of PCL and lignin. Previous studies have already been carried out on the blends of lignin and PCL obtained by mechanical mixing and other solution casting [15]. The corresponding results based on these blends had shown that the glass transition temperature, the melting temperature and the crystallinity of PCL were kept almost constant, until 40% of lignin incorporated in the blends. These previous results were totally different than those obtained in this study. For instance, at high lignin content (around 50%), no melting temperature is observed whereas a glass transition was observed at around -30°C. Then, it is obvious that the grafting of PCL onto lignin imparts to SLPCL polymers new thermal, mechanical, and rheological properties compare to conventional PCL/lignin blends.

3.3 A particular case: CL/OH ratio= 5

Considering the results and the specific behavior of the samples with a CL/OH ratio of 5, additional experiments have been carried out for this ratio value. The amount of $SnOct_2$ as catalyst and time of reaction have been studied to evaluate their influence on the final properties of the corresponding SLPCL samples. Each experiment has been carried out using the same quantities of lignin and CL, only the amount of catalyst varies from 30 to 120 $mol.mol^{-1}$ (Table II-5).

	Reaction parameters			DSC results	SEC results using UV detector	
Samples	OH/catalyst ratio (mol.mol^{-1})	Reaction time (h)	wt.% of lignin	T_g (°C)	M_n (10^3 g.mol^{-1})	PDI
S5 $_{30/14}$	30	14	53	-35	4.4	22.3
S5 $_{30/15}$		15	42	-47	5.6	16.1
S5 $_{30/18}$		18	37	-52	5.7	20.1
S5 $_{30/23}$		23	29	-52	6.0	16.5
S5 $_{60/14}$	60	14	52	-33	9.0	641
S5 $_{60/18}$		18	43	-45	4.3	24.2
S5 $_{60/21}$		21	40	-44	4.8	34.5
S5 $_{60/24}$		24	40	-45	5.0	11.4
S5 $_{60/38}$		38	29	-50	8.3	19.1
S5 $_{120/16}$	120	16	48	-40	4.9	351
S5 $_{120/18}$		18	42	-43	5.0	21.6
S5 $_{120/21}$		21	40	-45	4.5	16.0
S5 $_{120/24}$		24	33	-50	4.4	29.4

Table II- 5. Reaction parameters for SLPCL synthesis with SEC and DSC results.

It has already been shown that the kinetics of the chain propagation during the ROP of CL under conventional thermal conditions is first order and follows Equation (2), where k_p is the rate constant of chain propagation. $[P_n^*]$ represents the concentration of propagating species and t denotes the polymerization time.

$$\ln([CL]_0 /[CL]) = k_p[P_n^*]t \qquad (2)$$

According to Equation (2), the reaction time and the amount of catalyst have an influence on the kinetic of SLPCL polymerization.

Figures II-11 and II-12 show the relationships between the average number of CL units per grafted chain or conversion of monomer and the reaction time, respectively. The reported SEC and ^{1}H NMR results seem to point out that high catalyst content (i.e., low OH/catalyst ratio) gives high conversion rate and increase the number of CL units per grafted PCL chains. This complementary study reveals also that lignin's total hydroxyls are not all activated during the reaction. At high conversion rate (around 90%), the length of PCL grafts can reach a maximum of 16 units of CL, whereas the theoretical value should be 5 units. Moreover, the impact of catalyst content can influence the graft density of PCL chains onto lignin. For high

catalyst ratio, the graft density decreases thus conducting to the grafting of a higher length of PCL grafts.

Among all of experiments carried out, only five of them give SLPCL samples with an elastomeric behavior (oval area on Figure II-11). However, all of these samples have more or less the same T_g values. The increase of T_g compared to neat PCL can be attributed to a decrease of PCL chain's mobility due to the grafting. Moreover, as it has already been described in a previous study [17], the motion of the grafted chains can also be correlated to interactions between PCL and lignin. This interaction can probably be due to the beginning of the formation of a network based on hydrogen bonds, between carbonyl (PCL) and hydroxyl groups (lignin).

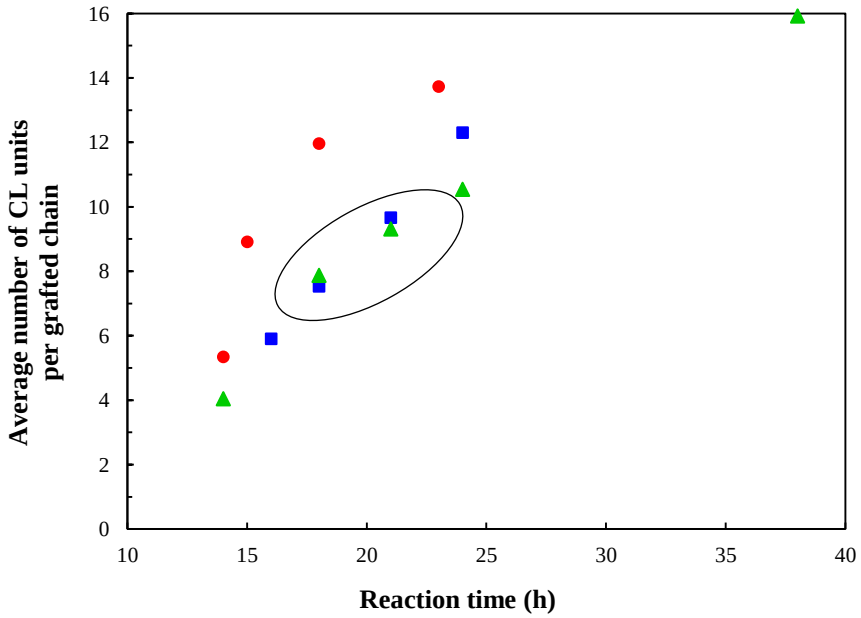


Figure II- 11. Relationships between the average-number of CL units per grafted chains and the reaction time for various OH/catalyst ratios. (●; 30, ▲; 60, ■; 120).

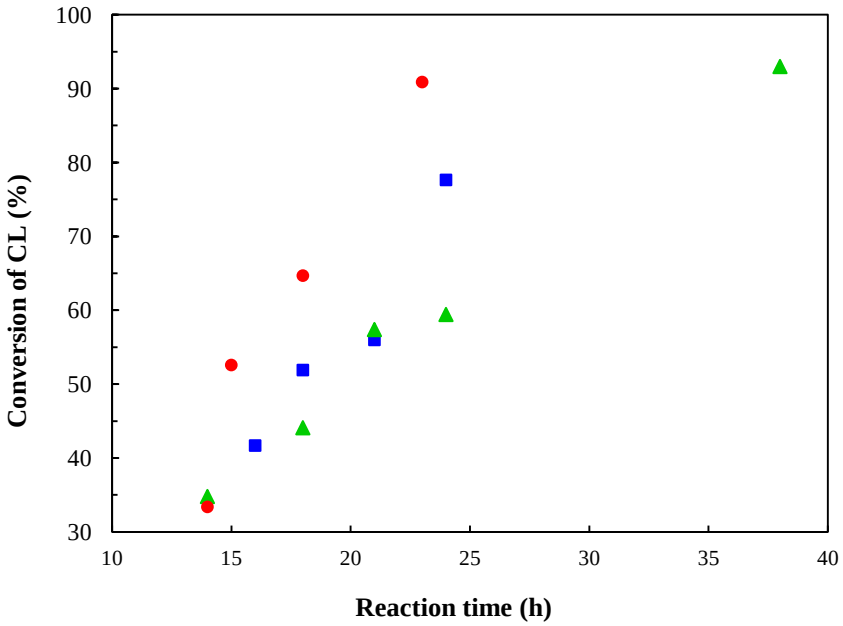


Figure II- 12. Relationships between the conversion of CL and the reaction time for various OH/catalyst ratios. (●; 30, ▲; 60, ■; 120).

Dynamic rheological analyses were performed on each experiment at a CL/OH ratio of 5. Figure II-13 shows only the data for dynamic storage modulus (G'), G' being always greater than the dynamic loss modulus (G''), which is not presented to ease the discussion. In previous experiments, we have shown that SLPL is an amorphous elastomeric polymer. However, a specific zone can be noticed at low frequencies where G' is independent of the frequency (Figure II-13) and could mean that highly branched amorphous copolymers have been synthesized. In this case, it can be said that at low frequencies, when G' reached a level-off, the value of G' is inversely proportional to the molar mass implicated between the linked chains.

It was found that a critical G' value could be highlighted. In fact, for samples S5 $_{60/18}$, S5 $_{60/21}$, S5 $_{60/24}$, S5 $_{120/18}$ and S5 $_{120/21}$, materials are soft and flexible whereas for S5 $_{60/14}$ and S5 $_{60/38}$, there are completely brittle. We can assume that a specific modulus G' range exists where the material shows flexibility.

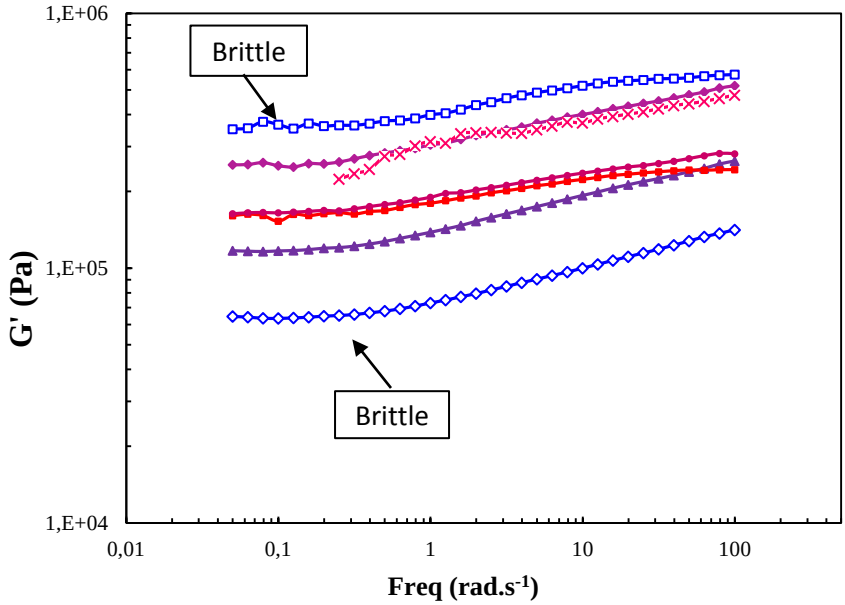


Figure II- 13. Isothermal dynamic frequency test of SLPCL samples.

S5 $_{60/14}$: G'(□)
S5 $_{60/18}$: G'(▲)
S5 $_{60/21}$: G'(■)
S5 $_{60/24}$: G'(●)
S5 $_{60/38}$: G'(◊)
S5 $_{120/18}$: G'(♦)
S5 $_{120/21}$: G'(X)

Uniaxial tensile tests were performed on samples to investigate the mechanical properties in the solid state. Maximum strength (σ), Young's modulus (E) and elongation at break (ε) were evaluated from the stress-strain curves. The main experimental results were presented in Table II-6. Highest Young's moduli were observed for samples synthesized with an OH/catalyst ratio of 60 while comparing to those prepared with a ratio of 120. In addition, the tensile strength is quite similar for all samples with an OH/catalyst ratio of 60 and higher, than that synthesized with lower catalyst content. These results suggest that the amount of catalyst used for these syntheses plays an important role in the final properties of the materials. As previously observed, the amount of catalyst has an impact on the graft density of PCL onto lignin. For low catalyst ratio, the number of grafted chains onto lignin increases whereas their lengths decrease. The difference between the four samples with "soft behavior" is the graft density, the chain's length for OH/catalyst ratio of 60 is quite high but we can suppose that there are fewer PCL grafts around lignin that allow having higher elongation at break.

Samples	OH/catalyst ratio (mol.mol^{-1})	Average units of CL per grafted chains	Traction		
			σ Maximum strength (MPa)	ε Elongation at break (%)	E Young's Modulus, (MPa)
$S5_{60/18}$	60	8.0	2.03 ± 0.11	33.0 ± 0.5	24.6 ± 4.5
$S5_{60/21}$		9.3	2.02 ± 0.05	33.5 ± 2.7	21.8 ± 1.3
$S5_{120/18}$	120	7.5	1.33 ± 0.06	28.1 ± 1.1	15.5 ± 2.4
$S5_{120/21}$		9.7	1.33 ± 0.21	29.0 ± 1.3	13.2 ± 1.4

Table II- 6. Uniaxial tensile tests results for samples with "soft behaviors".

4. Conclusion

Soda lignin-*grafted*-Poly(ε-caprolactone) can be synthesized by ROP in the presence of stannous octanoate by using hydroxyl functions of lignin. This reaction allowed converting hydroxyl groups of lignin into readily available reactive sites.

Different techniques have been used to determine the properties and structure of different lignin-*grafted*-Poly(ε-caprolactone) - SLPCL materials, compared to neat PCL. DSC, SEC, FT-IR and rheological characterizations have showed that the macromolecular organization of the different SLPCL structures varies, according to the length of the grafted chains and the synthesis conditions. This work allowed us to highlight two different behaviors, whose one lead to a material with remarkable intrinsic performances.

When the CL/OH ratio was 5, the corresponding polymer was mainly lignin and the carbonyl group C=O of PCL was possibly linked to phenolic hydroxyl group. Thus, amorphous materials based on 3D hydrogen bonds networks were synthesized. The synthesized products do not show a crystalline structure. Flexible polymers with specific properties are obtained. Rheological tests indicate that there is a critical G', corresponding to a specific interval of molar mass implicated between the cross linked chains of PCL.

For samples synthesized with a CL/OH ratio higher than 5, the grafted PCL chains form a semi-crystalline structure, which leads to PCL/lignin phases segregation. As a result, the intermolecular bonds between PCL and lignin decrease and the previous flexible network disappears. Brittle materials are obtained in this case.

These chemically modified lignins lead to long branched polyester with OH groups at the end that can constitute potential macropolyol (building blocks) with original structure, which could also be a macromolecular platform to synthesize different and original polymers. Polycondensation or polyaddition reactions can be considered from the OH reactive terminal sites.

Acknowledgments

We are grateful for Alsace Region, Oséo and ANRT for their financial supports. We also gratefully acknowledge Dr. Jairo H. Lora at Green Value for providing the lignin samples, Chheng Ngov for her help in SEC analysis and Sébastien Gallet for helpful discussion on chemistry.

III. Conclusion & perspectives de l'étude

Au terme de cette étude, différents polymères ont pu être synthétisés et les premières caractérisations de ces produits ont montré tout l'intérêt et le potentiel qu'offrait une stratégie de fonctionnalisation de la lignine. En effet, la polymérisation de l'ε-caprolactone à partir des fonctions hydroxyles de la lignine nous a permis de synthétiser différents matériaux qui peuvent se mettre en œuvre facilement, et qui présentent un large éventail de propriétés physico chimiques et mécaniques. L'influence des différents paramètres réactionnels sur les architectures macromoléculaires synthétisées a été mise en évidence.

Par ailleurs, grâce à l'optimisation des conditions opératoires, il a été possible de maitriser la longueur des chaines de polymères greffées mais également la densité de greffage sur la lignine. Cette première partie nous a permis de mettre en exergue différents points clés par rapport à l'application industrielle finale visée. En effet, l'utilisation de polymère fortement cristallin semble difficile à intégrer dans l'élaboration de ce type de matériau. Malgré de bonnes propriétés mécaniques et notamment des modules d'Young relativement élevés, le PCL associé à la lignine ne confère pas des propriétés de souplesse et d'élasticité suffisantes et nécessaires à la réalisation d'une membrane d'étanchéité (voir Annexe de ce manuscrit). Toutefois, dans certains cas et pour des degrés de polymérisation faibles (DPn≈5), des phénomènes très intéressants ont été observés démontrant la présence d'interactions faibles entre les chaines de polymères greffées et la lignine, responsables d'une certaine souplesse pour les matériaux obtenus (Figure II-14). Ces résultats prometteurs nous ont ainsi conduits à approfondir cette étude en faisant varier les temps de réaction et les quantités de catalyseurs sur ces systèmes.

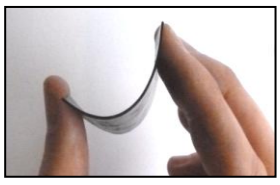
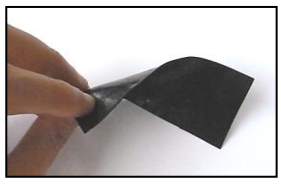
a)  b)  c) 

Figure II- 14. Photographies illustrant la flexibilité des matériaux synthétisés pour la série S5- a) S5 $_{120/21}$; b) S5 $_{60/18}$; c) S5 $_{60/21}$.

Par ailleurs, dans tous les systèmes élaborés à partir de lignine modifiée, cette dernière joue le rôle de point de réticulation physique et chimique et apporte généralement de la rigidité et parfois même de la fragilité au matériau synthétisé. Il est donc important d'apporter de la souplesse au système par l'introduction de chaines amorphes de faible T_g ou encore de polymères linéaires de masse molaire élevée. La lignine, de par sa structure, peut conférer au polymère final une certaine structuration et une rigidité, cependant, sa poly-fonctionnalité entraine inéluctablement la formation de réseau et la réticulation du matériau. L'espacement des molécules de lignine, le taux de réticulation et la présence de fonctions structurantes au sein des polymères ou molécules greffés sur la lignine sont autant de leviers permettant d'ajuster les propriétés finales des matériaux que nous allons moduler afin de développer un matériau répondant au cahier des charges. D'autres voies de modification chimique de la lignine ont donc été effectuées et sont présentées dans les chapitres suivants.

Notes et Références

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Chapitre III.

Estérification de la lignine avec l'acide oléique – Fonctionnalisation et Synthèse de polyuréthanes

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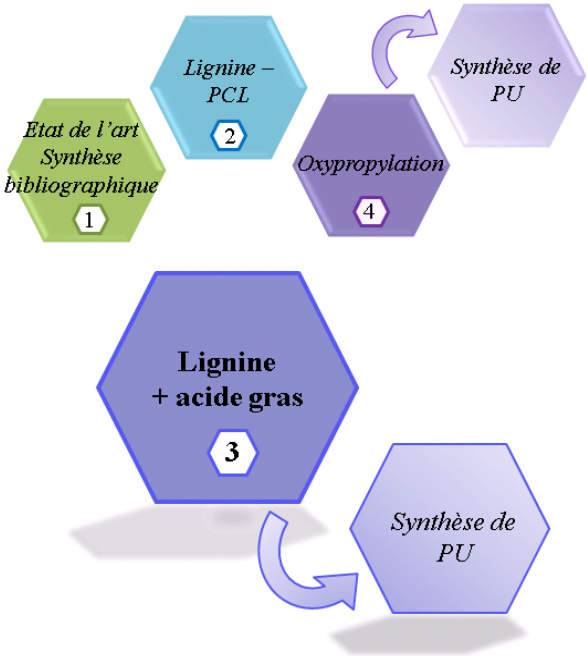


Introduction

La valorisation de la lignine pour la synthèse de polymères fonctionnels repose sur sa modification chimique préalable. Pour ce faire, notre démarche scientifique s'est axée sur la fonctionnalisation de la lignine afin d'en faire un synthon principal (polyol) dans la synthèse de PU pour une application dans le domaine des membranes d'étanchéité.

L'étude réalisée dans le Chapitre II a permis de développer une fonctionnalisation spécifique de la lignine permettant d'aboutir directement à un matériau qui a pu être mis en œuvre. L'objectif de ce nouveau chapitre est de proposer une alternative à l'utilisation du Poly(Caprolactone), dont la cristallinité s'est révélée être un point bloquant en vue de l'élaboration de matériaux souples et flexibles.

Les huiles végétales représentent une ressource naturelle abondante, variée, peu onéreuse et disponible. Majoritairement constituées de triglycérides, elles font l'objet de nombreux projets de recherches et apparaissent comme une alternative crédible pour répondre aux préoccupations environnementales. Les publications et brevets dans ce domaine attestent des nombreuses possibilités offertes par l'oléochimie pour l'élaboration de matériaux thermoplastiques ou thermodurs.

Dans cette optique, nous nous sommes donc tournés vers l'utilisation de dérivés des huiles végétales, et particulièrement les acides gras, pour modifier la lignine. Cette modification chimique fait écho aux techniques de fonctionnalisation du bois ou de la cellulose notamment à l'aide de dérivés d'acide gras. Dans un premier temps, nous présenterons l'oléochimie et développerons les principales voies de modifications chimiques des huiles végétales et de leurs dérivés aboutissant à l'introduction de fonctions hydroxyles. Enfin, nous présenterons les travaux originaux effectués au laboratoire mettant en jeu la lignine et un dérivé d'huile végétale afin d'élaborer un nouveau synthon bio-sourcé pour l'élaboration de polymères.

* * *

I. L'oléochimie et la modification des acides gras

De façon générale, l'oléochimie regroupe les transformations physico-chimiques appliquées aux huiles et aux graisses aussi bien animales que végétales. Utilisée depuis l'antiquité, notamment pour la fabrication des savons, l'oléochimie est actuellement présente dans de nombreux secteurs industriels allant de l'agro-alimentaire au secteur pharmaceutique en passant par la cosmétique ainsi que diverses industries (adhésifs, revêtements, détergents, lubrifiants, solvants…).

Dans le cadre de notre étude, une des stratégies de synthèse retenue est la fonctionnalisation des insaturations présentes sur les molécules d'acides gras (Tableau III-1). En effet, de nombreuses voies de modifications chimiques utilisant des doubles liaisons ont été étudiées et vont nous permettre d'envisager de nouvelles stratégies de synthèse à partir de la lignine estérifiée.

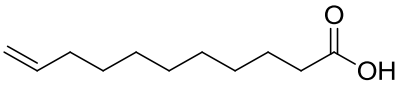
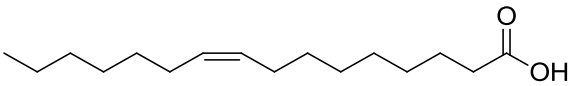
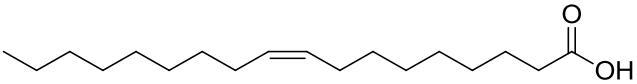
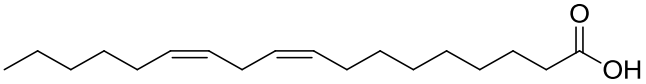
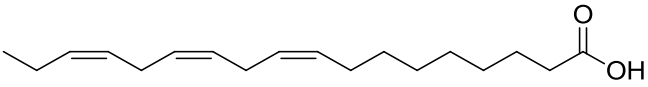
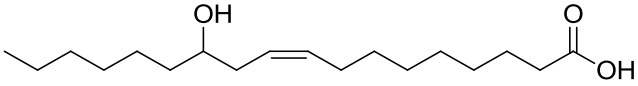
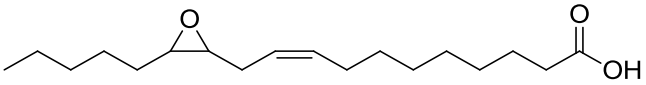
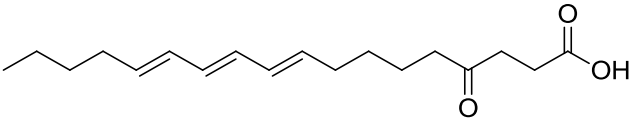
Acide gras	Formule brute	Structure
Acide undécylénique	$C_{11}H_{20}O_2$	
Acide palmitoléique	$C_{16}H_{30}O_2$	
Acide oléique	$C_{18}H_{34}O_2$	
Acide linoléique	$C_{18}H_{32}O_2$	
Acide linolénique	$C_{18}H_{30}O_2$	
Acide ricinoléique	$C_{18}H_{30}O_2$	
Acide vernolique	$C_{18}H_{30}O_3$	
Acide licanique	$C_{18}H_{28}O_3$	

Tableau III- 1. Formules brutes et structures des principaux acides gras contenant des insaturations.

L'objectif principal de cette fonctionnalisation repose sur l'introduction de fonctions hydroxyles dans la nouvelle architecture moléculaire élaborée à partir de lignine et d'acide gras. Il est à noter que certaines huiles végétales et leurs acides gras associés comme l'huile de ricin (acide ricinoléique) possèdent déjà des fonctions hydroxyles dans leurs structures. Pour les acides gras ne possédant pas ces fonctions, il est possible de les introduire en procédant à une ou des modifications chimiques. Les 6 voies principales de synthèse permettant d'aboutir à des fonctions hydroxyles à partir des insaturations présentes sur les acides gras sont représentées sur la Figure III-1 et détaillées dans la suite de ce manuscrit.

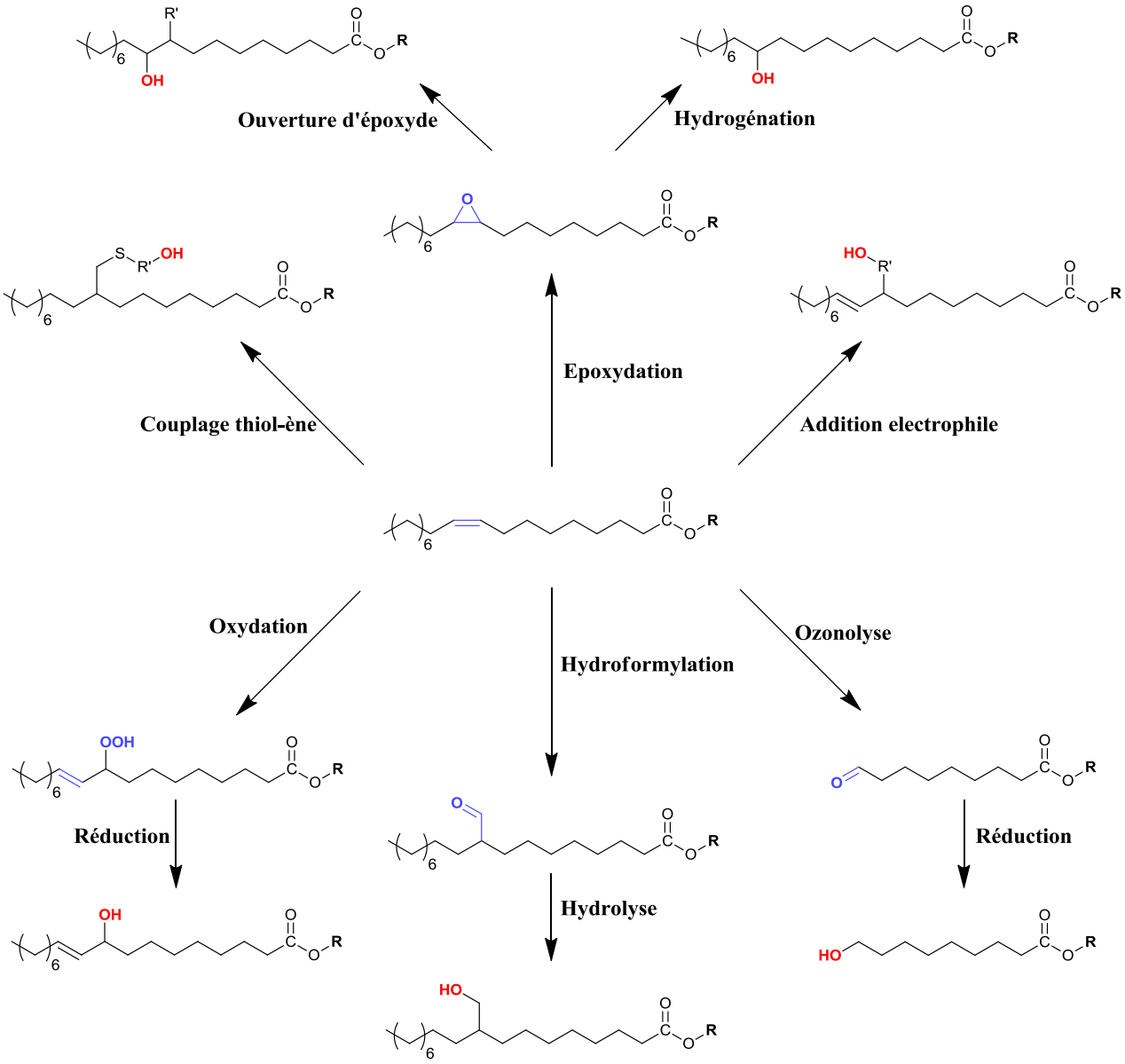


Figure III- 1. Résumé des divers composés obtenus à partir de la fonctionnalisation des insaturations présentes sur les dérivés d'huiles végétales.

1. Epoxydation des insaturations et conversion en alcool

La première voie de fonctionnalisation décrite repose sur l'époxydation des insaturations. La formation d'oxacyclopropane offre en effet la possibilité d'accéder à de nombreuses réactions par l'ouverture du cycle et permet ainsi d'envisager la fonctionnalisation de la chaîne grasse par l'ajout de nouveaux sites réactifs tels que les fonctions hydroxyles. L'époxydation constitue alors une première étape dans une stratégie de synthèse plus complexe faisant intervenir au minimum 2 étapes.

Parmi la multitude des acides gras que l'on peut trouver, seul l'acide vernolique est naturellement époxydé. Ce composé présente un intérêt majeur pour la fabrication d'époxydes entre autres mais n'est disponible qu'en très faibles quantités (extrait principalement des graines d'une plante originaire d'Afrique appelé *Vernonia galamensis*). Par ailleurs, il est possible de trouver des huiles époxydées commerciales qui ont déjà prouvé leur efficacité dans de nombreuses applications industrielles. On peut par exemple citer l'utilisation d'huile de soja époxydée (ESBO Epoxidized Soybean Oil) pour diminuer la dégradation thermique du PVC lors de son extrusion [1-3].

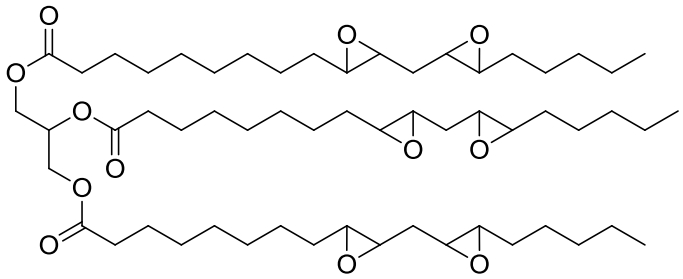


Figure III- 2. Structure de la linoléine époxydée.

L'époxydation d'une double liaison s'effectue par action d'un agent d'oxydation, classiquement un péracide (généralement *m*CPBA : acide *méta* chloroperoxybenzoïque) à température ambiante en présence d'un solvant inerte. Le mécanisme rentrant alors en jeu est un mécanisme de type électrophile. Les taux de conversion de cette réaction peuvent atteindre 100% [4]. Il est possible d'accélérer la réaction en enrichissant la double liaison à l'aide de groupes donneurs d'électrons. En revanche, si des groupes attracteurs d'électrons sont présents autour de cette double liaison, il sera plus difficile d'utiliser des peracides usuels. On aura alors recours à des péracides de type CF_3CO_3H. A plus grande échelle et, notamment

dans l'industrie, le *m*CPBA, explosif sous l'action de chocs, a été remplacé par le monoperoxyphtalate de magnésium (MMPP).

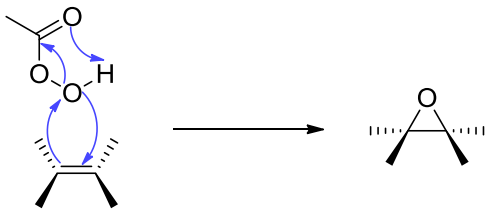


Figure III- 3. Formation d'une fonction époxyde sous l'action d'un péracide et mécanisme associé.

Le traitement des oxacyclopropanes pour obtenir des fonctions hydroxyles peut s'opérer de deux manières différentes. Dans le cadre de notre étude, on s'intéressera à l'ouverture de cycle en milieu acide ou basique ainsi qu'à l'hydrogénation catalytique.

L'ouverture des cycles époxydes peut s'effectuer aussi bien sous conditions acides que basiques ; on peut ainsi résumer cette réaction par le schéma suivant (Figure III-4) :

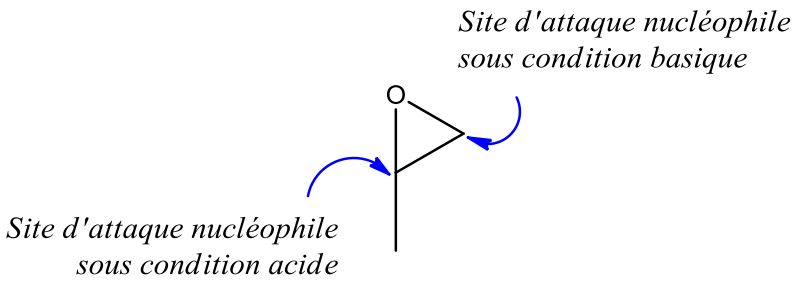


Figure III- 4. Ouverture du cycle époxyde.

En milieu basique, l'époxyde -relativement fragile- peut-être ouvert par un nucléophile qui attaque alors sur le carbone le moins encombré. Le mécanisme associé est de type SN_2 (Substitution Nucléophile d'ordre 2).

En milieu acide, le mécanisme est différent. Il y a formation d'un carbocation intermédiaire, l'oxygène est tout d'abord protoné, le carbone le plus substitué devient alors le plus riche en électrons et par conséquent le site préférentiel pour recevoir l'attaque nucléophile.

Les mécanismes réactionnels associés sont présentés sur la figure III-5:

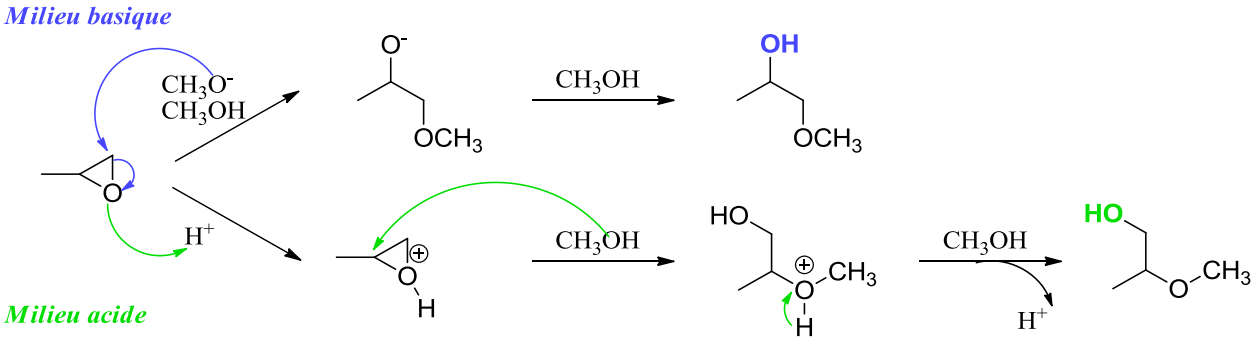


Figure III- 5. Mécanisme de l'ouverture du cycle époxy en conditions basique et acide.

En pratique, l'ouverture de la fonction époxyde se fait par hydrolyse, c'est-à-dire par action de l'eau en présence d'un catalyseur acide ou basique. Cette réaction fait ainsi apparaître deux nouvelles fonctions hydroxyles (alcools secondaires).

Enfin, l'utilisation d'un alcool en présence d'un catalyseur (acide ou basique) permet d'obtenir une seule fonction hydroxyle secondaire[4, 5]. La réaction consiste ainsi à chauffer le mélange réactionnel à la température de reflux de l'alcool (le méthanol est classiquement utilisé) en présence d'un catalyseur. Les catalyseurs généralement utilisés sont de l'acide sulfurique concentré, l'acide paratoluène sulfonique (APTS) ou encore une résine échangeuse d'ions (type Amberlyst 15).

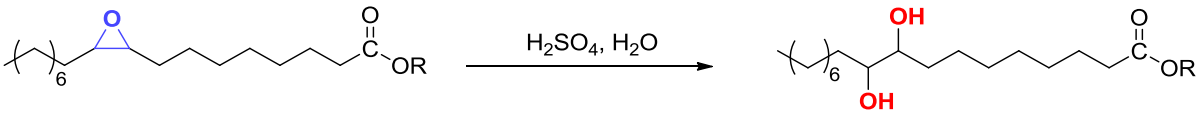


Figure III- 6 : Schéma général de la formation d'un diol vicinal à partir d'une fonction époxy.

Enfin, les époxydes sont susceptibles d'être directement hydrogénés par le dihydrogène en présence d'un catalyseur, généralement le nickel de Raney[6]. Les composés obtenus sont alors porteurs d'une seule fonction hydroxyle secondaire, le deuxième carbone impliqué dans la double liaison n'est quant à lui pas substitué. Cette méthode est largement utilisée pour les triglycérides car la suppression des insaturations améliore la tenue à l'oxydation des produits.

2. Oxydation des insaturations en péroxydes et réduction en alcool

Les doubles liaisons peuvent être oxydées pour former des hydro-peroxydes allyliques pouvant ensuite être réduits en alcools secondaires[7]. La réaction alors mise en jeu est une réaction photochimique. On utilise généralement un réacteur photochimique équipé d'une lampe à vapeur de sodium sous flux d'oxygène en présence de pyrophosphate de thiamine (TPP) et de dichlorométhane. Une fois le composé hydro-peroxyde formé, la réaction s'effectue à l'aide de borohydrure de sodium ($NaBH_4$) dans du méthanol à 0 °C.

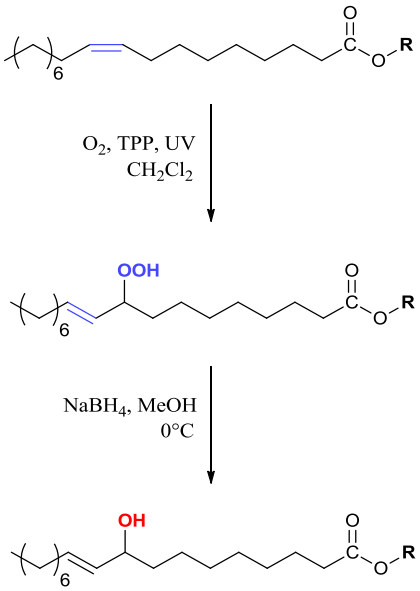


Figure III- 7. Synthèse d'hydroperoxydes allyliques réduits en alcools secondaires.

3. Mécanisme d'ozonolyse-réduction

La coupure oxydante d'une double liaison par l'intermédiaire de l'ozone (O_3) conduit à la formation d'un aldéhyde[8]. Une étape de réduction des aldéhydes en alcools primaires permet d'obtenir une fonction alcool.

L'ozone O_3 est un oxydant gazeux puissant, que l'on représente sous trois formes mésomères schématisées sur la Figure III-8:

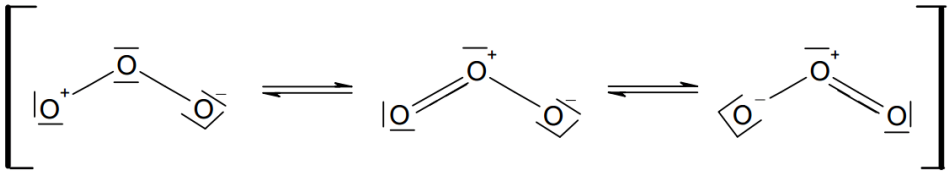


Figure III- 8. Les 3 formes mésomères de l'ozone.

Le mécanisme de la réaction d'ozonolyse implique, dans un premier temps, l'addition électrophile de l'ozone à la double liaison. Le composé intermédiaire alors formé est le 1,2,3-trioxolane ou molozonide. Ce complexe relativement instable forme un mélange d'entités carbonylées et un zwitterion (oxyde de carbonyle). La recombinaison de ces deux fragments aboutit à la formation de l'ozonide final ou 1,2,4-trioxolane. La deuxième étape consiste en la réduction de l'ozonide. Cette étape se fait par la mise en contact de l'intermédiaire avec du zinc dans de l'acide acétique ou encore par réaction avec le sulfure de diméthyle.

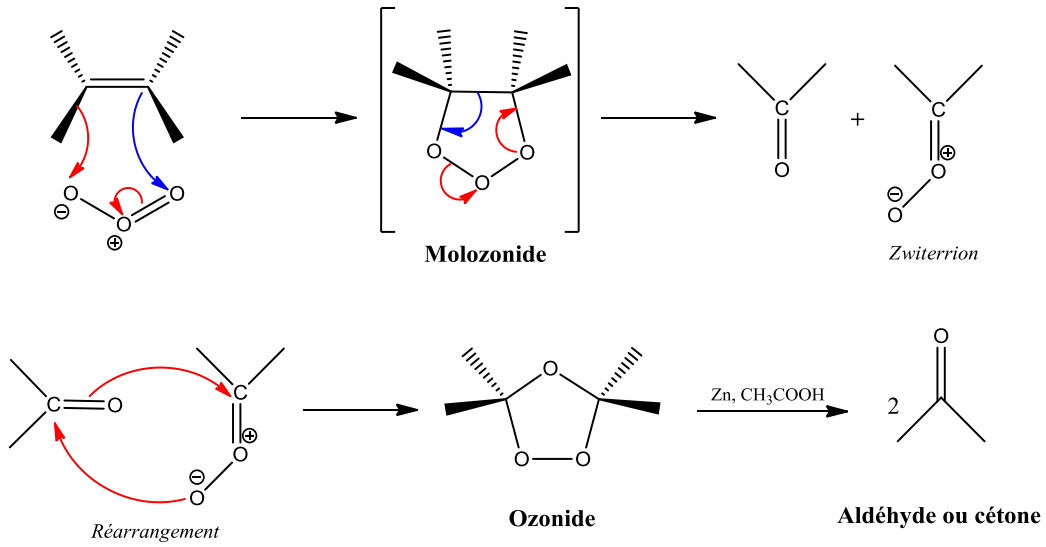


Figure III- 9. Schéma de la réaction d'ozonolyze des alcènes.

Le résultat global de cette séquence ozonolyse-réduction est la scission de la molécule au niveau de l'insaturation conduisant ainsi à la formation d'aldéhyde et/ou de cétone. Une étape supplémentaire de réduction des aldéhydes en alcools primaires permet d'obtenir des polyols à partir des dérivés d'huiles végétales[9-11]. Une fonctionnalité maximale de 3 peut alors être obtenue à partir de triglycérides insaturés, par exemple.

4. L'hydroformylation

L'hydroformylation, également appelée oxo-procédé, permet d'introduire une fonction aldéhyde sur les acides gras et triglycérides pouvant à son tour être modifiée pour aboutir à la formation d'alcools primaires.

De façon générale, l'hydroformylation consiste à faire réagir un composé oléfinique avec un mélange d'oxyde de carbone et d'hydrogène sous pression pour former un aldéhyde. Cette étape est généralement réalisée en présence d'un catalyseur. Les deux métaux les plus couramment utilisés sont le cobalt et le rhodium, les catalyseurs associés se présentent alors sous forme d'hydrures carbonylés[12-14] (rhodium dicarbonyl acétylacetonate par exemple) et sont solubles dans le milieu réactionnel : on parle alors de réaction catalytique homogène.

En pratique, la réaction s'effectue sous un courant d'un mélange de monoxyde de carbone et d'hydrogène à 110°C et permet d'obtenir des taux de conversion pouvant atteindre 95%. Les aldéhydes ainsi obtenus constituent des synthons de base et peuvent alors être convertis en alcools, esters, acides ou encore amines.
Dans le cas présent, nous nous intéresserons à l'étape d'hydrogénation qui, associée à l'hydroformylation, permet d'aboutir à la formation d'alcool primaire[15, 16]. Il s'agit simplement de la réduction de la fonction aldéhyde en alcool en présence d'un courant d'hydrogène et d'un catalyseur type Nickel de Raney.

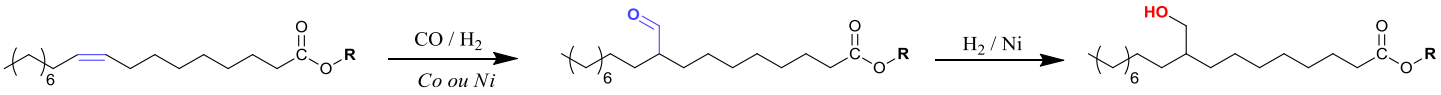


Figure III- 10. Réaction d'hydroformylation de l'insaturation suivie d'une hydrogénation catalytique.

Il est important de noter que cette réaction permet d'aboutir à une fonction alcool primaire contrairement aux étapes d'ouverture d'époxy qui génèrent la formation d'alcools secondaires. Comme cela a déjà été souligné dans plusieurs études, la nature du polyol tient un rôle très important dans la synthèse des PU et influence de façon significative les propriétés finales du matériau ainsi synthétisé[17].

5. Addition électrophile

Les électrons π appartenant à la double liaison sont relativement réactifs et sont donc susceptibles d'être attaqués par des espèces électrophiles. Ainsi, l'addition de formaldéhyde sur les acides gras insaturés permet d'accéder à de nouvelles chaines grasses di-fonctionnelles : des acides hydroxycarboxyliques[18, 19] (Figure III-11).

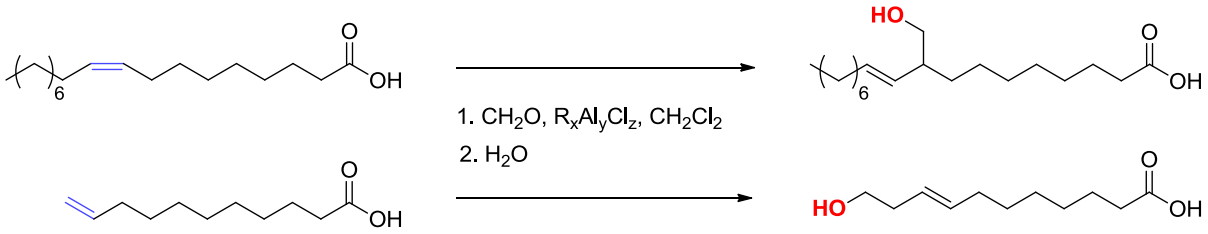


Figure III- 11. Addition de formaldéhyde sur l'acide oléique et l'acide undécylénique.

6. Couplage thiol-ène

Comme nous l'avons vu dans les sections précédentes, la plupart des fonctionnalisations d'huiles végétales se déroulent en deux étapes au moins et nécessitent l'emploi de catalyseurs souvent coûteux. La réaction thiol-ène permet quant à elle la synthèse de polyols porteurs d'alcools en une seule étape et représente une réaction versatile pour l'obtention d'intermédiaires fonctionnels bio-sourcés[20]. En effet, cette réaction de « click chemistry » est particulièrement intéressante ; insensible à l'oxygène, elle offre le choix d'une activation photochimique ou thermique et conduit à des rendements élevés. Récemment, le greffage de mercaptoéthanol sur les dérivés d'huiles a fait l'objet de plusieurs publications. Nous pouvons ainsi citer les travaux de Meier concernant le greffage de mercaptoethanol sur les dérivés d'huile pour la synthèse de polyesters[21].

Le mécanisme réactionnel sur lequel repose le couplage thiol-ène est celui de l'addition radicalaire de divers composés par l'intermédiaire de la double liaison particulièrement riche en électrons[22, 23] (Figure III-12).

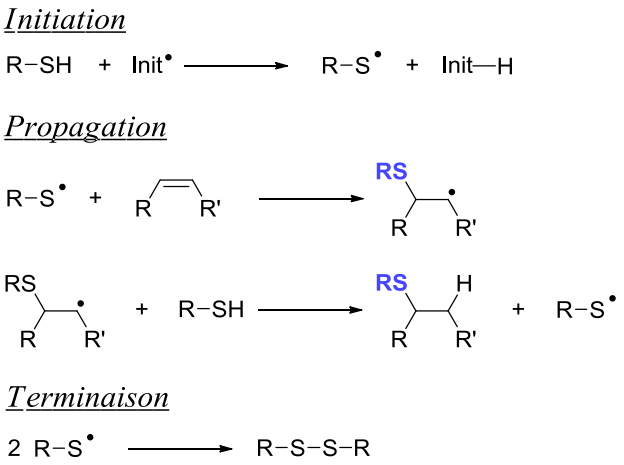


Figure III- 12. Mécanisme radicalaire de l'addition d'un thiol sur une double liaison.

La méthode thiol-ène connait un réel développement durant ces dernières années, avec un grand nombre de publications dédiées. Elle semble en effet particulièrement adaptée à la fonctionnalisation des huiles végétales étant donnée sa « robustesse » vis-à-vis des variations de qualité de la matière première, sa facilité de mise en œuvre et la diversité des fonctions réactives qu'elle permet de greffer. En outre, le couplage thiol-ène fait appel à des réactifs peu couteux et disponibles dans l'industrie. Cependant, cette réaction n'a pas été mise en place dans notre étude mais fera l'objet d'une étude plus approfondie si cette voie de fonctionnalisation se révèle prometteuse.

* * *

Dans le cadre de nos travaux de recherche, une nouvelle stratégie de synthèse a été retenue dans la perspective d'élaborer des macropolyols originaux à partir de lignine estérifiée par des acides gras. Cette stratégie de synthèse est présentée dans la partie suivante sous la forme d'une troisième publication.

II. Modification de la lignine par l'acide oléique, synthèse de polyuréthanes

La troisième publication reportée dans ce chapitre et intitulée "Original polyol based on organosolv lignin and fatty acids: new bio-based building blocks for segmented polyurethane synthesis" fait état de l'estérification de la lignine par un acide gras et de sa modification pour l'élaboration d'une nouvelle architecture de macropolyol. L'intégration de ce nouveau synthon dans la synthèse de PU est ensuite abordée. Afin d'étendre et de compléter ces résultats, divers paramètres ont été étudiés, notamment l'influence du ratio NCO:OH dans la formulation du PU mais également l'impact de la masse molaire des chaines de poly(propylène) oxyde introduites dans le système réactionnel.

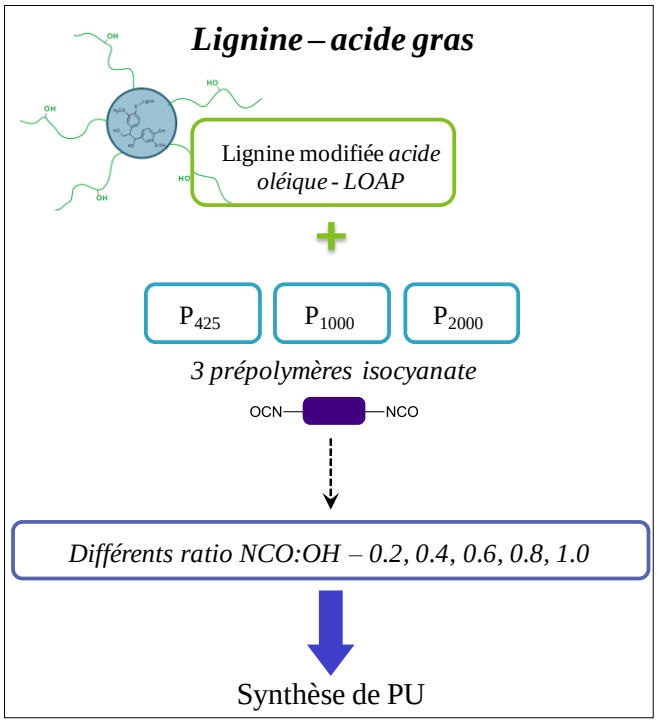


Figure III-13. Schéma récapitulatif de la stratégie de synthèse développée dans le chapitre III.

Original polyols based on organosolv lignin and fatty acids: new bio-based building blocks for segmented polyurethanes synthesis

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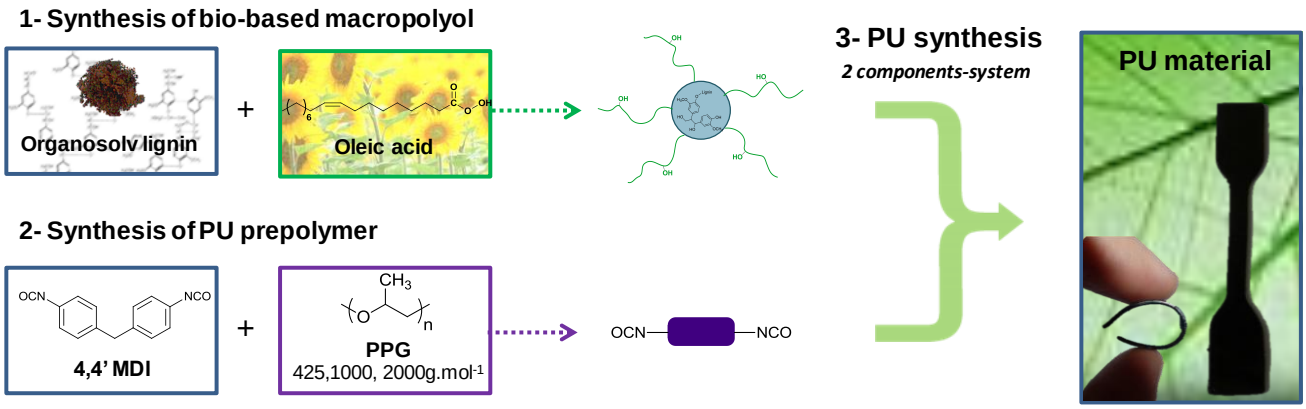
Green chemistry – Soumis ultérieurement



Abstract

Macropolyols were successfully prepared through combining two different biomolecules from biomass i.e., lignin and oleic acid, using a solvent-free and catalyst-free method. The chemical structures of this original lignin-fatty acid based polyol and its intermediates were determined by ^{1}H NMR and FT-IR analyses. A serie of polyurethanes (PUs) were then prepared on a two-step procedure. Three linear isocyanate prepolymers were first synthesized from 4,4' methylenebis(phenyl isocyanate) and different molecular weight poly(propylene) oxide (PPO - 425, 1000 and 2000 $g.mol^{-1}$). These intermediates were used to obtain different PUs macromolecular architectures by varying reaction parameters in presence of the lignin-fatty acid based macropolyol. The final lignin-based polyurethanes were thoroughly chemically characterized by FT-IR studies, whereas the properties of these polymers were assessed through DSC, TGA, DMTA, and tensile tests experiments. All this was performed in order to evaluate the influence of NCO:OH molar ratio (from 0.2 to 1.0) as well as the influence of PPO chain length. These new polymers with controlled architectures presented advanced properties. The high biobased content (until 89%) depicts an important output for the valorisation of the lignin and then may be an optimal alternative to conventional PUs.

Keywords:

Lignin, polyol, polyurethane, building-blocks, fatty acid.

1. Introduction

Renewable resources have recently gained interest as a petroleum substitute in chemical and polymer applications[24]. Biomass can also be the starting point of innovative pathways for designing new tailor-made building blocks and then original macromolecular architecture[25]. Among the multitude of resources which are extracted from the biomass, vegetable oils and lignocellulosic components represent a great potential and have attracted a lot of researches, notably to design monomers (mainly polyols) for the synthesis of bio-based polymers[26].

Lignin, a lignocellulosic component, represents after cellulose the most abundant biopolymer on Earth. It is a substituted hyperbranched polyphenol and constitutes a natural aromatic polymer that accounts for up 18-35% by weight of wood[27]. Lignin can be extracted from lignocellulosic biomass (wood, annual plants such as wheat straw and agricultural residues) by different extraction processes but its chemical structure still remains under investigation. It is an amorphous polymer consisting of phenylpropane units, originating from three aromatic alcohol precursors (monolignols), *p*-coumaryl, coniferyl and sinapyl alcohols[28]. Given its unattractive structure, lignin possesses therefore significant potential for being a source of macromolecular materials due to its huge availability and variety of functional groups. In fact, the numerous sites on the lignin backbone offer many opportunities for chemical modifications. Several studies have tried to take advantage of this aromatic structure by performing reactions that would confer to lignin higher reactivity and suitability for industrial applications, e.g. for the synthesis of polymers[29]. In that frame, chemical modification of lignin can be used to introduce reactive sites such as available hydroxyl groups and improve the capacity of hydrogen bonding with other components. The production of lignin-based polymers is however limited by its hindered structure i.e. its high crosslink density and the highly polydisperse molecular weight of the molecule.

Development of new advanced lignin-derived polymer is thus related to chemical modifications that can be carried out on this macromolecule. Similarly to thermoplastic cellulose ester derivatives, one method adopted to improve the properties and use of lignin as a thermoplastic polymer is by esterification. This procedure is an effective way to solubilise it in a common solvent and to easily characterize it. Various studies have been performed on lignin esterification by using organic acids such as acid anhydrides or acyl chlorides in presence of suitable acid or basic catalysts (sulfuric acid or pyridine). Lignin esterification using diacids has already been done[30, 31] but the use of fatty acid has only been seen for the

functionnalisation of wood to enhance its thermoplastic properties, flexibility and melting temperature [32, 33].

Recently, with the rapid development of green chemistry and engineering, a large quantity of polymeric materials mainly derived from plant oil and its derivatives have been reported[20, 34, 35]. During the last decades, a plentiful literature has been dedicated to the synthesis of polyol based on vegetable oil functionalization through their double bonds[36, 37]. These latter are generally performed by epoxidation and direct hydroformylation reactions whereas the ester bonds can be derivatized by e.g., transesterification or amidation. Those functionalization processes require the epoxidation of double bonds followed by the oxirane ring-opening by ozonolysis[9], hydroformylation[12] and more recently metathesis[38, 39] and thiol-ene coupling reactions[21, 40, 41] offer a new and green approach to modify fatty acids derivatives. In this way, a great variety of polyols based on vegetable oils have been synthesized and suggests interesting intermediates for designing e.g., polyurethanes (PUs) with new macromolecular architectures.

PUs represent one of the most important and versatile classes of polymeric materials. They can vary from thermoplastic to thermosetting materials with broad applications such as flexible or rigid foams, thermoplastic elastomers, adhesives and coatings[42]. The production of PUs is based on a polyaddition reaction between oligomeric polyol with terminal hydroxyl groups and a diisocyanate (or polyisocyanate)[43]. Thanks to the high variety of design for oligomeric polyols, it is possible to modulate the architecture and then final properties of PUs. Among them, we have mainly focused our investigations on segmented polyurethanes (PUs), well-known for their versatility with a wide range of behaviours and applications. They are multi-phase copolymers structured with soft and hard segments. The soft block is built out of a polyol responsible for the flexibility and elastomeric character of the PU whereas the hard block, constructed from a chain extender and isocyanate gives its toughness and physical performance properties.

Through an original approach we have used vegetable oils derivatives (triglycerides and fatty acids) as a raw material for lignin chemical modification. This methods depicts an innovative way for designing new tailor-made bio-based building blocks an then new macromolecular architectures[44]. The aim of this study is focused on the esterification of lignin with chlorinated fatty acid (oleoyl chloride) in a solvent-free system to develop a new polyol. The resulting biobased polyester, with an original core-shell structure, can represent a promising precursor for polymer synthesis.

This paper also reports the PUs synthesis in a two-step procedure with synthesized prepolymers. A total of three isocyanate prepolymers intermediates were produced with different molecular weight poly(propylene) oxide (PPO) i.e 425, 1000 and 2000 g.mol^{-1}. Final PUs were performed between the biobased macropolyol and the different isocyanate prepolymers. Properties of the resulting PUs were modulated by varying NCO:OH molar ratio from 0.2 to 1.0, and the PPO chain length. The synthesized chemicals (intermediates and lignin-based polyurethanes) were first analyzed by FT-IR and DSC. To further investigate the thermo-mechanical properties and their thermal stability, TGA, DMTA and tensile tests were performed to define the structure and determine the behaviour of the resulting polymers.

2. Experimental section

2.1 Raw materials

Organosolv lignin (Alcell) from hardwood was supplied by Lignol Company (Canada) and used as received without any further purification. Specific techniques for lignin characterization have been carried out according different methods previously reported[29] (Table III-1). Oleic acid (91% C18:1, 4% C18:2, 2% C16, 2% C18) was purchased from Croda. It is a yellowy transparent viscous liquid with an acid number of 199 mg KOH.g^{-1}. Peracetic acid (35 wt.% in an acetic acid solution), dichloromethane (DCM - 99.9%), methanol (99.6%), Tetrahydrofuran (THF - 99.8%), *para*-toluene sulfonic acid (APTS) and Dibutyl Tin Dilaurate (DBTDL - 95%) were all obtained from Sigma Aldrich. Poly(propylene) oxide polymers (PPO) of 425, 1000 and 2000 g.mol^{-1} were obtained from Acros and were dried under reduced pressure at 100°C before using. All of the solvents were distilled before their utilization for chemical synthesis.

Moisture content (%)		3.83
SEC analysis	M_n *(g.mol^{-1})*	1000
	M_w *(g.mol^{-1})*	2275
	PDI *(M_w/M_n)*	2.28
^{1}H NMR analysis	Total OH *(mmol.g^{-1})*	2.26
	OH phenolic *(mmol.g^{-1})*	1.30
	OH aliphatic *(mmol.g^{-1})*	0.96
	Average hydroxyl groups/ mol of lignin	2.26
Tappi method	Methoxy content *(mmol.g^{-1})*	2.07
DSC analysis	T_g (°C) *crude lignin*	76

Table III- 1. Analysis results performed on organosolv lignin.

2.2 General methods and analysis

^{1}H NMR were recorded in $CDCl_3$ on a Bruker UltraShield 300 spectrometer operating at 300 MHz. Chemical shifts (δ-ppm) are reported in parts per million relative to the internal standard tetramethylsilane (TMS, δ = 0.00 ppm). Polymer analysis was performed with a size exclusion chromatography (SEC) system from Shimadzu equipped with a pre-column PLGel 5µ, two PLGel 5µ Mixed-C 300 mm columns, one PL 100 Å 300 mm column and refractive index (RI) and ultra-violet (UV) detectors. All determinations of molar mass were performed relative to linear Polystyrene standards from 580 to 1,650,000 g.mol^{-1}.

Fourier Transformed Infra-Red spectroscopy was carried out with a Nicolet 380 FT-IR spectrometer working in Attenuated Total Reflectance Mode (FTIR-ATR). This analysis was used to detect specific chemical groups which provide direct evidence of different reactions performed onto lignin.

Differential scanning calorimetry (DSC) experiments were carried out with a TA DSC Q200 calorimeter, under nitrogen atmosphere using a sample mass in the range 2-5 mg. The samples were heated until 120°C with a heating rate of 10°C.min^{-1} (first heating scan), then cooled to -80°C at 10°C.min^{-1} and finally re-heated to 120°C at a heating rate of 10°C.min^{-1} (second heating scan). The glass transition temperature, T_g, is reported as the midpoint of the heat capacity change. These values were determined on the second heating scan in order to erase the previous thermal history of the samples during the first scan.

Thermogravimetric analyses (TGA) were performed on a Hi-Res TGA 2950 apparatus from TA Instruments at a heating rate of 10°C min^{-1} up to 750°C under a nitrogen atmosphere (flow rate = 25 mL.min^{-1}).

Dynamic mechanical thermal analysis (DMTA) was performed on polymers (with dimensions around 23 x 4 x 1 mm^3) with RSA-II apparatus from TA Instruments equipped with a liquid-nitrogen cooling system. Experiments were recorded on PU films with traction mode at a maximum strain from 0.003% to 0.9% and a frequency of 1Hz. The sample was heated from -100°C to 200°C at a heating rate of 2°C.min^{-1}.

Dynamic rheological analyses (DRA) were performed by using a strain-controlled rheometer (ARES, Rheometric Scientific) with parallel-plate geometry (25 mm in diameter). The dynamic storage modulus (G') and dynamic loss modulus (G'') were measured as a

function of the temperature ranging from 0°C to 200°C. A fixed strain was used to ensure that the measurements were taken well within the linear viscoelastic range of the material investigated. Results of rheological experiments are only presented in *Supplementary Information* section.

From uniaxial tensile tests, Young's modulus (E), ultimate strength (σ) and strain at break (ε) were obtained using a Zwick/Roell machine. The experiments were performed at room temperature, using a crosshead speed of 20 $mm.min^{-1}$ and a load cell of 20N sensitivity. After adjusting the parameters, experiments were carried out 5 times for each sample.

2.3 Synthesis and characterization of lignin-fatty acid based polyol

Lignin-fatty acid based polyol (LOAP) is performed in a multistep synthesis involving the esterification of lignin with oleic acid, followed by the epoxydation of the fatty acid double bond and then the oxirane ring-opening.

2.3.1 Esterification of organosolv lignin

Lignin esterification has been performed with oleic acid from sunflower oil (Figure III-14). In order to improve reactivity of the oleic acid, a chloration step of the compound has been carried out before esterification. According the procedure established by Thiebaud et al.[32, 33] , esterification has been then performed by a solvent-free and catalyst free reaction using oleoyl chloride.

Chloration step

The reaction took place into a three-necked 500 mL round-bottomed flask equipped with a magnetic stirrer, a nitrogen-gas bubbling system and an outlet connected to a wash-bottle containing an aqueous sodium hydroxide solution to trap the hydrogen chloride formed. The chloration step is carried out with an excess of oxalyl chloride, oleic acid:oxalyl chloride (1:2). Oleic acid (40.0 g; 0.14 mol) was first dissolved into ethyl acetate (300 mL) and was cooled to 0°C under nitrogen flow. An excess of oxalyl chloride (36.0 g; 0.28 mol) was then added drop by drop at 0°C (15 min) and finally heated at 50°C during 5h. The solvent and the excess of oxalyl chloride were then distilled out from the reactive mixture.

Oleoyl chloride (OC) was obtained as a yellow viscous product.

^{1}H-NMR (300MHz, $CDCl_3$, δ (ppm)): 0.88 (3H, t, C*H*$_3$), 2.87 (2H, t, C*H*$_2$-COCl), 5.32-5.38 (vinylic protons).
IR (cm^{-1}): 3005 (C=C-H), 1799 (C=O chloride group).

Esterification step

The esterification procedure was carried out in a 500 mL reactor having a mechanical stirrer, a nitrogen-gas bubbling system and an outlet connected to a wash-bottle containing an aqueous sodium hydroxide solution. Organosolv dried lignin (30.0 g; 67.8 mmol OH) and OC (40.7 g; 135.6 mmol) were successively introduced in the reactor. The reaction was then conducted at 130°C under agitation and a continuous nitrogen stream for 15h. At the end of the reaction a brown viscous but homogeneous product was obtained. The esterified lignin (EL) was washed with cold methanol in order to remove the excess of acid chloride.
The esterification reaction was confirmed by NMR and IR analyses and the remaining fatty acid has been quantified.

^{1}H-NMR (300MHz, $CDCl_3$, δ (ppm)): 0.88 (3H, t, C*H*$_3$), 2.29 (2H, t, C*H*$_2$-$COOCH_3$), 2.54 (2H, t, C*H*$_2$-COO-lignin), 3.88 (3H, OCH_3 lignin methoxy) 5.32-5.38 (vinylic protons).
IR (cm^{-1}): 3005 (C=C-H), 1761 and 1737 (ester band).

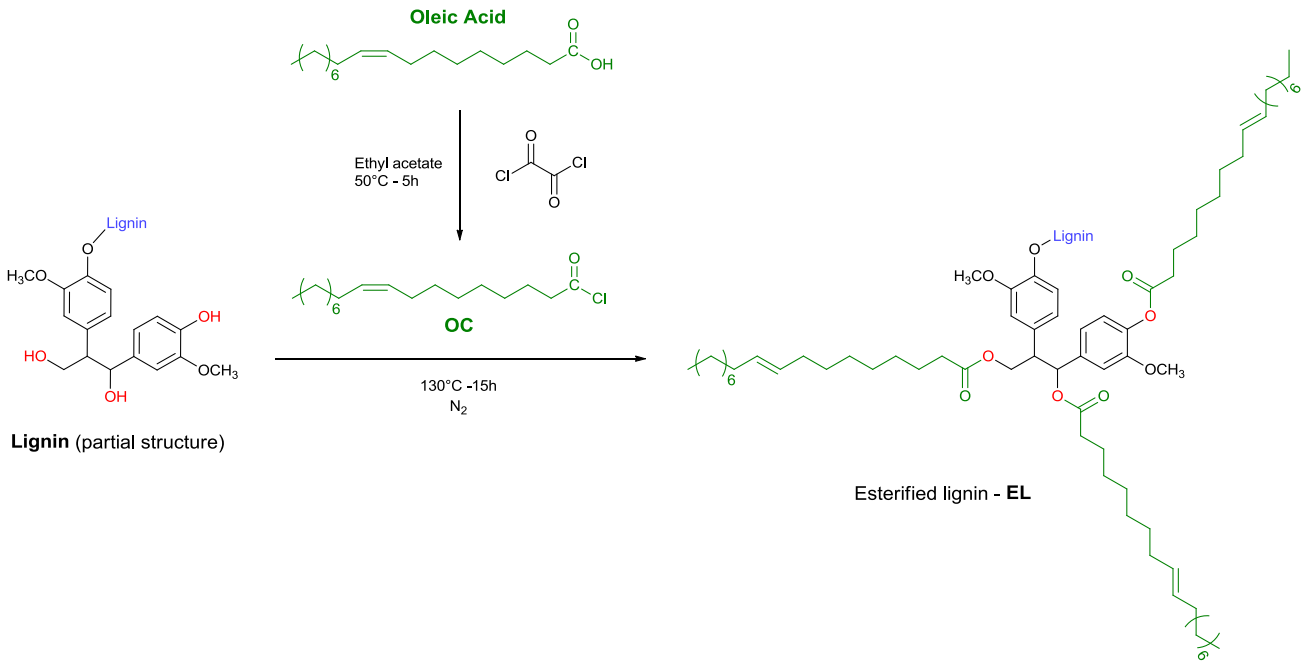


Figure III- 14. Reaction schemes for the synthesis of the esterified lignin – EL.

2.3.2 Epoxydation of oleic acid double bond

A 500 mL round-bottomed flask was charged with esterified lignin (EL) (45.0 g, 72 mmol of double bonds) dissolved into DCM (250 mL) and stirred until obtain homogenous solution. Peracetic acid (10.9 g; 144 mmol) was added in small portions. The reaction mixture was stirred at room temperature for 5 h. The organic layer was washed three times with brine and dried over sodium sulfate. The solvent was evaporated under reduced pressure and then dried under vacuum at 35°C for one night to obtain the epoxy-lignin oleate (ELO).

^{1}H-NMR (300MHz, $CDCl_3$, δ (ppm)): 0.87 (3H, t, C*H*$_3$), 1.20-1.70 (methylene protons), 2.29 (2H, t, C*H*$_2$-$COOCH_3$), 2.54 (2H, t, C*H*$_2$-COO-lignin), 2.89 (2H, epoxy ring proton).
IR (cm^{-1}): 1740 ($COOCH_3$ – ester bond), 841 (epoxy).

2.3.3 Oxirane Ring-Opening synthesis

A 500 mL round-bottomed flask was charged with epoxy lignin oleate (ELO), methanol, and APTS (2 wt.% vs. ELO) as the catalyst. The reaction mixture was stirred under reflux and nitrogen flow for 15h. After completion of the reaction, the methanol was distilled out under reduced pressure. The product was then dissolved in DCM and washed three times with brine to remove the catalyst. The organic layer was dried over sodium sulfate, filtered and evaporated under reduced pressure to obtain the lignin-oleic acid polyol (LOAP).

^{1}H-NMR (300MHz, $CDCl_3$, δ (ppm)): 0.88 (3H, t, CH_3), 120-1.70 (methylene protons), 2.29 (2H, t, C*H*$_2$-$COOCH_3$), 2.54 (2H, t, C*H*$_2$-COO-lignin), 2.99 (1H, dd, C*H*-OCH_3), 3.41 (3H, s, OC*H*$_3$), 3.49 (1H, m, C*H*-OH).
IR (cm^{-1}): 3480 (OH), 1740 ($COOCH_3$).

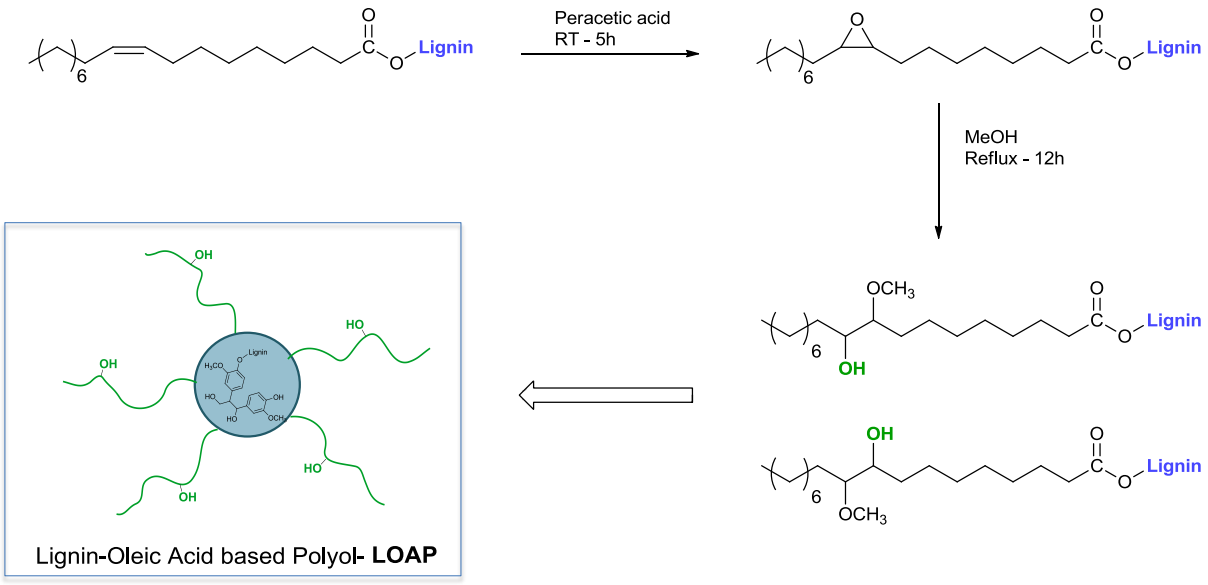


Figure III- 15. Synthetic pathway to macropolyol - LOAP (Lignin Oleic Acid Polyol) - from lignin and oleic acid. Schematic representation of lignin-fatty acid based polyol.

2.3.4 Characterization of the LOAP

Before the PU synthesis, the synthesized lignin-fatty acid based polyols have been characterized. A standard method has been developed to evaluate the amount of hydroxyl groups available for the reaction with isocyanates. This parameter is defined as the hydroxyl number or as the hydroxyl index.

Hydroxyl Index determination

The hydroxyl index of polyol has been determined and expressed as milligrams of potassium hydroxide equivalent for one gram of the sample (mg $KOH.g^{-1}$). The method used for hydroxyl index determination was adapted from the standard ASTM 4274-99 method. It is particularly recommended for polyester and polyether polyols containing primary and secondary hydroxyl groups. This method is based on the reaction of hydroxyl terminal groups with organic acids (acetic anhydride or phthalic anhydride). Two solutions were previously prepared, reactive solution (phthalic anhydride in pyridine-$1mol.L^{-1}$) and titration solution (sodium hydroxide in water-$1mol.L^{-1}$). 2g of polyol were introduced in Erlenmeyer with 20 mL of phthalic anhydride solution and stirred magnetically until complete dissolution. The reactive mixture was then heated under reflux at 130°C for 45 min. After the reflux, the flask was left to cool at room temperature before adding 30 mL of pyridine and 30 mL of deionized

water. The acid carboxylic groups resulting from the excess of phthalic anhydride were then titrated by a pHmetric method with a solution of sodium hydroxide. Titration was carried out 2 times and one blank was also performed. Hydroxyl index (I_{OH}) in mg of KOH.g^{-1}, was determined according to equation (1):

$$I_{OH} = \frac{(V_{blank} - V_P) \times C \times 56.1}{W_P} \qquad (1)$$

Where V_{blank} (mL) is the NaOH volume required for blank titration, V_P (mL) is the NaOH volume required for polyol sample titration, C (mol.L^{-1}) is the NaOH concentration and W_P (g) is the polyol weight.

2.4 Polyurethane synthesis

The general procedure followed for polyurethane (PU) synthesis is based on a two-step procedure. Firstly, three isocyanate prepolymers have been synthesized by varying the diol (PPO) molar mass while the molar ratio of isocyanate and hydroxyl groups remains constant. Then in a second step, different PUs are synthesised with the bio-based polyol building blocks and the prepolymers (Figure III-16).

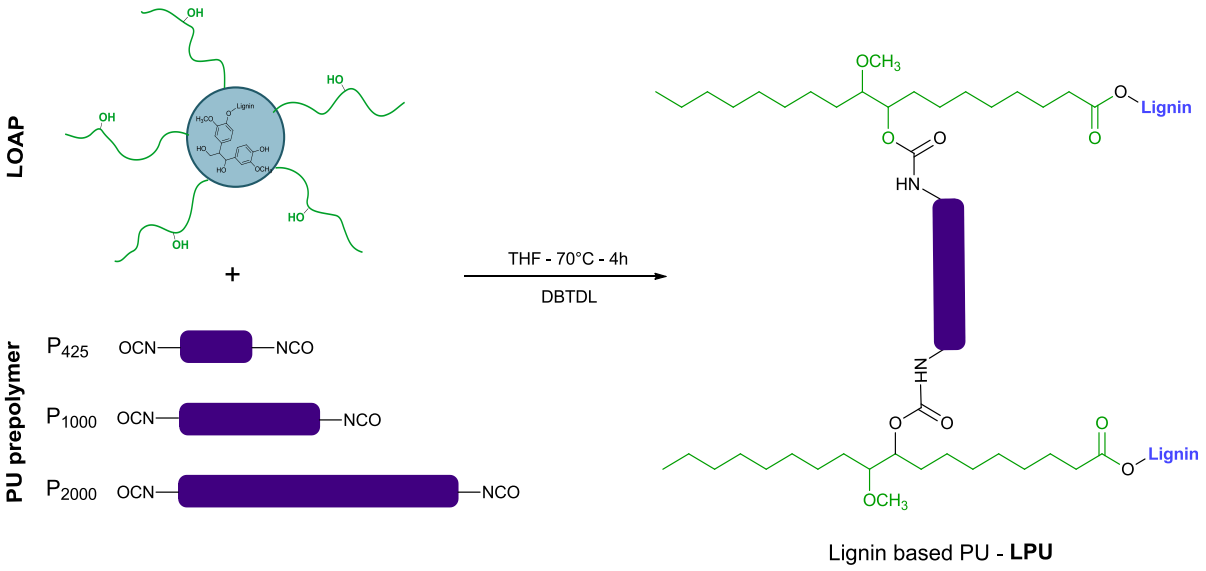


Figure III- 16. Synthesis of lignin based PU – LPU.

2.4.1 Prepolymer synthesis

A three-necked 250 mL round-bottomed flask was fitted with a nitrogen inlet tube and a mechanical stirrer. Poly(propylene) oxide and 4,4' MDI (f=2) were added into the flask and stirred at 70°C during 5 hours to yield isocyanate prepolymer with a 1.8 molar ratio of NCO:OH. The ensuing isocyanate prepolymers were coded as P_{425}, P_{1000} and P_{2000} for syntheses with PPO with molecular weights of 425, 1000 and 2000 $g.mol^{-1}$, respectively. The exact concentration of free isocyanate functions on the prepolymer was then determined.

NCO content determination

This method allows determining the amount of isocyanate which reacts with one equivalent of N-Dibutylamine, and gives NCO content by weight per cent.

$$\% \text{ NCO} = \frac{\left(V_{blank} - V_s\right) \times 42 \times 0.1}{W_P} \qquad (2)$$

Where V_{blank} (mL) is the hydrochloric acid volume required for blank titration, V_s (mL) is the HCl volume required for polyol sample titration and W_P (g) is the polyol weight.

2.4.2 Polymer synthesis

The typical procedure used is as follow: three-necked 100 mL round-bottomed flask equipped with a magnetic stirrer, nitrogen inlet and condenser was charged with LOAP and around 40 mL of anhydrous THF. The solution stirred at 70°C under nitrogen flow until the complete dissolution of polyol. Then, the isocyanate prepolymer previously dissolved in THF (P_{425}, P_{1000} or P_{2000}) and DBTDL (5 wt.% based on lignin monomers) were added. The NCO:OH molar ratios, also known as isocyanate index, were calculated on the basis of hydroxyl index of the polyol and NCO content from the prepolymers. Five different molar ratios were used for the syntheses: 0.2, 0.4, 0.6, 0.8 and 1.0. The reaction mixture was stirred at 70°C for 4h. After completion of the reaction, THF was evaporated and the PU was dried over one night at 35°C under vacuum. It may be noticed from Table III-2 that in PU series, up to 89 wt.% of lignin/oleic acid based macropoyol (LOAP) could be incorporated, highlighting the high content of biobased products in PU formulations. The resulting PUs were characterized to determine their structures and their physicochemical and mechanical properties by IR, DSC, DMTA, DRA and uniaxial tensile tests. Rheological and mechanical

tests were performed on PUs processed into films obtained by compression moulding between two plates, at 100-120°C.

Samples	Isocyanate prepolymer	NCO:OH molar ratio	% LOAP [a] (w/w)	PU formulation		
				OH from LOAP (mol)	PPO (mol)	NCO (mol)
LPU-1	P_{425}	0.2	89	3.67	1	1.8
LPU-2		0.4	81	1.83	1	1.8
LPU-3		0.6	74	1.22	1	1.8
LPU-4		0.8	68	0.92	1	1.8
LPU-5		1.0	63	0.73	1	1.8
LPU-6	P_{1000}	0.2	82	4.02	1	1.8
LPU-7		0.4	69	2.02	1	1.8
LPU-8		0.6	60	1.35	1	1.8
LPU-9		0.8	53	1.00	1	1.8
LPU-10		1.0	47	0.80	1	1.8
LPU-11	P_{2000}	0.2	78	5.35	1	1.8
LPU-12		0.4	64	2.70	1	1.8
LPU-13		0.6	54	1.80	1	1.8
LPU-14		0.8	47	1.35	1	1.8
LPU-15		1.0	42	1.10	1	1.8

Table III- 2. Synthesis of the different PUs with the corresponding designations and formulations.

[a] : % of biobased content (LOAP is composed by lignin and oleic acid)

3. Results and discussion

The results are presented in six sections. First, lignin has been characterized to clearly define its chemical properties in view of chemical modification. Afterwards, the polyol building block and PU were analyzed by FT-IR and ^{1}H NMR to confirm reaction and the properties of the resulting materials are discussed subsequently. The influence of reaction parameters such as NCO:OH molar ratio and PPO molar mass on PU materials are further investigated. In the last section, thermal stability of PU is also studied by TGA experiments.

3.1 Lignin characterization

The lignin was produced from an ethanol-water pulping (Alcell process) as already described elsewhere[45]. The main characteristics of this lignin have been reported in Table III-1. These data were found to be in the same range as that of others reported in the literature[46] and were also in good agreement with the values given by the supplier. The chemical data constitute a key point since the hydroxyl functions were functionalized. Total and phenolic hydroxyl contents were quantified according different techniques including chemical titration and ^{1}H NMR based on acetylated lignin and SEC in chloroform[47-49]. As can be observed from Table III-1, results found for Alcell lignin showed low hydroxyl content of 2.26 mmol.g^{-1} with a low number average molecular weight (M_n = 1000 g.mol^{-1}), compared to kraft lignin and lignosulfonate. Therefore, SEC results should be taken as “relative values”. This lignin is well known to present a high purity (low ash and sugar content) and also presents a good solubility in most solvent, particularly in THF and pyridine which must be considered as a great advantage for chemical modifications.

3.2 Synthesis and characterization of macropolyol

The main objective of this part was to synthesize a macromonomer. The resulting LOAP macropolyol with secondary hydroxyl groups was designed to react in a second time with isocyanate functions. LOAP was synthesized in a four step pathways (Figures III-14 and III-15). The structures of all the intermediates were analyzed. The targeted chemical structures were confirmed by FT-IR and ^{1}H NMR spectroscopy (Figures III-17 and III-18).

In the first step, chloration of oleic acid with oxalyl chloride yield OC. FT-IR of oleic acid shows a band at 1708 cm^{-1} linked to the carbonyl group (C=O) from carboxylic acid function

and a broad band from 3100 to 3500 cm^{-1} corresponding to the hydroxyl groups, while a C=C-H stretching vibration band is observed at 3005 cm^{-1}. The chloration of oleic acid was confirmed by the shift of the carbonyl group band from 1708 to 1798 cm^{-1} due to the formation of a more withdrawing chloride group and disappearance of hydroxyl band in the region of 3100-3500 cm^{-1}.

The esterification of lignin with OC gave EL as the main product along with oleic acid as remaining product from the corresponding synthesis. EL was characterized by FT-IR and ^{1}H NMR. Esterification reaction resulted in a drastic reduction of the OH absorption band along with the appearance of the ester bands at 1761 and 1737 cm^{-1}, corresponding to the esterification of aliphatic and phenolic hydroxyl groups, respectively. ^{1}H NMR spectrum of EL is presented in Figure III-18. The appearance of peaks at 3.60 ppm confirms the formation of ester protons whereas a peak at 2.34 ppm assigned to CH_2 to which carboxylic group is attached is still remaining and assigned to the presence of oleic acid in the final product. The amount of oleic acid chain present in this mixture was estimated by NMR integration at 80% of fatty acid grafted onto lignin whereas 20% are free chains. EL is a very viscous product where residual free oleic acid chains are partially imbedded due to a challenging incomplete extraction of the oleic acid in excess.

In the third step, EL was treated with peracetic acid to obtain epoxy lignin oleate (ELO). FT-IR spectrum of intermediate ELO shows the absence of a band at 3005 cm^{-1} which was linked to the C=C-H group. The corresponding molecular structure was also confirmed by ^{1}H NMR with the appearance of a new peak at 2.89 ppm due to the epoxy ring protons and the disappearance of the vinylic protons at 5.32 ppm. The fourth and last step of the reaction pathway consists in the ring-opening of epoxide using methanol in the presence of acid catalyst (APTS) to obtain a mixture of two regioisomers (4/4'- LOAP) containing secondary hydroxyl groups. Further onward, only one isomer structure will be used for the simplicity of the reaction scheme (see Figure III-15). FT-IR spectrum of the resulting macropolyol shows the appearance of a band at 3432 cm^{-1} due to the hydroxyl groups and another band at 1097 cm^{-1} attributed to ether bond. Moreover, the appearance of three new significant peaks at 2.99, 3.41 and 3.49 ppm in ^{1}H NMR spectrum confirmed the ring-opening of the epoxides. These peaks are attributed to CH to which methoxy groups is attached, methoxy protons and CH to which hydroxyl groups is attached, respectively. The resulting macropolyol was then characterized by pH metric titration; the hydroxyl value was estimated at 60 mg $KOH.g^{-1}$ of

sample. This value is in the range of hydroxyl value for bio-based polyester polyols usually used for PU synthesis (between 30 and 200 mg KOH.g^{-1})[50, 51].

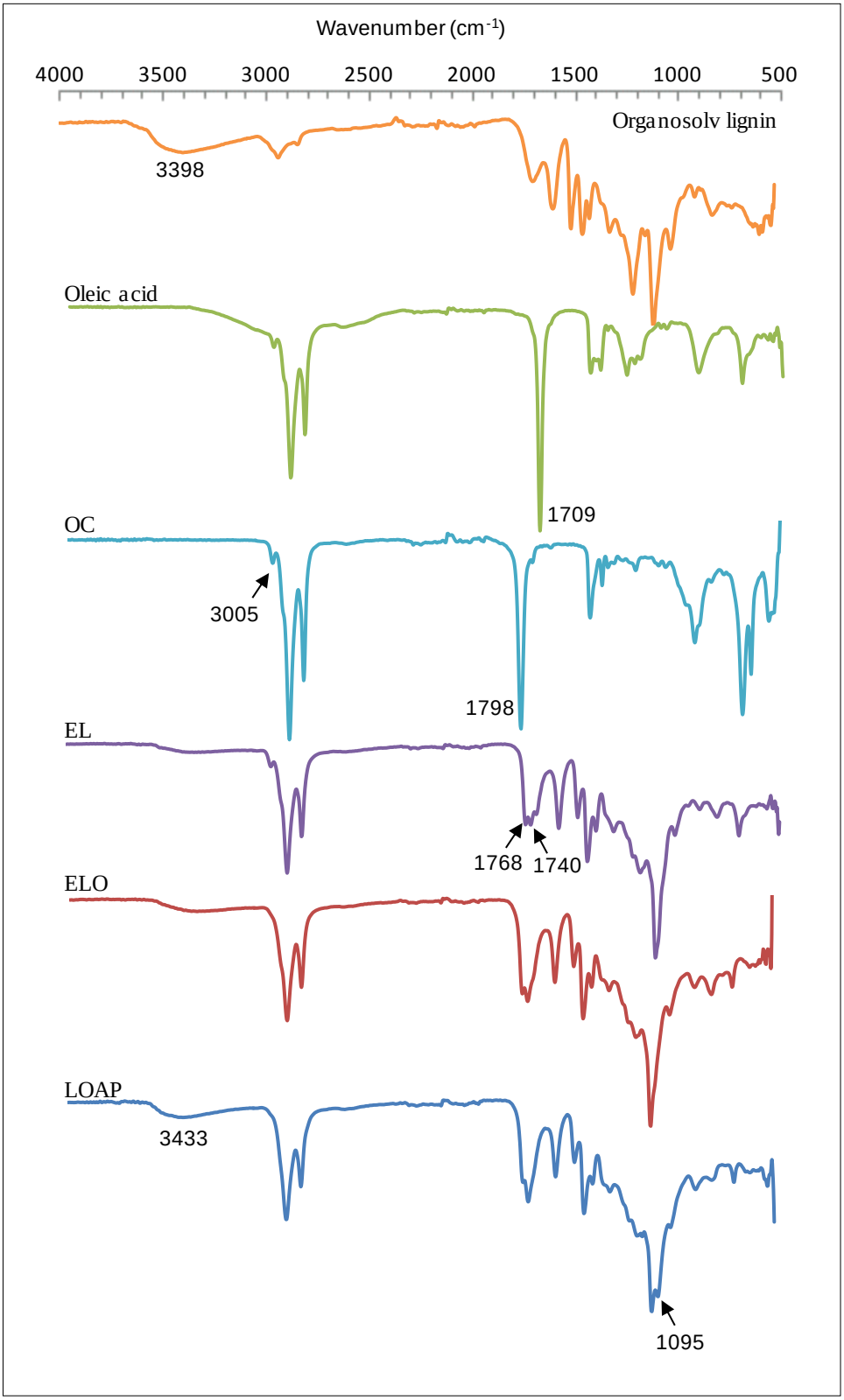


Figure III- 17. FTIR spectra of intermediates based on lignin and oleic acid.

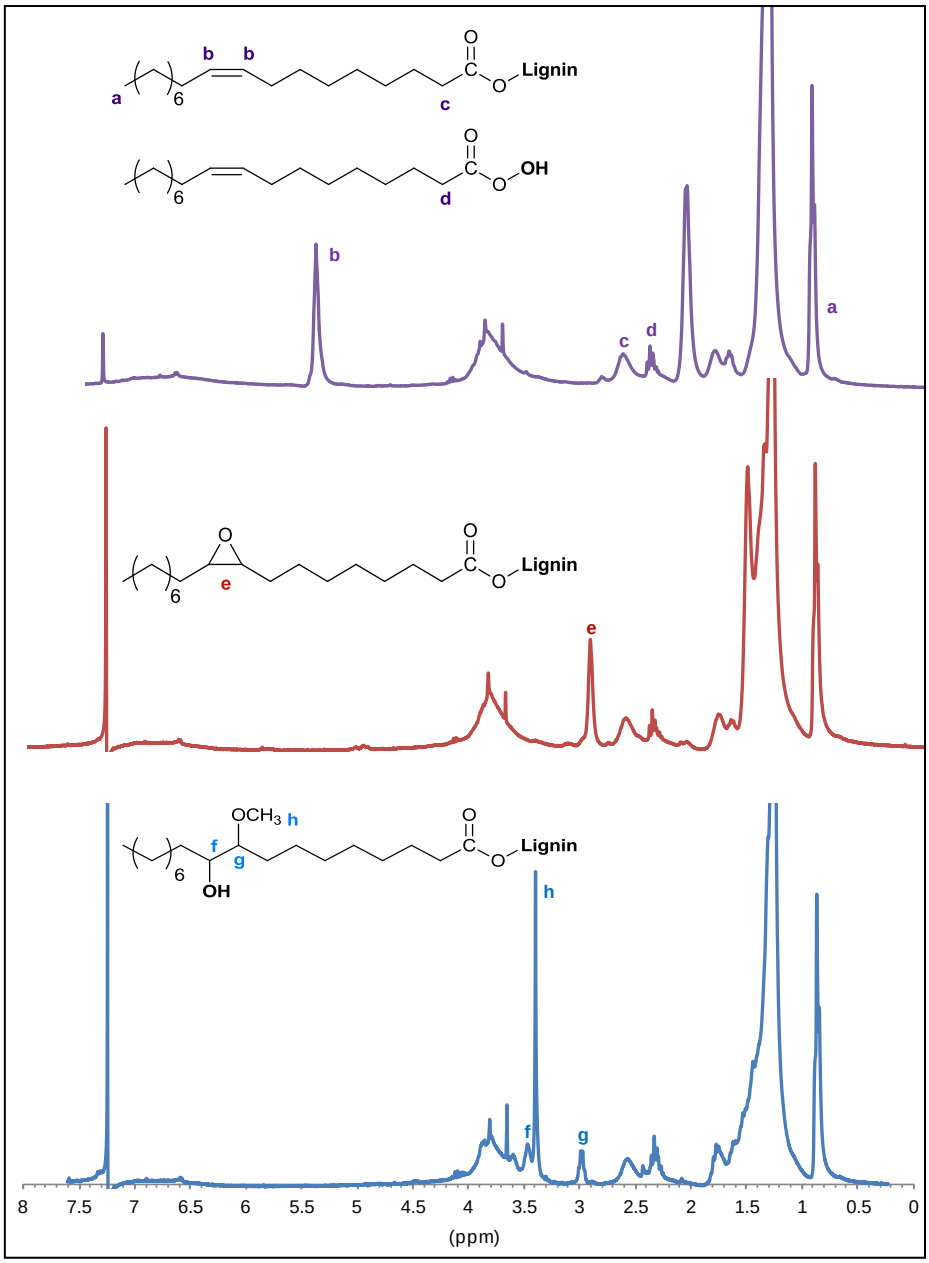


Figure III- 18. ^{1}H NMR spectra of intermediates based on lignin and oleic acid.

3.3 Synthesis and characterization of PUs

The reaction between LOAP and isocyanate was followed, analyzed and confirmed by FT-IR analyses. The isocyanate absorption band is assigned at approximately 2270 cm^{-1} and the absence of this absorbance can be used to monitor and check the isocyanate group conversion during the polymerization reaction. In this study, the absorbance corresponding to the NH stretching region, assigned at approximately 3300 cm^{-1} was used to follow and confirm the reaction between isocyanate and hydroxyl groups but also to qualitatively evaluate the effect

of the NCO:OH molar ratio. Figure III-19 shows the FT-IR spectra of PU samples synthesized with P_{425} at five different NCO:OH ratios. The signal attributed to OH stretching band at around 3500 cm^{-1} tends to decrease with increasing NCO:OH ratios whereas the NH stretching band becomes more intense. The conversion rate can be controlled and followed through the formation of urethane functions and the disappearance of the hydroxyl groups from macropolyol.

Concerning the properties of the synthesized PUs, thermal and mechanical behaviours should reflect the corresponding structural chemical organization, e.g., the cross-linking efficiency (related to the evolution of the NCO:OH molar ratio) and the chain prepolymer length in the flexible domain of the PU architecture. These statements will be investigated in the following sections.

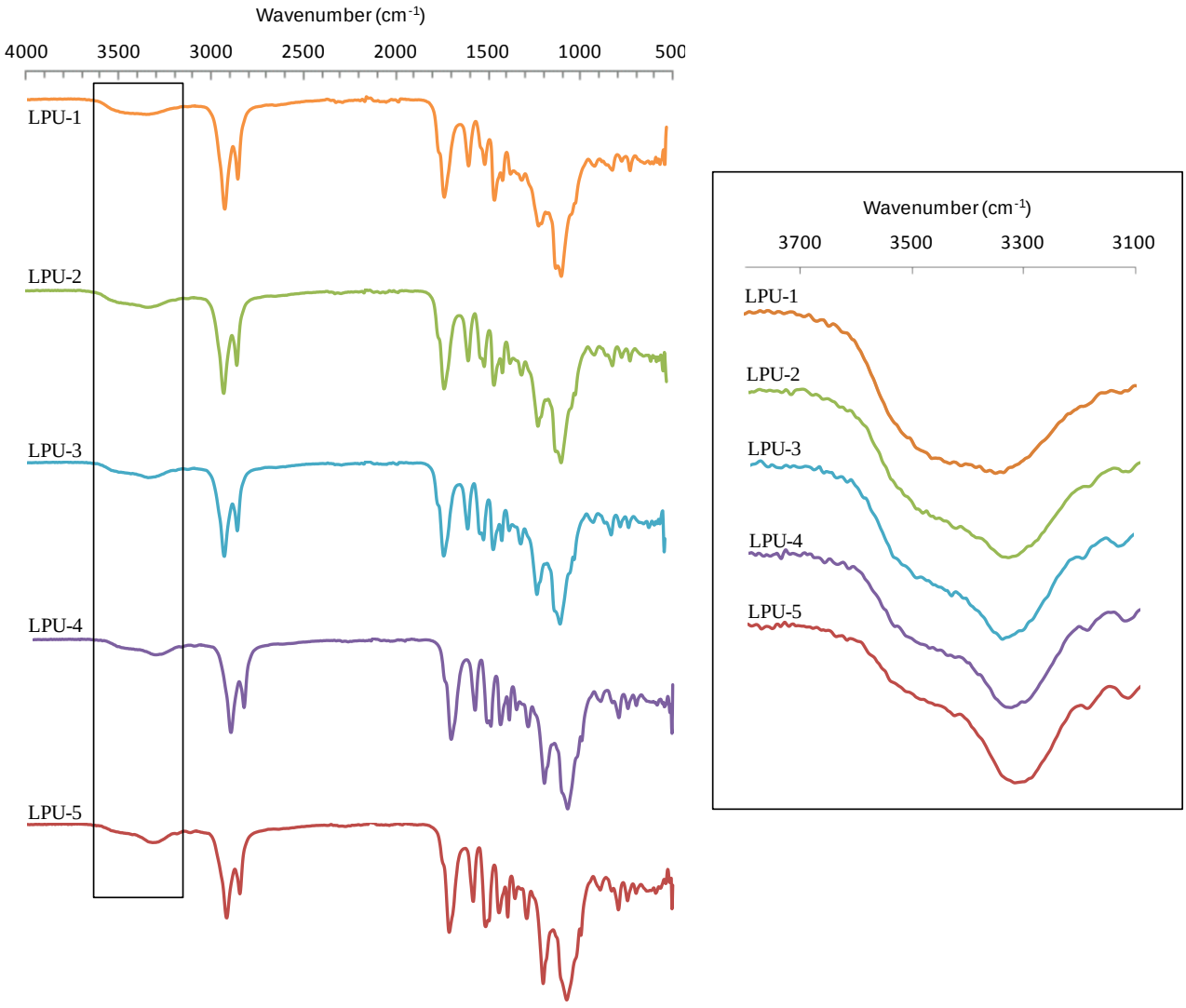


Figure III- 19. FTIR spectra of PUs synthesized with P_{425} and different NCO:OH molar ratios.

3.4 Effect of the NCO:OH molar ratio

Polyaddition reactions between LOAP and P_{425}, P_{1000} or P_{2000} were carried out at 70°C in anhydrous THF in the presence of DBTDL. The NCO:OH molar ratio was regulated based on the hydroxyl value and isocyanate index of the macropolyol and prepolymers respectively (Table III-3).

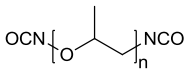
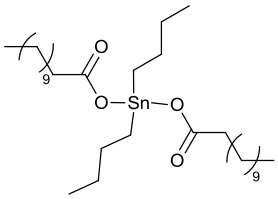
Designation	Description	Structural formula	I_{OH} (mg KOH.g^{-1})	% NCO	Functionality	T_g (°C)
LOAP	Polyol		60	-	-	-24
P_{425}	Isocyanate prepolymer		-	7.9	2	-11
P_{1000}			-	4.7	2	-30
P_{2000}			-	3.7	2	-48
DBTDL	Catalyst		-	-	-	-

Table III- 3. Chemicals and materials used in the PU synthesis with their corresponding properties.

In comparison with linear TPU resulting from the reaction between diols and diisocyanates molecules, we may obtain a highly branched and three-dimensional polyurethane network derived from the lignin macropolyols[52] (as suggested in Figure III-20). In these systems, lignin should act as a crosslinking point, covalently bonded with more or less flexible PPO-based chains.

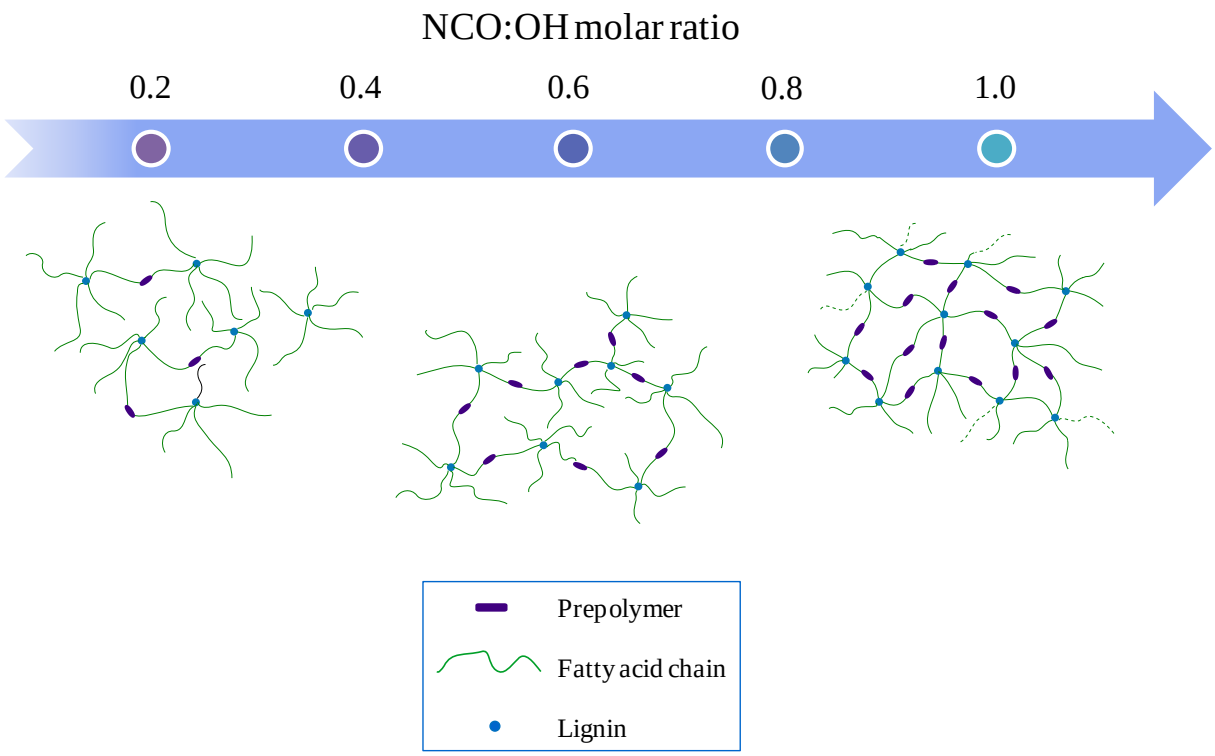


Figure III- 20. Schematic representation of PU networks with different NCO:OH molar ratios.

Table III-4 showed T_g data for synthesized PUs. Neither melting nor crystallization transition temperatures were observed by DSC, indicating the amorphous nature of these PUs. DMTA experiments were carried out in order to obtain further information on the morphology of these PUs. Figure III-21 shows storage modulus as function of temperature for PUs films based on different NCO:OH molar ratio, in a large temperature range from -100 to 140°C. With increasing temperature, all polymer materials showed a similar trend. In details, E' presents no variations in the glassy plateau from -100°C to around -50°C and show for some samples a very broad transition before reaching the rubbery state, or decreasing for the others until the limit of the measurement. All the samples with high NCO:OH molar ratio demonstrated a rubbery plateau confirming their high cross-linking density while those with low NCO:OH molar ratio display a decrease of storage modulus. The cross-linking density (ν_e) was calculated by Equation (3) derived from the theory of rubber elasticity[53, 54]:

$$\nu_e = \frac{E'}{3\ RT} \qquad (3)$$

Equation 3 establishes the relationship between crosslink density and Young's Modulus (E) of polymers above T_g. Since the storage modulus (E') obtained from DMTA can be associated to the elastic modulus (E) at temperature above T_g (in the rubbery region at T_g + 40°C), E' can be substituted in Equation (3) to determine ν_e. R is the gas constant (8,31 $J.mol^{-1}.K^{-1}$) and T is the temperature in Kelvin. The resulting data are summarized in Table III-4. As expected, for polymers presenting a rubbery plateau, the cross-linking density increases with the NCO:OH molar ratio[46], which confirm that a modulation of the properties of these PU systems is possible.

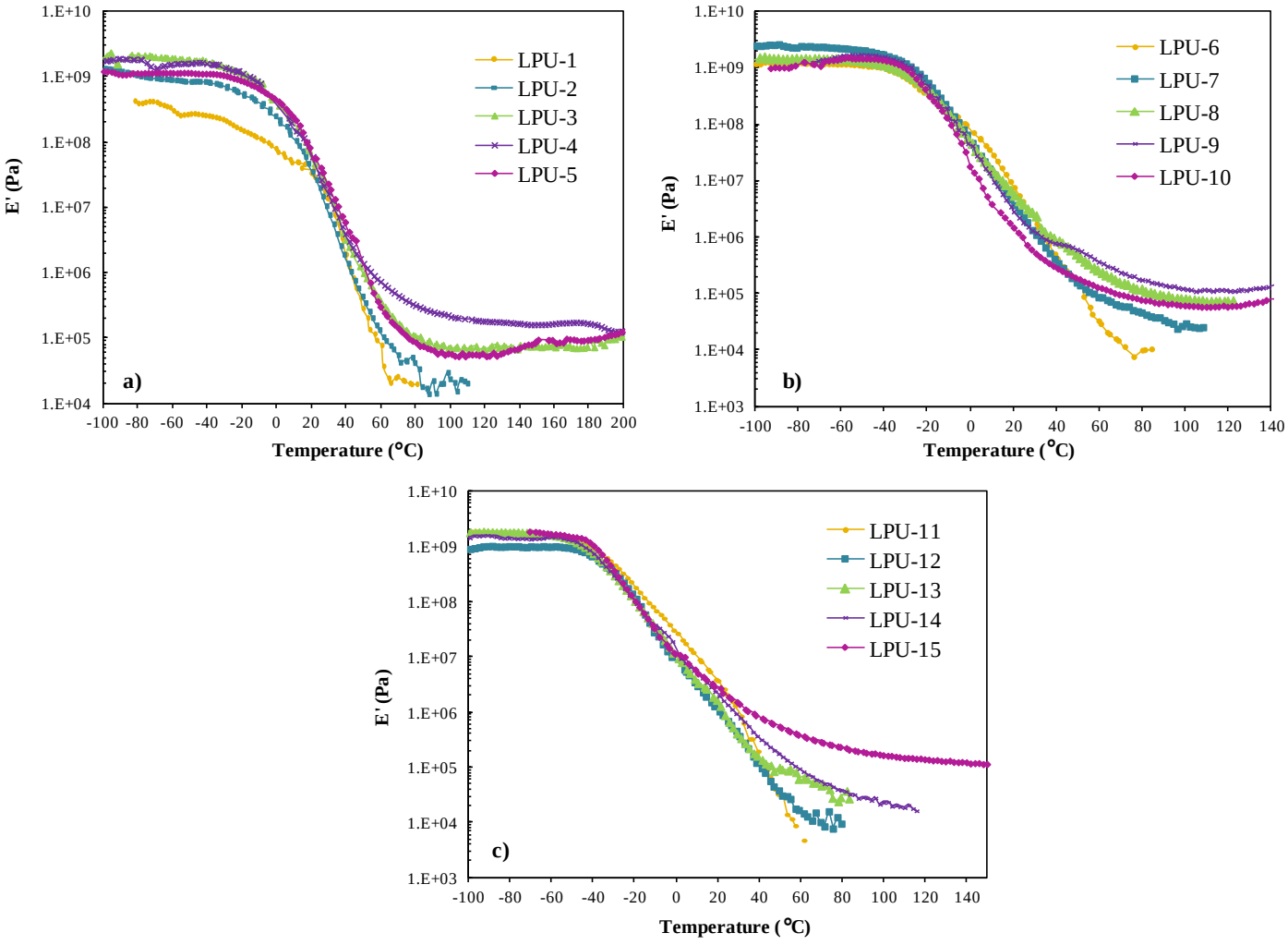


Figure III- 21. DMTA curves of the PUs (a : E' of PU based on P_{425} systems ; b :E' of PU based on P_{1000} systems; c: E' of PU based on P_{2000} systems).

As widely reported in literature on lignin and/or fatty acid based polymers and their corresponding morphological behaviours[55-58]; we should expect a phase separation on the segmented PU materials between soft and hard segments. Transition temperatures of both types of segments were determined by DSC and DMTA experiments.

The T_g of the prepolymers (i.e P_{425}, P_{1000} and P_{2000}) measured by DSC (Table III-3) were in the range of -48 to -10°C. These values were in good correlation with the first transition observed in DSC for PUs (Table III-4). This T_g can be attributed to the relative chain's motion of PPO soft segments into the PU architecture. It is also worth to mention, that the T_g of soft segment in PU material is related to the NCO:OH molar ratio, i.e the presence of crosslinking points.

A second transition (T_α) was observed at higher temperature by DMTA from the peak maximum in tan δ. This transition was also observed and then confirmed by DRA (*Supplementary Information*) which exhibit a relaxation temperature (maximum tan δ) in the same range than by DMTA. This second type of transition temperatures were above ambient temperature from 30 to 54°C. This relaxation temperature can be attributed to the transition linked to the hard segments motion, mainly composed by lignin-based crosslinking points and urethane bonds. Moreover, modulated DSC experiment carried out on crude organosolv lignin showed a T_g at 76°C (Table III-1). This glass transition can be associated to the relaxation temperature obtained from DMTA experiments with PU samples. In addition, this transition becomes closer to the T_g of crude lignin as the lignin content increases in the PU.

These different results may indicate a phase separation behaviour of PU samples, which is in good correlation with those reported in literature. While the T_g attributed to the soft segments is below the ambient temperature, the T_g of hard domains is above. In summary, these synthesized PUs might be at least partially described as amorphous segmented polyurethane with phase separation. Soft phase is composed by PPO polymer while lignin and urea groups form hard segment. This microphase separation is also responsible for the elastomeric properties of these polyurethanes as shown by ambient stress-strain curves [57]. Table III-5 presents main mechanical properties under uniaxial tensile tests including tensile strength, Young's Modulus and elongation at break, obtained from the corresponding stress-strain curves. At ambient temperature, these materials present rubbery behaviour with a high elongation at break from 170 to 360 % and corresponding quite low modulus, from 0.2 to 2.8 MPa. The maximum strength significantly increased with the NCO:OH molar ratio. These results can be explained by the increasing of cross-linking points between isocyanate and hydroxyl groups causing the formation of a PU with strong bonds, thus giving a more rigid

material. The highest value is obtained for PU synthesized with P_{425} and with the highest NCO:OH molar ratio (i.e., NCO:OH = 1.0) and reached 9.6 MPa.

Samples	Isocyanate prepolymer	NCO:OH molar ratio	DSC	DMTA	
			T_g (°C)	T_α (°C)	ν_e (mol.m^{-3})
LPU-1	P_{425}	0.2	-7	53	-
LPU-2		0.4	-7	49	20.6
LPU-3		0.6	-10	42	35.2
LPU-4		0.8	-7	42	75.6
LPU-5		1.0	-6	41	28.5
LPU-6	P_{1000}	0.2	-27	51	-
LPU-7		0.4	-19	44	10.1
LPU-8		0.6	-24	31	30.8
LPU-9		0.8	-19	29	43.0
LPU-10		1.0	-15	22	14.6
LPU-11	P_{2000}	0.2	-36	51	-
LPU-12		0.4	-39	50	1.8
LPU-13		0.6	-42	38	8.2
LPU-14		0.8	-41	34	12.2
LPU-15		1.0	-42	30	44.8

Table III- 4. Dynamical mechanical and thermal properties for the synthesized polyurethanes.

3.5 Effect of the prepolymer molar mass

The stress-strain curves of all the polymer materials show no decrease in the stress evolution vs. strain, until the rupture occurred. This typical mechanical behaviour can be compared to those of lightly crosslinked amorphous rubbers. The values of elongation-at-break display a very interesting trend which was linked to the evolution of the molar masses (M_n = 425, 1000 or 2000 g.mol^{-1}) of the prepolymers, P_{425}, P_{1000} and P_{2000}, respectively. The decreasing of PPO molecular weight results in the decreasing of elongation at break for all PUs series. In addition, longer soft segments are more able to respond to tensile deformations leading to higher elongations at break. As explained before, since the isocyanate prepolymers are incorporated into the PU network, the stretching distance between the macropolyol (LOAP) and isocyanate groups is modified by variation of the molecular weight of PPO. PPO chains provide flexibility to the resulting PUs and act as soft segment in the macromolecular architecture where lignin macropolyol acts as a cross-linking point. The increasing of ν_e is

linked to the decreasing of prepolymer molecular weight. PPO with low molecular weight bring stiffness and stability at high temperature (large rubbery plateau) whereas PPO with higher molecular weight bring flexibility at room temperature. However, it is relevant to notice that LPU 11 to 13 flow up to 80-100°C.

Samples	**Isocyanate prepolymer**	**NCO:OH molar ratio**	**Traction**		
			σ Maximum strength (MPa)	ε Elongation at break (%)	E Young's Modulus, (MPa)
LPU-1	P_{425}	0.2	2.7 ± 0.1	173 ± 22	1.6 ± 0.1
LPU-2		0.4	4.7 ± 0.7	235 ± 62	2.5 ± 0.2
LPU-3		0.6	6.6 ± 0.8	255 ± 34	2.3 ± 0.3
LPU-4		0.8	6.1 ± 0.2	201 ± 2	2.0 ± 0.2
LPU-5		1.0	9.6 ± 0.8	181 ± 10	2.8 ± 0.2
LPU-6	P_{1000}	0.2	3.2 ± 0.1	235 ± 22	0.8 ± 0.1
LPU-7		0.4	3.5 ± 0.2	240 ± 22	0.7 ± 0.1
LPU-8		0.6	4.1 ± 0.5	205 ± 15	0.7 ± 0.1
LPU-9		0.8	5.2 ± 1.0	202 ± 21	0.9 ± 0.0
LPU-10		1.0	-	-	-
LPU-11	P_{2000}	0.2	1.7 ± 0.1	317 ± 12	0.5 ± 0.0
LPU-12		0.4	1.5 ± 0.2	360 ± 6	0.2 ± 0.0
LPU-13		0.6	1.4 ± 0.1	230 ± 35	0.2 ± 0.0
LPU-14		0.8	1.5 ± 0.2	237 ± 6	0.2 ± 0.0
LPU-15		1.0	-	-	-

Table III- 5. Mechanical properties from uniaxial tensile tests of different synthesized PUs at ambient temperature with a crosshead speed of 20 $mm.min^{-1}$.

3.6 Thermogravimetric analysis

Segmented LPUs are mainly composed by two different structural blocks based on LOAP and isocyanate prepolymer, respectively. Their relative compositions affect their thermal degradation. Usually, PUs thermal decomposition is a multi-stage process with e.g., the decomposition of urethane bonds and the degradation of the soft segments[59]. Figure III-22 (a, b and c) displays the TGA and DTGA curves of PU samples under nitrogen atmosphere at $10°C.min^{-1}$. It can be observed that all of the PU materials show quite similar a two-step degradation behavior. First degradation step occurs between 200°C and 300°C (T_{1max}) and concerns decomposition of hard segments attributed to LOAP component. On the other hand

the second step is attributed to soft segments decomposition[50] with T_{2max} is between 350-400°C. In fact, the degradation of isocyanate prepolymer (P_{425}, P_{1000} and P_{2000}) is based on urethane bonds decomposition which begins at 240°C and reaches a maximum rate at 302-359°C depending on molar mass of PPO used. While LPU based on P_{2000} and P_{1000} show a clear two-step degradation mechanism, LPU-1 to 5, show a broader degradation with no distinctive peak on DTGA curves similar to LOAP behavior. However this LPU series shows the best thermal resistance compared to the others. This might be due to the high content of LOAP into the LPU matrix (from 89 to 63 % w/w). Figure III-22 also shows a char residue at 750°C for all LPUs materials. This high char residue (almost 20% of weight) is due to the high thermal resistance of lignin due to the large number of ether linkages and aromatic groups in its chemical structure[60].

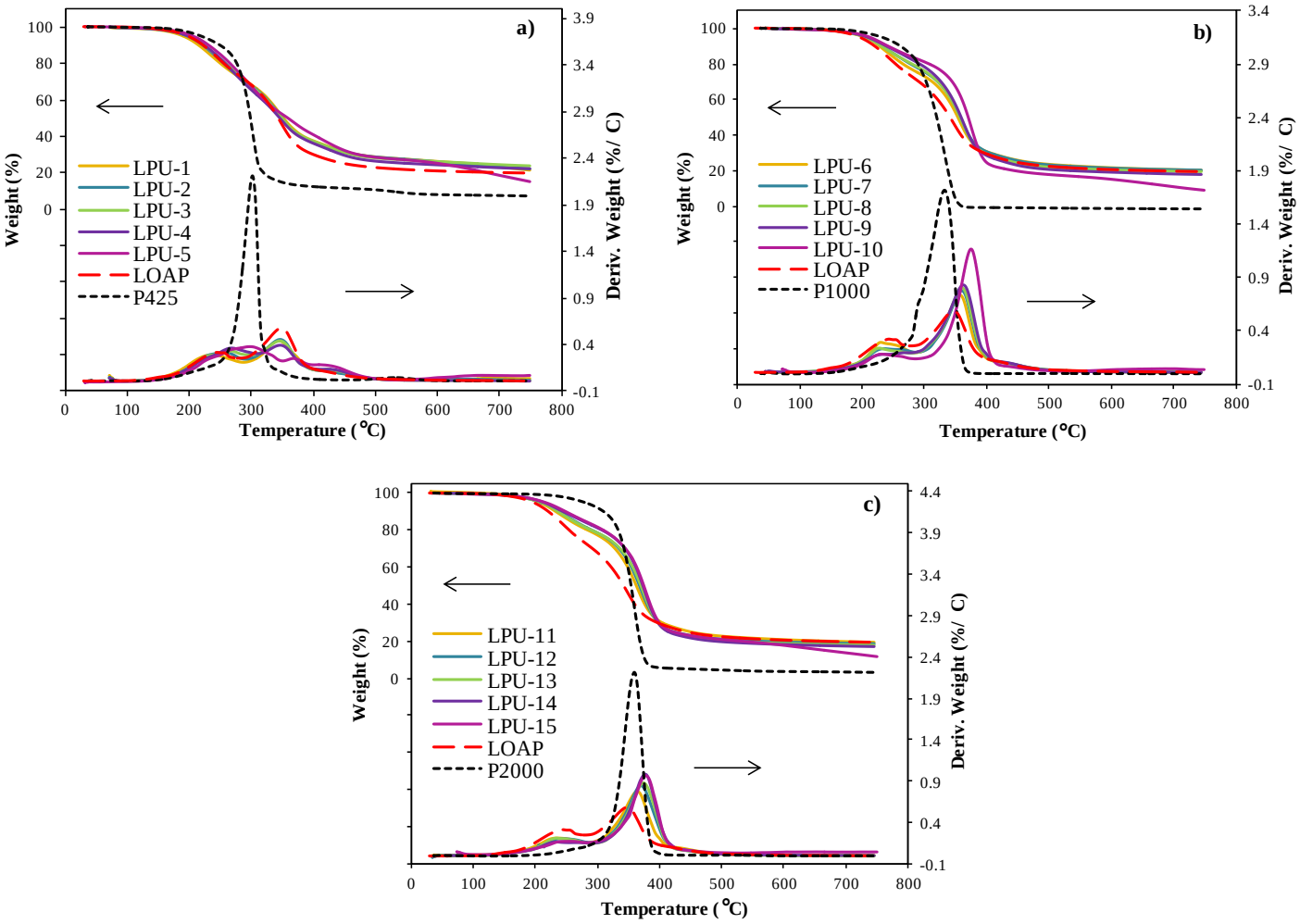


Figure III- 22. TGA/DTGA curves for PUs based on LOAP and isocyanate prepolymers (P_{425}, P_{1000} and P_{2000}).

a) LPU-1 to 5 and their respective components (LOAP and P_{425}).
b) LPU-6 to 10 and their respective components (LOAP and P_{1000}).
c) LPU-11 to 15 and their respective components (LOAP and P_{2000}).

4. Conclusion

The reaction conditions of lignin esterification and fatty acid modification were investigated leading to the synthesis of a new original macropolyol based both on lignin and fatty acid. This macropolyol was then characterized and subsequently used as an efficient building block for the synthesis of PU architectures. The macromolecular structure of the resulting PUs were designed in series by varying the NCO:OH molar ratio and the molecular weight of PPO soft segments. The thermal, mechanical and rheological properties of the corresponding LPUs were investigated by DSC, TGA, DMTA and uniaxial tensile tests.

For high NCO:OH molar ratio, LPUs exhibit a temperature independent rubbery plateau (indicated by dynamic mechanical thermal analysis) and a clear phase separation based on DSC and DMTA results. It has been concluded that soft segments were composed by PPO polymer chains and hard domains were mainly based on lignin crosslinking points. Each domain was characterized through their characteristic temperatures, which are below and above ambient temperature for soft and hard segments, respectively.

The increases in the molecular weight of PPO soft segments resulted in greater soft segment mobility and a lower glass transition temperature. In term of thermal stability of LPU samples, lignin confers to material a high thermal resistance compared to isocyanate prepolymer.

From this study, it can be concluded that a new type of macropolyol based on lignin can be used as a building block to design a new PU architecture with advanced properties. Such organized macromolecular systems with a high biobased content (up to 89%), might be foreseen to widen the scope of materials used for certain durable applications (e.g. in building and automotive industries). Hence, this work highlighted new possibilities for the valorization of crude lignin in comparison with its currently known applications. It is now worth considering the use of this industrial by-product for a larger range of green applications without competition with food.

Acknowledgements

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5. Supplementary information

To illustrate the influence of lignin-fatty acid based polyol (LOAP) on the PU network, three blank syntheses have been performed in the presence of Poly(Propylene) Oxide and 4,4' MDI. So far, three polyurethanes have been synthesized by varying the diol (PPO) molar mass (425, 1000 and 2000 g.mol-1) while the molar ratio of isocyanate and hydroxyl groups remains constant, i;e NCO:OH = 1.03.

Polymer synthesis procedure

A 250mL round-bottomed flask was fitted with a nitrogen inlet tube and a mechanical stirrer. Poly(Propylene) oxide and 4,4' MDI (f=2) were added into the flask and stirred at 70°C during 5 hours to yield PUs. The ensuing PUs were coded as BPU_{425}, BPU_{1000} and BPU_{2000} for blank syntheses with PPO with molecular weights of 425, 1000 and 2000 $g.mol^{-1}$, respectively.

Characterization of BPUs

The ensuing BPUs were analyzed by DSC and TGA according the procedure described in the publication (see Table III-S1 and Figure III-S1).

Samples	**T_g (°C)**
BPU_{425}	33
BPU_{1000}	-27
BPU_{2000}	-57

Table III-S1. T_g data obtained from DSC experiments for blank PUs.

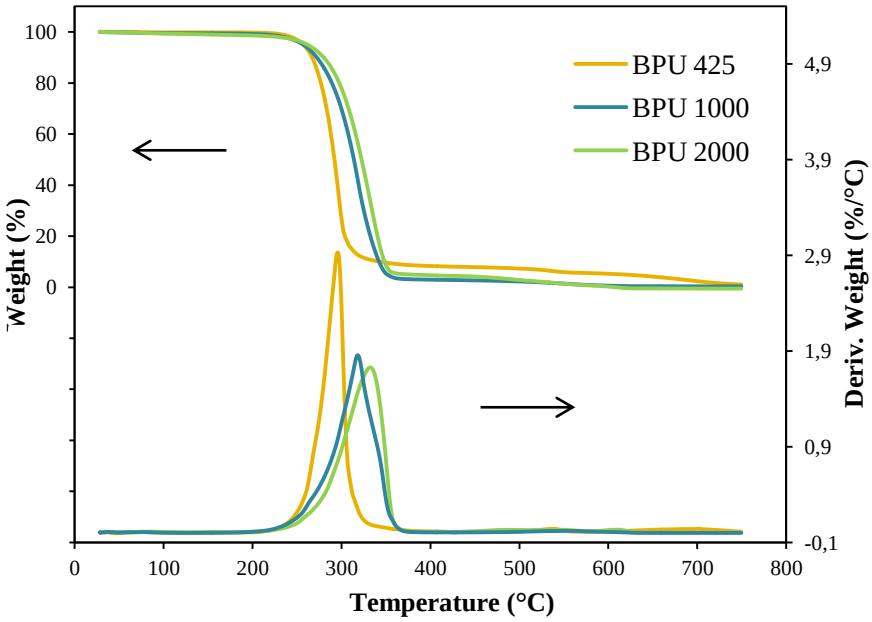

Figure III-S1.TGA/DTGA curves for BPUs based on PPO and 4,4' MDI (BPU_{425}, BPU_{1000} and BPU_{2000}).

The following figures III-S2 display the dependence of tan δ for the LPUs samples on temperature by DMTA.

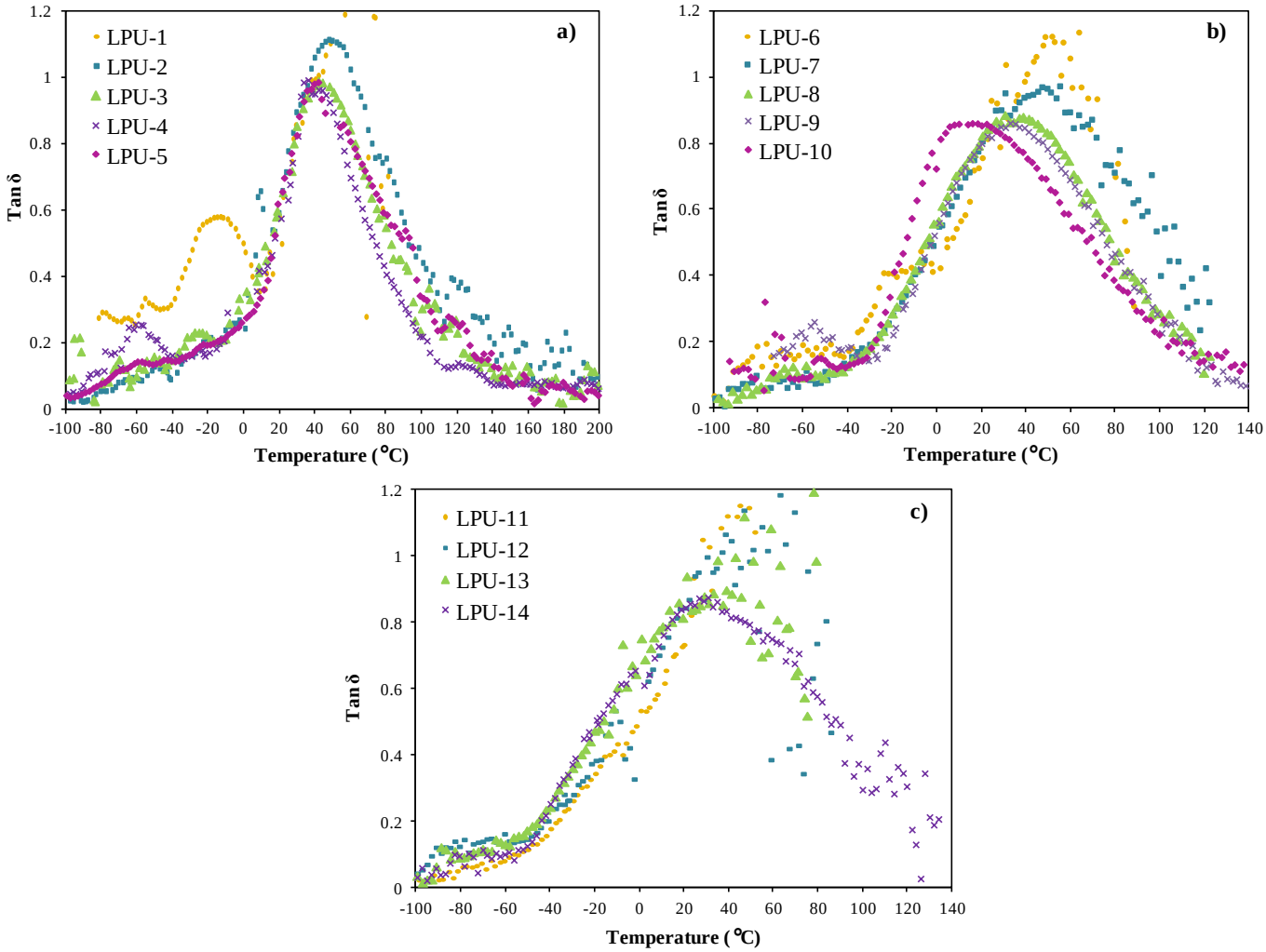

Figure III-S 2. Changes in the position and intensity of the relaxation transition (Tan δ) on the stoichiometric ratio of the component. (a: tan δ of PU based on P_{425} systems; b: tan δ of PU based on P_{1000} systems; c: tan δ of PU based on P_{2000} systems).

The following figures III-S3 display the dependence of tan δ for the LPUs samples on temperature. Analyses have been performed by DRA (Dynamic rheological analyses) at a heating rate of 2°C.min^{-1}.

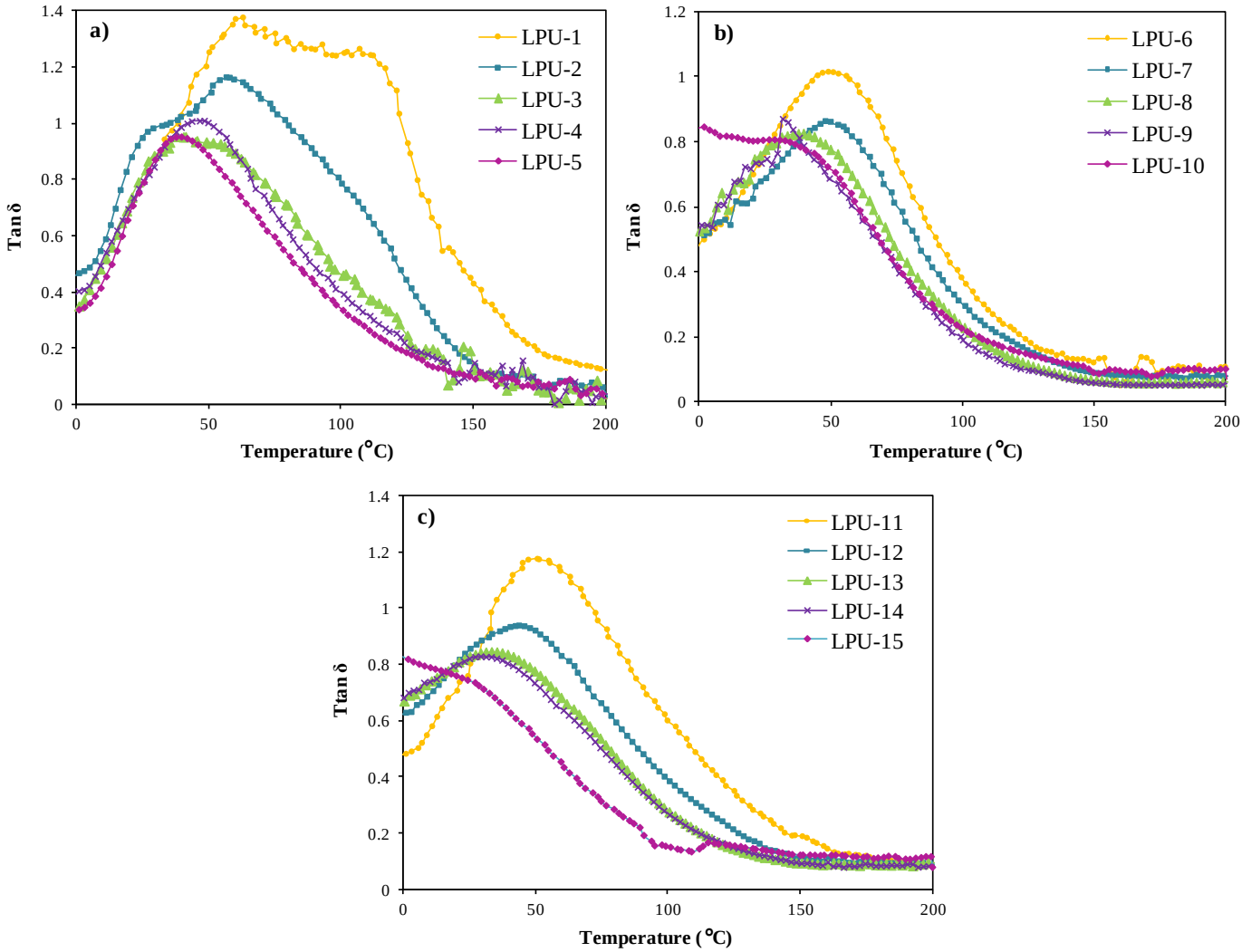

Figure III-S3. Temperature sweep of loss tangent (Tan δ) for synthesized PU performed by using a strain-controlled rheometer with parallel-plate geometry (a: tan δ of PU based on P_{425} systems; b: tan δ of PU based on P_{1000} systems; c: tan δ of PU based on P_{2000} systems).

Table III-S2 displays results obtained by means of DSC, DMTA and DRA. As can be seen, these results confirmed the previous comments. The difference observed between $T_{g\ SS}$ obtained from DSC and DMTA tests is caused by the nature of these two methods. DSC measures the change in heat capacity from frozen to unfrozen chains, while DMTA measures the change in the mechanical response of the polymer chains. However, these results seem to corroborate the phase separation behavior of LPUs samples with two different T_g attributed to soft segments and hard segments, respectively.

	$T_{g\ SS}$ (°C)		**$T_{g\ HS}$ - tan δ maximum (°C)**	
Samples	By DSC	By DMTA (max E'')	By DMTA	By DRA
LPU-1	-7	-18	53	63
LPU-2	-7	-11	49	57
LPU-3	-10	-	42	46
LPU-4	-7	11	42	47
LPU-5	-6	-7	41	40
LPU-6	-27	-54	51	49
LPU-7	-19	-35	44	58
LPU-8	-24	-38	31	38
LPU-9	-19	-	29	32
LPU-10	-15	-	22	-
LPU-11	-36	-48	51	51
LPU-12	-39	-60	50	44
LPU-13	-42	-64	38	34
LPU-14	-41	-44	34	29
LPU-15	-42	-	30	-

Table III-S2. Glass transitions of soft and hard segments in lignin-based polyurethanes. Comparison of data obtained by DSC, DMTA and DRA experiments.

* * *

III. Conclusion & perspectives de l'étude

Les réactions d'estérification figurent parmi les plus étudiées dans le domaine de la modification chimique du bois et généralement des matériaux lignocellulosiques. La bonne réactivité entre les fonctions hydroxyles (cellulose, bois…) et les groupements acides a permis le greffage de nombreux composés, souvent bi-fonctionnels dotés de propriétés variées. Toutefois à notre connaissance, aucune référence bibliographique ne fait état de l'estérification de lignines techniques par des dérivés d'acides gras. Ainsi, les travaux développés dans le cadre de cette thèse se positionnent comme des sujets novateurs associant alors deux composés issus de la biomasse et mettant en jeu des réactions chimiques appliquées aux dérivés d'huiles végétales.

A la suite de ces travaux, d'autres molécules issues d'huiles végétales ont été identifiées comme composés intéressants pour intégrer la stratégie de synthèse mise au point dans notre laboratoire. L'utilisation d'autres mono-acides gras présentant une ou plusieurs insaturations à des positions différentes sur la chaine alkyle pourrait en effet être étudiée.

La position et le nombre de groupements fonctionnels (insaturations), sites potentiels de réticulation dans un système PU, permettent une modulation très importante des architectures macromoléculaires résultantes et des propriétés thermo-mécaniques finales des matériaux correspondants.

Toutefois, une étude approfondie de ces systèmes serait nécessaire et plusieurs verrous technologiques sont encore à lever, notamment la maitrise des réactions secondaires (e.g., transestérifications dans le cas de l'acide ricinoléique) et le contrôle de l'indice d'hydroxyle des polyols finaux.

Cette étude a néanmoins mis en évidence l'efficacité de la réaction d'estérification, associée à la modification des insaturations pour la synthèse de polyols agro-sourcés. Le travail sur les conditions de synthèse en laboratoire a permis l'optimisation des paramètres et la mise en place d'un protocole opérationnel. Les deux matières premières rentrant en jeu dans la synthèse, à savoir la lignine et l'acide oléique sont disponibles à des échelles industrielles et nous permettent d'envisager dans un premier temps, un passage à l'échelle pilote avec l'entreprise partenaire du projet.

Ce changement d'échelle nous permettrait ainsi de réaliser de plus amples essais sur la synthèse de PU mais également sur la formulation complète de ces matériaux (charges, renforts, additifs…)

L'extrusion réactive représente également une alternative intéressante pour développer le procédé de synthèse d'estérification de la lignine. Cette méthode permet à la fois d'améliorer la mise en œuvre de la synthèse mais également facilite le passage de la réaction à plus grande échelle. Ce procédé continu ouvre ainsi la voie à la synthèse potentielle de PU en ligne sur une même extrudeuse.

Enfin, dans un souci de diminution du nombre d'étapes dans la stratégie de synthèse, une optimisation du procédé de synthèse est fortement encouragée. Comme évoqué dans la partie I de ce chapitre, la réaction thiol-ène, couramment classée parmi les réactions de « click chemistry » en raison de ses rendements élevés, de son adaptabilité et de sa facilité de mise en œuvre représente une excellente alternative. Appliquée sur des dérivés d'acide gras, cette méthode a permis le développement de nouveaux précurseurs pour la synthèse de polyuréthanes [61-64] et pourrait être un atout supplémentaire vers l'industrialisation de la synthèse de polyol à base de lignine et d'acide gras.

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Chapitre IV.

Oxypropylation de la lignine –Elaboration de macropolyols pour la synthèse de polyuréthanes

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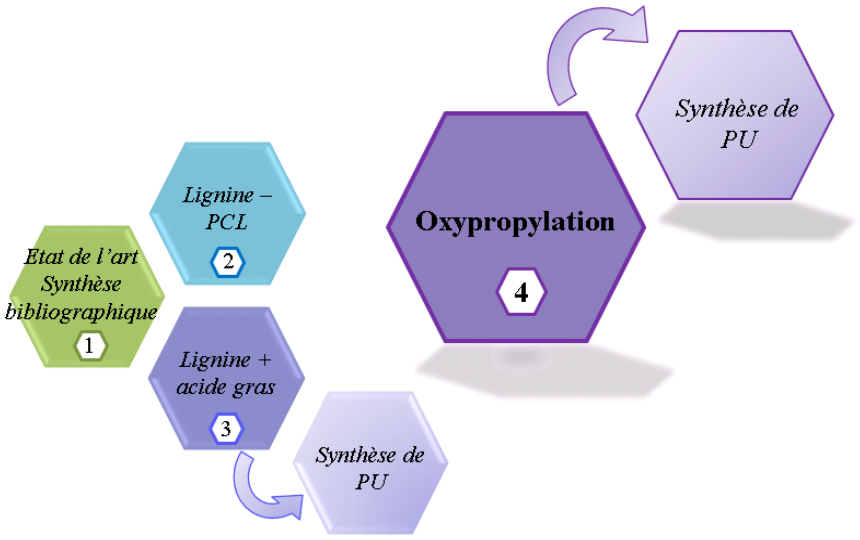

Introduction

Les polyuréthanes synthétisés par l'intermédiaire des synthons lignine-acide oléique (Chapitre III) ont démontré la possibilité d'élaborer des polymères aux propriétés intéressantes à partir de lignine fonctionnalisée. Cette voie de modification basée sur l'estérification de la lignine à partir d'acide gras suivie de réactions chimiques *in-situ*, confère à la biomacromolécule de nouvelles fonctionnalités. Les résultats prometteurs quant à l'obtention d'un nouveau polyol, ont toutefois soulevé quelques interrogations sur le scaling-up et l'industrialisation future de telles modifications (synthèse en trois étapes) sur une biomacromolécule de structure variable et non clairement définie. Cependant, l'étude développée dans le Chapitre II avait démontré le potentiel de la ROP comme voie de synthèse pertinente pour le greffage de chaines de polymères de longueur contrôlée. De ce fait, l'association des résultats obtenus dans les études précédentes (Chapitre II et III) nous a conduits à développer une réaction de polymérisation par ouverture de cycle pour la synthèse de matériaux PU.

Suite à l'étude bibliographique présentée dans le Chapitre I, il est apparu intéressant de s'orienter vers la réaction d'oxypropylation ou hydroxyalkylation des fonctions hydroxyles de la lignine. Cette technique, couramment utilisée sur des dérivés et résidus de la biomasse (cellulose, chitine, chitosane, résidu de liège, noyaux d'olive…) en raison de sa capacité à transformer des composés solides en produits liquides/visqueux, de sa rapidité et de sa facilité de mise en œuvre, permet en effet en une unique étape d'accéder à des synthons polyols polyethers. En outre, cette réaction présente l'avantage de reposer sur un procédé simple, limitant le nombre d'intermédiaires réactionnels, rendant cette modification facilement transposable en milieu industriel. L'oxypropylation s'est ainsi révélée être une excellente alternative dans une approche de chimie verte, car sans solvant et réduisant significativement le nombre d'étapes réactionnelles. Cette réaction nous a permis de développer des polyols à base de lignine conduisant à la synthèse de polyuréthanes.

Comme nous l'avons déjà évoqué, l'oxypropylation est une technologie déjà utilisée pour de nombreux composés hydroxylés issus de la biomasse. Elle a fait l'objet de nombreuses publications et brevets, dont l'exemple le plus souvent étudié est celui de lignine. La synthèse de polyuréthanes élastomères est quant à elle très peu décrite dans la littérature, la principale

application demeurant l'élaboration de mousses polyuréthane rigides. Ceci s'explique par un indice d'hydroxyle relativement élevé pour les polyols finaux.

L'oxypropylation est une voie de synthèse très adaptée puisqu'elle permet d'augmenter la réactivité de la lignine en lui conférant des fonctions hydroxyles plus accessibles et donc plus réactives, mais aussi une architecture macromoléculaire contrôlable par les paramètres réactionnels rentrant en jeu lors de la synthèse.

* * *

I. Oxypropylation de la lignine, synthèse de polyuréthanes

La quatrième publication présentée dans ce chapitre et intitulée "Novel segmented polyurethanes based on oxypropylated soda lignins: toward high performance materials" présente l'élaboration de polyuréthanes à partir de lignines qui sont oxypropylées. Différentes architectures macromoléculaires ont été synthétisées et caractérisées.

Dans un souci de cohérence de notre étude, la stratégie de synthèse élaborée dans ce chapitre s'est appuyée sur les résultats obtenus dans le chapitre précédent et sont présentés de la même façon. L'utilisation des polyols polyéthers à base de lignine oxypropylée a permis de développer cette stratégie de synthèse des PU préalablement mise au point. Un prépolymère isocyanate est par conséquent utilisé. Dans le cas présent (Figure IV-1), quatre polyols différents ont été élaborés pour la synthèse des polyuréthanes finaux. Quatre séries de PU ont donc été synthétisées et nous ont notamment permis d'étudier l'influence de la structure des lignines fonctionnalisées sur les propriétés finales des matériaux. Ainsi, contrairement à l'étude précédente, l'architecture macromoléculaire du polyol a été modulée afin d'évaluer son impact sur l'organisation des segments souples et rigides au sein du polymère.

Par ailleurs, l'influence du ratio molaire NCO:OH a été étudiée et son impact sur les propriétés des matériaux est discutée au travers des différentes analyses physico-chimiques et mécaniques réalisées.

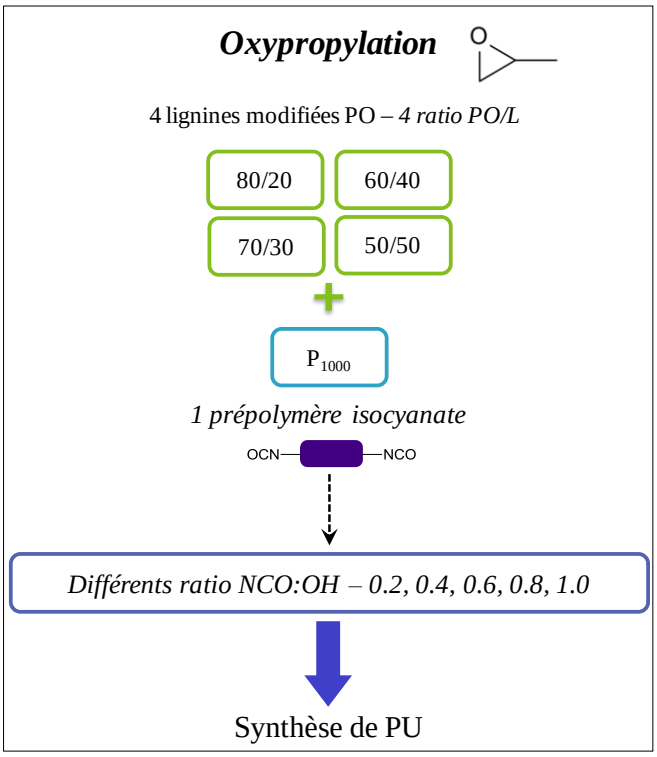

Figure IV-1. Schéma récapitulatif de la stratégie de synthèse développée dans le chapitre IV.

Novel segmented polyurethanes based on oxypropylated soda lignins: toward high performance materials.

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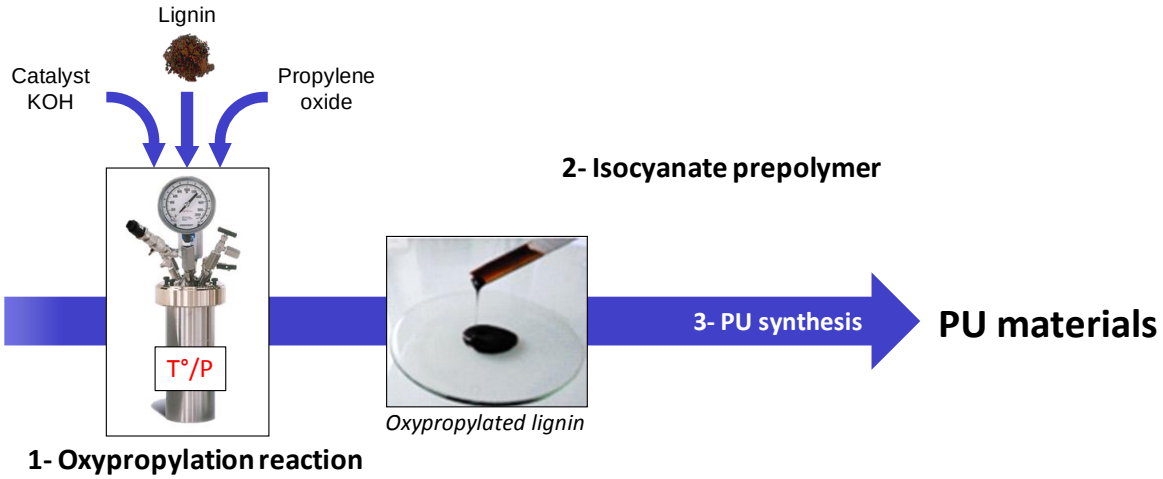

Abstract

Oxypropylation represents an excellent alternative to circumvent the problem of hydroxyl group's reactivity of lignin to produce attractive polymer precursors by transforming lignin into a reactive and biobased macropolyol. Oxypropylation reactions have thus been carried out onto soda lignin with different propylene oxide/lignin (PO/L) ratios. A series of four lignin-based polyether-polyols (oxypropylated lignins: OL) were synthesized and carefully characterized by several analytical methods (^{31}P and ^{1}H quantitative NMR, IR, SEC, DSC) in view of polymer synthesis. Various polyurethanes (PU) with different macromolecular architectures were subsequently synthesized with OL and isocyanate prepolymers. The ratio of the isocyanate and hydroxyl groups (NCO:OH ratio) was varied between 0.2 and 1.0. The influence of OL structure and NCO:OH molar ratio was investigated by DSC, DMTA and tensile test experiments. The NCO:OH molar ratio and the morphology of OL impacted the behaviour of the final PU materials such as the transition temperatures of the different phases and the mechanical properties. Preparing different OL enabled successful preparation of tailor-made segmented PU presenting a multiphase morphology based on soft and hard microphases, with some advanced properties and a biobased content up to 40 wt.%.

Keywords

Lignin, oxypropylation, ^{31}P NMR, segmented polyurethane.

1. Introduction

In the last decades, notable efforts have been directed toward the modification and the characterization of biopolymers extracted from the biomass for elaboration of high-value green chemicals and biobased materials[1]. Economic and environmental context, but also the increasing price of petroleum has thus encouraged industrials to find alternative to petrochemicals and their derivatives by promoting the use of sustainable sources of raw materials and the development of a greener chemistry.

Polyurethane polymers (PU) are among the most important polymers with a large scope of application as foams, thermoplastic elastomers, adhesives, coatings, sealants, fibers…[2] They can be produced, in one or several steps, by combination of poly(isocyanate) and polyol compounds. Despite the fact that all the history of PU was strongly linked to some renewable resources (glycerol)[3], the development of bio-based polyols has attracted several researches for the last decades. In this light, different biobased polyols have gained a recent interest, such as e.g., lignins. Its availability and the emerging of new types of technical lignins, namely sulfur-free lignins, also motivated by the recent development of biorefinery, have offered the opportunity to valorise this sustainable resource as a macromonomer in PU synthesis.

Lignin is the most abundant polyphenol occurring in vascular plants and the second most abundant natural polymer after cellulose. It acts as a bonding agent between the cell wall components, i.e. cellulose and hemicellulose[4]. From a chemical point of view, it comprises three monomeric units, namely, *p*-hydroxyphenyl, guaiacyl, and syringyl phenylpropanoïd units cross-linked together by enzymatic polymerization of three alcohol monomers (monolignols); *p*-coumaryl, coniferyl and sinapyl alcohols respectively[5]. The resulting macromolecule consists of a three-dimensional network with a highly complex and variable structure which still remains under investigations[6,7]. Lignin is a polyfunctional macromolecule including hydroxyl, methoxy, carbonyl and carboxyl groups present in various amount depending on its botanic origin (hardwood, softwood, annual plants...)[8] and the pre-treatment process. However, the hydroxyl groups are the most important and can be used as reaction sites[9] for e.g., polyester or polyurethane syntheses. Regarding to their accessibility, phenolic and aliphatic hydroxyls groups show different reactivity.

Currently considered as a by-product of pulp, paper and biofuel industries, only 2% of lignin production is nowadays valorised for different industrial applications (binders, adhesives, additives, surfactants...). Lignin is one of the major potential aromatic building block for the future, since this fragmented biomacromolecule doesn’t compete with food

resource. However, in light of the high variability of lignins in terms of structure and reactivity, few industrials applications have emerged. In order to widen the scope of lignin applications, it is necessary to overcome the poor reactivity and accessibility of its hydroxyl group. By making those hydroxyl sites more readily available, the reaction of lignin with isocyanate compounds can be considered to synthesize polyurethane materials (PU). Among all of chemical modifications performed on lignin, etherification reaction and particularly, oxypropylation of lignin, has been considered as the most viable and promising approach to add value to this industrial by-product[10]. Through an anionic ring-opening polymerization involving the use of propylene oxide (PO) and appropriate catalyst at elevated temperature and high pressure, polypropylene oxide chains are grafted from lignin. This reaction allows deploying hydroxyl groups entrapped inside the lignin molecule becoming then more reactive and free from steric and/or electronic hindrance. The chain extension yielded to a lignin-based macropolyol resulting in a viscous liquid product due to the introduction of ether moieties. Since the first studies carried out by Wu and Glasser on lignin[11,12], oxypropylation have been investigated extensively on different biopolymers and biobased materials bearing also hydroxyl groups such as chitosan[13], cork[14, 15], pine bark, corn starch[16], sugar beet pulp[17-19] and sugar cane bagasse. This reaction has also been applied for a partial modification by a superficial treatment on the surface of different polysaccharides[20-22].

Considering the number of publications and patents involved in this research area, oxypropylation reaction has attracted several academic and industrials researches in view of synthesizing renewable biobased polyols. Different technical lignins have already been modified by oxypropylation, namely sulfur and sulfur-free lignins[23, 24]. Both types of lignins are reactive through this modification but sulfur-free lignins reacted considerably faster than sulfur lignins. Soda lignin is therefore more reactive than organosolv thanks to its intrinsic structure that is richer in phenol propane moieties which are more reactive than hydroxyl from syringylic and guaiacylic units of organosolv lignin[25]. To that extent, we have decided to work with a lignin extracted from a soda process.

To consider new perspectives in this field, it is critical to precisely understand the chemical structure of oxypropylated lignin. Therefore, a fundamental study has been performed on four polyol systems by using four different propylene oxide/ lignin (PO/L: w/w) ratios: 80/20, 70/30, 60/40 and 50/50. In this study, we report the polyol purification and its complete chemical characterization in view of PU synthesis by FT-IR, ^{1}H and ^{31}P NMR. The synthesis of segmented and biobased polyurethanes with oxypropylated lignin and prepolymer with free

isocyanate groups has been carried out. For each oxypropylated lignin, a series of PUs were synthesized with 5 different NCO:OH molar ratios: 0.2, 0.4, 0.6, 0.8 and 1.0 with a biobased content up to 40%. An important objective was to determine the influence of oxypropylation parameters on the properties of lignin macropolyol. The stoichiometric balance (i.e. NCO:OH molar ratio) was also controlled to modulate the final architectures and the corresponding properties of the PU materials.

2. Experimental section

2.1 Raw materials

Soda lignin from wheat straw (Green Value - Protobind 1000) was used as the starting material. It was used as received without further purification.

Propylene oxide, Poly(propylene) glycol also named Poly(propylene) oxyde (PPO – 1000 $g.mol^{-1}$), Tetrahydrofuran (THF - 99.8%), and Pyridine were purchased from Sigma Aldrich. For NMR analyses, pentafluorobenzaldehyde (PFB), 2-chloro-4,4,5,5-tetramethyl-1,3,2-dioxaphospholane (TMDP), cholesterol and Chromium (III) acetylacetonate were also obtained from Sigma Aldrich and used as received without purification.

All of the solvents were distilled and PPO was dried under reduced pressure at 100°C before their utilization for chemical synthesis.

2.2 General methods and instrumentation

Chemical properties.

Infrared spectra were obtained on a Nicolet 380 FT-IR spectrometer using an attenuated total reflection (ATR) mode.

^{1}H NMR spectra were recorded using a Bruker UltraShield 400 MHz at room temperature by dissolving the samples in deuterated DMSO. In the present study, quantitative ^{1}H NMR was used to estimate the degree of polymerization of PO onto lignin. A standard solution of pentafluorobenzaldehyde (PFB) in DMSO-d_6 was prepared by weighting 33.0 mg of PFB diluted in 0.40 mL of DMSO-d_6. 20 mg of oxypropylated lignin (OL) was dissolved in 800 µL and an aliquot of the standard solution (0.10 mL) was added. The solution was then transferred into a 5 mm NMR tube for the NMR experiment. The relaxation delay was set to 10s with 32 scans.

Quantitative ^{31}P NMR spectra were acquired using a Bruker 400 MHz equipped with a "Quad probe" dedicated to ^{31}P, ^{13}C, ^{19}F and ^{1}H NMR acquisition. A relaxation delay of 10s was used, and the number of scans was 512. According previous procedure describe in literature, samples were prepared as follow. A solvent solution of anhydrous pyridine and deuterated chloroform (1.6:1, v:v) was first prepared. It was then used for the preparation of the relaxation reagent (Chromium (III) acetylacetonate, 5 $mg.mL^{-1}$) and the internal standard solutions (Cholesterol, 5 $mg.mL^{-1}$). Approximately 25-30 g of lignin sample or OL was dissolved in 800 µL of the solvent solution, followed by the addition of 100µL of the internal standard and relaxation solutions respectively. Finally, the mixture was treated with 100µL of phosphitylating reagent (2-chloro- 4,4,5,5-tetramethyl-1,3,2-dioxaphospholane,TMDP) and was transferred into a 5 mm NMR tube for subsequent NMR analysis. The reaction of TMDP with hydroxyl functional groups is illustrated in Figure IV-2. TMDP reacts with hydroxyl functional groups to give phosphite products which are resolvable by ^{31}P NMR into separate regions arising from aliphatic hydroxyl, phenolic, and carboxylic acids groups.

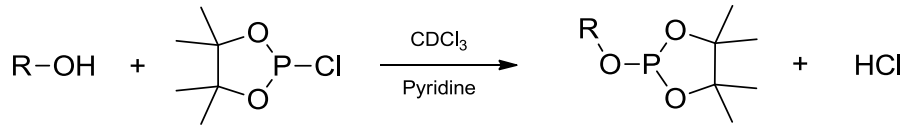

Figure IV-2. Derivatization of active hydrogen compounds with 2–chloro–4,4,5,5–tetramethyl– 1,3,2 dioxaphospholane (TMDP).

Size exclusion chromatography (SEC) analyses were performed in THF (HPLC grade–1 $mL.min^{-1}$) in a Malvern Instrument liquid chromatograph with a setup consisting of a thermostated oven with a 8µ guard column and three 6µ 300 mm-columns (50, 150 and 500 Å), and two online detectors : a refractive index detector (RI) and a UV detector. Molecular weights and polydispersity indexes were calculated using a calibration curve based on polystyrene standard from 162 to 20,000 $g.mol^{-1}$. Samples were dissolved in THF (concentration 5 $mg.mL^{-1}$) and filtered through a 0,2µ PTFE membrane.

Mechanical and physicochemical properties

Differential scanning calorimetry (DSC) were performed using a TA DSC Q200 calorimeter, under nitrogen atmosphere, at a heating rate of 10°C.min^{-1} from 25°C to 120°C to erase thermal history, cooled to -80°C at a cooling rate of 10°C.min^{-1}, and then heated again to 120°C at a heating rate of 10°C.min^{-1}. The second heating was selected to be analyzed for the collection of T_g data.

Thermogravimetric analysis (TGA) is used to determine lignin thermal stability by monitoring sample weight lost as a function of temperature. TGA was carried out on a Hi-Res TGA 2950 apparatus from TA Instruments. Samples were heated from 25°C to 750°C under dry Nitrogen at constant heating rate of 10°C.min^{-1}.

Dynamic mechanical thermal analysis (DMTA) were carried out on a RSA-II apparatus (TA Instruments) equipped with a liquid-nitrogen cooling system in the traction mode, with a constant heating rate of 2°C.min^{-1} from -100°C to 200°C. The size of samples was 23 x 4 x 1 mm^3. The measurements were performed with a maximum strain from 0.01 to 0.9% and at a fixed frequency of 1Hz.

Specimens for tensile measurements were cut out from the PU sheets using dumbbell specimens type H2 (ISO-527) (dimensions: 25 X 4 X 1 mm^3) standard. The tests were performed at room temperature using a Zwick Roell tensile test machine (model Z005 TN) equipped with a 20N load cell. The used cross-head speed was 20 mm.min^{-1}. At least five identical dumbbell-shaped specimens for each sample were tested, and their average mechanical properties are reported.

2.3 Syntheses

2.3.1 Lignin oxypropylation

The typical process used for OL synthesis is a bulk process, which constitutes an excellent alternative of reaction performed in aqueous or solvent media. In this light, the reaction was carried out in bulk using a 600 mL Parr pressure reactor (model N°4568) equipped with a heating mantle, mechanical stirrer, thermocouple and manometer. The grafting reaction was performed under stirring at 150°C in presence of the desire amount of lignin (L), PO and catalyst (C). In a general way, the reaction is catalyzed by basic catalyst such as potassium hydroxide (KOH) although acid catalysts can be used but they are therefore rarely used[3, 25]. In our case, KOH in fine powder was used. After reaching a maximum (P_{max} = 13-16 bars) the

pressure inside the reactor decreased almost instantaneously, in 1 to 3 minutes, reflecting the entire PO consumption. When the relative pressure ($P_{relative}$) reached zero, the reactor was cooled under stirring and the ensuing lignin-based macropolyol recovered.

Several studies have already investigated the influence of reaction parameters such as the type of lignin (kraft, lignosulfonate, soda or organosolv), PO/L ratio, temperature (80 to 200°C), the nature and amount of catalyst, on the properties of the resulting lignin-based macropolyol[17, 26]. OL were made by varying PO/L ratio (w/w) while keeping C/L ratio (w/w) constant, i.e. 5%. A total of four PO/L ratios were studied: 80/20, 70/30, 60/40 and 50/50 keeping always the same volume of PO introduced, i.e. 100 mL. The following terminology will be used to identify samples: $OL_{PO/L}$ (ratio between PO and lignin). For example, $OL_{80/20}$ means a sample with a PO/L ratio of 80/20 (w/w).

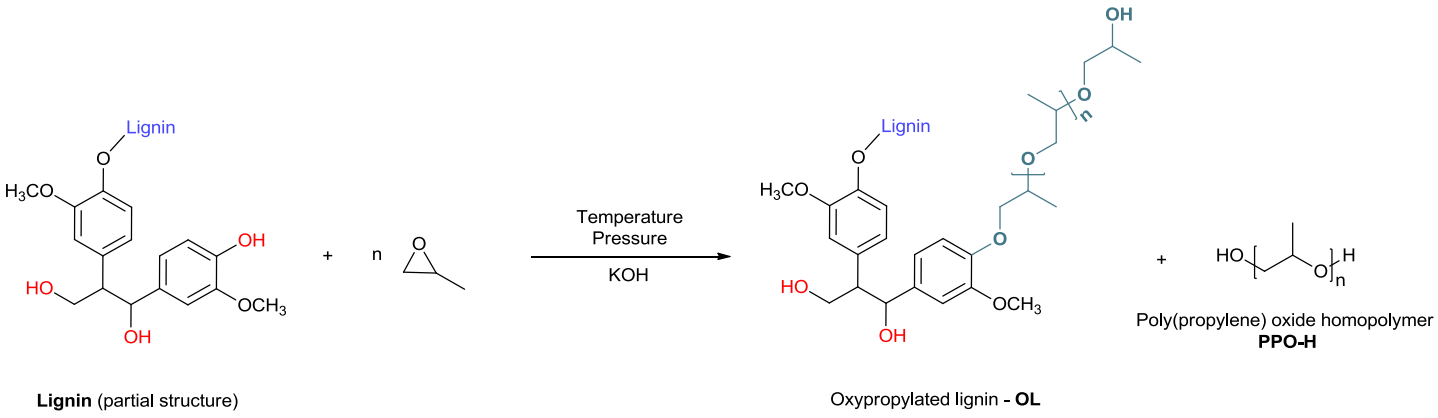

Figure IV-3. Reaction scheme for lignin oxypropylation.

Keeping in mind the future application of this new macropolyol in PU synthesis, the purification of OL was performed in two steps, involving firstly the removal of C following by the extraction of homopolymer (PPO-H) chains.

Catalyst removal. Oxypropylated lignin was first dissolved in dichloromethane and then washed twice with distilled water. The organic layer was then dried with anhydrous sodium sulfate and the product was evaporated at reduced pressure. The polyol mixture was dried under vacuum at 35°C for one night.

Homopolymer extraction. PPO-H chains were removed by extracting twice the polyol mixture with cyclohexane under reflux according to the method established by Pavier et al.[18]. The recovered fraction, OL and PPO-H were subsequently dried under vacuum at 60°C over one

night to remove cyclohexane. Both fractions were then weighted to determine the PPO-H content in the polyol mixture. The corresponding data are collected in Table IV-1 for each reaction parameters used.

Hydroxyl index (I_{OH}) in mg of KOH.g^{-1}, was determined according to Equation (1):

$$I_{OH} = \frac{(V_{blank} - V_P) \times C \times 56.1}{W_P} \qquad (1)$$

Where V_{blank} (mL) is the NaOH volume required for blank titration, V_P (mL) is the NaOH volume required for polyol sample titration, C (mol.L^{-1}) is the NaOH concentration and W_P (g) is the polyol weight.

	Oxypropylated samples	**$OL_{80/20}$**	**$OL_{70/30}$**	**$OL_{60/40}$**	**$OL_{50/50}$**
Reaction parameters	PO/L ratio (w/w)	80/20	70/30	60/40	50/50
	C/L ratio (%)	5	5	5	5
	Propylene oxide (mL)	100	100	100	100
	Lignin (g)	20.7	35.6	55.3	83.0
	T_{max} (°C)	231	248	233	223
	P_{max} (bar)	16.1	15.5	13.7	12.6
	Reaction time (h)	2.5	1.8	2.0	2.5

Table IV-1. Reaction parameters and operating conditions used during the oxypropylation.

2.3.2 Polymer synthesis

The preparation of polyurethanes (OLPU) based on OL has been performed by a two-step synthetic strategy. The first step is the prepolymerization reaction between PPO (1000 g.mol^{-1}) and an excess of MDI to prepare isocyanate-terminated prepolymers P_{1000} (T_g = -30.3°C, %NCO = 5.03). The second step is the reaction of OL with isocyanate prepolymer.

Polyurethane prepolymer synthesis.

A three-necked 250 mL round-bottomed flask was fitted with a nitrogen inlet tube and a mechanical stirrer. PPO (1000 g.mol^{-1}) and 4,4' MDI (fonctionnality = 2) were added into the flask and stirred at 70°C during 5 hours to yield isocyanate prepolymer with a 1.8 molar ratio

of NCO:OH. The ensuing isocyanate prepolymers was coded P_{1000}. The precise concentration of free isocyanate functions on the prepolymer was then determined.

NCO content determination. This method allows determining the amount of isocyanate which reacts with one equivalent of N-Dibutylamine, and gives NCO content by weight per cent according equation (2).

$$\% \text{ NCO} = \frac{(V_{blank} - V_s) \times 42 \times 0.1}{W_P} \qquad (2)$$

Where V_{blank} (mL) is the hydrochloric acid volume required for blank titration, V_s (mL) is the HCl volume required for polyol sample titration and W_P (g) is the polyol weight.

Polyurethane synthesis (OLPU).

Weighted quantity of OL and P_{1000} were separately solubilised in anhydrous THF. The solutions were stirred for 10-20 minutes at room temperature until all the components were completely dissolved. A three-necked 100 mL round-bottomed flask equipped with a magnetic stirrer, nitrogen inlet and condenser was charged with the solution of OL. The solution was stirred at 70°C under nitrogen flow and P_{1000} was added. The reaction mixture was stirred at 70°C for 4h. After completion of the reaction, the THF was evaporated and the OLPU was dried over one night at 35°C under vacuum. Four different OL samples were used to prepare OLPUs namely, $OL_{80/20}$, $OL_{70/30}$, $OL_{60/40}$ and $OL_{50/50}$ respectively. In this way, four different sets of OLPUs were prepared by varying the NCO:OH ratio of 0.2, 0.4, 0.6, 0.8 and 1.0. Reaction parameters and samples designations are given in Table IV-2.

The NCO:OH ratio was calculated according to the hydroxyl value of OL and the content of free NCO groups of the isocyanate prepolymer. PUs with different NCO:OH molar ratio are usually synthesized by changing chain extender content while keeping the same content of other components. In the present study, content of PPO and 4,4'MDI kept constants in PU formulation whereas the content of OL and thus lignin content varied (Table IV-3).

Dynamical and mechanical tests were performed on PUs processed into films obtained by compression moulding between 2 plates at 100 - 120°C.

Samples	Oxypropylated lignin samples	NCO:OH molar ratio	% OL (w/w)
OLPU-1	$OL_{80/20}$	0.2	70
OLPU-2		0.4	53
OLPU-3		0.6	43
OLPU-4		0.8	36
OLPU-5		1.0	30
OLPU-6	$OL_{70/30}$	0.2	68
OLPU-7		0.4	52
OLPU-8		0.6	42
OLPU-9		0.8	35
OLPU-10		1.0	30
OLPU-11	$OL_{60/40}$	0.2	64
OLPU-12		0.4	47
OLPU-13		0.6	37
OLPU-14		0.8	31
OLPU-15		1.0	26
OLPU-16	$OL_{50/50}$	0.2	69
OLPU-17		0.6	36
OLPU-18		1.0	26

Table IV-2. Reaction details for PU synthesis with four different oxypropylated lignins.

	PU formulation		
NCO:OH molar ratio	OH from OL (mol)	PPG (mol)	NCO (mol)
0.2	8.77	1	1.8
0.4	4.34	1	1.8
0.6	2.90	1	1.8
0.8	2.13	1	1.8
1.0	1.74	1	1.8

Table IV-3. Data concerning the PU formulations.

3. Results and discussion

3.1 Lignin characterization

It is widely accepted that lignin is not a clearly defined compound. Nevertheless, this physically and chemically heterogeneous material consists of phenylpropane units with hydroxyl groups, phenolic and aliphatic sites, respectively[9]. The extraction process and the botanical resource induce the amount and nature of the different functional groups, which control the chemical reactivity of the lignin. The lignin used in this study is extracted from wheat straw by a soda pulping process The main characteristics of this lignin are summarized in Tables IV-4 (SEC and DSC) and IV-7 (^{31}P NMR). The chemical and physical data were found to be in the same range to those reported from the literature, and in good correlation with values given by the supplier. As can be observed, results found showed a low number average molar mass (M_n = 1120 g.mol^{-1}) compared to sulfur lignins, namely Kraft and Lignosulfonates. The hydroxyl content and T_g values of soda lignin, determined according previous published method [27], will be then compared to those obtained for modified lignin.

Moisture content (%)		3.56
SEC analysis	M_n *(g.mol^{-1})*	1120
	M_w *(g.mol^{-1})*	4380
	M_w/M_n	3.9
DSC analysis	T_g (°C) *crude lignin*	143

Table IV-4. Analysis results performed on Soda lignin.

3.2 Synthesis and characterization of oxypropylated lignin macromonomers

Oxypropylation is a ring-opening polymerization through lignin hydroxyl groups which is always accompanied by the homopolymerization of propylene oxide through transfer reactions during the anionic grafting mechanism. In fact, alkoxy anions are formed from the hydroxyl groups of lignin in presence of KOH and the chain growth starts, but monomer transfer can lead to the removal of the anionic species and finally to PO homopolymerization (Figure IV-4)[25, 28]. The resulting product is then a mixture of PO oligomers, PPO-H, and OL. In our case, no specific study has been developed concerning the nature and amount of C used since previous studies demonstrated that KOH is an adequate choice for this type of reaction. Besides, Cateto et al. (2008) showed that the amount of catalyst did not influence significantly the formation of PPO-H and the viscosity of the resulting polyol mixture[29]. However,

temperatures involved during oxypropylation reaction can induce a self-condensation of lignin which can give insoluble fraction into the mixture[24, 30]. In the present study, the polyol mixtures are brown viscous products, without insoluble fraction.

The reaction parameters and the polymerization conditions are summarized in Table IV-1. It is worth mentioning that the reactor temperature set point was fixed at 150°C, but this temperature was always exceeded until it reached a maximum (T_{max}), e.g., 250°C for $OL_{70/30}$ synthesis with a subsequent increase of pressure inside the reactor. The pressure reached its maximum only during few seconds and then started to decline rapidly due to PO consumption accompanied by a temperature decrease until the set point (*Supplementary info*).

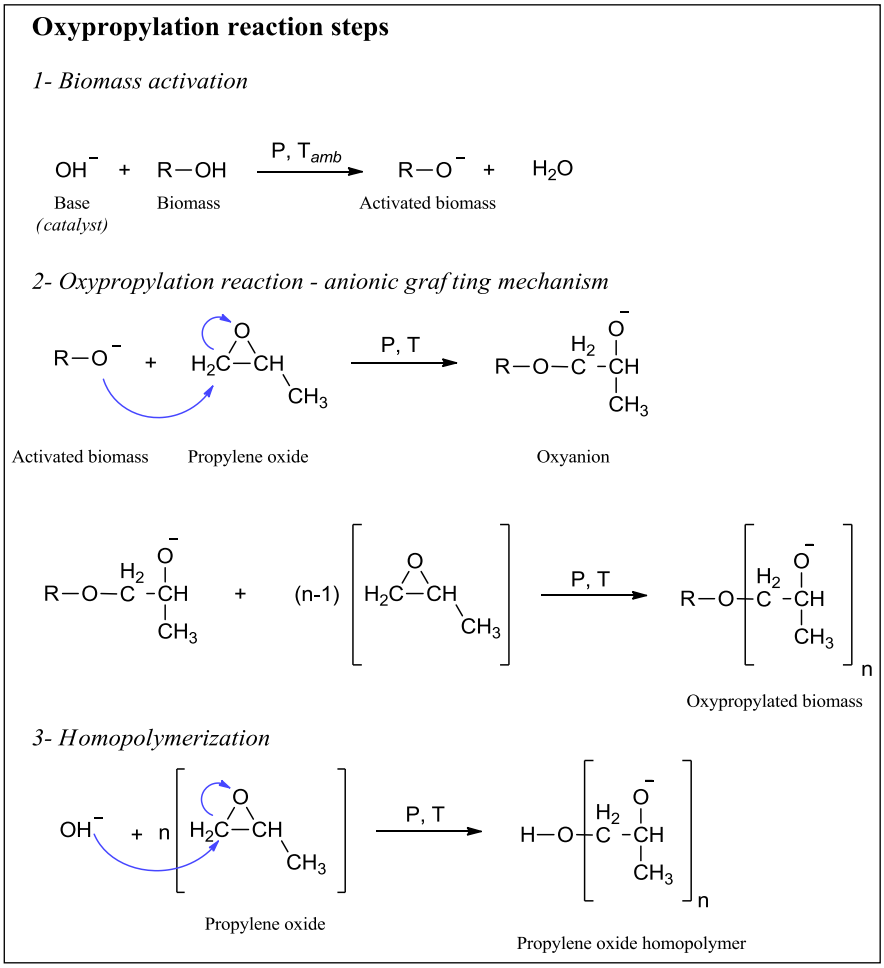

Figure IV-4. Schematic representation of the oxypropylation reaction mechanism; biomass activation, anionic grafting reaction on biomass and homopolymerization step are represented.

PO polymerization onto lignin was studied and followed by FT-IR and ^{1}H NMR. The FT-IR spectra of the soda lignin starting material and the $OL_{70/30}$ are presented in Figure IV-5. As

shown in FT-IR spectra, several characteristics bands indicated the grafting of PPO chains onto lignin such as (i) an increase in the aliphatic CH stretching region (2800-3000 cm^{-1}) with the appearance of a new peak at 2970 cm^{-1} attributed to the methyl groups from grafted PO units, (ii) a reduction in the intensity of carbonyl groups (1726 cm^{-1}), (iii) an increase in the C-O stretching region (1000-1110 cm^{-1}) associated to ether moieties and (iv) a new peak at 1375 cm^{-1}, confirming the introduction of CH_3 groups. Furthermore, it has to be mentioned that the relative increase in intensity of these peaks is related to the extent of oxypropylation. ^1H NMR also confirmed the reaction and allowed to quantitatively determine the structure of polyols by methods that are detailed in further sections.

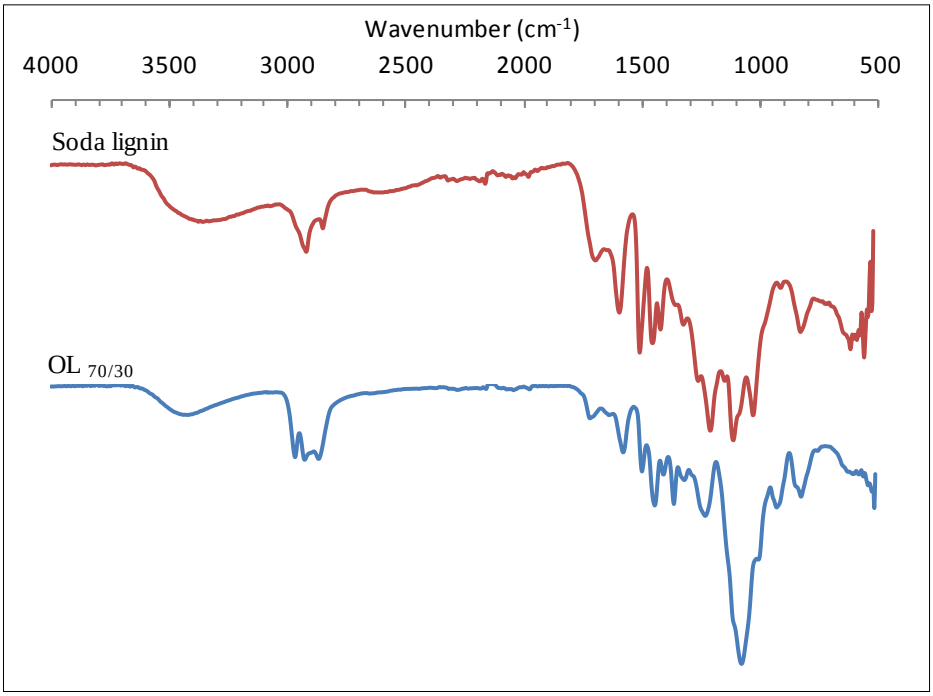

Figure IV-5. FTIR spectra of Soda lignin and oxypropylated sample ($OL_{70/30}$).

Tables IV-5 and IV-6 show a summary of the main properties obtained for lignin-based polyol mixture (i.e., homopolymer content, I_{OH}, number average molar mass (M_n) and T_g). SEC analyses have been performed on OL. The increase on M_n, which varied from 1200 $g.mol^{-1}$ for original soda lignin to 7700, 4600 and 3670 $g.mol^{-1}$ for $OL_{80/20}$, $OL_{70/30}$ and $OL_{60/40}$ respectively, confirmed also the grafting reaction. The result obtained for $OL_{50/50}$ was not expected and cannot be easily explained. The inspection of chromatographic profile as a function of PO/L content, and the corresponding SEC values reveals that molecular weight distribution shifts apparently towards lower molecular weight when PO/L ratio decreases. To

facilitate the analysis between the chromatographic profiles, normalized traces have been used (Figure IV-6). The same trend has also been observed in the case of the chromatographic profiles for PPO-H and polyol mixture (*Supplementary information*).

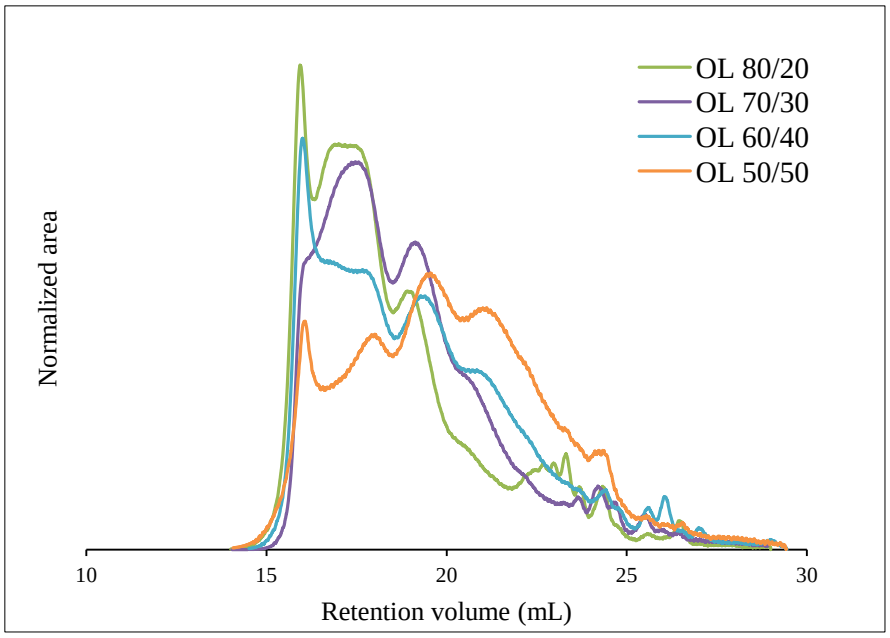

Figure IV-6. Chromatographic profile elution as a function of PO/L ratios.

The evolution of homopolymer content on polyol mixture revealed that the formation of neat PPO chains decreases with the increase of lignin content. This tendency has already been observed by Gandini's research groups for sugar beet pulp and lignin[21, 31]. It is interesting to note that polyol synthesized with high lignin content are sometimes brittle but often very viscous due to the presence of a small amount of residual PPO-H, which can play the role of plasticizer into the mixture. This plasticization effect can be also noticed through the evolution of the T_g of the corresponding mixture on Table IV-5, which depend on the PPO-H content. For a better understanding of OL structure, PPO-H has always been removed from the mixture. It is worth mentioning that the PPO-H content decreased as the lignin content increased resulting in a better polymerization of PO onto lignin. The PPO-H removed is a yellowy viscous product whose T_g is close to that of PPO oligomers (i.e., -70°C)[17]. From DSC experiments, theoretical T_g of polyol mixture could be determined according the following Fox Law Equation (3):

$$\frac{1}{T_{g\ \text{polyol mixture}}} = \frac{W_H}{T_{g\ H}} + \frac{W_{OL}}{T_{g\ OL}} \qquad (3)$$

In Equation (3), W_H and W_{OL} refer to the weight fraction of PPO-H and OL in the polyol mixture, respectively. As can be observed, from the data collected in Table IV-5, the T_g of polyol mixture seems to fit reasonably with the Fox theory and can thus be described as an homogenous mixture composed by PPO-H and OL.

The value of hydroxyl indexes (I_{OH}) for OL samples (without PPO-H) were about 150-200 mg $KOH.g^{-1}$. This index increased with increasing lignin content. The same tendencies were mentioned in previous studies and the results were in good correlation with data collected by Cateto et al. (2008) and Nadji et al. (2005)[26, 30]. Furthermore, it was also observed that I_{OH} values were quite lower than that of original lignin (258 mg $KOH.g^{-1}$) especially for reaction performed with low lignin content (i.e. PO/L of 80/20 and 70/30).

	Oxypropylated samples	**$OL_{80/20}$**	**$OL_{70/30}$**	**$OL_{60/40}$**	**$OL_{50/50}$**
	Extracted homopolymer content (%)[a]	56	39	23	12
	I_{OH} (mg $KOH.g^{-1}$)	149	155	188	193
DSC results	$T_{g\ polyol\ mixture}$ (°C)[b]	-61	-49	-19	32
	$T_{g\ H}$ (°C)	-65	-66	-63	-61
	$T_{g\ OL}$ (°C)	-37	-9	33	72
Theretical results	$T_{g\ polyol\ mixture}$ (°C)[c]	-53	-35	4	48

Table IV-5. Chemical and thermal properties of oxypropylated lignins (OL).

[a] Percentage of PPO-H extracted from the polyol mixture.
[b] Polyol mixture : OL + PPO-H (without catalyst).
[c] According calculations based on Equation (3)

	PO/L ratio (w/w)	80/20	70/30	60/40	50/50
OL fraction	M_n *(g.mol^{-1})*	7723	4601	3670	7410
	M_w *(g.mol^{-1})*	31700	19420	23001	27273
	PDI	4.1	4.2	6.3	3.7
PPO-H fraction	M_n *(g.mol^{-1})*	846	485	359	369
	M_w *(g.mol^{-1})*	1670	810	678	663
	PDI	2.0	1.7	1.9	1.8

Table IV-6. SEC results for OL and PPO-H fractions using PS standard.

Under basic conditions, it is well-known that monoalkyl-substituted epoxides react predominantly at the less substituted carbon, due to the steric effects. This reaction can be considered as an SN_2 type reaction (Figure IV-4). In the case of lignin oxypropylation, the rate constant of reaction (k) will greatly depend on the pKa of lignin hydroxyl groups with which the epoxide is reacting whereby: $k_{\text{phenolic OH}} > k_{\text{primary OH}} > k_{\text{secondary OH}} > k_{\text{tertiary OH}}$. The degree of derivatization of hydroxyl groups from lignin will be deeper investigated with following quantitative ^{31}P NMR results.

Quantitative ^{31}P NMR. Oxypropylation reaction was monitored and analyzed by quantitative ^{31}P NMR using previous published procedures[32-35]. According to the method developed by Argyropoulos's research group[32], the discrimination of the three forms of phenolic hydroxyl groups (*p*-hydroxyphenyl, guaiacyl, and syringyl structures), as well as aliphatic hydroxyl functions and carboxylic acid has been possible. The degree of oxypropylation of soda lignin could then be easily calculated. All chemical shifts reported are relative to the reaction product of water with phosphylating reagent, which has been observed to give a sharp signal in pyridine/$CDCl_3$ at 132.2 ppm. ^{31}P NMR spectra from OL (Figure IV-7) show that both condensed and non-condensed phenolic units were efficiently hydroxypropylated. COOH and aliphatic hydroxyl groups react also with PO but some of them remain unreactive. The different hydroxyl groups were obtained by integrating the following spectral regions: aliphatic hydroxyl groups (primary OH and new hydroxyalkylated OH) and phenolic units.

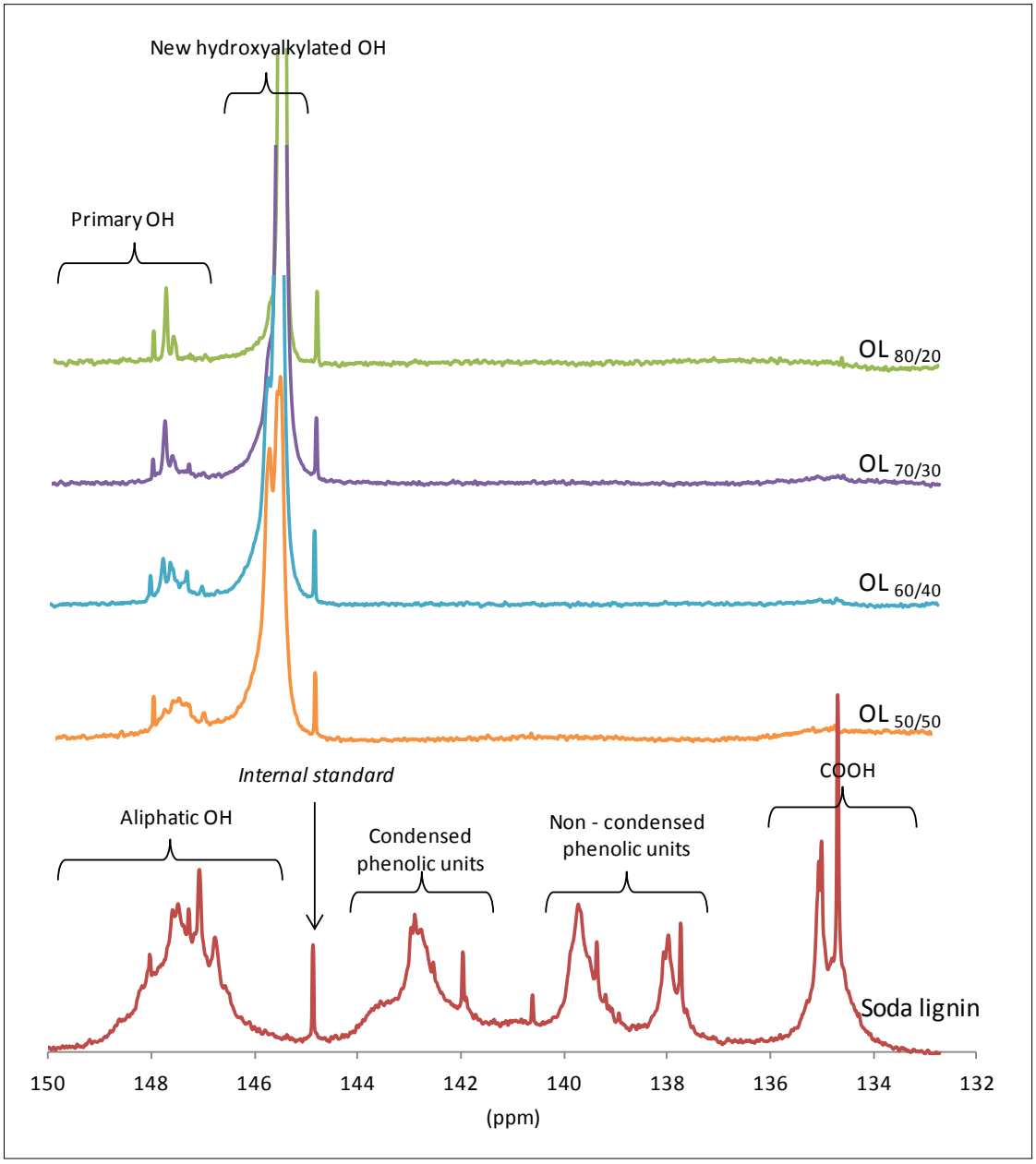

Figure IV-7. Quantitative ^{31}P NMR spectra of OL samples and soda lignin.

Quantitative ^{1}H NMR. Quantitative ^{1}H NMR spectra were recorded in an effort to accurately characterize OL, to estimate the average number of PO units appended to each OH function on lignin macromolecule, as described by Sadeghifar et al. (2012)[36]. Figure IV-8 illustrates the distinct regions attributed respectively to aromatic protons (6.0-8.0 ppm), methylene and methoxy protons (2.8-4.2 ppm) and new aliphatic methyl protons from PPO chains grafted onto lignin (0.2-1.5 ppm). Quantitative ^{1}H NMR allows estimating methyl groups formed during PO ring-opening. For example, 2.72 mmol.g^{-1} of new hydroxyalkylated hydroxyl groups were determined in $OL_{80/20}$ by quantitative ^{31}P NMR (Table IV-7) whereas 95.7

mmol.g^{-1} of methyl groups were estimated by ^{1}H NMR analyses. Hence, the average length of PPO chains grafted onto lignin after oxypropylation was approximately 35.2 units of PO per chain.

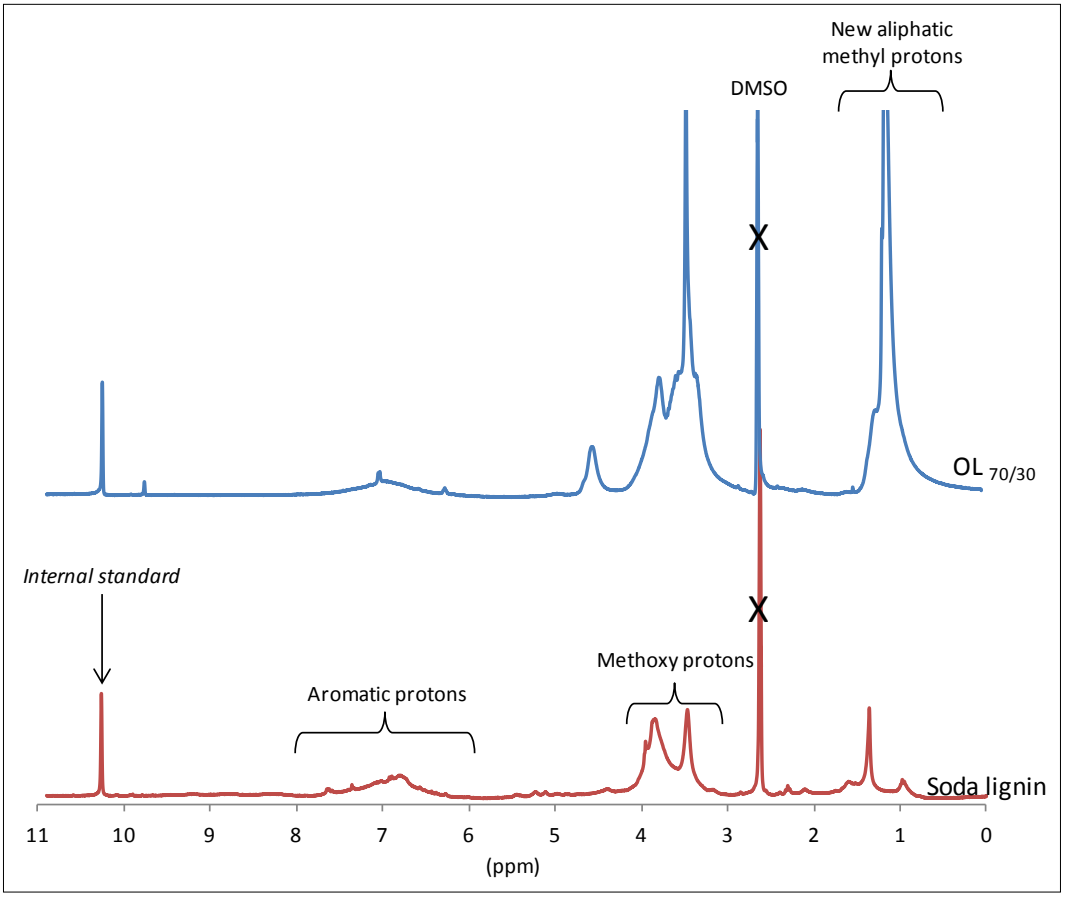

Figure IV-8. Quantitative ^{1}H NMR spectra of oxypropylated lignin sample ($OL_{70/30}$) and soda lignin.

Taking into account the data collected from ^{1}H and ^{31}P NMR, it has been possible to fully determine the main characteristics of OL. Table IV-8 gives some precise information concerning the chemical structure of OL, i.e., the average length of PO grafts and their number per lignin molecule. This characterization constitutes the key point of this study considering that OL is the starting point in PU synthesis. The average length of PPO grafts increases with the decreasing of lignin content, whereas the number of grafts increases. Furthermore, the number of grafted chains per lignin has to be compared to the number of phenolic hydroxyl groups per lignin macromolecule determined by ^{31}P NMR (i.e. 1.67 phenolic OH), which are the most reactive functions through oxypropylation reaction. As we can see, the number of grafts per lignin is lower than the number of phenolic hydroxyl groups, but in the same range. This tendency is in good correlation with hydroxyl index values and

confirmed that the increase of lignin content induced an increase of PPO grafts and simultaneous decrease of the average lengths of grafts. The determination of the number of grafts per lignin macromolecule has never been clearly determined in the literature and still remains investigated considering the high variability of the lignins structures. This result has thus to be considered as a first result to understand the lignin reactivity and then the properties of the resulting synthesized polymers.

Hydroxyl groups (mmol.g^{-1})	**Integration region (ppm)**	**Soda lignin**	**$OL_{80/20}$**	**$OL_{70/30}$**	**$OL_{60/40}$**	**$OL_{50/50}$**
Aliphatic –OH	145.3 – 150.0					
Hydroxyalkylated –OH	145.3 – 146.0	-	2.72	2.87	2.48	2.35
Primary –OH	146.5 – 150.0	1.49	0.18	0.52	0.32	0.58
Phenolic –OH	136.6 – 144.7	2.35	-	-	-	-
Total OH		3.84	2.90	3.39	2.8	2.93

Table IV-7. Signal assignments, hydroxyl content value and average arm lengths of PPO grafts from quantitative ^{31}P and ^{1}H analyses of soda lignin and OL samples.

	$OL_{80/20}$	**$OL_{70/30}$**	**$OL_{60/40}$**	**$OL_{50/50}$**
Number of PO units per chains (^{1}H NMR analysis)	35.2	21.3	16.5	11.2
Average number of hydroxyalkylated OH per lignin molecule	1.20	1.29	1.35	1.51

Table IV-8. Main characteristics of OL samples based on quantitative ^{1}H and ^{31}P NMR results.

It is well-known that chemical modification of lignin can affect its thermal properties such as glass transition temperature (T_g). As the degree of derivatization increases, the T_g of the lignin-based derivatives decreases (Table IV-5). This evolution is expected since the derivatizations affect the hydrogen bonding patterns of these materials. Depending on the structure and architecture of the substituent, the free volume of the new lignin-based polymer system may increase, resulting in the decrease of T_g. In this respect, T_g of polyol mixture increase with the decrease of PPO-H content formed during oxypropylation. As already mentioned previously, PPO acts as plasticizer with a decreasing of the T_g for resulting

products. When the PPO-H is removed from the mixture, the products become more viscous, and even brittle in the case of $OL_{50/50}$. The difference between T_g values of OL samples can be attributed to the PPO chains length grafted to lignin. Short chains grafted will give products with high T_g due to their low mobility, whereas long chains will provide more flexibility to samples and a resulting T_g below ambient temperature. The impact of T_g of these polyether macropolyols on the final polyurethane polymers will be discussed below.

In that frame, it is possible to understand that a wide range of macropoyol can be synthesized by modulating its properties, e.g. viscosity, T_g and hydroxyl index (I_{OH}). The high functionality and suitability of OL make them potential polyol for preparation of engineering plastic and synthesis of polyurethanes.

3.3 Synthesis and characterization of polyurethanes

The reaction between OL and the isocyanate prepolymer was confirmed by FT-IR analyses. The urethane link formation was monitored by some typical absorbance values such as (i) the carbonyl stretching vibration of polyurethane occurred at 1725 cm^{-1}, (ii) a combination of N-H deformation and C-N stretching vibrations at 1535 and 1225 cm^{-1}, respectively, and (iii) a new peak at 1309 cm^{-1} attributed at –OCONH asymmetric stretching vibrations. Moreover, the absence of the absorption band at approximately 2270 cm^{-1} confirmed the complete isocyanate group conversion during the polymerization reaction.

In this study, the absorbance corresponding to the NH stretching region, assigned at approximately 3300 cm^{-1} was used to assess the formation of urethane linkages but also to qualitatively evaluate the effect of NCO:OH ratio. Figure IV-9 shows the FT-IR spectra of the PUs samples synthesized with $OL_{60/40}$ and five different NCO:OH ratios. The broad band centred at 3500 cm^{-1}, corresponding to O-H stretching tends to decrease with the increasing of NCO:OH ratio whereas the NH stretching band (3295 cm^{-1}) becomes more intense. This observation also suggests that it is possible to control the conversion rate of hydroxyl groups from macropolyol by varying the NCO:OH molar ratio.

In the present study, block-copolymers were synthesized resulting in the creation of segmented structures. From an intensive literature survey on lignin based polyurethanes and their morphologies[37-39], we can expect a phase separation on segmented PU material between

soft and hard segments. Transition temperatures of soft and hard segments were determined by both DSC and DMTA experiments.

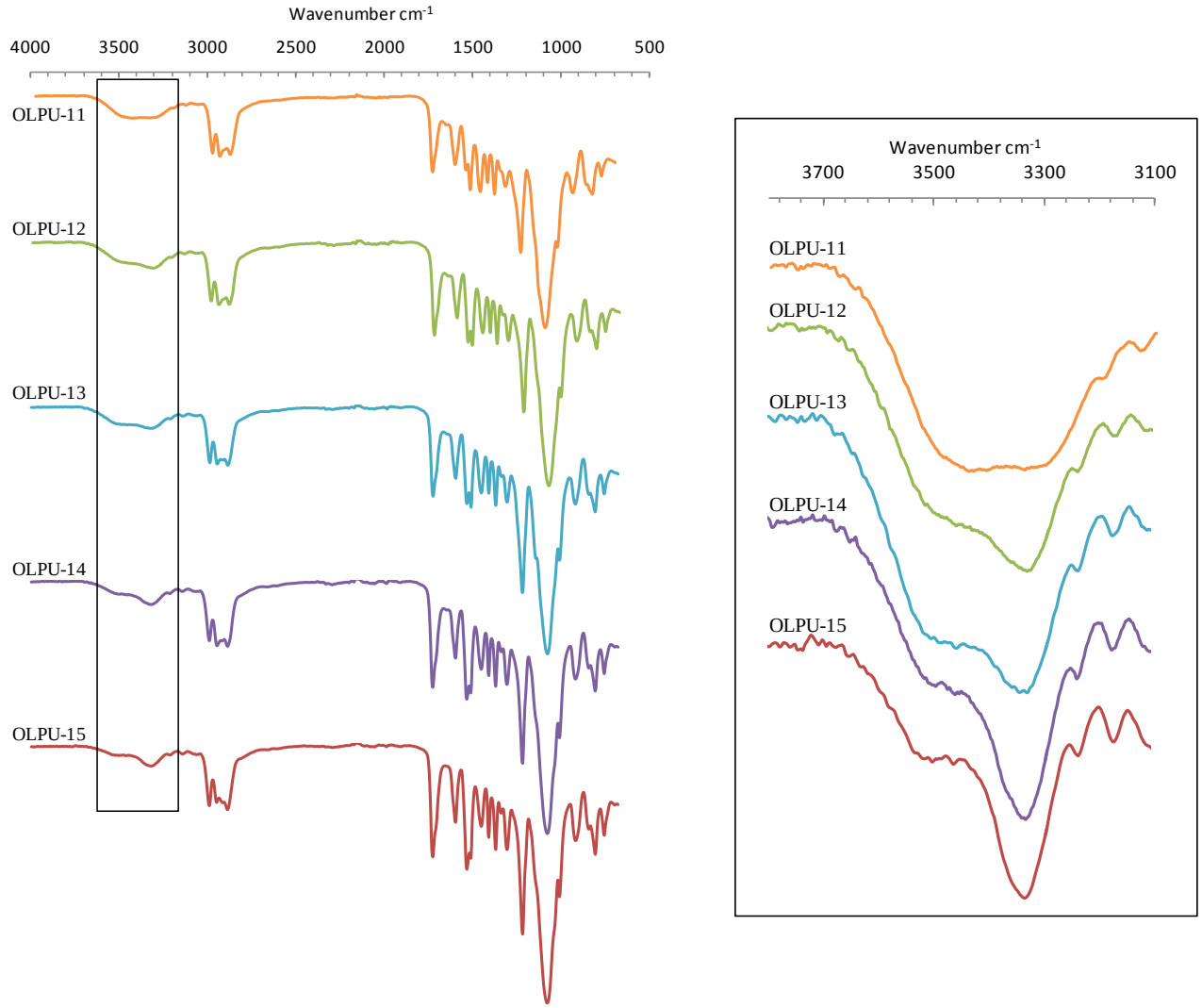

Figure IV-9. FTIR spectra of LPUs synthesized with P_{425} and different NCO:OH molar ratios.

3.4 Influence of NCO:OH molar ratio on polymer properties

A good understanding of the effect of NCO:OH molar ratio on the structure and the final polymer properties is essential for the elaboration of high performance PU materials. Consequently, a wide range of PUs was so far synthesized to investigate the level of cross-linking on the structures of the obtained materials.

The T_g values of OLPUs determined by DSC are shown in Table IV-9. In our case, the OLPUs synthesized do not present crystalline domain. Both block polymers (OL and isocyanate prepolymer) used in the synthesis were completely amorphous with one T_g respectively. For each OLPU series, the data clearly showed that T_g increased as expected

with the NCO:OH molar ratio and was correlated to a high degree of crosslinking. These T_g values seem to be associated of the soft segments ($T_{g\ SS}$) in OLPU architecture and attributed to the motion of the isocyanate prepolymer segments. The relative difference of structure of OL seems to affect the soft domain organization. Furthermore, we can observe that $T_{g\ SS}$ is not greatly impacted by the variation of the NCO:OH molar ratio.

Figures IV-10 and IV-11 show the temperature dependence of the storage modulus (E') and loss factor (tan δ) of the PUs. The dynamic mechanical properties of the OLPU were obtained as a function of temperature beginning in the glassy state (from -100 to -20°C) and ending into the rubbery plateau for each material (from 70 to 200°C). From the DMTA curves, the plateau of the elastic modulus in the rubbery state can be used to make qualitative comparisons of the level of crosslinking among the various polymers synthesized in each series. Table IV-9 summarizes value of crosslinking density (ν_e) determined from Equation (4).

$$\nu_e = \frac{E'}{3\ RT} \qquad (4)$$

Equation (4) is derived from the theory of rubber elasticity[40, 41], which establishes the relationship between crosslink density and Young's Modulus (E) of polymers above T_g. Since the storage modulus (E') obtained from DMTA can be associated to the elastic modulus (E) at temperature above T_g (in the rubbery region at T_g + 40°C), E' can be substituted in Equation 4 to determine ν_e. R is the gas constant (8,31 $J.mol^{-1}.K^{-1}$) and T is the temperature in Kelvin. As expected, the cross-linking density increases with the NCO:OH molar ratio[38]. It is thus possible to modulate PU properties by varying this parameter. Furthermore, the presence of a rubbery plateau for each OLPU revealed the elastomeric behaviour of these materials.

From DMTA data, relaxation temperature of crosslinked materials detected at the maximum of tan δ can be determined. As can be observed from Figure IV-11, the maximum of tan δ shifts towards higher temperature and the peak becomes broader as the NCO:OH molar ratio decreased, i.e. as the lignin content increased. As previously demonstrated in the case of PU based on vegetable oils[42], the maximum of tan δ is characteristic of the glass transition temperature of hard segment. This hard domain is mainly composed by lignin-based crosslinking points and urethane bonds. As the hard segment increased (% of OL in PU formulation), the transition temperature become higher reflecting in an organized structure of hard segments into the continuous soft segment phase.

Samples	Oxypropylated lignin samples	NCO:OH molar ratio	DSC	DMTA		
			$T_{g\ SS}$ (°C)[a]	$T_{g\ HS}$ (°C)[b]	ν_e (mol.m^{-3})	biobased content (%)
OLPU-1	$OL_{80/20}$	0.2	-36	-	-	32
OLPU-2		0.4	-26	-0.5	12.6	24
OLPU-3		0.6	-24	-3.8	22.7	19
OLPU-4		0.8	-27	-3.1	29.6	16
OLPU-5		1.0	-24	-5.4	51.7	14
OLPU-6	$OL_{70/30}$	0.2	-11	32.1	6.8	33
OLPU-7		0.4	-12	21.9	23.6	26
OLPU-8		0.6	-13	25.1	37.1	21
OLPU-9		0.8	-18	17.7	77.7	17
OLPU-10		1.0	-11	10.1	70.7	15
OLPU-11	$OL_{60/40}$	0.2	-5	60.2	57.8	33
OLPU-12		0.4	-6	50.5	49.8	24
OLPU-13		0.6	-6	40.5	42.5	19
OLPU-14		0.8	-4	36.7	75.3	16
OLPU-15		1.0	-7	36.2	140.9	13
OLPU-16	$OL_{50/50}$	0.2	1	90.7	15.8	39
OLPU-17		0.6	2	55.9	42.5	20
OLPU-28		1.0	-6	39.9	3.0	15

Table IV-9. Dynamical mechanical and thermal properties for the synthesized polyurethanes.

[a]: $T_{g\ SS}$: T_g of soft segment
[b]: $T_{g\ HS}$: T_g of hard segment

These different observations combining DSC and DMTA results may indicate the existence of two different phases in OLPU samples, in good correlation with the literature[43-46]. While the T_g of soft segment is observed by DSC below ambient temperature, the T_g of hard domains, is determined by DMTA in the range from -5 to 90°C. In summary, these series of polyurethanes might be partially described as amorphous segmented polyurethane where lignin hard segments are bridged with soft segments. The mobility of soft domain which is mainly composed by the isocyanate prepolymer is greatly affected by the structure of OL which forms the greatest part of the hard segment. This microphase separation is also responsible for the elastomeric properties of these polyurethanes[42].

Table IV-10 shows the mechanical properties of the OLPU based on $OL_{70/30}$ and $OL_{60/40}$, respectively, determined by uniaxial tensile testing. Samples synthesized with respectively, $OL_{80/20}$ and $OL_{50/50}$ were too soft and too brittle, to be investigated. As shown in Table IV-10, for materials synthesized with $OL_{70/30}$, there is no influence of the NCO:OH molar ratio, since the elongation at break varied from 296 to 400% whereas the modulus and the maximum strength remains quite constant. The tendency is different for OLPU based on $OL_{60/40}$: maximum strength and Young's Modulus significantly decrease with the increasing of crosslinking density. At that time, we can suppose that modified lignin plays an important role in segmented OLPU morphology. However it can be notice that OLPU-11 sample displays interesting mechanical properties with high strength at break and Young's Modulus, respectively.

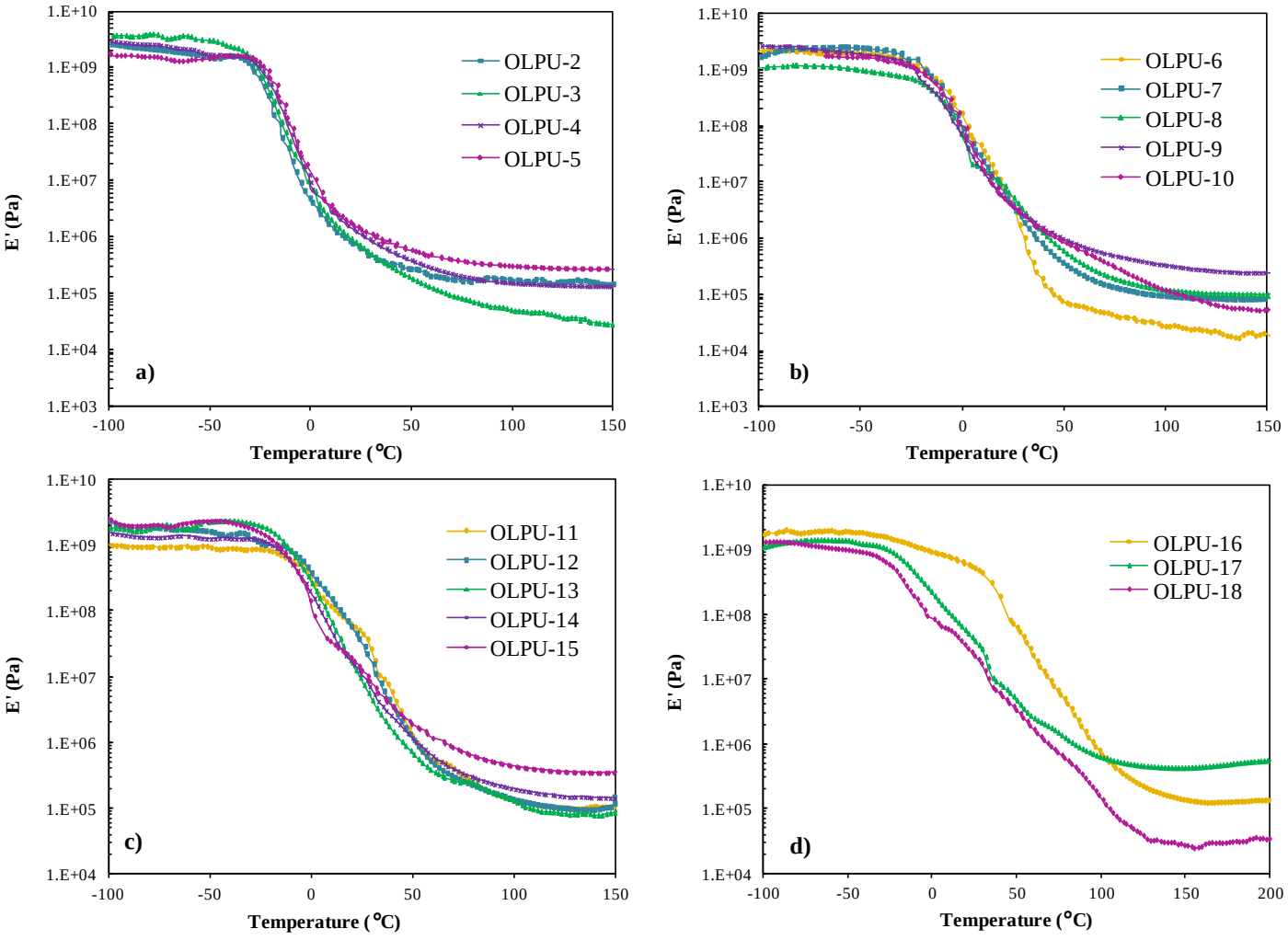

Figure IV-10. DMTA curves of the PUs (a: E' of PU based on $OL_{80/20}$; b: E' of PU based on $OL_{70/30}$; c: E' of PU based on $OL_{60/40}$; d: E' of PU based on $OL_{50/50}$).

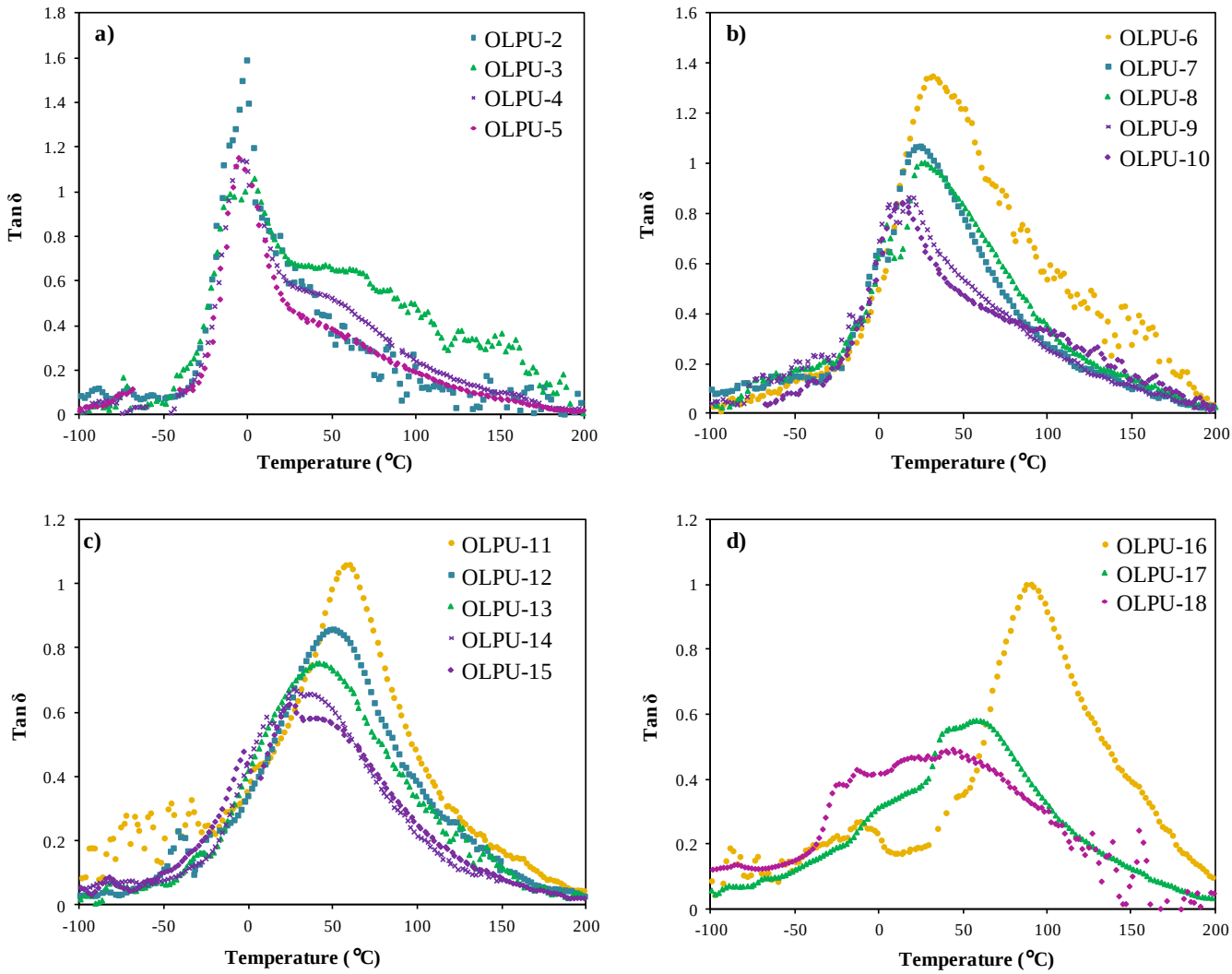

Figure IV-11. Evolutions in the position and intensity of the relaxation transition (Tan δ) on the stoichiometric ratio of the component. (a: tan δ of PU based on $OL_{80/20}$; b: tan δ of PU based on $OL_{70/30}$; c: tan δ of PU based on $OL_{60/40}$; d: tan δ of PU based on $OL_{50/50}$).

3.5 Influence of macropolyol structure on polymer properties

OL structures varied according to oxypropylation reaction conditions. Whether, numerous short PO chains (e.g. $OL_{60/40}$ and $OL_{50/50}$) were grafted to the lignin core, or the lignin only presented a few long PO grafted chains (e.g. $OL_{80/20}$ and $OL_{70/30}$). These differences in structures could also been observed in the thermal properties (DSC and DMTA). Indeed, for the lignin bearing long PO chains, the $T_{g\ HS}$ values are lower than for pure lignin. This can be explained by the fact that the PO chains act as a thermal plasticizer improving the chains motion and thus lower the obtained $T_{g\ HS}$. This observation is confirmed by the $T_{g\ SS}$ value that is close to the T_g of P_{1000} (T_g = -30 °C). We could then schematically represent the overall

structure by a two phases organization (Figure IV-12) where the hard segments are composed of lignin cores and the soft segment includes both the prepolymers and the long grafted PO chains. On the other hand, for $OL_{60/40}$ and $OL_{50/50}$, the hard segments are defined by lignin and short grafted PO chains. In this case, the $T_{g\ HS}$ values are closed to the one of pure lignin. It is worth mentioning that with this structure, the higher $T_{g\ SS}$ reflects the loss of mobility of the overall soft domain.

It has thus been proved that the OL chemical structure governs the general OLPU matrix self-organisation by well-defining the resulting soft and hard segments composition.

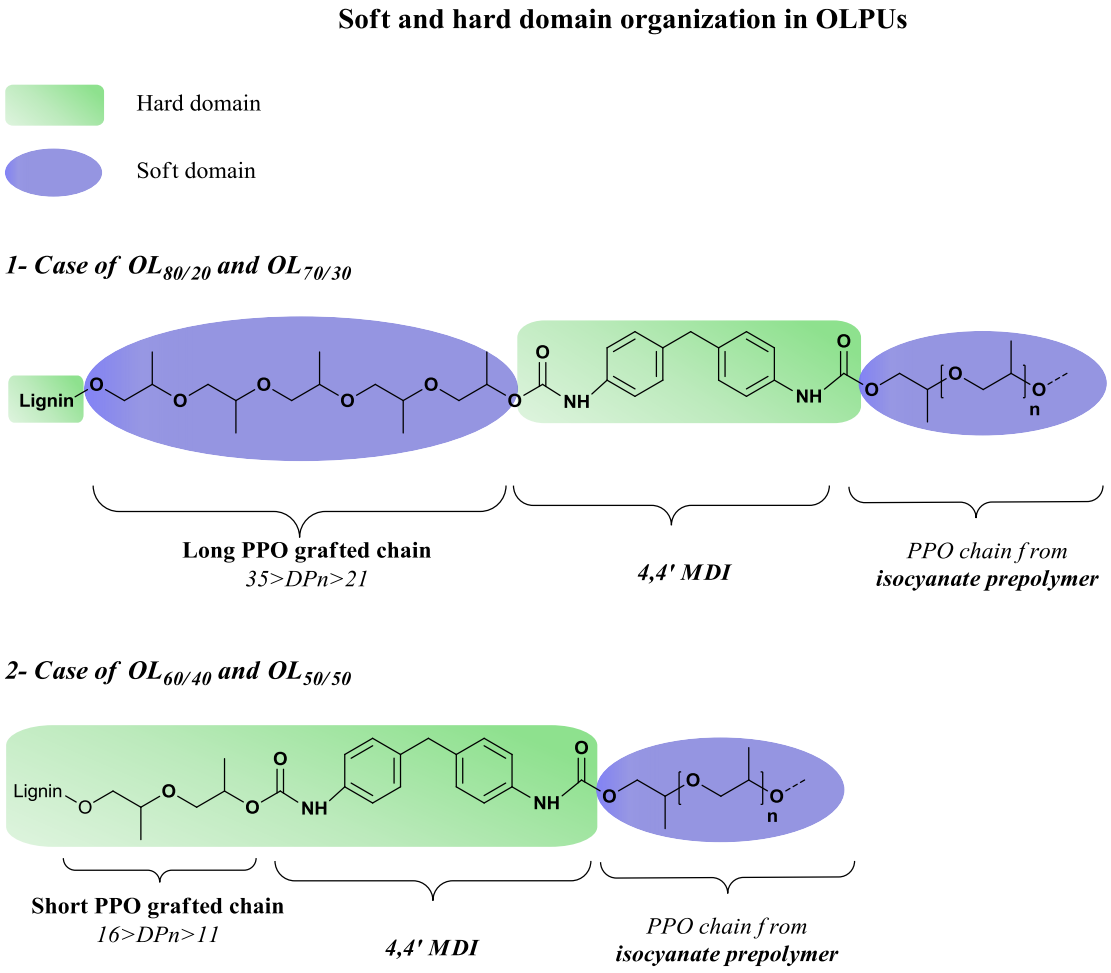

Figure IV-12. Schematic representation of OLPU domain organization – Partial structure of OLPU.

Furthermore, the presence of high lignin content gives appreciable stiffness to the network structure by increasing the Young's Modulus and maximum strength e.g., OLPU-11 is more rigid that OLPU-15. The average length of PO grafted impacts also the elongation at break.

Long grafted PO chains (high PO/L ratio) bring high elongation at break. This trend is in good correlation with the tendency observed for crosslink density.

To resume, the PO/L ratio plays an important role in the macromolecular structure of the macropolyol and consequently affects properties to the resulting PU materials. Thus, $OL_{70/30}$ and $OL_{60/40}$ seem to give PU materials with the highest mechanical properties, i.e. high elongation at break and high Young's Modulus. $OL_{70/30}$ with longer grafted chains provides high elongation at break whereas OLPUs with $OL_{60/40}$ polyol exhibit better mechanical resistance.

Samples	Oxypropylated lignin samples	NCO:OH molar ratio	**Traction**		
			σ Maximum strength (MPa)	ε Elongation at break (%)	E Young's Modulus, (MPa)
OLPU-6	$OL_{70/30}$	0.2	3.7 ± 1.0	296 ± 26	0.3 ± 0.1
OLPU-7		0.4	3.4 ± 0.1	404 ± 35	0.3 ± 0.0
OLPU-8		0.6	3.7 ± 0.6	325 ± 28	0.4 ± 0.0
OLPU-11	$OL_{60/40}$	0.2	9.8 ± 0.8	119 ± 29	7.0 ± 1.2
OLPU-12		0.4	6.9 ± 0.6	107 ± 9	4.4 ± 0.6
OLPU-13		0.6	2.6 ± 0.7	48 ± 16	2.0 ± 0.3
OLPU-14		0.8	2.6 ± 0.7	83 ± 19	1.8 ± 0.2
OLPU-15		1.0	5.2 ± 1.4	160 ± 59	1.9 ± 0.1

Table IV-10. Mechanical properties from uniaxial tensile tests of different synthesized OLPUs at ambient temperature with a crosshead speed of 20 $mm.min^{-1}$.

3.6 Influence of the residual PPO-H on the material properties

The role of the residual PPO-H into the polyol mixture after oxpropylation has been more particularly studied. In this case, only catalyst has been removed from the resulting mixture by liquid-liquid extraction with water. Consequently, the code used for these new starting polyols is $PM_{70/30}$ and $PM_{60/40}$ for polyol synthesized with PO/L of 70/30 and 60/40, respectively. The hydroxyl indexes of polyol mixtures (PM) were determined by chemical titration, the resulting I_{OH} are presented in Table IV-11 with the corresponding T_g values from DSC measurements. The NCO:OH ratio was varied from 0.2 to 1.0. As can be observed, the T_g values of soft segments are lower to those for PU synthesized with only OL. In this way,

the effect of the homopolymer chains as plasticizer in OLPU material is clearly demonstrated. In fact, free PPO-H can act as plasticizer but also as a chain extender for OLPU.

Samples	Polyol mixture	I_{OH} of Polyol mixture (mg KOH.g^{-1})[a]	NCO:OH molar ratio	DSC
				T_g (°C)
OLPU-16	PM $_{70/30}$	193	0.2	-38
OLPU-17			0.6	-33
OLPU-18			1.0	-27
OLPU-19	PM $_{60/40}$	219	0.2	-28
OLPU-20			0.4	-25
OLPU-21			0.6	-19

Table IV-11. DSC results obtained for OLPU synthesized with $PM_{70/30}$ and $PM_{60/40}$ with various NCO:OH molar ratio respectively.

[a]: determined by chemical titration

3.7 Thermal analysis

The original neat lignin was subjected to TGA analysis at a heating rate of 10°C.min^{-1} in a nitrogen atmosphere. For comparison, OL, PPO-H and polyol mixture thermal stability were also determined (Figure IV-13). An abundant literature on lignin thermal degradation reports the different radical coupling mechanisms occurring at pyrolitic temperatures[9, 47, 48]. TG curves indicated that thermal decomposition of lignin started at 200°C, while the slight mass decreasing between 0 and 150°C is attributed to vaporization of residual water in the sample. The maximum peak temperature appeared in derivative TG curve of crude lignin at 375°C and the residual mass of lignin at 500°C was 40% which is in good agreement with previous observation made by Hatakeyama and Hatakeyama (2010)[9]. Lignin derivatives (i.e., $PM_{80/20}$ and $OL_{80/20}$) show lower thermal stability due to the degradation of polyether chains grafted onto lignin. The TG curve of single PPO-H is on agreement with these previous results from Argyropoulos' team, which have highlighted the improved thermal stability of lignin by selective masking of phenolic hydroxyl groups[49]. After several repeated cycles of heating and cooling for up to three hours at 120°C, OL shows a higher stability compared to the neat lignin, regarding the evolution of molecular weight. This last behaviour may provide good perspectives for the use of OL samples for polymer processing.

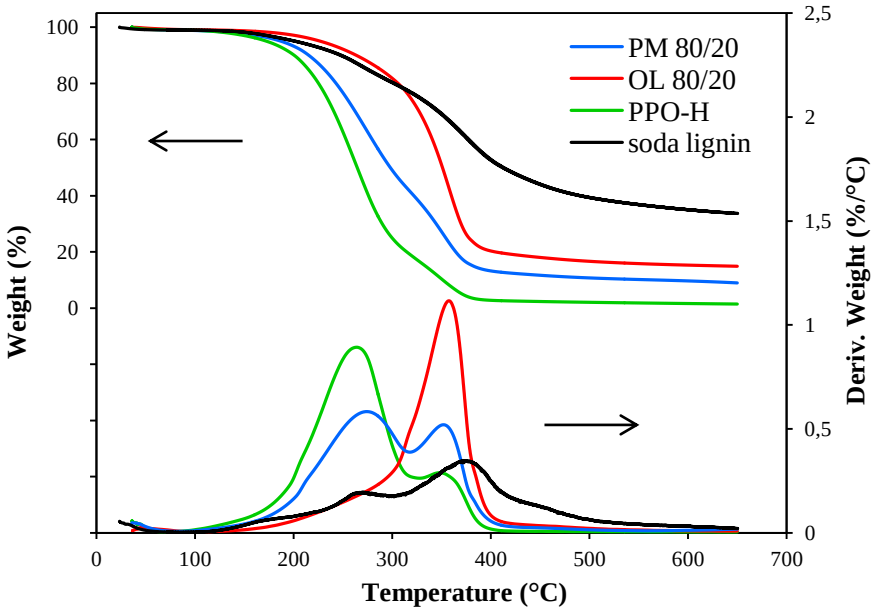

Figure IV-13. TGA/DTGA curves for soda lignin, PM, OL and PPO-H in case of PO/L of 80/20.

The thermal stability of the OLPU was also investigated by TGA, and the obtained weight loss curves of OLPU-11 to 15 are shown e.g., in Figure IV-14. A blank polyurethane synthesis (without lignin) has also been performed in order to compared the thermal behaviour of OLPUs samples to a PU synthesised with PPO (1000 $g.mol^{-1}$) and 4,4' MDI (NCO:OH = 1.03). This resulting PU is coded as BPU_{1000}.

Polyurethanes are well-known to have a relatively low thermal stability, mainly because of the presence of urethane bonds. In their study, Saunders et al.[50] proposed a three-step degradation mechanism of urethane bond decompositions consisting in (i) dissociation to isocyanate and alcohol, (ii) formation of primary amine and olefin and finally, and (iii) the formation of secondary amine. Taking into account that all of these reactions may proceed simultaneously.

As can be observed, the thermal behaviour observed for all OLPU samples is similar. This behaviour is not surprisingly considering that the PU structures are based on the same composition of polyols and isocyanate prepolymers. On the contrary, BPU_{1000} depicts a lower thermal stability with a T_{max} of 330°C and a residual mass at 500°C of 2.8%. For OLPUs a first shouldered peak in DTG curves (around 300°C) can be attributed to the main degradation of urethanes[51] whereas, the maximum peak can assigned to OL degradation. These results put

in evidence that lignin, as a macromer, promotes significant thermal stability of the polyurethanes, compared to those synthesized without it.

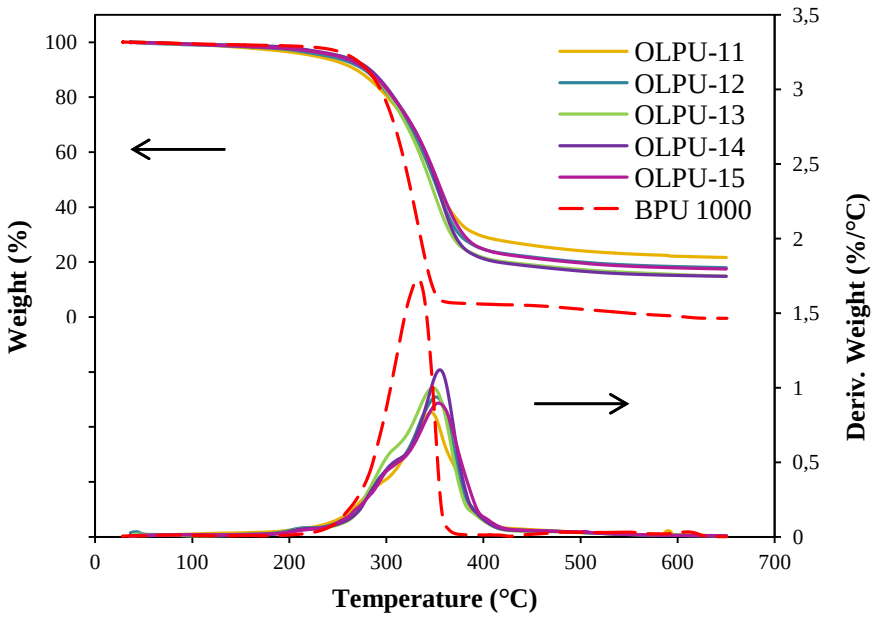

Figure IV-14. TGA/DTGA curves for OLPUs based on OL60/40 with various NCO:OH molar ratios.

4. Conclusion

Lignin-based polyether polyols were successfully synthesized by oxypropylation process. Lignin recovered from a soda process has been modified by varying PO/L ratio. Four sets of lignin derivatives have been synthesized and then fully characterized by various analytical methods in view of polyurethane synthesis. The structure of oxypropylated lignin was precisely investigated through quantitative ^{1}H and ^{31}P NMR analyses, demonstrating the control of poly(propylene) oxide chain lengths and the degree of pendant reactive sites (I_{OH}) by modulating oxypropylation reaction parameters. The potential of OL is clearly demonstrated, providing tailor-made polyols suitable for integration into various polymer systems. The use of these polyols as starting raw materials for biobased polyurethanes synthesis was investigated. PUs with different macromolecular architectures were designed in series by varying the NCO:OH molar ratio from 0.2 to 1.0 with a final biobased content up to 40 wt.%.

Thermal analyses performed by DSC and DMTA indicated two different transitions in these polymers. The two glass transition temperatures were assigned to the relaxation of soft and hard segments, respectively. The glass transition temperature of the hard and soft phases varies with the NCO:OH molar ratio and also lignin content, indicating changes in phase structure and in the composition of the phases. The mobility of soft segments is mainly affected by NCO:OH molar ratio whereas the motion of hard segments is more related to the amount and structure of lignin-based starting polyol. $OL_{80/20}$ and $OL_{70/30}$, with long and flexible grafted PPO chains, have a small influence on relaxation of hard segment mainly caused by the formation of urethane linkages whereas $OL_{60/40}$ and $OL_{50/50}$ significantly decrease motion of hard segments.

From this study, it has been concluded that $OL_{70/30}$ and $OL_{60/40}$ starting polyols were the most suitable for synthesizing lignin-derived polyurethanes with promising mechanical and thermal properties. Mechanical properties of the corresponding PUs depend strongly on the NCO:OH molar ratio and the chemical composition of OL. The data obtained were consistent with the fact that lignin with long grafted chains have high elongation at break with low modulus associated. On the contrary, $OL_{60/40}$ with shorter grafted chains greatly contributed to the formation of large and stiff phases yielding to rigid material with increased ultimate strength and Young's Modulus.

In order to improve the green balance of the system, we could suggest the use of residual PPO-H to synthesize PPO-based prepolymer instead of using exogenous PPO with highly controlled molar masses.

Oxypropylation process constitutes one of the most promising approach to develop lignin-based building blocks for high performance materials. These lignin-based materials have the potential to be used in conventional PU elastomer applications. This success opens up new perspectives to incorporate oxypropylated lignin as a component for high biobased content polymers. Besides, it is a promising modification to valorise lignin, since this renewable resource is a largely available by-product from different biorefinery processes, without competition with food. The resulting biobased polymers show advanced properties, which compete with synthetic polymers from fossil resources.

5. Supplementary information

The pressure reactor (Parr reactor) used for this study was equipped with sensors for online monitoring the evolution of pressure and temperature during the reaction. In figure IV-S1, the evolution of temperature and pressure with time is shown for each oxypropylation reactions carried out at different PO/L ratio: 80/20, 70/30, 60/40 and 50/50. As temperature increased, the vapor pressure of PO also increased thus raising the system's pressure level as illustrated in figure IV-S1 b).

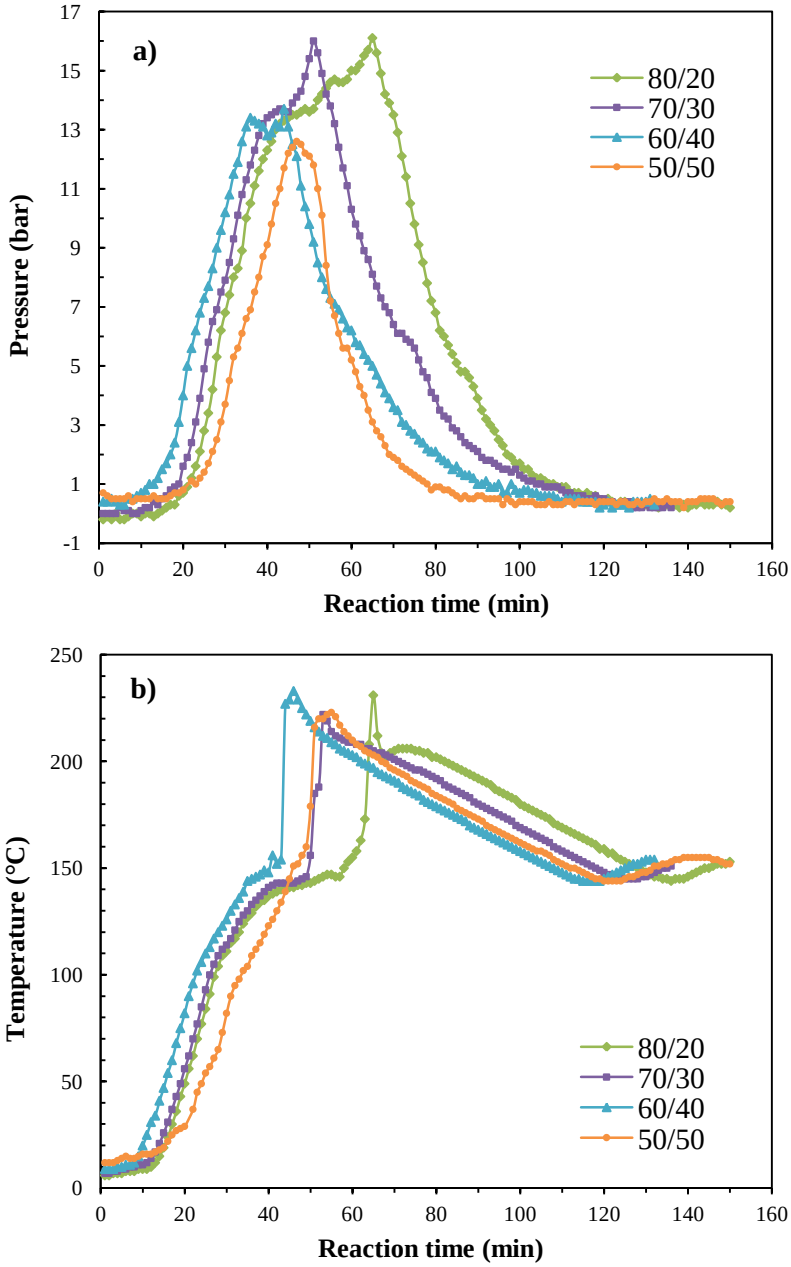

Figure IV-S1. Variation of pressure (a) and temperature (b) along time during the oxypropylation of soda lignin with propylene oxide at different PO/L ratios (80/20, 70/30, 60/40 and 50/50).

To illustrate the influence of PO/L ratio, chromatographic profiles elution of polyol mixtures (PM) and homopolymers (PPO-H) are shown on figures IV-S2 and IV-S3.

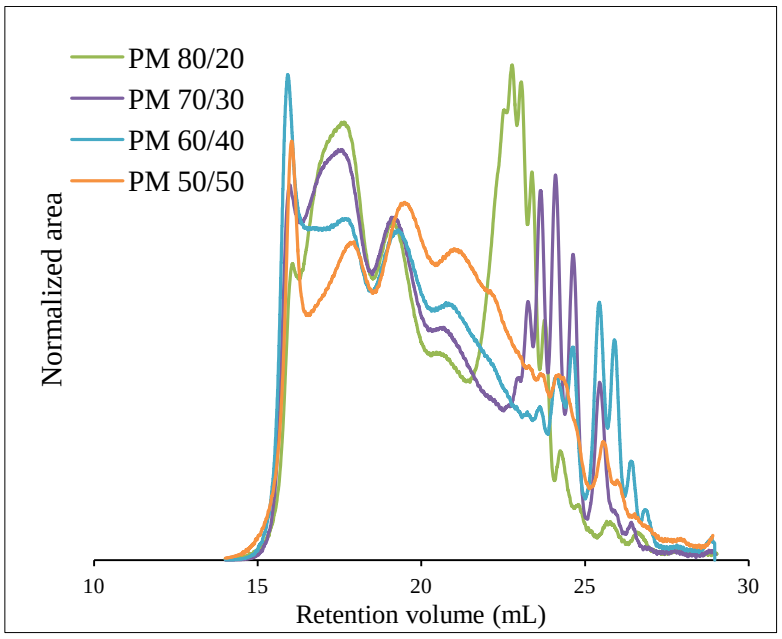

Figure IV-S2. Chromatographic profile elution of polyol mixtures (PM) as a function of PO/L ratios.

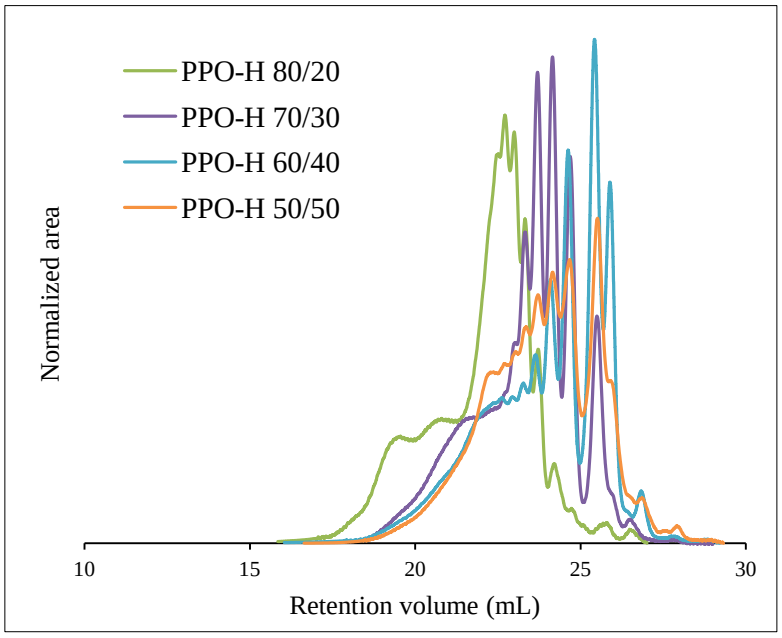

Figure IV-S3. Chromatographic profile elution of homopolymers (PPO-H) as a function of PO/L ratios.

Acknowledgements

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* * *

II. Conclusion & perspectives de l'étude

La réaction d'oxypropylation est une des voies de modification chimique de la lignine les plus étudiées, en vue de l'élaboration de matériaux polymères. De ce fait, dans le cadre de ce chapitre nous nous sommes intéressés à l'oxypropylation d'une lignine soda. L'objectif final de ce travail reposait sur l'élaboration et l'étude de polyuréthanes. La structure de la lignine oxypropylée et le taux de réticulation ont été les deux paramètres particulièrement étudiés et discutés.

Notre étude s'est tout d'abord orientée sur la purification et la caractérisation complète des lignines oxypropylées. Ce travail s'est appuyé sur de nombreuses méthodes analytiques RMN (^{1}H et ^{31}P), IR et DSC qui nous ont apporté des informations précieuses sur le degré de polymérisation et la densité de greffage des chaines de PPO sur la lignine. Les polyols ainsi obtenus ont pu être intégrés dans la synthèse de polyuréthanes faisant intervenir un prépolymère isocyanate à base de PPO. Grâce aux caractérisations préalables des polyols, associées aux analyses DSC, DMTA et mécaniques des polymères, il a été possible de mettre en avant la structuration des PU en deux phases distinctes : souple et rigide, conférant à chacun des polymères synthétisés des propriétés distinctes.

Ces résultats prometteurs nous ont conduits à envisager de nombreuses perspectives pour ce travail et notamment l'utilisation de la lignine oxypropylée sans extraction de l'homopolymère résiduel. Cette première voie a par ailleurs été évoquée dans ce chapitre soulignant le caractère plastifiant de l'homopolymère, se traduisant par une diminution de la T_g finale du matériau. Par ailleurs, l'homopolymère extrait pourrait être utilisé pour la synthèse du prépolymère isocyanate. L'ensemble des produits issus de l'oxypropylation serait ainsi valorisé permettant de s'inscrire dans une démarche complète de « chimie verte », avec une diminution des coproduits non valorisés.

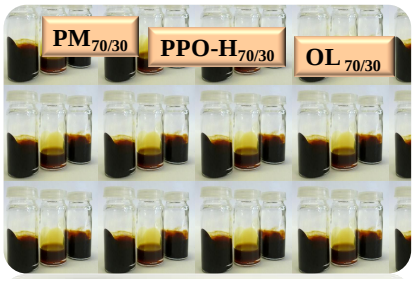

Figure IV- 15. Lignine oxypropylée avec un ratio PO/L = 70/30. De gauche à droite : Mélange obtenue en fin de réaction, homopolymère extrait (PPO-H), polyol purifié sans homopolymère.

D'autre part, la réaction d'oxypropylation est une réaction facile à mettre en œuvre et le passage à une production à plus grande échelle est actuellement envisagé. L'utilisation de lignines soda, Kraft et organosolve a été effectuée et les résultats prometteurs, sans présence de fractions solides insolubles nous encouragent à poursuivre dans cette voie de transposition avec un scaling-up graduel.

L'oxyde de propylène mais aussi l'oxyde d'éthylène ont été étudiés pour modifier la lignine par éthérification. Dans le cadre de notre étude, reposant sur l'élaboration de PU bio-sourcés, le remplacement de ces molécules par d'autres potentiellement biosoucées est aussi à mettre en avant. Dans cette même optique de valorisation de la biomasse, la transposition de la réaction d'oxypropylation à d'autres molécules est une autre voie à explorer. En effet, toute molécule présentant des fonctions hydroxyles accessibles peut être modifiée par ce type de réaction. Des polyols naturels de nature aromatique ou aliphatique (ramifiés ou linéaires) tels que les tannins, le glycérol ou des sucres sont des molécules pour lesquelles divers travaux de recherches sont engagés au sein de notre équipe *BioTeam*. Les perspectives de ce travail sont multiples et les choix des futurs travaux de recherches seront effectués en fonction des résultats obtenus avec la lignine.

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Conclusion générale & Perspectives

Ce travail de thèse pluridisciplinaire, associant la synthèse, la physico-chimie et la caractérisation des matériaux polymères avait pour objectif l'élaboration et l'étude de nouveaux matériaux bio-sourcés à base de lignine. La valorisation de la lignine en tant que matériau de substitution ou complémentaire aux polymères synthétiques classiques a ainsi été étudiée. De ce fait, la démarche scientifique retenue pour notre travail s'est axée autour du développement de nouvelles architectures (macro)moléculaires à partir de lignine pour l'élaboration de polymères fonctionnels. Dans notre cas, l'objectif final de ce travail de doctorat reposait sur l'utilisation de ressources renouvelables afin de développer des matériaux innovants et performants pour l'industrie du bâtiment et notamment l'étanchéité des toitures-terrasses.

L'étude bibliographique présentée dans le Chapitre I a dressé un état de l'art sur la lignine, ses modes d'extraction ainsi que les propriétés associées, mais aussi sur ses différentes voies de valorisation. Cette étape nous a permis de mettre en exergue les différents verrous technologiques qu'il reste à lever pour envisager l'utilisation de la lignine à l'échelle industrielle en tant que polyol bio-sourcé pour la synthèse de nouveaux polyuréthanes (PU). Le choix particulier du polymère est principalement lié au fait que les PU sont largement utilisés dans le domaine du bâtiment. Ils font également l'objet de nombreuses études en recherche académique pour l'élaboration de nouveaux polymères bio-sourcés.

Cet état de l'art nous a ainsi conduits à identifier et sélectionner des techniques de modification qui ont ensuite été approfondies lors de ce travail de recherche.

Les stratégies développées dans cette thèse et détaillées dans les chapitres II à IV sont basées sur l'utilisation de différentes lignines techniques, qui ont été préalablement analysées et caractérisées. Ces analyses nous ont conduits à la sélection de deux lignines techniques dites sans-soufre : une lignine soda et une lignine organosolve. Ce choix s'est révélé être un paramètre essentiel dans la suite de notre étude car la qualité de la lignine et principalement sa solubilité, conditionne les réactions chimiques développées sur cette biomacromolécule. Le développement de méthodes analytiques, à savoir la caractérisation et la quantification des principales fonctionnalités de la lignine ont constitué un des premiers axes de notre travail. Il a fallu ensuite développer une chimie spécifique permettant la modification de ce macromère. Une exploitation à plus grande échelle a orienté les choix de synthèse opérés. Par ailleurs, le respect des critères économiques inhérent à une future application industrielle a permis

d'envisager la lignine comme un candidat potentiel pour la substitution de monomères traditionnels issus du pétrole.

Les Chapitres II à IV reflètent les différentes stratégies mises en place pour la synthèse de polymères fonctionnels. Différents polyols ont effectivement été élaborés à partir de lignine, soit par réaction de polymérisation par ouverture de cycle (ROP) d'ε-caprolactone ou d'oxyde de propylène, soit par une estérification combinée à une fonctionnalisation des insaturations de l'acide gras (Figure C-1).

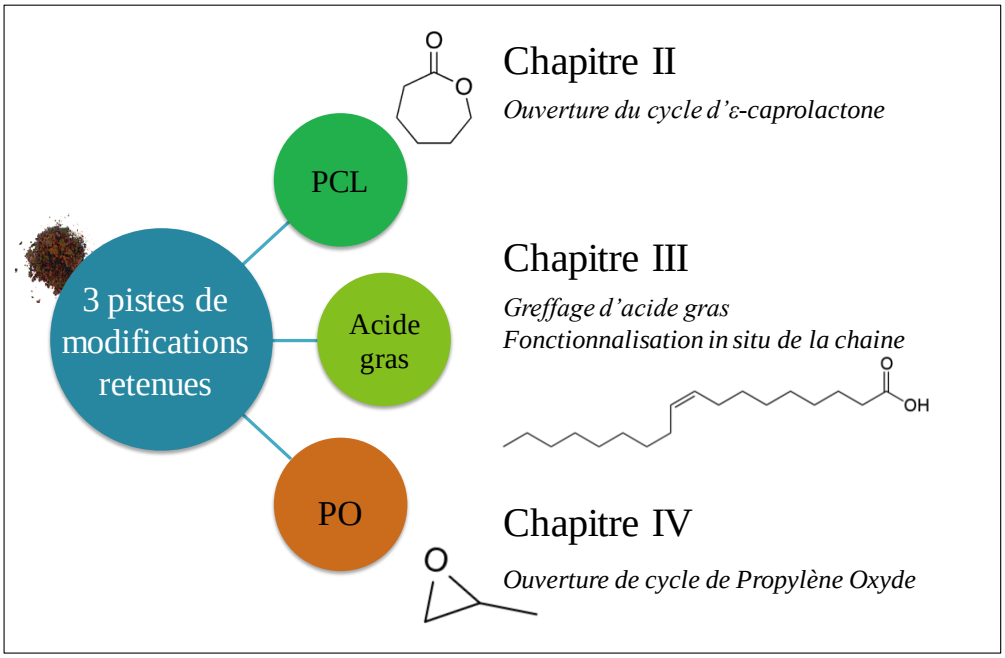

Figure C- 1. Schéma récapitulatif des différentes voies de modification chimique explorées.

Les réactions associées ont été optimisées et font l'objet d'études spécifiques notamment en ce qui concerne les différents paramètres réactionnels utilisés. Chacune de ces modifications s'est révélée très efficace pour la synthèse de nouveaux polyols bio-sourcés. Les polyols ainsi obtenus ont conduit à l'élaboration de matériaux originaux: poly(caprolactone) greffé sur la lignine (Chapitre II) ou PU (Chapitres III et IV). Les divers polymères obtenus ont été caractérisés par des analyses chimiques, physico-chimiques et mécaniques.

Le Chapitre II s'est focalisé sur la modification de la lignine par le poly(caprolactone). Par conséquent, les polymères résultants ont démontré un caractère cristallin très marqué engendré par la présence des chaines de PCL greffées. Afin d'apporter une véritable contribution et de répondre à certains questionnements scientifiques par rapport à la

bibliographie actuelle, deux paramètres réactionnels ont notamment été étudiés, à savoir le temps de réaction ainsi que la quantité de catalyseur (l'octanoate d'étain- $SnOct_2$). Nous avons montré au travers de méthodes de caractérisation complémentaires d'IR et de rhéologie, l'existence de liaisons intermoléculaires entre les chaines de PCL et la lignine. Ces dernières donnent lieu à la formation d'un réseau amorphe et flexible pour des degrés de polymérisation relativement faibles. Au-delà d'un certain seuil, le polymère devient semi-cristallin, rigide et cassant. Le comportement particulier observé pour les degrés de polymérisation faibles, a fait l'objet d'une étude scientifique approfondie dans le cadre de ce travail de doctorat. Compte tenu de l'application finale visée, ces matériaux n'ont pas été retenus pour envisager une future application industrielle. Ce travail a néanmoins permis (i) de développer des matériaux innovants avec de nouvelles architectures macromoléculaires, et (ii) de mettre en avant des relations spécifiques structure-propriétés conférant au matériau final des propriétés intéressantes, associées à une teneur en composés biosourcés importante (Tableau 1).

Le développement d'un nouveau polyester polyol pour la synthèse de PU originaux à base de lignine et d'acide oléique a été abordé dans le Chapitre III. L'intégration de ce nouvel intermédiaire dans diverses architectures PU a permis l'élaboration de différents réseaux polymères plus ou moins branchés et réticulés. La compréhension de l'organisation macromoléculaire a mis en évidence une séparation de phase du PU entre des segments souples et rigides, caractérisée par des températures de transition vitreuses respectives différentes.

La troisième et dernière approche développée dans le Chapitre IV présente une seule étape de synthèse pour l'élaboration du polyol de base. De nouveaux polyether polyols ont été obtenus par oxypropylation de la lignine en vue d'intégrer ces intermédiaires réactionnels dans la synthèse de PU. La structure macromoléculaire de ce synthon joue un rôle clé dans la structuration de la matrice polymère, dont les propriétés finales sont directement dépendantes. De la même façon qu'avec le système polyol-acide oléique, une séparation de phase a été mise en évidence et a révélé la coexistence de micro-domaines souples et rigides.

Les performances des matériaux obtenus à partir des trois voies de modification développées ont été comparées à celle d'un polymère conventionnel (TPU) qui rentre dans l'élaboration de membranes d'étanchéité commerciales. Les résultats sont présentés dans le tableau ci dessous (Tableau C-1) et permettent d'évaluer les différentes propriétés obtenues par rapport à cette référence. L'adéquation des différents matériaux développés par rapport au

cahier des charges a ainsi pu être appréciée. Ainsi, l'utilisation de polyol à base de lignine et d'acide gras semble à cet instant réunir de nombreux avantages ; notamment en termes de performances techniques en accord avec le cahier des charges mais aussi en terme de valorisation de la biomasse et de la lignine en particulier (forte teneur en composés biosourcés).

	PCL *Chapitre II*	**Acide gras** *Chapitre III*	**Oxypropylation** *Chapitre IV*	**Référence liant d'étanchéité**
Teneur en biosourcé (%)	48	42 – 89	13 - 39	0
T_g (°C)	-50 / -35	-42 / -7 ($T_{g\ SS}$) 22 / 53 ($T_{g\ SR}$)	-36 / 2 ($T_{g\ SS}$) -5 / 90 ($T_{g\ SR}$)	-45
$T_{mise\ en\ œuvre}$ (°C)	80-100	100-120	100	160
Module d'Young (MPa)	13 - 25	0.2 - 2.8	0.3 - 7	2.0 - 2.5
Allongement à la rupture (%)	28 - 30	170 – 360	50 - 400	300 - 400
Contrainte à la rupture (MPa)	1.3 - 2	1 – 10	2 - 9	2 - 3
$T_{dégradation}$ (°C)	520	300 – 400	250 - 400	300 - 400
Aspect matériau	Noir - Souple	Noir – Souple - Elastomère	Noir – Souple –Mise en œuvre parfois difficile	
Adéquation par rapport au cahier des charges	+/-	++	+	

Tableau C-1. Bilan des différentes caractéristiques des matériaux obtenus pour chacune des stratégies de synthèse retenues – Comparaison par rapport à un liant de référence pour une membrane d'étanchéité.

Enfin, cette thèse rédigée sous format articles nous a permis de soumettre trois publications scientifiques dans des journaux à comités de lecture et ainsi de valoriser notre travail. Parmi celles-ci une publication a d'ores et déjà été acceptée et publiée dans la revue *Polymer*, les deux autres articles sont en phase de révision. De plus, compte-tenu des résultats prometteurs et de l'originalité des travaux présentés, ces recherches ont fait l'objet d'un dépôt d'une

enveloppe Soleau avant la rédaction d'un éventuel brevet. Ainsi, un article complémentaire va être soumis prochainement dans la revue *Green Chemistry*.

* * *

Les résultats très encourageants obtenus lors de ces études n'ont pas permis à ce jour d'atteindre complètement l'objectif de formulation d'une membrane d'étanchéité à base de lignine. Cependant, l'élargissement récent des compétences de la société Soprema dans de nouveaux domaines d'activités permet d'envisager l'utilisation de certains polyols à base de lignine dans de nouvelles applications telles que les mousses d'isolations thermiques et phoniques...

Ce travail effectué dans le laboratoire au sein de l'équipe de recherche *BioTeam* était le premier sur le thème de la valorisation chimique de la lignine et a permis d'élargir les compétences de l'équipe dans ce domaine de recherche. Cette approche scientifique novatrice et différente des autres travaux de recherches précédents, associée à la mise au point de méthodes de synthèse réactionnelle a participé au développement d'une nouvelle expertise, actuellement étendue dans le cadre d'un autre sujet de recherche développé par la *BioTeam*. Les techniques de synthèses développées s'appuient essentiellement sur la modification des fonctions hydroxyles de la lignine, sites réactionnels abondants que l'on peut également retrouver dans plusieurs composés de la biomasse. Les approches de modification développées lors de ce travail peuvent ainsi s'appliquer à d'autres produits tels que les tannins ou les polysaccharides par exemple.

Ce sont principalement les PU élaborés au cours de cette étude qui retiennent notre attention. L'estérification de la lignine en l'absence de solvant et de catalyseur constitue une véritable avancée dans le domaine de la chimie de ce macromère. On peut envisager cette estérification avec différents types d'acides gras ou dérivés d'acides. Par ailleurs, la réaction thiol-ène (« click chemistry ») sur les acides gras représente une alternative prometteuse à la stratégie en deux étapes développée pour la modification de l'insaturation. Certains essais préliminaires et prometteurs ont d'ores et déjà été effectués au laboratoire et doivent encore être optimisés.

Enfin, un travail important reste à mener concernant la connaissance plus précise des mécanismes impliqués dans la réaction d'oxypropylation afin de contrôler de manière plus efficace la fonctionnalité d'une (macro)molécule de lignine oxypropylée. L'utilisation des techniques de RMN quantitatives ^{31}P et ^{1}H couplées à des méthodes de dosages chimiques sur des lignines modifiées doivent permettre une meilleure caractérisation de la structure en vue de l'élaboration de matériaux thermoplastiques élastomères (TPE).

Afin de pouvoir développer des membranes fonctionnelles pour l'industrie du bâtiment, la formulation complète de ces matériaux semble indispensable pour pouvoir répondre au cahier des charges fonctionnel en termes de résistance aux UV, tenue au vieillissement ou encore d'absorption d'eau... L'introduction de charges minérales mais aussi de fibres telles que les fibres ligno-cellulosiques permettra alors d'apporter des fonctionnalités complémentaires à ces matrices biosourcées (processabilité, résistance, ergonomie des membranes…). Un travail sur l'affinité fibre/matrice ou charge/matrice serait notamment nécessaire afin d'atteindre les propriétés mécaniques et physico-chimiques en accord avec l'application visée. Ces renforts mécaniques doivent être aussi associés à d'autres additifs tels que des antioxydants et anti-UV afin d'apporter aux matériaux finaux des propriétés d'usage avec une garantie d'utilisation décennale. Ce travail nécessite un fort développement en termes de formulation associé aux procédés de mise en œuvre des membranes d'étanchéité finales.

Enfin, dans le cadre de ce travail doctoral, des polymères originaux ont été développés et permettent d'envisager une utilisation dans d'autres domaines d'applications pour certains d'entre eux. Il serait alors intéressant d'identifier précisément ces domaines et de poursuivre le développement de formulations adéquates associé à des approches de scaling-up.

Par ailleurs, les enjeux industriels doivent également être pris en compte et l'ouverture des travaux vers l'utilisation de lignines techniques plus disponibles et moins coûteuses doit être envisagée. Les lignines Kraft représentent en ce sens la meilleure alternative et la transposition de nos travaux, notamment l'oxypropylation et l'estérification avec des acides gras doit se poursuivre.

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Annexes

I. L’étanchéité des bâtiments

L’étanchéité, permet sous différentes formes, de protéger un bâtiment ou un ouvrage de génie civil des intempéries et des diverses sollicitations climatiques.

L’étanchéité est généralement utilisée dans le cadre de toitures-terrasses plates ou inclinées, de murs enterrés, de balcons, de loggias ou de bassins de rétention d'eau... La mise en œuvre du revêtement d'étanchéité (en indépendance, en semi-indépendance, en adhérence ou fixé mécaniquement), varie en fonction de plusieurs paramètres à connaître, notamment la destination de l’ouvrage (accessible, non accessible, jardin,…) ainsi que l'élément porteur (bois, béton, acier,…), la pente de la toiture, l’isolant du support d'étanchéité et la protection.

Les différents revêtements d’étanchéité se classent en trois catégories principales:

- *Revêtement d’étanchéité bitumineux*
- *Membranes synthétiques*
- *Etanchéité liquide*

1. Revêtement d’étanchéité bitumineux

Les membranes d’étanchéité bitumineuses sont constituées de deux parties principales :

(i) Le liant bitumineux, mélange de bitume et d’un élastomère (SBS- Styrène-Butadiène-Styrène ou APP-Polypropylène Atactique) assurant l’étanchéité de façon durable.

(ii) Le renfort, constitué d’un « non tissé » à base de fibres de verre ou de polyester, renforçant la membrane tout en limitant son fluage lors du stockage, ou sur un toit lorsqu’elle est soumise à de hautes températures.

La face supérieure des membranes est toujours recouverte de paillettes d’ardoise ou d’une feuille d’aluminium dans le but de la protéger des agressions extérieures et plus particulièrement d’éviter la dégradation de l’élastomère (généralement le SBS) par les rayonnements ultraviolets du soleil. Une partie de la face supérieure, appelée galon, est laissée « nue » dans le but de pouvoir fusionner les lés de membranes entre eux lors de leur pose sur un toit et ainsi assurer des joints étanches, résistants et durables (Figure A-1).

Le liant d'étanchéité bitumineux est thermoplastique et l'application sur chantier se fait en fusionnant le liant de façon à le faire adhérer sur le support ou sur lui-même.

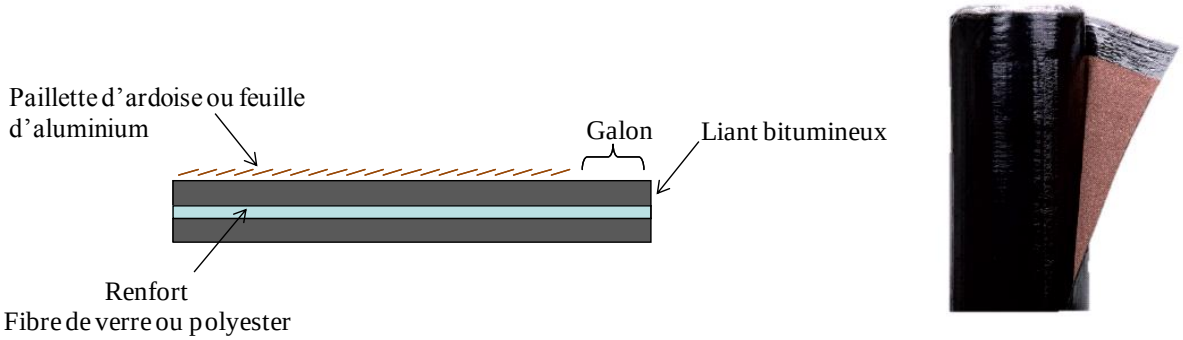

Figure A-1. Représentation d'une coupe transversale d'une membrane d'étanchéité – Photographie d'une membrane d'étanchéité SOPREMA à base de bitume élastomère et d'une armature en grille de verre/voile de verre auto protégée par des paillettes d'ardoise.

Les bitumes élastomères offrent par ailleurs les propriétés suivantes : (i) une grande élasticité, (ii) un meilleur comportement à basse température, (iii) de la souplesse, (iv) un grand pouvoir d'adhérence au support ainsi (v) qu'une étanchéité des joints fiable.

Les étanchéités bitumineuses représentent 75 à 80% du marché mondial de l'étanchéité des toitures terrasses.

2. Membranes synthétiques

Il existe plusieurs types de membranes d'étanchéité synthétiques, notamment les membranes PVC (Polychlorure de vinyle), les membranes TPE (Thermoplastiques élastomères) et les membranes TPO (polyoléfine thermoplastique). Ces membranes peuvent s'adapter à de nombreuses situations d'étanchéité de toiture-terrasse (accessible et non accessible) mais sont également destinées à l'étanchéité des bassins de rétention et des chéneaux. Ce sont elles aussi des membranes thermoplastiques qui sont mises en œuvre par soudure à air chaud ou par collage et généralement en monocouche (Figure A-2). Ces membranes d'étanchéité synthétiques s'adaptent aux principaux éléments porteurs avec ou sans isolant support.

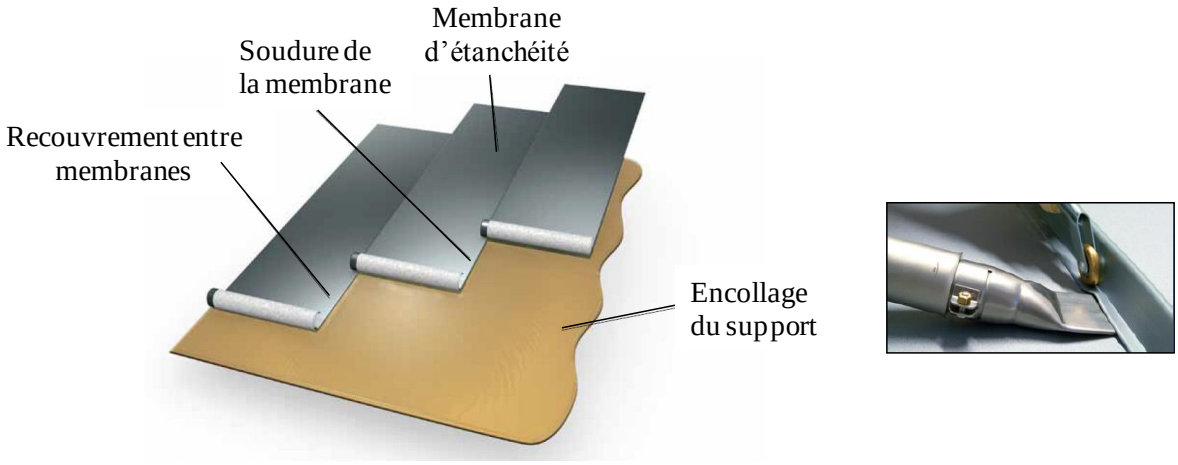

Figure A-2. Schéma de la mise en œuvre de membranes synthétiques – Soudure à air chaud d'un joint d'étanchéité.

Les procédés de fabrication généralement utilisés sont l'extrusion-calandrage dans le cas des membranes PVC plastifiés ou les polyoléfines, et l'enduction pour le PVC plastisol (mélange PVC + plastifiant).

Les étanchéités liquides représentent 15 à 20% du marché mondial et tendent à prendre une place de plus en plus importante.

3. L'étanchéité liquide

L'étanchéité liquide est particulièrement adaptée aux chantiers interdisant l'utilisation de flamme. Ce type d'étanchéité peut aussi être utilisé dans le cadre de traitement de points singuliers associé à des étanchéités bitumineuses. Le procédé est également adapté pour le traitement de petites surfaces telles que les balcons et loggias. Les étanchéités liquides du marché sont diverses: résine polyuréthanne, résine polyester, résine de polymères méthacryliques et polyuréthannes (PU), dispersion de polymères acryliques et résine en polyméthacrylate de méthyle (PMMA).

Ce sont des matériaux thermodurcissables pour lesquels le film assurant l'étancheité est généralement formé in situ. Les mécanismes réactionnels associés sont variés:

(i) Réaction de polyaddition avec l'humidité de l'air pour les PU mono composants,

(ii) Réaction de polyaddition après mélange des réactifs sur chantier (polyol + isocyanate par exemple)

(iii) Réaction radicalaire déclenchée après ajout de l'amorceur dans la résine sur chantier : peroxyde de benzoyle dans les résines PMMA.

Dans le cadre de notre travail de thèse, l'objectif principal était la synthèse d'un nouveau polymère biosourcé pouvant rentrer dans l'élaboration d'une nouvelle « éco-membrane ». Nous nous sommes donc concentrés principalement sur l'élaboration de nouveaux polymères pouvant s'intégrer dans la réalisation de membranes d'étanchéité thermoplastiques bitumineuses ou synthétiques. En outre, la nouvelle « éco-membrane » devra respecter un cahier des charges strict et fixé par l'industriel. Les caractéristiques principales de ce cahier des charges font l'objet de la seconde partie de cette annexe.

II. Le cahier des charges de la nouvelle « éco-membrane »

La nouvelle membrane d'étanchéité verte doit respecter un cahier des charges contraignant et strict. Il est attendu de cette dernière :

(i) d'être étanche et avoir une faible prise en eau,

(ii) qu'elle respecte la garantie décennale, règle imposée pour tout matériau du bâtiment,

(iii) qu'elle soit souple à basses températures et qu'elle ne flue pas à hautes températures,

(iv) qu'elle présente des joints fusibles, solides et durables.

Dans le cadre de nos travaux de recherche, il s'agit principalement de développer de nouveaux polymères fonctionnels pouvant s'intégrer totalement ou partiellement dans la formulation du liant d'étanchéité. Celui-ci doit respecter le cahier des charges présenté dans le tableau suivant (Tableau A-2).

Désignation	Critère	Propriétés
SERVICE	Etre étanche	Hydrophobe
MISE EN FORME	Résister aux conditions de mise en œuvre (enduction, mélange, extrusion…)	Viscosité, rhéologie,
	Résister aux hautes températures	Fluage
	Résister au calandrage	
MISE EN ŒUVRE / POSE DES MATERIAUX	Résister lors de la pose (allongement, résistance aux chocs, poinçonnement statistique, résistance à la déchirure)	Rémanence, viscosité
	Faciliter la pose des membranes	Soudabilité des membranes
		Caractère thermoplastique
VIELLISSEMENT ET DURABILITE	Suivre les mouvements du bâtiment	
	Résister à la lumière (UV)	Résistance à la fatigue
	Résister à l'oxygène (oxydation)	Aspect visuel
	Résister à l'humidité	Variation de masse
	Résister aux micro-organismes naturels (moisissures)	Hydrophobe
	Résister aux variations de températures	Fluage
	Résister au vent	Rémanence
	Résister à la pollution	
RESISTANCE AU FEU	Classement au feu	
STABIILITE DIMENSIONNELLE	Retrait libre	
DURABILITE	Garantie décennale	
AGREMENT / CONFORT	Etre facilement stockable	Volume occupé par un rouleau de membrane
	Etre facilement transportable	Poids du rouleau
	Etre esthétique	Couleur / Texture
COÛT / QUALITE / DISPONIBILITE	Respecter le coût du produit	Prix de revient d'un kilogramme de matière première
	Respecter la garantie de durabilité dans le temps	Garantie décennale
	Etre réalisable avec des matières premières disponibles	Tonnage des matières premières produites par an
RECYCLAGE	Etre recyclable	Etre valorisable/ broyable pour une utilisation future en tant que charge

Tableau A- 1. Cahier des charges d'une membrane d'étanchéité.

Résumé

De nouvelles architectures macromoléculaires ont été synthétisées à partir de lignine afin de développer des matériaux pour des applications dans le bâtiment. Trois voies différentes de modifications chimiques ont été retenues afin d'apporter de nouvelles propriétés à la lignine pour répondre à un cahier des charges précis. Dans un premier temps, des chaines de poly(caprolactone) ont été greffées sur la lignine par polymérisation par ouverture de cycle conférant ainsi à la lignine des propriétés particulières en fonction de la longueur des chaines de PCL greffées. La valorisation de la lignine pour la synthèse de polymères fonctionnels repose ainsi sur sa modification chimique. Notre démarche scientifique s'est par la suite axée sur la fonctionnalisation de la lignine afin d'en faire un synthon principal pour la synthèse de polyuréthanes (PU). Cette stratégie a été poursuivi avec l'addition d'acide oléique sur la lignine. Une réaction d'estérification a été mise au point par un procédé non solvanté en l'absence de catalyseur. Cet intermédiaire a été fonctionnalisé en vue d'obtenir un macropolyol réactif pour la synthèse de PU. Les propriétés des polymères ont été investiguées en modulant certains paramètres réactionnels. Les performances des matériaux obtenus ont montré l'intérêt de cette stratégie globale pour les applications finales visées. Enfin, dans une troisième et dernière approche, la réaction d'oxypropylation a été étudiée. Des chaines de polypropylène glycol ont été greffées sur la lignine aboutissant à l'obtention de quatre macropolyols différents avec des architectures macromoléculaires variées. Des PU ont été synthétisés à partir de ces macropolyols et les paramètres réactionnels ajustés en vue de moduler les propriétés finales des matériaux. Tous les PU réalisés ont démontré une séparation de phase attestant d'une organisation spécifique en segments souples/rigides et conférant des propriétés élastomères aux matériaux finaux. Cette étude a permis d'intégrer jusqu'à 89 % de matériaux biosourcés et renouvelables dans les polymères finaux et a montré le fort potentiel de la lignine pour l'élaboration de matériaux performants.

Mots clés : Lignine, Polyuréthane, estérification, éthérification, relation structure-propriétés.

Abstract

New macromolecular architectures have been performed by using lignin to develop new advanced materials for building applications. Three synthetic pathways have been carried out in order to impart specific properties to lignin-based materials. A Ring-Opening Polymerization has first been performed with ε-caprolactone to graft polymer chains onto lignin. Branching efficiency was confirmed by analysis and allows giving advanced properties to lignin materials. This first modification highlights the importance of lignin functionalization as building block for polymer synthesis. Then, we pursue the investigations by esterifying lignin with oleic acid by a solvent and catalyst-free method. Doubles bond were functionalized to obtain a lignin/fatty acid-based macropolyol that was then used for polyurethane synthesis (PU). Mechanical and thermal properties have been modulated by varying NCO:OH molar ratio and prepolymer molecular weight. Finally, oxypropylation was performed onto lignin by using various reaction parameters to obtain different macromolecular architectures for the resulting polyols. PUs have then been synthesized with the resulting macropolyols. The structure of macropolyols impacts greatly the thermal and mechanical properties of polymers, the influence of NCO:OH molar ratio was also studied.
All of the PU reported in this work presented a micro-phase separation resulting in a specific organization (rigid/soft segments) into the polymer matrix. The lignin-based material revealed advanced thermal and mechanical properties with a high bio-based content up to 89%. This work allows emphasizing the potential of lignin as a starting material in the synthesis of sustainable material for building applications.

Keywords: Lignin, Polyurethane, esterification, etherification, relationship structure-properties