



Utilisation de lignines Kraft comme agent de couplage dans des composites à base de polyéthylène de haute densité (HDPE) contenant des fibres d'écorce

Thèse

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Résumé

Ce travail de recherche se décompose en trois parties. Le premier volet fait part des différentes approches étudiées dans la littérature concernant les bois-plastiques (WPC) et de différentes possibilités existantes tout en mettant en avant les résultats préliminaires obtenus. Il rapporte aussi le potentiel des lignines comme agent de couplage. L'objectif du second volet est l'optimisation de l'efficacité de ce nouveau type d'agent de couplage en combinant des lignines modifiées à un agent de couplage commercial (le polyéthylène maléaté: MAPE). Finalement, le dernier volet reprend les connaissances développées dans les précédentes parties tout en ajoutant deux aspects : la résistance aux cycles de gel-dégel et l'effet des extractions à l'eau et à la soude.

Le problème des WPC est lié aux caractéristiques extrêmement opposées des fibres naturelles et de la matrice polymère, ce qui les rend incompatibles. Une multitude de traitements physiques ou chimiques peuvent améliorer la compatibilité et les interactions interfaciales entre les composants. L'impact environnemental et économique de l'utilisation de produits chimiques dérivés du pétrole et la demande de valoriser les coproduits du bois offrent la possibilité d'utiliser les lignines estérifiées dans la production d'une nouvelle génération de WPC. Nous avons démontré la faisabilité de composites à base de polyéthylène haute densité (HDPE) contenant 30% de fibres d'écorces d'épinette noire, avec 5% (basé sur la masse de l'écorce) de lignine Kraft estérifié à l'anhydride maléique. La combinaison de lignines Kraft estérifiées avec du MAPE (à teneurs égales) a permis d'optimiser l'efficacité de l'agent de couplage avec une nouvelle façon d'améliorer la compatibilité entre les fibres et la matrice. Étant donné que les fibres naturelles contiennent de la lignine, la lignine estérifiée (deux estérifications étudiées : succinique et maléique) a créé une structure qui agit comme un intermédiaire entre les fibres d'écorce et la matrice HDPE hydrophobe, grâce à sa haute porosité permettant un ancrage mécanique intéressant et des liaisons de type van der Waals ou d'interactions π - π donnant du liant à cette nouvelle structure. On a déterminé l'effet de la composition d'agent de couplage comme étant un facteur majeur sur les propriétés mécaniques. Une analyse statistique a

permis de trouver les meilleurs paramètres pour optimiser les propriétés mécaniques des composites et optimiser cette approche novatrice d'agent de couplage pour les WPC.

Il a finalement été décidé d'étudier l'effet d'extractions à l'eau ou à la soude des écorces sur les caractéristiques mécaniques tout en intégrant une analyse de la résistance aux cycles gel-dégel dans le cas d'une application extérieure du matériau, correspondant au contexte québécois. Il a été démontré que les différentes extractions n'altèrent pas les propriétés mécaniques en flexion et en traction. Mais le test de résistance aux gels-dégels met en valeur les caractéristiques des WPC. Un meilleur comportement a été trouvé pour les formulations avec un agent de couplage combinant les lignines estérifiées avec du MAPE.

Abstract

This research work is divided into three parts. The first part is dedicated to the review of different approaches discussed in the literature concerning wood-plastic composites (WPC) and different possibilities while highlighting the preliminary results obtained. It also reported the potential of lignin as coupling agent. In the second part, the optimization of the effectiveness of this new type of coupling agent combining modified lignin with a commercial coupling agent (polyethylene maleate: MAPE) is discussed. Finally, the performance of the selected composites upon the freeze-thaw resistance tests and the effect of extractions (water and soda) on the characteristics (flexural and tensile properties) of composites containing bark fibers and modified lignin are presented in the last part.

The problem of compatibility between the constituents of WPC is related to the extremely opposite characteristics of natural fibers and the polymer matrix. A multitude of physical or chemical treatments can improve compatibility and the interfacial interactions between components. The environmental and economic impact of the use of petroleum chemicals and the demand to valorize the co-products of wood transformation offers the possibility of using esterified lignin in the production of a new generation of WPC. We have demonstrated the feasibility of composite based on high density polyethylene (HDPE) containing 30% of black spruce bark fibers, with 5% (based on the mass of bark) of Kraft lignin esterified by maleic anhydride. The combination of esterified Kraft lignin with the MAPE (at equal levels) has been demonstrated to improve the compatibility between the bark fibers and the matrix. Given that natural fibers contain lignin, the esterified lignin (with succinic and maleic anhydride) is supposed to create a structure which acts as bond between the bark fibers and the hydrophobic matrix (HDPE). This action is related to the high porosity of esterified lignin as revealed by SEM, which allows for mechanical anchoring due to van der Waals or π - π interactions. The effect of the structure of coupling agent on the mechanical properties of the composites has been determined. A statistical analysis performed on the collected data made it possible to determine the best settings of parameters for optimal mechanical properties of composites, designed through

the innovative approach of using esterified Kraft lignin as a coupling agent for WPC. Finally, the effect of water and soda extractions of bark fibers prior to their incorporation into composites was studied, on the mechanical characteristics of the composites. The composites with best mechanical performance were finally tested regarding freeze-thaw resistance since an outside application of the material, is anticipated in the Quebec context. However, the test for resistance to freeze-thaw positively influences the characteristics of WPC. It has been shown that different extractions do not affect the mechanical properties (flexural and tensile). Better behavior was found for formulations with a coupling agent combining lignin esterified with the MAPE.

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Lexique

a* = Gamme de 600 niveaux sur l'axe rouge (+299 valeur positive) → vert (-300 valeur négative) en passant par le gris (0)

b* = Gamme de 600 niveaux sur l'axe jaune (valeur positive) au bleu (valeur négative)

DSC = Calorimétrie différentielle à balayage

E = Module de Young (MPa)

F = Force appliqué (N)

FQA = Analyseur de fibres

FTIR = Spectroscopie infrarouge à transformée de Fourier

G = Unité de structure de lignines de type guaiacyl

H = Unité de structure de lignines de type hydroxyphényle

HDPE = Polyéthylène haute densité

L* = Clarté, de 0 (noir) à 100 (blanc).

L/D = Rapport de forme Longueur / Diamètre

LDPE = Polyéthylène basse densité

LLDPE = Polyéthylène basse densité linéaire

MAPE = Polyéthylène maléaté

MaPO = Polyoléfine maléaté

MA-SEBS = Polystyrène-b-poly(éthylène-butylène)-b-polystyrène maléaté

MEB = Microscope électronique à balayage

MEB-EDS = Microscope électronique à balayage couplée avec spectroscopie de rayons X à dispersion d'énergie

S = Unité de structure de lignines de type syringyle

SEBS = Polystyrène-b-poly(éthylène-butylène)-b-polystyrène

TGA = Analyse thermogravimétrique

UV = Ultraviolet

WPC = Composites bois-plastique

Y = Flèche (mm)

ΔE = Distance entre deux couleurs placées dans l'espace L*,a*,b* de CIELab.

ΔH = Variation d'enthalpie correspond à la chaleur absorbée (ou dégagée)

ϵ = Allongement relatif (sans unité)

σ = Contrainte normale (MPa)

τ_M = Contraintes de cisaillement maximales (MPa)

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Avant-Propos

Le présent travail a été réalisé sous la direction de Mme Tatjana Stevanovic, professeure titulaire au Département des Sciences du Bois et de la Forêt de l'Université Laval et sous la codirection de M. Denis Rodrigue, professeur titulaire au Département de génie chimique de l'Université Laval, ainsi que la codirection de M. Xiang-Ming Wang, chercheur chez FPInnovations.

Ce travail de recherche a été effectué dans plusieurs laboratoires à Québec (FPInnovations, CRIQ, Centre de Recherche sur les Matériaux Renouvelables [CRMR] et au Centre de recherche sur les matériaux avancés [CERMA]) grâce aux financements offerts par le Fonds de Recherche du Québec – Nature et Technologies (FRQNT).

Ce document est présenté sous un format de thèse de publication. Il a été conçu selon les critères de présentation adoptés par la Faculté des études supérieures et postdoctorales (FESP) de l'Université Laval.

Cette thèse est constituée de cinq chapitres. Le premier chapitre est composé de trois aspects : (i) la littérature utile sur le projet (ii) la méthodologie nécessaire à la caractérisation du matériau, et (iii) une approche critique mettant en évidence les besoins de connaissances complémentaires dans ce domaine. Le chapitre 2 fait part des différentes approches étudiées dans la littérature afin de mettre en avant les résultats préliminaires obtenus, qui démontrent le potentiel des lignines comme agent de couplage et expriment des voies de développement à poursuivre. Le chapitre 3 présente les améliorations de propriétés des bois-plastiques par le biais d'une optimisation de l'efficacité de l'agent de couplage en combinant les lignines modifiées à un agent de couplage commercial. Le chapitre 4 développe les connaissances sur le potentiel démontré de la combinaison de MAPE et de lignines modifiées tout en ajoutant deux aspects : la résistance aux cycles gel-dégel et l'impact de

différentes extractions (à l'eau et à la soude). La conclusion générale et les recommandations, la bibliographie et les annexes constituent la dernière partie de cette étude. Ces annexes donnent des perspectives à ce travail écrit sous forme de note de recherche dans l'Annexe 1. Les Annexes 2 et 3 présentent des résultats préliminaires utiles à d'autres travaux possibles, écrits sous forme d'article de conférence.

Trois articles scientifiques rédigés en anglais sont présentés dans cette thèse :

Chapitre 1

Mariotti N., Stevanovic T., Rodrigue D., Wang X-M. (2013) Industrial Kraft lignin: a potential coupling agent for wood plastic composites (WPC). Sous Presse pour fin de publication dans le livre Lignin: Structural Analysis, Applications in Biomaterials and Ecological Significance by Nova Science Publishers, Inc.

Article 2

Mariotti N., Wang X-M., Rodrigue D., Stevanovic T. (2014) Combination of esterified Kraft lignin and MAPE as coupling agent for bark/HDPE composites. Publié dans la revue Journal of Materials Science Research. <http://dx.doi.org/10.5539/>

Article 3

Mariotti N., Grenier D., Wang X-M., Rodrigue D., Stevanovic T. (2014) Performance and properties of HDPE composites containing bark fibers and esterified Kraft lignin upon exposure to freeze-thaw tests. À soumettre aux fins de publication dans une revue avec comité de lecture.

L'étudiant Nicolas Mariotti auteur de cette thèse est le principal auteur des articles ci-haut mentionnés. Sa contribution dans chacun de ces articles était : planification et réalisation expérimentale, programmation et interprétation des résultats statistiques, ainsi que la rédaction entière des articles. Tatjana Stevanovic, professeure au Département des Sciences du Bois et de la Forêt de l'Université Laval, Denis Rodrigue, Professeur au Département de Génie Chimique de l'Université Laval, et Xiang-Ming Wang, chercheur chez FPInnovations sont les coauteurs des deux premiers articles ci-haut mentionnés. Daniel Grenier, chercheur au CRIQ est un coauteur actif du dernier article. Leurs rôles dans chacun de ces articles étaient de : vérifier l'ensemble des résultats, aider l'auteur principal à interpréter certains résultats et apporter des corrections nécessaires aux articles avant leur soumission dans les revues scientifiques choisies.

Les résultats issus de ce travail de recherche ont également fait l'objet de présentations orales et d'affiches techniques lors de congrès scientifiques.

Présentations orales :

1. Mariotti N., Stevanovic T., Rodrigue D., Wang X-W., Grenier D. (2013). New composites containing bark and industrial lignins as coupling agent. 99th Annual meeting, PaperWeek Canada 2013; 4-7 Février 2013, Montréal (QC), Canada (Annexe 3).
2. Mariotti N., Stevanovic T., Rodrigue D., Wang X-W. (2013). Bio-Composites à base de polyéthylène haute densité contenant des lignines Kraft et des écorces. Colloque du CRB : Développement de produits renouvelables à base de bois, Pavillon Gene-H.-Kruger, Université Laval, 30 Novembre 2012; Québec (QC), Canada.
3. Mariotti N., Stevanovic T., Rodrigue D., Wang X-W. (2012). Valorisation des écorces et des lignines industrielles dans les biocomposites. Colloque Facultaire de la FFGG, Pavillon Gene-H.-Kruger, Université Laval, 14-15 Novembre 2012, Québec (QC), Canada.

4. Mariotti N., Hu L., Schorr D., Stevanovic T., Rodrigue D., Wang X-W., Niokhor Diouf P., Grenier D. (2012). Utilisation des lignines industrielles comme agent de couplage dans les composites contenant de l'écorce. 80ième Congrès de l'ACFAS, « Transformation de la matière ligneuse en bioproduits », 10 Mai 2012, Montréal (QC), Canada.

Affiches techniques :

1. Mariotti N., Stevanovic T., Rodrigue D., Wang X-W., Grenier D. (2014). Biocomposites HDPE / bark: development of a Kraft lignin based coupling agent. Colloque annuel du CRMR, 14 mai 2014, Trois Rivières (QC), Canada.

2. Mariotti N., Stevanovic T., Rodrigue D., Wang X-W., Grenier D. (2013). Biocomposites HDPE / bark: development of a Kraft lignin based coupling agent. 6th International Wood Fibre Polymer Composites Symposium, 23-24 septembre 2013, Biarritz, France.

3. Mariotti N., Hu L., Schorr D., Stevanovic T., Rodrigue D., Wang X-W., Niokhor Diouf P., Grenier D. (2012). New Bio-composites Containing Industrial Lignins. 55th International Convention of Society of Wood Science and Technology, 27-31 août 2012, Beijing, Chine (Annexe 2).

4. Mariotti N., Stevanovic T., Rodrigue D., Wang X-M. (2011). Utilisation des lignines industrielles comme agents de couplage dans des biocomposites contenant des écorces de bouleau jaune. Journée du CRB, Pavillon Gene-H.-Kruger, Université Laval, 25 novembre 2011, Québec (QC), Canada.

*À ma famille
À mes ami(e)s : ici et là-bas
À mes amours : passés et futurs
Pour le soutien et l'énergie reçus!*

*Parce que la vie avance et chaque étape
apporte autant de bonheur que
nous décidons de conserver en mémoire*

Introduction

Les composites à base de matériaux naturels ont été utilisés depuis l'ère égyptienne. En effet, cette civilisation si mystérieuse, qui possédait une technologie très avancée pour l'époque utilisait déjà des mélanges de paille et d'argile qui, après séchage au soleil, étaient employés dans la construction résidentielle [1]. Par la suite, c'est en 1896 que les premiers sièges d'avion et réservoirs de carburant ont été fabriqués de fibres naturelles avec de faibles quantités de liants polymères. En Inde, le gouvernement a encouragé les projets utilisant la fibre de jute en agent de renfort à des résines de polyester pour les bâtiments résidentiels [1].

Il est vrai que dans les dernières décennies, la société dans son ensemble est devenue plus sensible à l'impact environnemental de l'utilisation de la ressource pétrolière et des conséquences de l'exploitation des ressources naturelles. Cette contribution importante a été apportée par des organisations non gouvernementales (ONG) telles que Greenpeace ou WWF (parmi les plus connues). Cette nouvelle conscience collective pousse les gouvernements à légiférer de façon plus stricte la protection de l'environnement afin de léguer aux générations futures des solutions pour l'avenir ou un problème moindre qu'en continuant de négliger cet aspect de notre chère planète bleue. À l'heure actuelle, il existe un commun accord entre les chercheurs, les institutions scientifiques, les industries, les centres de recherche et de développement, ainsi que les gouvernements, qu'il existe un réel besoin de l'intensification des activités permettant le développement de matériaux contenant des polymères issus de ressources renouvelables. Ce consensus abouti sur de nombreux projets scientifiques dont ce projet de thèse fait partie, car il intègre deux départements de l'Université Laval (SBO et GCH) et deux industriels (FPInnovations et le CRIQ).

Les matériaux composites sont définis comme étant des combinaisons de deux ou plusieurs matériaux qui sont constitués généralement, d'une matrice (polymère, métallique ou céramique) et d'une armature ou agent de renfort (farines, particules ou fibres) [2]. La simple introduction de ressources renouvelables dans des matrices de polymères synthétiques offre une myriade de combinaisons en raison de la variété de

structures disponibles dans la nature. Toutefois, il ne faut pas avoir un optimisme naïf concernant cette grande diversité de fibres naturelles exploitables. En effet, certaines combinaisons seront de faible intérêt, tandis que d'autres répondront parfaitement aux divers besoins croissants de la population et donc de remplacer progressivement les produits de synthèse actuels, apportant un impact économique tout en étant respectueux de l'environnement [3]. Dans ce sens, le bois a été introduit comme un agent de renfort biosourcé pour augmenter la rigidité et la résistance de composites à base de polyoléfine connus comme les composites bois-plastique (WPC) [4]. La principale difficulté dans la conception, l'optimisation et la réalisation de ce type de matériau afin d'obtenir de bonnes propriétés réside dans les propriétés chimiques différentes des matrices polyoléfines hydrophobes et hydrophiles des fibres de bois [5]. Cette différence notable entraîne une mauvaise compatibilité entre les deux composants de ces WPC. En vue d'améliorer l'interaction entre une matrice de polyoléfine et des fibres lignocellulosiques (ce qui est le cas de la très grande majorité des fibres naturelles), un agent de couplage est généralement requis. Au fil des ans, le polyéthylène greffé d'anhydride maléique (MAPE) a démontré son efficacité à lier les fibres naturelles avec le polyéthylène [4, 6-8]. L'interface entre ces composants étant améliorée, il en résulte de meilleures propriétés mécaniques des WPC offrant des perspectives économiquement intéressantes à ce nouveau type de matériel. De plus, les fibres renouvelables lignocellulosiques sont généralement moins abrasives par rapport à des charges minérales résultant en une durée de vie des équipements de fabrication plus durable [4, 9].

L'industrie du bois produit de grandes quantités d'écorces, 438000 tonnes métrique anhydre étaient disponibles en 2010 au Québec [10]. Ce coproduit est actuellement presque entièrement utilisé pour la production d'énergie thermique, Ministère des Ressources Naturelles et de la Faune du Québec [10-11]. Des travaux de recherches sont faits pour utiliser l'écorce dans des produits à forte valeur ajoutée, par exemple comme une source alternative de fibres pour la fabrication de panneaux de particules et de fibres de moyenne densité (MDF) [12-15]. Il pourrait donc être intéressant de profiter du savoir-faire et de l'expertise qui a été développée pour les WPC en l'appliquant à ce coproduit qui mérite tout notre intérêt. Les écorces présentent un avantage par rapport au bois de par sa composition chimique, car elles possèdent un certain potentiel dans des applications pharmacologiques ou alimentaires grâce aux extractibles à l'eau d'écorce d'épinette noire (par exemple, mais le bouleau jaune et d'autres essences pourraient être mis en avant dans ce secteur en plein essor) [16]. Les propriétés spécifiques des écorces

laissent entrevoir la possibilité de profiter de la richesse de ses extraits tout en laissant les fibres d'écorce extraites disponibles pour d'autres applications, comme la fabrication de WPC. Récemment, des études ont porté sur la fabrication de composites biosourcés de particules d'écorce à base de matrices polyoléfiniques afin d'en démontrer le potentiel. L'incorporation de fibres naturelles peut améliorer la stabilité thermique des matériaux polymères, mais elles agissent comme charge et non comme agent de renfort [17-18]. L'impact de l'extraction à l'eau chaude de particules d'écorce d'épinette noire avant l'incorporation dans le polyéthylène haute densité (HDPE) n'est pas néfaste sur les propriétés des composites obtenus [19].

Les lignines sont des polymères naturels ayant un noyau aromatique le plus disponible sur Terre, mais leurs structures dépendent de l'origine végétale et du processus d'extraction. Leur contenu varie en moyenne entre 20% et 35% selon l'origine de la plante [20]. La plupart des résidus de l'industrie des pâtes et papiers ou produits du bois restent sous-exploités, malgré les efforts de recherche importante pour développer de nouveaux produits. Récemment, il a été démontré que les lignines Kraft pourraient être précipitées des liqueurs noires sans affecter négativement le procédé Kraft [21]. Des quantités importantes de ce type de lignines industrielles pourraient devenir disponibles à l'aide du procédé breveté LignoBoost® développé en Suède dans la dernière décennie [22]. Cette précipitation des lignines contenues dans les liqueurs noires permettrait d'utiliser une source de CO₂ disponible dans le procédé Kraft, réduisant ainsi les impacts environnementaux de cette technologie qui tente de devenir neutre concernant les émissions polluantes et concernant la consommation énergétique [23].

L'intégration d'écorces dans les WPC et la nécessité de concevoir un agent de couplage pour ce nouveau composite permet d'entreprendre une réflexion sur l'utilisation de lignines industrielles Kraft dans ce rôle primordial à l'obtention d'un bon produit. La teneur importante en lignine dans les écorces permet d'émettre l'hypothèse que les lignines provenant de l'industrie papetière auraient une affinité avec l'agent de renfort ciblé. Afin d'améliorer la compatibilité avec la matrice, des modifications par estérification sont envisagées, car le greffage de chaînes carbonées sur cette macromolécule pourrait assurer des mécanismes de liaison entre les différents composants de ce nouveau WPC. Les applications potentielles des WPC sont dans l'aérospatiale, l'emballage, les composants électroniques, la marine, les revêtements extérieurs, la construction et l'industrie automobile.

D'un point de vue scientifique, les résultats issus de ce travail de recherche contribueront à la littérature sur l'utilisation de fibres raffinées d'écorces d'épinette noire comme agent de renfort (ou de charge) et de lignines Kraft estérifiées comme agent de couplage (ou combiné à du MAPE) pour la fabrication de WPC. Quant au point de vue industriel et économique, ces résultats seraient utiles aux industries de pâtes et papiers, de la transformation du bois et par conséquent à la plasturgie. Ceci donnerait plus d'intérêt à l'exploitation des coproduits papetiers (liqueurs noires) et du bois (écorces) dans la fabrication de composites à valeur ajoutée dont le champ d'application est très diversifié.

I. Revue de littérature et objectifs de recherche

I.1. Revue de littérature

I.1.1. Connaissances scientifiques sur les composites bois-plastiques (WPC)

La conception de composites bois-plastique (WPC) repose sur une volonté de s'intégrer dans l'ingénierie verte dont les principes exposés par Anastas et Zimmerman [24], sont les suivants :

Principe 1 : Le concepteur doit veiller à ce que toutes les matières, les énergies et les produits utilisés soient intrinsèquement les moins dangereux possible.

Principe 2 : Il est préférable d'éviter la production de déchets à la source plutôt que de collecter et de traiter les déchets produits.

Principe 3 : Les opérations de séparation et de purification doivent être conçues de façon à minimiser la consommation d'énergie et les quantités de matières utilisées.

Principe 4 : Les produits, procédés et systèmes doivent être conçus de manière à obtenir la meilleure efficacité en termes de quantités de matières, d'énergie, d'espace et de temps.

Principe 5 : Les produits, procédés et systèmes doivent être dimensionnés par les quantités à produire (*output pulled* ou flux tirés) et non par les quantités entrantes disponibles (*input pushed* ou flux poussés), tant pour ce qui concerne l'énergie que les matériaux.

Principe 6 : Il convient de veiller à ce que l'entropie et la complexité intégrées soient minimales en investissant dans un choix de conception de recyclage, de réutilisation ou de valorisation.

Principe 7 : Lors de la conception, la durabilité et une durée de vie raisonnable (non éternel) doivent être des objectifs prioritaires.

Principe 8 : Une capacité de traitement superflue, nominale ou maximale, est à considérer comme défaut de conception lors de la conception d'un procédé (le concept « une taille unique suffit pour tout » est à rejeter).

Principe 9 : La diversité des matières mises en œuvre dans les produits doit être réduite autant que possible afin d'en faciliter la déconstruction et la valorisation.

Principe 10 : La conception de produits, de procédés et de systèmes doit intégrer et interconnecter les flux d'énergie et de matières.

Principe 11 : Les produits, procédés et systèmes doivent être conçus pour en permettre la valorisation après leur cycle de vie.

Principe 12 : Les matières premières et les énergies doivent être renouvelables plutôt qu'épuisables (ex. énergie d'origine fossile).

Ce document prouvera tout au long de son développement que la conception du matériau présenté ici prend en compte ces concepts.

1.1.1.a. Les bois-plastiques (WPC)

Généralités et développement des connaissances sur les WPC

Gauthier *et al.* [25] ont décrit les caractéristiques de la cellulose pure et des fibres de bois lorsqu'elles sont associées à des matrices thermoplastiques formant ainsi des composites bois-plastiques (WPC). La modification chimique de la cellulose est réalisée afin de permettre une bonne compatibilisation. Les agents de couplages les plus efficaces pour les composites à base de polymères hydrophobes contenant les fibres cellulosiques doivent posséder les caractéristiques suivantes : une forte réactivité avec les groupements hydroxyles de la cellulose ou des fibres de bois et une chaîne non polaire compatible avec une structure polymère. Les traitements réalisés dans cette étude modifient considérablement le caractère hydrophile de la surface de la cellulose et jouent un rôle majeur pour une meilleure mouillabilité de la fibre de bois, conduisant à une meilleure adhérence. Les propriétés mécaniques globales sont ensuite améliorées. Le vieillissement lié à l'humidité est généralement préjudiciable aux propriétés mécaniques, mais ce phénomène est limité par le traitement chimique effectué sur les fibres.

L'intérêt croissant pour les fibres lignocellulosiques est principalement lié à leur production économique avec peu d'exigences pour l'équipement et un faible poids, qui se traduit par une meilleure résistance spécifique à la traction et en terme de rigidité spécifique par rapport aux composites renforcés de fibres de verre. Ils présentent également des avantages de manutention plus sûre et plus durable et démontrent de meilleures conditions de travail par rapport aux renforts synthétiques. Les fibres naturelles

lignocellulosiques sont non abrasives, ce qui peut contribuer à la réduction significative des coûts de fabrication [26-27]. L'aspect le plus intéressant sur les fibres naturelles est leur impact positif sur l'environnement. Elles constituent une ressource renouvelable avec une production nécessitant peu d'énergie. De plus, le « bilan carbone » de ces fibres est neutre; c'est-à-dire qu'elles ne renvoient pas d'excès de gaz carbonique dans l'atmosphère lorsqu'elles sont compostées ou brûlées. Il est possible de faire du recyclage thermique. Mais aussi, sa structure cellulaire poreuse fournit de bonnes propriétés acoustiques et isolantes. Finalement, sa disponibilité dans le monde entier est un autre facteur attractif pour ce type de charge dans les WPC [28].

Cependant, la nature polaire et hydrophile des fibres lignocellulosiques et les caractéristiques non polaires de la plupart des thermoplastiques se traduisent par des difficultés de fabrication menant à une dispersion non uniforme des fibres au sein de la matrice qui altère l'efficacité du composite [29-30]. Il s'agit d'un inconvénient majeur des composites renforcés de fibres naturelles. Un autre problème est que la température de transformation des matériaux composites est limitée à 200°C comme les fibres d'origine naturelles subissent une dégradation à ces températures (hémicellulose), ce qui limite le choix de la matrice. Un autre revers est l'absorption en humidité élevée des fibres naturelles, conduisant à la présence de vides à l'interface, qui se traduit par de mauvaises propriétés mécaniques et diminue la stabilité dimensionnelle des composites. Afin de pallier à ce problème, un séchage est nécessaire sur les fibres préalablement à la fabrication des WPC. Ces propriétés posent aussi de sérieux problèmes durant l'expédition, le stockage et la transformation des composites. La non-uniformité et les changements de dimensions des fibres et de leurs propriétés mécaniques (même entre les plantes individuelles dans la même culture) posent un autre problème sérieux. Il est clair que les avantages l'emportent sur les inconvénients et la plupart des lacunes ont des mesures correctives [28].

Afin d'améliorer l'affinité et l'adhérence entre les fibres du bois et les matrices thermoplastiques, les agents de couplage chimique ont été introduits [31-34]. Ces agents de couplage sont des substances utilisées en petites quantités, généralement entre 2 et 10% en masse de fibres intégrées au WPC, pour qu'une liaison se forme entre le renfort et les matrices thermoplastiques [35]. Elles servent de ponts qui relient les fibres lignocellulosiques et polymères thermoplastiques par un ou plusieurs des mécanismes suivants : liaison covalente, enchevêtrement de chaînes polymères et fortes interactions secondaires comme dans le cas des liaisons hydrogène [36-37]. Une possibilité, qui est plus rare, est l'utilisation des agents couplant non-réactifs pour les composites bois-plastique. Dans le cas où la lignine et le polyéthylène forment un mélange

de polymères, l'ajout de polystyrène-b-poly(éthylène-butylène)-b-polystyrène (SEBS) interagit avec les constituants des composites par des liaisons chimiques faibles comme des liaisons hydrogène ou des forces de van der Waals [38]. De façon plus conventionnelle, des compatibilisants sont utilisés pour assurer la compatibilité par le biais de la réduction de la tension à l'interface [35]. Ils baissent l'énergie de surface de la fibre et la rendent moins polaire, plus semblable à la matrice en plastique. Certains agents de liaison, tels que le polypropylène maléaté (MAPP), le styrène maléaté-éthylène-butylène-styrène (MA-SEBS) et l'anhydride maléique-styrène (MA-S), agissent également comme compatibilisants dans les WPC [39-41]. Des agents dispersants peuvent être employés afin de réduire l'énergie à l'interface fibre-matrice afin d'obtenir une dispersion uniforme des fibres de bois dans la matrice polymère sans agrégation et faciliter ainsi la formation de nouvelles interfaces [42-43]. En général, compatibilisants et agents dispersants ne forment pas de forte adhérence à l'interface fibre-matrice [44]. Ainsi, les agents de couplage sont donc actuellement la méthode la plus efficace pour obtenir de bonnes propriétés. Cependant, il existe également plusieurs types d'agent de couplage [4, 6, 26, 45] déjà étudiés et dont nous pouvons utiliser les résultats pour choisir la meilleure référence possible dans nos travaux.

Le marché des WPC et ses perspectives

Les fibres naturelles lignocellulosiques ont été utilisées dans les matériaux composites depuis de nombreuses années. Récemment, un regain d'intérêt est apparu, car une nouvelle génération de composites a fait son apparition grâce aux recherches qui ont permis de mieux comprendre leur comportement et par conséquent, les performances se sont améliorées et de nouvelles opportunités ont été identifiées. Les tendances récentes telles que le désir de diminuer la dépendance au pétrole, la volonté d'augmenter l'aspect « *ecofriendly* » de nos produits de consommation, la production commerciale de nanocellulose et les marchés changeants jouent un rôle majeur dans l'avenir de ces composites [46].

Le marché mondial (Figure I-1) pour les applications des composites bois-plastique (WPC), matières plastiques cellulosiques et les composites de fibres naturelles a été estimé à environ 2,4 millions de tonnes en 2011. D'ici 2016, on l'estime à près de 4,6 millions de tonnes et en hausse avec un taux de croissance (moyen) de 13,8%, selon le BCC Research [46]. Le marché des produits de construction devrait connaître la plus forte croissance avec un taux de croissance annuel composé de 12,4% au cours des 5 prochaines années. Ce secteur avait une productivité de 1,7 million de tonnes en 2011 et pourrait atteindre près de 3,2 millions de tonnes en 2016. Le marché des applications automobiles a été estimé à 350000 tonnes en 2011 et devrait passer à 800000 tonnes en 2016, soit un taux de 17,1% de croissance annuelle.

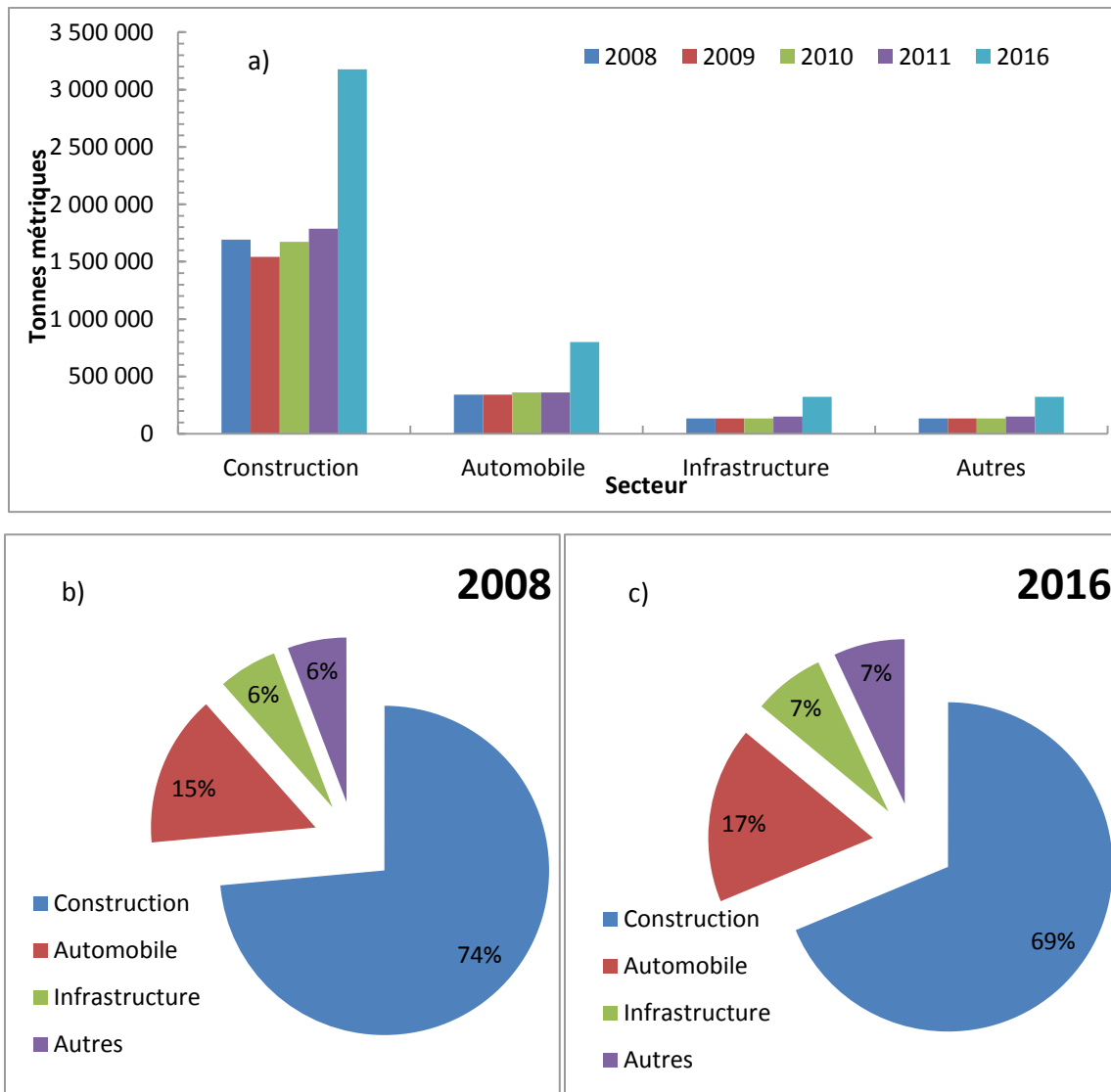


Figure I-1 Évolutions du marché des WPC entre 2008 et 2011 avec les perspectives 2016 (a), parts de marchés pour les WPC en 2008 (b) et 2016 (c). (Adapté du rapport de BCC Research paru en juin 2011).

La demande aux États-Unis de composite bois-plastiques devrait progresser d'environ 13%, à 5,4 milliards \$US en 2015, créant un marché important pour ces matériaux. La poursuite de la croissance, sur le marché nord-américain, sera renforcée en augmentant la demande des consommateurs pour la construction de produits à base de structures composite, au lieu des matériaux plus traditionnels, comme le bois. Les composites offrent un large éventail de propriétés de performance favorable, la durabilité, un minimum de maintenance, une résistance à la dégradation, et la capacité d'être coupé et taillé facilement. La perception de ces matériaux étant comme des produits « verts » qui réduisent la déforestation soutiendra également la demande. Le platelage, qui était la principale utilisation des composites bois-plastique en 2010, connaîtra

un élargissement de sa demande jusqu'en 2015. En effet, les propriétaires de maison vont installer d'autres installations avec des WPC (Figure I-2) comme des terrasses en ces matières au lieu du bois traditionnel parce que les terrasses en bois-plastiques nécessitent moins d'entretien annuel, ont des durées de vie plus longues et coûtent moins cher à long terme, puisqu'elles ne nécessitent pas de peinture annuelle ou de traitements fongiques. Par la suite, ceux-ci vont installer des clôtures faites de vinyle et autres matériaux en raison de leurs propriétés mécanique et leur résistance au pourrissement. La demande de structures en composites bois-plastique, dans le paysage et les produits d'extérieur tels que les fenêtres, les portes et les autres applications, est garantie par la reconnaissance des consommateurs des performances de ce matériau. L'augmentation des parts de marché des WPC sera pilotée par l'intérêt des consommateurs vers ce matériau comme substitut du bois naturel dans des applications telles que les terrasses et les clôtures, puis d'autres développements de ce matériau (Figure I-2), Wolcott et Smith [47]. Et tout ceci, parce que les structures en composite bois-plastique intègrent des matériaux recyclés, il est considéré comme un matériau de construction écologique. La demande de bois-plastique devrait augmenter d'environ 11% par an, à 2,8 milliards \$US en 2015. Des gains seront stimulés par l'intérêt accru des consommateurs en raison de ses propriétés et de son faible entretien. Les efforts des fabricants pour créer des bois plastiques variés avec des textures « bois » plus réalistes en surface contribueront également à soutenir la demande [46].

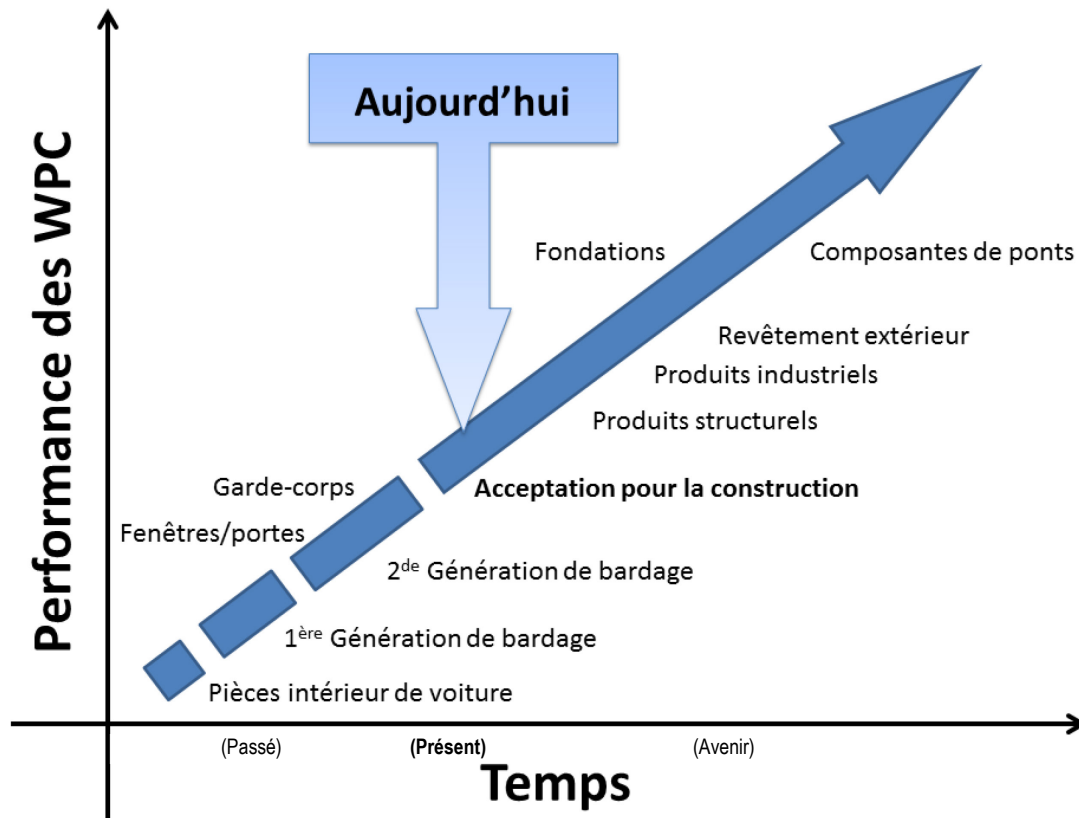


Figure I-2 Évolutions des performances des WPC dans le temps et marchés actuels et potentiels. (Adapté de Wolcott et al. 2005).

Selon les recherches et les marchés, la croissance de l'industrie des bois plastiques est prévue en Europe malgré les difficultés financières. Après un démarrage lent dans le secteur de l'automobile il y a une quarantaine d'années, la production européenne de composites bois-plastiques a diversifié ses offres et augmenté rapidement sa production au cours des cinq dernières années pour atteindre 193000 tonnes en 2010. Il est prévu de poursuivre la croissance à près de 360000 tonnes d'ici à 2015, ce qui représente une croissance annuelle moyenne de 13%, mais qui représente un ralentissement de la croissance par rapport à la période 2005-2010 en raison des difficultés persistantes dans les économies européennes. Le platelage est de loin le plus grand domaine d'application avec 75% de part de marché (hors secteur automobile), mais les arguments pour l'utilisation de WPC dans d'autres applications extérieures et intérieures sont importants et se développent par le biais de projets de recherche. Une grande partie de la croissance prévue devrait être dans les applications de la construction. En effet, ce secteur, en plus du platelage, comprend le bardage ou le parement, les clôtures et les fenêtres. L'Allemagne, la France et la Belgique sont parmi les pays d'Europe les plus actifs producteurs dans le domaine des WPC, ces fabricants anticipent plus ardemment d'autres applications de volume élevé en dehors du platelage. En plus de la

fabrication européenne, les importations de WPC provenant des États-Unis et de l'Asie sont devenues de plus en plus importantes sur le marché européen, en particulier dans le secteur de la construction [46]. Les WPC ont un excellent impact écologique et ont un énorme potentiel d'accroissement à l'avenir.

L'utilisation de fibres naturelles permettrait de sauver certaines ressources nécessaires pour cultiver ces types de fibres et de préserver les sources de pétrole non renouvelable pour produire des fibres synthétiques. Plus de 9 millions de tonnes de fibres lignocellulosiques représentant une valeur potentielle de 19 milliards de \$ et avec un potentiel en valeur ajoutée d'au moins 12 milliards de \$ qui pourrait être disponible chaque année [28].

1.1.1.b. L'optimisation des propriétés des WPC

Les prétraitements des fibres naturelles

Les traitements de fibres naturelles sont généralement nécessaires afin d'améliorer leur compatibilité avec les matrices polyoléfiniques. Ces traitements sont en général destinés à purifier, oxyder et/ou activer la surface des fibres lignocellulosiques. Ainsi, le traitement Corona, plasma et, plus récemment, laser, rayons X et UV ont été explorés. Les traitements plasma sont les plus couramment utilisés et ont démontré leur efficacité pour améliorer la compatibilité des fibres lignocellulosiques avec la matrice. Les traitements chimiques avec de la soude, du silane, isocyanate, siloxane, alcalino-terreux, des agents d'oxydoréduction ou de maléate sont conçus pour améliorer l'interface entre la fibre naturelle hydrophile polaire et avec la matrice de polymère généralement non polaire et hydrophobe [1, 27, 48-50]. Sans traitements physique ou chimique, la surface de la fibre resterait inerte vis-à-vis des interactions désirées avec des polymères.

Certains traitements physiques et chimiques changent les propriétés de structure et de surface des fibres lignocellulosiques et influencent ainsi leurs liaisons avec la matrice polymère. Le traitement physique « Corona » est l'une des techniques les plus efficaces pour l'activation et l'oxydation de surface [48-50]. Cette décharge « Corona » de haute énergie provoque des changements dans les liaisons moléculaires à la surface, conduisant à la formation de radicaux libres et d'autres espèces réactives dans l'environnement hautement actif de cette décharge. Les fibres traitées Corona ont démontré de bonnes capacités de réticulation de surface avec une matrice polymère [1]. Le traitement de plasma est une autre façon d'améliorer l'adhérence à l'interface entre les fibres lignocellulosiques et la matrice. Le principe du

traitement plasma est similaire au traitement Corona. Le traitement plasma à basse température provoque la formation de radicaux libres, ce qui apporte des changements physiques, principalement la rugosité de surface menant à une adhérence accrue [49]. Le plasma peut être généré sous pression atmosphérique ou en présence de gaz choisi. Les propriétés du plasma sont exploitées pour obtenir des changements de la surface d'un matériau selon le type et la nature du gaz utilisé. L'énergie de surface peut être augmentée ou diminuée à l'aide de radicaux instables qui convertissent des groupes fonctionnels tels que les alcools, aldéhydes, cétones et acides carboxyliques [49].

Un des traitements chimiques les plus anciens et le plus souvent utilisé est la mercerisation des fibres lignocellulosiques qui est un traitement alcalin. La mercerisation dépend du type et de la concentration de la solution alcaline, du temps de traitement et de la température. Des conditions optimales sont à déterminer pour assurer l'amélioration des propriétés en traction [48]. Ce procédé réduit le diamètre de la fibre, augmente ainsi le rapport de forme (L/D) et conduit au développement d'une topographie de surface plus rugueuse qui se traduit par une meilleure adhérence au niveau de l'interface fibre-matrice et une augmentation des propriétés mécaniques [45, 51]. L'hémicellulose, qui est composée essentiellement de xylanes, polyuronides et hexoses, est très sensible à l'action de la soude caustique, qui n'exerce qu'un faible effet sur la lignine ou l' α -cellulose. Lorsque les hémicelluloses sont dissoutes, la région interfibrillaire est susceptible d'être moins dense et moins rigide, ce qui confère aux fibrilles la capacité de se réorganiser dans la direction de déformation en traction. Lorsque les fibres naturelles sont sous tension, ces réarrangements entre les fibrilles entraînent une meilleure répartition des contraintes et permettent donc de résister à des charges plus élevées dans la fibre [1]. L'étude de Chand et Rohatgi [52] sur les fibres de sisal ont montré des modifications morphologiques après un traitement alcalin dans une solution de NaOH à 8%. Une augmentation de 100% de la résistance à la traction a été obtenue pour ces fibres de sisal dans une matrice polyester. La mercerisation augmente le nombre de sites réactifs et permet un meilleur mouillage de la fibre dans la matrice polymère [45]. De plus, une augmentation de qualité des composites est à prévoir en raison de la meilleure adhésion fibre – matrice [1, 52]. Ce traitement peut également améliorer la résistance à la pourriture et l'hydrophobicité de fibres lignocellulosiques [48].

Les agents de couplages

Les agents de couplage dans les composites contenant des fibres de bois (WPC) jouent un rôle important dans l'amélioration de la compatibilité et l'adhérence entre les fibres polaires et des matrices non polaires. Lu *et al.* [4] discutent des agents de couplage, prétraitements et combinaisons de ces deux technologies

dans la fabrication de WPC. Depuis 2000, plusieurs agents de couplage avaient été explorés. Ces agents sont classés dans les groupes organiques, inorganiques et organiques-inorganiques, parmi lesquels les agents organiques conviennent mieux que les agents inorganiques en raison de la plus forte adhérence interfaciale. Les agents de couplage sont habituellement enduits sur la surface de la fibre lignocellulosique, polymère ou par mélange, trempage, pulvérisation ou d'autres méthodes. Le choix de l'agent de couplage est donc très important pour optimiser les propriétés ciblées pour le matériau développé.

Les travaux d'Abdelmouleh *et al.* [53] portent sur les matériaux composites basés sur des fibres de cellulose (brutes ou chimiquement modifiées) comme éléments de renfort. Des matrices thermoplastiques ont été préparées et caractérisées, en termes de performances mécaniques, comportement à l'absorbance d'eau et résistance thermique. Quatre fibres lignocellulosiques différentes et deux polymères thermoplastiques (LDPE et caoutchouc naturel) ont été employés comme matrices. Les fibres ont été incorporées dans les matrices, brutes ou après modification chimique de surface impliquant trois agents de couplage de type silane, à savoir γ -methacryloxypropyltriméthoxysilane (MPS), γ -mercaptopropyltriméthoxysilane (MRPS) et hexadecyltriméthoxysilane (HDS) (Figure I-3). Les propriétés mécaniques des composites préparés avec des fibres dont la longueur moyenne a été augmentée, sont améliorées. Seulement pour l'HDS portant une chaîne aliphatique simple, Abdelmouleh *et al.* [53] observent une faible amélioration des propriétés des composites, avec des gains de seulement 5% du module de Young et de la résistance en traction, à cause de l'incapacité de l'HDS de permettre la formation des liaisons covalentes avec la matrice. Les silanes de type MPS et MRPS offrent une interface adéquate et forte entre les fibres lignocellulosiques et la matrice (Figure I-4 pour le silane de type MPS), avec des gains de 20% et 10% respectivement pour le module de Young et des augmentations de leurs résistances en traction de 25% (avec du MPS) et 10% (avec du MRPS).

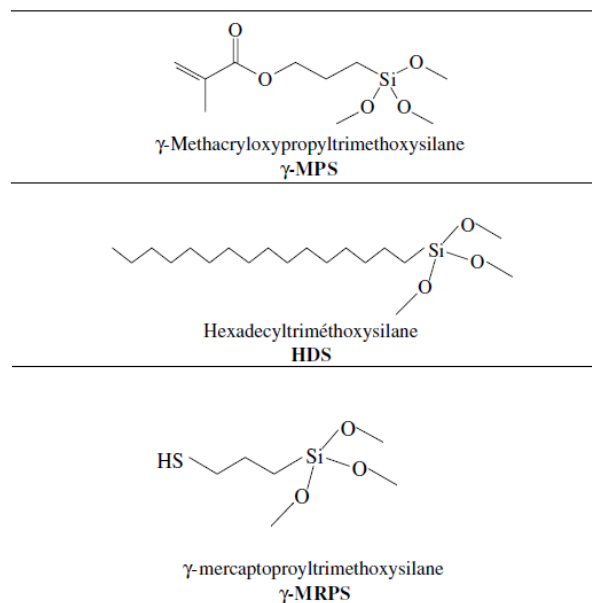


Figure I-3 Les agents de couplage de type silane utilisés par Abdelmouleh *et al.* (2007).

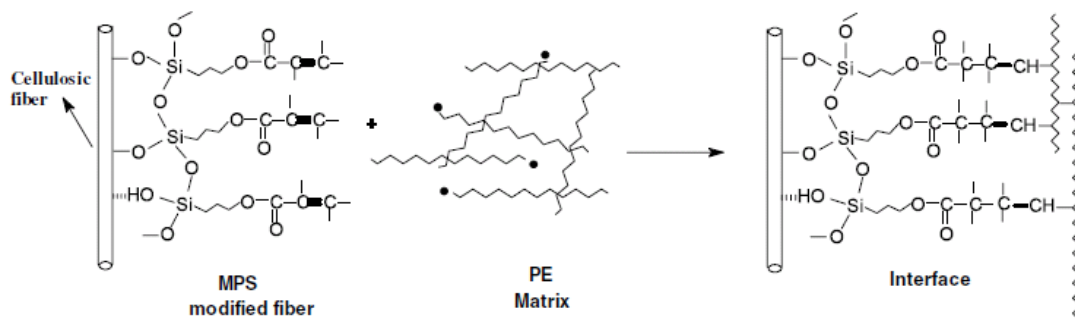


Figure I-4 Illustration schématique de la zone interfaciale des composites contenant des fibres lignocellulosiques modifiées avec du MPS et du LDPE (Adapté de Abdelmouleh *et al.*, 2007).

Colom *et al.* [5] ont étudié les caractéristiques chimiques et mécaniques des bois plastiques constitués de HDPE (polyéthylène de haute densité) et de fibres lignocellulosiques (en présence ou en absence d'agent de couplage). Les effets interfaciaux (Figures I-5 à I-7), morphologiques, liés à l'estérification des fibres de peuplier faux-tremble et l'agent de couplage a été analysé par de la spectrophotométrie infrarouge à transformée de Fourier (FTIR) et de la microscopie électronique à balayage (MEB). La variation de l'absorption dans les bandes spectrales a été déterminée afin d'évaluer l'influence des agents de couplage ainsi que la teneur en fibres lignocellulosiques. Des observations MEB démontrent l'effet « pont » provoqué par l'agent de couplage entre la matrice HDPE et les fibres lignocellulosiques. Les propriétés mécaniques, résistance à la traction, module de Young, l'allongement à la rupture et la dureté, ont été analysées. Les

différences observées entre les différentes formulations de composites étudiés s'expliquent par des mécanismes spécifiques d'adhésion (Figures I-5 à I-7).

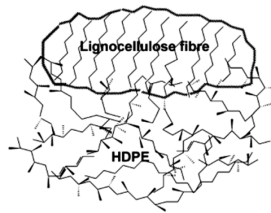


Figure I-5 Mécanisme d'adhésion pour des composites HDPE – fibres lignocellulosiques non traités (Tiré de Colom *et al.*, 2003).

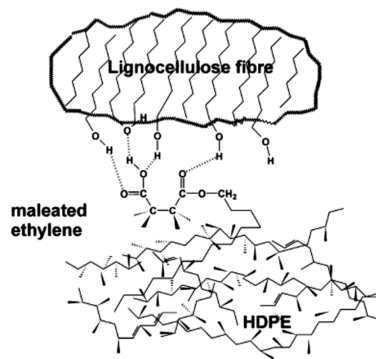


Figure I-6 Mécanisme proposé pour l'adhésion entre le HDPE et les fibres lignocellulosiques traitées avec de l'Epolene (MAPE). Les liaisons ester entre le MAPE et les hydroxyles du bois introduisent la partie lipophile de ces esters qui fait le pont avec le polymère (Tiré de Colom *et al.*, 2003).

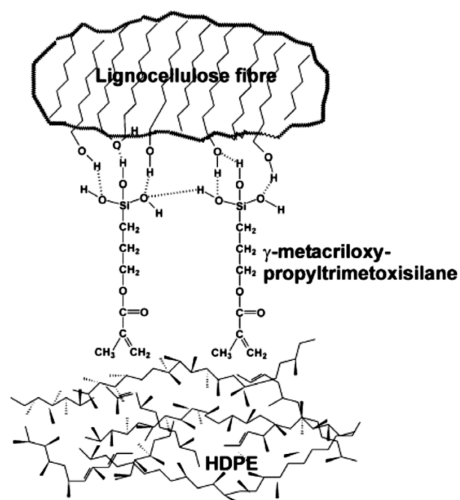


Figure I-7 Mécanisme d'adhésion pour des composites HDPE – fibres lignocellulosique traité avec du silane (Tiré de Colom *et al.*, 2003).

Les travaux de Colom *et al.* [5] indiquent que les propriétés macroscopiques des WPC dépendent de la teneur en fibres lignocellulosiques et de l'utilisation d'un agent de couplage. Les observations MEB des surfaces de fracture montrent que l'ajout d'agents de couplage favorise la dispersion dans la matrice de HDPE. Ils montrent également que l'agent de couplage silane facilite le contact direct entre les fibres lignocellulosiques et semble plus efficace que l'Epolene (MAPE) ou sans agent de couplage. Les différences observées entre les divers composites étudiés sont expliquées par des mécanismes d'adhérence différents. Plusieurs mécanismes d'adsorption-mouillabilité et quelques liaisons chimiques ont été proposés dans les composites traités avec de l'Epolene® (un produit de type MAPE, commercialisé par Westlake Chemical Corporation). L'adhésion dans les composites modifiés avec du silane est principalement un mécanisme chimique de liaisons covalentes simples et des ponts hydrogène.

Les travaux de Yang *et al.* [26] sur les composites contenant des farines lignocellulosiques, de bois et de balle de riz, avec du polypropylène maléaté (MAPP) ou du polyéthylène maléaté MAPE ont montré que ces composites avaient des propriétés mécaniques différentes. Quelques ruptures de type *pulled-out* étaient visibles sur les observations au microscope électronique à balayage des composites constitués de MAPP, alors qu'aucun *pulled-out* ont été observés dans les composites utilisant du MAPE. La présence de *pulled-out* démontre une mauvaise adhésion entre les particules lignocellulosiques (ici de bois ou de balle de riz) et la matrice polymère ce qui est néfaste pour les propriétés mécaniques, car les contraintes ne sont pas transmises aux interfaces qui deviennent des zones de fragilités du WPC. La raison est qu'il y a un meilleur mouillage du MAPE avec la matrice de polyéthylène, qui a conduit à la plus forte liaison interfaciale entre le renfort et la matrice polymère. Les bonnes qualités des zones d'ancrage du MAPE avec la matrice de polyéthylène s'expliquent par le fait qu'il s'agisse du même matériau de base (le PE). Le MAPE est recommandé dans le système composite de polyéthylène, car il permet d'augmenter de 60% la résistance en traction pour du bois et de 75% pour des balles de riz en utilisant du LDPE et de 30% pour des balles de riz en utilisant du HDPE, en raison de sa meilleure compatibilité par rapport au MAPP, qui améliore la résistance en traction pour du LDPE de 20% avec du bois et de 25% avec des balles de riz et de 20% pour du HDPE avec ces dernières fibres lignocellulosiques.

Le greffage de polyéthylène sur des poudres de lignosulfonate de sodium a été étudié par Casenave *et al.* [54] avec des propriétés mécaniques améliorées de façon significative pour les WPC fabriqués. Cette technique est cependant très coûteuse et ne sera pas développée dans cette thèse. Par contre, des modifications chimiques (estérifications) sur les lignines ont démontrées un potentiel à développer pour les

WPC en se basant sur les travaux de Jandura *et al.* [55] sur de la cellulose purifiée de pâte sulfite blachie (40% *Pinus radiata* et *Tsuga heterophylla*) et de Nadji *et al.* sur des lignines Soda d'herbacées (*Stipa tenacissima*) [56].

I.1.1.c. Valorisation de coproduits dans une nouvelle génération de WPC

Le choix de la matrice polyoléfine (HDPE)

En raison des différences de structure, il existe différents types de polyéthylènes qui ont des applications et des propriétés différentes. Les propriétés principales qui différencient ces types sont : la masse moléculaire, la distribution de masse moléculaire, la densité, le pourcentage de cristallinité et le degré de ramification à longue chaîne ou à chaîne courte. La masse moléculaire et la distribution des poids moléculaires sont les principaux facteurs qui influencent les propriétés mécaniques du polyéthylène. Les types sont classés en quatre catégories de densité selon les normes ASTM, comme illustré dans le Tableau I-1 [57].

Table I-1 Classification des types de polyéthylène par densité (Adapté de Cheng 2008).

Type de PE	Densité (g/cm ³)
Faible densité	0,910-0,925
Moyenne densité	0,926-0,940
Haute densité	0,941-0,959
Homopolymère de haute densité	supérieure à 0,960

La Figure I-8 montre l'impact des variations de densité sur les changements dans la morphologie du polyéthylène et de sa cristallinité. Le polyéthylène linéaire de basse densité (LLDPE) et le HDPE ont une morphologie lamellaire et sphérolitique. Une augmentation de cristallinité, d'où une augmentation de la densité en polyéthylène augmente la rigidité et la résistance à la traction du matériel [57].

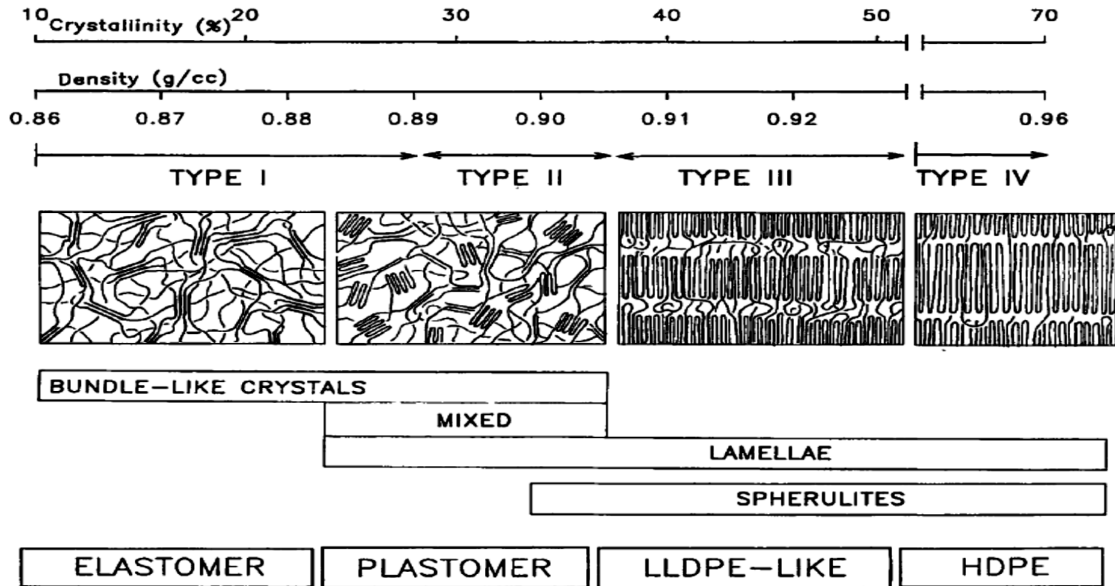


Figure I-8 Les différentes structures cristallines du polyéthylène (Tiré de Bensason et al., 1996).

D'éventuelles chaînes de ramifications affectent la densité et d'autres propriétés (principalement les propriétés rhéologiques) du polyéthylène. Il existe deux types de ramifications, celles à chaîne de ramification courte (RC), principalement en raison de l'introduction de co-monomère, et celles à longues chaînes (LC), formées à partir de réactions secondaires lors de la polymérisation. Comme illustré à la Figure I-9, le HDPE est généralement linéaire à faible teneur en RC. Le LLDPE a une teneur supérieure en RC que le HDPE avec peu ou pas de branches à longue chaîne (LC). Par contre, le polyéthylène de basse densité (LDPE) est connu pour avoir une haute teneur en ramification à chaîne courte (RC) et à longue chaîne (LC). La présence de branches à chaîne courte interfère avec la formation de lamelles, le LDPE a une teneur plus élevée en RC que le LLDPE et présente donc une densité plus faible. La distribution de branches à chaîne courte est contrôlée par le type de catalyseur utilisé pendant le processus de polymérisation. L'influence de la teneur en RC n'est pas négligeable sur les propriétés mécaniques du polyéthylène [57-58].



Figure I-9 Ramification générale des structures de polyéthylène : a) haute densité (HDPE); b) basse densité linéaire (LLDPE); c) basse densité (LDPE) (Tiré de Cheng 2008).

L'intégration des écorces dans les WPC

La variabilité des fibres de bois a un effet significatif sur les propriétés mécaniques et physiques des WPC, selon l'étude de Bouafif *et al.* [59]. Cet effet s'explique par les variations des propriétés de surface des fibres, ainsi que la cristallinité relative, la dégradation thermique et la masse volumique spécifique du bois. Les matériaux composites contenant des particules d'écorce présentent moins d'absorption d'eau (1,2% d'humidité) par rapport à celles faites avec des particules de bois (1,6% d'humidité). Cependant, les propriétés mécaniques en flexion de WPC de bois de pin gris sont plus performantes que les écorces de cette essence, pour les mêmes dimensions, de 55% de mieux pour le module de Young et de 50% en résistance à la flexion. Les différences de composition chimique entre l'écorce et le bois sont une des explications plausibles pour les différences dans l'absorption d'eau et de résistance mécanique (des fibres plus courtes possèdent un module plus faible). L'augmentation de la taille des fibres, pour une teneur de 45%, améliore le module de Young en flexion de 25% en passant de particules de 65 mesh (soit, environ 0,27mm) à 24 mesh (environ 0,7 mm).

L'ajout de farine d'écorce d'argousier centenaire (*Azadirachta indica*), selon les résultats des travaux de Sewda et Maiti [17], modifie les propriétés mécaniques du HDPE. Le module élastique en traction, la force et l'élongation à la rupture sont détériorés proportionnellement à l'augmentation des concentrations en écorce et la cristallinité du composite diminue avec un ajout important d'écorce. A 26% de teneur en écorce, ils ont déterminé un taux de cristallinité de 56% tandis qu'à 3% ils obtiennent 64% de cristallinité et l'ensemble de valeurs mesurées présente une valeur de r^2 de 0,9 avec une régression linéaire. On explique

la détérioration du module de Young et de la résistance par ces deux effets opposés ainsi que par une concentration de contrainte à l'interface. Par les contraintes mécaniques et les concentrations de contraintes, la ductilité des composites a diminué conduisant à une diminution de l'allongement à la rupture et résistance à l'impact Izod des composites. En présence de l'agent de couplage, HDPE-g-MAH, l'élongation était plus faible que celle déterminée pour le système précédent en raison d'une adhérence améliorée à l'interface. Les observations MEB indiquent que les particules de fibres d'écorce ne sont pas adhérentes avec la matrice HDPE. En présence de l'agent de couplage, en imagerie MEB, les limites de particules ne sont pas visibles et le type de fracture prouve une amélioration de l'adhérence à l'interface.

Des WPC ont été extrudés par Ngueho Yemele *et al.* [18] avec du HDPE et des fibres non raffinées d'écorce d'épinette noire ou d'écorce de peuplier faux-tremble. Les fibres d'écorce agissent comme une charge et non pas comme un agent de renforcement dans les composites obtenus. En effet, par rapport à de l'HDPE seul, le module de Young en flexion est diminué de 15% pour la meilleure formulation contenant des écorces d'épinette noire et dégradée de 40% pour la meilleure contenant des écorces de peuplier faux-tremble alors qu'il est augmenté de 55% pour le témoin de bois plastique (farines de pin). Concernant le module de Young en traction, les écorces semblent être plus efficace, mais restent nettement moins efficaces que pour le témoin en farine de bois, les améliorations sont de 240%, 130% et 90% pour le bois, les écorces d'épinette noire et les écorces de peuplier faux-tremble respectivement. Ces résultats sont probablement dus à l'inefficacité de l'agent de couplage MAPE à former des liaisons covalentes (simples ou doubles) avec la fibre d'écorce. Les effets des espèces, des proportions d'écorce et des dimensions des fibres sur les propriétés mécaniques sont significatifs. Afin d'ajouter des connaissances importantes, une étude a été menée sur les effets de l'extraction à l'eau chaude de l'écorce et l'ajout de l'agent de couplage et de lubrifiants sur les propriétés en flexion et en traction des composites écorce/HDPE, par Ngueho Yemele *et al.* [19]. Les résultats ne montrent aucun impact significatif de l'extraction à l'eau chaude sur les propriétés en flexion et en traction des composites d'écorce/HDPE. Ainsi, le module de Young en flexion des composites d'écorce d'épinette noire non raffinée diminuent de 1% après extraction et de 10% avec les écorces de peuplier faux tremble et en traction, le module de Young est dégradé de 2% après extraction à l'eau chaude pour les deux essences. Toutefois, la résistance en traction après l'extraction a été améliorée de 5% pour les deux essences. Les écorces présentent des extraits sollicités en pharmacologie et pour les adhésifs, qui pourraient être extraits et les résidus restants servant à la fabrication de matériaux composites. Le lubrifiant et l'agent de couplage utilisés ont sensiblement amélioré les propriétés mécaniques des composites

Dans ce projet, des fibres raffinées d'écorce d'épinette noire (résineux) seront développées, car elles semblent avoir un meilleur potentiel que les particules d'écorce de bouleau jaune (feuillus) à disposition (Annexe 2).

L'opportunité de valoriser les lignines industrielles

La lignine est un terme général qui est utilisé pour décrire une gamme de polymères de structure phénylepropane qui constitue les parois des cellules des plantes vasculaires. Il faut également faire la distinction entre la *protolignine* (dans l'arbre) et les lignines extraites de l'arbre, lesquelles sont des dérivés fortement dégradés de cette *protolignine*. De plus, il existe une variété de types de lignines selon la source botanique et le procédé d'isolement. Les lignines forment un groupe important de polymères aromatiques. Il s'agit du polymère naturel le plus important au monde comportant un noyau aromatique. En effet, tous les végétaux possédant des tissus vasculaires ont une certaine forme de lignine. La différence entre les résineux qui ont des lignines constituées presque uniquement d'unités guaiacyl (G) et les feuillus qui sont composés de façon presque égale d'unités guaiacyl (G) et syringyl (S), comme le montre les Figures I-10 et I-11.

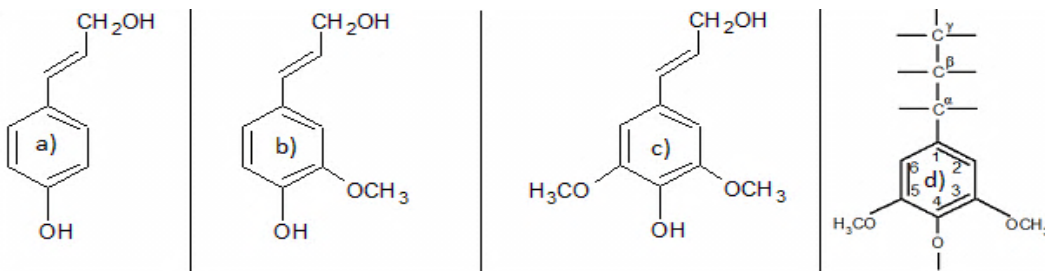


Figure I-10 Unités composantes des lignines naturelles (ou monolignols) : a) unité hydroxyphényle (H -alcool p-hydroxyphényle), b) unité guaiacyl (G - alcool coniférylique), c) unité syringyl (S – alcool sinapylique), d) notation commune pour les différents atomes de carbone au sein de chaque unité de phényle propane.

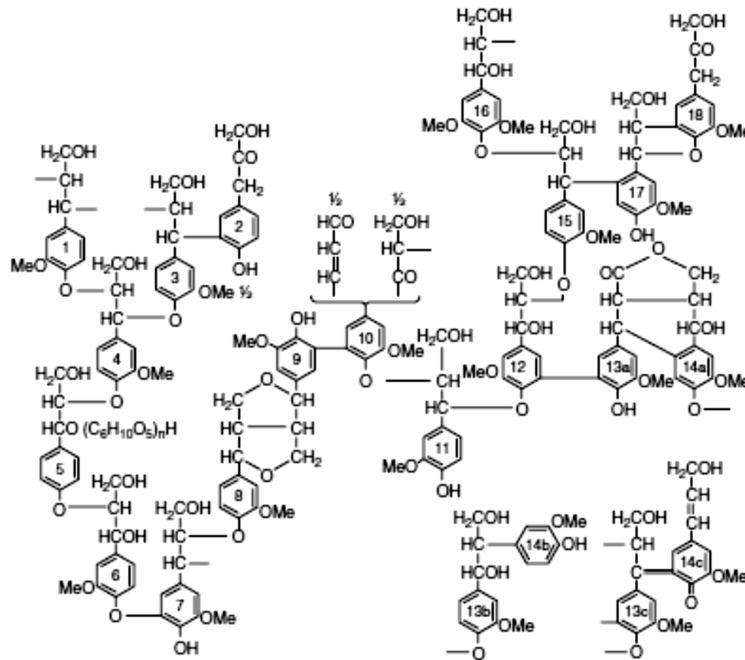


Figure I-11 Exemple de modélisation schématique d'une lignine de résineux, d'épicéa de Norvège (Europe) *Picea abies* (L.) Karst. (adapté de Gellerstedt et Henriksson, 2008).

Des composites bois-plastiques (WPC) à base de LDPE ont été préparés avec une lignine (de Sigma Aldrich qui ne précise pas son origine végétale) par Sailaja et Deepthi [60]. Afin d'améliorer l'hydrophobicité de la lignine, celle-ci a été estérifiée avec de l'anhydride phtalique avant de la mélanger. Du LDPE greffé avec de l'anhydride maléique a été utilisé comme agent de couplage, à une teneur de 6%, pour améliorer l'adhérence interfaciale. Une amélioration des propriétés mécaniques en traction a été obtenue avec du LDPE maléaté, en raison d'une meilleure adhérence entre la matrice LDPE et la lignine estérifiée. Cependant, les WPC fabriqués restent plus faibles mécaniquement que du LDPE en terme de résistance en traction avec une diminution de 10% avec 40% de lignines estérifiées. L'aspect positif démontré est une augmentation en termes de module de Young respectif de 130% et de 150% en intégrant 20% et 40% de lignines phtalique. Cela est particulièrement vrai dans le cas de la résistance à la traction des mélanges avec des valeurs approchant le LDPE, et ce, même avec 40% de lignine. La morphologie du mélange a montré une surface très déformée indiquant la bonne adhérence et confirmée par les micrographies MEB de surface. Une analyse TGA a montré une perte de poids plus faible pour les composites contenant de l'agent de couplage qui semblent démontrer une meilleure interaction des lignines avec la matrice par l'action du LDPE greffé avec de l'anhydride maléique. En effet, cette étude caractérise une perte de masse totale de 86% et 78% pour les composites contenant 20% et 40% de lignines estérifiées à 91% et 81% en

ajoutant 6% d'agent de couplage. Une étude en DSC a montré une légère augmentation des valeurs de cristallinité de 20% et de 10% avec l'ajout de la lignine estérifiée à 20% et 40%, respectivement, ce qui peut prouver une amélioration de la compatibilité des composants.

Le procédé Kraft est le plus présent dans l'industrie papetière et il a été démontré que des lignines Kraft provenant de liqueurs noires seraient disponibles par l'utilisation du procédé LignoBoost®, breveté récemment [22].

I.1.2. Approche critique et connaissances scientifiques complémentaires à développer pour une meilleure compréhension des WPC

La revue de littérature présentée dans ce chapitre nous a permis de faire le point sur : (i) les composites bois-plastiques (WPC), en identifiant le HDPE comme la matrice la plus utilisée et représentant l'objet d'étude le plus intéressant (ii) l'importance de l'interface fibre-matrice sur les propriétés des WPC et (iii) les connaissances requises pour le développement d'un nouvel agent de couplage à base de lignine industrielle provenant du procédé Kraft.

- (i) Les composites bois-plastique (WPC) présentent un potentiel de développement important sur le marché actuel et futur. La diversité des fibres lignocellulosiques et de matrice polymère disponible permet de répondre à divers besoins de la société. Cependant de nombreux défis doivent être relevés pour optimiser les propriétés des WPC en améliorant l'interface entre les fibres lignocellulosiques et la matrice de polyéthylène haute densité. Le choix du HDPE réside dans la volonté de concevoir un WPC disposant de propriétés intéressantes pour la réalisation de produit à forte valeur ajoutée.

- (ii) Deux approches et plusieurs méthodes existent pour améliorer cette interface en faisant des prétraitements sur les fibres lignocellulosiques afin de les rendre moins polaires pour ainsi, les rendre plus compatibles avec la matrice non polaire. L'autre approche est d'utiliser un intermédiaire qui servirait de pont entre les fibres et la matrice. Cette approche semble la plus efficace, surtout avec du polyéthylène maléaté (MAPE). L'optimisation des propriétés des WPC dépend directement de la performance de cet agent de couplage qui doit être adapté pour

chaque système fibres-matrice. Dans ce travail nos connaissances sur les WPC avec des écorces sont assez restreintes et se composent de quelques articles sur son utilisation sous forme de farine ou de particules (*fiber-like*) uniquement. Nous étudions dans ce projet les fibres d'écorce d'épinette noire issues du raffinage. Il est intéressant de noter qu'une extraction à l'eau chaude sur ces fibres a été ajoutée aux objectifs de ce projet pour anticiper une disponibilité de ces écorces après l'extraction. Les extractibles d'intérêt agroalimentaire, pharmaceutique ou cosméceutique ont été déterminés dans des études antérieures (Garcia Perez *et al.*, 2012). On a étudié l'impact de l'extraction sur les propriétés des WPC contenant des fibres d'écorce d'épinette noire. D'autre part, la teneur importante en lignine de ces fibres laisse entrevoir un potentiel intéressant pour la valorisation des lignines (modifiées ou non) comme agent de couplage.

- (iii) Notre approche critique porte sur le manque de travaux visant à investiguer : (i) l'utilisation de lignines estérifiées comme agent de couplage, (ii) la valorisation des fibres raffinées d'écorce comme agent de renfort et (iii) les champs d'application extérieurs possibles pour ce nouveau matériau de type « WPC ».

I.2. Objectifs de recherche

I.2.1. Objectifs généraux et spécifiques du projet

I.3.1.a. Objectifs généraux

Optimiser le procédé de mise en œuvre des composites de type bois-plastiques (WPC) fabriqués à la base de matrice (HDPE) avec des fibres d'écorce.

Réaliser des modifications chimiques sur les lignines et utiliser ces lignines estérifiées comme agents de couplage, afin d'améliorer la compatibilité entre les fibres naturelles et le polyéthylène (hydrophobes).

Déterminer l'influence de la composition chimique et de la morphologie des fibres d'écorce extraite sur les WPC fabriqués.

1.3.1.b. Objectifs spécifiques

Déterminer le potentiel de l'utilisation de la lignine commerciale Indulin AT, et des lignines industrielles de type Kraft (une de feuillue provenant de la liqueur noire de Domtar, Windsor et une de résineux provenant de la liqueur noire de Kruger, Wayagamack) comme agent de couplage.

Comparer l'efficacité des différentes lignines Kraft avec un agent de couplage commercial : l'Epolene (MAPE).

Étudier l'efficacité de la combinaison de lignines Kraft estérifiées avec du MAPE comme agent de couplage entre les fibres d'écorce et la matrice polyoléfine (HDPE).

Déterminer le potentiel de l'utilisation des écorces extraites d'épinette noire.

Analyser les propriétés physico-chimiques et mécaniques des WPC et envisager les différents domaines d'applications possibles d'un tel matériau.

I.3. Hypothèses de recherche

Les lignines estérifiées vont agir en tant qu'agent de couplage efficace, en remplacement du MAPE, pour les composites bois-plastiques (WPC) d'écorces et de polyéthylène de haute densité (HDPE).

Les fibres raffinées d'épinette noire (extraites ou non) agiront comme élément de renfort dans la matrice HDPE.

Les WPC ainsi obtenus seront utilisables pour des produits à forte valeur ajoutée.

I.4. Apports scientifiques du projet

L'étude des composites bois-plastiques (WPC) contenant des fibres lignocellulosiques a attiré beaucoup d'attention ces dernières années. Cependant, il existe peu de travaux portant sur l'incorporation d'écorces dans du HDPE contenant des lignines industrielles, et aucune ne porte sur des fibres d'écorces raffinées (de type fibres de panneau MDF). L'extraction de l'écorce peut être envisagée dans le contexte de bioraffinage de la biomasse forestière, mais une seule étude [19] sur des particules *fiber-like* d'écorce a montré qu'une extraction à l'eau chaude était possible sans influence néfaste sur les composites fabriqués. Les extraits pouvant être dirigés vers la filière des produits forestiers non ligneux (pharmacologie, nutrition ou cosmétique) et les fibres restant après l'extraction trouvant une application à valeur ajoutée (WPC).

Des études portent sur l'incorporation des lignines modifiées comme renfort ou charge dans des matrices de polyéthylène. Cependant, il n'existe presque pas de travaux portant sur l'utilisation de lignines industrielles modifiées comme agent de couplage à des fibres lignocellulosiques provenant de l'écorce. Les lignines Kraft sont devenues partiellement disponibles grâce aux développements récents (brevet pour le procédé LignoBoost® par Tomani [22] et la valorisation de ce coproduit est devenue intéressante de par sa disponibilité.

I.5. Structure d'approche du projet

Les connaissances générales sur les bois-composites (WPC), avec les perspectives prometteuses de ce type de matériau, mais également les possibilités de prétraitements des fibres lignocellulosiques et l'importance du choix de l'agent de couplage, ont été développées dans la revue de littérature afin de mieux appréhender la conception, la réalisation, la caractérisation et l'optimisation d'un composite bois plastique (WPC) contenant des fibres d'écorces, des lignines estérifiées et du polyéthylène haute densité (HDPE) qui est l'aboutissement de cette thèse. La partie II est un chapitre de livre ayant été accepté pour publication par l'éditeur *Nova Science Publisher* qui a été conçu comme une revue de littérature sur les WPC en y incluant de façon pédagogique des résultats préliminaires étudiant plusieurs facteurs afin de se familiariser avec les difficultés de mise au point du matériau visé. Ainsi, le potentiel des lignines brutes et estérifiées y est développé, mais également l'effet de l'extraction à l'eau chaude sur des fibres d'épinette noire (*Picea mariana*). Cependant, les résultats sont inférieurs à la référence contenant l'agent de couplage commercial

usuellement employé dans ce genre de matériau (MAPE). Par la suite, la combinaison de ce MAPE avec des lignines modifiées sera développée dans la partie III sur des fibres d'écorces d'épinette noire raffinées, mais non extraites, sous forme d'un article scientifique ayant été publié par le *Journal of Materials Science Research*. Les résultats prouveront une amélioration des propriétés en utilisant ce genre d'agent de couplage dans nos WPC. Finalement, la partie IV, rédigée sous forme d'article qui sera soumis à un journal avec comité de relecture, étudiera l'impact de l'extraction à la soude et à l'eau chaude sur les propriétés des composites ainsi que l'efficacité de ce nouveau type d'agent de couplage (combinaison lignines estérifiées-MAPE) entre la matrice (HDPE) et l'agent de renfort (les fibres d'écorces). Afin de tester l'applicabilité des matériaux pour une utilisation extérieure, un test normalisé de résistance aux cycles gel-dégel a été réalisé démontrant un potentiel intéressant avec une amélioration des propriétés mécaniques.

Ces études pourront être faites afin de développer de nouvelles connaissances dans le développement de ce nouveau matériau ou en vue de commercialisation du produit. Une note de recherche écrite pour le *Centre de recherche sur les matériaux renouvelables* (CRMR) est intégrée en annexe 1 de cette thèse, car elle représente des résultats indirectement liés au projet, mais permettant d'envisager de nouvelles perspectives à cette étude.

II. Méthodologie

II.1. Propriétés chimiques des fibres d'écorce

La composition chimique de l'écorce de l'épinette noire a été étudiée en déterminant les teneurs en cellulose, lignine hémicellulose (pentosanes), taux de cendre ainsi qu'en extractibles à l'eau, éthanol-toluène et à la soude. Afin de la caractériser chimiquement, l'écorce est tamisée pour conserver la fraction comprise entre les tamis de 40 et 60 mailles.

II.1.1. Extraction des écorces dans l'eau, solvant organique et inorganique

L'écorce est extraite avec trois solvants, un mélange normalisé éthanol anhydre-toluène (40:60) puis, après séchage à l'air, à l'eau chaude durant trois heures et une troisième, normalisée (ASTM D1109 [61]), à l'hydroxyde de sodium (NaOH, soude à 1%). Le mélange (éthanol anhydre-toluène) est un mélange azéotropique de l'alcool éthylique anhydre et du toluène. Ces proportions de mélange sont un litre d'alcool éthylique anhydre et 427 mL de toluène. Une détermination quantitative du pourcentage d'extractibles sur une fraction de la sciure est réalisée pour chaque extraction.

II.1.2. Cellulose

Le taux de cellulose dans les écorces est déterminé par la méthode de Kurschner et Hoffner [62]. L'écorce est soumise à l'attaque d'un mélange d'acide nitrique et d'éthanol. La lignine est transformée en produits nitrophénoliques solubles dans l'alcool et insolubles dans l'eau. Les hémicelluloses sont en grande partie hydrolysées, dégradées et passent en solution. La cellulose subit également une dégradation, mais négligeable, l'éthanol jouant un rôle de protecteur vis-à-vis de cette dernière.

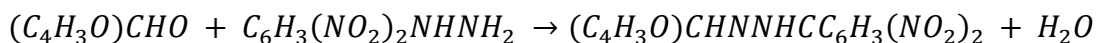
II.1.3. Lignines

Une variante non normalisée de détermination de la lignine Klason [62] modifiée à l'autoclave est employée. La lignine insoluble à l'acide sulfurique est déterminée par mesure de masse et la lignine soluble à l'acide mesurée par spectrophotométrie sur le premier filtrat.

II.1.4. Hémicelluloses (Pentosanes)

Afin d'obtenir une approximation de la teneur en hémicelluloses, l'évaluation des pentosanes selon la norme CPPA-G-12 utilise l'indice de furfural. La détermination des hémicelluloses est complexe, car seule une évaluation des pentosanes peut être obtenue : l'indice de furfural. L'écorce est soumise à l'attaque de l'acide chlorhydrique concentré (azéotrope à 131 +/- 0,5 g/L). Le furfural obtenu par action d'un acide sur les matériaux cellulosiques provient de plusieurs sources : des pentosanes, ou des acides uroniques qui accompagnent toujours les polyosides (abondants dans les matières pectiques), ou des hexosanes (de la cellulose par exemple) moins réactifs que les pentosanes, mais qui peuvent conduire à la formation de faibles quantités d' ω -hydroxyméthylfurfural.

Le rendement en furfural n'est pas quantitatif pour ces produits, cependant, il est possible de déterminer le rendement en furfural à partir de xylose et d'arabinose. Le furfural obtenu est dosé par action de la dinitro-2-4-phénylhydrazine sur le groupement aldéhyde.



Par pesée de l'hydrazone formée, il est possible de remonter au poids de furfural et en tenant compte du rendement en furfural, au taux de pentosanes.

II.1.5. Cendres

Le contenu en cendres est une détermination approximative du contenu en matière minérale et d'autres matières inorganiques se retrouvant dans les écorces. On détermine en réalité le résidu après une combustion complète de la matière organique. Le contenu en cendres sur les écorces non extraites est inspiré de la norme ASTM D 1102 [63]. Un four à moufle est employé pour cette détermination.

II.2. Procédé de fabrication des composites

II.2.1. Le mélangeur interne

Un mélangeur interne (*Haake Buchler Rheomix*, Figure II-1) a été utilisé pour préparer les composites biosourcés avec des fibres d'écorce d'épinette noire. Trois mélanges par formulation ont été réalisés pour pouvoir obtenir une caractérisation pertinente. Une vitesse de rotation de 60 rpm, à une température fixe de 160°C pendant 9 minutes pour obtenir un matériau le plus homogène possible. Le minutage utilisé a été le suivant :

- $t_0 = 0$ minute : Départ du cycle lors de l'incorporation du HDPE dans le mélangeur
- $t_1 = 3$ minutes : Ajout de l'agent de couplage à base de lignine et/ou du MAPE (dans l'ordre lignine puis MAPE lorsque les deux sont utilisés).
- $t_2 = 4$ minutes : Intégration des fibres d'écorce d'épinette noire pendant cinq minutes.
- $t_3 = 9$ minutes : Fin du cycle.



Figure II-1 Mélangeur interne de 40 cm³ (Haake Buchler Rheomix).

II.2.2. Réalisation des échantillons pour effectuer les caractérisations

Afin de pouvoir tester les bio-composites, la réalisation de plaques par thermocompression (Figure II-2) est la solution choisie, à cause de la faible quantité de matériel utilisée et des trop grandes pertes engendrées par l'utilisation de la machine de moulage par injection. Les paramètres de compression du matériel, conditionné pendant 48h à température ambiante, ont été : la température de 175°C avec une pression de trois tonnes pendant cinq minutes. Ces plaques, de 10 cm × 10 cm × 3 mm, sont ensuite refroidies dans la presse par circulation d'eau puis découpées aux dimensions ASTM standardisées pour toutes les différentes caractérisations voulues (flexion en accord avec ASTM D790 [64] et traction avec une éprouvette de type V selon ASTM D638 [65]).



Figure II-2 Presse hydraulique de thermocompression.

II.3. Propriétés physiques

II.3.1. Densité (Ultra-pycnomètre)

L'utilisation de l'ultra-pycnomètre « Ultrapyc 1200e Quantachrome », selon la norme ASTM D 2856 [66], permet la mesure de la densité des produits de base (HDPE, fibres d'écorce, lignine). Mais également les mesures de la densité de certaines formulations de WPC seront obtenues.

II.3.2. Densité (rayon X)

Pour mesurer la masse volumique des composites, un densitomètre à rayons X est utilisé avec l'équipement suivant : QMS Density Profile System v1.25. Cet appareil donne des informations sur le profil de densité en épaisseur de la formulation de WPC étudiée. Il est ainsi possible de vérifier l'homogénéité de ce matériau tout en caractérisant sa densité par une moyenne avec un écart-type.

II.3.3. Analyseur de fibres (FQA)

L'utilisation du FQA, disponible au laboratoire d'anatomie, permet d'obtenir des informations sur la longueur des fibres d'écorces, leur diamètre et le ratio de la longueur sur le diamètre (avec des corrections adaptées), ainsi que la distribution de ses dimensions caractéristiques dans les différents lots de fibres étudiées. La norme ISO 16065 – 2001 « Pâtes -- Déterminations de la longueur de fibre par analyse optique automatisée » est employée avec le système FQA code LDA 02.

II.3.4. Résistance au gel-dégel

Pour déterminer la dégradation des propriétés mécaniques après exposition aux cycles gel-dégel, des éprouvettes des composites sélectionnés ont été submergées sous l'eau pendant une période de 24 h. Elles ont ensuite été placées dans un congélateur à $-29\pm 2^{\circ}\text{C}$ pendant 24 h. Ce processus comprend un cycle hygrothermique. La procédure, correspondant aux normes ASTM D7031 et D7032 [67-68], a été répétée deux autres fois, pour un total de trois cycles. Une caractérisation complète (propriétés physiques et mécaniques) est faite avant et après ces essais pour déterminer la résistance au gel-dégel de chaque formulation dans le but de valider le potentiel des WPC pour une application extérieure.

II.3.5. Colorimétrie

Un appareil de colorimétrie (Color-guide 20 mm avec blanc standard de marque BYK-Gardner USA) a été employé afin de déterminer les valeurs L^* , a^* et b^* (sans unité) puis par simples calculs ΔL^* (sans unité), Δa^* (sans unité), Δb^* (sans unité) et ΔE^* (sans unité). L'appareil employé répond aux normes DIN 5033,

5036, 6174, ASTM D2244, E308, E1164 et ISO 7724. Ces valeurs permettront de définir avec précision le changement de couleur dû au test de résistance au gel-dégel, selon la formule (1). Quatre mesures ont été effectuées directement sur chaque placage avant et après le test. Les valeurs L, a* et b* étaient données directement par l'appareil. Les différences (Δ) en terme de L, a* et b* donneront des informations sur la modification en clarté (L), niveau de rouge (a*) et niveau de jaune (b*). Le changement de couleur global est évalué par le ΔE dont la formule est donnée ci-dessous :

$$\Delta E = \sqrt{(L_{av.}^* - L_{ap.}^*)^2 + (a_{av.}^* - a_{ap.}^*)^2 + (b_{av.}^* - b_{ap.}^*)^2} \quad (1)$$

où L* = Niveau de clarté de 0 (noir) à 100 (blanc).

a* = Gamme de l'axe rouge (valeur positive) au vert (valeur négative): 0 = neutre.

b* = Gamme de l'axe jaune (valeur positive) au bleu (valeur négative): 0 = neutre.

av. = avant test de résistance au gel-dégel

ap. = après test de résistance au gel-dégel

ΔE = Distance entre deux couleurs placées dans l'espace L*,a*,b* de CIELab.

II.3.6. Microscopie électronique à balayage

Un microscope électronique à balayage (MEB) JEOL JSM-840A est utilisé pour les caractérisations morphologiques. Chaque échantillon WPC sera brisé à l'azote liquide afin d'obtenir une surface propre avec une zone de rupture nette pour l'observation. Pour permettre l'observation, la surface sera revêtue avec un alliage d'or/palladium à basse pression. La tension utilisée sera de 15 kV en utilisant différents agrandissements.

Lors d'un examen à spectroscopie de rayons X à dispersion d'énergie (EDS), le module d'analyse émet des rayons X ayant des caractéristiques d'énergie de chaque élément. La détection et la mesure de l'analyse élémentaire ont une limite de détection de 1%. L'EDS peut également fournir une analyse qualitative de la composition élémentaire de la région sélectionnée sur l'observation au MEB. Il est important de noter qu'il

n'y a pas de détection d'élément en dessous du carbone (C) en utilisant cet équipement, ainsi l'hydrogène (H) n'est pas observable. Ce module est utilisé pour identifier chacun des composants de nos WPC.

II.4. Propriétés thermiques des composites et de leurs constituants

II.4.1. Calorimétrie différentielle à balayage (DSC)

L'appareil de calorimétrie différentielle à balayage (DSC) est utilisé pour déterminer le taux de cristallinité du polymère [17], sa température de fusion et de cristallisation. Le programme de contrôle de la température est composé de trois étapes, une première montée en température de 50 à 200°C avec un chauffage de +10°C/min puis une diminution de la température de 200 à 100°C avec un refroidissement de -10°C/min et finalement une remontée en température de 100 à 200°C avec un chauffage de +10°C/min. Cette analyse pourra être utile pour suivre son taux de cristallisation dans les composites bois-plastique réalisés. Ce test est un outil d'interprétation pour expliquer l'interaction entre l'agent de couplage, les lignines et les fibres d'écorces sur la cristallisation du polyéthylène.

II.4.2. Analyse thermogravimétrique (TGA)

Les tests thermogravimétriques vont fournir des informations nécessaires pour définir et valider la plage de températures à utiliser lors du procédé de fabrication et déterminer la résistance thermique des matériaux testés. La plage de température programmée pour la TGA est de 50°C à 900°C dont le chauffage est régulé à +10°C/min sous atmosphère d'azote (50mL/min). L'exploitation de cette technique, en utilisant la dérivée du signal (DTG), permettra une analyse compositionnelle [69] du matériau ainsi que la détermination de la température(s) de décomposition et la stabilité thermique.

II.5. Propriétés mécaniques des composites

II.5.1. Flexion trois-points

Les propriétés en flexion (module de Young, contrainte à la rupture ou contrainte maximale, élongation à la rupture ou à la contrainte maximale et contraintes de cisaillement) ont été déterminées selon la norme ASTM D790, calculé selon les formules (2) et (3), sur des échantillons, des composites fabriqués avec le

mélangeur interne, ayant $80,0 \times 12,8 \times 2,5 \text{ mm}^3$ dimensions avec une distance entre les supports de 60 mm avec une vitesse de traverse de 10 mm/min. Six répétitions par formulation ont été effectuées en utilisant un modèle de banc d'essai mécanique universal-5565 (Instron, USA) avec une cellule de charge de 50 N afin d'avoir une précision optimale.

$$\sigma_R = \frac{3F_R D}{2bh^2} \quad (2)$$

$$\varepsilon_R = \frac{6hY_R}{D^2} \quad (3)$$

Avec F_R = force à la rupture (ou force maximale ou force à la limite de linéarité),

Y_R = flèche correspondante,

D = distance entre appuis,

b = largeur de l'éprouvette,

h = épaisseur de l'éprouvette.

Le module d'Young E peut être calculé à partir de la pente F/Y (formule (4)) de la tangente à l'origine de la courbe force F -flèche Y , suivant la relation :

$$E_R = \frac{D^3}{4bh^3} \frac{F}{Y} \quad (4)$$

On notera aussi que pour une sollicitation en flexion trois points, l'effort tranchant engendre non seulement des contraintes normales de traction-compression, mais également des contraintes de cisaillement maximales (τ_m) données par la relation :

$$\tau_m = \frac{3F}{4bh} \quad (5)$$

L'influence des contraintes de cisaillement sur la déformation de l'éprouvette et sur la rupture peut être notable, afin de vérifier son impact, ces contraintes seront calculées dans la dernière partie de cette étude.

II.5.2. Traction

Les propriétés en traction (module de Young, contrainte à la rupture ou contrainte maximale et élongation à la rupture ou à la contrainte maximale) ont été étudiées selon la ASTM D 638, calculé selon les formules (6) et (7), sur des éprouvettes de type V. Six répétitions par formulation ont été effectuées en utilisant un banc d'essai mécanique universal-5565 (Instron, USA) avec une cellule de charge de 500 N.

$$\sigma = \frac{F}{el} \quad (6)$$

$$\varepsilon = \frac{L_f - L_0}{L_0} \quad (7)$$

Le module d'Young correspond à la pente à l'origine de la courbe contrainte - allongement obtenu à faible vitesse (1 mm/min), ou plus précisément, à la pente de la droite passant par deux points de la loi de comportement correspondant à deux valeurs de déformation prescrites (0,25 % et 0,5 %). Il est également nécessaire de vérifier la linéarité de la courbe de traction lors du calcul de ce module, en s'assurant d'une corrélation linéaire à plus de 99%. Ces prérogatives permettent de répondre aux critères de la loi d'élasticité qui est la loi de Hooke.

III. Lignine industrielle Kraft: un agent de couplage potentiel pour les composites bois plastique (WPC)

Chapter 11 (pages 283-308):

Esterified Kraft Lignin: A Potential Coupling Agent For Wood Plastic Composites (WPC)

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In:

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III.1. Résumé

L'utilisation de fibres naturelles, en particulier celles de composition lignocellulosique, comme renfort dans des matrices de polyoléfine a fait l'objet de nombreuses études au cours de la dernière décennie. Il a été démontré qu'il est important d'utiliser un agent de couplage adapté pour chaque matrice polyoléfine/fibre. Les agents de couplage examinés jusqu'à présent sont des dérivés de polyoléfine et la référence est de la famille des polyoléfines maléates (MaPO) provenant de ressources pétrochimiques qui visait à améliorer la compatibilité entre une matrice thermoplastique et de fibres lignocellulosiques. Dans cette étude, la capacité d'estérification (avec des anhydrides succiniques et d'acide maléique) de lignines Kraft afin d'améliorer leur potentiel d'action comme agents de couplage entre les fibres naturelles et polyéthylène haute densité (HDPE) a été menée. Les propriétés mécaniques (résistance à la traction et en flexion) et la morphologie (microscopie électronique à balayage, MEB) ont été utilisées pour évaluer les performances des composites bois-plastiques (WPC). Les résultats obtenus indiquent que la lignine Kraft précipitée de liqueur noire avec du dioxyde de carbone puis modifiée par estérification possède un potentiel pour atteindre l'efficacité d'un agent de couplage commerciale (polyéthylène maléate: MAPE) lorsqu'il est appliqué à du HDPE contenant des fibres d'écorce d'épinette noire (*Picea mariana*). Les procédures expérimentales utilisées dans cette recherche ont été conçues pour définir la proportion optimale de lignine Kraft estérifiée à fibres d'écorce d'épinette noire et de produire des WPC de bonne qualité. Le mécanisme par lequel les lignines Kraft estérifiées ont agi est proposé, permettant d'améliorer les propriétés des composites étudiés. Il peut être prévu que la production de ce type de WPC contribuera à la séquestration du CO₂ à plusieurs niveaux : par précipitation de lignine de la liqueur noire qui consomme du CO₂ et en remplaçant les polymères synthétiques (matrice et agent de couplage conventionnel) d'origine pétrochimique par des fibres naturelles renouvelables (écorces) et des polymères naturels (lignine).

III.2. Abstract

The use of natural fibers, particularly those of lignocellulosic composition, as reinforcement in polyolefin matrices has been the object of numerous studies in the last decade. It has been demonstrated that it is important to use a coupling agent adapted for each fiber/polyolefin matrix. The coupling agents examined so far are polyolefin derivatives and the reference is maleated polyolefin (MaPO) derived from petrochemical resources which was designed to improve compatibility between a thermoplastic matrix and lignocellulosic fibers. In this study, the capacity of esterified (with succinic and maleic acid anhydrides) and neat Kraft lignin to act as coupling agents between natural fibers and high density polyethylene (HDPE) was investigated. Mechanical properties (tensile and flexural) and morphology (scanning electron microscopy, SEM) were used to examine the wood plastic composites (WPC) performance. The obtained results indicate that Kraft lignin precipitated from black liquor with carbon-dioxide and modified through esterification has a potential to reach the efficiency of a commercial coupling agent (maleated polyethylene: MAPE) when applied in HDPE containing black spruce (*Picea mariana*) bark fibers. The experimental procedures applied in this research were designed to define the optimal proportion of esterified Kraft lignin to black spruce bark fibers and produce good quality WPC. The mechanism by which the esterified or neat Kraft lignins are enhancing the properties of the studied composites is proposed. It can be anticipated that the production of this type of WPC will contribute to the sequestration of CO₂ on several levels: through precipitation of lignin from black liquor which consumes CO₂ and by replacing synthetic polymers (matrix and conventional coupling agent) of petrochemical origin with renewable natural bark fibers and lignin polymers.

III.3. Introduction

Composites based on natural materials have been used since the Egyptian era. Indeed, that civilization had already used mixtures of straw and loam which, after sun drying, were used in construction, to build family houses [1]. In 1896, the first aeroplane seats and fuel-tanks were made of natural fibers with small quantities of polymeric binders. In India, the government promoted projects using jute reinforced polyester resins for buildings (Madras-House in 1978). In the past decades, the whole society became more sensitive to the environmental impact of petrol derived chemicals, with important contribution of non-governmental organizations (NGO) such as Greenpeace. This collective consciousness is thus pushing governments to legislate more stringent rules promoting environmental protection for future generations.

Composite materials are defined as a combination of two or more materials which typically consist of a matrix (polymeric, metallic or ceramic) and a reinforcing or filler phase (sheets, fibers, particles or flour). In this chapter, only composites containing a polymeric matrix are discussed. Traditional composite structures containing glass, mica, talc, calcium carbonate, carbon, or aramid fibers are considered disadvantageous because of potential environmental problems related to the fact that these materials are not biodegradable, and may have possible dermal and respiratory irritation effects [8]. Furthermore, their removal after the end of service is difficult [70]. These unwanted properties of the traditional materials explain the growing interest for composites containing renewable natural fibers. The advantages of natural fibers are multiple: lower cost and density, better specific strength, thermal insulation properties, better flexibility and less machine wear during processing than that of traditional composites, no health hazards (no dermal or respiratory irritation), possibility of recycling and good biodegradability [6, 8, 71]. Therefore lignocellulosic materials are regarded as extremely beneficial from an environmental point of view. The use of lignocellulosic fibers as reinforcement in polyolefin matrices has been studied in several wood plastic composites (WPC) where the name "wood" stands not just for wood but also for any lignocellulosic fibers which can be integrated in a matrix. Potential WPC applications are in aerospace, packaging, electronic components, marine, construction and automotive industries [27]. The results of the studies on WPC indicate the importance of using a coupling agent adapted for each lignocellulosic fiber / polyolefin matrix pair. The coupling agents examined included polyolefin derivatives, such as maleated matrices, silanes as organic-inorganic agents, isocyanate and terpolymers [1, 45, 48-50, 72]. The coupling agents studied were designed to improve compatibility between thermoplastic matrices and lignocellulosic fibers. Thus, the potential of butyrate Kraft lignin as compatibilizing agent for natural fiber in styrene matrix was investigated [73]. Here, we report on a

preliminary analysis of the capacity of esterified Kraft lignins (with succinic and maleic acid anhydrides) to act as coupling agents between black spruce bark fibers and HDPE [74] in comparison to the industrial coupling agent, maleated polyethylene (MAPE).

III.4. Natural fibers

There are three main categories of natural fibers: mineral, animal and plant fibers [9]. For the sake of space limitation, only two examples per category are presented.

III.4.1. Animal fibers

Silk is an animal fiber. It is obtained from cocoons made by the larvae of the silkworm *Bombyx mori* reared in captivity (sericulture) [9]. Another kind of silk comes from spiders. They are the strongest animal fibers known so far. The Alpaca (*Vicugna pacos*) is the main special fiber produced in South America (Peru, Bolivia and Chile). Alpaca fibers are known for their fineness, softness, exceptional warmth, hygroscopic features, resistance, elasticity, and natural colors. Their soft touch property is only related to the fineness of this fiber, but also to the arrangement of the scales along the fiber [75].

III.4.2. Mineral fibers

Asbestos is represented by a group of minerals resistant to heat/fire and is also a poor conductor of electricity. Amosite asbestos was generally used in mixture with cement as building material because of fire retardant and thermal insulation properties [9]. Nonetheless, the Joint Policy Committee of the Societies of Epidemiology (JPC-SE) [76] banned this material because prolonged inhalation of asbestos fibers can cause serious illnesses including malignant lung cancer, mesothelioma, and asbestosis (a type of pneumoconiosis). Mica is the name of a group of minerals; i.e. silicates group from the subgroup of phyllosilicates, formed mainly of aluminum silicate and potassium. The properties of mica such as transparency, heterogeneity, as well as the thermal and insulation properties, make it good material for acoustic insulation (automobiles) or for fire retardant barriers (fire doors). Mica is used as a dielectric

(insulator) in high frequency and high voltage capacitors. Deshmukh and Rao [77] studied mica dielectric properties in a polyvinyl chloride (PVC) matrix by manufacturing electric cables and wires.

III.4.3. Plant fibers

There are six types of plant fibers: stem fibers (e.g. jute extracted from the ribbon of stem, used for packaging and decorative items), leaf fibers (e.g. sisal from *Agavaceae*, mainly used for mats and other reinforcement materials), seed fibers (e.g. cotton in textile industry, hemp for ropes and sails or textiles), fruit fibers (e.g. coir as coconuts, strong and light, fibers obtained from the husk of the fruit of coconut palm), stalk fibers (e.g. extracted from stalks of plants such as rice, bamboo or grass and cereal straws), and wood fibers which will be discussed in this chapter [9]. Wood is a natural material used by humans since the prehistoric era, and it is green and renewable and highly variable depending on the species (e.g. there are more than 10,000 known wood species) [78]. There are two main subgroups: hardwoods and softwoods. The growing and environmental conditions have also influence on the physical, mechanical and chemical properties of wood, which amplifies their variability even within the same species. Wood is a highly hygroscopic material, which is the main problem limiting its use. To solve this problem, a polymer matrix is used to protect wood fibers from water in WPC and, in addition, to make their properties more homogeneous. Mechanical and physical properties of wood are related to its anatomy. Good knowledge of wood anatomy is important for adequate selection of the manufacturing method of engineering new materials. Direct use of softwoods is easier due to their simpler structure (compared to hardwoods), based essentially on two cell types (tracheid and parenchyma) and relatively little variation in structure [79]. Hardwoods have greater structural complexity because of a greater number of cell types and a greater degree of variability within cell types [80]. The single most important distinction between the two types of wood is that hardwoods have characteristic vessel elements [81]. Wood and vascular plants are composed of cellulose, hemicelluloses, lignin and/or pectin, wax, extractives, and their chemical compositions vary depending on species and plant (tree) part. A comparison of the chemical composition of softwoods versus hardwoods [82] is presented in Table III-1.

Table III-1 Comparison of general chemical composition of softwood versus hardwood.

	Softwoods	Hardwoods
Cellulose	40-50%	40-50%
Lignin	25-35%	20-25%
Hemicelluloses	20-30%	25-40%
Extractives	0-25%	0-25%

Additionally, the chemical composition of wood varies across the cell walls [79-83]. Mechanical and physical properties of wood are dependent on both anatomical and chemical characteristics. Bark, together with sawdust, represents a co-product of wood transformation and is only marginally studied. It is nowadays mainly used to generate energy by combustion. Bark is generally considered to have higher lignin and extractives content than wood, which is related to the protection role of this specialized part of the tree against bacterial, fungal and other pathologies. Bark anatomy is more complex than that of wood [84-85]. One of the most important differences between wood and bark is their functionality. Wood is the vital and structural part of a tree, while bark acts as a barrier against exterior environment and contaminations.

Animal fibers have a large variability which is at the origin of the success of the textile industry, but their use in composites is rare. However, the know-how acquired in the weaving of these fibers could provide original ideas of how to explore the engineering and development of WPC with improved properties depending on the targeted applications. Mineral fibers have been integrated in composites for construction, such as asbestos, but their adverse effects on human health and skin or respiratory irritation resulted in their reduced use. New applications of mineral fibers are proposed, such as the manufacture of electric wires with mica which could further enhance the application of this type of material in composites.

Only plant fibers are discussed in more detail here.

III.5. Treatments of natural plant fibers destined for WPC

Treatments of natural plant fibers are generally required in order to enhance their compatibility with polyolefin matrices. These treatments are usually aimed to purify, oxidize and/or activate the surface of lignocellulosic fibers. Thus, corona, dielectric barrier and plasma discharges and, more recently, laser, γ -ray and UV irradiations have been explored [1, 27, 48-50]. Corona and plasma treatments are the most commonly used and have been demonstrated to be the most efficient techniques to improve the compatibility of lignocellulosic fibers with the matrix. Chemical treatments with silane, isocyanate, siloxane,

alkaline, redox agents or maleate are designed to improve the interface between the polar and hydrophilic natural fiber with the commonly nonpolar and hydrophobic polymer matrix. Without physical or chemical or both treatments, the fiber surface would remain inert for interaction with polymers.

III.5.1. Physical treatments

Physical treatments change structural and surface properties of the fiber and thereby influence mechanical bonding to polymers. Corona treatment is one of the most effective techniques for surface oxidation activation [48-50]. To obtain good adhesion to materials having low surface energy (i.e. low or non-polar materials like PP, PE), high voltage and high frequency electrical discharge in close proximity to the surface to be treated is created. This high energy corona discharge is causing changes in molecular bonds on the surface, leading to the formation of free radicals and other reactive species in the highly active corona discharge environment. Corona-treated fibers were demonstrated to participate in surface cross-linking with a polymeric matrix [1]. Owing to difficulties in effective treatment of three-dimensional objects with corona discharge, the increase of polarity of treated matrices is relatively small [50]. The effect of corona treatment on PET film hydrophobicity can be evaluated by contact angle measurements as described in the literature [86].

Plasma treatment is another potential way to improve interface adhesion between the matrix and natural/plant fibers. Plasma treatment is similar to corona treatment. Low temperature plasma treatment causes mainly chemical implantation, etching, polymerization, free radical formation, and crystallization, whereas sputter etching brings about chiefly physical changes such as surface roughness leading to increased adhesion and decreased light reflection [49]. Low temperature plasma uses electron, ion, radical and excited molecules produced by electrical discharge, to modify the treated surface. Low temperature plasma can be generated under atmospheric pressure or in the presence of selected gas. The property of plasma is exploited to induce changes on the surface of a material. A variety of surface modifications can be attained depending on the type and nature of the gases used. Reactive free radicals and groups can be produced by plasma treatment. The surface energy can be increased or decreased and surface cross-linking can be introduced using unstable radicals that convert functional groups such as alcohols, aldehydes, ketones and carboxylic acids. Electrical discharge methods are used for cellulose fiber

modification in order to decrease the melt viscosity of cellulose-polyethylene composites and to improve the mechanical properties of WPC [49].

III.5.2. Chemical treatments

One of the oldest and most frequently used chemical treatment methods is fiber mercerization which is an alkaline treatment of lignocellulosic fibers. The parameters for this kind of treatments include the type of chosen solution (generally sodium hydroxide, NaOH), solution concentration, as well as time and temperature [49]. The chemical effect of mercerization is the solubilisation of small quantities of remaining lignin and hemicelluloses from the treated fibers. These are attacked during the mercerization process by disruption of the hydrogen bonding network structure of the treated fibers. Physically, it may reduce fibers diameter, thus changing (increasing) aspect ratio and roughness [50, 72]. These chemical modifications result in an improvement of interfacial adhesion between the lignocellulosic fibers and the matrix because of the higher number of reactive sites available and a lower polarity (due to the -OH disruption as shown in Figure III-1).



Figure III-1 Chemical reaction during an alkaline treatment onto lignocellulosic fibers.

These physical evolutions will improve roughness and theoretically improve WPC strength because of increased aspect ratio as discussed by Faruk *et al.* [50] and Kalia *et al.* [45] in their reviews. Also, it can improve rot resistance and hydrophobicity of the composites.

Isocyanate treatment consists of mixing lignocellulosic fibers into a solution of 1,6 diisocyanatohexane or another isocyanate at different concentrations [87]. This isocyanate will react with the hydroxyl group on the fibers surface. Through this reaction mechanism, the free superficial -OH groups of cellulose react with the -NCO groups of diisocyanate. The polarity and the hydrophilicity of the fiber are reduced and this contributes to the improvement of the interface between the matrix and the plant fibers. In the study of Qiu *et al.* [85], this treatment was applied to a maleated polypropylene (MAPP) coupling agent with the aim of improving its efficiency. An improvement of the WPC was attributed to an increased interface adhesion

between the fibers and the matrix (polypropylene, PP). Without the addition of a maleated matrix, Botaro and Gandini [88] showed that isocyanate treatment on cellulosic fibers results in grafting alkenyl functions onto the surface and leads to the creation of covalent bonds with a polymeric matrix.

III.6. Coupling agents of natural plant fibers destined for WPC

III.6.1. Coupling agents for biocomposites: WPC

The first coupling agent was developed by Bridgeford (1963) who grafted olefin monomers onto wood fibers with a catalyst system containing ferrous cations and hydrogen peroxide. Lu *et al.* [4] published a review article on coupling agents available for WPC and proposed a classification in three categories: organic agents, inorganic agents, and organic-inorganic agents. In 2000, there have been already tried 10 subclasses of organic agents (acrylates, amides, imides, anhydrides, chlorotriazines, epoxides, isocyanates, organic acids, monomers or polymers, and copolymers) to produce 38 different coupling agents. Two subclasses of inorganic-organic coupling agents (silanes and titanates) and one inorganic coupling agent (sodium silicate) were also studied.

Organic coupling agents can react with the –OH groups on the surface of lignocellulosic fibers to form covalent or hydrogen bonding with their own grafted functions/groups. The other functionalizations are to modify the polymer matrix by grafting copolymerization or crosslinking at the interface in order to obtain a strong adhesion between the matrix and the fibers. Inorganic coupling agents do not truly act for this purpose, but allow improving WPC properties by their dispersive actions. This reaction mechanism is potentially counteracting the surface polarity of natural fibers and improving the interface between the non-polar matrix and the polar natural fiber. Organic-inorganic coupling agents have a hybrid structure. Generally, one metallic function combined to an organic polymeric partner surrounding the titanium atom (for example). It is the functionality of the organic part that determines the effectiveness of this kind of coupling agent in WPC [4].

III.6.2. New developments in coupling agent formulations

An application of a new chemical treatment on the fibers using the redox system H_2O_2/Fe^{2+} to graft methyl methacrylate (MMA) onto thermomechanical pulps from softwoods and hardwoods has been proposed [89]. In fact, it represents an improvement of the first coupling agent developed by Bridgeford in 1963. Other systems are under development, such as grafting with reagents bearing two (or more) identical reactive functions [4, 45, 48]. The hypothesis is that only one of the functions can react with a fiber –OH groups, while others will be available to copolymerize with the polymer matrix [48]. Actually, most of the coupling agents are bi-functional, Panthapulakkal *et al.* [72] explored the application of a terpolymer as coupling agent. Again, coupling efficiency depends on the nature of the interface formed between the matrix and the natural fibers used. These new coupling agents have been tried with rice-husk in HDPE and both were found effective for this composite system.

II.6.2.a. Silane coupling agent

The general formula $R-(CH_2)_n-Si(OR')_3$ represents a silane coupling agent molecule where $n = 0-3$, OR' is the hydrolyzable alkoxy group, and R the functional organic group. The organic part is reacting with the polymeric matrix and co-polymerizing and/or forming an interpenetrating network. The OR' groups undergo hydrolysis and then could participate in condensation reactions forming bonds or interacting with the hydroxyls of the natural fiber resulting in polysiloxane structures formation [1].

Abdelmouleh *et al.* [53] used LDPE and five types of natural fibers: Avicel fibers from Sigma-Aldrich®, bleached soda softwood (pine) fibers, alfa fibers (*Alfa tenassissima*) and two dissolving pulp cellulose fibers (Technocel-2500 and Technocel-50). They chose three commercial silanes (γ -methacryloxypropyltrimethoxysilane [γ -MPS], hexadecyltrimethoxysilane [HDS], and γ -mercaptoproyltrimethoxysilane [γ -MRPS]) at different concentrations in the composites to determine the best coupling agent. The addition of these silanes contributed to the improvement of some of the mechanical properties of WPC, the best results for strength being obtained with γ -MPS probably due to the formation of better interface network. Raj *et al.* [90] studied the effect of two different functionalizations on silane molecules, vinyl (VTS) and methacryl (MPS), at a level of 4 wt. % of this coupling agent in a HDPE matrix with 30% content of chimicothermomechanical pulp (CTMP) of aspen. Better efficiency was

determined for the addition of silanes with vinyl function (VTS) [90] showing a 45% improvement of tensile modulus and 70% in tensile strength, as compared to the silanes with methacryl function (MPS) showing the improvement of only 40% in tensile strength and 15% in the tensile modulus for the WPC system were determined (ASTM D638). In the studies of Wong and Varall [91] and Bengston and Oksman [92-93], the use of 40% wood flour in HDPE with 2 wt. % silane (VTS) improved by 90% flexural strength (ASTM D790), 20% flexural modulus and 100% impact strength (ASTM D256). Valadez-Gonzalez *et al.* [94] and Herrera-Franco and Valadez-Gonzalez [71, 95] used 1 wt. % silane (VTS) as coupling agent in HDPE and 20% henequen fibers and 30% improvement in tensile strength was found in each of these studies.

II.6.2.b. Maleated matrices as coupling agent

The traditional industrial method to produce maleated polyolefins (MaPO) was briefly described by Keener *et al.* [7] as a reactive extrusion process. This extrusion process is typically realized in a short residence time with the selected polyolefin, maleic anhydride, and peroxide. These conditions allow for the acid number of the polymer to be controlled to a desired level, independently of the viscosity. Patented processes have been developed to manufacture MaPO. In a recent study, Zhang *et al.* [96] developed a new economical method, to prepare maleic anhydride grafted polypropylene (PP-g-MAH) in suspension with high polymer content and easy product purification with a well-defined molecular structure. A good efficiency indicator is the amount of maleic anhydride functions determined in the polymer. The ASTM D1386 standard presents a method to determine the acid number of maleic anhydride grafted polyolefin. The protocol for getting the same acid number by saponification was described in the literature [7]. Once grafted onto the selected polyolefin, the MaPO can react with the fibers through esterification [1, 6, 26] via the –OH groups available on their surfaces, as shown in Figure III-2.

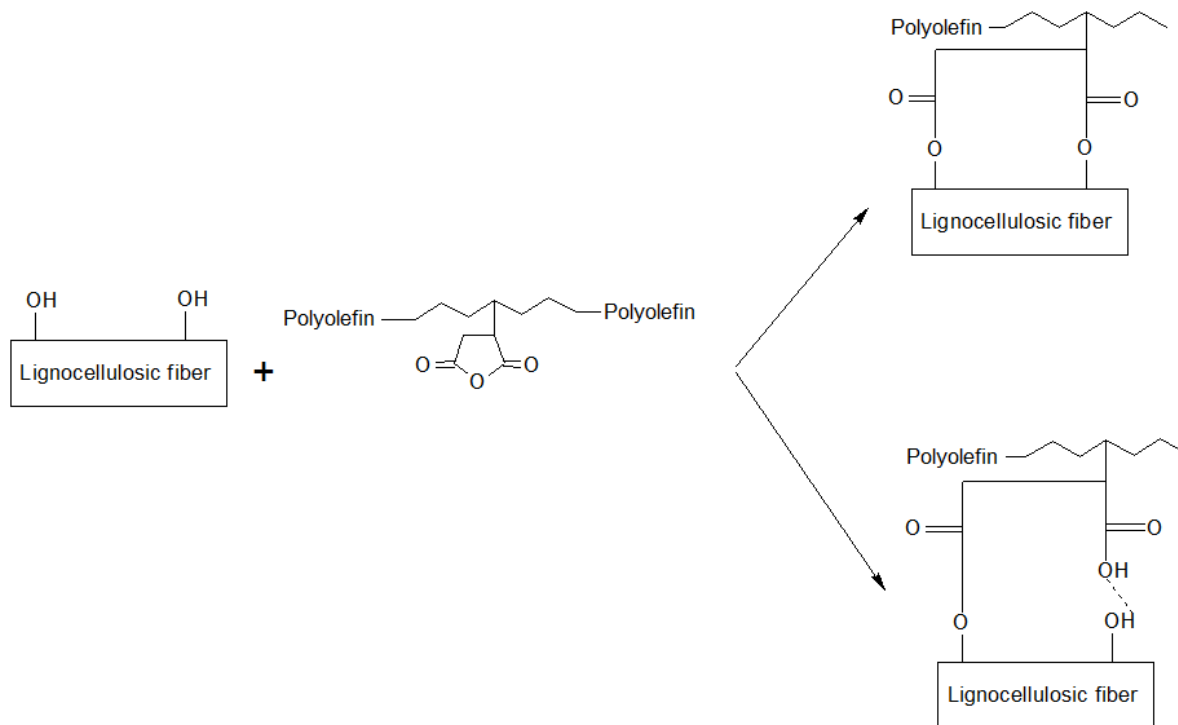


Figure III-2 Maleated polyolefin (MaPO) grafting mechanism on a lignocellulosic fiber.

Li and Matuana [6] compared the efficiency of maleated anhydride versus acrylic acid functionalized coupling agent in wood flour – polyolefin composites. They studied these coupling agents in polyethylene (HDPE) versus polypropylene (PP) matrix and found that in the case of HDPE, the coupling agent should be based on the same polyolefin (PE in this case) and that the maleated functionalization gave a better coupling agent than acrylic acid. Park *et al.* [8] studied the interface of modified jute and hemp in PP using two coupling agents (silane and maleic anhydride polypropylene, MAPP), and evaluated the effect of alkaline versus thermal pre-treatments on these fibers. They showed that MAPP was better in this kind of WPC and that alkaline pre-treatment was a good solution to improve the properties [91, 94] of the obtained material. Mechraoui *et al.* [97] used PP with hemp fibers and MAPP as coupling agent at a large range of concentrations based on bark fibers mass. They found that the optimal quantity of MAPP for this system was 2-4wt. % (fibers weight basis).

In conclusion, an efficient coupling agent can be defined as:

- A molecule capable to create bonds both with matrices and fillers (such as lignocellulosic fibers). These agents are usually created through adapted grafted functionalization with the chosen

polymer matrix or based on it to ensure a strong adhesion and wettability between the coupling agent and the matrix.

- The same molecule should have a good affinity for –OH groups on the surface of natural plant fibers which should lead to formation of covalent bonds or at least strong hydrogen bonds between the coupling agent and the fibers.

The results presented so far indicate that MaPO coupling agents seem to be the best solution for composites containing natural fibers. Therefore, we explored the concept of HDPE composites containing black spruce bark fibers and natural coupling agents based on Kraft lignin in comparison to those containing MAPE alone.

III.7. Utilization of Kraft lignin as coupling agent

A decline in demand for pulp and paper products has forced this industry to integrate the concept of bio-refinery in existing plants. The valorization of industrial lignin is one of such solutions. We are presenting here a study of Kraft lignin used as coupling agent in WPC based on high density polyethylene (HDPE). Black liquor from Quebec pulp and paper industry (Kruger Wayagamack) was used to precipitate Kraft lignin which was examined in composite application. Its characterization is described in detail by Schorr *et al.* [98]. Two lignin modifications are presented here: esterification with maleic or succinic acid anhydride. Butyric, stearic and maleic esterifications were previously explored [73] for Indulin AT, a commercial Kraft lignin obtained from Westvaco Corporation. Maleic esterification was also performed on Wayagamack Kraft lignin precipitated in our laboratory using CO₂. The results obtained for esterified Indulin AT Kraft lignin samples indicated that maleic esterification produced coupling agents with better performance than esterification with butyric or stearic acid anhydrides. Therefore, the Wayagamack Kraft lignin esterified with maleic anhydride was further explored as coupling agent in comparison to the esterified (with the same anhydride) commercial Indulin AT Kraft lignin for production of WPC based on HDPE containing black spruce bark fibers. The combination of modified lignin with maleated polyethylene (MAPE) is not explored in the literature. Thielemans and Wool [73] examined the potential of butyrate Kraft lignin as coupling agent in a styrene matrix with flax fibers and obtained a 40% increase in flexural strength with 5 wt. % of modified lignin based on fiber mass (ASTM D790). Their results indicated that the improvement in stress transfer

between the polymeric matrix and the natural fiber depends on the type of fiber used in WPC. The design of wood fiber composites studied in this research is based on several principles of sustainable chemistry and engineering [24]: utilisation of renewable resource-residues from wood processing (bark), while reducing the use of petrochemical origin polymers and contributing to the sequestration of carbon dioxide through lignin precipitation from black liquor.

III.7.1. Lignin precipitation, esterification and application in WPC

In Latin, the word lignum mean wood and it is the botanist A.P. Candolle (1778-1841) who is believed to be the first to use the term “lignin” [99-100]. Lignin is the most abundant polymer containing an aromatic moiety in nature [99-106]. The structure of lignin is based on three types of monolignols: p-coumaryl alcohol (at origin of hydroxyphenyl-H-units), coniferyl alcohol (G-unit for guaiacyl), and sinapyl alcohol (S-unit for syringyl). These monolignols are combined to form different inter-unit linkages C-O-C such as β -O-4, α -O-4, 4-O-5 or C-C linkages such as β -5, 5-5, β -1 or β - β [100-101]. All these combinations are at the origin of the molecular complexity of lignin. Nevertheless, the most important linkage is β -O-4. Lignin structure is complex not only due to its multiple units, but also to variability caused by family group of the plants; e.g. softwood lignin is composed mainly of G unit whereas hardwood and grass lignins contain different ratios of G, S and H units [99-102].

The most prevalent pulping process worldwide is the Kraft process. For that reason, our focus was on this type of lignin source. Moreover, the highly engineered Kraft process has the advantage to include a recovery system at every level of production. This is the key for an economic and environmental performance of this technology which generates an excess of energy relative to its needs and produces exportable electricity [103]. The recent LignoBoost® process [22, 107] allowed Kraft pulp mills to control their overproduction of black liquor and use a precipitation process based on CO₂ available from the Kraft pulp mill [23, 108-109]. The fields of application of Kraft lignin can be extended to new products such as WPC, as proposed here. In order to enhance the compatibility with the polymer matrix (HDPE) and bark fibers, the esterification of Kraft lignin with maleic or succinic acid anhydride was applied in this study. Other systems have been explored in the past for modification of wood fibers in order to enhance their compatibility with the polymer matrices.

The commercial Kraft lignin (Indulin AT) developed as described in our preliminary study in 2012 [110] has been incorporated as coupling agent (5 wt. % of bark fibers mass) into a WPC system based on HDPE (70%) and black spruce bark or yellow birch bark fibers (30%). Compared to the integration of 5 wt. % MAPE (based on bark fibers mass), the incorporation of non-modified Indulin AT had negative effect on all tensile properties of HDPE composites containing yellow birch and black spruce bark fibers (Table III-2).

Table III-2 Effect of the introduction of commercial Kraft lignin (Indulin AT) in WPC on tensile properties compared to a formulation without any coupling agent.

Bark	Formulation			Gain (%)		
	Lignin	MAPE	Bark species	Modulus	Stress at Break	Strain at Break
30%	5% <i>Indulin AT</i>	0%	BSP	12	-20	15
30%	0%	5% MAPE	BSP	5	43	31
30%	5% <i>Indulin AT</i>	0%	YB	-90	41	-24
30%	0%	5% MAPE	YB	13	25	24

BSP: black spruce, YB: yellow birch.

The results obtained in that study indicated that it was necessary to chemically modify Kraft lignin in order to improve its capacity to act as a coupling agent.

III.7.2. Esterification of wood and lignin for applications in WPC

The esterification of southern yellow pine (*Pinus spp.*) was explored using maleic anhydride versus succinic anhydride at different temperatures between 60 and 200°C [111]. The aim was to determine which one was the best to esterify wood by measuring acid values, saponification values of neat and esterified wood, monoester and the diester content for both esterifications. Hon and Xing [111] found that beyond 140°C a large amount of diester was formed which proved the efficiency of the esterification. However, it was impossible to determine at which of wood components the esterification took place. It was also impossible to evaluate if the treatment was effective for long term (stable) or was reversible. We developed a protocol for lignin esterification and the determination of the effectiveness of esterification based on Stevanovic *et al.* [110]. In 2008, Bouafif *et al.* [112] examined the esterification of wood particles from: eastern white cedar (*Thuja occidentalis*), black spruce (*Picea mariana*), wood of jack pine (*Pinus banksiana*) and bark of jack pine, using MAPE as esterification agent and matrix in this WPC. Their study showed that lignin

concentration may be the major hindrance for esterification since bark fibers (particle having the highest lignin content) did not show a response to the MAPE treatment.

In a patent published in 2010, Gifford *et al.* [113] presented methods to esterify softwood Kraft and organosolv lignins with various mixtures of reactants (such as acetic anhydride combined with valeric anhydride, acetic anhydride with hexanoic anhydride, acetic anhydride with lauric anhydride, acetic anhydride with stearic anhydride and propionic anhydride with hexanoic anhydride). All these combinations used 1-methylimidazole as a catalyst. This work from the Weyerhaeuser Company has provided some solutions for efficient esterification of lignins. The work of Maldhure *et al.* [114-115] focused on thermal (TGA, DSC), structural (wide-angle X-ray and SEM) and mechanical properties (tensile strength) of PP blended with industrial Kraft lignin esterified by maleic anhydride (ASTM D790). They demonstrated that the addition of esterified lignin increased thermal stability because of lignin antioxidant properties, while it decreased the glass transition temperature and melting temperature of the composite with higher crystallization temperature and crystallinity. SEM observations indicated a good dispersion and miscibility of the esterified lignin in PP proving the efficiency of this kind of modification in this system. Nevertheless, a reduction in tensile strength of the blend versus neat PP was determined in that study (ASTM D638). In 2010, Sailaja and Deepthi [60] introduced 40 wt. % esterified alkali lignin (by using phthalic anhydride) into LDPE with maleic anhydride grafted LDPE as compatibilizer to improve the interfacial adhesion. They observed a drastic reduction (caused by addition of lignin) in relative impact strength (ASTM D1822) and relative tensile strength (ASTM D1708), following the addition of esterified lignin as the only coupling agent, but the addition of maleated LDPE minimized this effect. Olsson *et al.* [116] introduced softwood Kraft lignin esterified with acetic and propionic anhydride into LDPE. The addition of 10 wt. % of esterified lignin into LDPE matrix reduced the tensile strength of the composite (ASTM D638). In a previous study [110], they explored the application of softwood commercial Kraft lignin (Indulin AT) esterified with butyric anhydride or stearic chloride in HDPE. It was demonstrated that both esterifications were accomplished, but the tensile properties of the produced composites indicated that esterified lignin did not contribute to the improved interface properties. Despite modulus increased by 30%, tensile strength and elongation at break (ASTM D638) were drastically lower than those of neat HDPE, mainly due to the bark content. The addition of MAPE (6 wt. %) did not significantly improve the mechanical properties of this system.

II.7.2.a. Effect of hot water extraction of bark fibers used in WPC

Hot water extracted bark fiber has been used in manufacture of WPC. 50% black spruce bark fibers (non-extracted and extracted) were used in three formulations: 1. without any coupling agent; 2. with 5% MAPE based on fiber mass; 3. with 5% commercial Kraft lignin (Indulin AT) based on fiber mass. Less difference was found between non-extracted and extracted bark when used in the formulation with Indulin AT as coupling agent, although the mechanical properties of WPC were too low to have any interesting application. It is interesting that the composites made with hot water extracted bark fibers and MAPE as coupling agent had comparable mechanical properties. The fact that no significant influence of bark fibers extraction prior to their incorporation into formulations was found (Table III-3) provides an opportunity to generate a new co-product, bark extractives, from this forest biorefinery [19].

Table III-3 Effect of hot water extraction of black spruce bark on tensile properties of the formulation based on HDPE.

Formulation (%)			Tensile properties / Gain after hot water extraction					
Bark	Lignin	MAPE	Modulus (MPa)	Gain (in %)	Stress at Break (MPa)	Gain (in %)	Strain at Break (%)	Gain (in %)
50	0	0	264	14	9.5	28	8	44
50	0	5	421	-42	18.9	-16	7	22
50	5	0	282	3	9.6	14	9	20

Slight improvements of tensile properties observed for the formulations with commercial Kraft lignin could be explained by the effect of hot water extraction treatment on fibers in a way that it reduced the diameter of the agglomerations of fibers. However, this effect was less pronounced than mercerization treatment reported in the literature [45, 49-50]. These results indicated that the use of modified lignin as a coupling agent would allow using the extracted bark fibers and MAPE to make WPC with promising mechanical properties in the future, while the generated hot water extractives from bark could be used for pharmaceutical or other purposes [16].

II.7.2.b. Esterified commercial Kraft lignin (Indulin AT) as coupling agent versus MAPE for production of WPC containing black spruce bark fibers

The butyric and stearic esterified commercial Kraft lignin developed in our preliminary study [110] have been used as coupling agents (5 wt. % on fibers mass) in a WPC system based on HDPE (70%) and extracted black spruce bark fibers (30%). We have demonstrated previously that the extraction of bark fibers prior to their incorporation in the composites based on HDPE did not have adverse effects on the properties of the composites [19]. These formulations were designed to explore the potential of commercial Kraft lignin, Indulin AT (with and without modification), using MAPE as a reference. The tensile properties (ASTM D638) presented in Figure III-3 show a low applicability of this type of lignin as a coupling agent for the studied system.

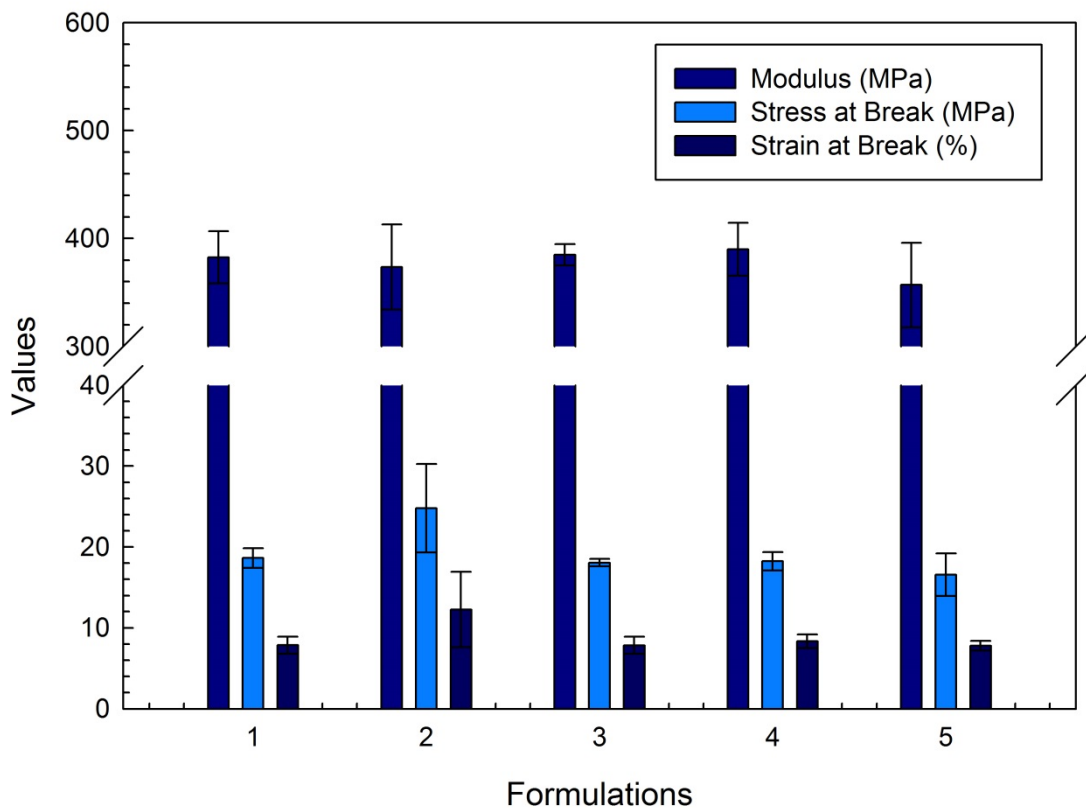


Figure III-3 Tensile properties of different formulations (HDPE 70% + Black spruce bark 30%) : 1 = without any coupling agent; 2 = MAPE (5 wt. %); 3 = Indulin AT (5 wt. %); 4 = Butyric Indulin AT (5 wt. %); 5 = Stearic Indulin AT (5 wt. %) as coupling agent.

Indeed, as can be seen from the results presented in Table III-4, MAPE was effective as its addition improved the properties of the composite such as stress at break (33%) and strain at break (56%), while the addition of commercial Indulin AT Kraft lignins, esterified or not, did not seem to improve the interaction between the lignocellulosic fiber and matrix, which could indicate that they acted rather as fillers or dispersants in the WPC formulation.

Table III-4 Tensile properties of WPC based on HDPE containing extracted black spruce bark fibers and MAPE or commercial Kraft lignin (Indulin AT) as coupling agent.

Formulation			Gain (%)		
Bark	Lignin	MAPE	Modulus	Stress at Break	Strain at Break
30%	0%	5%	-2	33	56
30%	5% <i>Indulin AT</i>	0%	1	-3	0
30%	5% <i>Indulin AT</i> Butyric	0%	2	-2	6
30%	5% <i>Indulin AT</i> Stearic	0%	-7	-11	-1

This result is in accordance with our previous study in which we demonstrated that good interaction between esterified lignin and HDPE could not be achieved [110]. However, this cannot be extrapolated to other types of esterified commercial lignins because other esterification systems could be more favorable to the improvement of targeted mechanical properties of the studied WPC.

II.7.2.c. Modified Wayagamack softwood Kraft lignin as coupling agent for WPC based on HDPE matrix containing extracted black spruce bark fibers

It is hypothesized that lignin modified by esterification would be acting as a coupling agent between the hydrophobic HDPE matrix and hydrophilic bark fibers thus improving the compatibility or acting as dispersing agent in combination with MAPE. The following possibilities were examined in the present study:

- Wayagamack Kraft lignin esterified with maleic and succinic acid anhydrides could act as a coupling agent and/or dispersant, when used without MAPE, between the HDPE matrix and bark fibers.

- The performance of esterified Wayagamack Kraft lignin would be comparable or superior to that of the esterified commercial Kraft lignin (Indulin AT) when used in the same system for composite production.

We are presenting here the results about mechanical properties of HDPE composites made of black spruce bark fibers and maleated or succinicated softwood Wayagamack Kraft lignin as coupling agent and comparison with the composites containing MAPE as coupling agent.

III.8. Materials and methods

III.8.1. Bark fibers used for composites- conditions of refining for black spruce

Refined black spruce (*Picea mariana*) bark was obtained from FPInnovations (Quebec, Canada). The raw bark samples were obtained from Scierie Leduc sawmills (Quebec, Canada). After removing the contaminants by sieving at 10 mesh, the bark was conditioned and refined using an Andritz disk refiner at FPInnovations' MDF pilot plant as specified in the studies by Fang *et al.* [117] and Gao *et al.* [15]. The refining parameters used to obtain bark fibers were: steam pressure of 12 bars, plate distance of 0.1 mm, plate speed of 2200 rpm and a retention time of 3.5 min at 189°C. No wax or resin was added during refining. The bark fibers used in this study did not contain any wood.

III.8.2. Esterifications of lignin for WPC applications

Lignin precipitated from black liquor with CO₂ and purified with sulfuric acid, was first dried in a vacuum oven at 60°C for 24 hours and esterified with maleic or succinic acid anhydride following the procedure described by Schorr *et al.* [98].

III.8.3. Fabrication of HDPE composites

An internal batch mixer (Haake Büchler Rheomix) was used to prepare the WPC containing black spruce bark fibers. The black spruce bark fibers were dried at 80°C overnight before processing. Three batches

were prepared for each formulation. Rotational speed was set at 60 rpm in order to minimize the shearing effect on the natural fibers. The mixture was kept at a temperature of 160°C for 9 minutes in order to minimize material degradation (thermo-oxidation), and to obtain a homogeneous material. The following protocol was applied for each batch: at t0 the HDPE was introduced and melted while mixing, after three minutes the coupling agent was added (esterified lignin and/or MAPE respectively) while continuous mixing was applied in order to distribute the material, and after four minutes from the start the black spruce bark fibers were finally added, and mixed for another five minutes (nine minutes total). In order to produce the WPC, the mixtures were molded by compression using a laboratory Carver press at 175°C using a force of three tons for five minutes in a mould with dimensions of 115 mm x 115 mm x 2.7 mm.

III.8.4. Mechanical properties determination

Flexural properties of the composites, including modulus of elasticity (MOE), tensile properties, including modulus of elasticity, strength at break and strain at failure, were determined. The three-point bending tests were performed according to ASTM D790. Samples having $80.0 \times 12.8 \times 2.5 \text{ mm}^3$ in dimensions were tested with a support span of 60 mm at a cross-head speed of 10 mm/min. ASTM D 638 was used to determine the tensile modulus of elasticity, strength and strain at break of the samples. Dimensions were consistent with type V specimen. Both characterizations were obtained using a universal mechanical tester model 5565 (Instron, USA) with an adapted cell load (500 N for bending and 5 kN in tension).

III.8.5. Scanning electron microscopy (SEM)

A JEOL JSM-840A scanning electron microscope was used for morphological characterizations. Each WPC sample was broken using liquid nitrogen to expose the internal structure and obtain a clean surface for scanning. To allow observation, the surface was coated with a gold/palladium alloy under low pressure and observation was made at 15 kV using different magnifications.

III.9. Results and discussion

III.9.1. Esterified Wayagamack Kraft lignins as coupling agents

WPC composites were produced by the same protocol (internal batch mixer at 60 rpm and 160°C for 9 minutes) from MAPE and bark fibers in formulations with addition of Wayagamack Kraft lignin esterified with maleic or succinic acid. The morphology of the produced composites was examined by SEM (Figure III-4). The mechanical properties of the composites could be related to a certain extent to the observations by SEM.

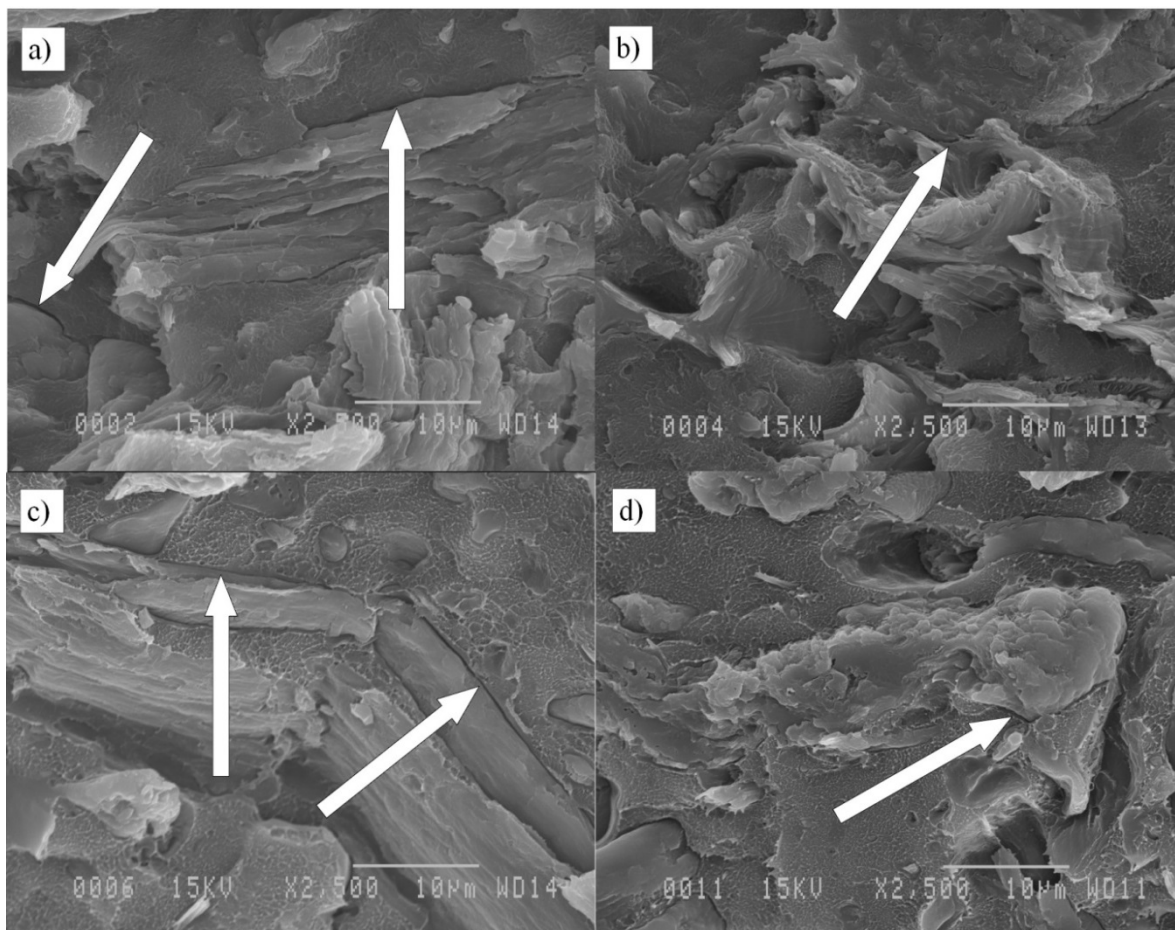


Figure III-4 Scanning electron micrographs (SEM) at 2500x: a) without any coupling agent; b) MAPE (5 wt. %); c) Maleic Wayagamack lignin (5 wt. %); d) succinic Wayagamack lignin (5 wt. %) as coupling agent. The arrows indicate a fiber-matrix interface.

In Figure III-4 (a), representing the composite without any coupling agent, a gap between bark fiber and HDPE can be observed, which could explain the poor adhesion between the polar hydrophilic lignocellulosic fiber and the non-polar hydrophobic matrix. On the other hand, the strongest interfacial adhesion was observed for composites containing MAPE (no space can be seen) in Figure III-4 (b) due to the presence of the commercial coupling agent (MAPE). The capacity of esterified lignin to be positioned between bark fibers and the matrix would be the first proof of its acting as true coupling agent. The interface between bark fiber and HDPE matrix appears to be slightly better when using esterified lignin as shown in Figure III-4 (c) and d) versus Figure III-4 (a). It is impossible on this SEM to exactly locate the esterified lignin in the structure of this WPC, but interface adhesion between lignocellulosic fiber and HDPE seems to be quite well established.

III.9.2. The potential of esterified Kraft lignin as coupling agent

Comparison of SEM micrographs presented in Figure III-4 indicates that maleated lignin (Figure III-4c) is better than succinated lignin (Figure III-4d) for application as a coupling agent in HDPE based composites. However, acting as a dispersant and/or a compatibilizing agent, succinated lignin could have a positive effect to improve the properties of the WPC. This improvement could also be explained by the high porosity of the esterified lignin offering the possibility to form mechanical bonding [97]. The determined mechanical properties of these composites (Tables III-5 and III-6) are comparable to those reported for HDPE composites containing wood or bark fibers [5, 18, 59, 118].

Table III-5 Tensile properties of WPC based on HDPE with extracted black spruce bark fibers: without any coupling agent, with MAPE or Wayagamack Kraft lignin as coupling agents.

Formulation			Gain (%)		
Bark	Lignin	MAPE	Modulus	Stress at Break	Strain at Break
30%	0% Waya	5%	7	20	21
30%	5% Waya Ma	0%	-22	-42	-7
30%	5% Waya Su	0%	8	-62	-31

Lignin and MAPE content are expressed based on bark mass (wt. %)

Legends: Waya = *Wayagamack* Kraft lignin; Ma = Maleated; Su = Succinated

Table III-6 Gain in flexural modulus of WPC based on HDPE matrix with extracted black spruce bark fibers: without any coupling agent, with MAPE or Wayagamack Kraft lignin as coupling agents.

Formulation			Gain (%) Modulus
Bark	Lignin	MAPE	
30%	0% Waya	5%	7
30%	5% Waya Ma	0%	17
30%	5% Waya Su	0%	-1

Lignin and MAPE content are expressed based on bark mass (wt. %)

Legends: Waya = *Wayagamack* Kraft lignin; Ma = Maleated; Su = Succinicated

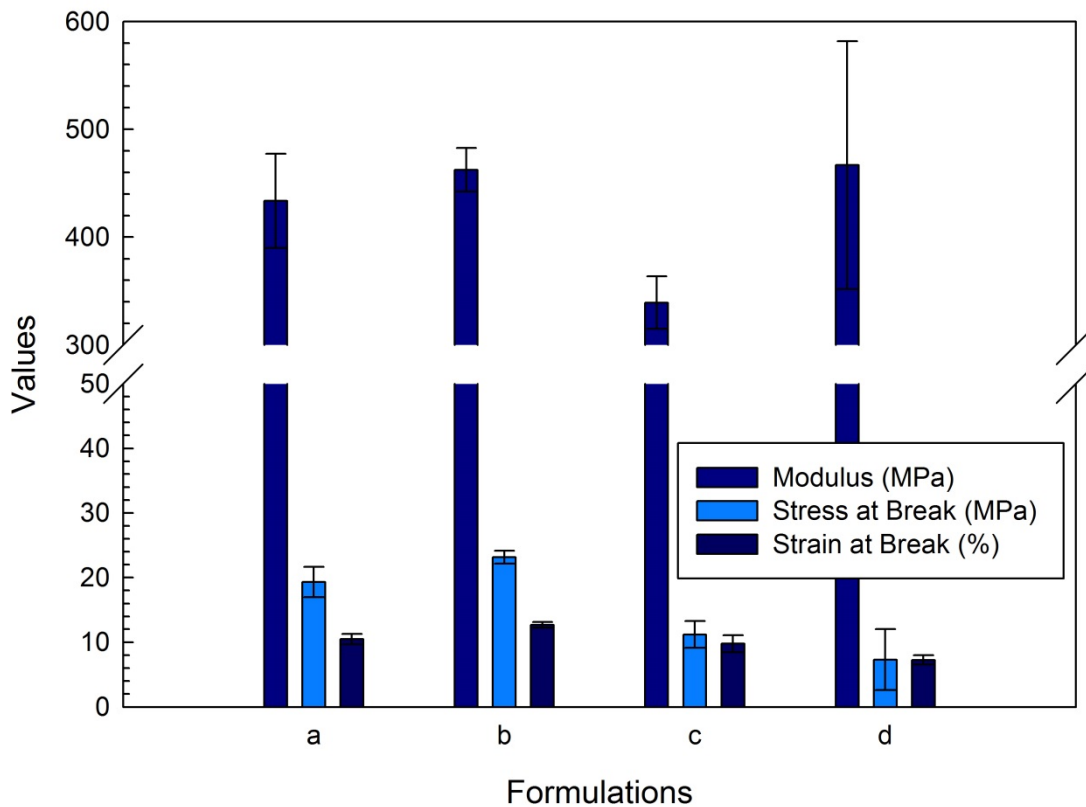


Figure III-5 Tensile properties of different formulations (HDPE 70% + black spruce bark fibers 30%): a) without any coupling agent; b) MAPE (5 wt. %); c) Maleic Wayagamack lignin (5 wt. %); d) succinic Wayagamack lignin (5 wt. %) as coupling agent.

Tensile properties (using ASTM D638) (Figure III-5 and Table III-5) determined for the composites containing 30% of black spruce bark fibers in HDPE matrix indicated that MAPE seems to be an efficient coupling agent contributing to the enhanced tensile properties of the composites, such as stress at break

(+20%) and strain at break (+21%), with small improvement in modulus (+7%) because this property is mostly dependent on fibers content [47]. The results obtained for the composites using esterified Kraft Wayagamack lignins as coupling agents indicated that the use of Wayagamack Kraft lignin esterified with succinic acid anhydride contributed to a slight increase in modulus (+8%), but to a drastic decrease in stress (-62%) and strain at break (-31%) of the composites, showing poor compatibility and performance of this Kraft lignin as coupling agent. Similar results were obtained for composites containing maleated Wayagamack Kraft lignin, for which the decrease of 22% for modulus, 42% for stress at break and 7% for strain at break were found.

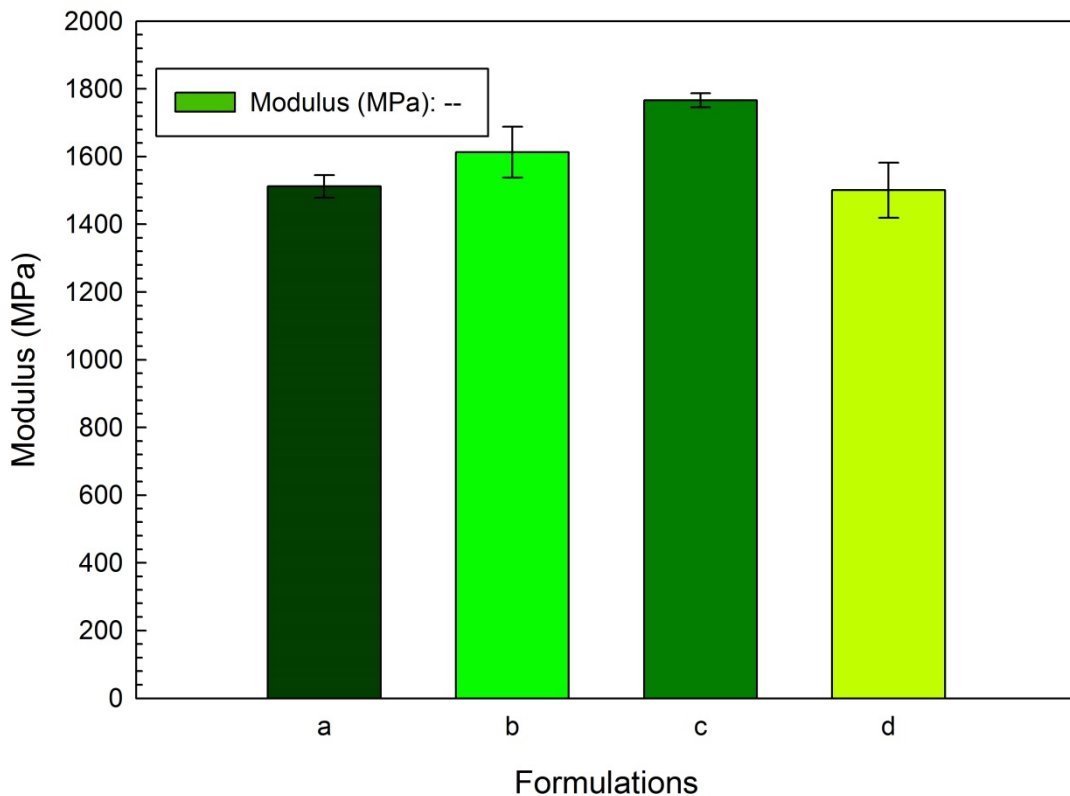


Figure III-6 Flexural modulus of different formulations (HDPE 70% + black spruce bark fibers 30%): a) without any coupling agent; b) MAPE (5 wt. %); c) Maleic Wayagamack lignin (5 wt. %); d) succinic Wayagamack lignin (5 wt. %) as coupling agent.

However, the flexural modulus (Figure III-6 and Table III-6) determination for the studied composites provides additional information on the performance of modified Kraft lignins as coupling agents (using ASTM D790). Indeed, in three-point bending experiments, the addition of 5 wt. % (based on fiber mass) of

Wayagamack Kraft lignin esterified with maleic anhydride contributed to the best improvement of flexural modulus with +17% versus +7% using the reference MAPE. The formulation containing succinic esterified Kraft lignin did not change this property (-1%). Therefore, the admixtures of lignin esterified with maleic acid anhydride and MAPE should be further explored for the production of HDPE composites containing bark fibers.

III.10. Conclusions

Society is nowadays sensitive to the environmental incidence of processing industries. This important awareness is growing and forcing different governments to adopt more restrictive legislation against industrial pollution with potential negative effects for future generations. This worldwide mindset is helpful for the research sector to promote natural or bio-sourced products. The variability of lignocellulosic fibers available in nature represents a great challenge for researchers to further explore this type of materials. The knowledge about anatomy and chemical composition remains the key to the design of new products for selected applications (automotive, aerospace, construction or packaging). The problem with WPC is related to the extremely opposite characteristics of natural fibers and polymer matrices, which make them incompatible. A multitude of physical and/or chemical treatments may improve compatibility and interfacial interactions through the formation of covalent bonds between all the components. Such modifications or improvements are possible for the engineering design of WPC by using a new coupling agent based on totally or partially esterified lignins. Maleated polyolefin (MaPO) still remains the best coupling agent available for application in WPC based on polyolefins. Nevertheless, environmental and economic impact of using chemicals derived from petrol and the demand to valorize the co-products from wood or agricultural industries offer an opportunity to use esterified lignins in production of new WPC. In that context, the potential of using esterified Kraft lignin as coupling agent in HDPE composites containing black spruce bark fibers explored in this study contributes to the future developments of biocomposites. We have demonstrated that for HDPE composites containing 30% of black spruce barks fibers, maleic anhydride esterified Kraft lignin addition at 5 wt. % level (based on bark mass) improved flexural modulus by 20%, while tensile properties were somewhat diminished. The results from our study on HDPE composites containing black spruce bark fibers suggested that combination of esterified Kraft lignin and MAPE would be a promising option for future studies. Such formulations could potentially improve stress transfer between the polymer matrix and lignocellulosic fiber in WPC. The WPC developed in this study apply several

sustainable engineering and green chemistry principles: using co-products, Kraft lignins and bark fibers, which are renewable resources, as partial replacement of polyethylene matrix of petrochemical product, while contributing to sequestration of CO₂ both through lignin precipitation and by diminishing the use of synthetic products.

IV. La Combinaison de Lignines Kraft Estérifiées et de MAPE Comme Agent de Couplage pour des Composites d'Ecorces / HDPE

Combination of Esterified Kraft Lignin and MAPE as Coupling Agent for Bark/HDPE Composites

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IV.1. Résumé

Des fibres d'écorce d'épinette noire raffinée et du polyéthylène haute densité (HDPE) ont été utilisées pour produire des composites bois-plastique (WPC) tout en explorant pour la première fois la possibilité d'utiliser des lignines Kraft estérifiées comme agent de couplage. Deux types d'estérification de lignines (anhydrides d'acide succinique et acide maléique) ont été examinées seules ou en combinaison avec du polyéthylène maléaté (MAPE) et par rapport à un agent de couplage commercial : du polyéthylène maléaté (MAPE). Trois teneurs en agent de couplage (2%; 5%; 10%) ont été employées et trois combinaisons de lignines modifiées et MAPE (50:50, 100:0; 0:100), tandis que la quantité de fibres d'écorce contenues dans le WPC a été maintenue constante à 30%. La morphologie (microscopie électronique à balayage équipée d'un module d'analyse dispersive en énergie [MEB-EDS]); thermique (analyse thermogravimétrique [ATG], analyse calorimétrique différentielle [DSC]) et des propriétés mécaniques (résistance à la traction et en flexion) des composites ont été mesurées. Deux formulations optimales ont été déterminées selon la meilleure interface matrice - écorce conduisant à des propriétés mécaniques plus élevées : un contenu égal de lignines estérifiées avec de l'anhydride d'acide maléique et du MAPE à 5%, ou un contenu égal de lignines estérifiées avec de l'anhydride d'acide succinique et du MAPE à 2%.

IV.2. Abstract

Refined black spruce bark fibers and high density polyethylene (HDPE) were used to produce wood plastic composites (WPC) while exploring for the first time the potential of using esterified Kraft lignin as a coupling agent. Two types of lignin esterification (succinic acid and maleic acid anhydrides) were examined alone or in combination with maleated polyethylene (MAPE), and compared with a commercial coupling agent: maleated polyethylene (MAPE). Three contents of coupling agents (2%; 5%; 10%) were considered for esterified lignin and three combinations of lignin and MAPE (100:0; 50:50; 0:100), while bark fibers content was kept constant at 30%. Morphological (scanning electron microscopy - energy dispersive X-ray spectroscopy [SEM-EDS]), thermal (thermogravimetric analysis [TGA] and differential scanning calorimetry [DSC]) and mechanical properties (tensile and flexural) of the composites were measured. Two optimum formulations were determined based on the best bark-matrix interface leading to highest mechanical properties: an equal content of maleic acid anhydride esterified lignin and MAPE at 5%, or an equal content of succinic esterified lignin and MAPE at 2%.

IV.3. Introduction

It is a common consent now among research scholars, scientific institutions, industries, research and development centers, as well as governments, that there is a real need for intensification of activities enabling the development of materials containing polymers derived from renewable resources. The simple introduction of renewable resources into synthetic polymer matrices offers a myriad of combinations due to the variety of structures available from nature. However, as noted by Gandini [3], one should not base a naive optimism merely on multiple possibilities of combination between different polymers available and high diversity of exploitable natural fibers. Some specific combinations will definitely be of low interest, while others will answer the diverse needs of the world's growing population and therefore gradually replace current synthetic products, bringing an economic impact while being eco-friendly for our society.

Most of the residues from the pulp and paper or wood products industry remain underexploited, despite important research efforts made to develop new products or uses. For decades, wood has been introduced as a filler to increase stiffness and strength of polyolefin-based biosourced composites, known as wood plastic composites (WPC) [4-5]. The main difficulty in developing good properties resides in the different chemical properties between hydrophobic polyolefin matrices and hydrophilic wood fibers, resulting in poor compatibility. In order to improve the interaction between a polyolefin matrix and lignocellulosic fibers, a coupling agent is generally required. Polar functionality and molecular weight of coupling agent are optimized to provide a good interface between the matrix and reinforcements or fillers such as glass, wood fibers, minerals, metals or bark fibers. Over the years, maleic anhydride grafted polyethylene (MAPE) has been shown to be a good material to link natural fibers with polyethylene, as improved mechanical properties of the resulting WPC were obtained [3-5]. This favorable effect is attributed to the capacity of MAPE to form hydrogen (or covalent) bonds with lignocellulosic fillers to obtain good compatibility and adhesion with the matrix.

Lignocellulosic renewable materials are generally less abrasive compared to inorganic fillers resulting in a more sustainable process life of the equipment. Recently, some studies focused on the manufacture of biosourced composites based on polyolefin matrices in order to demonstrate the potential of bark particles to act as filler in WPC [17, 19]. The incorporation of natural fibers may improve thermal stability of the polymer materials [17-18]. Ngueho-Yemele *et al.* [19] studied the impact of hot water extraction of black spruce bark particles before incorporation in high density polyethylene (HDPE). On the other hand, interesting chemical

composition of the water extracts of black spruce bark qualifies them for pharmacological or alimentary applications [16], while leaving extracted bark fibers available for their conventional applications as fiber sources or energy production. Large quantities of bark produced in Quebec are presently almost entirely used for thermal energy production [11]. Numerous research efforts have been made to use bark for high value-added products, for example as an alternative source of fibers for particleboard and medium density fiberboard manufacturing [12, 14-15].

Lignins are the third most available natural polymers and their structures depend on plant origin and extraction process. They are the most abundant aromatic polymers on earth, and their content varies on average between 20% and 35% depending on plant origin [20]. Recently, it has been demonstrated that Kraft lignins could be precipitated from residual black liquor without negatively affecting the Kraft process [22]. Significant amounts of Kraft lignin could become available using the LignoBoost® patented process developed in Sweden [22]. Kraft pulp mills could thus maintain the same pulp production capacity, while precipitating a portion of lignin from black liquor. It is estimated that in Quebec, 130,000 tons of black liquor could be used for lignin precipitation annually, without disturbing mill production [21]. On the other hand, environmental problems are related to carbon dioxide emissions. Inside a pulp and paper Kraft industry, a source of 0.166 tons of CO₂ per ton of produced pulp is available at the lime kiln stage [119]. Kraft lignin can be precipitated from black liquor following the procedure proposed by LignoBoost [23, 109], which explored the possibility to use this source of CO₂ from the process itself. A protocol inspired by the same process was applied for lignin precipitation in this research.

This work presents an original integration of the concept of bio-refinery via the use of Kraft lignin in combination with black spruce bark (*Picea mariana*) fibers to produce WPC based on high density polyethylene. The general objective of the study was to investigate the potential of esterified Kraft lignins, alone or in combination with maleated polyethylene, to act as a coupling agent between high density polyethylene and black spruce bark fibers. The effect of esterified lignin addition on flexural and tensile properties of HDPE composites containing bark fibers was studied in comparison with composites made with a commercial coupling agent (MAPE).

IV.4. Experimental

IV.4.1. Materials

High density polyethylene was used as the polymer matrix. ExxonMobil HD 6605 (Exxon Chemicals) has a melt flow index of 5 g/10 min (ASTM D 1238 at 190°C and 2.16 kg) and a density of 948 kg/m³. A commercial coupling agent, Epolene C-26, was used as a base of comparison. This polyethylene grafted with maleic anhydride (MAPE) has an acid number of 8 (mg KOH/g) and a molecular weight of 65,000 g/mol (Westlake Chemicals Corporation). Refined black spruce bark (*Picea mariana*) fibers were obtained from FPIinnovations (Quebec, Canada). The raw bark samples were obtained from Scierie Leduc sawmill (Quebec, Canada). After removing the contaminants by sieving at 10 mesh, bark was conditioned and refined with an Andritz disk refiner at the FPIinnovations' MDF pilot plant as specified in Fang *et al.* [17] and Gao *et al.* [15]. The refining parameters used to obtain bark fibers included steam pressure of 12 bars, plate distance of 0.1 mm, plate speed of 2,200 rpm and retention time of 3.5 min at 189°C. No wax or resin was added during refining and bark fibers did not contain any wood. The size distribution of bark fibers was investigated with a fiber quality analyzer (Fiber Quality Analyzer Code LDA02 from OpTest Equipment Inc.). The anhydrous density of bark was determined by a gas (nitrogen) pycnometer, ULTRAPYC 1200e (Quantachrome Instruments) and cellulose content was determined by the Kurschner and Hoffner method [120]. Lignin content was determined by an alternative non-standard method for Klason lignin (ASTM D1106), modified by the integration of an autoclave Stevanovic [62]. Pentosans content was determined following protocols developed in our laboratory Stevanovic [62]. Determination of ash content was based on ASTM D1102 using a muffle furnace. For extractives content determination, bark fibers were extracted with water, a mixture of anhydrous ethanol:toluene (40:60) and sodium hydroxide (NaOH 1%) as specified in ASTM D1109. Three quantitative extractions were performed to determine the extractives content in each solvent.

IV.4.2. Precipitation and esterification of lignin

Black liquor from a pulp and paper industry (*Kruger Wayagamack*, Quebec) containing a mixture of softwood species (black spruce/balsam fir/jack pine) was used to precipitate lignin. Carbon dioxide was used to precipitate lignin by decreasing the pH of black liquor from 13-14 to 8-9 following the procedure

inspired by the LignoBoost process [22, 107-108]. A purification step consisted of washing lignin with sulfuric acid and then with distilled water. The precipitated lignin was dried in a vacuum oven at 60°C overnight before esterification. The esterification protocol with maleic or succinic anhydride was optimized as presented in a previous report by Stevanovic *et al.* [110].

IV.4.3. Composites compounding

An internal batch mixer (*Haake Büchler Rheomix*) was used to prepare WPC containing black spruce bark fibers. The fibers were dried at 80°C overnight before processing. Three mixtures were prepared for each WPC formulation. A rotational speed of 60 rpm was set to minimize mechanical shearing effect on the natural fibers. The mixture was kept at a temperature of 160°C for 9 minutes in order to minimize material degradation (thermo-oxidation), and to obtain homogeneous materials. The following protocol was applied for each batch: at t0 HDPE was incorporated and melted while mixing; after three minutes the coupling agent was added (esterified lignin and/or MAPE) while continuous mixing was applied to distribute it evenly. Finally, after four minutes from the start, black spruce bark fibers were incorporated and mixing was performed for another five minutes (nine minutes total). In order to obtain WPC plates, the compounds were compression moulded in a laboratory Carver press at 175°C with a force of 3 tons for 5 minutes in a mould with dimensions of 115 mm x 115 mm x 2.7 mm. The resulting plates were cut into standard dimensions for further characterizations.

IV.4.4. Thermal characterizations

Thermogravimetric (TG) measurements were performed by heating around 30 mg of material between 50 and 900°C in a platinum cell using a heating rate of 10°C.min⁻¹. The analyzer was a model Q5000IR from *TA Instruments*. The samples were placed in a high quality nitrogen (99.5% nitrogen) atmosphere with a flow rate of 50 mL.min⁻¹. The software *TA Universal Analysis* was used to calculate the first derivative (DTG) and obtain the temperature of maximum degradation rates (DTG max). Thermal stability was characterized by the starting decomposition temperature calculated as the temperature at which 5% mass loss was produced. The solid residues at 900°C were also determined. Differential scanning calorimetry (DSC 822e

Mettler Toledo) measurements were performed on 15 mg samples under a nitrogen atmosphere. *STARe Thermal Analysis Software 9.01* was used to calculate enthalpies and crystallinity.

IV.4.5. Scanning electron microscopy (SEM) coupled with energy dispersive X-ray spectroscopy (EDS)

A *JEOL JSM-840A* scanning electron microscope was used for morphological characterizations. Each WPC sample was broken using liquid nitrogen to expose the internal structure and obtain a clean surface for scanning. To allow observation, the surface was coated with a gold/palladium alloy under low pressure and observation was made at 15 kV using different magnifications. Interaction of the primary beam with atoms in the sample causes shell transitions which result in the emission of an X-ray. The energy dispersive X-ray spectroscopy (EDS) analysis module emits X-ray having energy characteristics of each element. The detection and measurement of the energy permit elemental analysis with a detection limit of 1%. EDS can also provide qualitative analysis of elemental composition of the selected area on SEM observations. It is important to notice that no detection of the element below carbon (C) is available using this equipment, so hydrogen (H) is not observable. This module is used to identify each component in a WPC.

IV.4.6. Physical and mechanical testing

Density of bark fibers and composites was determined by a gas pycnometer, *ULTRAPYC 1200e* from Quantachrome Instruments, using nitrogen as the gas phase. The results were reported as the average of five measurements with standard deviation. Flexural (modulus of elasticity, MOE) and tensile properties, including modulus of elasticity, stress at break and strain at break, were determined. Three-point bending tests were performed according to ASTM D790 on samples having $80.0 \times 12.8 \times 2.5 \text{ mm}^3$ dimensions with a support span of 60 mm at a cross-head speed of 10 mm/min. ASTM D 638 was used to perform tensile measurements on type V specimen. In each case, six repetitions per formulation were done using a universal mechanical tester model 5565 (Instron, USA) with a 500 N (flexural) or 5 kN (tensile) load cell.

IV.4.7. Statistical analyses

Experiments were conducted according to a D-Optimal design (Table IV-1). The factors studied included two lignin modifications (esterified with maleic or succinic anhydride) compared to MAPE, three levels of coupling agent content (2, 5 and 10%), and three compositions of coupling agent (CA) (100% modified lignin, 100% MAPE and 50:50 lignin:MAPE). Thus, 12 combinations with three replicates were produced, for a total of 36 compounds. Three control blends without bark fibers were also manufactured under the same conditions. *Statistical Analysis System (SAS) 9.3* was used for the statistical analysis. An analysis of variance (ANOVA) was performed on this experimental plan (three factors for 12 treatments). A control with neat HDPE and a reference of WPC containing bark fibers without any coupling agent were used to discuss the results. Contrasts were performed to determine interactions between the factors studied. Finally, comparisons between treatments were performed following the Duncan method to determine the best formulation(s).

Table IV-1 Bark-HDPE WPC formulations: Design of experiment from D-Optimal in SAS 9.3.

Coding	Coupling agent (CA)	CA content (%)	CA composition (Lignin:MAPE)
a	Succinic	2	100:00
b	Succinic	5	100:00
c	Succinic	10	100:00
d	MAPE	2	00:100
e	MAPE	5	00:100
f	MAPE	10	00:100
g	Succinic + MAPE	2	50:50
h	Succinic + MAPE	5	50:50
i	Succinic + MAPE	10	50:50
j	Maleic + MAPE	5	50:50
k	Maleic	5	100:00
<i>l</i>	<i>30% bark without any coupling agent</i>		
<i>m</i>	<i>HDPE</i>		

IV.5. Results and discussion

IV.5.1. Black spruce fibers characteristics

It is well known that natural fibers are characterized by an important variability of their chemical and physical properties (Table IV-2). Nevertheless, the results obtained in this study are similar to those published in the literature for black spruce bark [18], with somewhat lower cellulose and hemicellulose contents, which could be explained by the fact that bark was refined prior to chemical analyses, while the literature results reported untreated bark. Indeed, the Andritz disk refiner used at an elevated temperature could cause some hemicellulose (pentosan) losses. The anhydrous density (Table IV-2) of the bark determined by a volumetric method was 639 kg/m^3 for black spruce bark [19], but this technique gives the apparent bulk density without taking the porosity of the studied material into account. Here, a gas pycnometer with nitrogen was applied to measure density and the obtained results correspond to the density of the cell walls [121-122]. Fiber sizes determined by the fiber quality analyzer (FQA) are presented in Table IV-2 and aspect ratios (L/D) were found to be comparable to the findings of Ngueho-Yemele *et al.* [18-19], while the main difference found in the average fiber length between both studies could be again attributed to the use of the disk refiner which separated longer fibers. Differences in hemicellulose content and FQA properties can explain physical and mechanical properties as indicated by Bouafif *et al.* [59] who showed that increasing fiber size improved strength, but reduced elongation at break.

Table IV-2 Properties of black spruce refined bark.

Chemical composition ^a (%)					Extractives (%)		
	Cellulose ^b	Lignin ^c	Pentosan ^b	Ash ^d	Hot Water	Organic [*]	Inorganic ^{**}
Value	47.3	43.6	7.5	1.9	12.7	7.8	18.9
(SD)	(4.0)	(3.2)	(0.8)	(0.1)	(0.9)	(0.6)	(1.4)
Physical properties							
	Density (kg/m ³)	L (mm)	D (μm)	Aspect ratio (L/D)			
Value	1557	1.02	37.8	10.9			
(SD)	(28)	(0.05)	(1.8)	(1.7)			

^a : Calculation based on anhydrous mass of bark

^b : On extracted fibers with toluene, ethanol and boiling water

^c : On extracted fibers with ethanol, boiling water and sodium hydroxide (1%)

^d : On non-extracted fibers

^{*} : With ethanol-toluene mixture

^{**} : With sodium hydroxide (1%)

IV.5.2. Thermal stability (TGA results)

Several steps of mass loss can be observed on the thermal analysis curves, as was previously found for HDPE composites with bark [18]. An initial mass loss observed below 120°C is attributed to the gradual evaporation of water and of some volatile compounds. A second mass loss observed between 200 and 400°C is due to the decomposition of lignocellulosic constituents, namely hemicelluloses (around 250°C and 300°C), cellulose (around 350-365°C), lignin (between 270 and 410°C as proved by Stevanovic *et al.* [110]), and finally HDPE (at 450°C) [18]. The results obtained for starting decomposition temperature, temperature of maximum degradation rates (DTG max), and solid residues at 900°C are presented in Table IV-3. These results indicate the influence of natural fibers on WPC thermal degradation which starts around 260-300°C due to poor thermal stability of hemicelluloses from black spruce fibers. Temperature of maximum degradation rates for all the formulations are above 450°C corresponding to HDPE as the major component (70%). Solid residues at 900°C were low (about 1%) indicating a potential of energy recovery by combustion, useful at the end of life cycle.

Table IV-3 TGA and DTG results for each formulation [Letter a to k refer to the formulation given in Table III-1].

Sample	Starting decomposition temperature (°C)	DTG max (°C)	Residues at 900°C (%)
a	271	450	1.0
b	306	457	0.5
c	263	454	1.5
d	274	449	0.7
e	275	451	0.8
f	304	447	0.5
g	298	450	0.6
h	283	457	0.8
i	261	452	0.3
j	271	454	0.9
k	269	446	0.9

IV.5.3. Scanning electron microscopy (SEM) coupled to energy dispersive X-ray spectroscopy (EDS)

Before analyzing the interface between bark fibers and HDPE matrix, it is important to recognize each component in the WPC. In this work, three different components are present in the composites: HDPE, black spruce bark fibers and esterified Kraft lignin. It is impossible to observe the difference between HDPE and MAPE since both are mainly composed of H and C, and the oxygen content in MAPE (less than 1%) is below the detection limit of the instrument. To well recognize each component, not only by their morphological appearance, chemical differences between them should be exploited. HDPE is based on H and C atoms, with a formula $(C_2H_4)_nH_2$ compared to bark fibers composed of H, C and O. Therefore, they can be distinguished by SEM-EDS. The characteristic presence of S atom in Kraft lignin, which is not the case with native lignin, helps distinguish between the fibers and esterified Kraft lignin. The problems are that SEM-EDS has a detection limit of 1% and the sulphur (S) peak is very close to the peaks of gold (Au) and palladium (Pd) which are used for surface coating. Theoretically, it would be possible to observe the esterified Kraft lignin due to its S content, because the first gold peak will become larger and the peak of the sulphur atom will appear if enough S content is detected. The observations in SEM coupled to energy dispersive X-ray spectroscopy (EDS), as presented in Figure IV-1, show the chemical distinction of each component which helped to relate the morphological appearance to the chemical distinction of each component. In Figures IV-1 a1) and a2), the HDPE matrix with smooth surface was analyzed (the examined area is indicated by the square) and confirmed by SEM-EDS. Typical morphology of this component was

confirmed by chemical compositions based only on C atoms. In Figures IV-1 b1) and b2), the presence of O atoms proved that it is related to black spruce bark fiber, a raw material recognized by tracheids with bordered pits clearly visible on SEM, morphologically very different from the matrix. Finally in Figures IV-1 c1) and c2), esterified lignin was characterized by the presence of S atoms (on EDS), which proved that esterified Kraft lignin has a very porous aspect, probably due to esterification.

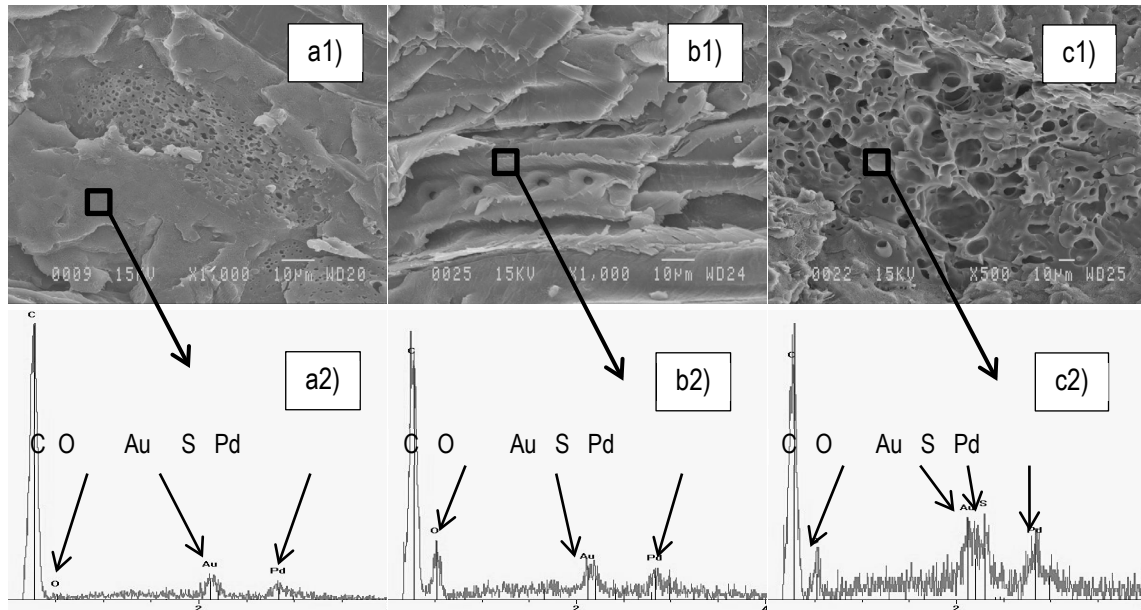


Figure IV-1 SEM observations (top row) coupled with EDS analyses (bottom row) to identify each component of the WPC: a1) and a2) HDPE; b1) and b2) bark fibers; c1) and c2) esterified Kraft lignin. The square indicates the analyzed area (EDS).

IV.5.4. Scanning electron microscopy (SEM) observations of the bark fiber-HDPE matrix interface

Scanning electron micrographs were used to investigate the interface quality between black spruce bark fiber, esterified lignin, MAPE and HDPE, in a similar way as reported by Colom *et al.* [5] and Ramezani *et al.* [118]. Figure IV-2 shows micrographs from the fractured surfaces of the composites containing black spruce fibers (at 30%) and their composition (a to k) is presented in Table IV-1. These representative formulations were examined to understand the effect of coupling agent (MAPE, esterified lignin, or combination of lignin and MAPE) on interfacial adhesion between the polyolefin matrix and black spruce bark fiber. Composites having poor matrix-fiber interaction would not be able to support a significant part of the load and have weaker mechanical properties [118]. The differentiation between morphological

appearance of each component (lignin, HDPE or black spruce fiber) was based on the results presented in Figure IV-1.

III.5.4.a. Esterified Kraft lignin as coupling agent

SEM micrographs of the formulations containing esterified Kraft lignin as coupling agent are shown in Figures IV-2a, IV-2b and IV-2c for succinic esterified lignin and in Figure IV-2k for maleic esterified lignin. The references with MAPE as coupling agent are presented in Figures IV-2d, IV-2e and IV-2f. Weak adhesions between black spruce bark and HDPE can be seen for all contents of succinic esterified Kraft lignin (i.e., 2, 5 and 10%) in Figures IV-2a, IV-2b and IV-2c, respectively. It is possible that succinic esterified lignin has a dispersive effect on black spruce fibers but no observation could validate the hypothesis that esterified lignin is acting as a coupling agent. The possible effect of esterified lignin acting as dispersing agent could be verified through improvements in mechanical properties. For formulations containing MAPE (5 and 10%), no interfacial void can be observed in Figures IV-2e and IV-2f, indicating strong interfacial adhesion. However, the formulation with only 2% MAPE has poor interface as observed in Figure IV-2d, just slightly better than succinic esterified lignin alone. These observations on MAPE reveal that a minimum content is necessary and the fact that no difference observed between 5% and 10% indicates that the optimal MAPE content is around 5%. This value is consistent with the work of Mechraoui *et al.* [97] for which the optimum coupling agent content was around 4% for a system composed of polypropylene and hemp fibers with maleated polypropylene as a coupling agent. In another system containing basalt fibers in HDPE (from recycled WPC), Chen *et al.* [123] determined an optimal MAPE content of 5-8%. Formulation containing 5% maleic esterified Kraft lignin is presented in Figure IV-2k, in which the interface looks slightly better than for formulations containing succinic acid esterified lignin, but not better than formulations containing 5% or 10% MAPE, and similar to the interface of formulation with 2% MAPE. To act as a coupling agent, esterified lignin needs to be attached to the black spruce bark fibers at the interface between fibers and matrix. This capacity of esterified lignin to be positioned between bark fibers and HDPE has been observed for maleic esterified lignin which was found to be positioned near black spruce fibers. The best interface was nevertheless obtained with 5% MAPE (Figure IV-2e) and will be used as reference to discuss the next part of SEM observations.

III.5.4.b. Combination of esterified Kraft lignin with MAPE as coupling agent

The combinations of succinic esterified Kraft lignin:MAPE at 1%:1% and 2.5%:2.5% (Figures IV-2g and IV-2h) have good interfaces similar to the actual reference obtained with 5% of MAPE (Figure IV-2e). However, this type of composite formulation was found to have a less effective interface than for the level of 5% MAPE: 5% lignin (Figure IV-2i). Although succinic esterification may have a positive impact, with an optimal content, in producing esterified lignin acting as dispersant of the black spruce bark fibers and MAPE (enhancing the efficiency of this commercial coupling agent) and/or compatibilizing agent and thus improving the properties of WPC. Esterification with maleic anhydride on the other hand has good potential even without MAPE (Figure IV-2k), but the combination of Kraft lignin esterified with maleic anhydride with MAPE at the same level of 2.5% (Figure IV-2j) seems to produce the same interface aspect as the reference with 5% MAPE alone. This could mean that maleic esterification has a higher potential as coupling agent when combined with MAPE than succinic anhydride alone.

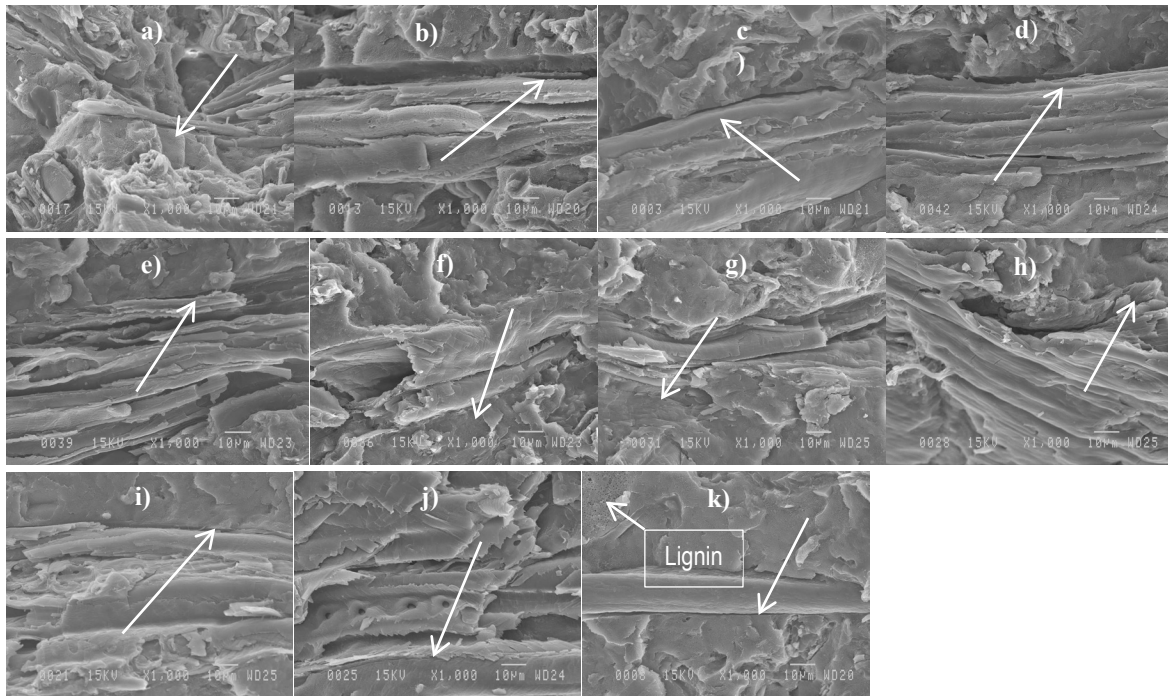


Figure IV-2 Scanning electron micrograph (SEM) of the WPC (letter a to k refer to the formulations described in Table III-1).

IV.5.5. Crystallinity and density

The results of HDPE and WPC crystallinity obtained using DSC measurements, with a calculation based on the enthalpy of the tested WPC compared with a theoretical value of an HDPE crystal ($\Delta H = 293$ J/g, as Wunderlich [124]), are presented in Table IV-4. The obtained results reflect the importance of coupling agent and fibers contents. Sewda and Maiti [17] found a linear decrease of crystallinity with increasing bark fibers content (*Azadirachta indica*) in HDPE formulations. At 26% bark content, they determined a crystallinity of 56% which is similar to the values determined here (between 45 and 55%) at 30% bark fibers. As for esterified Kraft lignin, crystallinity was determined to be maximum at 5% of succinic (or maleic) acid esterified lignin, alone or combined with MAPE. On the contrary, MAPE used as a sole coupling agent at 5% produced composites with the lowest crystallinity. There are situations where crystallinity may increase with the addition of contaminant (such as bark fibers or esterified lignin) which is adding nucleation points. However, if compatibility was not good, the crystals formed around the multiple nucleation points could be smaller than in the presence of a lower number of nucleation points having better compatibility. The use of 5% coupling agent seems again to be the optimum content in this context. One can hypothesize that higher crystallinity and better compatibility between bark fibers and HDPE may result in better mechanical properties, which was validated by the results presented in Table IV-4. The density results are also presented in Table IV-4. Higher density of the composites, compared to HDPE, is due to the presence of 30% fiber because HDPE has a density of 940 kg/m³ (Table IV-4), while bark fibers density is 1557 kg/m³ (Table IV-2) corresponding to the cell wall density as determined by pycnometry [121-122]. These results can be related to mechanical properties because density has a positive impact on these properties, as can be seen from the results presented in Table IV-4.

Table IV-4 Properties of black spruce refined bark.

Coding	Crystallinity (%)	Density (kg/m ³)	Flexural properties	Tensile properties		
			MOE ¹ (MPa)	MOE ¹ (MPa)	Stress at break (MPa)	Strain at break (%)
a	48.8	1049	1429 ^B	423 ^{AB}	11.1 ^C	9.4 ^{EF}
	(0.7)	(1)	(50)	(20)	(0.8)	(0.8)
b	54.6	1052	1473 ^B	403 ^{AB}	9.0 ^C	6.8 ^F
	(0.8)	(2)	(37)	(31)	(0.4)	(0.4)
c	47.0	1037	1547 ^{AB}	435 ^{AB}	9.8 ^C	9.7 ^{DE}
	(0.7)	(2)	(20)	(33)	(0.4)	(0.9)
d	55.4	1058	1449 ^B	396 ^{AB}	20.3 ^A	12.2 ^{CD}
	(0.8)	(2)	(45)	(10)	(0.8)	(1.6)
e	47.9	1000	1551 ^{AB}	445 ^A	21.3 ^{AB}	12.1 ^{CD}
	(0.7)	(2)	(56)	(18)	(1.2)	(0.4)
f	52.4	1008	1433 ^B	384 ^{AB}	21.4 ^{AB}	18.5 ^A
	(0.8)	(1)	(106)	(21)	(1.2)	(1.1)
g	52.8	1011	1545 ^{AB}	445 ^A	25.1 ^A	12.6 ^C
	(0.8)	(1)	(56)	(10)	(0.8)	(0.6)
h	56.5	1016	1614 ^{AB}	413 ^{AB}	22.3 ^{AB}	12.8 ^C
	(0.8)	(1)	(41)	(14)	(0.9)	(0.9)
i	46.6	1010	1530 ^{AB}	396 ^{AB}	23.0 ^{AB}	15.5 ^B
	(0.7)	(1)	(54)	(14)	(1.2)	(0.8)
j	55.6	1019	1618 ^{AB}	431 ^{AB}	22.4 ^{AB}	13.0 ^{BC}
	(0.8)	(1)	(73)	(14)	(1.9)	(0.8)
k	51.6	1026	1667 ^A	370 ^B	11.2 ^C	8.9 ^{EF}
	(0.8)	(1)	(60)	(26)	(0.8)	(0.6)
<i>Without C-A²</i>	47.5	1009	1495	434	19.3	10.5
	(0.6)	(1)	(18)	(11)	(0.6)	(0.2)
<i>100% HDPE</i>	40.2	940	1050	349	13.1	122.6
	(0.5)	(1)	(46)	(5)	(0.1)	(0.3)

1: MOE = Modulus of elasticity; 2: Without C-A = without any coupling agent. Standard deviation is in brackets. For each property, values followed by the same letter are not significantly different and values followed by different letters are significantly different at 0.05 probability level (letter a to k refer to formulations given in Table III-1).

IV.5.6. Mechanical properties

The results of flexural and tensile measurements are presented in Table IV-4. Flexural modulus (MOE) is in the range from 1,400 to 1,700 MPa which represents a 30 to 60% improvement compared to neat HDPE

(1,050 MPa). Tensile MOE are in the range from 350 to 450 MPa (350 MPa for HDPE), giving a maximum improvement of 30%. Stresses at break are between 9 and 25 MPa (13 MPa for HDPE) which corresponds to a maximum improvement of 90%. This substantial increase indicates the clear effect of coupling agent addition. Finally, tensile strain at break values are in a range from 5 to 20% for WPC (125% for HDPE) corresponding to a less elastic behavior of the material as expected. The determined mechanical properties are in the same range as those reported by Bouafif *et al.* [59] for HDPE composites containing bark “fiber-like” particles, having a modulus of elasticity equal to 1,600 MPa, a tensile strength of 22 MPa and a strain at break of 6.6%. Similar results were obtained by Ngueho-Yemele *et al.* [19] for WPC containing bark “fiber-like”, with a flexural modulus of elasticity equal to 1,436 MPa, a tensile modulus of elasticity of 1,766 MPa (the only property much higher than here), a tensile strength of 10.6 MPa and a strain at break of 2.8%. The results of Table IV-4 are also slightly better than those reported for composites containing hemp fibers by Ramezani Kakroodi *et al.* [118] having for 30% of hemp a tensile modulus of elasticity of 340 MPa, a tensile strength of 15.3 MPa and a strain at break of 17%.

III.5.6.a. Esterified Kraft lignin as coupling agent

Analyzing the flexural modulus results for formulations a, b and c (Tables IV-1 and IV-4), increasing succinic esterified lignin content had a positive influence on this property, but no difference was found in terms of tensile modulus and stress at break. Concerning strain at break, no clear tendencies were observed for the three WPC formulations studied. Composites using MAPE as coupling agent (d to f) have higher strain at break with increasing MAPE content, probably due to the intrinsic elasticity of this commercial coupling agent. Flexural modulus and tensile properties (modulus of elasticity and stress at break) of these formulations increased with increasing MAPE content, except for tensile modulus which increased until a MAPE content of 5% was reached, after which tensile modulus decreased. This optimal coupling agent content, in terms of mechanical properties, validates the previous SEM observation (Figure IV-2) in terms of better bark fiber-HDPE interface quality. This optimal MAPE content is also in agreement with Mechraoui *et al.* (2007) whose work established the best content near 4% (based on fibers mass) and with Chen *et al.* (2013) with an optimal content of 5-8% (based on fiber mass). To compare the best modification between succinic and maleic esterification, analysis of formulations a, b, c (for succinic esterification) and k (for maleic esterified lignin) was done via a Duncan test. This analysis proved that composites containing maleic anhydride esterified lignin had significantly higher modulus of elasticity (+7.2%) than composites containing

succinic modified lignin, but no statistical difference in terms of stress and strain at break (Table IV-4) could be determined. Further analysis of mechanical performance, with a simple calculation of the gain (in %) of each property measured relative to the neat HDPE matrix (Table IV-5), indicates that no clear tendencies could be found for succinic esterification. However, the best Kraft lignin content for this type of modification was determined to be 10% (succinic esterified lignin content based on fiber mass), with increases of 25% and 47% for flexural and tensile modulus of elasticity respectively, but with losses of 25% on stress at break and 92% on strain at break. An optimum MAPE content was found to be 5% with improvements of 27% and 48% for flexural and tensile modulus, 63% stress at break, but a 90% loss on strain at break (less elastic material). Maleic esterified lignin alone had a limited effect on WPC properties since gains in terms of tensile properties were much lower: 6% increase for modulus of elasticity, with 14% stress at break and 93% strain at break losses. The addition of maleic anhydride esterified lignin appears to be intermediate between succinic anhydride Kraft lignin and MAPE as coupling agents. Finally, maleic esterification of Kraft lignin had the best effect on flexural modulus of elasticity with an improvement of 59%.

Table IV-5 Tensile and flexural properties gain (in %) for WPC formulations using MAPE or esterified lignin alone.

Bark	Formulation (%)			Tensile properties gain (%)			Flexural MOE gain (%)
	Lignin Succinic	Wayagamack Maleic	MAPE	MOE (MPa)	Stress at break (MPa)	Strain at break (%)	
30	2	0	0	21	-15	-92	36
30	5	0	0	15	-31	-94	40
30	10	0	0	25	-25	-92	47
30	0	0	2	13	56	-90	38
30	0	0	5	27	63	-90	48
30	0	0	10	10	64	-85	36
30	0	5	0	6	-14	-93	59

III.5.6.b. Combination of esterified Kraft lignin with MAPE as coupling agent

The combination of succinic esterified lignin with MAPE as coupling agent (formulations g to i) confirmed the trends observed with MAPE alone, with the best properties obtained at a total coupling agent content of 5%. The Duncan statistical test (Table IV-4) showed that the best coupling agent is to combine equal amounts of MAPE and maleic esterified lignin at 5% total which yields the best combination of flexural and tensile properties. Similar optimal coupling agent content was reported in the literature on WPC with other types of

lignocellulosic fibers [97, 123]. It is important to notice that the combination of MAPE with maleic esterified lignin produced WPC with better mechanical properties than using MAPE alone (4.1% increase of flexural modulus of elasticity, 7.7% decrease of tensile modulus of elasticity, 4.9% increase in stress at break and an increase of 6.9% for strain at break). It seems that MAPE has a strong affinity towards HDPE, while modified lignin has good compatibility with native lignin from bark fibers, as maleic functions grafted on it recognize similar functions in MAPE thus creating a new combination of coupling agents. This result concerning the combination of MAPE and maleated Kraft lignin is corroborated by SEM observation because the interface of this formulation (Figure IV-2k) is very similar to the reference with 5% MAPE (Figure IV-2e). The results of Bouafif *et al.* [112] indicated certain limitations of using MAPE as coupling agent with jack pine bark fibers (*Pinus banksiana*) in composites based on HDPE. Here, the addition of esterified (succinic and maleic) Kraft lignin in HDPE composites has proved to positively influence MAPE efficiency as a coupling agent and improved the interface between natural fibers (bark) and polyolefin matrix, perhaps due to the high porosity of esterified Kraft lignin (Figure IV-1 c1), which is offering space to create mechanical bonds with the matrix) and thus resulting in production of WPC with better mechanical properties. Using the calculations on gain in the studied properties of these formulations based on a combination of MAPE and esterified Kraft lignins and taking the WPC with optimal MAPE content (5%) as reference, the obtained results made it possible to identify the best combination of MAPE and modified lignin (Table IV-6). Indeed, the combination of MAPE (1%) with succinic Kraft lignin (1%) produced composites with better properties than MAPE (5%) alone: +27% tensile modulus of elasticity, +92% stress at break, -90% strain at break, and +47% flexural modulus. This combination is very favorable as it decreases considerably the content of synthetic coupling agent (MAPE) by a factor of five, while introducing natural polymer. As for the combination of maleated Kraft lignin (2.5%) with MAPE (2.5%), the tensile properties are similar to MAPE (5%) alone with +23% tensile modulus, +71% stress at break and -89% strain at break reducing by a half the MAPE content in WPC. However, this combination is the best solution to optimize also flexural modulus with an increase of +54%. The potential of application of esterified lignin combined with MAPE is based on two different mechanisms of action and has the advantage to offer sites for mechanical bonding to the matrix through the high porosity of esterified lignin. Succinic esterified Kraft lignin seems to act as a very efficient dispersant, improving the action of MAPE yielding the best formulation at 1% lignin:1% MAPE, while maleic esterified Kraft lignin is forming a good interaction between the maleated parts of MAPE (grafted maleated function) with the esterified lignin part preserving its affinity towards bark fibers. Thus, a new coupling agent with an affinity to the matrix through MAPE and a good

affinity to the fibers through the esterified Kraft lignin is created through the combination of MAPE with Kraft lignin esterified with maleic acid anhydride.

Table IV-6 Tensile and flexural properties gain (in %) for WPC formulations using a combination of MAPE and esterified lignin. The first line is the best formulation from Table IV-5 (5% MAPE).

Bark	Formulation (%)			Tensile properties gain (%)			Flexural MOE gain (%)
	Lignin Succinic	Wayagamack Maleic	MAPE	MOE (MPa)	Stress at break (MPa)	Strain at break (%)	
30	0	0	5	27	63	-90	48
30	1	0	1	27	92	-90	47
30	2.5	0	2.5	18	71	-90	54
30	5	0	5	13	76	-87	46
30	0	2.5	2.5	23	71	-89	54

IV.5.7. Statistical analysis

The results of the analysis of variance (ANOVA) are presented in Table IV-7 and show a significant effect of the interaction between the type of esterification (Typ) and the composition (Comp) of the formulations on tensile modulus at 0.05 probability level. No main effects are significant for tensile modulus. This interaction is illustrated in Figure IV-3 with the surface response helping to understand its influence on WPC. It can be assumed that it is due to the favorable presence of MAPE and of appropriate esterification to optimize the system. Furthermore, the micrographs and mechanical properties indicated the influence of the esterification method and the effectiveness of MAPE on the morphological structure of black spruce bark fibers-HDPE composites (Figure IV-2) and on WPC tensile modulus. Tensile stress at break, as shown in Table IV-7, reveals no significant interaction. But the main effect of coupling agent composition is significant at the 0.01 probability level. This result proves the potential of MAPE combined with esterified Kraft lignin, giving better properties to the composites. To conclude on tensile properties, the strain at break presented in Table IV-7 was examined and no significant interaction was found. The composition and content are significant at 0.01 probability level, allowing confirming that the combination of MAPE with esterified lignin is a potential way to optimize bark/HDPE WPC. Nevertheless, an optimum coupling agent (or combination) content needs to be determined (for each composition) because it is highly significant for strain at break. Finally, the ANOVA analysis can be used to examine how the studied parameters influence the flexural modulus (Table IV-7). There were no statistically significant interactions determined by this analysis, and the main effect of esterification type (Typ) is the only significant factor at the 0.01 probability level. This

result is contributing to new information about this novel type of coupling agent (esterified Kraft lignin) proving the potential of maleic esterification. This statistical analysis result was confirmed by SEM observations (Figure IV-2) and through mechanical properties previously discussed (Tables IV-4, IV-5 and IV-6).

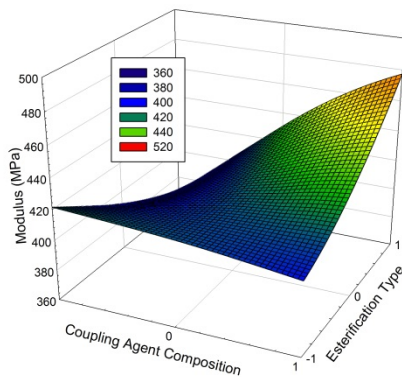
Table IV-7 ANOVA results (F-values) for tensile and flexural properties of bark/esterified lignin/HDPE WPC.

Source of variation	Tensile properties			Flexural property
	MOE (MPa)	Stress at break (MPa)	Strain at break (%)	MOE (MPa)
<i>Main effect</i>				
Type (Typ)	0.63 ^{NS}	1.32 ^{NS}	2.19 ^{NS}	8.80 ^{**}
Content (Cont)	1.35 ^{NS}	0.31 ^{NS}	18.3 ^{**}	1.15 ^{NS}
Composition (Comp)	0.64 ^{NS}	93.6 ^{**}	28.4 ^{**}	1.29 ^{NS}
<i>Interaction effect</i>				
Typ*Comp	4.83 [*]	1.61 ^{NS}	0.53 ^{NS}	1.84 ^{NS}
Cont*Comp	1.46 ^{NS}	0.79 ^{NS}	2.28 ^{NS}	0.85 ^{NS}

NS : Not significant at 0.05 probability level

* : Significant at 0.05 probability level

** : Significant at 0.01 probability level



Legend

Coupling agent composition (Axis)

-1 = 100% Lignin
 0 = 50% Lignin + 50% MAPE
 1 = 100% MAPE

Esterification type (Axis)

1 = Maleic esterified lignin
 0 = Maleated polyethylene
 -1 = Succinic esterified lignin

Figure IV-3 Surface response explaining the interactions observed in the statistical analysis: Tensile modulus (MPa) as a function of coupling agent composition and esterification type.

IV.6. Conclusions

In this study, composites based on HDPE with refined black spruce bark fibers (30% wt.) and coupling agents were produced. In particular, a novel way to improve compatibility between bark fibers and HDPE through the use of esterified Kraft lignins and a combination of these lignins with MAPE at equal amounts is presented. Since natural fibers contain lignin, lignin esterification created a structure which acted as a coupling agent between the hydrophobic HDPE matrix and hydrophilic bark fibers, while also improving compatibility by acting as a dispersing agent in combination with MAPE, due to partial similarity of chemical structures. The effect of coupling agent composition was determined to be highly significant on mechanical properties. The type of coupling agent (MAPE versus esterified lignin versus a mixture of them) was significant on flexural modulus, while coupling agent content (2, 5, and 10%) was significant for tensile strain at break.

Finally, coupling agent composition (MAPE:lignin ratio) was significant for stress at break. An interaction between coupling agent content and composition was significant on tensile modulus only. Each significant factor and the interaction give important knowledge which helped to understand how esterified Kraft lignin was acting inside the WPC.

The statistical analysis of interactions between composition and type of lignin esterification made it possible to find the best parameters to optimize the mechanical properties of the composites. A combination of maleic anhydride esterified Kraft lignin with MAPE, at a level of 5% total content (MAPE:esterified lignin of 2.5%:2.5%) allowed to reduce by half the use of commercial petrochemical coupling agent (MAPE), while succinic anhydride esterified Kraft lignin with MAPE, at a level of 2% total content (MAPE:esterified lignin; 1%:1%) allowed to cut MAPE content by five while producing composites with better properties.

These are important results since this research indicated the possibility of reducing the quantity of synthetic coupling agent (MAPE) and replacing it by esterified Kraft lignin while getting better mechanical results than MAPE alone. Keeping in mind these four refining principles used in this study:

- 30% of petrochemical matrix (HDPE) was replaced by black spruce bark fibers,
- Kraft lignin was obtained by precipitation from black liquor using CO₂ produced inside this pulp and paper process,
- precipitated Kraft lignin was esterified and the results obtained in this study indicate that it can be used to replace half of the synthetic coupling agent MAPE, or even to reduce its quantity to one fifth,
- these new WPC can be used to produce energy at the end of their life cycle, since they are constituted almost entirely of C, H and O.
- the development of biosourced composites studied in this research is therefore incorporating several sustainable chemistry and engineering principles [24].

V. Performance et propriétés des composites contenant du HDPE, des fibres d'écorce raffinées et des lignines Kraft estérifiées lors de tests de résistance aux gel-dégel

En voie de soumission dans un journal avec comité de lecture.

Performance and properties of HDPE composites containing refined bark fibers and esterified Kraft lignin upon exposure to freeze-thaw resistance tests

By:

Nicolas Mariotti, Daniel Grenier, Xiang-Ming Wang, Denis Rodrigue and Tatjana Stevanovic

V.1. Résumé

Des fibres d'écorce d'épinette noire raffinées et du polyéthylène de haute densité (HDPE) ont servi à produire des composites bois-plastiques (WPC) contenant des lignines Kraft estérifiées combinées à du polyéthylène maléaté (MAPE) comme agents de compatibilisation. La stabilité des produits qui en résulte a été étudiée par des expériences de gel-dégel. On a examiné l'effet de trois types d'extraction (non-extrait, eau ou soude) sur les fibres d'écorce pour trois proportions de lignines estérifiées Kraft (soit avec l'anhydride maléique ou succinique): MAPE (50: 50, 100: 0; 0: 100). La teneur en fibres d'écorces est maintenue constante à 30 % alors que la teneur totale en agent de couplage a été fixée à 5 %. Une analyse morphologique par microscopie électronique à balayage (MEB) a montré une bonne interface fibre-matrice pour toutes les préparations. Les résultats ont été complétés par calorimétrie différentielle à balayage (DSC), densité et propriétés mécaniques (en traction et en flexion). La formulation de WPC optimale (ayant des proportions égales de lignines estérifiées à l'anhydride maléique et MAPE avec une concentration totale de 5 %), ont montré une augmentation de 90 % du module de flexion, 70 % en traction, 75 % de résistance à la flexion et 25 % de résistance en traction par rapport au HDPE. Après le test de gel-dégel, les propriétés des WPC ont présenté une augmentation de 20 % du module de flexion et résistance à la flexion, tandis qu'une augmentation de 25 % pour le module d'élasticité en traction et de la résistance à la traction a été mesurée.

V.2. Abstract

Refined black spruce bark fibers and high density polyethylene (HDPE) were used to produce wood plastic composites (WPC) containing modified Kraft lignin with maleic polyethylene (MAPE) as compatibilizing agents. The stability of resulting products was investigated via freeze-thaw experiments. The effect of three types of extraction (none, water or soda) on bark fibers was examined for three proportions (100:0; 50:50; 0:100) of either esterified Kraft lignin (maleic or succinic anhydride) or MAPE. Bark fibers content was kept constant at 30% while coupling agent content was fixed at 5%. Morphological analysis through scanning electron microscopy (SEM) showed a good fiber-matrix interface for all formulations. The results were completed by differential scanning calorimetry (DSC), density and mechanical properties (tensile and flexural). The optimized WPC (equal proportions of maleic lignin and MAPE at a total concentration of 5%), showed an increase of 90% in flexural modulus, 70% in tensile modulus, 75% in flexural strength, and 25% in tensile strength compared to neat HDPE. After the freeze-thaw tests, the WPC properties showed an increase of 20% of flexural both modulus and strength, while an increase of 25% for tensile modulus and tensile strength were measured.

V.3. Introduction

Recently, the rise of environmentalism across the world made many people think on using “greener” materials and products following important contributions of non-governmental organizations [125]. Several studies have been performed on the design and manufacture of new eco-friendly materials. The most important argument is life cycle and sustainability of the materials developed [24]. Martinez *et al.* [126] analyzed the life cycle of a bio-composite plate (1 m²) made of recycled polyolefin (HDPE and PP), rice husks, and cotton fabric waste. The results showed that these bio-composites have potential to minimize impact on the environment compared to conventional production of plastics based products [24, 125-127].

Bark is produced in large quantities from wood transformation industries, but still lacks adequate uses due to several economic conditions [10]. Bark can be used as a source of extracts with important bioactive properties [16, 128]. Also, numerous research efforts have been made to use bark for high value-added products in various applications such as insulation boards, hardboards, fiberboards, and particleboards [12, 15, 117]. Recent studies focused on the manufacture of composites based on polyolefin matrices containing bark [17-19, 129]. The incorporation of bark particles can improve thermal stability and mechanical properties of wood plastic composites (WPC) [17-18].

For optimal results, the fiber-matrix interface must be improved in formulations using lignocellulosic fibers as reinforcement for most polyolefin matrices. Physical and chemical treatments were proposed to modify the fiber-matrix interface and increase adhesion in order to improve the mechanical properties of the resulting composites [1, 45, 48, 51-52]. However before incorporation, bark particles can be treated. Indeed, Ngueho-Yemele *et al.* [19] studied the impact of hot water extraction of black spruce bark “fibers-like” particles before their incorporation in high density polyethylene (HDPE). The interesting chemical compositions of the water extracts qualify for various valuable applications [19], while the extracted bark fibers remain available for conventional fiber applications or energy production.

On the other hand, Kraft lignins are becoming more available following several extraction methods like the LignoBoost process [22, 107-108]. These renewable polymers are now being explored for the design of eco-friendly industrial products [22, 100, 105, 107-108], which could become source of extra revenues for their producers.

The aim of the present study is to give an added-value to bark fibers by investigating the influence of two different extractions (boiling water and mercerization) towards the properties improvement of composites based on HDPE. Also, esterified Kraft lignins (with maleic or succinic anhydride) alone or in synergy with maleated polyethylene (MAPE) were explored as compatibilization agents between high density polyethylene and black spruce bark fibers by measurement of flexural and tensile properties of the resulting composites [129]. The performance of these bio-composites was also examined via freeze-thaw resistance test which is an important characterization to include in the development of new materials for outdoor applications in cold weather although very few data can be found in the literature. For example, Bengtsson *et al.* [130] found no statistical decrease in properties for WPC containing 40% pine flour with silane as coupling agent in HDPE following the freeze-thaw test. Tamrakar and Lopez-Anido [131] observed no significant effect of the freeze-thaw resistance test on the mechanical properties (quasi-static bending) for WPC containing 46% pine flour in polypropylene (PP).

V.4. Experimental

V.4.1. Materials

High density polyethylene, *Petromont* DMDC-6400, was used as the matrix. This polymer has a melt flow index of 7 g/10 min (ASTM D1238 at 190°C and 2.16 kg) and a density of 960 kg/m³. A commercial coupling agent (Epolene C-26), a maleated polyethylene (MAPE), was obtained by *Westlake Chemicals Corporation*, and used as reference. This MAPE has an acid number of 8 (mg KOH/g) and a molecular weight of 65,000 g/mol. Refined black spruce bark (*Picea mariana*) fibers were obtained from FPIInnovations (Quebec, Canada). The refining parameters are described in Fang *et al.* [17] and Gao *et al.* [15].

V.4.2. Precipitation and esterification of lignin

Black liquor from pulp and paper industry (*Kruger Wayagamack*, Quebec) containing a mixture of softwood species (black spruce/balsam fir/jack pine) was used to precipitate lignin. Carbon dioxide was used to precipitate lignin by decreasing the pH of black liquor from 13-14 to 8-9 following the procedure inspired by the *LignoBoost* process [22, 107-108, 132]. Lignin esterification protocol with maleic or succinic anhydride was optimized as presented in a previous report by Schorr *et al.* [132].

V.4.3. Bark fiber extractions and preparation

Two different extractions were done on bark fibers. A first batch was submitted to hot (boiling) water extraction with a fiber concentration of 30 g/L for three hours [19]. A second batch was extracted with 1% sodium hydroxide containing 10 g/L of fibers following ASTM D1109. Mass before and after each extraction was taken to determine weight loss caused by this pre-treatment. Humidity of bark fibers was measured, using three batches (5 g each) of fibers, after 48 h drying in an oven at 80°C.

V.4.4. Morphology and chemical characterisation of bark fibers

The size distribution of bark fibers was characterized with a fiber quality analyzer (*Fiber Quality Analyzer Code LDA02* from *OpTest Equipment Inc.*) using ISO 16065 to measure 5,000 fibers. Three repetitions on each batch of fibers (un-treated, hot water extracted and mercerized) were performed for average and standard deviation calculations. The chemical composition of the bark and wood fibers used in this study was determined in a previous study by Mariotti *et al.* [129].

V.4.5. Composites compounding

An internal batch mixer (*Haake Büchler Rheomix*) was used to prepare WPC containing black spruce bark fibers. Three mixtures were prepared for each WPC formulation. A rotational speed of 60 rpm was set to minimize mechanical shearing on the natural fibers. The mixture was kept at a temperature of 160°C for 9 minutes in order to minimize material degradation (thermo-oxidation), and to obtain homogeneous materials. The following protocol was applied for each batch: at t_0 HDPE was incorporated and melted while mixing; after three minutes the coupling agent was added (esterified lignin and/or MAPE) while continuous mixing was applied. Finally, after four minutes from the start, black spruce bark fibers were incorporated and mixing was performed for another five minutes (nine minutes total). In order to obtain WPC plates, the compounds were compression molded in a laboratory *Carver* press at 175°C with a load of 3 tons for 5 minutes in a mold with dimensions of 115 mm x 115 mm x 2.7 mm. The resulting plates were cut into standard dimensions for further characterization.

V.4.6. Surface coloration

Spectral measurements were made with a portable *spectrocolorimeter Color-guide 45/0 (BYK-Gardner)* using a 10° standard observer and standard illuminant D65. CIEL*a*b* color coordinates were calculated from the measured spectra. Four random measurements were done on each formulation and the parameters ΔL , Δa , Δb , and $\Delta E = \sqrt{(\Delta L)^2 + (\Delta a)^2 + (\Delta b)^2}$ were calculated to characterize the color change during freeze-thaw resistance test.

V.4.7. Crystallinity

Differential scanning calorimetry (*DSC 822e Mettler Toledo*) measurements were performed on 15 mg samples under a nitrogen atmosphere (flow of 50 ml/min) using a heating rate of 10°C.min⁻¹ over a temperature range from 50 to 200°C. *STARe Thermal Analysis Software 9.01* was used to calculate enthalpies and crystallinities from the melting endotherm. Equation (1) is used to measure the corrected crystallinity which takes into account the addition of bark fibers as:

$$\text{Corrected crystallinity (\%)} = \frac{\frac{\Delta H_{\text{bio-composite}}}{\Delta H_{\text{pure HDPE}}}}{1 - (\text{Bark \%})} \quad (1)$$

Where:

$\Delta H_{\text{bio-composite}}$ = Enthalpy of fusion, of the bio-composite (J/g);

$\Delta H_{\text{pure HDPE}}$ = Enthalpy of fusion, of a theoretical Polyethylene having a structure totally crystalline = 293 J/g (Wunderlich [124]);

Bark % = Bark content in bio-composite (%).

V.4.8. Density

Density of bark fibers was determined by a gas pycnometer, *ULTRAPYC 1200e* from *Quantachrome Instruments*, using nitrogen as the gas phase. The reported results are an average of five measurements

with standard deviation. For the density of the composites, an X-ray densitometer applying the program *QMS Density Profile System v1.25* was used. The density profile of the WPC is presented as the average with standard deviation.

V.4.9. Microstructural characterization

A *JEOL JSM-840A* scanning electron microscope (SEM) was used for morphological characterization. Each sample was broken using liquid nitrogen to expose the internal structure. The exposed surface was coated with a gold/palladium alloy under low pressure and observation was made at 15 kV using different magnifications.

V.4.10. Mechanical properties

Flexural and tensile properties, including modulus of elasticity, tensile or flexural strength and strain at yield, were determined. Three-point bending tests were performed according to ASTM D790 on samples having $80.0 \times 12.8 \times 2.5 \text{ mm}^3$ dimensions with a support span of 60 mm at a cross-head speed of 10 mm/min. ASTM D638 was used to perform tensile measurements on type V specimen at a cross-head speed of 1 mm/min. In each case, six repetitions per formulation were done using a universal mechanical tester model 5565 (Instron, USA) with a 50 N (flexural) or 500 N (tensile) load cell.

V.4.11. Statistical analyses

Experiments were conducted according to a D-Optimal design (Table V-1). The factors studied included three extractions (un-extracted, water extracted and soda extracted) and two lignin modifications (esterified with maleic or succinic anhydride) compared to MAPE from different proportions (100% modified lignin, 100% MAPE and 50:50 modified lignin:MAPE). Thus, 10 combinations (entries 2 to 11 in Table V-1) with three replicates were produced, for a total of 30 compounds. Three control blends without bark fibers were also manufactured under the same conditions (Entry). *Statistical Analysis System 9.3 (SAS)* was used for the statistical analysis. An analysis of variance (ANOVA) was performed on this experimental plan (three factors for 11 treatments). A control with neat HDPE (entry 1 in Table V-1) was used to discuss the results.

Contrasts were performed to determine interactions between the factors studied. Comparisons between treatments were performed following the Duncan method to determine the best formulation(s). This implies that all the formulations were examined by freeze-thaw test in order to compare the performance of the studied WPC before and after this test. Finally, a statistical two-sample t-test will be used on mechanical results, before versus after freeze-thaw, to determine if the null-hypothesis of equality of variances is validated or not.

Table V-1 Bark–HDPE WPC formulations: Design of experiment from D-Optimal in SAS 9.3.

Entry	Bark fibers content (%)			Coupling agent content (%)		
	Un-extracted	Hot water extracted	NaOH extracted	Maleic lignin	Succinic lignin	MAPE
1	HDPE					
2	0	0	30	5	0	0
3	0	0	30	0	0	5
4	0	0	30	2.5	0	2.5
5	0	30	0	0	5	0
6	0	30	0	5	0	0
7	0	30	0	0	2.5	2.5
8	0	30	0	2.5	0	2.5
9	30	0	0	5	0	0
10	30	0	0	0	2.5	2.5
11	30	0	0	2.5	0	2.5

V.4.12. Freeze-thaw resistance test

To determine the variation of the mechanical properties after freeze-thaw exposure, test specimens were submerged underwater for a period of 24 h. The specimens were then placed in a freezer at $-29 \pm 2^\circ\text{C}$ for 24 h. Once frozen, the specimens were brought to room temperature during a period of 24 h. This process represents one hydrothermal cycle. The above procedure (following ASTM D7031 and D7032) was repeated two more times for a total of three cycles of water submersion, freezing, and thawing. A complete characterization (physical and mechanical properties) was done before and after these tests to determine the effect of freeze-thaw cycles on these WPC.

V.5. Results and discussion

V.5.1. Black spruce fibers characteristics

The chemical composition of the refined black spruce bark fibers was analyzed for the same batch and the results reported previously [129]. These results show that bark fibers are composed of $47\pm 4\%$ cellulose, $44\pm 3\%$ lignin, and $8\pm 1\%$ pentosans (hemicelluloses) and extractives with hot water ($13\pm 1\%$), ethanol-toluene mixture ($8\pm 1\%$) and sodium hydroxide at 1% ($19\pm 1\%$) (the same extractives can be found in the different extracts). Indeed, the Andritz disk refiner used at an elevated temperature could cause some hemicelluloses losses. The anhydrous density of the bark determined previously by a nitrogen gas pycnometer was determined to be 1557 kg/m^3 , corresponding to the density of the cell walls [121-122, 129]. It is important to mention that the same type of extractives could be found in the studied extracts and that the extractives contents are obtained by independent extractions and not by successive ones. An important quality factor for integration of lignocellulosic fibers in WPC is their humidity content during processing. This content needs to be as low as possible. Therefore, the fibers were oven dried at 80°C for 48 h before processing and the humidity content was determined as average of three measurements. The results presented in Table V-2 show that humidity content is in the range of 3 to 3.5%.

V.5.2. Effects of extractions on black spruce fibers morphology

Fiber sizes determined by the fiber quality analyzer (FQA) are presented in Table V-2 together with aspect ratios (L/D). Because of the refining process used, the aspect ratio almost tripled compared to the value determined by Nguého-Yemele *et al.* [18]. The fibers used here have been already refined by Andritz disk and the water extraction did not seem to affect their aspect ratio. The hot water extraction caused 18% weight loss (Table V-2) following the solubilization of various classes of extractives [128]. In order to further increase the aspect ratio of the refined bark fibers, mercerization with 10% of NaOH according to ASTM 1109 was applied, since previous studies reported favourable results [45, 48]. The results presented in Table V-2 show a positive impact of mercerization, with an increase of 65% of aspect ratio. However, soda extraction resulted also in 36% weight loss which could be explained by the fact that this solvent system is reported to extract various classes of polyphenols, including some bark lignin, hemicelluloses, and suberin fragments [128]. Differences in hemicellulose content and FQA properties were used to explain physical and mechanical properties by Bouafif *et al.* [59] who showed that increasing fiber aspect ratio contributed to

improved strength, but also reduced elongation at break. The alkaline treatment (mercerization) was expected to improve the fiber aspect ratio and the fiber-matrix interface adhesion and therefore to increase the mechanical properties [1, 45, 48, 51-52].

Table V-2 Fibers dimensions measured using a fibers quality analyzer (FQA) and weight loss.

			Length (mm)	Diameter (μm)	Aspect ratio L/D	Weight loss during extraction (%)	Humidity during processing (%)
Refined	bark	fibers	0.89	46	28	0%	3.1%
	non-extracted		(0.03)	(2)	(1)	(0)	(0.1%)
Refined	bark	fibers	0.84	49	29	-18%	3.5%
	Water extracted		(0.03)	(2)	(1)	(2%)	(0.0%)
Refined	bark	fibers	1.00	32	46	-36%	3.5%
	Soda extracted		(0.03)	(1)	(2)	(3%)	(0.1%)

L/D = Length to diameter; Standard deviation is in parenthesis.

V.5.3. Effects of freeze-thaw resistance test on WPC

IV.5.2.a *Impact of the freeze-thaw resistance tests on mass and color of WPC*

As the freeze-thaw resistance test imposes water immersion during 24 h at 25°C, it was necessary to follow the mass variation to verify if the bark fibers inside the WPC formulations absorbed humidity during this test. This change is presented in Figure V-1. The obtained results indicate very low mass increase following the water uptake for all WPC (under 0.4% for the final evolution), but still somewhat higher than neat HDPE (nearly 0%) due to the hydrophobic nature of this polymer. This result indicates that the matrix can well protect the hydrophilic bark fibers from water absorption.

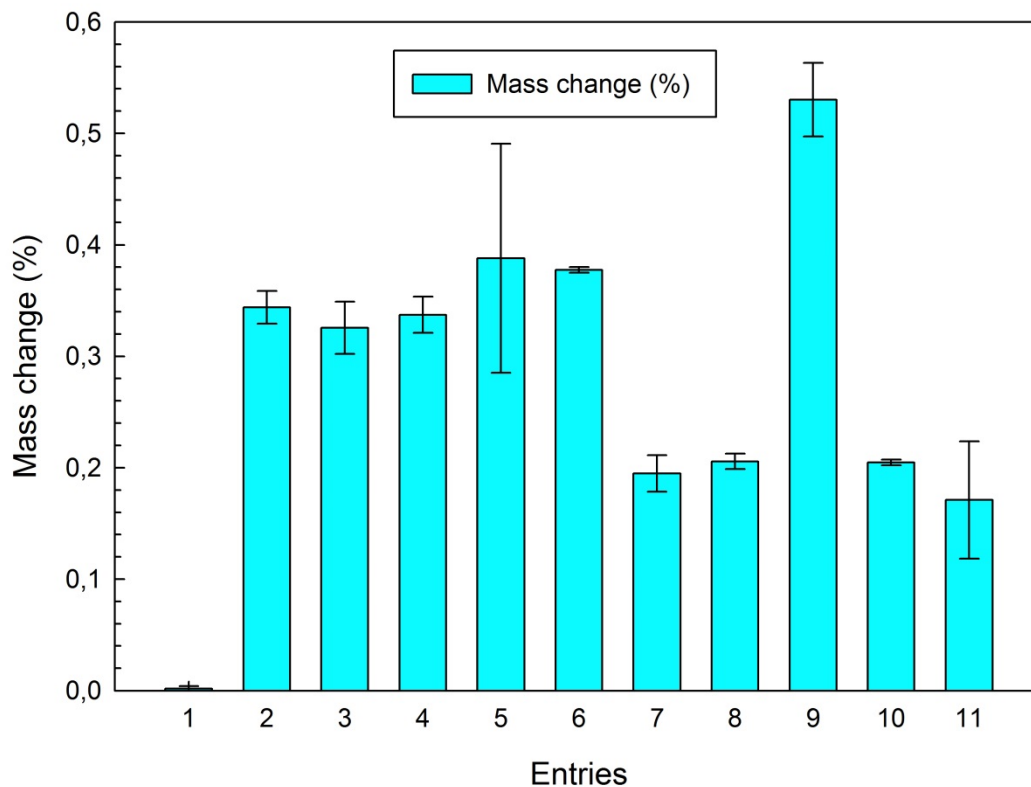


Figure V-1 Mass change of WPC during freeze-thaw resistance test (entries 1 to 11 refer to the formulations described in Table IV-1).

Due to the harsh test conditions applied during freeze-thaw cycles, it was considered important to check if color changes were present. It was important to determine if the WPC color had changed due to potential appearance of fungus or surface oxidation during water immersion over three days. The results presented in Table V-3 show that no such changes occurred during this test since no variations in terms of ΔE were obtained, indicating that no color modifications occur. ΔL^* , corresponding to the evolution in lightness (positive when closer to white), showed no change either (Table V-3). The parameters Δa^* and Δb^* were not affected, and the WPC formulations did not change in redness or blueness neither. Therefore the freeze-thaw tests did not induce any color changes which are otherwise related to UV-A or UV-B exposure, as reported in the literature [133].

Table V-3 Color evolution of WPC after freeze-thaw resistance test (entries 1 to 11 refer to the formulations described in Table IV-1).

Entry	ΔL	Δa	Δb	ΔE
1	0.7 (0.5)	0.2 (0.0)	-2.1 (0.5)	2.2 (0.6)
2	-1.6 (0.5)	0.6 (0.2)	0.1 (0.0)	1.7 (0.6)
3	-0.1 (1.7)	0.2 (0.3)	-0.1 (0.9)	1.4 (1.0)
4	0.9 (1.9)	-0.1 (0.4)	0.5 (0.5)	1.8 (1.1)
5	-0.6 (0.2)	-0.2 (0.3)	0.1 (0.5)	0.8 (0.2)
6	-0.2 (0.9)	-0.1 (0.3)	0.1 (0.2)	0.8 (0.4)
7	0.4 (0.7)	0.2 (0.2)	0.2 (0.4)	0.8 (0.4)
8	-1.1 (0.5)	0.0 (0.4)	0.3 (0.3)	1.2 (0.5)
9	-0.7 (0.7)	0.2 (0.2)	0.3 (0.3)	0.9 (0.5)
10	0.0 (0.2)	0.1 (0.2)	0.2 (0.2)	0.4 (0.1)
11	1.6 (1.0)	0.1 (0.5)	-0.3 (0.5)	1.8 (0.8)

Standard error is in parenthesis; Entries 1 to 11 refer to the formulations described in Table V-1.

IV.5.2.b *Impact of the freeze-thaw resistance tests on crystallinity and density*

The results shown in Figure V-2 illustrate that no significant difference for composites **1** (neat HDPE), **4** (a combination of maleic esterified lignin 2.5% and MAPE 2.5% with soda extracted bark fibers 30%) and **7** (a combination of 2.5% succinic lignin and 2.5% MAPE with water extracted fibers) for both density and crystallinity before and after the freeze-thaw resistance test. Moreover, the WPC composed of 30% non-extracted bark using a combination of maleic lignin and MAPE (**11**) had decreased crystallinity and increased density after the thaw-freeze tests. Improvements of flexural and tensile properties were possible. Nevertheless, other formulations having a different behaviour showed a constant crystallinity but a decrease in density as determined for the WPC composed of 30% soda extracted bark and 5% maleic lignin (Figure V-2b) and for 30% water extracted fibers and 5% maleic lignin (**6**). The composite incorporating 30% water extracted bark and a combination of maleic lignin and MAPE (**8**), or the one with 30% un-extracted bark and

maleic lignin (9) were determined to have stable density and increased crystallinity. The bio-composite made with 30% water extracted bark and 5% succinic esterified lignin (5) was determined to have higher density combined with a constant crystallinity. The formulation composed of 30% soda extracted bark and 5% MAPE (3) was constant in terms of density, but has decreased crystallinity. Finally, increase of density combined with a decrease in crystallinity has been demonstrated for WPC made from un-extracted bark fibers and a combination of succinic esterified lignin-MAPE (10). For formulations 2, 3, 5, 6, 8, 9 and 10 no clear tendencies are exposed in density and crystallinity results.

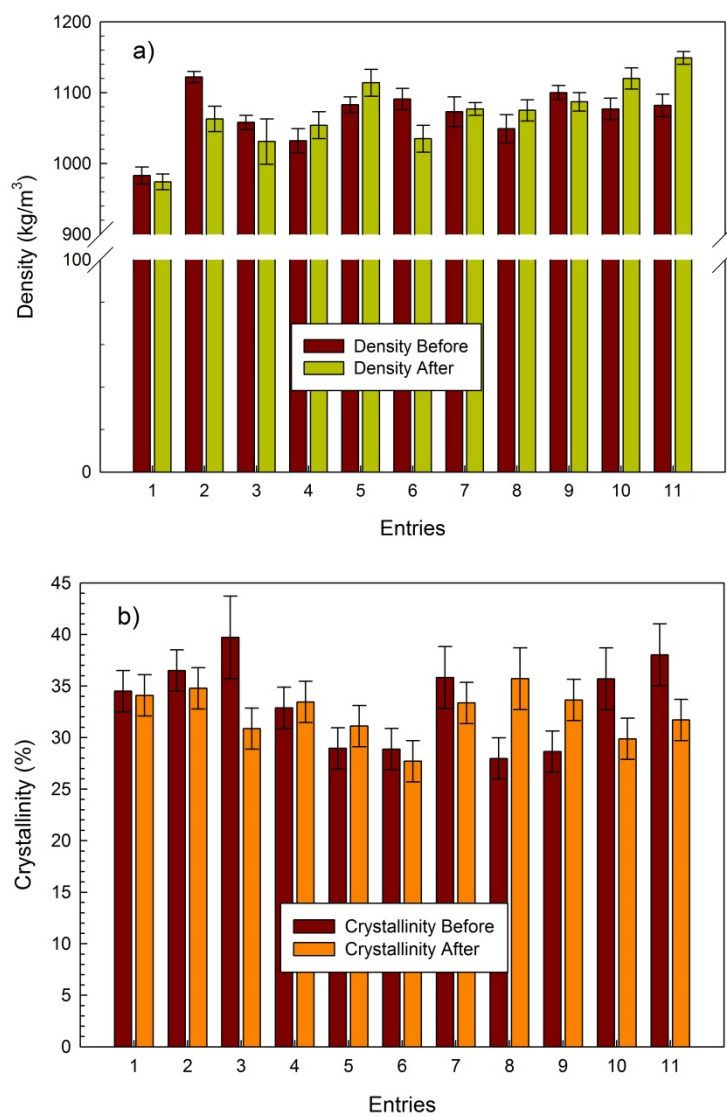


Figure V-2 Evolution of (a) density and (b) crystallinity caused by freeze-thaw resistance test (entries 1 to 11 refer to the formulations described in Table IV-1).

IV.5.2.c Impact of freeze-thaw resistance tests on the interface fiber-HDPE

Scanning electron micrographs were used to investigate the interface between black spruce bark fiber, esterified lignin, MAPE, and HDPE in a similar way as reported by Colom *et al.* [5] and Ramezani Kakroodi *et al.* [118]. The micrographs of the fractured surfaces of the composites containing 30% of black spruce are presented in Figures V-3 to V-12. These representative formulations were examined to understand the effect of MAPE or esterified lignin alone, or in combination, on interfacial adhesion. Composites having poor matrix-fiber interaction would not be able to support a significant part of the load and have weaker mechanical properties [118]. The differentiation between morphological appearance of each component (lignin, HDPE or black spruce fiber) was described in previous report [129], using SEM-EDS analyses.

After the freeze-thaw tests, all the formulations seem to have a good interface between the matrix and fibers (2 to 11 of Figures V-3 to V-12) or similar to the actual reference obtained with 5% of MAPE (3, Figure V-4). Moreover, the matrix seems to penetrate inside the pores of the fiber cells as shown in Figures V-5a (4), V-8a (7), and V-11a (10), possibly resulting in some improvements of the mechanical properties. Moreover, the weakest interface seems to be the one exposed after braking the composite containing 5% of maleic esterified Kraft lignin alone as coupling agent and un-extracted bark fibers in Figure V-10a (9), which was improved after the freeze-thaw tests, as can be observed in Figure V-10b (9). This could be explained by fibre swelling (Figure V-1) occurring during the freeze-thaw resistance tests leading to the fibers to “fill the gaps” observed at the interface in Figure V-10a (9). The slight fiber swelling observed which seems to help fill the gaps at the fiber-matrix interface, may have a positive influence on the mechanical properties due to a better stress transfer as can be observed in Figure V-10 (9). Observations made from Figures V-7a, V-7b (6) and V-10b (9) indicate important affinities, particularly between bark fibers and maleic. In addition, these observations confirm better affinity of maleic lignin than succinic lignin for extracted and un-extracted bark fibers. Since WPC were prepared by adding esterified lignin and MAPE before fibers are introduced in the HDPE matrix, it can be assumed that no chemical reaction occurs between esterified lignin and MAPE prior to fiber incorporation. Three hypotheses about interactions between lignin and fibers are available: Firstly, free carboxylic acid group present at esterified lignin after reaction with anhydride, reacts with OH groups from fibers forming covalent bonds (ester), in addition to π - π interaction which occurs between aromatic moieties of esterified lignins and lignin from bark fibers in combination with van der Waals interactions between the HDPE and the polyethylene side chain of MAPE. Indeed, as reported in the literature about π - π interaction [134-135], the properties of our material induced by the covalent linkage, could be reinforced

by intermolecular π - π system in addition to a van der Waals interaction. The second reaction is that of MAPE with OH groups of fibers by covalent bonds and leading to dipole-dipole interaction with HDPE in addition to aromatic stacking between bark and lignin for interaction reinforcing. The third hypothesis is that the previous two are occurring simultaneously. Therefore, according to obtained results we could propose the third hypothesis being the most probable.

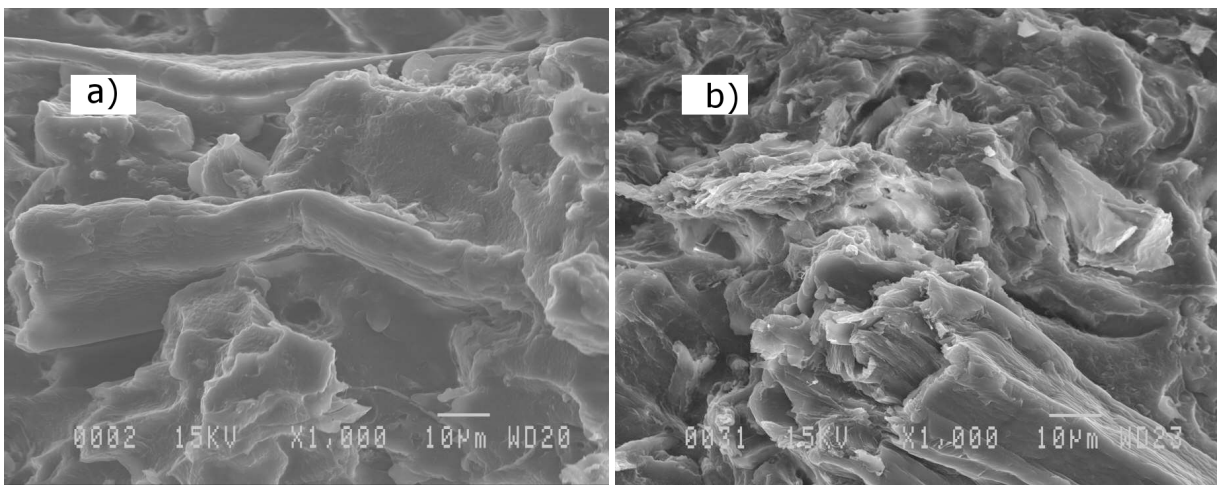


Figure V-3 WPC containing 30% soda extracted fibers and 5% maleic lignin: a) before freeze-thaw resistance tests; b) after freeze-thaw resistance tests.

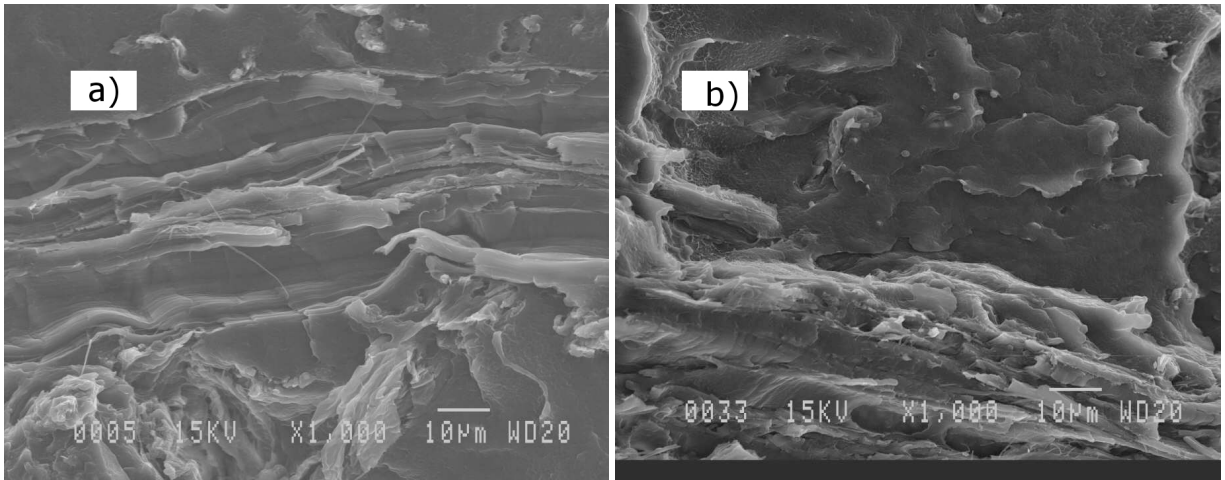


Figure V-4 WPC containing 30% soda extracted fibers and 5% MAPE: a) before freeze-thaw resistance tests; b) after freeze-thaw resistance tests.

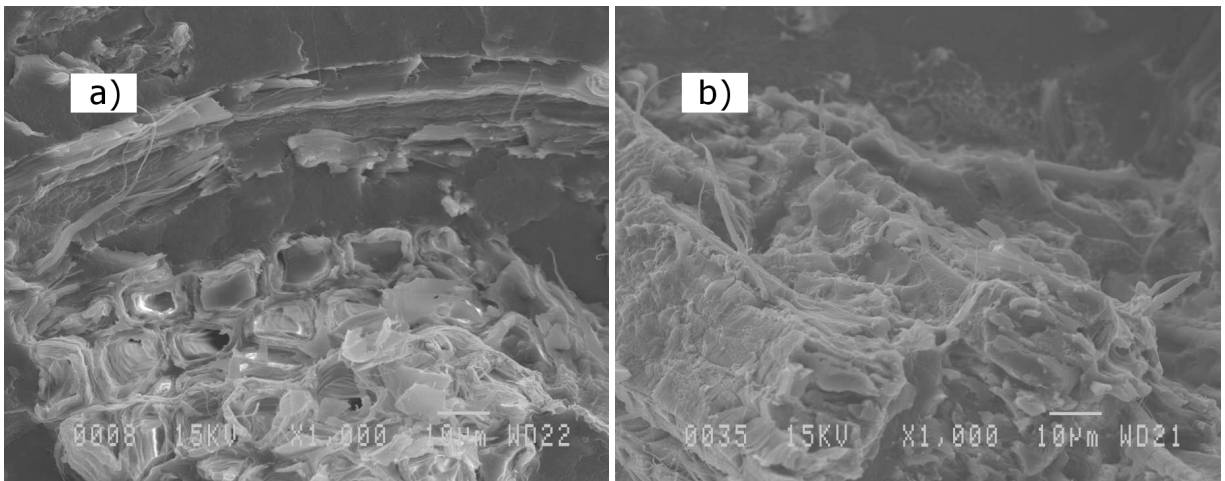


Figure V-5 WPC containing 30% soda extracted fibers and a combination of 2.5% maleic lignin with 2.5% MAPE: a) before freeze-thaw resistance tests; b) after freeze-thaw resistance tests.

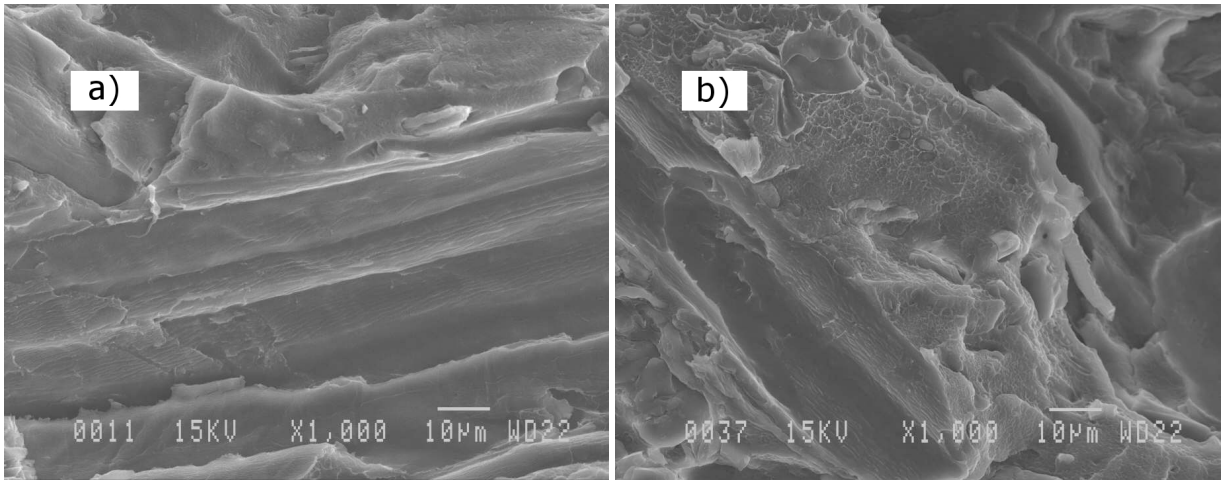


Figure V-6 WPC containing 30% water extracted fibers and 5% succinic lignin: a) before freeze-thaw resistance tests; b) after freeze-thaw resistance tests.

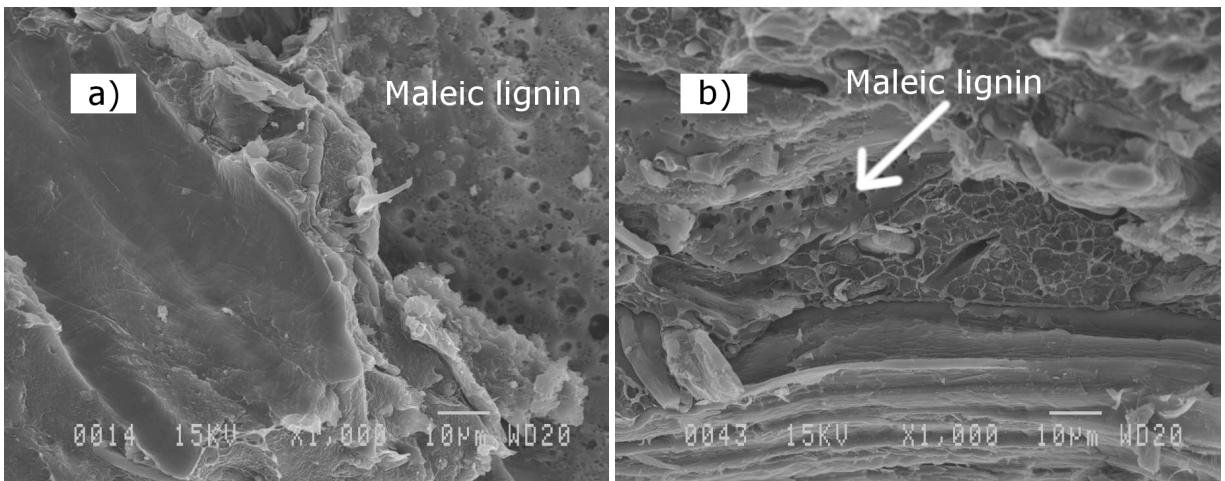


Figure V-7 WPC containing 30% water extracted fibers and 5% maleic lignin: a) before freeze-thaw resistance tests; b) after freeze-thaw resistance tests.

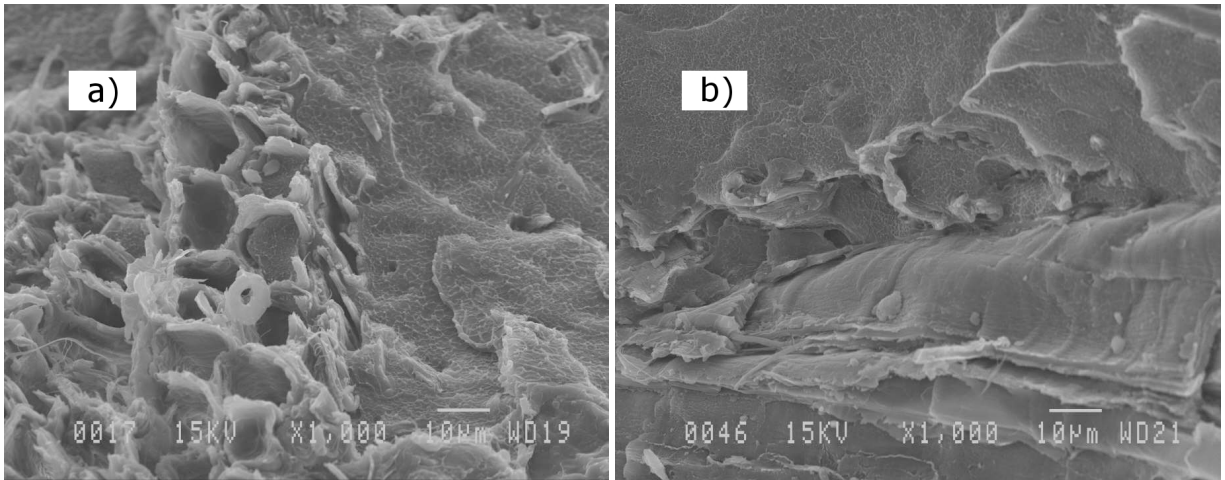


Figure V-8 WPC containing 30% water extracted fibers and a combination of 2.5% succinic lignin with 2.5% MAPE: a) before freeze-thaw resistance tests; b) after freeze-thaw resistance tests.

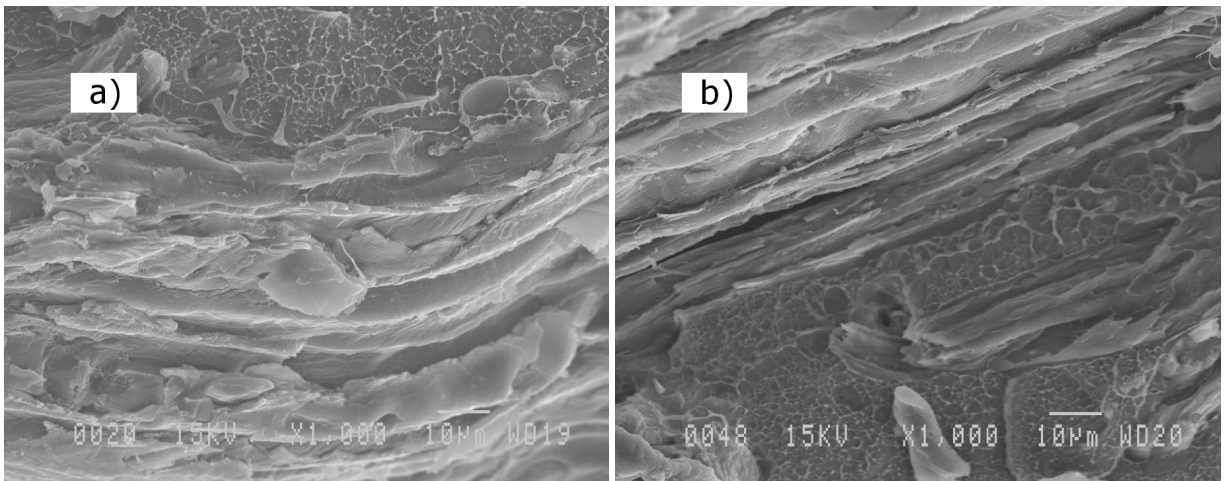


Figure V-9 WPC containing 30% water extracted fibers and a combination of 2.5% maleic lignin with 2.5% MAPE: a) before freeze-thaw resistance tests; b) after freeze-thaw resistance tests.

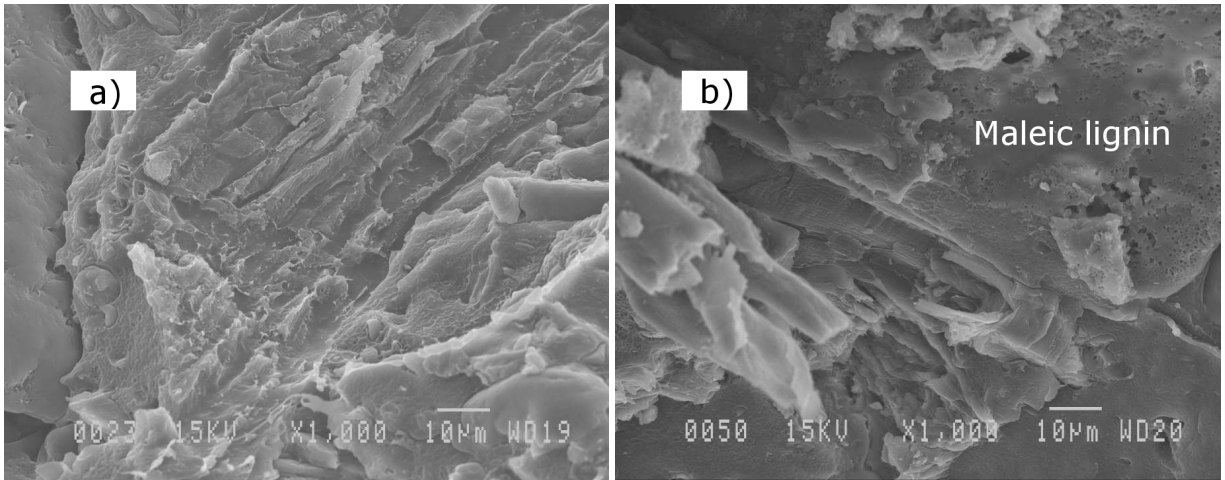


Figure V-10 WPC containing 30% non-extracted fibers and 5% maleic lignin: a) before freeze-thaw resistance tests; b) after freeze-thaw resistance tests.

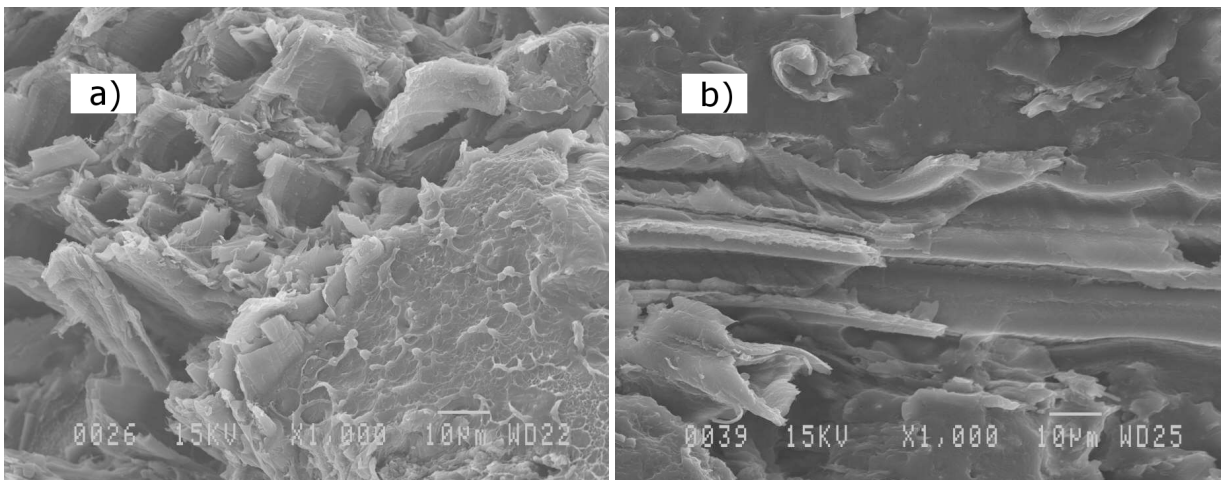


Figure V-11 WPC containing 30% non-extracted fibers and a combination of 2.5% succinic lignin with 2.5% MAPE: a) before freeze-thaw resistance tests; b) after freeze-thaw resistance tests.

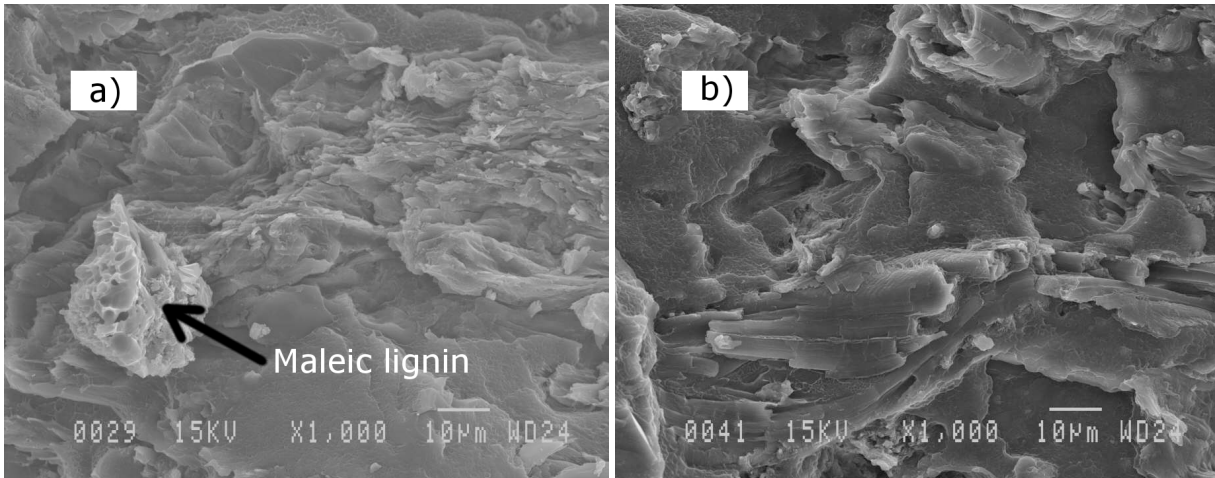


Figure V-12 WPC containing 30% non-extracted fibers and a combination of 2.5% maleic lignin with 2.5% MAPE: a) before freeze-thaw resistance tests; b) after freeze-thaw resistance tests.

V.5.4. Mechanical properties of WPC

IV.5.3.a Impact of freeze-thaw resistance test on flexural properties

The flexural Young modulus (MOE) was determined to be in the range from 1,000 to 1,365 MPa, for the composites before freeze-thaw test (Figure V-13a), which represents a 60 to 110% improvement compared to neat HDPE (650 MPa). The composition of coupling agent is highly significant (Table V-4) confirms that the efficiency of the combination of the esterified Kraft lignin depends on the chemical properties of the fibers surface. The flexural strength was determined to vary in the range from 18 to 29 MPa (versus 16 MPa for neat HDPE). Using the coefficient of determination (Table V-4), the composition of coupling agent was the only factor that explained 55% of these results. The flexural strain had a maximum decrease of 25% corresponding to a less elastic behavior of the material as expected, with a strain of 6% for WPC versus 9% for the HDPE. The only significant factor revealed was the composition of coupling agent (Table V-4) this only factor could explain 55% of the results obtained for the flexural strain. The extraction effect was determined to never be significant for the flexural properties (Table V-4), thus confirming that it would be possible to use the extracted black spruce bark fibers leaving the extractives available for value added-applications such as in pharmaceutical or nutraceutical area [16, 19, 128].

After the freeze-thaw resistance tests (Figure V-13b), flexural modulus was in the range from 1,130 to 1,400 MPa, representing a 50 to 85% improvement compared to neat HDPE (760 MPa). The statistical model developed using SAS 9.3 explained only 29% of the results for the Young modulus (MOE in MPa) for flexural test (Table V-4) proving that other factors not considered here may have an impact on this property. This low level could also be explained by the technical difficulties while trying to obtain enough precision when measuring the low deformation in the elastic zone of the WPC. Flexural strength was determined to

vary in the range from 22 to 32 MPa (versus 17 MPa for neat HDPE), indicating an increase from 25 to 85% compared to neat HDPE. The effect of composition of coupling agent was highly significant for this mechanical indicator (Table V-4). The flexural strain had a maximal decrease of 20% corresponding to a less elastic behavior of the material as expected, with a minimum strain of 6% for the composite versus 8% for the neat HDPE explained by the composition of coupling agent. These results were similar to those reported by Ngueho-Yemele *et al.* [19] for the HDPE composites containing “fiber-like” particles of black spruce bark, with a flexural modulus of 1,436 MPa and a flexural strength of 16 MPa. The composition of coupling agent was the major factor for the flexural properties. The type of extraction effect was determined to be never significant for flexural properties (Table V-4), confirming the possibility of using bark extractives without damaging effect on the composites [16].

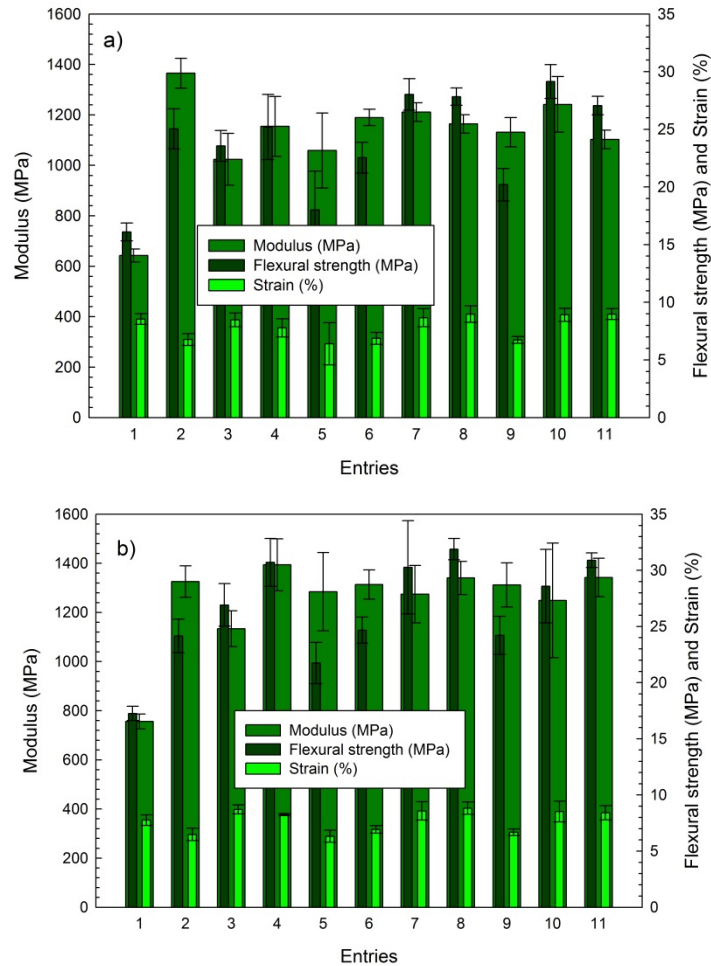


Figure V-13 Flexural properties of WPC (entries 1 to 11 refer to the formulations described in Table IV-1): a) before freeze-thaw resistance tests; b) after freeze-thaw resistance tests.

Table V-4 ANOVA results (F-values) for flexural properties of bark/esterified lignin/HDPE composites.

Source of variation	Flexural properties					
	Before freeze-thaw resistance test			After freeze-thaw resistance test		
	MOE (MPa)	Flexural strength (MPa)	Strain (%)	MOE (MPa)	Flexural strength (MPa)	Strain (%)
<i>Main effect</i>						
Extraction (Ext)	0.43 ^{NS}	2.42 ^{NS}	2.01 ^{NS}	0.13 ^{NS}	0.56 ^{NS}	0.66 ^{NS}
Esterification type (Typ)	4.11*	0.15 ^{NS}	4.04 ^{NS}	9.93**	1.67 ^{NS}	8.46*
Composition (Comp)	11.4**	60.3**	32.2**	2.65 ^{NS}	57.8**	68.4**
<i>Interaction effect</i>						
Ext*Typ	8.75*	13.7**	0.71 ^{NS}	0.28 ^{NS}	0.04 ^{NS}	1.23 ^{NS}
Ext*Comp	8.81**	15.0**	1.99 ^{NS}	0.22 ^{NS}	0.42 ^{NS}	0.42 ^{NS}
Typ*Comp	5.59*	8.39*	0.05 ^{NS}	0.12 ^{NS}	0.46 ^{NS}	0.50 ^{NS}
<i>Coefficient of determination</i>						
Model (%)	60	82	66	29	75	79
Extraction (%)	0.8	2.3	3.5	0.5	0.7	0.7
Esterification type (%)	4.0	0.2	3.5	17.6	1.0	4.5
Composition (%)	23	55	55	9.4	72.4	72.3
Ext*Typ (%)	8.7	6.5	0.6	0.5	0.1	0.7
Ext*Comp (%)	18	14	3.4	0.8	0.5	0.5
Typ*Comp (%)	5.5	4.0	0.0	0.2	0.3	0.3

NS = not significant at 0.05 probability level; * = significant at 0.05 probability level; ** = significant at 0.01 probability level.

IV.5.3.b Impact of freeze-thaw resistance tests on tensile properties

Before freeze-thaw resistance test (Figure V-14a), tensile MOE values were in the range from 325 to 400 MPa (215 MPa for HDPE), giving an improvement from 50 to 85%. The statistical model explained only 30% of the results about the Young modulus in Table V-5, other factors not considered here may have an impact on this property. The tensile strength of the WPC was in the range from 12 to 22 MPa corresponding to a maximum improvement of 25% compared to neat HDPE. The interaction between the type of esterification and the composition of coupling agent was highly significant (Table V-5), explaining 55% of these results. This observation confirms that the efficiency of the combination of esterified Kraft lignin with the fibers surfaces depended on their chemical properties which then helped to create the optimum interactions between bark fibers, esterified Kraft lignin, MAPE, and HDPE. As expected, the tensile strain has a maximum decrease of 70%, proving a less elastic behavior from 8 to 15% for WPC versus 24% for the neat HDPE. The interaction between the extraction and the composition of coupling agent was

significant (Table V-5). The composition of coupling agent was still the main factor. The type of esterification is significant, this new significant interaction factor was important because it can explain differences between the efficiency of maleic and succinic esterification (Figures 7 (6), 10b (9) and 12a (11)). Again, removing the extractives from the black spruce bark fibers did not produce mechanical properties changes for the composites.

After freeze-thaw resistance tests (Figure V-14b), tensile MOE values were in the range from 320 to 440 MPa (260 MPa for HDPE), giving an improvement from 25 to 70% compared to neat HDPE. The statistical model explained only 39% of the results about the Young modulus, other factors will have to be considered. The tensile strength of the WPC was in the range from 12 to 24 MPa corresponding to a maximum improvement of 25% compared to neat HDPE. The composition of coupling agent was still main factor (Table V-5). As expected, the tensile strain has a maximum decrease of 70%, proving a decreased elastic behavior from 7 to 16% for WPC versus 24% for the HDPE. The tensile strain was explained by the model at 77% (Table V-5) and the composition of coupling agent is still the main factor. Contrary to flexural and tensile properties before freeze-thaw resistance tests (Table V-4), extraction was a significant factor for tensile properties (Table V-5) after freeze-thaw resistance tests.

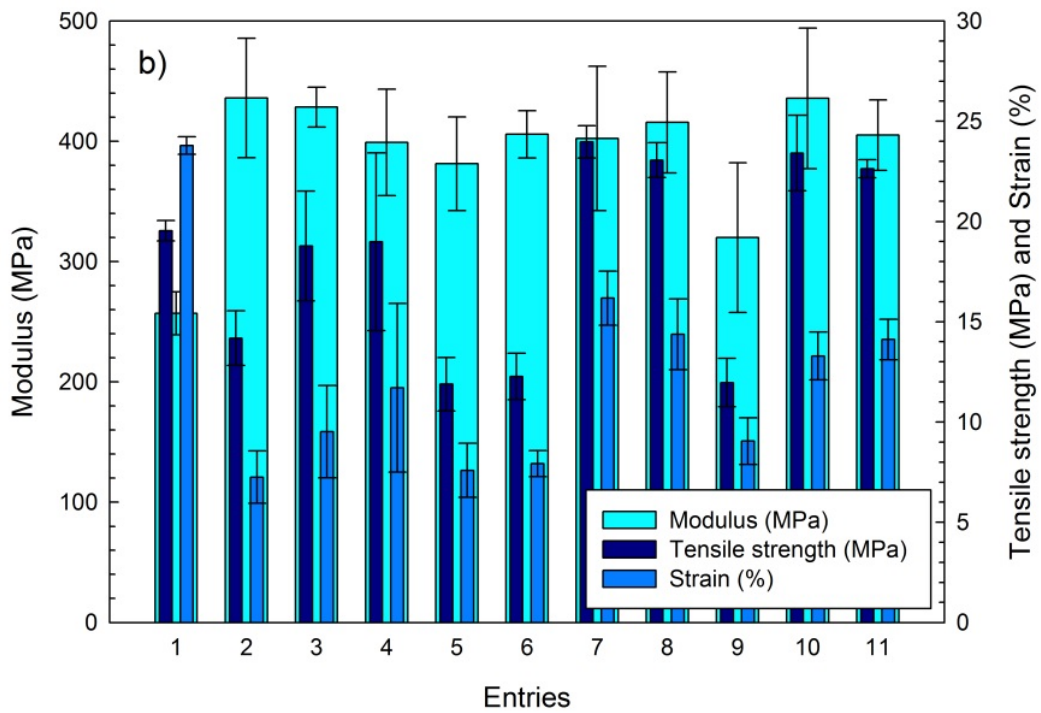
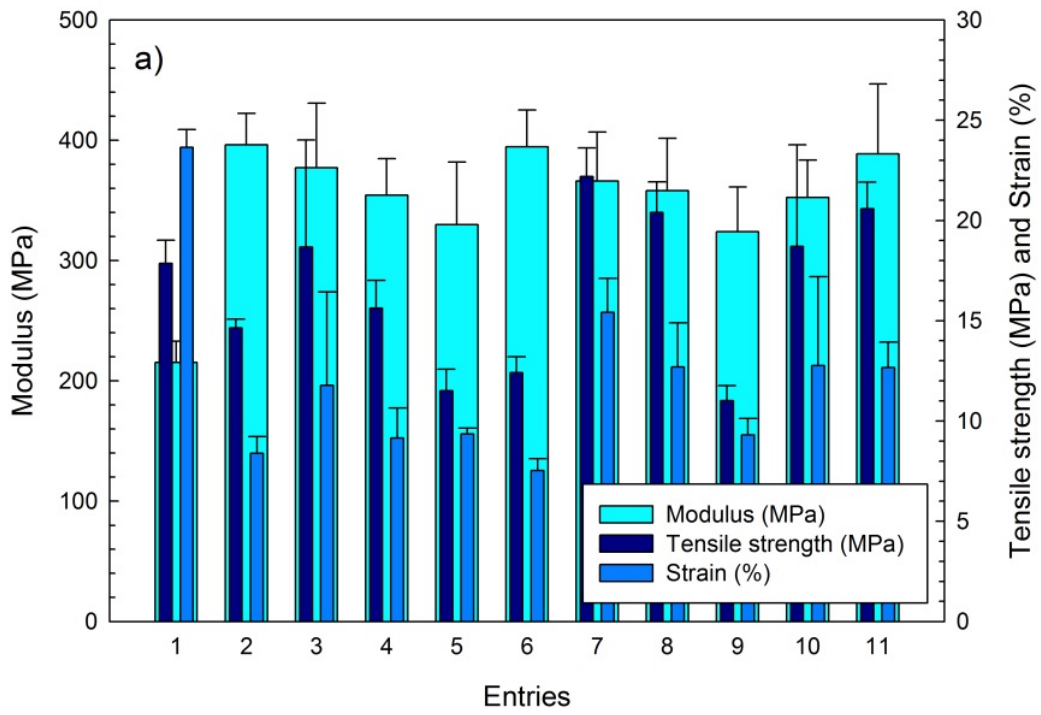


Figure V-14 Tensile properties of WPC (entries 1 to 11 refer to the formulations described in Table IV-1): a) before freeze-thaw resistance tests; b) after freeze-thaw resistance tests.

The determined mechanical properties were lower than those reported by Bouafif *et al.* [59] for HDPE composites containing bark “fiber-like” particles, having a modulus of elasticity equal to 1,600 MPa, a tensile strength of 22 MPa and a strain at break of 7%. These differences were probably due to a different grade of the HDPE used. Nevertheless, the results of Figure V-14 are slightly better than those reported for composites containing hemp fibers by Ramezani Kakroodi *et al.* [118] who observed a tensile modulus of elasticity of 340 MPa, a tensile strength of 15.3 MPa and a strain at break of 17% for composites containing 30% of hemp fibers.

Table V-5 ANOVA results (F-values) for tensile properties of bark/esterified lignin/HDPE composites.

Source of variation	Tensile properties					
	Before freeze-thaw resistance test			After freeze-thaw resistance test		
	MOE (MPa)	Tensile strength (MPa)	Strain (%)	MOE (MPa)	Tensile strength (MPa)	Strain (%)
<i>Main effect</i>						
Extraction (Ext)	0.98 ^{NS}	0.12 ^{NS}	2.59 ^{NS}	2.20 ^{NS}	4.38*	8.27**
Esterification type (Typ)	1.09 ^{NS}	7.45*	11.7*	1.47 ^{NS}	18.6**	2.18 ^{NS}
Composition (Comp)	0.47 ^{NS}	42.8**	12.7**	2.01 ^{NS}	127**	52.5**
<i>Interaction effect</i>						
Ext*Typ	0.52 ^{NS}	0.43 ^{NS}	2.04 ^{NS}	6.40*	0.55 ^{NS}	2.34 ^{NS}
Ext*Comp	4.19*	10.3**	3.65*	4.68*	9.96**	2.73 ^{NS}
Typ*Comp	3.79 ^{NS}	1.40 ^{NS}	0.19 ^{NS}	0.08 ^{NS}	0.54 ^{NS}	1.60 ^{NS}
<i>Coefficient of determination</i>						
Model (%)	30	74	56	39	88	77
Extraction (%)	3.6	0.2	5.7	6.7	2.5	9.6
Esterification type (%)	2.0	4.7	13	2.2	5.4	1.3
Composition (%)	1.8	55	27	6.1	74.0	60.6
Ext*Typ (%)	0.9	0.3	2.1	9.7	0.2	1.4
Ext*Comp (%)	15	13	8.0	14.2	5.7	3.2
Typ*Comp (%)	6.7	0.8	0.2	0.1	0.2	0.9

NS = not significant at 0.05 probability level; * = significant at 0.05 probability level; ** = significant at 0.01 probability level.

IV.5.3.c Change in flexural and tensile properties due to the WPC formulations efficiency

The best formulations in terms of general mechanical properties (tensile and flexural) were obtained using a Duncan statistical test as shown in Table V-6, in which the mercerized fibers were used with 5% MAPE or with the combination of 2.5% maleated lignin with 2.5% MAPE. For the WPC using water extracted bark fibers, the best formulations were with 5% maleated lignin, or the combination of 2.5% succinic lignin with 2.5% MAPE, or the combination of 2.5% maleated lignin with 2.5% MAPE. Finally, using un-extracted bark fibers, the only good formulation was determined to be the combination of 2.5% succinic lignin with 2.5% MAPE, as found in our previous work [129]. A difference in gain can be observed in tensile and in flexural properties. This can be explained because in tension, the macromolecules are clearly stretched, whereas in flexural testing a portion of the macromolecules is in tensile while another portion is in compression mode. Moreover, the stress direction versus the fibers direction in the matrix is different in tensile (parallel to fiber) and in flexural (perpendicular to the fibers) tests. The mercerization was expected to improve mechanical properties of WPC due to a better aspect ratio (Table V-2). But the statistical analyses before freeze-thaw resistance tests (Tables V-4 and V-5) proved the non-significance of the extraction factor. It is possible that the diameter of the bark fibers was too low (Table V-2) for the bark fibers to act as reinforcing agent.

Table V-6 Flexural and tensile properties change (in %) for WPC formulations compared to WPC before freeze-thaw resistance tests (entries 1 to 11 refer to the formulations described in Table IV-1).

Entry	Change in flexural properties (%)			Change in tensile (%)		
	Modulus	Flexural strength	Maximum strain	Modulus	Tensile strength	Maximum strain
2	112 ^A	56 ^{BC}	-21 ^{CD}	84 ^A	-18 ^{DEF}	-65 ^E
3	59 ^E	46 ^{CD}	-1 ^{AB}	75 ^{AB}	5 ^{BC}	-50 ^{CD}
4	80 ^{BCD}	56 ^{BC}	-9 ^{BC}	64 ^{AB}	-12 ^{CDE}	-61 ^{DE}
5	65 ^{ED}	12 ^{EF}	-25 ^D	53 ^B	-36 ^{FG}	-60 ^{DE}
6	85 ^{BC}	40 ^D	-20 ^{CD}	83 ^A	-31 ^{EFG}	-68 ^E
7	88 ^{BC}	74 ^A	1 ^{AB}	70 ^{AB}	24 ^A	-35 ^B
8	81 ^{BCD}	73 ^A	5 ^A	66 ^{AB}	14 ^{AB}	-46 ^{BC}
9	76 ^{CDE}	25 ^E	-21 ^{CD}	50 ^B	-38 ^G	-61 ^{DE}
10	93 ^B	81 ^A	4 ^A	64 ^{AB}	5 ^{BC}	-46 ^{BC}
11	72 ^{CDE}	68 ^{AB}	5 ^A	80 ^A	15 ^{AB}	-46 ^{BC}

For each property, values followed with the same letter are not significantly different and values followed with different letters are significantly different at 0.05 probability level, using a statistical test of Duncan

IV.5.3.d Change in flexural and tensile properties due to the freeze-thaw resistance tests

Table V-7 shows an increase of the flexural properties after the freeze-thaw test, which was unexpected. A decrease of less than 5% was obtained for the formulation containing soda extracted bark fibers using maleic esterified Kraft lignin as coupling agent, for flexural modulus, flexural strength and strain. But the flexural strength of all the other formulations was determined to increase up to 20% for the composites based on a combination of maleic lignin with MAPE as coupling agent with soda extracted or un-extracted fibers. The increase of flexural and tensile properties is not related to mass change (Figure V-1) or to crystallinity or density (Figures V-2-a, and V-2-b) nor to the morphology (Figures V-3 to V-12) as demonstrated by the obtained testing results. A complementary study to find an explanation to this behavior will be conducted in the future. Concerning the tensile properties, Table V-8 shows the increase of tensile properties after the freeze-thaw test. An increase of up to 25% was determined for flexural properties for the formulation using a combination of succinic lignin with MAPE as coupling agent with un-extracted fibers. The statistical analysis on tensile properties after freeze-thaw resistance test (Table V-5), indicates that the extraction of fibers has a significant negative impact on tensile strength and strain of WPC only due to soda extraction, no statistical differences are obtained due to water extraction.

Table V-7 Change due to freeze-thaw resistance test on flexural and tensile properties of WPC combined to a two-sample t-test to validate the difference between before and after this test (entries 1 to 11 refer to the formulations described in Table IV-1).

Entry	Change in flexural properties (%)			Change in tensile properties (%)		
	Modulus	Flexural strength	Maximum strain	Modulus	Tensile strength	Maximum strain
1	18 ^{NS} (4)	7 ^{NS} (4)	-9 ^{NS} (5)	19 ^{NS} (7)	9 ^{NS} (4)	1 ^{NS} (3)
2	-3 ^{NS} (4)	-4 ^{NS} (6)	-4 ^{NS} (7)	10 ^{NS} (8)	-3 ^{NS} (6)	-14 ^{NS} (13)
3	11 ^{NS} (7)	14 ^{NS} (6)	3 ^{NS} (5)	14* (8)	0 ^{NS} (19)	-19 ^{NS} (29)
4	21 ^{NS} (8)	22 ^{NS} (8)	6** (5)	13 ^{NS} (9)	21* (14)	28 ^{NS} (23)
5	21 ^{NS} (12)	21 ^{NS} (12)	-1* (17)	16 ^{NS} (12)	3 ^{NS} (9)	-19* (9)
6	10 ^{NS} (3)	9 ^{NS} (5)	1 ^{NS} (6)	3 ^{NS} (6)	-1 ^{NS} (7)	5 ^{NS} (7)
7	5* (5)	8 ^{NS} (8)	-1 ^{NS} (8)	10 ^{NS} (12)	8 ^{NS} (4)	5 ^{NS} (9)
8	15 ^{NS} (4)	15 ^{NS} (3)	-2 ^{NS} (6)	16 ^{NS} (10)	13 ^{NS} (5)	13 ^{NS} (13)
9	16 ^{NS} (5)	20 ^{NS} (6)	-1 ^{NS} (4)	-1 ^{NS} (14)	9 ^{NS} (8)	-3 ^{NS} (10)
10	1 ^{NS} (12)	-2 ^{NS} (7)	-4 ^{NS} (8)	24 ^{NS} (10)	25 ^{NS} (6)	4* (20)
11	22 ^{NS} (4)	14 ^{NS} (2)	-6 ^{NS} (6)	4 ^{NS} (10)	10 ^{NS} (4)	11 ^{NS} (8)

Standard deviation are in parenthesis. NS = the null-hypothesis of equality of variances is not significant at 0.05 probability level; * = the null-hypothesis of equality of variances is significant at 0.05 probability level; ** = the null-hypothesis of equality of variances is significant at 0.01 probability level.

The best formulations in terms of general mechanical properties (tensile and flexural), after the freeze-thaw resistance tests, were determined using a Duncan statistical test as presented in Tables V-4 to V-7. These best formulations were based on un-extracted fibers with a combination of maleic esterified Kraft lignin with MAPE or those based on water extracted bark fibers with a combination of maleic or succinic Kraft lignin with MAPE or one with soda extracted fibers with maleic lignin and MAPE. These results are confirming our previously published findings on the combination of esterified Kraft lignin (succinic or maleic) with MAPE as optimized coupling agents [129].

V.6. Conclusions

In this study, composites based on HDPE with refined black spruce bark fibers (30% wt.) and different coupling agents were produced. A novel way for improving compatibility between bark fibers and HDPE reported here is through the use of esterified Kraft lignins in combination with equal quantity of MAPE. The extractions were performed in order to determine the efficiency of this combination to act on bark fibers surfaces properties. These extractions had different effects on the dimensions of the fibers, with no changes using water extraction, but an improvement of the aspect ratio using soda extraction. Nevertheless, the mechanical properties of the WPC formulations tested were not affected by these treatments. The efficiency of the combination of esterified lignins with MAPE at an equal content was better than using MAPE alone. Implementation of this green engineered WPC product will have a positive impact on local economic development and environmental protection. The economic influence can be realized by using the valuable asset of residues of wood transformation (bark) in a high value added composite product. The sustainability of these WPC products and their impact on the environment can be outlined as follows:

- ✓ 30% of petrochemical matrix (HDPE) is replaced by black spruce bark fibers,
- ✓ Kraft lignin is obtained by precipitation from black liquor using CO₂,
- ✓ the efficiency of the combination of esterified Kraft lignins with MAPE indicates that it can be used to replace half of the synthetic coupling agent MAPE,
- ✓ the possibility of replacement of synthetic materials by these new composites,
- ✓ the availability of extractives, thus a co-product of bark extractions, for food, nutraceutical or pharmaceutical applications,
- ✓ the freeze-thaw resistance tests had no impact on WPC color for the conditions tested,
- ✓ no clear tendencies are observed on change of density and crystallinity due to the freeze-thaw resistance tests,
- ✓ the fiber-matrix interface did not change after freeze-thaw resistance tests,
- ✓ the impact of freeze-thaw resistance tests depends on WPC formulation; the best improvements were 20% in flexural properties and 25% in tensile properties.

VI. Conclusion générale et Recommandations

Conclusion générale

La mise au point de composites bois-plastiques, à base de polyéthylène de haute densité (HDPE), avec des fibres raffinées d'écorce d'épinette noire et de lignine Kraft, en appliquant les principes de l'ingénierie verte nécessite qu'une attention particulière soit accordée au choix des paramètres du procédé utilisé et des composantes à utiliser pour la préparation des formulations afin d'optimiser les performances du matériau conçu. L'évaluation des propriétés des composites bois-plastique fabriqués dans ce projet permet :

- (i) de déterminer le potentiel de l'utilisation des lignines non modifiées ou estérifiées comme agent de couplage en se basant sur la littérature;
- (ii) de déterminer la meilleure combinaison de lignines estérifiées-MAPE et la meilleure formulation de composites fabriqués;
- (iii) d'étudier la possibilité d'avoir une source d'extractible en parallèle de la fabrication de WPC ainsi que l'applicabilité de ce matériau en vue d'une exploitation en extérieur.

Ce travail de recherche peut se séparer en trois parties. Le premier volet avait comme objectif général de déterminer le potentiel d'utilisation de lignines non modifiées et estérifiées pour améliorer les propriétés des composites développés dans ce projet. Quant au second volet, l'objectif visait à optimiser les performances des WPC fabriqués avec des fibres raffinées d'épinette noire, par combinaison de l'agent de couplage commercial (MAPE) à des lignines estérifiées à différentes concentrations. Et finalement, le dernier volet examinait la faisabilité technique à l'échelle laboratoire de la fabrication de ce nouveau type de composite en intégrant deux facteurs supplémentaires : l'extraction et la résistance aux cycles gel-dégel. Le but de ce travail visait à vérifier les hypothèses de recherche formulées *a priori* :

1. Les lignines Kraft de résineux estérifiées vont agir comme agent de couplage efficace, en remplacement de l'agent de couplage commercial (le polyéthylène maléaté: MAPE). pour les composites constitués de fibres d'écorce d'épinette noire et d'une matrice de polyéthylène de haute densité (HDPE),

2. Les fibres raffinées d'épinette noire (extraites ou non) agiront comme élément de renfort dans la matrice,
3. Les composites conçus à la base de HDPE avec des fibres d'écorce d'épinette noire et la lignine Kraft seront utilisables pour des produits à forte valeur ajoutée.

Les conclusions suivantes, sont formulées à la base des résultats obtenus sur la recherche réalisée dans le cadre de cette thèse, affirment ou pas ces hypothèses.

1. Il a tout d'abord été démontré que les lignines Kraft de résineux non modifiées ou estérifiées n'agissent pas comme agent de couplage appliquées seules sur les fibres d'écorce, car les propriétés mesurées étaient plus faibles qu'en utilisant le MAPE qui servait de référence.
2. Cependant, l'application des lignines Kraft de résineux estérifiées par l'anhydride maléique en combinaison avec du MAPE permet d'améliorer la performance des composites en renforçant la structure à l'aide des interactions entre les lignines estérifiées et lignines dans les fibres d'écorce, reposant sur des mécanismes de type π - π . Les lignines estérifiées agissent alors en renforçant l'efficacité de l'agent de couplage commercial MAPE, par son remplacement partiel, dans les composites contenant les fibres d'écorces d'épinette noire dans la matrice de polyéthylène de haute densité (HDPE).
3. Les composites contenant les fibres d'écorce d'épinette noire présentent des propriétés toujours supérieures à la référence de HDPE confirmant ainsi l'hypothèse de recherche sur le rôle de renfort des fibres raffinées d'écorce d'épinette noire.
4. Une extraction à l'eau a été réalisée sur les fibres d'épinette noire. La morphologie des fibres d'écorce avant et après l'extraction a été étudiée, en mettant l'accent sur le rapport de forme (L/D), à l'aide de l'analyseur de fibres (FQA). Les fibres non extraites et extraites à l'eau ont une morphologie quasiment identique, démontrant que le traitement à l'eau n'affecte pas la forme des fibres. Toutefois, une perte massique de 18% a été mesurée, ce qui prouve que les extraits à l'eau et d'autres éléments non structuraux sont éliminés durant ce traitement. Les résultats obtenus, sur les composites fabriqués avec des fibres d'écorce extraites démontrent que cette extraction des fibres d'écorce d'épinette noire n'a pas d'effet significatif sur les propriétés mécaniques des composites.

5. La valorisation des extraits disponibles (un coproduit, lorsque les fibres sont extraites) pour la nutraceutique ou les industries agro-alimentaires ou pharmaceutique est donc envisageable et présente un intérêt important en vue de la production de produits à haute valeur ajoutée.
6. Une mercerisation (à la soude à 10%) a également été testée sur ces mêmes fibres d'épinette noire. Le rapport de forme a été augmenté de 64% après traitement accompagné d'une perte de masse de 36%. La solution de soude a pu extraire une partie de la lignine et hémicelluloses, mais également de la subérine des écorces. L'amélioration morphologique obtenue laissait espérer des améliorations mécaniques mais la perte de masse a contrebalancé cet apport en fragilisant l'apport mécanique des fibres dans les composites fabriqués, qui n'ont pas été affectés par ce prétraitement des fibres.
7. Les résultats obtenus sur les propriétés des composites à base de HDPE contenant les fibres d'écorce (30%) et de la lignine Kraft de Wayagamack (5% en masse de fibres d'écorce) démontrent que ces composites peuvent trouver des applications à forte valeur ajoutée, comme la réalisation de patios de piscine ou du bardage. Les résultats obtenus sur les tests gel-dégel confirment la possibilité d'une utilisation extérieure en prouvant une bonne aptitude du matériau à résister à des cycles de gel-dégel correspondant au contexte québécois.
8. Les résultats des essais de résistance aux cycles de gel-dégel ont démontré qu'il n'y avait aucun impact de ce test sur la masse ou la couleur des composites testés. Aucune tendance claire n'est observée sur l'évolution de la densité et la cristallinité après ce type d'essais. L'interface fibre-matrice, observée à l'aide d'un microscope électronique à balayage (MEB), n'a pas changé après les tests de gel-dégel. L'impact des essais de résistance aux gel-dégel dépend de la formulation du WPC, la meilleure amélioration obtenue pour le composite contenant 30% de fibres d'écorce et 5% d'agent de couplage (2,5% de MAPE et 2,5% de lignines Kraft estérifiées avec de l'anhydride maléique) est une augmentation de 20 % des propriétés en flexion et une augmentation de 25 % des propriétés en traction.

Le respect de concepts de l'ingénierie verte impliqués dans la conception de composites engendre un impact positif sur l'environnement de ce matériau dont 30% de la matrice pétrochimique (HDPE) est remplacée par des fibres d'écorce d'épinette noire. Ces écorces d'épinette noires étant de très faible valeur marchande, leur valorisation a un intérêt économique et social. D'autre part, la lignine Kraft obtenue par précipitation de la liqueur noire en utilisant du CO₂ présente un intérêt écologique évident. L'efficacité de la combinaison de lignines Kraft estérifiées et de MAPE indique qu'il est possible de remplacer la moitié de l'agent de couplage MAPE synthétique par un polymère renouvelable. Et finalement le remplacement possible de matériaux synthétiques par des matériaux renouvelables aurait un impact positif sur le cycle de vie.

Recommandations

Les principes de la chimie verte ont été utilisés dans ce travail de recherche comme approches afin de concevoir un nouveau composite contenant des fibres d'écorce et des lignines dans une matrice de HDPE pour une application à forte valeur ajoutée. Les résultats montrent qu'il est possible d'améliorer l'efficacité de l'agent de couplage commercial (MAPE) en employant des lignines Kraft estérifiées. De plus, la valorisation des extraits issus des écorces est possible, car les propriétés des composites fabriqués n'ont pas été diminuées après extraction. Cependant, certains aspects n'ont pas été étudiés par choix, mais présentent un intérêt scientifique pour les études futures.

Les recommandations suggérées pour des travaux futurs portent sur les aspects suivants :

- Investigations complémentaires sur les différents aspects suivants :
 - (i) traitements des surfaces de fibres de renforts (Annexe 1);
 - (ii) durabilité fongique;
 - (iii) vieillissement naturel et accéléré;
 - (iv) recyclage du composite fabriqué;
 - (v) analyse du cycle de vie.

- Dans le but de valoriser les écorces d'épinette noire et les lignines estérifiées, il pourrait être envisagé de changer de matrice polymère, en prenant un thermoplastique biosourcé (HDPE, LDPE, etc.) e.g. à partir de cannes à sucre. Ou de changer de types de fibres lignocellulosiques en prenant d'autres essences de bois (feuillus ou résineux). Le bouleau jaune a été étudié, de façon préliminaire, sur des particules d'écorces et les résultats obtenus ont été présentés dans des articles de conférences (Annexes 2 et 3).

- Étude chimique plus poussée des composites afin de vérifier la formation, ou l'absence, de liaisons covalentes entre :
 - (i) l'agent de couplage (MAPE) et les fibres d'écorces;
 - (ii) les lignines non estérifiées et cet agent de couplage;
 - (iii) les lignines estérifiées et le MAPE;
 - (iv) les lignines estérifiées et les fibres d'écorces (difficilement concevable).

Une étude RMN (à définir) pourrait permettre de mieux comprendre les mécanismes réactionnels mis en place lors de la fabrication du composite.

- Mises à l'échelle industrielle en trois étapes :
 - (i) utilisation d'une extrudeuse d'échelle laboratoire;
 - (ii) utilisation d'une extrudeuse à l'échelle pilote;
 - (iii) utilisation et optimisation des paramètres d'une presse de moulage par injection.

Les résultats préliminaires sur les composites extrudés avec des écorces de bouleau jaune obtenus sur ce projet de doctorat sont présentés en Annexes 2 et 3.

- Modélisation du composite fabriqué par régression, en réalisant au minimum six concentrations en fibres d'écorces, afin d'obtenir les informations supplémentaires nécessaires pour la conception de ce nouveau matériau :
 - (i) importance de la matrice dans les propriétés du WPC fabriqué;
 - (ii) impact de l'agent de renfort (fibres d'écorces) sur les propriétés du WPC;
 - (iii) importance de l'ajout de lignines estérifiées dans l'optimisation de l'effet de l'agent couplant (MAPE);
 - (iv) obtenir des informations sur l'interface des composants du composite bois-plastiques fabriqué.

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Annexe 1 : Note de Recherche publiée au CRMR

Cette note de recherche porte sur des traitements testés sur des fibres d'épinette noire sans les intégrer dans des bois composites (WPC) : Extraction à l'eau chaude, extraction à soude, triturations, macération, sonication.

L'aspect anatomique, avec une observation au microscope optique, et morphologique des fibres, avec le rapport de forme, y est présenté. Ce document conduit à une réflexion sur le potentiel des applications des fibres d'écorces et de ces traitements en vue de l'optimisation des propriétés des fibres pour leur intégration dans les composites (WPC). Cela pourrait servir de base à des pistes de développements futurs pour les WPC mais également d'autres matériaux.

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Accessible sur internet à l'adresse suivante :

[http://www.materiauxrenouvelables.ca/files/content/sites/crmr/files/Notes%20de%20recherche/Note%20Recherche%20\(No4\)_Impact%20de%20l'extraction%20et%20preparation%20des%20fibres%20d'ecorces.pdf](http://www.materiauxrenouvelables.ca/files/content/sites/crmr/files/Notes%20de%20recherche/Note%20Recherche%20(No4)_Impact%20de%20l'extraction%20et%20preparation%20des%20fibres%20d'ecorces.pdf)

1. Analyse de l'impact de l'extraction à l'eau et à la soude ainsi que la préparation des fibres d'écorces sur leurs longueurs, diamètres et ratio L/D

Les écorces représentent des résidus générés en quantités importantes lors de la transformation du bois, cependant, elles ne sont pas valorisées (actuellement elles sont brûlées pour produire de l'énergie). Les fibres lignocellulosiques sont ajoutées couramment dans des matrices polymères en tant qu'agent de renfort pour produire des composites bois plastiques (Wood – plastic composites - WPC). Les écorces ont un potentiel à déterminer pour ce type de composites (WPC). Cette étude a été menée afin de mesurer les dimensions des fibres d'écorce d'épinette noire (*Picea mariana*), car leurs morphologies ne sont pas référencées dans la littérature. Les longueurs (L), diamètres (D) et leur rapport de forme (L/D) donnent des indices sur l'efficacité de ces fibres à agir en tant qu'agent de renfort (le plus élevé le ratio L/D, le plus élevée l'efficacité) dans les WPC. De plus, l'extraction de molécules bioactives représente une valorisation très intéressante des écorces dans le contexte actuel de bioraffinage forestier. Le rapport de forme des écorces a été modifié par extraction à l'eau (-14% L/D) et à la soude (+55% L/D) mais également par les trois techniques de préparation des fibres post-extraction, soit une macération (+33% L/D), une trituration (+45% L/D) ou une sonication (+49% L/D). Cette analyse démontre l'intérêt d'étudier l'effet de l'extraction à la soude ainsi que la préparation par sonication sur des fibres d'écorces avant leurs usages dans un WPC afin d'optimiser leur potentiel d'action en tant qu'agent de renfort dans ce matériau.

INTRODUCTION

Les dimensions des fibres d'écorces sont peu étudiées. Le rapport de forme, correspondant au ratio longueur/diamètre (L/D), constitue un paramètre majeur pour les propriétés de composites bois plastique (WPC). En effet, avec un rapport de forme faible (<10), les fibres agiraient plus en tant que charge, n'ayant pas d'influence sur les caractéristiques mécaniques du matériau. Un ratio L/D plus élevé (>30), par contre, offre une morphologie plus allongée avec une surface spécifique intéressante pour obtenir un WPC plus performant. Les extractions et traitements post-extraction peuvent améliorer le rapport de forme des fibres d'écorces. D'autre part, le problème majeur dans les WPC est la nature hydrophile et polaire des écorces (ou fibres lignocellulosique) qui est incompatible avec la matrice polyoléfine non-polaire et hydrophobe. Cette difficulté pourrait être surmontée grâce à une extraction à l'eau ou à la soude [49], qui rendrait la fibre

moins polaire en ayant permis d'extraire certains composés hydrophiles et polaires. De plus, la présence d'extractibles dans l'écorce d'épinette noire a un certain potentiel dans les domaines de la nutraceutique et pharmaceutique qui a déjà été démontré avec extraction à l'eau [16].

I. MATÉRIEL ET MÉTHODE

Les fibres d'écorces raffinées d'épinette noire (*Picea mariana*) ont été obtenues de *FPIInnovations*® (Québec, Canada). Après avoir enlevé les contaminants par tamisage à 10 mesh, l'écorce a été conditionnée et raffinée avec un disque de raffinage *Andritz*. Les paramètres de raffinage utilisés étaient : une pression de vapeur de 12 bars, une distance de plaque de 0,1 mm, une vitesse de rotation de 2200 rpm et un temps de rétention de 3,5 min, le tout à 189°C. Une fraction a été gardée, après séchage, pour les mesures avec l'analyseur de fibres (FQA). Les fibres ont été observées au microscope optique à des grossissements de x100 et de x400 avec une coloration au phloroglucinol (Figure 1-1 A1).

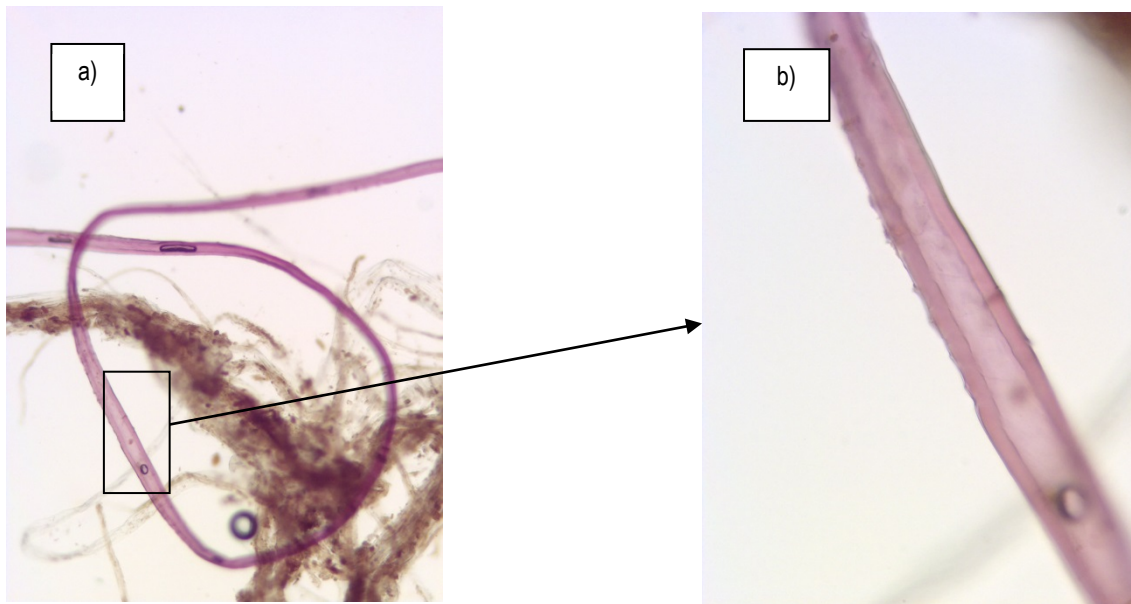


Figure 1-1 Observations au microscope optique de fibres d'écorces après raffinage *Andritz* et coloration au phloroglucinol ([a] 100X et [b] 400X).

Une partie des écorces obtenues ont été extraites à l'eau, en accord avec la littérature [19], avec une concentration en écorces de 30 g/L pendant trois heures à ébullition. Il en résulte une perte de 18% en masse des fibres d'écorces. Une fraction a été prélevée, avant séchage, pour les mesures FQA.

Une autre partie a été extraite à la soude selon la norme ASTM D1109 avec une concentration d'écorce de 20 g/L pendant une heure à ébullition. 36% de perte de masse a été mesurée après extraction. Une fraction a été prélevée, avant séchage, pour les mesures FQA.

La macération post-extractions (à l'eau ou à la soude) des fibres, après séchage, a été réalisée avec de la liqueur de Franklin (50% peroxyde d'hydrogène à 20% et 50% d'acide acétique à 100%) à ébullition pendant 20 minutes. Une analyse FQA a été réalisée avant séchage.

Trois triturations de 1200 tours ont été réalisées post-extractions, après séchage, en diminuant la concentration en fibres dans le triturateur après chaque cycle. Le tout a été filtré sur Büchner avec papier filtre Whatman #1. Ces fibres ont été analysées avant séchage avec le FQA.

La sonication post-extraction a été réalisée avec une sonde à ultrason pendant 15 minutes dans de l'eau distillée sur des fibres d'écorces après séchage. Avant séchage, une analyse FQA a été effectuée sur ces fibres.

II. RÉSULTATS ET DISCUSSION

Une analyse statistique (ANOVA, Tableau 1-1 A1), permet de découvrir qu'il existe une interaction entre le type d'extraction (eau ou soude) et la préparation post-extraction (macération, trituration ou sonication). Il est logique que la préparation agisse de façon différente en fonction de la morphologie initiale des fibres qui semble différente avant versus après extraction.

Table 1-1 Résultat de l'ANOVA (valeurs de F) du rapport de L/D

<i>Facteur simple</i>	L/D
Extraction	634**
Préparation	1580**
<i>Interaction</i>	
Extraction * Préparation	141**

N.B. : ** = significatif à un niveau de probabilité de 0,01.

Les fibres d'écorces raffinées par disque *Andritz* ont une longueur ($0,89 \pm 0,03$ mm) plus faible que les fibres de xylème macérées ($1,42 \pm 0,02$ mm) qui ont été utilisées comme témoin dans ce travail. Ce résultat n'est pas surprenant, car les fibres de xylème des résineux sont théoriquement plus longues que celle des écorces. D'autre part, le diamètre des fibres d'écorces (46 ± 2 µm) est semblable à celui des fibres de

xylème macérés ($43 \pm 1 \mu\text{m}$), ce qui tend à prouver que le raffinage par disque *Andritz* est efficace pour séparer les fibres. Le rapport de forme (L/D) est supérieur pour les fibres de xylème (36 ± 1) par rapport aux fibres d'écorces (28 ± 1). Il faut donc prévoir un traitement après le raffinage à disque pour rendre les écorces plus intéressantes que les fibres de xylème en vue d'une utilisation en tant qu'agent de renfort dans les WPC.

L'extraction à l'eau n'a pas d'influence sur les dimensions (L, D et L/D) des fibres d'écorces (Figure 1-2 A1). Toutefois, l'extraction à la soude (NaOH) contribue à un défibrage (mise en pâte - séparation des fibres par une délignification) proche du procédé papetier Soda, en diminuant le diamètre des fibres et en les « dépliant », ce qui fait augmenter leur longueur et donne ainsi un L/D amélioré significativement par rapport aux écorces raffinées par disque *Andritz* (Figure 1-2 A1).

La macération a un effet de séparation des fibres, diminuant leur diamètre, et tend aussi à les « déplier », augmentant leur longueur par rapport aux fibres raffinées sans traitement ni extraction. Ces deux actions permettent d'augmenter le rapport L/D (Figure 1-2 A1). La trituration a un effet similaire à la macération (Figure 1-2 A1).

La sonication est la technique la plus rapide pour améliorer le rapport de forme (L/D) de façon significative (Figure 1-2 A1) par rapport aux extractions et aux autres traitements post-extraction étudiés ici.

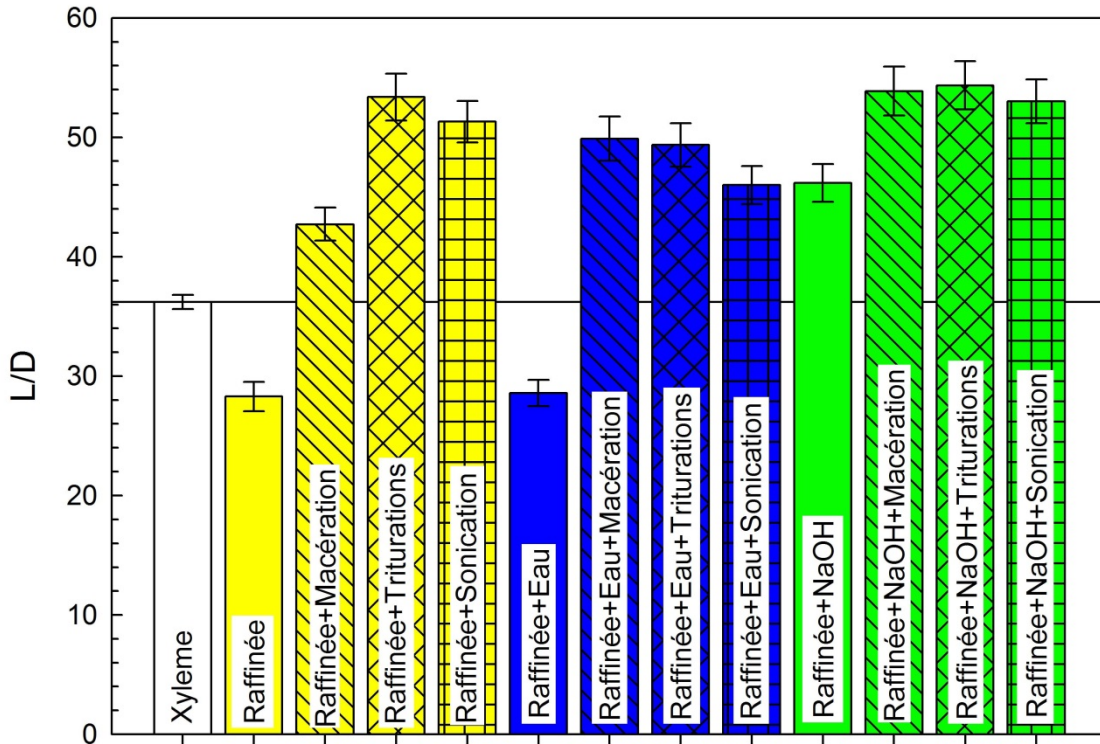


Figure 1-2 Évolution du rapport de forme L/D pour chaque traitement étudié.

III. CONCLUSIONS

Les résultats démontrent que les fibres d'écorces ont une longueur plus faible que celles du xylème, et ainsi un rapport de forme L/D significativement inférieur.

L'extraction à la soude est la plus efficace, versus celle à l'eau, pour modifier les dimensions des fibres d'écorces et augmenter le rapport de forme L/D.

La sonication est un traitement plus rapide ayant un impact plus significatif que les autres traitements, donnant ainsi les meilleurs rapports de forme (L/D), qui peuvent doubler.

Le traitement par sonication peut être un prétraitement à étudier sur des fibres raffinées (*Andritz*) avant de les intégrer dans des WPC afin d'optimiser leur potentiel d'action en tant qu'agent de renfort dans ce nouveau matériau.

Annexe 2: Article de conférence pour “55th International Convention of Society of Wood Science and Technology” à Beijing (Chine), les 27-31 août 2012

Cet article de conférence porte sur l'utilisation de lignines Kraft commerciales et industrielles en tant qu'agent de couplage dans des bois composites (WPC).

Trois lignines Kraft ont été évaluées en termes de potentiel d'action en tant qu'agent de couplage : Lignine commerciale de résineux : IndulinAT, Lignine industrielle de résineux : Wayagamack et Lignine industrielle de feuillus : Windsor. Deux essences ont été étudiées et comparées : bouleau jaune et épinette noire. Deux procédés de fabrication ont été utilisés : extrudeuse bi-vis et mélangeur interne.

Une extraction à l'eau est également étudiée ici et n'a pas eu d'influence sur les propriétés mécaniques. Cependant, des résultats peu encourageants concernant l'utilisation de la lignine Kraft en tant qu'agent de couplage ont été mis en évidence. Le potentiel des fibres d'écorce d'épinette noire était plus important que les particules d'écorce de bouleau jaune en tant qu'agent de renfort.

Accessible sur internet à l'adresse suivante :

<http://www.swst.org/meetings/AM12/pdfs/Full%202012%20Proceedings.pdf>

2. New Bio-composites Containing Industrial Lignins

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Abstract

An important decrease in demand for the pulp and paper products in the last decade has caused the shift of this industry towards the integration of biorefinery concept into existing mills. The valorization of industrial lignins is one of such solutions. In this research we have explored the application of Kraft lignins in two types of bio-composites based on high density polyethylene (HDPE): one with esterified lignin, coupling agent and HDPE and another with HDPE, lignin or coupling agent and bark fibers (extracted or not). Tensile properties of the produced composites were determined by standard tests. The results of these tests indicated the positive effect of utilization of coupling agents along with lignins on good mixing and homogeneity of HDPE based composites. The production of such composites could contribute to the sequestration of CO₂ on several levels: by replacement of synthetic polymers by renewable lignins and bark fibers and through the process of lignin precipitation from black liquor itself (with CO₂ provided from Kraft pulping plant). The pre-extraction of the bark fiber was determined not to cause any deterioration of tensile properties of the bio-composites containing them, and the integration of extraction step could therefore yield interesting co-products with high added value (pharmaceutical, cosmeceutical, nutraceutical), transforming this process into real biorefinery.

Keywords:

Kraft lignins, esterified lignin, chemical properties, thermal properties, HDPE, composites, bark fibers (extracted or not), tensile properties, sequestration of CO₂.

Introduction

Lignins are renewable and natural polymers the structure of which varies depending on plant origin and process of isolation. They are the most abundant aromatic polymers on earth and second only after cellulose. Lignin content varies from 20% to 35% depending on the plant origin [20]. Lignins are the main components of residual liquors from chemical pulping, notably black liquor from the Kraft process. It is estimated that in Quebec, 130,000 tons of black liquor containing lignin could be used for lignin precipitation annually, without disturbing the mill production [21]. In this investigation, two lignins were precipitated from black liquor obtained from two Quebec pulp and paper mills (*Domtar Windsor* and *Kruger Wayagamack*), following a procedure inspired by LignoBoost protocol, using carbon dioxide to decrease the pH. A comparison of these Kraft lignins with a commercially available Kraft lignin (IndulinAT) was performed. Kraft lignins were modified by esterification in order to improve their compatibility with a polymer matrix (HDPE) and consequently the tensile properties of the bio-composites produced from that materials. In the second application, the use of non-modified and esterified lignins as coupling agent between HDPE and yellow birch (*Betula alleghaniensis*) or black spruce (*Picea mariana*) bark fibers was examined.

Materials and Methods

Materials.

Two Kraft black liquors from Quebec pulp and paper industry (*Kruger Wayagamack* and *Domtar Windsor*) were used to precipitate Kraft lignin. A commercial Kraft lignin (IndulinAT) was received from *Westvaco Corporation*. The high density polyethylene (HDPE) from *Exxon Chemicals* used in this study has a melt index of 5 g/10 min (ASTMD 1238) and a density of 948 kg/m³. Maleic anhydride grafted to polyethylene (MAPE) was used as a coupling agent for the manufacture of composites based on polyethylene (PE). The Epolene C-26 (MAPE) used here was gratefully donated by *Westlake Chemicals Corporation*. Yellow birch (*Betula alleghaniensis*) bark splinters were obtained directly after the rosser-head debarker, from the sawmill *Bois Poulin North Inc.*, St-Jacques de Leeds, Quebec, Canada. The bark was air dried at ambient temperature until reaching constant moisture content (9%) and stored adequately. Size separation was carried out by sieving after drying. Fibers of black spruce (*Picea mariana*) bark were obtained by refining at the pilot plant of *FP Innovations* installations in Quebec, QC, Canada. The weight and moisture of this bark were measured (above 5% moisture content) and stored properly.

Precipitation of industrial lignins.

Carbon dioxide was used to precipitate lignin by decreasing the pH of black liquor (*Kruger Wayagamack* and *Domtar Windsor*) from the initial pH 13-14 to 8-9 following the procedure inspired by LignoBoost process [106, 136]. A purification step consisted of washing lignins with sulfuric acid and distilled water. These precipitation and purification protocols are designed to contribute to greenhouse gas sequestration (CO₂) and sustainable chemistry.

Characterization of lignins.

Klason lignin and ash content were analyzed in order to determine the purity of lignin samples [110, 137-139]. The spectral characteristics of lignin samples were analyzed by Fourier Transform Infrared (ATR-FT-IR/FT-NIR Perkin Elmer Spectrum 400) both for non-modified and esterified lignins. The thermal properties were studied by thermogravimetric analysis (TGA/DTA 851e METTLER TOLEDO), differential scanning calorimetry (DSC 822e METTLER TOLEDO) (ASTM D3418) and thermo-mechanical analysis (TMA/SDTA 640 METTLER TOLEDO).

Esterifications of lignins with butyric anhydride.

The commercial Kraft lignin (Indulin AT) was dried in an oven at 80°C overnight. Various amounts of butyric anhydride were added to the reaction system to obtain a desired substitution degree. 1,4-dioxane and 1-methylimidazole were used as solvent and catalyst, respectively. The reaction was conducted at 60°C for two hours. The product was precipitated by adding distilled water to the solution and then washed with 0.5 M solution of NaHCO₃ and distilled water. The esterified lignins were dried at 60°C under reduced pressure overnight.

Esterifications of lignins with stearyl chloride.

Esterification applied acid chloride rather than the anhydride and the reaction time was extended to 5 hours at a temperature of 70°C [140]. By the end of reaction, 100 ml of hexane were added to the system and the precipitated esterified lignin was repeatedly washed with a total of 220 ml of hexane and 220 ml of distilled water. The product was finally dried at 60°C under reduced pressure overnight.

Water extraction of barks.

The black spruce bark fibers (obtained from disk-refiners) and the yellow birch bark particles were each extracted with boiling distilled water (30 g oven dry bark with 1L distilled water) for two hours. The objective of extraction was to determine its impact on the properties of the bio-composites. The hypothesis was that the removal of hydrophilic extractives would increase the hydrophobicity of the bark fibers and thus improve their compatibility with hydrophobic polyethylene matrix.

Manufacturing process of bio-composites.

Modified and non-modified lignins and bark fibers were previously dried at 80°C overnight. In order to study the effect of esterification on compatibility of lignins with HDPE, a comparison with a commercial coupling agent, polyethylene-graft-maleic anhydride (MAPE), was made. Blends of HDPE with lignin were prepared in various proportions by melt-processing using a twin-screw extruder (Haake TW-100). The temperature was set between 150°C (at the supply) and 165°C (at the output of the extruder) with a screw speed of 40 rpm. The amount of MAPE in the blends was selected to be similar to the lignins content. An internal mixer (Haake Buchler Rheomix) at temperature fixed at 165°C for 10 minutes was used to prepare the bio-composites containing black spruce bark fibers (30%) or the yellow birch particles (50%) to prepare the HDPE-lignin bio-composites. All blends were pelletized and compression molded at 160°C for 5 minutes under 3 tons pressure.

Tensile characterization of bio-composites.

From the plates produced, dumbbell shaped specimens (type V) were cut following ASTM D-638. Tensile properties of the bio-composites HDPE - lignins specimens were investigated using an Instron 5565 universal tester without extensometer at room temperature with a crosshead speed was 5 mm/min. For the bio-composites HDPE - coupling agent – barks, an MTS Qtest/5 was used at regulated temperature and humidity with an extensometer MTS 634.11F-24, with a crosshead speed of 1 mm/min as specified in ASTM D-638. Young's modulus and yield stress were obtained from the stress-strain curves.

Experimental Results

Characterization of non-modified lignin: Purity of the Kraft lignins (Wayagamack, Windsor and Indulin AT).

The purity of Kraft lignins was higher than 96% [110], in agreement the results obtained by El Mansouri [137-138]. Both lignins precipitated (Wayagamack and Windsor) in our laboratory have low ash content (less than 1%). These results suggest that the precipitation and purification protocols were well defined. The commercial Kraft lignin samples, Indulin AT had somewhat higher ash content (above 3%) than the lab precipitated lignins.

Thermal analyses of non-modified lignin: Thermogravimetric analysis (TGA-DTG).

The lignin degradation was observed under nitrogen in a large range of temperature (150-700°C). The degradation of Kraft lignins started at temperatures higher than 260°C. At 700°C under nitrogen atmosphere, lignins were not completely decomposed but remain in form of highly condensed char-like structures (27-45% of initial mass). These results confirm the strong reticulation and good thermal properties of Kraft lignin [110].

Thermal analyses of non-modified lignin: Differential scanning calorimetry (DSC) versus thermomechanical analysis (TMA).

The melting temperatures (T_m) were determined by DSC and TMA (Figure 2-1 A2). The differences between these results reflect the differences of principles of measurements by these two analytical methods. For DSC the measurement principle is calorimetric while it is physical for TMA. The comparable T_m values were obtained for all Kraft lignins.

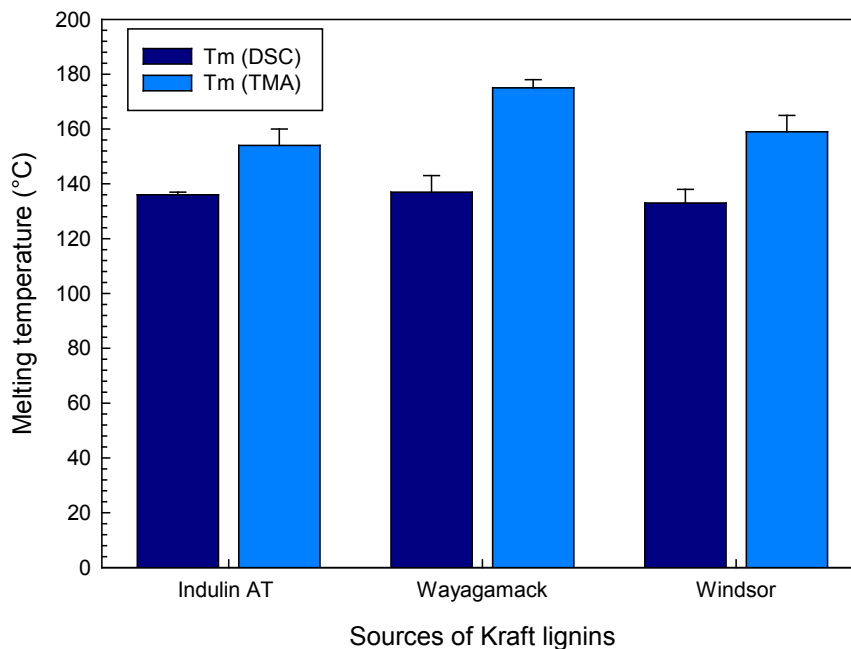


Figure 2-1 Comparisons of two techniques (DSC versus TMA) used to determining the melting temperature of different sources of Kraft lignins.

Esterification of IndulinAT lignin.

The extent of esterification with butyric and stearic anhydride was analyzed by ATR FT-IR spectroscopy. The decrease in O-H stretching bands (3400-3500 cm^{-1}), C-H stretching band (2850-2950 cm^{-1}) and C-O bending band (1030 cm^{-1}) of primary alcohol group and the increase in the bands attributable to ester groups (absorption at 1730 cm^{-1} assigned to C=O bond in the ester group) were taken as indication of good esterification [110].

Characterization of HDPE-MAPE-lignins blends.

The addition of lignins into HDPE had an effect on the increase of the Young's modulus of the composite, while the addition of esterified lignin had slightly less effect on the modulus (Figure 2-2 A2). Compared to HDPE alone, the addition of esterified lignin did not seem to be beneficial to tensile strength properties. The tensile strength increased however significantly with the addition of 6 wt% MAPE, especially high tensile strength being determined for the composite containing 40% Lignin – 6% MAPE – 54% HDPE which is now comparable to that of neat HDPE. Luo *et al.* [141] have already observed a high increase in tensile strength

with MAPE addition. These results showed that lignin compatibility with HDPE was improved by MAPE addition.

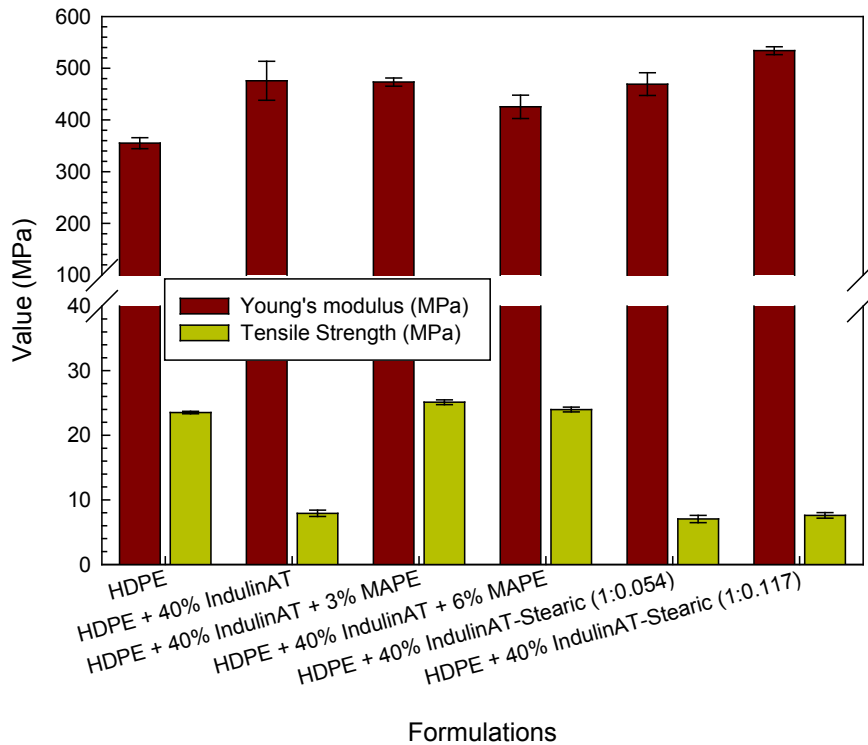
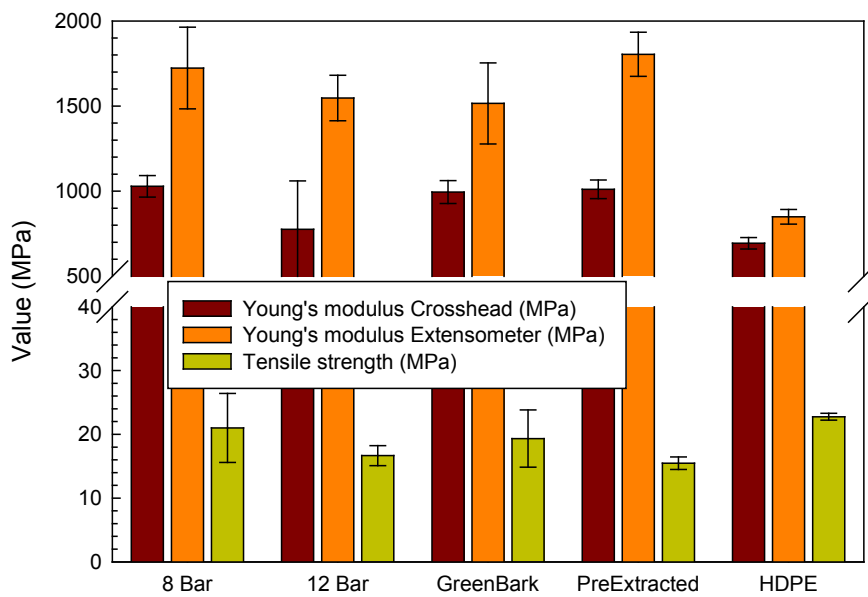


Figure 2-2 Tensile properties of lignin based composites (Young's modulus calculated without extensometer [crosshead], gage length of 7.62 mm [13]).

Characterization of blends HDPE-coupling agent-bark fibers: Bio-composite made by black spruce fibers bark (~30%) with different refining conditions, HDPE (~70%) and coupling agents (~5% w/w of barks).

No significant differences of mechanical properties were observed for bio-composites made with black spruce bark fibers from four different refining conditions (GreenBark, rotation rate = 2200 rpm, time =10.1 min, p=12 bar, distance between discs= 3.5 mm; Pre-Extracted Bark; rotation rate = 2200 rpm, 13.5 min, 12 bar, 0.1 mm; 12 bar = dry bark, 2200 rpm, time- 13.5 min, p=12 bar, distance between discs = 0.5 mm; 8 bar = dry bark, 2200 rpm, 13.5 min, 8 bar, 0.1 mm) (Figure 2-3a A2). Two refining conditions parameters seemed however to be slightly more favorable (8 bar and green bark conditions). The bark extraction that carried out for 2 hours in boiling water had no significant effect on the tensile properties (Figure 2-3b A2). This observation allows us to envisage the use of extracts of bark for other applications with added value. Three options have been considered for improving composite properties by using the coupling agent

versus, without (without coupling agent), lignin indulinAT and MAPE (Figure 2-3c A2). The MAPE could improve the bio-composite properties as observed by Ngueho-Yemele *et al.* [18], but unmodified lignin indulinAT was not an effective coupling agent. The Young's modulus calculated from the extensometer (gage length 12.5 mm corresponds to the dimension of extensometer) is systematically higher than that calculated from the crosshead movement (gage length 24.5 mm equal to the distance between grips, ASTM D638), but the tendencies are similar. This difference can be explained by the fact that the crosshead integrates the phenomena of slip in the grips and other mechanical noise associated to this test. With the extensometer, the strain measured solely from the area solicited by the tensile test is without errors implicated in the previous technique. The accuracy and sensitivity of the extensometer is designed to gather the intrinsic value of the test material.



a) Refining conditions effect

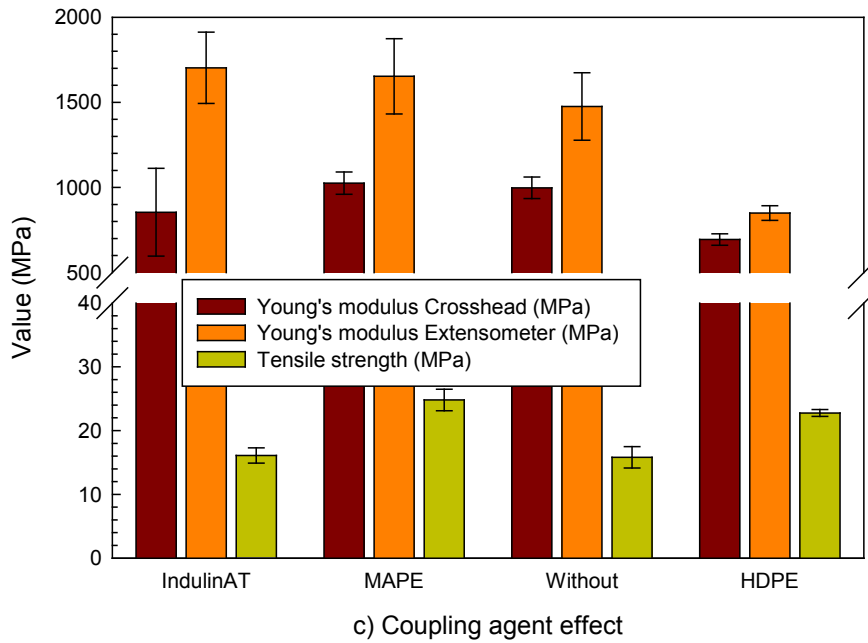
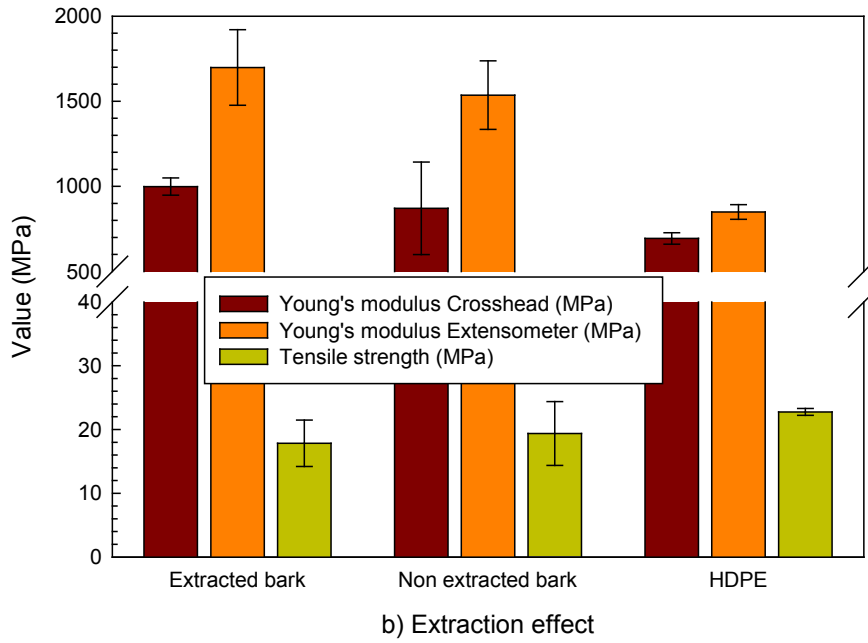


Figure 2-3 Analysis of simple effects on bio-composites for black spruce bark fibers; a) refining conditions effect, b) extraction effect, c) coupling agent effect.

Characterization of blends HDPE-coupling agent-bark fibers: Black spruce barks fibers (~30%) versus yellow birch bark particles (~30%) with HDPE (~70%) and coupling agents (5% w/w of barks).

Better composites properties have been determined for composites containing black spruce bark than for those with yellow birch bark particles (Figure 2-4 A2). The addition of the non-modified indulinAT, or of IndulinAT esterified with butyric anhydride or stearoyl chloride did not bring any improvements of the bio-composites properties. The properties of the bio-composites containing MAPE have, however, been determined to be significantly improved [18]. Young's modulus calculated from the extensometer is higher than the crosshead. An estimate of measurement errors associated to both techniques (crosshead versus extensometer) will be carried out in future work.

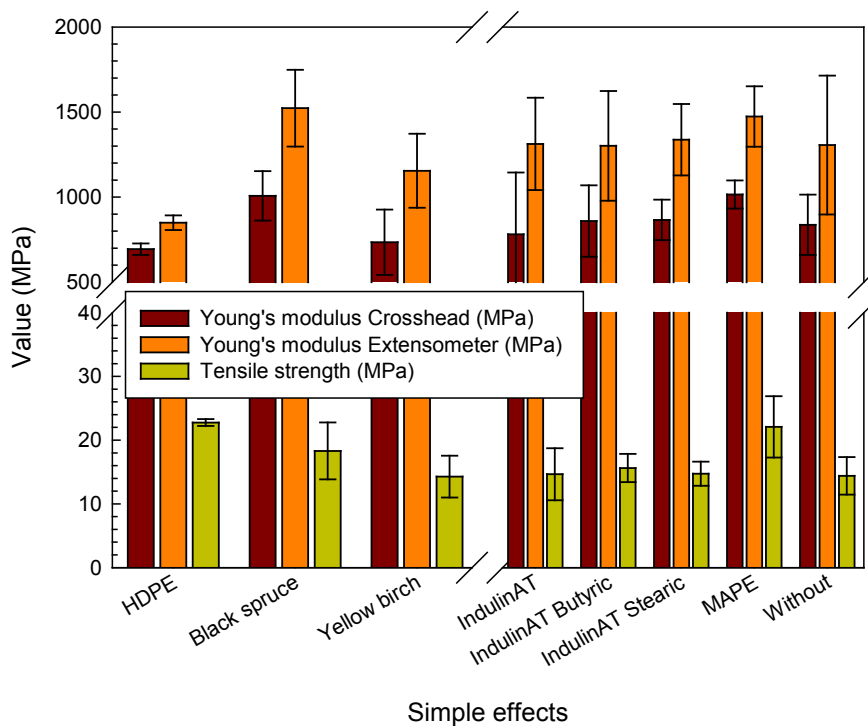


Figure 2-4 Analysis of simple effects; left: the effect of bark species; right: different coupling agent effect.

Characterization of blends HDPE-coupling agent-bark fibers: Bio-composite made with yellow birch barks particles (~50%) with HDPE (~50%) and coupling agents (~5% w/w barks).

The influence of particle sizes of yellow birch bark on the composite properties was measured and there was no significant difference, so the results are not presented here. Two extrusion temperatures were analyzed and there were not to be significant impact on the tensile properties (and other measured

properties, not shown here). As observed for black spruce, the extracted bark had no significant effect on the tensile properties (Figure 2-5a A2). As compared to the non-extracted bark, allowing the potential use of extractives for other value added products. IndulinAT lignin was demonstrated to be inefficient as coupling agent, since the properties of the composite based on HDPE and bark fibers did not improve upon its addition (Figure 2-5b A2). Contrary to the observation by Sewda and Maiti [17], we observed an improvement of the modulus with addition of bark but a decrease of tensile for these composites. MAPE was determined to be a good coupling agent for this type of material [18].

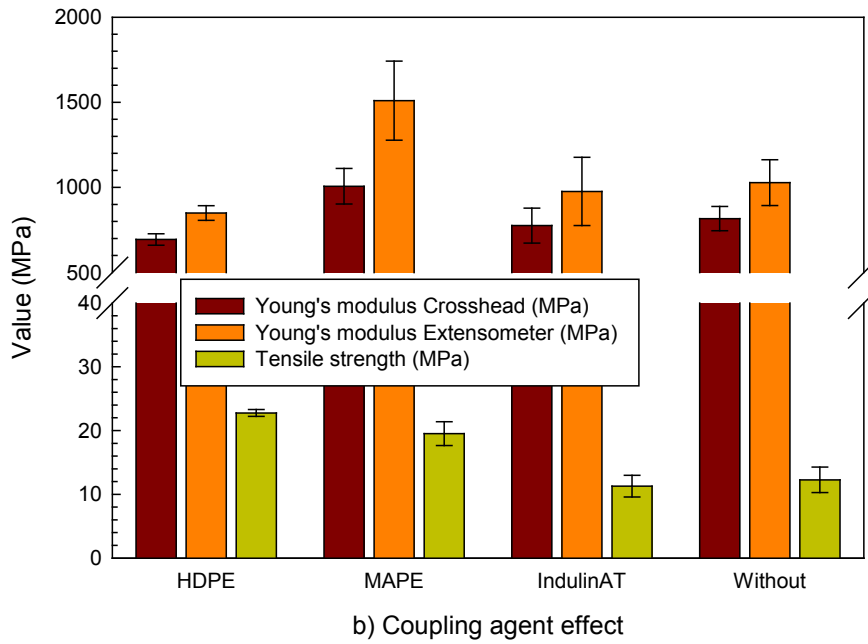
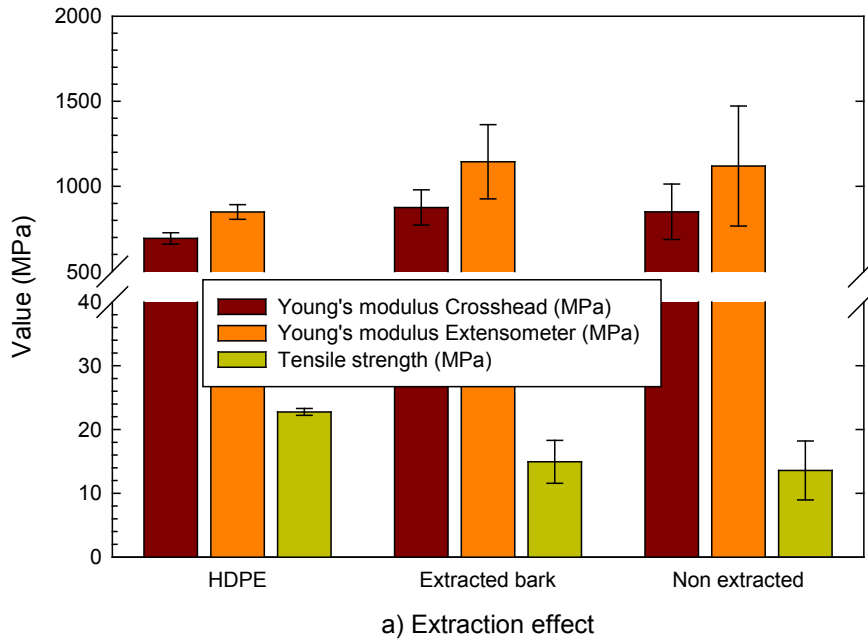


Figure 2-5 Analysis of simple effects on bio-composites for yellow birch bark particles; a) extraction effect, b) coupling agent effect.

Conclusion

Two Kraft lignins have been precipitated by carbon dioxide from the black liquor provided by Domtar–Windsor and Kruger-Wayagamack pulp and paper mills in Quebec. The purification protocol was confirmed by their high purity and low ash contents. Esterification reactions were performed on IndulinAT with butyric anhydride and stearoyl chloride to improve lignin compatibility with HDPE but proved to be insufficient. Stearate lignin was incorporated into HDPE matrix by melt blending. However, the tensile properties of blends were not improved by incorporation of esterified lignins only, but were possible with the standard compatibilizer (MAPE).

For blends produced with HDPE–Indulin AT lignin (esterified with butyric anhydride or or stearoyl chloride and non-modified) no improvements of mechanical properties of the composites have been observed, which indicated that lignins esterified as mentioned were inefficient as coupling agents. The commercial coupling agent, MAPE, was however determined to be a good compatibilizer for this kind of material. The composites made with black spruce bark fibers have been determined to have superior properties to those determined for the composites produced with yellow birch bark particles. The water extraction of the bark fibers prior to their incorporation was determined not to have significant impact on the tensile properties of the bio-composites produced with them. The pre-extraction of the bark fibers was determined not to cause any deterioration of tensile properties of the bio-composites containing them.

Therefore the integration of extraction step could yield interesting co-products with high added value (pharmaceutical, cosmeceutical, nutraceutical), completing thus the biorefinery concept studied here. Other acid anhydrides will be tested for lignin esterification, the cyclic anhydrides, maleic and succinic, in order to examine thus modified lignins as coupling agents in manufacturing the HDPE-bark fibers blends and their properties.

Acknowledgments

The authors are grateful to the Fonds Québécois de la Recherche sur la Nature et les Technologies (FQRNT) for financial support, Kruger-Wayagamack and Domtar-Windsor for black liquors and FPIinnovations and Les bois Poulin Inc for bark fibers supply. David Lagueux, Flavien Mattesi, Yann Giroux, and Yves Bédard are gratefully acknowledged for their technical support.

Annexe 3 : Article de conférence pour “99th Annual Meeting, PaperWeek Canada” à Montréal (Canada), les 4-7 février 2013

Cet article de conférence porte sur l'utilisation de lignines Kraft industrielles en tant qu'agent de couplage dans des bois composites (WPC). Deux essences ont été étudiées et comparées : bouleau jaune et épinette noire. Deux procédés de fabrication ont été utilisés : extrudeuse bi-vis, mélangeur interne.

La nature hydrophobe des WPC a été mise en évidence par des mesures d'angles de contact. Des mesures de résistance à l'impact Charpy ont également été menées avec des résultats plus faibles pour les WPC versus l'HDPE. Une extraction à l'eau n'a pas eu d'impact sur les propriétés mécaniques mesurées. Des résultats concernant l'utilisation de la lignine Kraft en tant qu'agent de couplage ont mis en évidence son manque d'efficacité.

3. New composites containing bark and industrial lignins as coupling agent

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Abstract:

Softwood and hardwood Kraft lignins have been precipitated by carbon dioxide using black liquor from two pulp mills in Quebec (*Domtar Windsor* and *Kruger Wayagamack*) following a procedure inspired by LignoBoost protocol, using CO₂ to decrease the pH. These lignins were also esterified with stearic acid anhydride in order to improve their compatibility with high density polyethylene (HDPE). A commercially available Kraft lignin (Indulin AT) was used for comparison. The use of non-modified and esterified lignins as coupling agents in comparison to MAPE between polymer matrix HDPE and yellow birch (*Betula alleghaniensis* Britton) or black spruce (*Picea mariana*) bark fibers was examined. The chemical compositions of the barks fibers were determined as well as the thermal, mechanical and wettability (contact angle) properties of the composites. The pre-extraction of bark fibers did not show any significant effect on the tensile properties of the bio-composites. The extraction step could therefore be used to extract interesting co-products with high value-added, transforming this process into a real biorefinery, while contributing to CO₂ sequestration.

Keywords:

Kraft lignins (esterified or not), thermal – mechanical - physical - rheological properties, HDPE, composites, bark fibers (extracted or not), CO₂ sequestration.

INTRODUCTION

Pulp and paper industries produce tons of lignins (in black liquor) of which only 2% find applications other than for energy recovery. Lignins are renewable and natural polymers [20, 104, 106] and their structure varies depending on plant origin and isolation process [99]. It is estimated that in Quebec, 130,000 tons of black liquor containing lignin could be used for lignin precipitation annually, without disturbing the mill production [21]. Large quantities of bark produced in Quebec are mainly or totally used for thermal energy production [11]. In this work, an original integration of the concept of biorefinery is presented by using Kraft lignins combining with yellow birch (*Betula alleghaniensis*) or black spruce (*Picea mariana*) bark to produce bio-composites based on high density polyethylene (HDPE).

MATERIALS AND METHODS

HDPE and Commercial Coupling Agent

The high density polyethylene (HDPE HD 6605) from *Exxon Chemicals* used in this study has a melt index of 5 g/10 min (ASTM D1238) and a density of 948 kg/m³. Maleic anhydride grafted polyethylene (MAPE) was used as a coupling agent for the manufacture of composites based on polyethylene (PE). Epolene C-26 was obtained from *Westlake Chemicals Corporation*.

Black Liquors and Commercial Kraft Lignin

Two Kraft black liquors from the pulp and paper industry in Quebec (*Kruger Wayagamack* and *Domtar Windsor*) were used to precipitate Kraft lignin. The precipitation protocol is described in *Stevanovic et al.* [110]. A commercial Kraft lignin (Indulin AT) was supplied by *Westvaco Corporation*.

Bark Fibers and Bark Particles

Particles of yellow birch (*Betula alleghaniensis*) bark splinters were obtained directly after the roller-head debarker, from the sawmill *Bois Poulin North Inc.*, St-Jacques de Leeds, Quebec, Canada. The bark was air dried at ambient temperature until reaching constant moisture content (9%) and stored adequately. A second batch of particles of yellow birch barks were obtained from *Precitech Int. Inc.* located in Sainte-Rose de Watford, Quebec, Canada. Fibers of black spruce (*Picea mariana*) bark were obtained by refining (disk-refiners) in the pilot plant of *FPInnovations* installations in Quebec, Canada. The weight and moisture of this bark were measured (above 5% moisture content) and stored properly. A second batch of black spruce

barks were obtained from *Boisaco Inc.*, located in Sacré-Coeur, Québec, Canada, and this one has a particle-like morphology versus the “fiber-like” aspect of the barks from *FPIinnovations*. Size separation was carried out by sieving after drying.

Hot Water Extraction of Barks

It was initially expected that this kind of treatment should remove the hydrophilic extractives and increase hydrophobicity by decreasing the polarity of the bark fibers and would improve their compatibility with hydrophobic and non-polar polyethylene matrix. The black spruce barks and the yellow birch barks were each extracted separately with boiling distilled water (30 g oven dry bark with 1 L distilled water) for two hours. The objective of these extractions was to determine their impact on the properties of the bio-composites. Extracted bark was finally air-dried, after water extract elimination by filtration.

Chemical Characterizations of Barks

The cellulose content was determined by the Kurschner and Hoffner method [120]. The bark is subjected to a mixture of nitric acid and ethanol, allowing the nitration of the lignin and fragmentation of hemicellulose. However, the cellulose is resistant to this kind of attack because it is a supra-molecule. The lignin content was determined by an alternative non-standard method for determining the Klason lignin (according to ASTM D1106, modified by the integration of an autoclave to obtain this characterization; Stevanovic [62]). Lignin insoluble in sulfuric acid was determined by measuring the mass and the lignin soluble in this acid measured by spectrophotometry in the first filtrate after a controlled dilution ratio.

To obtain an approximation on the hemicelluloses content, pentosans assessment according to the standard CPPA G-12, using indirect titration according to the index of furfuraldehyde was used. Determination of the ash content was based on ASTM D1102. A muffle furnace was used for this quantification.

Barks were extracted with three solvents, including water, a normalized mixture of anhydrous ethanol - toluene (40:60) and sodium hydroxide (NaOH 1%) as specified in ASTM D1109. Three quantitative extractions on each bark were done to determine the content of extractives in each of the solvents used.

Manufacturing Process of Bark Plastic Composites

Modified and non-modified lignins and bark fibers were previously dried at 80°C overnight in order to obtain dry ligno-cellulosic materials. Then, two different processing methods were applied to produce the bio-composites: a twin-screw extruder and a batch mixer. To study the effect of esterification on lignin compatibility with HDPE, a comparison with a commercial coupling agent, polyethylene-graft-maleic anhydride (MAPE), was made.

For extrusion (HAAKE Rheomex TW-100), the temperature profile was set between 150°C (feed) and 165°C (die) with a screw speed of 75 rpm. The amount of MAPE in the blends was selected to be similar to the lignin contents.

For the internal batch mixer (Haake Buchler Rheomix), a rotation speed of 85 rpm, at a fixed temperature of 165°C for 10 minutes, was used to prepare the bio-composites containing black spruce bark fibers (30%) or yellow birch particles (50%).

Finally, all the blends were compression molded at 160°C for 5 minutes under 3 tons of pressure.

Characterizations of Bio-Composites Obtained

To determining the crystallinity (Equation (1)) of the polymer in the composite, differential scanning calorimetry (DSC) measurements were performed. The control program was decomposed in three steps, a first rise in temperature from 50 to 200°C with a heating rate of 10°C/min, followed by a decrease in temperature from 200 to 100°C with a cooling rate of 10°C/min and finally a temperature increase from 100 to 200°C with a heating rate of 10°C/min. This analysis may be useful to monitor the rate of crystallization in bio-composites produced, as a useful tool of interpretation for explaining the interaction between the coupling agent, lignins and bark fibers on polyethylene crystallization. Crystallinity values are calculated comparing the enthalpy of fusion to the theoretical value of 100% crystalline PE as:

$$\text{Equation (1): Crystallinity (\%)} = \frac{\Delta H_{\text{bio-composite}}}{\Delta H_{\text{pure HDPE}}}$$

where:

$\Delta H_{\text{bio-composite}}$ = Enthalpy of the bio-composite (J/g);

$\Delta H_{\text{pure HDPE}}$ = Enthalpy of a theoretical polyethylene having a structure totally crystalline = 293 J/g;

We propose equation (2) to measure the corrected crystallinity which takes into account the addition and the content of bark fibers:

$$\text{Equation (2): Corrected crystallinity (\%)} = \frac{\frac{\Delta H_{bio-composite}}{\Delta H_{pure HDPE}}}{1 - (Bark \%)}$$

where:

$\Delta H_{bio-composite}$ = Enthalpy of the bio-composite (J/g);

$\Delta H_{pure HDPE}$ = Enthalpy of a theoretical Polyethylene having a structure totally crystalline = 293 J/g;

Bark % = Bark content in bio-composite (%).

Three-point bending tests were performed to get MOE and MOR (when breakup occurred), according to ASTM D790. Also, a study of the Charpy impact resilience according to ASTM D256 was done. The aim was to explore the applicability of the bio-composites obtained.

Tensile properties were studied using dumbbell shaped specimens (type V) that were cut following ASTM D638. An MTS Qtest/5 was used at regulated temperature and humidity with an extensometer MTS 634.11F-24, having a crosshead speed of 1 mm/min and with a gauge length of 7.62 mm as specified in ASTM D638. Young's modulus and yield stress were obtained from the stress-strain curves.

The FTÅ200, from First Teen Ångstrom Inc., is a flexible video system coupling with a CCD camera, Sanyo VCB 3512T, which is able to measure the contact angle on the bio-composite surface. The solution used in this study was distilled water, put on the surface via a syringe with a diameter of 0.7 mm, a pump speed of 5.00 $\mu\text{L/s}$, and a falling-drop of 5.7 mm. Contact angles were automatically determined for the first 20 seconds for three repetitions on each sample.

Experimental Design and Data Analyses

The definition of design of experiments related to the project is developed with the SAS statistical software module and experimental design which integrates the function of D-optimal optimization. This method D-optimal based on matrix calculation to define the test formulations for analysis of good value by limiting to single effects quadratic interaction effects. Duncan test was also performed to determine the best formulation according to the properties measured.

RESULTS AND DISCUSSION

The differential scanning calorimetry (DSC) characterizations allow obtaining two important parameters on our composites (Table 3-1 A3). The melting temperature is interesting, because this parameter has to be lower than the processing temperature in order to have an efficient process. The results showed that the

melting temperature is the same for each formulation. The crystallinity is very important because it is used as a quantitative value about the compatibility between bark and lignins with the HDPE and also because it is important. The hypothesis made is that higher crystallinity is a signal of good compatibility in bio-composites. Eqs. 1-2 are used to account for bark content. Another hypothesis was that the lignin content is insignificant versus the bark content. The only significant factor having impact on crystallinity (Table 3-1 A3) seems to be the extraction with hot water of the barks. It is interesting to note that extracted barks have better compatibility inside the bio-composites than the non-extracted ones. Contrary to the findings of Sewda and Maiti [17], the crystallinity obtained from our study does not decrease significantly in the bio-composite compared to HDPE crystallinity.

Table 3-1 Crystallinity (using Eqs. 2-3) and melting temperatures of the extruded formulations.

Formulations (Description)				Bark content (%)	Crystallinity (%)	Corrected crystallinity (%)	Melting temperatures (Tm) (°C)
HDPE 150°C				0.0	41.3	41.3	130
HDPE 160°C				0.0	40.2	40.2	130
Non Extracted	50% YB [0.5-1.0]	Without	150°C	50.4	18.2	36.7	132
Non Extracted	50% YB [0.5-1.0]	MAPE	150°C	48.2	20.7	40.0	131
Non Extracted	50% YB <0.5	Without	150°C	52.4	21.1	44.3	135
Non Extracted	50% YB <0.5	MAPE	150°C	50.1	18.4	36.8	132
Non Extracted	50% YB [0.5-1.0]	Without	160°C	50.4	21.3	43.0	131
Non Extracted	50% YB [0.5-1.0]	MAPE	160°C	48.2	19.5	37.5	131
Non Extracted	50% YB <0.5	Without	160°C	52.4	19.0	39.9	135
Non Extracted	50% YB <0.5	MAPE	160°C	50.1	17.1	34.3	132
Non Extracted	50% YB [0.5-1.0]	IndulinAT	160°C	48.2	25.3	48.8	131
Non Extracted	50% YB <0.5	IndulinAT	160°C	50.2	19.8	39.8	131
Non Extracted	50% YB <0.5	IndulinAT	150°C	50.2	20.1	40.3	132
Non Extracted	50% YB [0.5-1.0]	IndulinAT	150°C	48.2	21.9	42.3	133
Non Extracted	50% YB [0.5-1.0]	IndulinAT	150°C	48.2	20.4	39.5	131
Extracted	50% YB <0.5	IndulinAT	150°C	50.2	27.1	54.4	131
Extracted	50% YB [0.5-1.0]	IndulinAT	150°C	48.2	27.1	52.4	130
Extracted	50% YB <0.5	IndulinAT	160°C	50.2	24.2	48.6	132
Extracted	50% YB <0.5	MAPE	160°C	50.1	25.9	51.9	129
Extracted	50% YB <0.5	MAPE	150°C	50.1	20.3	40.6	135
Extracted	50% YB [0.5-1.0]	MAPE	150°C	48.2	27.5	53.0	129
Extracted	50% YB [0.5-1.0]	MAPE	160°C	48.2	26.3	50.7	131
Extracted	50% YB [0.5-1.0]	IndulinAT	160°C	48.2	25.9	49.9	132
Extracted	50% YB <0.5	Without	150°C	52.4	18.9	39.7	132
Extracted	50% YB <0.5	Without	160°C	52.4	28.1	58.9	129
Extracted	50% YB [0.5-1.0]	Without	160°C	50.4	27.3	55.1	131
Extracted	50% YB [0.5-1.0]	Without	150°C	50.4	25.8	52.0	131

(1) Calculated during the temperature decrease

(2) Calculated during the second temperature rise

YB = Yellow birch; [0.5-1.0] = particles size between 0.5 and 1.0 mm; <0.5 = particles size

Two hypotheses can be advanced to explain differences between black spruce barks and yellow birch barks. The first one would be that the particle size will have a significant influence on the results, which was the reason why characterization of the dimensions is needed. There are also possible differences in morphology (particle geometry). It is supposed that “fiber-like” barks will have better properties than particle ones. The second hypothesis would be that the chemical characteristics of barks (Table 3-2) have an important influence on their compatibility with HDPE, explaining the properties of our bio-composites. Five batches of barks were characterized. The general chemical composition of the studied barks are rather similar, the only significant difference found was the higher ash content of yellow birch bark which was

possible to relate to its higher sand content at reception from sawmill *Bois Poulin* (BP). The black spruce bark was furnished by *FP Innovations* (FPI) after being refined, which could explain its lower hemicellulose content the part of which is known to be lost during the refining process (with disk-refiners) at high temperature. Finally, high content of extractives (ethanol-toluene, hot water and NaOH) were found for each bark species. Sodium hydroxide extraction gave the highest yields since it is likely to extract some of the structural components as well.

Table 3-2 Chemical characterizations of different barks batches.

		Wood constituents (%)				Extractives (%)		
		Cellulose ¹ (%)	Lignin ¹ (%)	Hemicellulose ¹ (%)	Ash ¹ (%)	Ethanol-Toluene ¹ (%)	Hot water ¹ (%)	NaOH ^{1,2} (%)
YB-NE BP	Value (+/-)	35.0% (6.9%)	41.0% (11.6%)	24.7% (3.4%)	8.9% (0.1%)	4.8% (0.1%)	6.6% (0.1%)	25.1% (0.3%)
YB-E-BP	Value (+/-)	35.5% (7.2%)	44.0% (13.6%)	28.5% (3.2%)	9.3% (0.2%)	2.3% (0.0%)	5.1% (0.1%)	20.8% (0.3%)
YB-NE Pr	Value (+/-)	31.9% (0.5%)	38.9% (5.1%)	27.7% (1.1%)	2.2% (0.1%)	7.4% (0.1%)	5.1% (0.1%)	42.0% (0.5%)
BISp-NE Bs	Value (+/-)	42.3% (1.1%)	30.8% (2.0%)	16.4% (0.8%)	2.5% (0.1%)	11.4% (0.2%)	14.8% (0.3%)	31.9% (0.6%)
BISp-NE FPI	Value (+/-)	47.3% (4.0%)	43.6% (3.2%)	7.5% (0.8%)	1.9% (0.1%)	7.8% (0.6%)	12.7% (0.9%)	18.9% (1.4%)

1 : Calculated on the oven-dry mass of bark
2 : May contain cellulose and hemicellulose

YB = Yellow birch / BISp = Black spruce / NE = Non extracted / E = Extracted with hot water
BP = Bois Poulin / FPI = FP Innovations (batch "Green Bark") / Pr = Precitech / Bs = Boisaco

Mechanical Properties

Bending characterization (Table 3-3), gave the results which were contradictory to those by Ngueho-Yemele *et al.* [18] who examined HDPE containing black spruce and trembling aspen bark fibers. The bending modulus, in our study, increases with bark incorporation in the bio-composites. But according to the study by Ngueho-Yemele *et al.* [18], the maximum strength varied depending on the content of each components of the bio-composite tested. Another important result was that no significant difference between extracted and non-extracted barks was determined for our formulations according to Ngueho-Yemele *et al.* [19].

Table 3-3 Bending properties (ASTM D790) of the extruded formulations.

Formulations (Description)				MOE (GPa)		Maximum strength (MPa)	
HDPE 150°C				0.879	(0.053)	26.1	(0.5)
HDPE 160°C				0.948	(0.056)	26.5	(0.7)
Non Extracted	50% YB [0.5-1.0]	Without	150°C	1.31	(0.061)	24.1	(0.5)
Non Extracted	50% YB [0.5-1.0]	MAPE	150°C	1.652	(0.047)	35.6	(2.1)
Non Extracted	50% YB <0.5	Without	150°C	1.526	(0.036)	25.9	(0.6)
Non Extracted	50% YB <0.5	MAPE	150°C	1.57	(0.068)	36.3	(0.6)
Non Extracted	50% YB [0.5-1.0]	Without	160°C	1.094	(0.050)	22.1	(0.4)
Non Extracted	50% YB [0.5-1.0]	MAPE	160°C	1.574	(0.153)	32.8	(2.3)
Non Extracted	50% YB <0.5	Without	160°C	1.259	(0.131)	25.0	(1.2)
Non Extracted	50% YB <0.5	MAPE	160°C	1.635	(0.040)	35.3	(2.6)
Non Extracted	50% YB [0.5-1.0]	IndulinAT	160°C	1.166	(0.029)	21.2	(1.9)
Non Extracted	50% YB <0.5	IndulinAT	160°C	1.192	(0.055)	18.9	(0.7)
Non Extracted	50% YB <0.5	IndulinAT	150°C	1.388	(0.034)	25.1	(1.9)
Non Extracted	50% YB [0.5-1.0]	IndulinAT	150°C	1.266	(0.068)	24.1	(1.7)
Non Extracted	50% YB [0.5-1.0]	IndulinAT	150°C	1.165	(0.045)	25.2	(1.2)
Extracted	50% YB <0.5	IndulinAT	150°C	1.359	(0.053)	24.8	(0.3)
Extracted	50% YB [0.5-1.0]	IndulinAT	150°C	1.252	(0.116)	25.2	(0.4)
Extracted	50% YB <0.5	IndulinAT	160°C	1.305	(0.045)	26.9	(1.0)
Extracted	50% YB <0.5	MAPE	160°C	1.199	(0.045)	31.8	(0.6)
Extracted	50% YB <0.5	MAPE	150°C	1.598	(0.032)	34.2	(1.9)
Extracted	50% YB [0.5-1.0]	MAPE	150°C	1.193	(0.034)	31.5	(1.1)
Extracted	50% YB [0.5-1.0]	MAPE	160°C	1.206	(0.080)	31.5	(1.4)
Extracted	50% YB [0.5-1.0]	IndulinAT	160°C	1.238	(0.019)	25.3	(1.0)
Extracted	50% YB <0.5	Without	150°C	1.306	(0.083)	24.6	(0.8)
Extracted	50% YB <0.5	Without	160°C	1.315	(0.071)	27.8	(0.3)
Extracted	50% YB [0.5-1.0]	Without	160°C	1.233	(0.069)	26.3	(1.0)
Extracted	50% YB [0.5-1.0]	Without	150°C	1.275	(0.019)	27.7	(0.9)

Charpy impact resilience (ASTM D256) characterization (Table 3-4) give results similar to Sewda and Maiti [17] with an important decrease on the impact strength values with and without notch. The reason may be the difference in interphase between the bark particles and the matrix HDPE. When adding MAPE, which is an efficient commercial coupling agent, better properties were obtained as already observed by Sewda and Maiti [17] and Colom *et al.* [5]. So the chemical interaction between the components of the bio-composites is important. Scanning electron microscope (SEM) observations need to be done to check this hypothesis.

Table 3-4 Charpy impact resilience (ASTM D256) of the extruded formulations.

Formulations (Description)				Without notch (J/m ²)		With notch (J/m ²)	
HDPE 150°C				58 660	(5348)	6 096	(653)
HDPE 160°C				51 520	(6230)	5 112	(344)
Non Extracted	50% YB [0.5-1.0]	Without	150°C	5 782	(644)	3 138	(169)
Non Extracted	50% YB [0.5-1.0]	MAPE	150°C	7 686	(1291)	3 120	(307)
Non Extracted	50% YB <0.5	Without	150°C	5 696	(702)	2 892	(274)
Non Extracted	50% YB <0.5	MAPE	150°C	10 808	(653)	2 980	(209)
Non Extracted	50% YB [0.5-1.0]	Without	160°C	4 596	(373)	2 898	(204)
Non Extracted	50% YB [0.5-1.0]	MAPE	160°C	5 946	(839)	3 128	(294)
Non Extracted	50% YB <0.5	Without	160°C	6 062	(607)	2 934	(245)
Non Extracted	50% YB <0.5	MAPE	160°C	8 314	(2011)	3 108	(261)
Non Extracted	50% YB [0.5-1.0]	IndulinAT	160°C	4 534	(618)	3 008	(518)
Non Extracted	50% YB <0.5	IndulinAT	160°C	4 626	(533)	2 550	(275)
Non Extracted	50% YB <0.5	IndulinAT	150°C	5 572	(779)	3 082	(455)
Non Extracted	50% YB [0.5-1.0]	IndulinAT	150°C	5 250	(1275)	2 910	(285)
Non Extracted	50% YB [0.5-1.0]	IndulinAT	150°C	5 944	(1370)	3 724	(153)
Extracted	50% YB <0.5	IndulinAT	150°C	5 820	(407)	3 082	(361)
Extracted	50% YB [0.5-1.0]	IndulinAT	150°C	5 306	(298)	3 232	(299)
Extracted	50% YB <0.5	IndulinAT	160°C	7 046	(576)	2 932	(287)
Extracted	50% YB <0.5	MAPE	160°C	11 616	(1806)	3 140	(307)
Extracted	50% YB <0.5	MAPE	150°C	10 072	(1144)	3 338	(246)
Extracted	50% YB [0.5-1.0]	MAPE	150°C	7 913	(733)	3 318	(151)
Extracted	50% YB [0.5-1.0]	MAPE	160°C	9 990	(2474)	3 744	(492)
Extracted	50% YB [0.5-1.0]	IndulinAT	160°C	5 218	(1047)	2 996	(105)
Extracted	50% YB <0.5	Without	150°C	5 720	(993)	2 562	(305)
Extracted	50% YB <0.5	Without	160°C	7 190	(1314)	3 218	(401)
Extracted	50% YB [0.5-1.0]	Without	160°C	6 562	(1219)	3 216	(204)
Extracted	50% YB [0.5-1.0]	Without	150°C	5 708	(535)	3 098	(54)

Before presenting the tensile and wettability properties, an explanation on the experimental plan used with the internal mixer must be done. First of all, we chose this process because of the very small quantities of esterified lignin and black spruce bark available. The experimental design included three steps. In Table 3-5 the results obtained for nine formulations used to select the best batch of barks fibers from *FPIinnovations* are presented and the experiment was designed to select the one with the best performance to be used in the following experiments (and future ones). A second factor in these experiments was to analyze the effect of hot water extraction. This plan used non-esterified lignins only.

Table 3-5 Formulations used in the internal mixer 1.

A1	BISp FPI	30:70	Non Extracted	12 Bar	IndulinAT
B1	BISp FPI	30:70	Non Extracted	8 Bar	MAPE
C1	BISp FPI	30:70	Non Extracted	GreenBark	Without
D1	BISp FPI	30:70	Extracted	12 Bar	Without
E1	BISp FPI	30:70	Extracted	PreExtracted	IndulinAT
F1	BISp FPI	30:70	Extracted	8 Bar	IndulinAT
G1	BISp FPI	30:70	Extracted	GreenBark	MAPE
H1	HDPE 150	-	-	-	-
I1	HDPE 160	-	-	-	-

The second step (Table 3-6) was designed to compare the best batch of black spruce bark fibers with the yellow birch used in the extruded formulations, therefore the comparison is made between “fiber-like” particles of black spruce bark with particles from *Bois Poulin*. Another factor (the modification type of lignins) was analyzed here, because two different esterifications on Indulin AT lignins were integrated in the formulations. Esterified lignins (with stearic and butyric anhydride) were compared to non-esterified lignins and to commercial coupling agent (MAPE).

Table 3-6 Formulation used in the internal mixer 2.

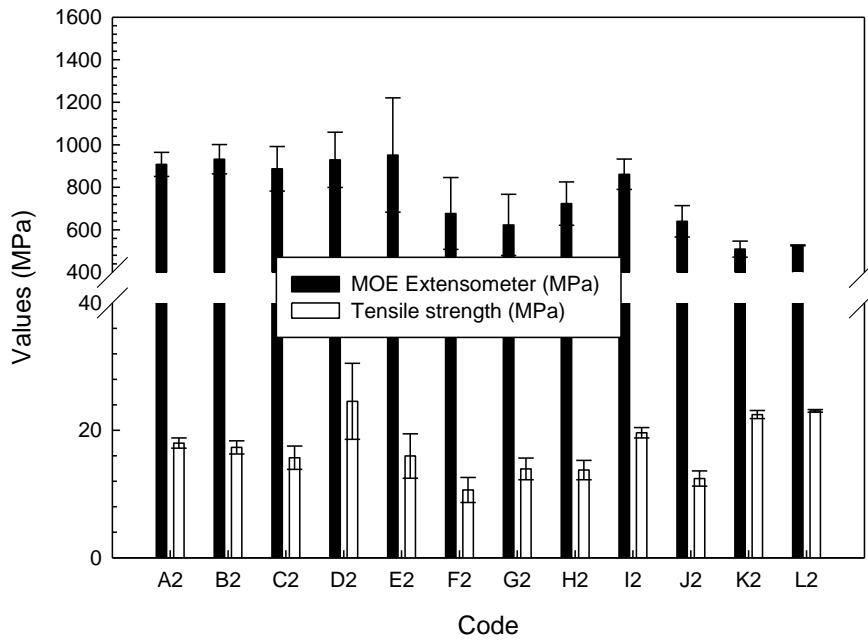
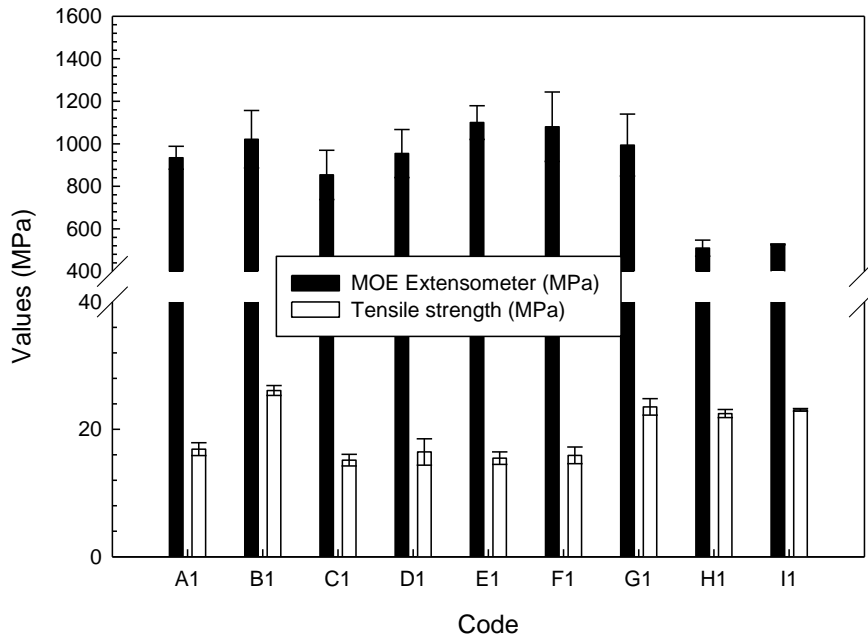
A2	BISp FPI	30:70	Non Extracted	GreenBark	IndulinAT
B2	BISp FPI	30:70	Non Extracted	GreenBark	IndulinAT Butyric
C2	BISp FPI	30:70	Non Extracted	GreenBark	IndulinAT Stearic
D2	BISp FPI	30:70	Non Extracted	GreenBark	MAPE
E2	BISp FPI	30:70	Non Extracted	GreenBark	Without
F2	YB BP	30:70	Non Extracted	<0.5mm	IndulinAT
G2	YB BP	30:70	Non Extracted	<0.5mm	IndulinAT Butyric
H2	YB BP	30:70	Non Extracted	<0.5mm	IndulinAT Stearic
I2	YB BP	30:70	Non Extracted	<0.5mm	MAPE
J2	YB BP	30:70	Non Extracted	<0.5mm	Without
K2	HDPE 150	-	-	-	-
L2	HDPE 160	-	-	-	-

The third step (Table 3-7) was to compare all the batches of barks available in small quantities and to analyze yet another esterification (with maleic anhydride) on two different lignins to determine which one has more potential to be used as coupling agent. All these formulations gave useful data to compare our bio-composites containing lignins to the formulations containing commercial coupling agents.

Table 3-7 Formulation used in the internal mixer 3.

A3	YB BP	50:50	Non Extracted	[1.0 ; 1.4]mm	MAPE
B3	BISp FPI	30:70	Non Extracted	GreenBark	MAPE
C3	YB P	50:50	Non Extracted	[1.0 ; 1.4]mm	Wayagamack Maleic
D3	YB BP	30:70	Non Extracted	[1.0 ; 1.4]mm	Wayagamack Maleic
E3	BISp Bs	30:70	Non Extracted	Span	Wayagamack Maleic
F3	YB P	50:50	Non Extracted	Span	Without
G3	YB BP	50:50	Non Extracted	Span	Without
H3	BISp Bs	30:70	Non Extracted	[1.0 ; 1.4]mm	Without
I3	BISp FPI	50:50	Non Extracted	GreenBark	Without
J3	YB P	30:70	Non Extracted	[1.0 ; 1.4]mm	IndulinAT Maleic
K3	BISp Bs	50:50	Non Extracted	[1.0 ; 1.4]mm	IndulinAT Maleic
L3	HDPE 150	-	-	-	-
M3	HDPE 160	-	-	-	-

Our tensile characterization results (Figure 3-2) were contrary to those of Sewda and Maiti [17], the tensile strength decreased with addition of bark fibers. However, according to the work of Ngueho-Yemele *et al.* [18], the tensile modulus increased when barks were added. According to Ngueho-Yemele *et al.* [18], the maximum strength was significantly reduced in the bio-composite versus HDPE except for the formulations containing the commercial coupling agent (MAPE). Colom *et al.* [5] explained that the chemical interaction between the components of the bio-composites was not efficient enough without MAPE. An important result was however that no significant difference between performance of formulations containing extracted or non-extracted. This is an important result because it leaves the space for potential future applications of extractives which could be obtained from the bark fibers prior to their incorporation into the composites.



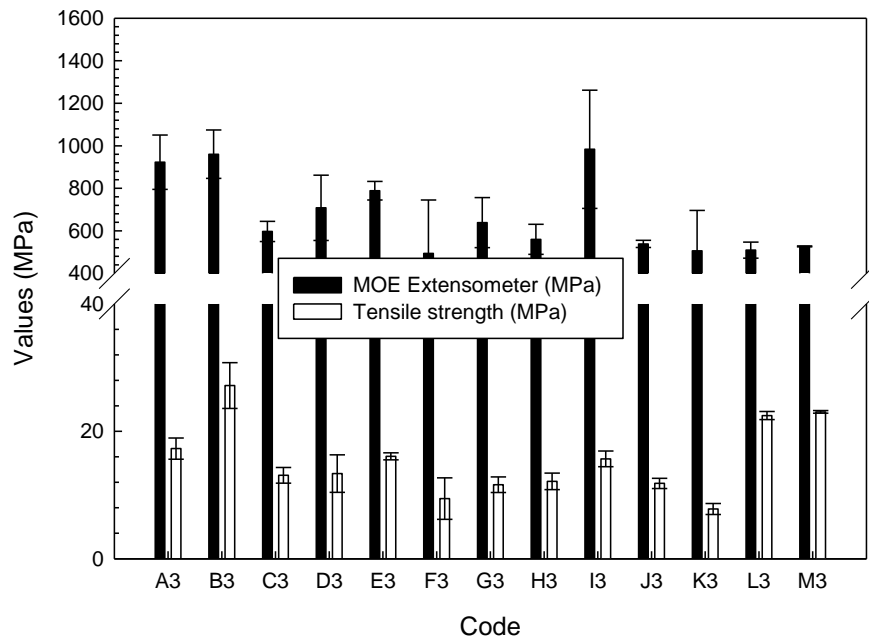
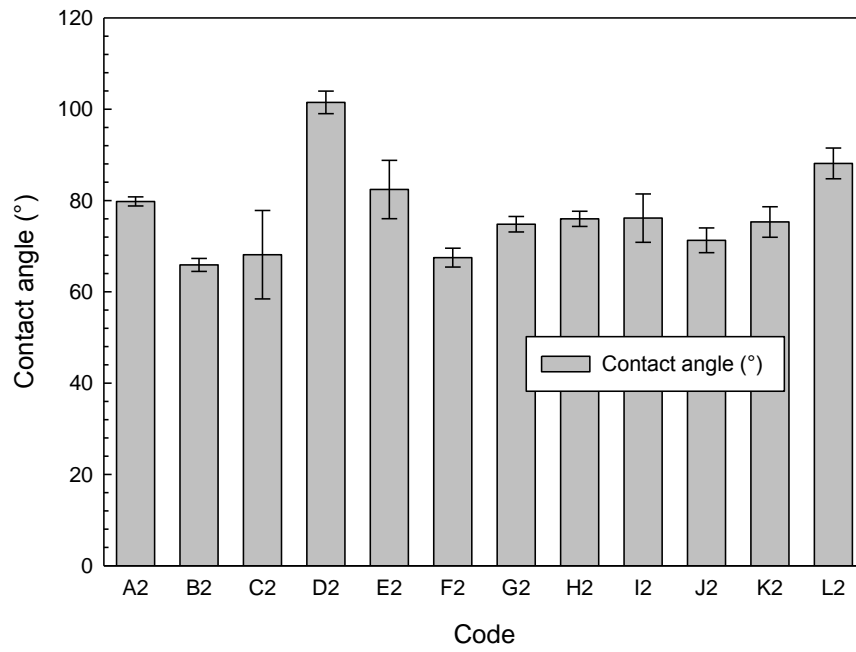
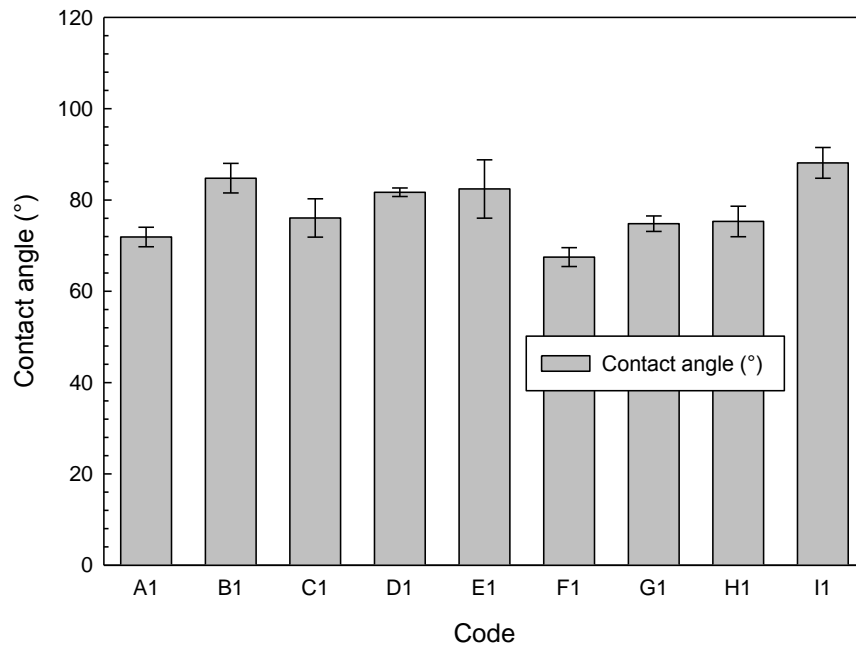


Figure 3-1 Tensile properties (MOE using extensometer and Tensile strength): a) internal mixer 1 (Table 3-5); b) internal mixer 2 (Table 3-6); c) internal mixer 3 (Table 3-7).

Wettability (Contact Angle)

In order to examine the potential of our bio-composite for outdoor applications, wettability in terms of contact angle was measured (Figure 3-3). The results showed good hydrophobicity of all the formulations tested. It is important to notice that the bio-composites containing extracted bark had the best hydrophobic performance. This is another property which is allowing imagining the extraction of bark prior to its incorporation, while yielding the extractives from the bark for high-value applications [16]. These data are to be further verified by the swelling based on ASTM D7031, in which samples are mechanically tested after swelling tests to confirm the hydrophobic nature of the composites.



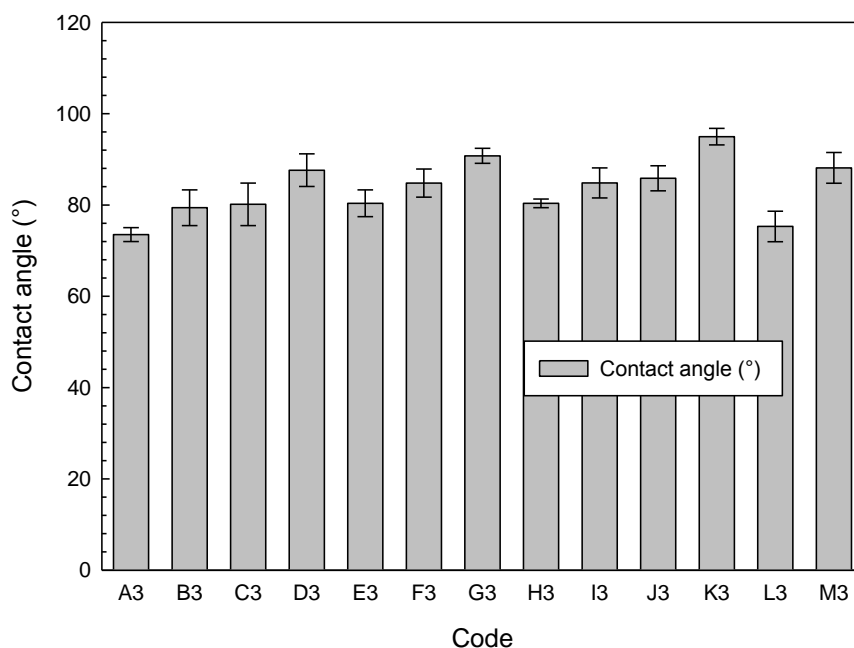


Figure 3-2 Wettability property (Contact angle °): a) internal mixer 1 (Table 3-5 A3); b) internal mixer 2 (Table 3-6 A3); c) internal mixer 3 (Table 3-7 A3).

CONCLUSIONS

The rheological measurements may give important tools to control and optimize the processing of bio-composites. Differential scanning calorimetry (DSC) data confirmed that some materials obtained in this study indicate to a good compatibility between the components, the bio-composites containing extracted bark preserving higher crystallinity than their non-extracted counterparts. This information is important for further study. Mechanical properties (bending, Charpy impact resilience and tensile) indicate that bio-composites containing extracted bark are not significantly different from those with non-extracted bark. This point is important for potential future applications of extractives (pharmaceutics, nutraceutics, cosmetics) has to be explored. Finally, wettability measurements indicate that these products could be used for outdoor applications, but this point has to be confirmed in the future with long term mechanical characterizations and swelling tests.

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