Universidad de Huelva

Departamento de Ingeniería Química, Química Física y Ciencias de los Materiales

Development of new thickening and/or gelling agents of vegetable oils from different lignocellusic fractions chemically modified through epoxidation

Memoria para optar al grado de doctora presentada por:

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Fecha de lectura: 18 de enero de 2019

Bajo la dirección de los doctores:

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Huelva, 2019

UNIVERSITY OF HUELVA

Department of Chemical Engineering, Physical Chemistry and Materials Science

DEVELOPMENT OF NEW THICKENING AND/OR GELLING AGENTS OF VEGETABLE OILS FROM DIFFERENT LIGNOCELLUSIC FRACTIONS CHEMICALLY MODIFIED THROUGH EPOXIDATION

Ph. D. Thesis

Doctoral Program in Industrial and Environmental Science and Technology

ESPERANZA CORTÉS TRIVIÑO

2019

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Dr. José María Franco Gómez

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UNIVERSIDAD DE HUELVA

Departamento de Ingeniería Química, Química Física y Ciencias de los Materiales

DESARROLLO DE NUEVOS AGENTES ESPESANTES Y/O GELIFICANTES DE ACEITES VEGETALES A PARTIR DE DIFERENTES FRACCIONES LIGNOCELULÓSICAS MODIFICADAS QUÍMICAMENTE MEDIANTE EPOXIDACIÓN

Ph. D. Thesis

Programa de Doctorado en Ciencia y Tecnología Industrial y Ambiental

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2019

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Research memory presented by Esperanza Cortés Triviño to apply for a Doctoral degree with International Mention at the University of Huelva.

Esperanza Cortés Triviño

The present Dissertation has been performed at the Department of Chemical Engineering, Physical Chemistry and Materials Science of the University of Huelva, under the auspices of Dr. José María Franco Gómez and Dr. Concepción Valencia Barragán, which approve its defence:

Dr. José María Franco Gómez   Dra. Concepción Valencia Barragán

Huelva, December 2018

Universidad de Huelva
Escuela de Doctorado

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Título: **Desarrollo de nuevos agentes espesantes y/o gelificantes de aceites vegetales a partir de diferentes fracciones lignocelulósicas modificadas químicamente mediante epoxidación**
Programa Oficial de Doctorado al que se adscribe y órgano responsable: **Ciencia y Tecnología Industrial y Ambiental**
Línea de investigación a la que se adscribe y órgano responsable: **Ingeniería de Procesos y Productos Químicos**
Rama de Conocimiento **(marcar casilla)**: ☐ Arte y Humanidades ☐ Ciencias ☐ Ciencias de la Salud ☐ Ciencias Sociales y Jurídicas ☒ Ingeniería y Arquitectura

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Acknowledgements

The completion of this Doctoral Thesis could not have been possible without the support and advice of those who have always been by my side on this long journey, enriching me and helping me to become a better person, both at personal and professional levels. My most heartfelt thanks.

Firstly, to my Thesis supervisors, to Dr. José María Franco Gómez, for giving me the opportunity to begin this uncharted road to me, for his assistance, support and ability to calm me down in most situations; and to Dr. Concepción Valencia Barragán, for trusting me from the beginning and being always with me for whatever and at any time, giving me advice and staying with me on this journey. Thank you both for the help and understanding, and above all for being capable of enduring my worst moments.

To Dr. Inmaculada Martínez García, a teacher at the beginning and a great friend at the end, for listening me and providing me advice and her office as a shelter against any situation. Thank you so much for your unconditional support.

To Dr. Erik Kuhn, for hosting me in his "*house*" and making me feel at home, and to all the members of the Tribology Laboratory of University of Hamburg, Ms. Nazli Acar, Mr. Thomas Rhieling and Mr. Niels Eiben, for guiding me and helping during those three wonderful months.

To Junta de Andalucía (TEP-1499), for granting me a Research Fellowship, and to El Ministerio de Economía y Competitividad (CTQ2014-56038-C3-1R), for allowing the execution of these projects that have enabled the development of this Doctoral Thesis.

To all the members of Pro^{2}Tecs and Fluid Complex Laboratory. Thanks for introducing me into the Rheology world and providing me with unforgettable moments throughout this period of my life. In particular to my mates of the shared office on the third and fourth floors of the Experimental Sciences Faculty (Rocio, my predecessor in the world of greases, Antonio, Isa, Ortega, Mauricio, and many others). Thank you for sharing with me all this time full of moments hard to forget.

To Adrian, for being my friend, my partner, my close confidant, specially, for becoming HOME. I would not have been able to move forward without his overwhelming support. Thank you wholeheartedly for staying with me at every step of the way, even at those moments in which even I could not be. And, of course, thanks for understanding, for loving me and for making me the happiest woman in the universe.

To my family, my parents Esperanza and Antonio, and my brother, Antonio, for being the pillars unconditionally underpinning my life, despite the distance. Without them, I would not be able to become who I really am, and, obviously, I could not have reached any of my goals. To Belen, for being part of my family, and to my grandparents, uncles and cousins, for making me feel such a special person. And, finally, to these persons that, unfortunately, are no longer with me, to my grandfather and my uncle. I am sure that they would be proud to see the person I have become.

My heartfelt thanks.

Agradecimientos

Esta Tesis Doctoral no hubiese podido ser realizada sin la ayuda de todos aquellos que, junto con sus consejos, han estado a mi lado en este largo camino, enriqueciéndome y convirtiéndome en mejor persona, tanto a nivel personal como profesional. Gracias de corazón.

En primer lugar, a mis directores de Tesis, al Dr. José María Franco Gómez, por ofrecerme la posibilidad de comenzar este camino que para mí era desconocido, guiarme, apoyarme y ser capaz de calmarme en la mayoría de las situaciones, y a la Dra. Concepción Valencia Barragán, por confiar en mí desde el principio y estar siempre ahí, para cualquier cosa y a cualquier hora, por aconsejarme y acompañarme en este viaje. Gracias a ambos por la ayuda y comprensión, y sobre todo por ser capaces de soportarme en mis peores momentos.

A la Dr. Inmaculada Martínez García, profesora al principio y gran amiga al final, por escucharme, aconsejarme y brindarme su despacho como refugio ante cualquier situación. Gracias por estar conmigo en lo bueno y en lo malo y por ofrecerme un apoyo incondicional.

Al Dr. Erik Kuhn, por acogerme en su casa y hacerla mía, y a todos los miembros del laboratorio de Tribología de la Universidad de Hamburgo, Nazli Acar, Thomas Rieling y Niels Eiben, por guiarme y ayudarme durante esos tres maravillosos meses.

A la Junta de Andalucía (TEP-1499) y al Ministerio de Economía y Competitividad (CTQ2014-56038-C3-1R), cuya financiación ha hecho posible el desarrollo de esta Tesis Doctoral, junto con la Beca de Formación del Personal Investigador otorgada por la Junta de Andalucía.

A todos los integrantes de Pro^{2}Tecs y del Laboratorio de Fluidos Complejos, y a los que ya no están pero que estuvieron en mis inicios. Gracias por introducirme en el mundo de la Reología y conseguir que este periodo de mi vida sea inolvidable. Mención especial a mis compañeros de las salas de becarios 3 y 4 de la Facultad de Experimentales (Rocío, mi predecesora en el mundo de las grasas, Antonio, Isa, Ortega, Mauricio… y a todos los demás), gracias por compartir conmigo todo este tiempo lleno de miles de momentos que jamás olvidaré.

A Adrián, por ser mi amigo, mi compañero, mi confidente; en especial, por ser CASA. Sin su inmenso apoyo no hubiese sido capaz de seguir adelante. Gracias de corazón por estar siempre ahí, incluso en momentos en los que ni yo misma estaría. Y por supuesto, gracias por entenderme, por amarme y por hacerme la mujer más feliz del universo.

A mi familia, mis padres Esperanza y Antonio, y a mi hermano Antonio, por ser los pilares que sostienen mi vida de forma incondicional y a pesar de la distancia. Sin ellos no sería quien soy, y obviamente, no hubiese conseguido ninguno de mis objetivos. A Belén, por formar parte de mi familia, y a mis abuelos, tíos y primos, por hacerme siempre sentir especial. Y, por último, a las personas que, desgraciadamente, ya no están a mi lado, mi Abuelo y mi Tío, estoy segura de que estarían realmente orgullosos de ver en lo que me he convertido.

Gracias de corazón.

"*When you are inspired by some great purpose, some extraordinary project, all your thoughts break their bonds: Your mind transcends limitations, your consciousness expands in every direction, and you find yourself in a new, great and wonderful world. Dormant forces, faculties and talents become alive, and you discover yourself to be a greater person by far than you ever dreamed yourself to be.*" — Patanjali.

To my parents.

"*Cuando estas inspirado por algún gran propósito, por algún extraordinario proyecto, los pensamientos rompen las barreras; la mente trasciende sus limitaciones, la conciencia se expande en todas direcciones y te encuentras en un nuevo mundo maravilloso. Las fuerzas, las facultades y los talentos dormidos cobran vida. En ese momento te das cuenta de que eres mucho más grande de lo que jamás hubieras soñado.*" — Patanjali.

A mis padres.

Content

Chapter 1

Introduction

Resumen

Durante las últimas décadas, se ha desarrollado una mayor concienciación sobre la contaminación y los efectos negativos que los diferentes productos químicos y/o de uso final ejercen sobre el medioambiente, especialmente aquellos que proceden del petróleo. En este sentido, la industria de los lubricantes ha aumentado también su sensibilidad sobre el impacto de estos materiales en el medioambiente y está intentando reemplazar el uso de materias primas no renovables por aquellas procedentes de fuentes renovables. El primer objetivo de esta iniciativa fue la sustitución de los aceites minerales por otras bases lubricantes amigables con el medioambiente, tales como aceites vegetales, o derivados de ellos, cuyas propiedades los convierte en candidatos prometedores como bases lubricantes biodegradables. Sin embargo, en relación con las formulaciones de grasas lubricantes, éstas, además, contienen generalmente espesantes no naturales, tales como jabones metálicos y poliureas, cuyo uso implica una reducción de las características biodegradables del producto final. De esta forma, y con objeto de producir formulaciones de grasas lubricantes completamente biodegradables y renovables, existe un campo abierto hacía la búsqueda de bio-espesantes basados en productos renovables cuyas características proporcionen las propiedades adecuadas al producto final. Con este objetivo, en este trabajo se pretende desarrollar dispersiones tipo gel biodegradables constituidas por un aceite vegetal (aceite de ricino) y materiales lignocelulósicos químicamente modificados que actúen como espesantes para su aplicación como grasas lubricantes.

De este modo, materiales lignocelulósicos como la lignina, la cual está considerada un subproducto residual en la fabricación de la pasta de papel y producción de bioetanol, con una gran producción a nivel global; y la pasta de celulosa, compuesta por celulosa, hemicelulosa y lignina y que representa una materia prima renovable, abundante y asequible para muchas aplicaciones, han sido seleccionadas como biopolímeros para reemplazar los espesantes basados en jabones metálicos tradicionalmente empleados en grasas lubricantes. Con este

propósito, se modificaron químicamente estos biopolímeros usando compuestos epoxídicos, tales como epiclorhidrina y derivados del glicidil éter, variando tanto la naturaleza del epóxido como la proporción utilizada en la reacción de epoxidación, y después se dispersaron en aceite de ricino con objeto de obtener geles químicos físicamente estables. Con el fin de evaluar el grado de modificación de los diferentes materiales lignocelulósicos y las propiedades de las grasas bio-lubricantes, se aplicaron diferentes técnicas de caracterización. Así, se realizaron ensayos de determinación del índice de epóxido, espectroscopía infrarroja, análisis termogravimétrico y calorimetría diferencial de barrido para verificar la modificación química de los biopolímeros. Además, se realizó una amplia caracterización reológica y tribológica de los oleogeles obtenidos, estudiando también la microestructura de algunos de ellos.

En general, un mayor índice de epóxido, es decir un mayor grado de epoxidación de los materiales lignocelulósicos estudiados, mejoran la compatibilidad con el aceite de ricino y favorecen la estabilidad física de los oleogeles resultantes, como consecuencia del entrecruzamiento químico producido entre los grupos epóxidos libres y los grupos hidroxilos del aceite de ricino. Estas interacciones químicas son, por otra parte, las responsables de las propiedades finales de estos oleogeles. Así, se obtienen propiedades reológicas más adecuadas para su uso como grasa bio-lubricante cuando la lignina o la pasta de celulosa poseen un alto índice de epóxido. El grado de modificación de estos materiales lignocelulósicos puede controlarse variando las condiciones de la reacción de epoxidación (temperatura, tiempo y proporción de reactivos). Por otra parte, el uso de epóxidos aromáticos como agentes modificadores permite obtener, en general, propiedades reológicas y tribológicas más adecuadas en relación a las obtenidas utilizando epóxidos alifáticos, para el mismo grado de epoxidación del material lignocelulósico, debido a un mayor nivel de entrecruzamiento en la red tridimensional de los oleogeles químicos. De este modo, el comportamiento reológico de una gran parte de los oleogeles desarrollados fue muy similar al de las grasas lubricantes tradicionales. Por otro lado, las formulaciones espesadas con pasta de celulosa epoxidada muestran una excelente estabilidad térmica, sin cambios significativos en las propiedades reológicas hasta 150 ºC. Además, tanto la fricción como el desgaste, evaluados en un contacto tribológico, disminuyeron al introducir los bio-espesantes consistentes en material lignocelulósico epoxidado en las formulaciones, en comparación con el uso de aceite de ricino como único lubricante. Como principal resultado de esta investigación, puede concluirse que todas las formulaciones estudiadas y sintetizadas con compuestos procedentes de recursos completamente renovables, presentan propiedades adecuadas para ser propuestas como alternativas prometedoras a las grasas lubricantes convencionales.

1. Summary

During the last decades, the world is really concerned about the pollution and the negative effects that most chemicals and/or end-used products are causing on the environment, especially those derived from crude oil. In this sense, the lubricant industry has also become more sensitive to the needs of the environment and it is fostering the replacement of non-renewable raw materials by others coming from natural resources. The first objective of this tendency was the substitution of mineral oils by other more eco-friendly lubricating base oils, by using vegetable oils or some derivatives, whose properties make them promising candidates to be employed as biodegradable lubricants. However, regarding lubricating grease formulations, these are generally composed of non-natural thickeners, like metallic soaps and poliureas, with the subsequent impact on the biodegradable characteristics of the final product. In this sense, in order to produce completely renewable and biodegradable lubricating grease formulations, there is an open research field aiming to find new bio-thickeners based on natural resources, whose characteristics provide suitable properties to the final bio-lubricating grease. With this aim, this work claims to develop biodegradable gel-like dispersions constituted by a vegetable oil (castor oil) and chemically modified lignocellulosic materials able to act as efficient thickeners in these formulations to be applied as lubricating greases.

Lignocellulosic materials such as lignin, which is considered a residual fraction of cellulose pulping and bioethanol production, with a great global manufacture; and cellulose pulp, composed of cellulose, hemicellulose and lignin, and constituting a renewable, abundant and inexpensive raw material for many applications, have been selected as biopolymers to replace the metallic soaps traditionally employed as thickeners in lubricating greases. For this purpose, these biopolymers have been chemically modified by using epoxy compounds, such as epichlorohydrin and glycidyl ether derivatives, by varying both the nature of the epoxide and the proportions used in the epoxidation reaction, and afterwards dispersing them into castor oil, in order to obtain physically stable chemical gels. With the aim of assessing the extent of the biopolymers epoxidation and the properties of resulting biolubricating greases, different characterization techniques have been used. Thus, epoxy index determination, infrared spectroscopy, thermogravimetric analysis and differential scanning calorimetry tests were carried out to verify the chemical modification of biopolymers. Moreover, oleogels were fully characterized from a rheological and tribological point of view, also studying the microstructure of some of them.

In general, a higher epoxy index, i.e. a higher epoxidation degree of the lignocellulosic materials studied, improves the compatibility with castor oil and favours the physical stability of the resulting oleogels, as a consequent of the chemical cross-linking produced between the free epoxy groups and the hydroxyl groups of castor oil. These chemical interactions are also responsible for the final properties of these oleogels. Thus, more suitable rheological properties are obtained for their use as bio-lubricating greases when the lignin or cellulose pulp have a high epoxy index. The degree of modification of these lignocellulosic materials can be controlled by varying the conditions of the epoxidation reaction (temperature, time and proportion of reagents). On the other hand, the use of aromatic epoxides as modifying agents provides, in general, more convenient rheological and tribological properties compared to their aliphatic counterparts, for the same epoxidation degree of the lignocellulosic material, due to a higher level of cross-linking achieved in the three-dimensional network of chemical oleogels. In this way, the rheological behaviour of most oleogels developed was very similar to that found in traditional lubricating greases. On the other hand, the formulations thickened with epoxidized cellulose pulp show excellent thermal stability, without significant changes in rheological properties up to 150 ºC. In addition, both friction and wear, evaluated in a tribological contact, were reduced by introducing the bio-thickeners consisting of epoxidized lignocellulosic material in the formulations, in comparison to the castor oil as the sole lubricant. Overall, it may be concluded that all formulations synthetized from completely renewable materials, showed suitable properties to be proposed as promising alternatives to conventional lubricating greases.

2. Justification

In this age, climate change, pollution and preservation of the environment are important aspects that greatly disturb people in a society which tries to minimize the impact that consumer goods are causing on nature. In fact, most of the government directives of many countries are implementing several remediation measures, which comprise the replacement of petroleum-based materials and the use of renewable raw materials in multiple applications. In this sense, the lubricant industry, whose current production is fully controlled by crude oil derivatives, tends to increase the pollution levels every year, because of products like engine, hydraulic or industrial oils, are usually percolated or poured into the environment through ground or waterways. Moreover, its combustion drastically affects the global warming as a consequence of the production of greenhouse gases.

With the aim of minimising the environmental impact, the lubricant sector is compelled to find new alternatives to their traditional raw materials, which include green practices and must entail no changes in the bulk properties of the final products. This implies the use of renewable and biodegradable materials that provide similar thermal, mechanical, rheological and tribological behaviours to those shown nowadays by petroleum-based lubricant formulations. In this sense, an extensive research has been focused on the development of biodegradable products, which was firstly approached by the replacement of traditional liquid lubricants, i.e. mineral oils, by vegetable oils. However, regarding lubricating grease formulations, thickeners generally based on metallic soaps takes part of their composition as a major component, whose characteristics do not satisfy the tenets of sustainable chemistry and engineering. In this way, the synthesis of lubricating greases involving vegetable oils and cellulosic derivatives thickeners has been widely studied, as can be seen in the recent literature of this subject. Notwithstanding, these oleogels generally showed a limited stability over time, resulting in oil bleeding problems, as well as a reduced mechanical stability after working in a tribological contact in comparison with conventional products.

In order to solve these drawbacks, chemical modifications of cellulosic natural thickeners by using isocyanates as reactive chemical modifiers have been employed during the last years, yielding stable chemical oleogels. Nevertheless, although similar properties to those shown by conventional lubricating greases are achieved by inducing chemical crosslinking with diisocyanate groups, the use of such compounds cannot be considered as a green practice since their toxicity and hazardous nature has been rigorously evidenced. In addition to this, the synthesis of these NCO-based thickeners for lubricant applications comprises some solvents and catalysts, such as toluene and amines, that pose a risk to the environment. Consequently, this investigation deals with the use of epoxy compounds as reactive chemical groups to chemically modify lignocellulosic materials, like cellulose and lignin, with the aim of producing more sustainable chemical oleogels, once dispersed in castor oil, with similar properties than those found in conventional lubricating greases.

3. Objectives

The main objective of this Doctoral Thesis is the production of completely biodegradable lubricating greases formulations from castor oil and bio-thickeners derived from lignocellulosic materials by means of a previous chemical modification of these biopolymers with reactive epoxy groups.

In relation to the specific goals of this work, the first proposal was to modify the hydroxyl groups of lignocellulosic materials (lignin and cellulose pulp) with epoxy compounds, evaluating their modification degree as a function of reaction conditions (temperature and time), proportion of both epoxy compound and catalyst (if required), and the reactive compound chemical structure. Once verified the chemical modification of these bio-thickeners through their chemical characterization (i.e., determination of epoxy index, spectroscopy, thermogravimetric analysis and differential scanning calorimetry), they were dispersed in castor oil in order to promote chemical crosslinking in the oil medium.

The second target of this research was the full rheological and tribological characterization of the resulting oleogels as a function of the epoxidation degree and concentration of bio-thickeners in order to assess the performance properties and efficiency of these bio-sourced formulations.

4. Structure

This Doctoral Thesis is divided in five chapters, including this present introductory chapter. Chapter 2, covers the state of the art on this topic, providing an in-depth description of lignocellulosic materials and the corresponding pre-treatments applied for the separation of the three main components, i.e., cellulose, hemicellulose and lignin, as well as the numerous possibilities for increasing their chemical reactivity through chemical modification, specifically by using epoxidation reactions. In addition, oleogel term has been defined from a chemical, physical and macroscopic point of view, providing information about its properties and applications, including lubricants. In this sense, a general description of lubricants, and specially lubricating greases, is also detailed, describing their fundamental characteristics and the typical rheological and tribological properties of these products. Moreover, bio-sourced formulations, focussing on these based on lignocellulosic materials and vegetable oils are described. On the other hand, a detailed description of the materials used to produce the biolubricating greases is included in Chapter 3, as well as the synthesis protocols and all the techniques employed to characterize both modified thickeners and the resulting gel-like dispersions. Chapter 4 contains the experimental results and their discussion of the different studies raised in this Doctoral Thesis. As a compendium of articles, this chapter is divided into 4 different subsections, each one comprising an article, three of them published and one of them pending acceptance, in several well reputed scientific journals, which concerns, respectively, the assessment of lignin epoxidation conditions on the physical stability and rheological properties of gel-like dispersions in castor oil, using epichlorohydrin as epoxidation agent; the influence of lignin/poly(ethylene glycol) diglycidyl ether ratio on the performance properties of resulting oleogels, i.e., rheological, tribological and thermal characteristics; the effect of cellulose pulp epoxidation on the rheological properties of the resulting gel-like dispersions in castor oil by analysing the influence of cellulose pulp epoxy index and chemical structure of the epoxy compounds; and a detailed insight into the thermo-rheological and tribological behaviour, at different temperatures, of oleogel formulations based on castor oil and epoxidized cellulose pulp. Finally, chapter 5 sets out the most relevant conclusions deduced from this research.

Chapter 2

State of the art

1. Lignocellulosic materials

The world biomass production is about 220 billion tons/year on land, among which 82% is related to forest industries, while the rest corresponds to agricultural residues, water plants, grasses, and other plant substances (Kumari and Singh, 2018). In particular, lignocellulosic materials are agro-industrial resources, which are considered renewable materials from biomass, and whose annual worldwide production involves between 10 to 50 billion tons on dry weight. Their abundant availability makes them relatively inexpensive, and together with their biodegradable character and environmental eco-friendly practices, turn them into potential products for the development of high added-value chemicals and biomaterials production (Winarni et al., 2013). Moreover, these materials possess attractive properties to be used as renewable raw materials, amongst which some highlights include its light weight, low density, low thermal expansion and high specific strength. In general, lignocellulosic biomass is composed of cellulose, hemicellulose and lignin, making up cell walls and being responsible for the wood physical and chemical properties. However, as shown in Table 1, the relative proportion of these constituents is largely determined by their origin and species, which includes a small content of extractives, i.e. terpenes, fats, and waxes (Jönsson and Martín, 2016).

Cellulose is the main component of lignocellulosic materials, which is assembled in a lignin matrix and connected through hemicellulosic polymers. Lignin thus has a binding function in the polysaccharide matrix, holding the hemicellulose and cellulose microfibres, where all chains are bonded together by hydrogen and covalent bonds forming a complex structure (Karumuri et al., 2015; Thakur and Thakur, 2015). In order to fully exploit the opportunities of lignocellulosic biomass, each component should be ideally isolated into their basic chemicals, thus maximizing its yield, and used them in bio-product development. However, this is specially complicated due to the natural recalcitrance of the plant cell walls and the cellulose accessibility, which limit the enzymatic degradation of its carbohydrates (Chandel and Silvério, 2013; Meng and Ragauskas, 2014; Zhao et al., 2012). Nevertheless, some studies have revealed that the enzymatic hydrolysis of lignocellulose components can be balanced by applying different pre-treatments, which will be described later, allowing to remove the recalcitrant barriers and solubilize the different lignocellulosic biomass components (see Figure 1) (Kumari and Singh, 2018; Mosier et al., 2005; Scheper, 1999; Sun and Cheng, 2002).

Table 1. Chemical composition of lignocellulosic materials (%) (Hon, 1995)

Lignocellulosic source	Cellulose	Hemicellulose	Lignin	Extract
Hardwood	43-47	25-35	16-24	2-8
Softwood	40-44	25-29	25-31	1-5
Abaca	63.72	5-10	21.83	1.6
Bagasse	40	30	20	10
Coir	32-43	10-20	43-49	4.5
Corn cobs	45	35	15	5
Corn stalks	35	25	35	5
Cotton	95	2	0.9	0.4
Flax (retted)	71.2	20.6	2.2	6
Flax (unretted)	62.8	12.3	2.8	13.1
Hemp	70.2	22.4	5.7	1.7
Henequen	77.6	4-8	13.1	3.6
Istle	73.48	4-8	17.37	1.9
Jute	71.5	13.6	13.1	1.8
Kenaf	36	21.5	17.8	2.2
Ramie	76.2	16.7	0.7	6.4
Sisal	73.1	14.2	11	1.7
Sunn	80.4	10.2	6.4	3
Wheat straw	30	50	15	5

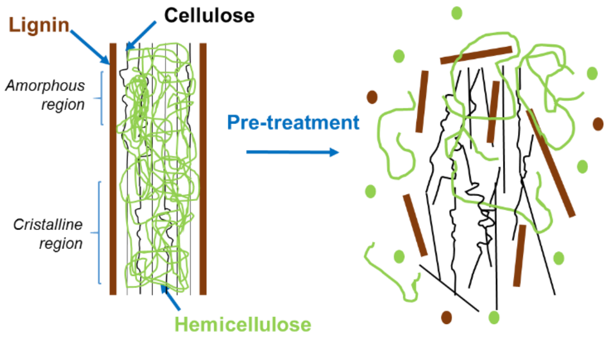


Figure 1. Effect of lignocellulose biomass pre-treatment (Mosier et al., 2005)

Cellulose is a linear polysaccharide consisting of ß(1→4) glycosidic linked D-glucopyranose units that form linear polymeric chains of about 8000-12000 glucose units. Its structure is formed by two different regions, the crystalline and the amorphous one. In the crystalline structures, cellulose chains are packed together by means of hydrogen bonds, generating highly insoluble structures known as microfibrils, which are assemblies of about 36 hydrogen-bonded glucan chains. These hydrogen bonds are responsible for the recalcitrant character of cellulose, which hinder their enzymatic and microbial attack. On the other hand, the amorphous regions are located within the microfibrils previously described, whose molecules are easily hydrolysed and less compact. In this way, the cellulose microfibrils are cross-linked by hemicellulose/pectin matrixes, giving rise to macrofibrils that stabilise the plant cell wall (Ding and Himmel, 2006). Glucose monomers of cellulose, characterized by their ability to rotate, are shown in Figure 2.

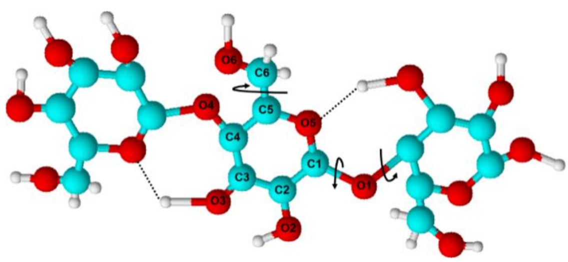


Figure 2. Chemical structure of cellulose with its possible rotation angles (Hon, 1995)

Hemicellulose is another of the main components constituting the lignocellulosic biomass. This short and highly branched heteropolymer is composed of pentoses (D-xylose and L-arabinose), hexoses (D-galactose, D-mannose and D-glucose) and small amounts of acetic and uronic (D-glucuronic, D-4-O-methyl- glucuronic and D-galacturonic acids) acids (Carpita and Gibeaut, 1993; Peng et al., 2009). Although xylose is the main carbohydrate in the hemicellulosic fraction (around 80% of total sugars), it can also contain small amounts of other sugars like L-rhamnose and L-fucose (Chandel and Silvério, 2013). Hemicellulose is relatively easy to hydrolyse and is linked to cellulose through hydrogen bridges and physical interactions, giving rise to a network that constitutes the backbone of the plant cell wall (Freudenberg, 1965; Kim, 2018). Its chemical structure differs greatly from cellulose, since it is composed of different sugar units, its polymerization degree is much lower and essentially has an amorphous structure due to its chain branching (see Figure 3) (Saha et al., 2016).

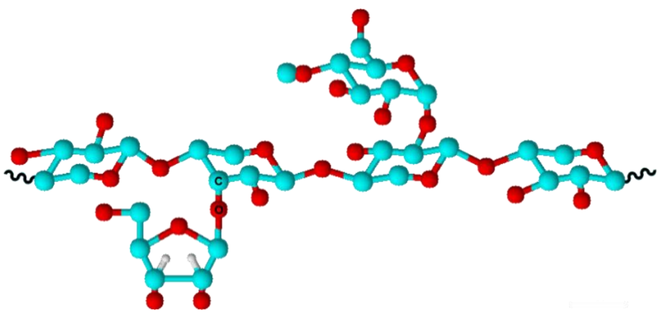


Figure 3. Chemical structure of hemicellulose (Ndibewu and Pierre, 2018)

Lignin is a natural phenolic macromolecule composed of a large number of aromatic rings, which result in a complex three-dimensional structure. Its main function consists of giving mechanical strength and structural support to plant cell walls, since it acts as a continuous matrix component, as well as facilitating water transport and protecting the cell wall from destructive pathogens. As can be seen in Figure 4, lignin is formed by three kinds of phenyl propanol units, i.e., p-coumaryl alcohol (p-hydroxy phenyl propanol, **H**), coniferyl alcohol (guaiacyl propanol, **G**) and sinapyl alcohol (syringyl alcohol, **S**), which are mainly linked by two different linkages, C−O−C and C−C, whereas other bonds include β−O−4, 5−5−, α−O−4, β−5, β−β, 4−O−5 and β−1) (Chen et al., 2015; Singh et al., 2012). In general, C−O−C ether linkages are the most abundant linkages present on lignin, in particular β−O−4 aryl ether, 45-60%, which are less resistant to chemical attacks, becoming susceptible to cleavage in lignin depolymerization processes. In this sense, the composition of lignin depends on the source from which it is derived, thus varying the proportion of G, S and H units. For instance, softwood lignin is mainly composed of G units, while equal amounts of G and S and a mix of the three monolignols compose the hardwood and the grass lignin, respectively (Adler, 1977).

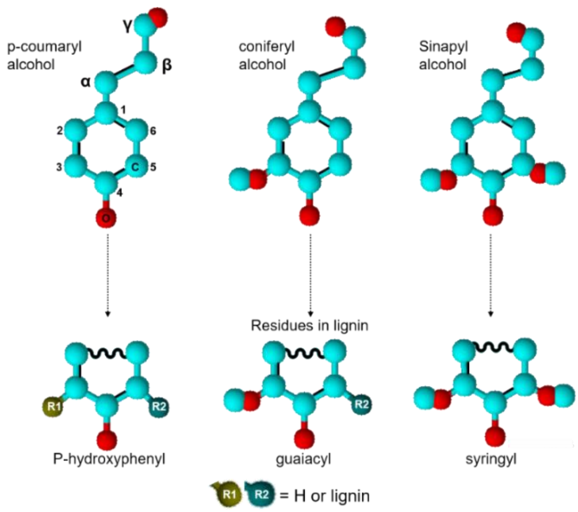


Figure 4. The three main precursors of lignin (monolignols) and their corresponding structures in lignin polymers (Laurichesse and Avérous, 2014)

1.1. Reactivity and functionalities of lignocellulose

Lignocellulosic materials possess fundamental qualities to be considered as raw materials in a wide range of applications, owing to their low toxicity, biodegradability, great availability, low cost and renewable nature (Thakur and Thakur, 2015). As previously discussed, nowadays there is a great interest in diversifying the use of lignocellulose as feedstock for the biomaterials production.

However, the original lignocellulosic components may not show the required properties for using them in a particular application, being necessary the modification of their structure in order to broaden the range of use. This means inducing new properties that allow to increase the added-value of final end-use products. In this way, although lignocellulosic materials can be different as far as their composition is concerned, in general all of them show very similar properties and possess many functional groups susceptible to reaction, which comprise primary and secondary hydroxyl, carbonyl and carboxyl groups, as well as carbon-carbon, ether, ester and acetal linkages (see Figure 5).

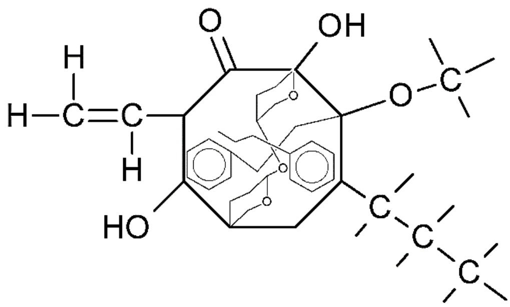


Figure 5. Functional site present in lignocellulosic materials (Hon, 1995)

In this way, carbohydrates units within cellulose and hemicellulose macromolecules are connected through covalent ethers, while covalent ester linkages within hemicellulose give rise to carboxyl groups or carboxyl salts. Moreover, cellulose and hemicellulose chains have free hydroxyl groups, which are linked by hydrogen bonds. In addition, lignin is composed by ether and carbon-carbon bonds between monomers that are connected with cellulose and hemicellulose by means of hydrogen bonds. This kind of bonds also links cellulose with the hemicellulose within lignocellulosic macromolecule (Saha et al., 2016). Table 2 summarizes the typical bonds found in lignocellulose macromolecules.

Table 2. Chemical linkages of lignocellulosic materials (Saha et al., 2016)

Linkage	Bonds	Occurrence
Intra-polymeric linkages	Ether	Lignin, cellulose and hemicellulose
	Carbon-carbon	Lignin
	Hydrogen	Cellulose
	Ester	Hemicellulose
Inter-polymeric linkages	Ester	Hemicellulose-lignin
	Hydrogen	Cellulose-hemicellulose, cellulose-lignin, hemicellulose-lignin
	Ether	Lignin-polysaccharide

Therefore, lignocellulosic materials show a wide range of possibilities for their chemical modification, which may involve a chemical reaction between the different selected functional sites and chemical reagents, either with or without a catalyst, generating new covalent linkages. Catalysts generally prevent the extensive degradation of lignocellulosic materials and allow for the swelling of cell wax matrix structure, favouring the penetration of different reagents (Rowell, 2012). It is worth to point out that hydroxyl modifications are the most common chemical reactions used to increase the compatibility of lignocellulosic materials due to the great availability of these groups and their high reactivity with many other functional groups and/or different reagents. These methods entail the substitution or blocking of hydroxyl groups by hydrophobic functional groups or polymeric chains, among which esterification, etherification and urethanization are the most remarkable ones.

1.1.1. Esterification reactions

Esterification of lignocellulosic materials consists of the replacement of their hydroxyl groups by an ester group by using different chemical compounds, such as anhydrides (like acetylation with acetic anhydride), acyl chlorides and carboxylic acids. In general, acetylation is the most popular reaction, where the accessible hydroxyl groups in the cell wall are esterified with or without a catalyst giving rise to the corresponding ester and acetic acid as by-product (see Figure 6) (Hon, 1995).

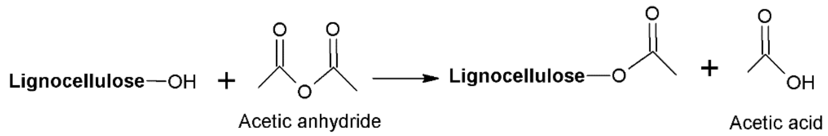


Figure 6. Acetylation reaction of lignocellulose

Moreover, other anhydrides like propionic, butyric, succinic and maleic can be used for the lignocellulose esterification. The two last ones provide thermoplastic properties to the lignocellulose, thus allowing its thermoconforming into high-density composites. Acid chlorides generate the ester-based lignocellulose of related acid chloride and hydrochloric acid as by-product. On the other hand, the use of carboxylic acids also enables the esterification of lignocellulosic materials, achieving a slight increase of its solubility in organic solvents, which is hampered by lignin and hemicellulose compounds (Rowell, 2012).

However, a special case occurs when lignocellulose is reacted with β-propiolactone (Figure 7), being possible two different reactions as a function of pH. Thus, an ether bond is formed under acid conditions, with a free acid-end group, while under basic conditions, an ester bond with a primary alcohol end group is created. However, this reaction is not generally promoted due to the carcinogenic nature of this reactive (Hill, 2006).

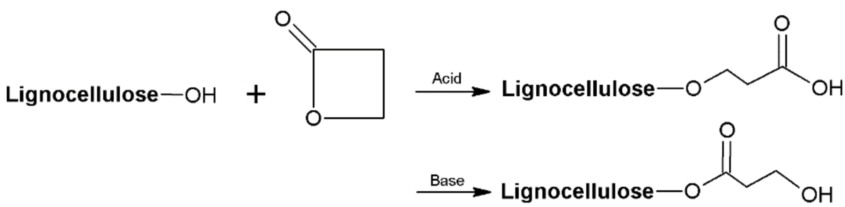


Figure 7. Modification of lignocellulose with β-propiolactone

1.1.2. Etherification

In the etherification process, hydroxyl groups are dehydrated to form an ether group. Although methylation is the simplest etherification pathway of lignocellulose, commonly carried out with dimethyl sulphate or methyl iodide (see Figure 8), alkyl chlorides and acrylonitrile can be also used for the etherification process (Rowell, 2012).

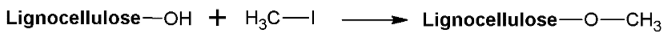


Figure 8. Methylation of lignocellulose

On the other hand, the use of epoxides allows the formation of an ether linkage by means of the reaction between the cell wall hydroxyl groups and the highly strained three-membered ring of the oxirane group. This reaction needs to be acid or base catalysed and gives rise to a new hydroxyl group formation that can further react with another epoxide (see Figure 9) (Hon, 1995).

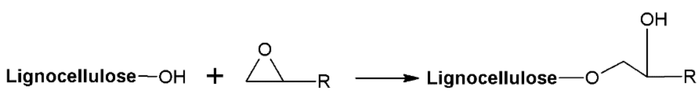


Figure 9. Etherification of lignocellulose with epoxides

1.1.3. Urethanization

Hydroxyl groups of lignocellulosic materials can also react with isocyanate compounds, forming a urethane bond, i.e. a nitrogen-containing ester (see Figure 10). This reaction is generally catalysed by acids or bases, being the last ones most frequently used. It is worth to point out that isocyanates are highly reactive with water, yielding a di-substituted urea, so it is necessary to remove the lignocellulose moisture before urethanizacion (Hill, 2006).

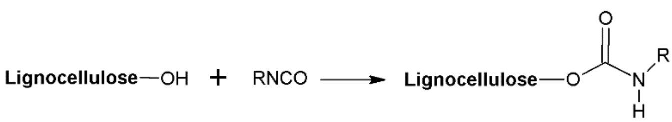


Figure 10. Chemical modification of lignocellulose with isocyanates

1.2. Pre-treatments for the lignocellulosic components isolation

As previously mentioned, natural recalcitrance of the plant cell wall and the cellulose accessibility limit the range of possibilities of lignocellulosic resources to be chemically modified and used as raw materials for multiple applications. For this reason, one of the most important goals of biomass refining consists in fractionating the lignocellulose into its three main components, namely, cellulose, hemicellulose and lignin, in order to exploit all the chemical functionalities previously described (Popa and Volf, 2018).

In general, when a pre-treatment is applied to the lignocellulosic materials, their natural binding characteristics are modified by tailoring the supramolecular structure of cellulose-hemicellulose-lignin matrix. There are many methods for the lignocellulose fractionation, which usually hydrolyse hemicellulose into its water-soluble sugars, keeping cellulose and lignin in the non-soluble part. From this ensuing product, lignin is extracted with the aid of chemical solvents, which will be detailed below, while cellulose with some remaining lignin residues, can be hydrolysed into water-soluble sugars, generating lignin and unreacted carbohydrates as residue. This residual lignin generally shows lower quality than the directly extracted lignin from biomass, but can be also used for many applications (Bungay, 1992). In this way, physical, chemical, physicochemical and biological methods can be used for the lignocellulose pre-treatment.

- Physical procedures include milling, pyrolysis, gasification, gamma irradiation, microwave, infrared radiation or sonication, and allow to increase the accessible surface area and decrease the cellulose crystallinity. In detail, milling is used for reducing the crystallinity of cellulose, while sonication leads to the rupture of cellulose and hemicellulose fractions allowing the enzymatic degradation of cellulose into simpler reducing sugars (Kumar and Sharma, 2017).
- Chemical processes involve acids, alkalis, ozone, peroxide and organic solvents. Regarding the acid pre-treatment, it can be carried

out by means of dilute-acid or concentrated-acid methods, being the sulfuric acid the most popular chemical due to its low cost. On the other hand, sodium hydroxide is usually employed for the alkaline hydrolysis of lignocellulose, where the side chains of esters and glycosides are degraded allowing the structural modification of lignin, cellulose swelling and hemicellulose solvation. Moreover, with the organosolv process, lignin network and hemicellulose are decomposed, thus exhibiting the cellulose fibres for their enzymatic hydrolysis (Popa and Volf, 2018).

- Physicochemical pre-treatment. Steam explosion methods are the most popular for hemicellulose removal, since their use of chemicals is limited and they have low energy requirements. In addition, other procedures comprise the utilization of ammonia, like ammonia fibre explosion (AFEX), ammonia recycled percolation (ARP), and soaking aqueous ammonia (SAA), where the swelling and phase change in cellulose crystallinity allow to increase the products' reactivity. On the other hand, biomass can be also treated by CO_2 explosion methods (Sun and Cheng, 2002).
- Biological pre-treatments. A low hydrolysis degree of lignocellulose is achieved by using biological methods, which need a long period of time. Lignin and hemicellulose are usually degraded by microorganisms, but cellulose shows a strong resistance to biological attack (Taherzadeh and Karimi, 2008).

Focusing on lignin isolation from lignocellulosic biomass, in particular, there are many methods that involve its progressive break down into lower molecular weight products. Figure 11 shows the most common industrial processes for the extraction of lignin (Belgacem and Gandini, 2008; Galkin and Samec, 2016), which depend on several factors, such as temperature, pH, pressure and type of solvent, and will condition the physicochemical properties of isolate lignin (see Table 3).

In the Kraft pulping process, high temperatures and pH values are used for lignin delignification, by employing sodium hydroxide and sodium sulphite. The cleavage of ether linkages is first produced, increasing the number of phenolic hydroxyl groups that lead to lignin solubilization and finally, an acid solution allows the precipitation of lignin from the alkaline solution (Azadi et al., 2013). On the other hand, sulphite process comprises the reaction between lignin and a metal sulphite and sulphur dioxide. Calcium, magnesium or sodium act as counter ions, which aids the lignin hydrolysis by means of the introduction of polar sulfonic acid groups to its backbone. In this method, lignosulphonate molecular weight is higher than Kraft lignin due to the incorporation of sulfonate groups into the lignin skeleton (Zakzeski et al., 2010).

Regarding the non-sulphur lignin, this is obtained by two different methods. Soda pulping is similar to the Kraft process, but anthraquinone is also used as a catalyst to decrease the carbohydrates degradation and dissolve lignin, whose extraction by filtration is limited due to its high carboxylic acid content (Galkin and Samec, 2016). Conversely, organosolv is the most promising method that preserves the native lignin structure. It uses mixtures of organic solvents and water as delignifying agents, employing precipitation or solvent evaporation processes for the lignin recovery (Figueiredo et al., 2018).

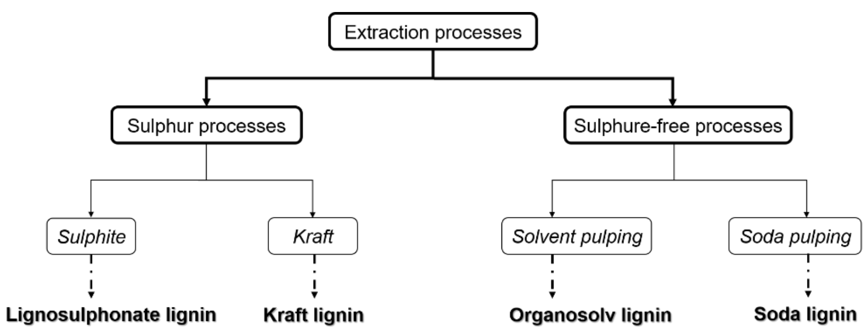


Figure 11. Extraction process of lignin from lignocellulosic biomass (Laurichesse and Avérous, 2014)

Table 3. Characteristics of isolation treatments of lignin (Figueiredo et al., 2018)

Extraction process	Conditions	Solubility	Lignin MW (Da)	Functional groups (%)		
				COOH	OH phen.	O-CH_3
Kraft	• NaOH and/or Na_2S (pH 13-14; ≈170ºC) • Sulfuric acid (pH 5-7.5)	Alkali; organic solvents	1000-15000	4.1	2.6	14
Sulfite	Metal sulphite +HSO_3^- (pH 2-12, ≈120-180ºC, 1-5h)	Water	1000-50000			
Soda	13-16% NaOH (≈140-170ºC) + anthraquinone	Alkali	1000-3000	7.2-13.6	2.6-5.1	10-16
Organosolv	Organic solvents + H_2O (≈170-190ºC)	Wide range of organic solvents	50-5000	3.6-7.7	3.4-3.7	15.1-19

1.3. Chemical modification of cellulose and hemicellulose

As previously discussed, lignocellulosic materials present a high chemical reactivity, which makes them susceptible for a wide range of chemical modifications. However, many efforts have been also focused on the modification of each lignocellulose components, i.e. cellulose, hemicellulose and lignin, in order to extend the range of applications and increase the chemical reactivity of these individual materials.

In this sense, although the esterification of cellulose with carboxylic acids is the most popular transformation, this reaction can be also produced by reacting with acid chloride, anhydrides or unsaturated agents (CS_2 or urea). These compounds leading to a disruption of the hydrogen bonding by a combination of steric interactions, decreasing the number of hydroxyl groups available for hydrogen bonding and replacing them by acyl groups. Etherification reactions by alkali-catalyzed substitution or addition reactions are produced in cellulose compounds by using alkyl, aryl halides or sulphates to obtain alkyl ethers, alkene oxide to yield hydroxylalkyl ethers, and unsaturated agents like diazomethane, acrylonitrile and acrylamide forming methylcyanoethyl and carbamoethyl derivatives. In addition, cellulose can be also oxidized yielding carbonyl or carboxyl groups (Hon, 1995).

Moreover, the cellulose modification can be performed by means of nucleophilic displacement reactions, where hydroxyl groups are partially or completely replaced by other functional groups. In this sense, the chemical modification of cellulose fibres seems to be really interesting and not only involves the traditional processes like esterification or etherification reactions, but also includes the grafting of new chemical groups at the surface through cellulose hydroxyl groups. Thus, coupling reactions with acids and anhydrides, silane, isocyanates, via free-radical initiation and via ring opening polymerizations can help to increase the chemical reactivity of cellulose-based products (see Figure 12) (Belgacem and Gandini, 2008).

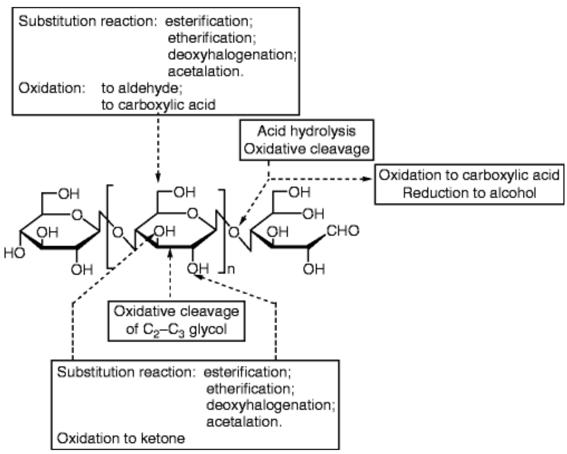


Figure 12. Chemical modification of cellulose (Figueiredo et al., 2010)

Consequently, different previous investigations reported chemical modifications of cellulose, its derivatives, and diverse cellulose pulps for several applications. Thus, this group studied the use of methylated (Núñez et al., 2012), ethylated (Martín-Alfonso et al., 2011) and acid-treated (Núñez et al., 2011) cellulose pulps to produce gel-like dispersions for lubricant applications. Moreover, Gallego et al. (2015a) induced the crosslinking of this raw material and other cellulosic derivatives (Gallego et al. 2013a) with HMDI in order to obtain alternative products to commercial lubricating greases. Adhesive applications were also explored by this research group by using isocyanate-functionalized cellulose acetate and castor oil (Tenorio-Alfonso et al., 2018, 2017).

On the other hand, Pahimanolis et al. (2011) increased the reactivity of nanofibrillated cellulose through etherification reactions with azide groups and their further amino functionalization, while different chemical modifications of microfibrillated cellulose were reported by Stenstad et al. (2008). In addition, polymer composites were studied by Cai et al. (2003), who worked with grafting reactions onto the cellulose fibres, while hydrogels applications by means of cellulose modification with poly(ethylene glycol) diglycidyl ether as a cross-linker were investigated by Kono (2014) and Kono et al. (2016).

Regarding the hemicellulose, only few studies are available in the scientific literature concerning its chemical modification, but its carbohydrates can be modified by means of esterification and etherification reactions. Hemicellulose esterification reduces the absorptive capacity and crystallinity, and increases its solubility. Acetylation reactions with anhydrides and carboxylic acids can be carried out to increase the functionality of hemicellulose. On the other hand, etherification reactions, such as carboxymethylation, methylation, hydroxyalkylation, or sulfoalkylation allows to increase its solubility, stability against microorganisms and viscosity (Dumitriu, 1998).

Zoldners and Kiseleva (2013) modified hemicellulose with the aid of polycarboxylic acids in order to improve its water resistance and impart it new properties for film development. Moreover, its hydrophilic character was also enhanced by Ren et al. (2009), who worked on the quaternization of the hemicellulose hydroxyl groups for the paper quality improvement.

1.4. Chemical modification of lignin

Lignin has a great variety of functional groups like aliphatic and phenolic hydroxyls, carboxylic, carbonyl and methoxyl groups, which offer a wide range of possibilities for chemical modifications. Apart from the chemical change of its hydroxyl groups, lignin can be also depolymerized in order to be used as a carbon source or cleavage it into aromatic monomers, or modified by creating new chemical active sites (Figueiredo et al., 2018).

In this way, fragmentation of lignin allows obtaining low molar mass compounds, which are valorised into different lignin-based products that are used for further applications, and also aids to elucidate its composition and structure. Pyrolysis, oxidation, hydrogenolysis and gasification are the thermochemical methods applied for the lignin depolymerization (Meister, 2008; Pandey and Kim, 2011). A summary of these modifications with associated methodologies and the corresponding conditions is showed in Figure 13.

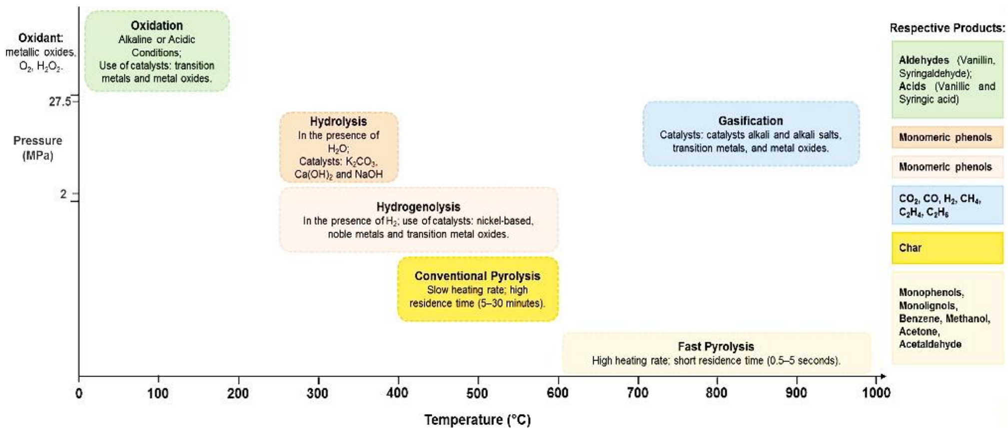


Figure 13. Methods for the lignin depolymerization (Figueiredo et al., 2018)

On the other hand, the chemical reactivity of lignin macromolecules can be modified through the increase of hydroxyl groups reactivity or creating new reactive sites that also provide it with new properties. These reactions include hydroxyalkylation, amination, nitration, sulfomethylation and sulfonation (see Figure 14).

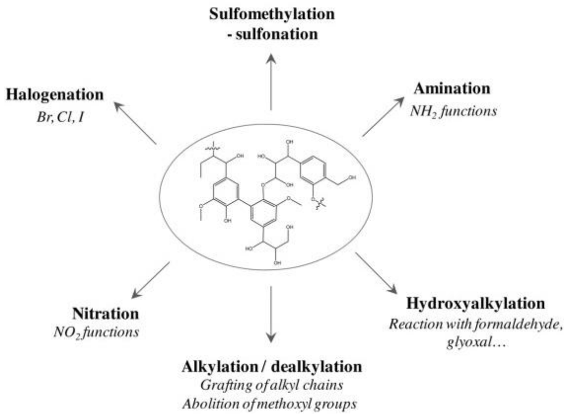


Figure 14. Different reactions for the synthesis of new chemical active sites on the lignin macromolecule (Laurichesse and Avérous, 2014)

However, as previously discussed, the most important lignin functionalization reactions affect its hydroxyl groups, both phenolic and aliphatic ones, which are located in the lignin structure at the C-γ and C-α position on the side chain, respectively. Phenolic hydroxyls are usually the most reactive groups of the lignin molecule. Figure 15 shows the different reactions associated to the lignin hydroxyl groups.

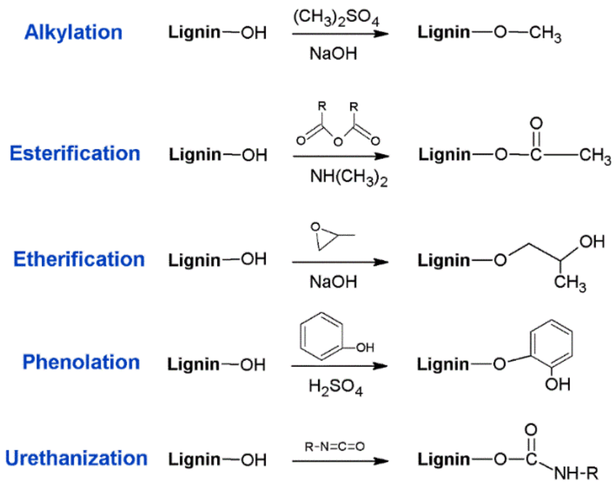


Figure 15. Typical reactions of lignin hydroxyl groups functionalization (Figueiredo et al., 2018)

Alkylation reactions of lignin are produced in the oxygen atoms of the hydroxyl groups via chemical interaction with three different chemical compounds, diazoalkanes, alcohols (with the aid of a catalyst) or alkylsulfates, and sodium hydroxide (Meister, 2008). On the other hand, lignin esterification is carried out by means of different routes, such as ring opening reactions with cyclic esters, condensation polymerization with carboxylic acid chloride, and dehydration polymerization with dicarboxylic acids (Matsushita, 2015), while the etherification process comprise the polymerization of lignin with alkylene oxides (ethylene oxide and propylene), epichlorohydrin, cross-linking with diglycidyl ethers, and solvolysis with ethylene glycol (Figueiredo et al., 2018). Regarding the phenolation process, lignin is treated with phenol in acid medium, increasing its reactivity as a phenol substitute (Effendi et al., 2008). Finally, lignin urethanization involves the use of isocyanate groups, which form a urethane linkage with their hydroxyl groups, leading to the preparation of a wide range of products (Ionescu, 2007).

Thus, Zhao et al. (2017) studied the chemical modification of lignin through acetylation in order to increase its reactivity. Yang et al. (2014) employed three different methods for its modification, i.e., hydroxymethylation, epoxidation and phenolation, subsequently used as raw material for the synthesis of polyurethane foams. The first type of reaction was also studied by Câpraru et al. (2012), who modified two kinds of lignins through hydroxymethylation for increasing their functionality and used them as a component in adhesive systems. In the adhesive field, Jin et al. (2010) explored the modification of phenol-formaldehyde adhesives by replacing part of the phenol with enzymatically hydrolysed lignin.

On the other hand, Chen et al. (2016) investigated the epoxidation and etherification of lignin hydroxyl groups in order to obtain water-soluble derivatives for detergent, emulsifier and additives to improve enzymatic hydrolysis efficiency and bioethanol production, while bio-based hydrogels and superabsorbents applications were explored by Passauer et al. (2012), who carried out the lignin modification with poly(ethylene) glycol diglycidyl ether (PEGDGE) as a cross-linker through the etherification of its phenolic hydroxyl groups. Moreover, this cross-linker was also used to modify an acetic acid-modified lignin in order to produce lignin-based gels (Nishida et al., 2003).

On the other hand, esterification reactions with maleic anhydride were studied by Maldhure et al. (2011), who devoted their investigation to change the lignin polarity and increase its solubility and compatibility in polypropylene-based blends. Additionally, the use of isocyanate-functionalized lignin was explored by Borrero-López et al. (2018, 2017) in order to develop chemical oleogels based on vegetable oils.

1.5. Epoxidation of lignocellulosic materials

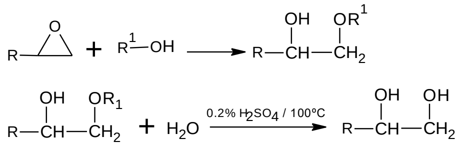
As previously discussed, epoxidation consists of the etherification of lignocellulose hydroxyl groups, giving rise to an ether linkage and producing new hydroxyl groups. In this way, low molecular weight epoxides are able to penetrate into the wood cell walls or fibrillated structures, reacting with the hydroxyl groups through stable chemical bonds (Hon, 1995).

In general, epoxy groups show a high reactivity with some compounds containing hydroxyl or amino groups as a consequence of the high tension in the oxirane ring and the polarity instigated by the oxygen atom (Doszlop et al., 1978). These reactions involve either electrophilic attack on the oxygen atom or nucleophilic attack on one of the ring carbon atoms, allowing the opening of the three-membered ring. As a result, factors such as reagent or catalyst nature, the influence of substituent and the relative steric hindrance of carbon atoms will condition the opening reaction of oxirane group. In general, when the reaction is carried out by an amine, carboxylic acid or thiol, a secondary hydroxyl group is formed as a consequence of the pair of unshared electrons donated to the methylene group (Ellis, 1993). These ones and others reactions including epoxy groups are summarized in Table 4.

Table 4. Most typical reactions of epoxy groups (Ellis, 1993)

1. Addition reactions by nucleophilic substitution

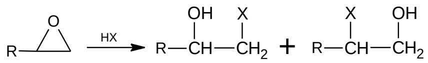
a. Hydroxylic nucleophiles



R^1 = alkyl,alcohol; R^1 = aryl,phenol

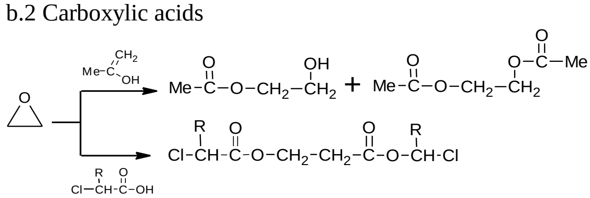
b. Acids

b.1 Mineral acids

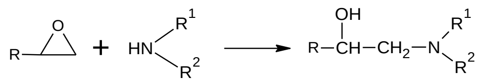


X = F,Cl,Br,I

b.2 Carboxylic acids



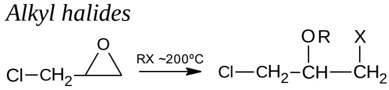
b.3 Ammonia and amines



R^1,R^2 = H: ammonia R^1 = H; R^2 = alkyl, aryl: primary amina R^1,R^2 = alkyl, aryl: secondary ami

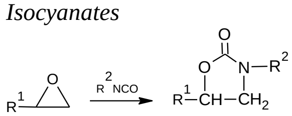
2. Electrophilic additions

a. Alkyl halides

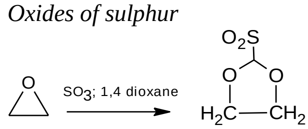


X=Br; X=I; R=Et; R=Me, Et, Pr

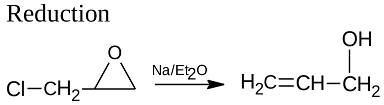
b. Isocyanates

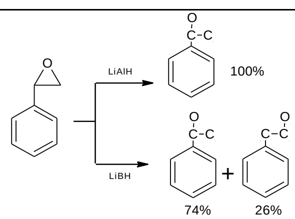


c. Oxides of sulphur

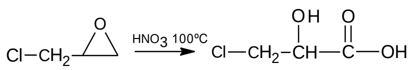


3. Reduction





4. Oxidation



In connection with the chemical modification of lignocellulosic materials via epoxidation reactions, this method seems to be really interesting in order to increase their functionalities as well as the application field. In this way, the introduction of epoxy groups into lignocellulose chemical structure has been widely explored, providing certain capacities to these materials and increasing their solubility in some common organic solvents.

For instance, Chen et al. (2016) produced water-soluble lignin derivatives by means of epoxidation with epichlorohydrin, also using this modified lignin as an additive to improve the enzymatic hydrolysis efficiency. Likewise, the enzymatic hydrolysis of a residual lignin in substrates was improved by Lai et al. (2017) through the in situ modification of corn stover with poly (ethylene glycol) diglycidyl ether (PEGDGE) during low temperature alkali pre-treatment.

On the other hand, the use of PEGDGE as a cross-linker was also investigated by Kono et al. (2016), who reported the production of cationic cellulose hydrogels from quaternized celluloses. Moreover, neopentyl glycol diglycidyl ether (NPGDGE), a similar diglycidyl derivative, was used to modify cotton fabrics by Xiao et al. (2017).

Films based on epichlorohydrin-cross-linked hydroxyethyl cellulose and soy protein were developed by Zhao et al. (2016) for tissue engineering applications. In addition, Ferdosian et al. (2012) carried out the functionalization of an organosolv lignin by grafting epoxy groups into the lignin structure in order to extend its application field as biomaterials, while coatings applications based on epoxidized lignin were studied by Singh et al. (2012).

On the other hand, the epoxy resins field has been widely studied by many researchers. Thus, Soto et al. (2005) evaluated the chemical reactions between tannins isolated from Pinus radiata D. Don bark and several epoxy resins of diglycidyl and polyglycidyl ether, obtaining an improvement of the viscoelastic properties in comparison with a tannin-p-formaldehyde resin. Similarly, Karumuri et al. (2015) studied the improvement of the epoxy thermosets by addition of lignocellulosic particles and their corresponding epoxide-hydroxyl reactions. Lignin-based epoxy resins were also synthesized in many works through reaction of lignin with epichlorohydrin in alkaline medium with the presence of a catalyst (Chen et al., 2015; Ferdosian et al., 2015). Moreover, bio-based epoxy resins were studied by Delmas et al. (2013) by using wheat straw lignin and PEGDGE and obtaining promising results in relation with their properties.

2. General overview of gels

2.1. Fundamentals of gels

Over the last several decades, there have been different ways of defining a gel. The first one was proposed in 1861 by Thomas Graham, which assumed a gel as colloid that possesses "energia" (Graham, 1861), and although there were many authors who provided other definitions, nowadays the proposal of Almdal et al. (1993) is one of the most accepted. In this sense, a gel-like substance must fulfil two overarching requirements;

- It must be formed by two or more components, such as a liquid found in significant quantities and a gelling substance,
- And the system should show solid-like rheological properties, that means, considerably higher values of the storage modulus G'(ω) than the viscous ones G''(ω), and also G'(ω) must show a plateau extending to times at least in the order of seconds (rheological properties of gels will be described in more detail in section 4).

According to the nature of the liquid, gels can be divided in two different categories, hydrogels and organogels. While in the former, cross-linked hydrophilic polymers are swollen in water or in an aqueous environment, the latter include a liquid hydrophobic component such as an organic solvent or an oil (Balasubramanian et al., 2014).

In general, organogels are classified as a function of the kind of gelator employed to form the gel, i.e., polymeric or low-molecular weight organogelators. In the last case, gel is constituted by using small amounts of low molecular weight organic compound, and two different categories, viz., crystalline dispersions and lyotropic phases, can be distinguished depending on whether system is formed by two or three phases, respectively (Co and Marangoni, 2012). On the other hand, the use of polymer organogelators comprises the formation of a polymer network surrounded by solvent molecules, which is stabilized by physical interactions.

Organogels based on low-molecular weight compounds are usually prepared by warming a gelator in the organic liquid until its complete dissolution, leading to the formation of a network of self-assembled molecules, which forms a thermally reversible gel upon cooling and allows for the liquid encapsulation (see Figure 16). The mechanisms of gel formation generally include the existence of three different structures, specifically, primary structure, where gelator molecules are unidirectionally aggregated (Å to nm scale), secondary structure (nm to μm scale), which is composed by micelles, vesicles or fibres (the aggregates morphology), and the tertiary one, where the gel network is formed by the interaction of these aggregates (μm to mm scale) (Balasubramanian et al., 2014). Hence, the sol-gel conversion process involves the formation of a continuous microscopic structure with macroscopic dimensions, which should be permanent on the time scale (Marangoni and Garti, 2011).

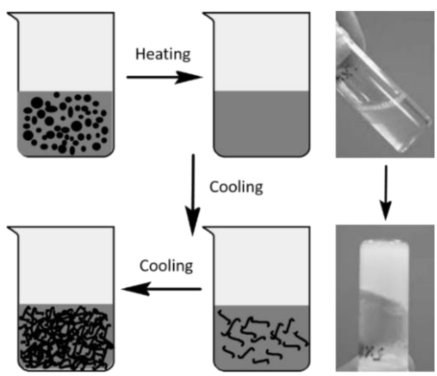


Figure 16. Mechanism of gel formation by heating process (Kidowaki et al., 2006; Mishra, 2015)

This process implies the transition from sol to gel, that means, the free monomers start to link up with each other, giving rise to an infinite network. At this point, solute molecules and solvent are forming a three-dimensional connection, and the minimum amount of gelator necessary to form this network is known as "gel point" (Tanaka, 2001). In general, the aggregation process and the final gel structure will depend on the strength of binding forces between the different molecules, being thus possible to differentiate among two kinds of gels, i.e., the physical and chemical ones. In this way, physical gels are "self-healing" materials in which molecules are held together by weak intermolecular forces like hydrogen bonds, electrostatic or Van der Waals forces, and π-π stacking. On the contrary, chemical reactions by means of covalent bonding are produced in the chemical gels (Mishra, 2015). Organogels usually have thermo-reversible properties, that means, they can return of the gel-to-sol state by temperature application, which provides external energy to the system and disrupt the three-dimensional structure (Sahoo et al., 2011).

In addition, two different kinds of three-dimensional networks and gels can be differentiated according to their macroscopic behaviour. In this sense, "strong" or "true gels" are characterized by a strong three-dimensional network and have "finite energy" in terms of dynamic mechanical analysis. Moreover, these gels show highly reduced molecular rearrangements within their structure over time and have a solid-like behaviour. On the other hand, those gels whose network can be easily broken by applying a high stress and are transient in time, also showing hyperentanglements, are known as "weak gels". In this case, viscoelastic moduli show a higher dependence on frequency and a lower difference between their values (see Figure 17) (Clark and Ross-Murphy, 1987; Doublier et al., 1992; Rao, 2013).

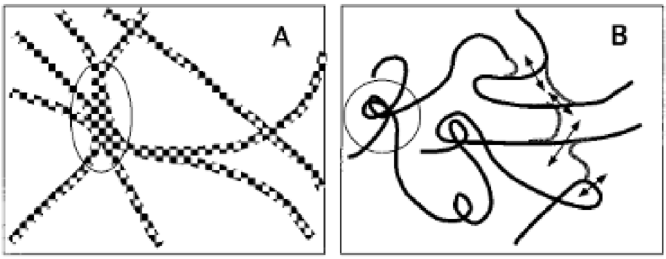


Figure 17. Typical networks of strong (a) and weak (b) gels (Terech and Weiss, 1997)

On the other hand, many polymers (linear, hyperbranched or star shaped) can induce organogelation, even at very low concentrations, by physical entanglement or chemical crosslinking. In general, these kinds of organogelators show a lower gel-to-sol transition temperature and possess gel strengths higher than gels based on low-molecular weight organogelators (Mishra, 2015).

2.2. Gels properties and their applications

Gels based on organic solvents present physicochemical properties that, naturally, depend on the kind of gelator and the amount used for the three-dimensional network development. In general, viscoelasticity, related to the viscous and elastic properties of materials, is one of the most important characteristics of these compounds. They display solid-like behaviour at low shear rates. However, when shear rate is increased, the three-dimensional network loses its structure because of the physical interaction points start to weaken, until they finally are disrupting and the system starts flowing (Abdallah et al., 2000; Toshiyuki et al., 2003; Van Esch and Feringa, 2000). Moreover, these materials have non-birefringence properties, in other words, their isotropic nature does not allow the polarized light to pass through their matrix (Lv et al., 2017). As above discussed, organogels generally exhibit thermo-reversibility and are capable of changing their solid- or liquid-like structures by modifying the temperature (Nazir et al., 2016). They are inherently thermostable, since the gelator ability to self-assembly allows to turn them into low-energy thermostable systems (Escuder et al., 2005). Moreover, organogels can vary their optical clarity as a function of their composition, which can be transparent or opaque. Finally, they can also show some chiral centers within the gelators, helping the molecules to aggregate and providing thermodynamic stability to the system (Sahoo et al., 2011).

All of the gel properties are measured by means of different tests that allow to define its nature as well as its application range. Therefore, rheological tests provide information about mechanical characteristics of organogels, thus evaluating the aggregates network nature. Methods like steady shear, oscillation, stress relaxation or creep can be used to measure the flow properties of gel-like systems. In general, oscillatory tests by applying a small strain/stress within the linear range help to evaluate the elastic and viscous components (Nazir et al., 2016). On the other hand, thermal analyses allow to establish the sol-to-gel transition temperature, which can be easily quantified through differential scanning calorimetry (DSC) or temperature sweep rheological tests. Molecular properties of organogels are assessed by different spectroscopy experiments (IR, NMR, etc), which provide information about their chemical fingerprint and are able to understand the chemical interactions between gelator and solvent, like inter/intra-molecular hydrogen bonding or π-π stacking (Mishra, 2015). Furthermore, the microscopic characteristics of gels, studied through optical, electron or scanning probe microscopic, allow to study the formation of the three-dimensional network structure (Mishra, 2015; Terech and Weiss, 1997).

In this way, the numerous properties of gels make them into potential products for a wide range of applications, particularly in fields such as food industry (Marangoni and Garti, 2011; Martins et al., 2018), cosmetics (Lupi et al., 2016, 2015), bioengineering (Kalcioglu et al., 2013; Ramanujan et al., 2009), lubricants (Lea, 2002; Salomonsson et al., 2007), bioseparations (Kim and Park, 1998; Liang et al., 2007), biosensors (Gogoi et al., 2017; Kartha et al., 2012), agriculture (Jadhav et al., 2011; Wang et al., 2016), medicine (Satapathy et al., 2013; Silverman et al., 2017), proteins (De Vries et al., 2017) and pharmaceutical industry (Adhikari et al., 2016; Lupi et al., 2016).

3. Lubricants

Nowadays, there are many kinds of machines that need the use of lubricants in the most of their components. In particular, engines are formed by multiple metal parts, which are in continuous movement, generating friction and heat as a consequence of their contact, resulting in a loss of material, i.e., wear (Miller et al., 2007). In general, lubricants are used to reduce this friction and the subsequent heat generation, also allowing to decrease the wear and extending the service life of the equipment. For this reason, the consumption of lubricants has been rising with time, achieving a global demand of around 36.1 million tons in 2017, with the Asia Pacific consuming about 43 % (see Figure 18).

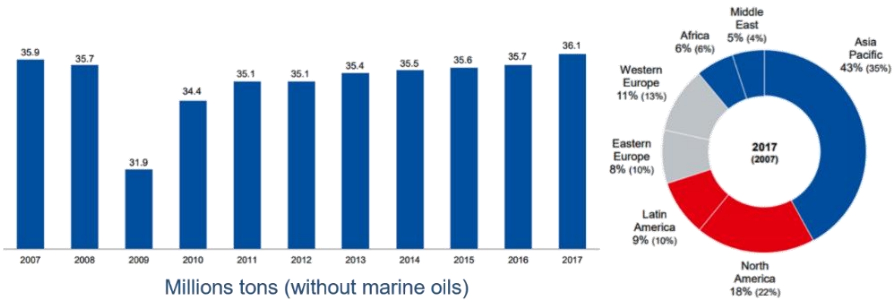


Figure 18. Global lubricant demand (Dagmar Steinert, 2018)

Therefore, lubricants play an important role in enhancing the durability and efficiency of automotive engines and industrial machinery, as they enable the creation of a protective film between two surfaces that are on the move, reducing the friction and wear and preventing damage by scoring. Although the most commonly employed lubricants are the lube oils (Figure 19), there are other different products depending on their final application, inter alia emulsions, water-based solutions, greases or solid lubricant suspensions (Mang and Dresel, 2007).

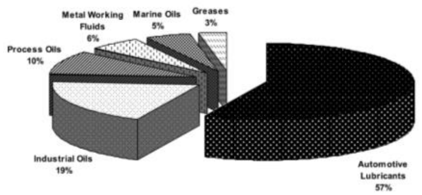


Figure 19. Production of different lubricants in the world (Rizvi, 2009)

3.1. Lubricating greases

Lubricant greases are considered two-component systems formed by a liquid dispersion medium and a thickener solid-like dispersed phase. They have intermediate properties between liquid (oils) and solid lubricants and offer all the advantages related to their gel-like characteristics. In general, lubricating greases are usually employed in several applications where liquid lubricants cannot be conveniently applied, since their semisolid character allows them to remain in place during operation without leaking, also acting as a seal against contaminants. They show solid-like properties under small loads action at normal temperatures, but they are capable of flowing like a liquid at loads close to a critical value, returning to their original state when loading ceases (Ishchuk, 2006). Therefore, this singular characteristic, as well as their ability to prevent wear, their valuable service properties, low specific consumption and high corrosion protection properties, turn them into added-value materials with numerous advantages over the lube oils. Moreover, they are user-friendliness by extending the machinery service life and cutting down the maintenance costs due to their ability to intensify the relubrication intervals, also reducing noise and vibration (Lugt, 2009). In this way, new applications of these products are emerging in modern cars and construction vehicles, especially for hard-to-reach places or high-speed bearings where leakage and sealing are particular concerns and need the use of lubricating greases (Salomonsson et al., 2007). In addition, there are other many applications in the industry that require their use, such as bearing, gears, universal joints, chassis, electric motors, couplings, centralized lubrication systems, wipe ropes and chains, among others (Rizvi, 2009).

Lubricating greases are highly structured systems composed of a thickener, which is dispersed in a lubricating liquid, and that might contain some kinds of additives for improving their properties (NLGI, 1994). Overall, a grease can hold from 65 to 95 wt.% of base oil, whose viscosity usually determines their application conditions, and between 5 to 35 wt.% of thickeners, which are responsible for maintaining the solid structure of grease, providing consistency and mechanical stability. In its structure, the latter is maintained inside of the base oil through Van der Waals or capillary forces, while dipole-dipole interactions are produced between the different gelling molecules (entanglements) (Mang and Dresel, 2007). In general, these formulations involve alkali metal or metal complexes soaps, mineral oils (the most widely used) and some additives such as oxidation inhibitors, rust and corrosion inhibitors, colour stabilizers, metal passivators, water repellents and viscosity index improvers. Some examples of the main components of lubricating greases are showed in Table 5.

Table 5. Common components employed to produce lubricating greases (Lansdown, 2004)

Base oils	**Thickeners**	**Additives**
Mineral oils	Sodium soap	Anti-oxidants
Synthetic hydrocarbons	Calcium soap	Anti-wear additives
Di-esters	Lithium soap	EP additives
Silicones	Aluminium soap	Corrosion inhibitors
Phosphate esters	Lithium complex	Molybdenum disulphide
Perfluoropolyethers	Calcium complex	Friction modifiers
Fluorinated silicones	Aluminium complex	Metal deactivators
Chlorinated silicones	Bentonite clay	VI improvers
Polyglycols	Silica	Pour-point depressants
	Carbon/graphite	Tackiness additives
	Polyurea	Water repellants
	PTFE	Dyes
	Polyethylene	Structure modifiers
	Indantherene dye	
	Phthalocyanine dye	

The most common soap-based grease consists of a long-chain fatty acid (between 16 to 18 carbon atoms) neutralized by a metal, such as aluminum, barium, calcium, lithium, magnesium, sodium or strontium, which is located in the form of fibres with the suitable size to be dispersed into oily medium (see Figure 20). A combination of different-size fibres is required to achieve a suitable thickening, since large fibres provide them with a good shear stability while small ones favour a good oil retention (Mang and Dresel, 2007). In general, more than 85% of commercial greases contain lithium soaps as thickeners.

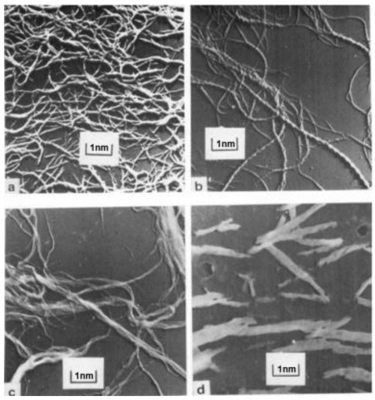


Figure 20. Soap fibers obtained as a function of raw materials used in the greases production: a), b) lithium 12-hydroxystearate, c) lithium oleate and d) calcium-sodium soap (Dorinson and Ludema, 1985)

In this way, the greases properties will be defined, not only by the kind of raw materials used for their synthesis, but also by the way in which thickeners and oils are mixed to generate the final product. The manufacture procedure includes addition of metal soap as an aqueous solution into the base oil, which is previously heated in an open vessel equipped with a mixing stirrer at around 90 ºC (saponification process). After that, temperature is raised up to a temperature which depends on the type of metal soap (i.e. 115-150 ºC for lithium soaps) to facilitate the soap dispersion, which must be subsequently dehydrated by increasing the temperature till around 200 ºC. Then, the mixture is cooled down to favour the crystallization and a further amount of base oil is added to the mixer. Finally, the addition of additives is carried out at around 80 ºC, just before homogenization of the product (Jones, 1968). It should be noted that cooling is the most important stage of the lubricating grease manufacture process due to the formation of crystal nuclei (associates and micelles), their growth (aggregation of micelles for the production of fibres), and the development of the three-dimensional network, which determines the stability and properties of these products (Ishchuk, 2006).

As previously detailed, a thin film of grease is usually placed on the contact surfaces to reduce the friction effect, which is converted into heat and block the distribution of grease in a large volume. But even higher amounts of lubricant can hamper the grease flow, avoiding the convective cooling and provoking its greater oxidation. Therefore, the main property of greases is their ability to create such film, which is a function of the thickener concentration, the oil viscosity and the manufacturing process (Ishchuk, 2006). In fact, three kinds of greases can be distinguished as a function of their hardness or softness (consistency), like soft, semi-liquid or hard greases (Lansdown, 2004). However, the grease consistency can be modified when it is subjected to high mechanical shear or load, being necessary to determine its mechanical stability after being worked. This parameter is analysed in term of penetration by using a standard cone, according to ASTM D 217/D 1403, and it is quantified by means of NLGI classification (National Lubricating Grease Institute), as shown in Table 6. Nevertheless, the consistency of greases may be slightly altered due to the tendency of these materials to suffer a certain oil separation ("oil bleeding") during storage and application (Ishchuk, 2006).

Consequently, the consistency of greases is closely related to their bulk viscosity. These products generally have a high initial resistance to flow, due to their semi-solid nature, but they are vulnerable to the shear action, which reduces this resistance. In this case, when grease starts to flow under high-shear action, its viscosity is greatly determined by the viscosity of the base oil rather than by the original consistency of the grease (Lansdown, 1982).

Table 6. NLGI Grease classification (Gale and Totemerier, 2003)

NLGI grade	Worked penetration range (0.1 mm)	Description
000	445–475	Very fluid
00	400–430	Fluid
0	355-385	Semi-fluid
1	310–340	Very soft
2	265-295	Soft
3	220-250	Semi-firm
4	175-205	Firm
5	130-160	Very firm
6	85-115	Hard

Other important factor to be considered is the thermal behaviour of greases, i.e., the temperature at which the structure changes from semi-solid to a liquid state. The penetration value slowly increases until this critical temperature, which is known as dropping point and delimits the operating range of the lubricating grease. Consequently, heating above the dropping point can result in permanent changes in the grease consistency, inducing softening and bleeding and, thus losing its semi-solid lubricant properties. Moreover, the base oil can be burned or evaporated at extremely high temperatures. This point generally depends on the type of thickener used in the grease manufacture (see Table 7). On the other hand, greases also show a low-temperature limit, which is related to the base oil crystallization, where the grease is too hard to be used (Lansdown, 2004).

Moreover, the application of high temperatures can accelerate the oxidation of lubricating greases, which reduces their application range and determines their service life. This property is also conditioned by the heat generated by working due to the grease limitations to flow, what hinders the heat transfer. The oxidation is characterized by darkening, carbonization and hardening of the grease (Lansdown, 1982).

Table 7. Properties of lubricant greases as a function of thickener (Lansdown, 1982; Rizvi, 2009)

Thickener	Low-temperature limit	Drop point (ºC)	Water Resistance	Mechanical stability	Corrosion protection
Sodium soap	-20	150-200	Poor	Fair	Fair
Calcium soap	-20	60-100	Excellent	Good	Very good
Lithium soap	-40	170-250	Good	Good	Very good
Aluminium complex	-30	200-260	Very good	Very good	Very good
Calcium complex	-30	230-270	Very good	Very good	Excellent
Lithium complex	-35	230-270	Very good	Good	Excellent
Sodium complex	-30	240	Good	Good	Excellent

Other important factors of lubricating greases are their water resistance capability, since their structure can be destroyed under the influence of water or aqueous medium, losing their lubrication ability (Peterson, 1951), and their corrosion-preventive characteristics, i.e., reducing the chemical action of corrosive components on metallic surfaces and friction units (Ishchuk, 2006). These properties are usually conditioned by the thickening agent (Table 7), and just like the others, they are tested according to different standardized methods (see Table 8).

Table 8. Standard methods to evaluate the lubricating greases properties (Rizvi, 2009)

Property	**ASTM Test Method**
Mechanical stability	ASTM D217 / D1831 / D4290 / IP 50
Dropping point	ASTM D2265 / D566
Oxidation resistance	ASTM D942 / D3527 / D3336 / DIN 51806 / SKF RDF / IP 142
Water resistance	ASTM D1264 / D4049 / IP 215
Bleed resistance	FTM 321.3 / ASTM D1742
Leakage	ASTM D1263
Evaporation	ASTM D972 / D2595
Extreme pressure/antiwear	ASTM D2596 / D2509 / D2266 / D4170 / D3233 / IP 326 / IP 239
Corrosion	ASTM D1743 / D4048 / D5969 / IP 220 / EMCOR (D6138)
Apparent viscosity	ASTM D1092
Pumpability	ASTM D4693 / US Steel LT37
Elastomer compatibility	ASTM D4289
Identification and Quality Control	ASTM D566 / D2265

Apart from all the benefits of using lubricating greases previously discussed, they show some disadvantages related to their resistance to flow and the instability of the gel structure. In general, they show a reduced heat transfer capacity; limitations on bearing speed, because of the grease overheating; poor storage stability, since oil may be separated, softening/hardening or darking after long period of time; heterogeneity, as they are generally produced in batches; compatibility problems with other greases, and low resistance to oxidation because of their pronounced ionic character (Lansdown, 1982; Mang and Dresel, 2007).

However, the most important problem of lubricating greases is their environmental impact, usually quantified through grease-to-nature contact and its corresponding consequences, but also in terms of energy consumption and the equipment service life in the different applications (Lugt, 2016). In this way, as previously detailed, these products come from distillation of crude oil, since they are formed by petroleum-based raw material, and thus entail an environmental threat to both aquatic and terrestrial ecosystems. The large production of lubricating greases generally results in their huge loss in the environment (45 million tonnes per year), which affect water and soil, also producing air contamination by volatile haze because of their combustion, thus increasing the greenhouse gases that affect global warming. Moreover, lubricating greases are composed of a number of components that imply toxicity, carcinogenicity and mutagenic activity, affecting the human health either directly or via indirect routes through the environment (Ssempebwa and Carpenter, 2009). In this sense, different governments are applying some mandatory regulations in the lubricant industry regarding the release of these products into the environment. Thus, "Blue Angel", "White Swan" or "Green Cross" are different environmental acceptability eco-labelling schemes that include ecological tests requirements, prohibitions and manufacture's declarations (Van der Waal and Kenbeek, 1993).

Another aspect of note is the availability of raw materials to produce lubricating greases. As it is known, mineral oils are fossil materials that emerged from sediments of plant biomass in the forests millions of years ago, which were transformed into bitumen and mineral oil under specific conditions. Since this process took place during thousands of years, the ratio between the replenishment of these mineral oil deposits and their used is not balanced out, turning them into a finite resource (Willing, 2001). This implies certain politic considerations that involve a price rise of fossil products, becoming less affordable for the lubricant industry.

Therefore, the increase of prices, the consumption of petroleum natural reserves in the world and the need for environmental protection have compelled the search for new alternatives to traditional lubricating greases.

3.2. Rheology of lubricating greases

Lubricating greases, in contrast with liquid lubricants, are known as viscoelastic materials consisting of two-phase colloidal suspensions with a three-dimensional gelling network formed by the base oil and the thickener (Mas and Magnin, 1994), which show intermediate properties between purely elastic and viscous systems. This viscoelastic behaviour makes them excellent materials for many applications, like bearing lubrication, where liquid oils cannot be employed. In this way, the elasticity of lubricating greases prevents their leakage from joints, while the fluidity aids to their pumpability and lubricating efficiency (Salomonsson et al., 2007).

In this sense, the study of rheological behaviour of lubricating greases has been very helpful to understand the microstructure of these materials and their response under quiescent state or small deformations, but also to predict their flow characteristics under specific working conditions (Balan, 2000). In general, lubricating greases show a non-Newtonian behaviour from very low shear rates and pressures, mainly due to the thickener structure and its interaction with the base oil. In comparison with Newtonian liquid oils, the viscoelastic response of these materials is the result of elastic and viscous forces, related to the thickener network and the base oil, respectively, both determining the grease microstructure (Lugt, 2009).

From a rheological point of view, the evolution of viscoelastic moduli of lubricating greases is usually studied inside the linear viscoelastic region by means of small-amplitude oscillatory shear (SAOS) experiments, i.e., applying frequency sweep tests at a constant amplitude. Figure 21 shows the mechanical spectrum for a typical lithium lubricating grease, which is quite similar to that exhibited by gel-like colloidal structures and highly entangled polymers (Almdal et al., 1993). Therefore, under small deformations, both elastic and viscous responses are represented by the storage (G’) and the loss (G’’) moduli, respectively, which will be raised by increasing the thickener concentration, from a liquid-like behaviour until reaching a certain point, where a continuous three-dimensional network between all disjointed thickener fibres and their aggregates will be formed, resulting in a dramatically increase of the storage modulus and the corresponding free-flow loss of the lubricating grease (Li et al., 2015). However, most of lubricating greases display shear-thinning characteristics when increasing the strain rate, generating a permanent destruction of a part of their microstructure and the subsequent thickener degradation. This structural degradation affects the mechanical stability, leading to changes in the consistency after working the grease (Hamnelid, 2011).

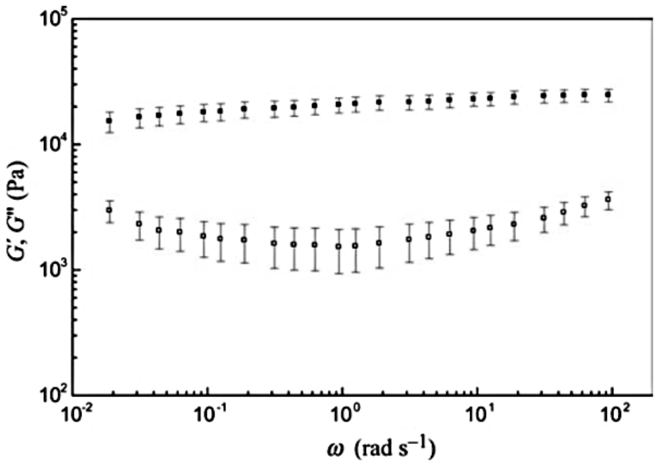


Figure 21. Typical rheological response for lubricating greases (Delgado et al., 2005)

In general, when the applied shear stress is larger than the critical yield stress (σ_y), the internal structure of lubricating grease will be broken, giving rise to its plastic deformation before flow starts, and must be restored when the stress is ceased (Hamnelid, 2011). This yield stress is traditionally characterized by means of consistency or penetration tests (NLGI consistency number), although it can also be measured with a rheometer through the yield value or the "cross-over stress" in SAOS amplitude sweep tests (Couronne et al., 2000). Thus, amplitude sweep tests are usually used to determine the extension of the linear viscoelastic region (LVR) but also to estimate the yield stress in lubricating greases. In this region, viscoelastic functions (G' and G'') do not depend on the amplitude, being the stress proportional to the strain (see Figure 22). Moreover, LVR is characterized by the application of small oscillatory stress or strain amplitudes, which prevents the grease internal microstructure destruction and inhibits the measurement effects over the material properties (Li et al., 2015). On the other hand, the apparent yield stress can be deduced as the value from which both viscoelastic moduli start to decrease, taking place their crossover at higher stresses (also known as flow point), and indicating a liquid-like structure (Heyer and Läuger, 2009).

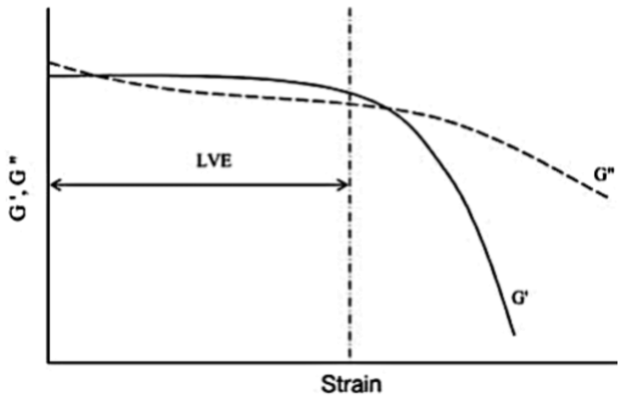


Figure 22. Amplitude sweeps to determine the linear viscoelastic region (Salomonsson et al., 2007)

Regarding the influence of thickener concentration on the lubricating grease rheological properties, Delgado et al. (2006a) showed that an increase in the soap content produced a rise of viscoelastic functions values. This effect reveals the formation of a stronger microstructure network by increasing the thickener amount, while the values of the loss tangent remained almost constant, meaning, there was no variation in the relative elasticity of samples (see Figure 23). Moreover, an increase of both viscoelastic moduli was generally observed by decreasing the base oil viscosity, also influencing the relative elasticity, as can be inferred from Figure 24.

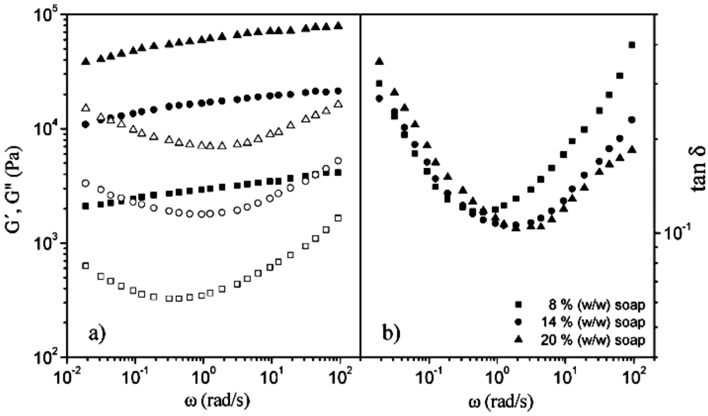


Figure 23. Rheological response of lubricating greases as a function of soap concentration (Delgado et al., 2006a)

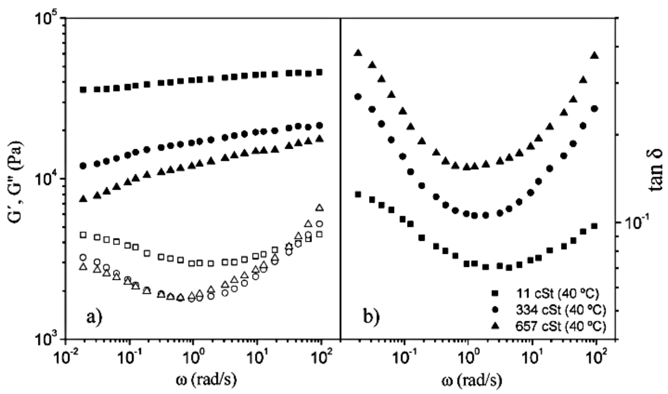


Figure 24. Influence of the base oil viscosity on the greases rheological properties (Delgado et al., 2006a)

Furthermore, the study of rheological properties shows a great interest due to the effect of several parameters, like temperature, time-dependence or shearing action. In general, viscoelastic functions tend to decrease by increasing temperature, as has been shown in many investigations (Cheng et al., 2016; Delgado et al., 2006b; Karis et al., 2003). Moreover, the time-dependence shows a great importance (thixotropic properties), since the lubricating greases can undergo shear-induced microstructural changes (as illustrated in Figure 25 (Delgado et al., 2009)), thus affecting to their lubricating properties. The time-dependent rheological response is the result of microstructural changes arisen during the application of a shearing action or temperature (see Figure 26).

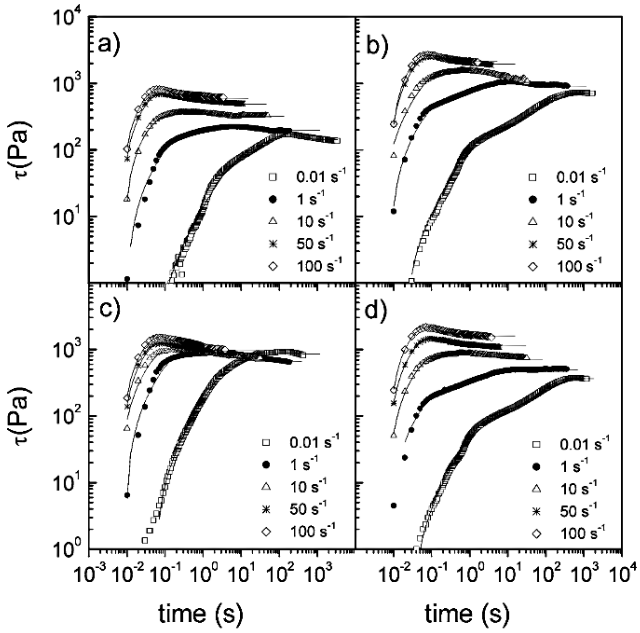


Figure 25. Shear stress-time dependence for lithium lubricating greases at different constant shear rates (Delgado et al., 2009)

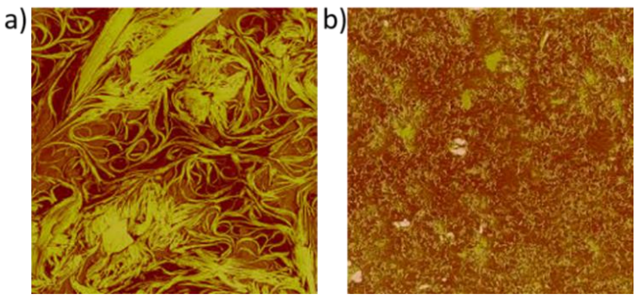


Figure 26. Microstructural changes of a lithium-based lubricating greases before (a) and after (b) applying a shearing action for 10 hours at 0.01 s^{-1} and 120 ºC (20µm x 20µm) (Paszkowski, 2013)

However, there are many problems concerning the rheological characterization of lubricating greases. Thus, wall slip, fracture and subsequent ejection of sample from the gap, beyond a certain level of deformation, are important phenomena in connection with lubrication properties. A summary of these effects can be seen in Figure 27.

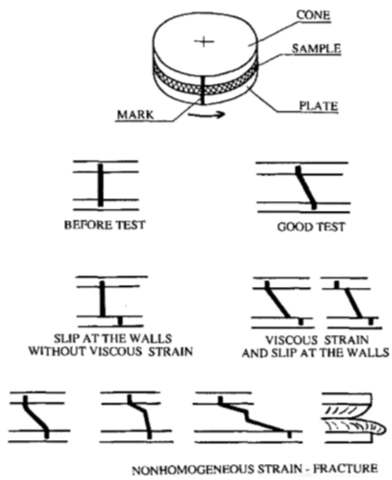


Figure 27. Typical problems occurring during lubricating greases shear tests (Magnin and Piau, 1990)

In this way, wall depletion effect is characterized by the formation of a film layer (around microns of thickness) next to the wall, whose viscosity is much lower than the viscosity of the grease. Alternatively, shear banding includes the formation of different layers and, consequently, non-homogeneous velocity gradients during the experiments (Balan and Franco, 2001). It is worth to point out that these effects may produce the grease fracture, also inducing its ejection from the gap at high strain rates. The expulsion of sample in rotational experiments is usually related to the centrifugal force, which produce a contact surface diminution between sample and geometry, resulting in wrong characterizations (Dobson and Tompsett, 1973).

Many researchers have devoted their investigation to the origin of these phenomena, which includes the fibres contacts rupture (Forster et al., 1956), a lower thickener particle concentration around the wall (Bramhall and Hutton, 1960), the type of wall material (Czarny, 2002) or the kind of thickener (Paszkowski, 2013), as well as their possible solutions. In this sense, it is generally accepted that the use of serrated geometries in rheological experiments can overcome the wall slip effects, although this practice favours the fracture of lubricating grease sample. In addition, this phenomenon is also affected by the magnitude of roughness and the geometry dimensions (Balan and Franco, 2001).

3.3. Tribological properties of lubricating greases

Tribology is the science related to friction and wear of materials, which are controlled by means of lubrication. Generally, friction is the resisting force to the relative movement between two surfaces in contact, which can be low and steady, resulting in a smooth and easy sliding, or so great that produces overheating and the consequent loss of material (Lansdown, 1982).

As described above, lubricating greases are usually used in journal bearings and show some advantages compared to liquid lubricants in terms of their leakage from the bearing and sealing properties. In general, tribological properties of lubricating greases depend on the film formation between two surfaces and its corresponding thickness (see Figure 28), which is usually affected by the NLGI grade, the kind of thickener and the viscosity of the base oil (Cann, 1996). Traditionally, lubrication properties of greases have been mainly attributed to the base oil, however, nowadays, many researches have demonstrated the noticeable influence of thickener particles (Åström and Venner, 1994; Cann and Hurley, 2002; De Laurentis et al., 2016; Lu and Khonsari, 2007). On the other hand, working conditions will also modify the mechanisms of the film formation, giving rise to important changes in its thickness, and consequently, in the lubrication efficiency.

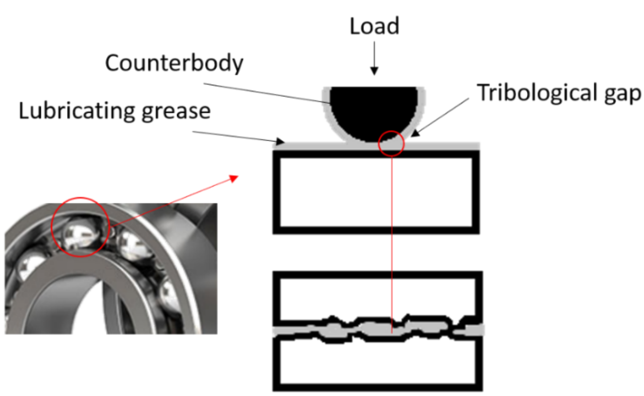


Figure 28. Tribological system scheme in a ball rolling bearing (BearingAdmin, 2013)

In a classical experimental approach, the tribological behaviour is usually characterized by means of the Stribeck curve, where the evolution of the friction factor (μ) is evaluated as a function of the working conditions and the lubricant properties, i.e., through the Sommerfeld number, which includes tangential speed (U), normal contact load (F_N) and lubricant dynamic viscosity (η) (Brandão et al., 2012; Lu and Khonsari, 2007). Under heavy loads, lubricating film starts to become progressively thinner, sometimes achieving a magnitude of the order of nanometers or even less when the contact pressure exceeds a certain value. In this sense, the lubrication mechanism can be altered from the hydrodynamic or elastohydrodinamic (EHL) to the mixed lubrication regime if the magnitude of surface roughness is higher than the film thickness.

Therefore, in the hydrodynamic lubrication regime, although the film thickness is generally much higher than the roughness, there is no direct contact between the surfaces, which can be slightly produced in the elastohydrodynamic lubrication regime despite the thickness is still high enough. On the contrary, a very thin film unable to resist the load is formed in the boundary lubrication regime, with the subsequent production of a high friction by virtue of asperities contact. Finally, the mixed lubrication regime is characterized by a lubricant film formation but associated to still incomplete separation of the rubbing surface, i.e., the lubricant film is not thick enough and all lubrication regime are simultaneously produced (Brandão et al., 2012; Xiao et al., 2012). A summary of the lubrication regimes as a function of thickness film is shown in Figure 29.

However, although the previously mentioned Sommerfeld number is usually used for lubricating oils, i.e., Newtonian systems, some researchers have applied this to lubricating greases, analysing the effect of soap thickener particles using the value of the base oil dynamic viscosity (Baker, 1958; Biresaw et al., 2017; Lu and Khonsari, 2007).

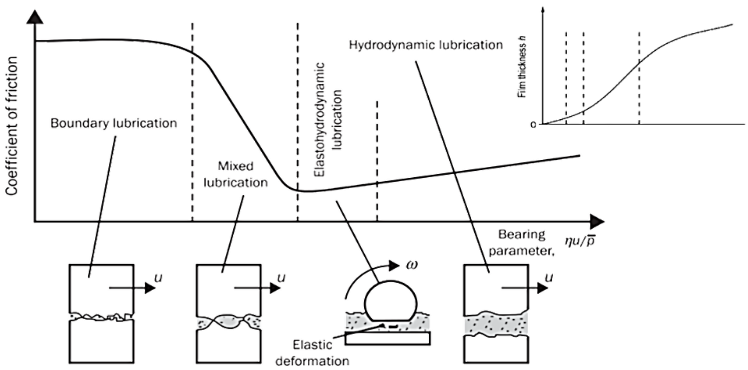


Figure 29. Stribeck curve (Davim, 2011) (Mang et al., 2010)

In this way, Lu and Khonsari (2007) studied the impact of thickener particles on the contact surfaces in comparison with the corresponding lubricant base oil, obtaining lower values of the friction coefficient for lubricating greases in the boundary or mixed lubrication regimes. This effect is related to the entrainment of thickener particles into the contact, giving rise to the increase of deposited film viscosity and thus reducing the asperities interaction. In addition, De Laurentis et al. (2017, 2016) not only confirmed the influence of thickener particles in the film thickness at low speeds, but also attributed the friction coefficient values in the high-speed regions mainly to the effect of the base oil viscosity, i.e., the bleeded oil.

On the other hand, measurements under sliding working conditions are also performed in lubricating greases in order to evaluate the values of the friction coefficient under specific situations, as well as the examination of the corresponding wear marks obtained as result of friction. In general, wear is quantified as the volume loss from solid surfaces that is usually related with the surface roughness, hardness, ductility, surface oxide films, tribolayers and transfers process, just as friction (Davim, 2011). Thus, the surface wear is influenced by different mechanisms, such as surface fatigue, abrasion, tribochemical and adhesion processes, which are summarized in Figure 30.

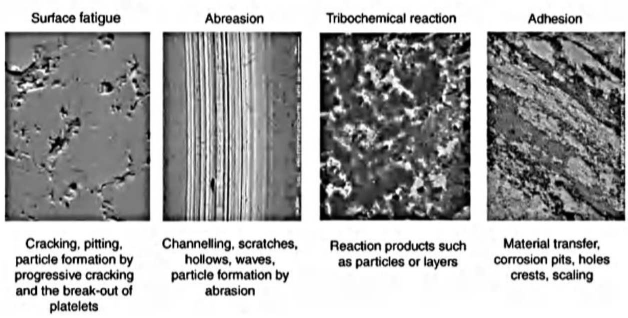


Figure 30. Wear mechanism (Mang et al., 2010)

Therefore, the tribological characterization of lubricating greases includes the study of the friction coefficient, and the subsequent characterization of wear, which are strongly related to their viscoelastic properties, as pointed out by Couronné et al. (2003). Overall, physico-chemical properties of the base oil, the kind of thickener and its concentration, as well as the characteristics of the three-dimensional network formed as a result of the thickener-base oil interactions, will affect both rheological and tribological properties of lubrication greases.

4. Bio-based lubricants

It is estimated that approximately 55% of the total amount of lubricants traded worldwide per year (45 million tonnes) end up in the environment due to losses, volatility, spills or accidents (Syahir et al., 2017). The global consumption of lubricating greases is estimated at 1.3 million tonnes, of which 90% is processed from mineral oils, 9% from synthetic oils and only 1% from biodegradable oils (Panchal et al., 2017). Considering that lubricating greases are mainly made up of mineral or synthetic oils and non-biodegradable metal soaps (85% lithium soaps), there is a widespread concern in this industrial sector to replace these components by others, biodegradable or obtained from natural resources, so that the lubricating greases maintain their functionality while reducing their impact on the environment.

The term bio-based lubricant or bio-lubricant is associated with those lubricants derived from natural resources, i.e. vegetable oils, animal fats or any other environmentally benign material. First attempts to produce bio-based lubricating greases were focussed on the replacement of the mineral base oil by natural products, like vegetable oils, whose substitution proved to be relatively simple and effective since vegetable oils and their derivatives exhibit excellent lubricating properties. However, given that the thickener content can vary between 5 to 35 wt. %, and that the thickeners with the best technical performance and most widely used in industry are lithium soaps, there is a clear need to develop new renewable thickening agents that also provide adequate technical performance. Moreover, harmful synthetic additives should be avoided, without compromising the lubricating greases properties. In this way, a bio-lubricant should be a biodegradable and renewable lubricant, non-toxic and also involving net zero greenhouse gas emissions.

4.1. Vegetable oils and derivatives

Regarding the base oil, vegetable oils are usually used to replace the petroleum-based oils, owing to their outstanding properties. In detail, they are inherently biodegradable, have low ecotoxicity and low toxicity towards humans, are derived from renewable resources and contribute with no volatile organic chemicals (Salimon and Salih, 2010).

In general, vegetable oils are composed of triglyceride molecules, which are essentially composed of glycerol and three fatty acids. Their fatty acid profile strongly depends on the plant, thus differing in chain length and number of double bonds (Wagner et al., 2001). Table 9 shows the composition of the most common vegetable oils, which will predetermine the physicochemical properties of bio-based formulations, and whose influence can be seen in Table 10.

Table 9. Fatty acid composition of some vegetable oils (Zainal et al., 2018)

Fatty acid (%)	C8:0	C10:0	C12:0	C14:0	C16:0	C16:1	C18:0	C18:1	C18:2	C18:3	C18:1:OH	C20:0	C20:1	C22:0	C22:1	C24:0
Neem oil				0.26	14.9	0.1	20.6	43.9	17.9	0.4		1.6		0.3		0.3
Calophyllum inophyllum L. oil					17.9	2.5	18.5	42.7	13.7	2.1						2.6
Pongamia pinnata Pierre oil					10.6		6.8	49.4	19.0			4.1	2.4	5.3		2.4
Karanja oil					11.65		7.5	51.59	16.64			1.35		4.45		1.09
Jatropha curcas L. oil				1.4	15.6		9.7	40.8	32.1			0.4				
Coconut oil	9.5	4.5	51.0	18.5	7.5		3.0	5.0	1.0							
Sunflower oil					6.18		2.16	26.13	65.52							
Soybean oil					11.28		2.7	24.39	56.29	5.34						
Rapeseed oil					4.8		1.8	62.7	19.5	8.6		1.7			1.0	
Canola oil					3		3	60	30	7						
Castor oil					2.63		1.51	4.74	8.36		82.80					
Palma oil			0.46	1.22	47.9		4.23	37.0	9.07	0.26		0.31				
Olive oil					11.7	0.8	3.0	77.9	7.2							

Table 10. Influence of the fatty acid characteristics on the vegetable oils physicochemical properties (Zainal et al., 2018)

Physicochemical properties	Viscosity index	Kinematic viscosity	Low temperature properties	Oxidation stability
Increase of the chain length	Positive	Positive		
Increase of chain branching	Negative		Positive	Positive
Higher degree of unsaturation	Positive	Negative	Positive	Negative

Viscosity is one the most important properties of lubricating oils, which is related to the resistance to flow and shows a vital role in the friction and wear reduction. An increase of viscosity may produce large increments of oil temperature in a lubricated contact and drag, while low viscosities give rise to an increase of the metal-to-metal contact friction. This property depends on temperature, pressure and fatty acid profile, influencing the film formation. At room temperature, the presence of double bonds in the fatty acid chains (unsaturations) produces a decrease of the oil viscosity, which increases by increasing the hydrocarbon chain length due to increment in random intermolecular interactions (Syahir et al., 2017).

On the other hand, the temperature dependence of viscosity is usually measured through the viscosity index (VI). In this way, a high value of this parameter indicates a slight temperature influence in the oil viscosity, allowing its use in a wide range of temperatures, while a large viscosity modification is characterized by small values of VI, generating the thinning of the film oil at elevated temperatures. Vegetable oils usually have higher values of VI than mineral oils, which indicates that the first ones are able of resisting high temperatures by keeping the oil film thickness (Zainal et al., 2018).

Another related parameter is the pour point, which refers to the lowest temperature at which the oil stars to flow or pour. This property is important for low-temperature lubrication, showing vegetable oils lower values of pour point than the mineral counterparts and being more effective for cold starts. Low values of pour point are required to prevent the excessive friction, wear and heating in the system, leading to the equipment failure. In general, a high unsaturation degree of fatty acid chain or the introduction of branched molecules produces a reduction in the pour point (Mobarak et al., 2014).

On the other hand, flash and fire points indicate the lubricant volatility and fire-resistance properties, respectively. In general, the mixture of lubricant with the air produces its ignition but not its burning. Therefore, heating temperature limit for the start of vaporized lubricant ignition is measured through the flash point, while fire point is associated with the combustion temperature of lubricants. Vegetable oils show higher flashpoint values than fossil-based ones, revealing their non-volatile nature and ensuring safer for transportation and storage stages (Mobarak et al., 2014).

Other important factors are the cloud point and the acid or neutralization number. The first one is the temperature of solids dissolution in oil, i.e., wax crystallizes at lower temperatures than cloud point, which would provoke the clogging of filters and hinder a good lubrication process at low temperatures (Syahir et al., 2017). The acid or neutralization number gives information about the amount of acid or base content required for lubricant neutralization (Mobarak et al., 2014).

In addition, biolubricants should show oxidation stability properties, i.e., they have to exhibit resistance for the oxide formation. The oil oxidation is promoted by metal surfaces, temperature, contaminants, pressure, agitation and water, increasing the oil thickness and producing its polymerization, also making it more volatile and corrosive. In detail, saturated vegetable oils show better oxidative stability than unsaturated oils at high temperatures, while among the last ones, the existence of double bonds, which easily react with oxygen to form free radicals, harms the oxidation stability (Zainal et al., 2018). Hence, they need to prevent the rust, that is, the chemical reaction between water and ferrous metals; and the corrosion obtained by interaction of chemicals and metals. In general, vegetable oils show better prevention properties than mineral oils, since they are nontoxic and less reactive (Mobarak et al., 2014). Finally, anti-wear properties are necessary for low-speed and low-pressure applications, showing vegetable oils better properties than mineral counterparts.

Therefore, bio-based oils generally show high flash point, high viscosity index, higher lubricity, low evaporative losses, and good metal adherence, as well as low friction and wear characteristics in comparison with petroleum-based lubricant oils (see Table 11). Table 12 shows the physicochemical properties of some vegetable oils.

Table 11. Fundamental properties of vegetable oils compared with the mineral ones (Mobarak et al., 2014)

Properties	Vegetable oils	Mineral oils
Density (20ºC, kg/m^3)	940	880
Viscosity index	100…200	100
Pour point	-20…+10	-15
Cold flow behaviour	Poor	Good
Oxidation stability	Moderate	Good
Hydrolytic stability	Poor	Good
Seal swelling tendency	Slight	Slight

Table 12. Physicochemical properties of some vegetable oils (Syahir et al., 2017)

	Density 15ºC (kg/m^3)	Kinematic viscosity 40ºC (mm^2/s)	Kinematic viscosity 100ºC (mm^2/s)	Viscosity index	Flash point (K)	Pour point (K)	Acid value (mg KOH/g)
Castor	0.95-0.97	220.6	19.72	220	523	246	1.40
Soybean	0.922-0.934	28.86	7.55	246	598	264	0.30
Olive	0.914-0.925	39.62	8.24	190	591	270	1.10
Sunflower	0.920-0.927	40.05	8.65	203	525	261	0.30
Rapeseed	0.910-0.917	45.60	10.07	180	513	261	1.50
Jathopha	0.917	40.0	5.50	170	546	270	4.65
Coconut	0.919-0.937	24.8	5.5	169	598	294	
Rice bran		40.6	8.7	201	591	260	
Palm		39.4			525	297	0.50
Cottonseed	0.917-0.931	33.86	7.75	211	525		
Sesame		27.33	6.3	193	589	268	2.00
Moringa		44.88			477		
Corn	0.916	32.41	8.06	238	597	259	0.30

Apart from all the advantages that vegetables oils show over mineral ones, the most relevant characteristic is their biodegradability, i.e., their ability to be broken down by microorganisms. In general, a lubricant is broken down into simpler compounds by means of microbial attack by bacteria and fungi present in soil or water, losing their functionality. Then, these compounds are converted by microorganisms into carbon dioxide, water, inorganic salts and new microbial cells (Battersby, 2005).

In order for a lubricant to be considered as biodegradable, it is necessary that its degradation percentage in a standard test exceeds a certain marked level. In general, vegetable oils show good biodegradable characteristics, much better than petroleum-based oils (see Figure 31). Moreover, biodegradation process for bio-based oils depends on the fatty acid chains forming the triglyceride, being the degradation of linear-chained compounds more easily than branched ones.

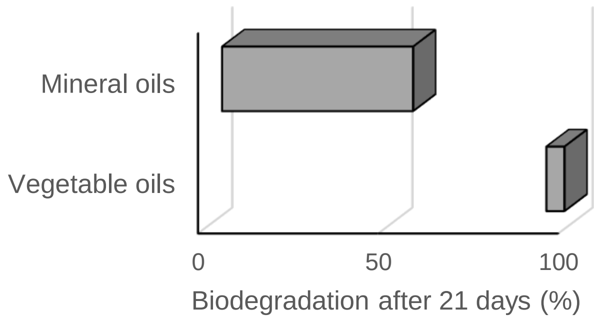


Figure 31. Biodegradation of bio-based lubricants and traditional ones (Battersby, 2005)

Despite vegetable oils are good alternatives to replace mineral oils in the production of lubricating greases, their direct application shows some limitations regarding their properties, being solely possible their use under low thermal stresses. The presence of unsaturations and the β-CH group of the alcohol in the chemical structure provides the lubricant with low oxidative stability and poor low-temperature properties, due to the ability of double bonds to react with oxygen and the easy rupture of the molecular structure through β-hydrogen atom in glycerol. These properties can be improved by means of chemical modifications, including addition reactions to the double bonds present on the unsaturated fatty acids alkyl chains (see Figure 32) (Salimon et al., 2010), such as transesterification (Bokade and Yadav, 2007; Panchal et al., 2017; Zainal et al., 2018), estolides formation (Cermak et al., 2013; McNutt and He, 2016), and epoxidation (McNutt and He, 2016; Zainal et al., 2018) reactions.

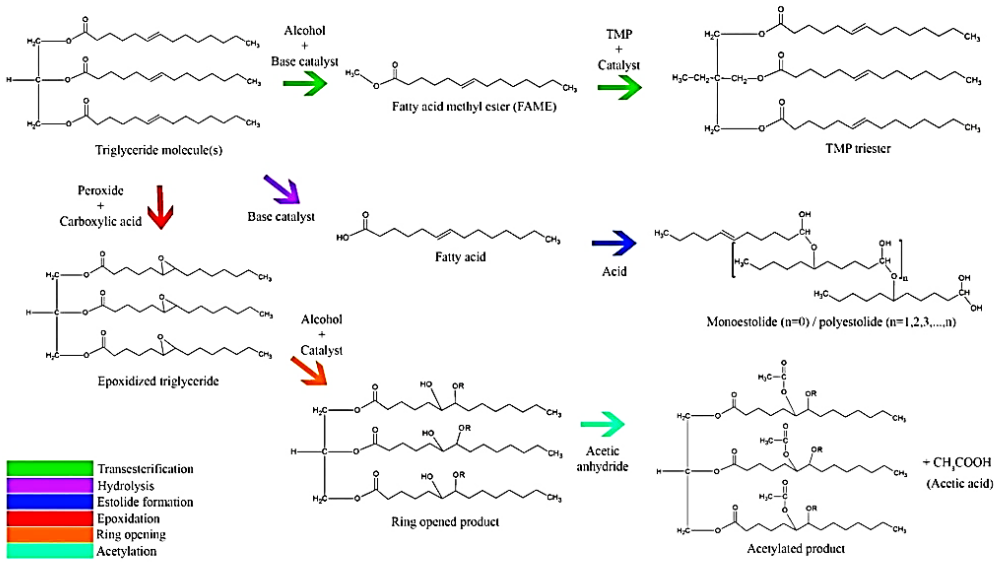


Figure 32. Chemical modification of vegetable oils (Syahir et al., 2017)

In this way, many researchers have explored the use of chemically modified vegetable oils for lubricants applications. Arumugam et al. (2015) sought to improve the thermo-oxidative stability of rapeseed oil by means of epoxy-based modification and a successive transesterification process, achieving better results of this property with the epoxidation method.

The effectiveness of using epoxidized soybean oil against its non-modified counterpart for high-temperature lubricant applications was studied by Adhvaryu and Erhan (2002). The low-temperature and oxidation stability of this oil was improved by Hwang and Erhan (2001) through a ring-opening reaction with alcohols followed by esterification of the resulting hydroxy groups.

Estolides from high-oleic sunflower and olive pomace acid oils (García-Zapateiro et al., 2013) and their ester from castor and lesquerella oil (Cermak et al., 2006) were synthesized with suitable properties for lubricant applications.

On the other hand, the replacement of mineral oils by vegetable ones in bio-lubricating greases has been widely explored by Panchal and Chauhan (2014), who proved the use of Tobacco oil, previously modified by esterification with different alcohol groups, in comparison with a petroleum-based all-purpose grease. The results showed that bio-based grease had good and competitive tribological properties against traditional greases. This research group also studied the properties of biolubricants based on modified Karanja oil and lithium-12-hydroxy stearate, whose promising characteristics were comparable to their petroleum counterparts (Panchal et al., 2015).

Nagendramma and Kumar (2015) used vegetable oil residues, like Jatropha vegetable residual oil, for the production of bio-lubricating greases based on lithium soap and multifunctional additives. Modified refined bleach deodorized palm oil as base oil and lithium soap as thickener were also produced by Sukirno et al. (2009), giving rise to lubricating greases with promising protection or antiwear properties. In addition, Sterpu et al. (2016) developed new bio-lubricating greases by using calcium stearate soap as thickening agent dispersed in corn, olive and palm oils. Castor oil was also used by Dwivedi and Sapre (2002) in the manufacture of lubricating greases, together with sodium and lithium soaps as thickeners.

4.2. Bio-thickeners

Nowadays bio-lubricating greases cannot be considered totally biodegradable, since their thickeners are still mainly based on metallic soaps and polyureas, which cannot be regarded as biodegradable components. Thus, these thickeners are being used in the industry for biodegradable greases production, just dispersing them into vegetable oils matrixes, i.e., they have the same composition of non-biodegradable products excepting for their base oil. For this reason, the scientific community is looking for new alternatives to traditional gellants, which should be bio-based, non-toxic, and derived from renewable resources like biopolymers. However, the dispersion of this kind of materials in vegetable oils seems to be really complicated from a chemical point of view, since they show a limited compatibility with most of the vegetable oils (Gallego et al., 2013a). In addition, the replacement of soap-based thickeners by renewable raw materials implies not only the need to maintain certain properties, i.e., suitable rheological characteristics, but also these must provide thermal and mechanical stability to the bio-lubricating greases. For this reason, the chemical modification of biopolymers with functional reactive groups seems to be an appealing strategy to facilitate the chemical compatibility, also allowing to obtain the desirable properties of these materials. In this sense, an intense investigation has been carried out over years aiming to increase the compatibilization of natural polymers and oil media for the development of oleogels or stable dispersions based on natural fibres and biopolymers in oil. This stabilization can be attained physically, by reducing the polymer polarity, making them more similar to the oil medium, for example by inserting methyl, ethyl or acyl groups into their structure, or chemically, by functionalization with reactive groups able to produce covalent interactions with the oil, thus promoting a certain degree of cross-linking between medium and thickener.

Regarding lignocellulosic components, they offer a wide range of possibilities to be used as renewable raw materials for several applications, since they show fundamental qualities and, as previously discussed, possess many functional groups susceptible to chemical modifications. In particular, some previous investigations have been focused on the use of lignocellulose as bio-thickener in the formulation of bio-lubricating greases. For instance, Núñez et al. (2012) evaluated the use of an industrial cellulose pulp and its methylated derivatives as thickening agents for bio-lubricating applications, obtaining an improvement of the thermal resistance for biogreases in comparison with standard products (see Figure 33).

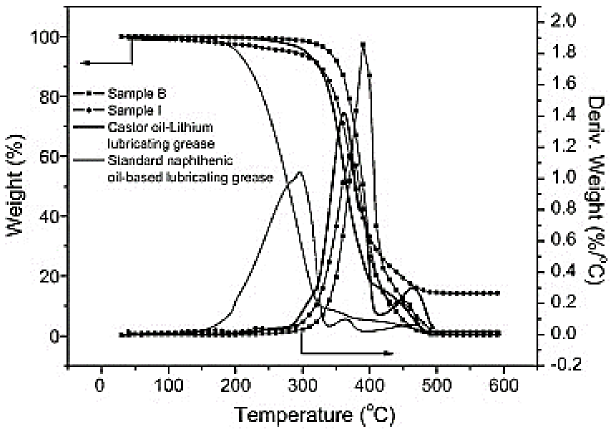


Figure 33. Thermal decomposition of two biodegradable lubricating greases (Sample B and I) in contrast with a standard grease and a partially biodegradable product (Núñez et al., 2012)

Martín-Alfonso et al. (2011) also used a Kraft cellulose pulp as thickener in castor oil dispersions, where ethylation reactions of this raw material were carried out in this case in order to improve the compatibilization with the oil medium and increase the physical stability of resulting products. In general, non-ethylated Kraft cellulose pulps produced highly strong gel-like dispersions with very high values of the viscoelastic moduli, much more than required for commercial greases (see Figure 34), also showing oil phase separation after few days. On the contrary, ethylated cellulose pulp significantly decreased these moduli, imparting a much more convenient rheological response.

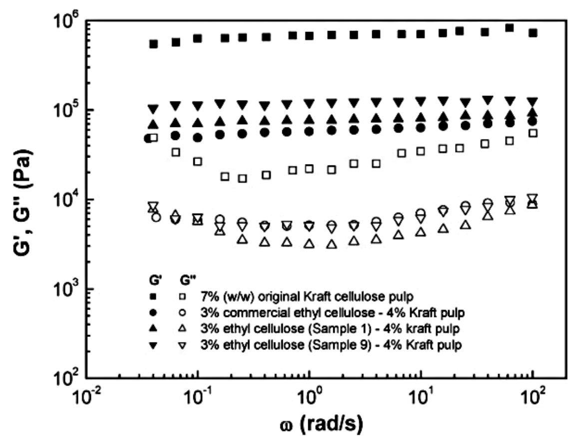


Figure 34. Viscoelastic functions of ethylated cellulose pulp (Martín-Alfonso et al., 2011)

Likewise, different cellulose pulps (Gallego et al., 2015a) and a commercial methyl cellulose (Gallego et al., 2013a), functionalized with isocyanate groups in this case, were employed to synthetize green lubricating greases formulations with suitable rheological and tribological properties. Moreover, these authors also studied the gelling effect of several isocyanate-functionalized commercial cellulose derivatives, allowing to alter the rheological behaviour of the resulting gels, from solid-like to weak ones, and their oil medium affinity, according to the polarity of cellulose derivative substituents (see Figure 35) (Gallego et al., 2015b).

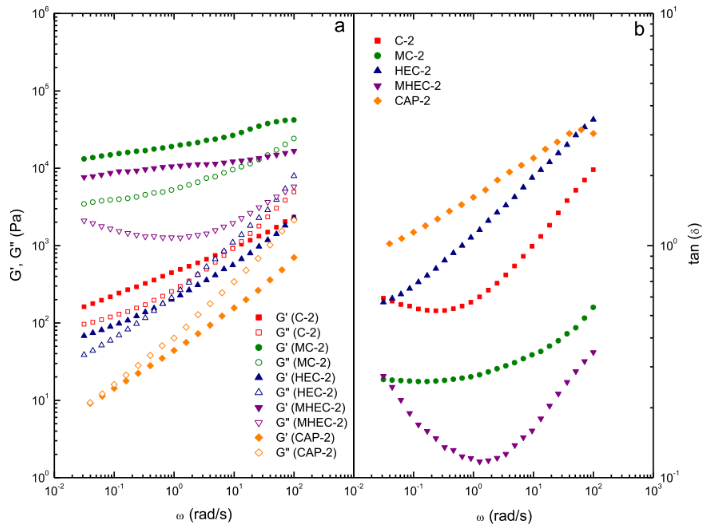


Figure 35. Rheological behaviour of several isocyanate-functionalized commercial cellulose derivatives gel-like dispersions in castor oil (Gallego et al., 2015b)

Table 13. Penetration, NLGI and friction coefficients for isocyanate-modified lignin-based oleogels compared to commercial commercial lubricating greases (Borrero-López et al., 2018)

Sample	Unworked penetratrion (dmm)	NLGI	Friction coefficient
GKL1-20	330	1	0.086
GKL2-20	287	2	0.083
GKL2-30	198	4	0.089
Lithium-based grease	260	2-3	0.108
Calcium-based grease	279	2	0.107

Lignin has been also recently employed as thickener for bio-lubricating greases production by Borrero-López et al. (2018), who functionalized a Kraft lignin with isocyanate groups for its dispersion in castor oil, resulting in chemical gels with enhanced tribological properties in comparison with soap-based greases, as can be seen in Table 13.

On the other hand, other non-lignocellulosic biopolymers have been also chemically modified for their utilization as bio-thickeners in the production of bio-lubricating greases. For example, Sánchez et al. (2014) synthetized acylated chitosan-based biodegradable lubricating greases, obtaining very similar rheological properties to those shown by lithium commercial lubricating greases, as can be seen in Figure 36. Moreover, Gallego et al. (2013b) also studied the rheological and thermal properties of gel-like systems based on chitin and chitosan for lubricant applications, but using isocyanate groups as crosslinking agents.

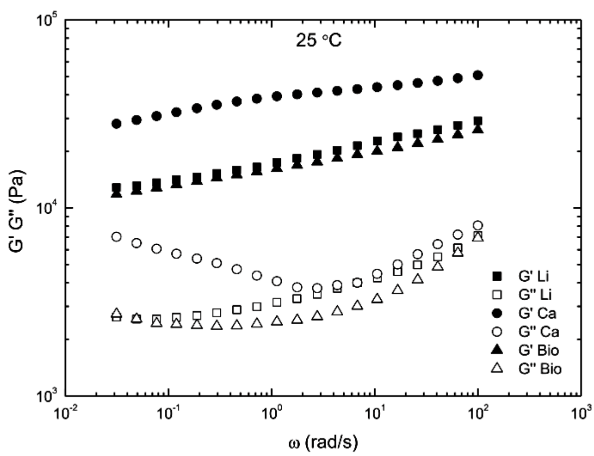


Figure 36. SAOS functions for lithium and calcium greases in comparison with an acylated chitosan-based biodegradable one (Sánchez et al., 2014)

Finally, Abdulbari et al. (2011) used waste cooking oil and spent bleaching earth derived from natural clay for the development of lubricating greases, discovering excellent thickening properties of this raw material in bio-lubricant formulations.

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Chapter 3

Materials & Methods

1. Materials

1.1. Bio-sourced raw materials employed for the production of thickening agents

1.1.1. Kraft Lignin

A commercial alkali softwood lignin from the Kraft process was used as raw material in the production of bio-lubricating greases. The generic chemical structure of this compound, which was provided by Sigma Aldrich in powder form, is shown in Figure 37.

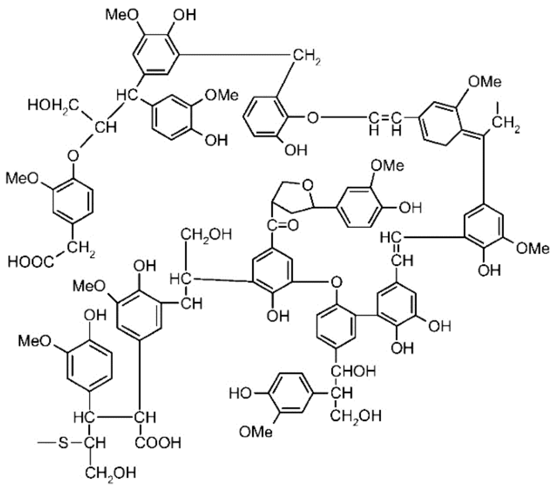

Figure 37. Kraft lignin molecular structure (Norgren and Edlund, 2014)

1.1.2. Cellulose pulp

An industrial grade Kraft bleached cellulose pulp, from *Eucalyptus globulus* sheets, supplied by ENCE, S.A. (Spain) was also employed as feedstock. Its chemical composition, measured by oven-dried weight, as well as the intrinsic viscosity are collected in Table 14. The average polymerization degree is around 1640, estimated from the intrinsic viscosity value.

Table 14. Characteristics of a commercial grade Kraft bleached cellulose pulp (Núñez et al., 2012)

Components	
α-cellulose (wt.%)	85.1±0.13
Hemicellulose (wt.%)	13.1±0.01
Lignin (wt.%)	0.3±0.28
Intrinsic viscosity (cm^3/g)	688±27

1.2. Epoxide components used to modify lignocellulosic materials

1.2.1. Epichlorohydrin

Lignin was functionalized with epichlorohydrin (purum grade, ≥99%), purchased from Sigma Aldrich (St. Louis USA). The chemical structure can be seen in Figure 38.

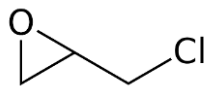

Figure 38. Chemical structure of epichlorohydrin

1.2.2. Glycidyl ethers

Some di- or tri- functional epoxy compounds from glycidyl ethers were also used to modify the lignocellulosic materials. Thus, glycidyl ethers such as poly (ethylene glycol) diglycidyl ether (PEGDGE, ~M_n 500 g/mol), neopentyl glycol diglycidyl ether (NPGDGE, M_w 216 g/mol), bisphenol A diglycidyl ether (BADGE, M_w 340 g/mol), resorcinol diglycidyl ether (RDGE, M_w 222 g/mol) and trimethylolpropane triglycidyl ether (TMPTGE, Mw: 302 g/mol), whose chemical structures are summarized in Figure 39, were kindly supplied by Sigma Aldrich (St. Louis USA).

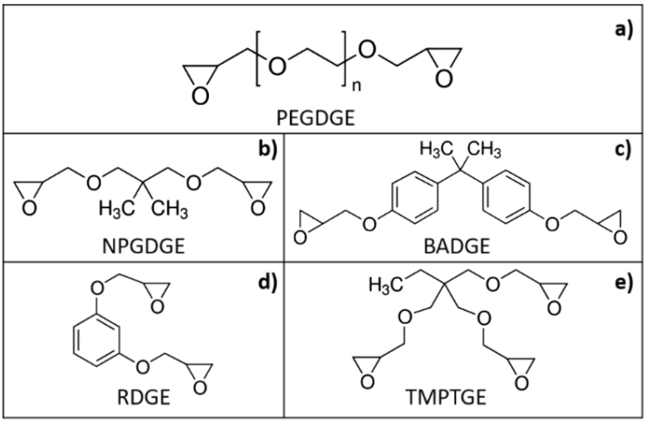

Figure 39. Chemical structure of different di- or tri- epoxides

In these cases, the modification of lignocellulosic materials was intended to do by linking their hydroxyl groups to one terminal epoxy ring of these epoxides, giving rise to a new hydroxyl group as a consequence of epoxy ring opening and keeping the others free end-epoxy ring available to further react with the hydroxyl groups of castor oil.

1.3. Castor oil

Castor oil, supplied by Guinama (Valencia, Spain), has been selected as biodegradable lubricating base oil. It is mainly composed of glycerol triricinoleate, i.e., esters of 12-hydroxy-9-octadecenoic (ricinoleic acid) and other fatty acids. The predominant chemical structure and fatty acid profile can be seen in Figure 40 and Table 15, respectively. Castor oil is characterized by the existence of three different functionality points, such as carboxyl groups, the single point of unsaturation and the hydroxyl groups, making it suitable for many chemical reactions and modifications (Ogunniyi, 2006). Moreover, the presence of hydroxyl groups with their corresponding hydrogen bridges, provides it exceptional viscosity properties, thus favouring the reduction of friction in a tribological contact, in comparison with other vegetable oils (Boyde, 2002; Ogunniyi, 2006).

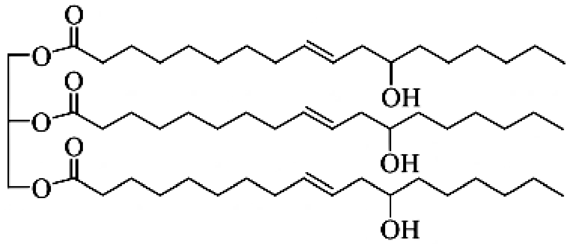

Figure 40. Triricinolein molecule (Ghosh et al., 2017)

Table 15. Fatty acids composition of castor oil (Quinchia et al., 2010)

Fatty acids	Concentration (%)
Myristic C14:0	trace
Palmitic C16:0	1.70
Palmitoleic C16:1	trace
Stearic C18:0	1.96
Oleic C18:1	5.34
Ricinoleic C18:1:OH	82.48
Linoleic C18:2	7.01
Linolenic C18:3	1.51
Arachidic C20:0	trace
Lignoceric C24:0	trace
Saturated	3.66
Monounsaturated	87.82
Polyunsaturated	8.52

1.4. Other chemicals

Some common solvents and other chemicals, such as sodium hydroxide (pellets ≥97%), hydrochloric acid (37%), acetic anhydride (≥98%), glacial acetic acid (99.7%), chloroform (≥99.5%), perchloric acid (70%), potassium hydrogen phthalate and crystal violet were purchased from Sigma Aldrich (St. Louis, USA).

2. Experimental procedures

2.1. Epoxidation of lignocellulosic materials

2.1.1. Lignin-epichlorohydrin reaction

The reaction between an alkali lignin and epichlorohydrin was carried out in alkaline medium (see Figure 41) according to El Mansouri et al. (2011) in order to promote the interaction between hydroxyl groups of lignin and the epoxy ring. The opening of oxirane ring gave rise to a new hydroxyl group, which reacts with NaOH leading to the closing again the epoxy ring and producing NaCl as by-product. In essence, lignin and a sodium hydroxide solution (20 wt.%) were mixed until complete lignin dissolution in a round-bottom flask equipped with a thermometer and a dropping funnel. Then, epichlorohydrin was slowly added during 1 hour while stirring at constant temperature. Reaction conditions, i.e., time, temperature and the reagent amounts, were varied and discussed in terms of the functionalization degree of lignin samples (see Chapter 4). The final blend was centrifugated, washed with distillate water and dried in an oven, obtaining the epoxidized lignin as a brown powder. The reactive proportions and the reactions conditions used in the lignin functionalization process are summarized inTable 16.

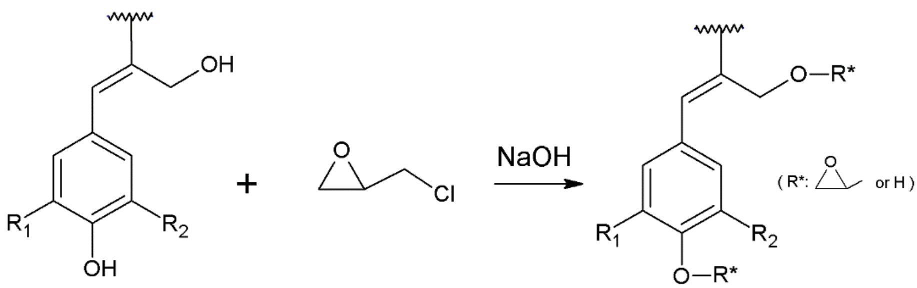

Figure 41. Epoxidation reaction of lignin with epichlorohydrin

Table 16. Reaction conditions for the functionalization of lignin with epichlorohydrin

Sample code	Temperature (ºC)	Time (h)	Lignin/NaOH (wt.)	Concentration (%)
EL1	120	3	1/3	1/10
EL2	100	3	1/3	1/10
EL3	60	3	1/3	1/10
EL4	30	3	1/3	1/10
EL5	10	3	1/3	1/10
EL6	30	6	1/3	1/10
EL7	30	24	1/3	1/10
EL8	30	3	1/3	**1/20**
EL9	30	3	**1/5**	1/10

2.1.2. Lignin modification with PEGDGE

Lignin was also chemically modified by using poly (ethylene glycol) diglycidyl ether (PEGDGE) as crosslinking agent. The reaction protocol was similar to those employed for epichlorohydrin-based lignin functionalization, but a lignin/NaOH weight ratio of 1/3, 3 hours and 30 ºC were fixed as reaction conditions in this process. However, the amount of epoxy compound was altered to determine the effect of modification degree of biopolymer, which was separated from mixture through centrifugation, vacuum filtration and later dried. A summary of these proportions is shown in Table 17.

Table 17. Lignin and PEGDGE weight ratios used in the lignin epoxidation process

Sample	Lignin (g)	PEGDGE (g)
EAL1	10	2.5
EAL2	10	5
EAL3	10	10
EAL4	10	20
EAL5	10	50

2.1.3. Cellulose pulp epoxidation with several glycidyl ether compounds

Cellulose pulp (CP) epoxidation process was carried out by using several glycidyl ethers compounds (see Figure 39), which were mixed with the cellulose pulp in an open vessel in an aqueous medium. In general, this raw material was dispersed in water under mixing with the aid of a RW 20 (Ika) device, at 1200 rpm, and the epoxy compound was then added at different concentrations (see Table 18). The reaction was performed at room temperature during 3 hours, obtaining the final product after centrifugation, washing with distillate water and freeze-drying, in a Virtis Advantage lyophilizer. Figure 42 shows the most possible chemical structure of this chemically modified raw material as an example when using NPGDGE as crosslinking agent.

Table 18. Epoxy/CP weight ratio used in the cellulose pulp chemical modification as a function of the epoxy compound

Sample code	Di- and tri- functional epoxide	CP/Epoxy w. ratio
ECPN-0.25	NPGDGE	1/0.25
ECPN-1		1/1
ECPN-2		1/2
ECPN-5		1/5
ECPN-10		1/10
ECPN-20		1/20
ECPB	BADGE	1/2
ECPR	RDGE	1/2
ECPT	TMPTGE	1/5

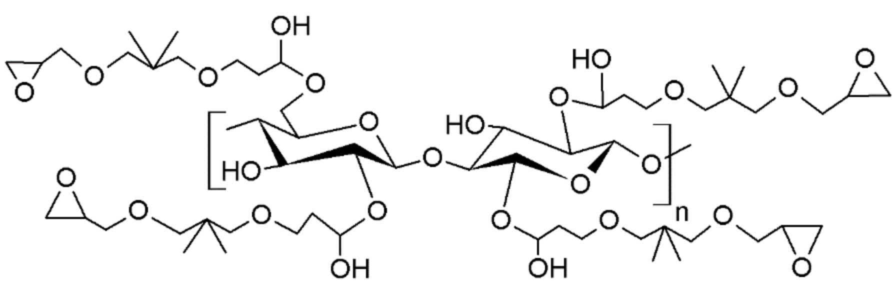

Figure 42. NPGDGE-modified cellulose pulp chemical structure

2.2. Preparation of gel-like dispersions.

Modified biopolymers and castor oil were mixed in an open vessel at 70 rpm using a controlled-rotational speed mixing device (RW 20, Ika) equipped with an anchor impeller, at room temperature during 24 and 3 hours for lignin-based and cellulose pulp-based oleogels, respectively. During the mixing process, the reaction of free epoxy groups and castor oil hydroxyl groups is promoted. Finally, the resulting gel-like dispersions were homogenized with an Ultra-Turrax T-25 (Ika) rotor-stator turbine for 1 min at 10,000 rpm.

3. Characterization techniques

3.1. Determination of epoxy index

Epoxidized lignocellulosic materials were chemically analysed in order to quantify the availability of free epoxy groups in their chemical structure. In this way, epoxy groups of epichlorohydrin-based lignins were calculated by means of their hydrolysis with HCL (0.1N), quantifying the excess of acid by neutralization with NaOH aqueous solution (0.1N) (El Mansouri et al., 2011). On the other hand, a standard titration method (ISO 3001:1990(E)) was employed for the epoxy index determination in diglycidyl ethers-based biopolymers. In this method, free epoxy groups reacted with nascent hydrogen bromide, which was produced as a consequence of the addition of a perchloric acid solution and tetraethylammonium bromide. The reaction end-point was established with the aid of crystal violet. Epoxy index was expressed as the moles of epoxy groups contained in 1 kg of epoxidized sample.

3.2. Infrared spectroscopy

FTIR spectra were obtained by using a FT/IR-4200 spectrometer (JASCO, Tokyo, Japan) within the wavenumber range from 4000 to 400 cm^{-1}, at 4 cm^{-1} resolution, in the transmission mode. In general, biopolymers in powder form were analysed by means of KBr pellets, while an attenuated total reflectance (ATR) accessory provided with monolithic diamond crystal, was coupled to the spectrometer and used for modified cellulose pulp measurements. In addition, two KBr disks were used to characterize the resulting gel-like dispersions in castor oil, by placing a small drop of sample between both disks.

3.3. Themogravimetric analysis

Q-50 thermal analyser (TA Instruments, USA) and Exstar TG/DTA 6200 device (Seiko, Chiba, Japan) were employed under nitrogen atmosphere to determine the thermal degradation of samples. In general, the measure of the mass loss of the different materials as a function of temperature was carried out by placing 10-20 mg of samples into a platinum pan and increasing the temperature from 30 ºC to 600 ºC at 10 ºC min^{-1}.

3.4. Differential scanning calorimetry

Typically, sealed aluminium pans with 5-10 mg of sample were placed in a Q100 differential scanning calorimeter (DSC) (TA Instruments, USA) under a 50 ml min^{-1} nitrogen purge and a temperature program from -80 to 200 ºC, at 10 ºC min^{-1}, was applied.

3.5. Morphological characterization

Morphological characterization of gel-like related dispersions was carried out by using an optical microscope (Olympus BX51) connected to a digital camera (dp70).

3.6. Rheological characterization

Rheological properties of gel-like dispersions were studied by using a Physica MCR 501 (Anton Paar, Austria) controlled-stress rheometer, equipped with a Peltier temperature controller. In general, all samples were firstly analysed by applying stress sweep tests at 1 Hz from 0.01 to 5000 Pa in order to determine the extension of the linear viscoelastic range (LVR). Once the LVR was established, small-amplitude oscillatory shear (SAOS) frequency sweep tests were performed inside the linear viscoelastic region in a frequency range of 0.03-100 rad/s. In addition, viscous flow tests were carried out by applying stepped-shear rate ramps in a 10^{-2}-10^{2} s^{-1} shear rate range. On the other hand, some selected formulations were subjected to rheo-destruction experiments at 25ºC in oscillatory mode by applying a stepped-shear stress program, inside (1 Pa) and outside (100, 500, 1000 Pa) the LVR for 15 and 30 min, respectively. A stress program of 1-100-1 Pa was also applied at 95ºC to study the influence of temperature in rheo-destruction experiments. In general, all measurements were done by using a serrated plate-plate geometry (25 mm and 1 mm gap) to prevent wall-slip effect (Balan and Franco, 2001). Although rheological properties were generally studied at 25 ºC, different temperatures from -5 to 150 ºC were also applied in some cases to evaluate their influence over the viscoelastic functions. Moreover, the effect of ageing time over the rheological behaviour of samples was also quantified by testing gel-like dispersions during time, i.e., one day, 1 month and 2 months after sample preparation. At least two replicates of each test were done on fresh samples.

3.7. Tribological measurements

A ball-on-three plates tribological cell coupled to the Physica MCR 501 rheometer (Anton Paar, Austria) was used to carry out the tribological characterization. This system is composed of two different geometries, the lower one formed by three 45º inclined steel plates (1.4301 AISI 304), where the lubricant is located, and the upper one, which is continuously rotating and contains a fixed bearing ball (1.4401 grade 100 AISI 316, 6.35 mm) (Heyer and Läuger, 2009). A scheme of this tribological system can be seen in Figure 43.

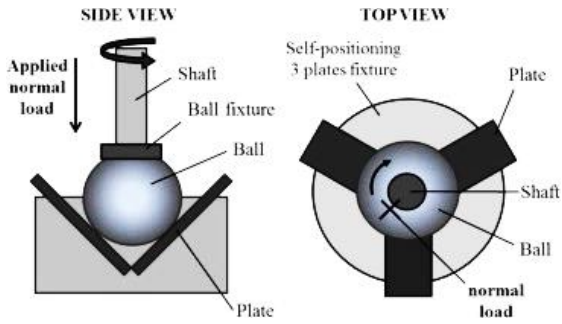

Figure 43. Tribological cell scheme (Martín-Alfonso and Valencia, 2015).

Tribological characterization of samples was performed by applying two different tests. Firstly, the evolution of the friction coefficient (μ) was monitored by stablishing a constant normal force of 20N and a rotational speed sweep from 0.01 to 1000 rpm. Furthermore, stationary friction tests at a constant rotational speed (10 rpm) and 20N normal force were done for 10 min. These tests were performed at two different temperatures (25 and 95 ºC) and at least five replicates on fresh samples were carried out.

On the other hand, steel plates surfaces were analysed after performing the constant rotational speed friction tests, in order to quantify the produced wear scar. For this purpose, a JXA-8200 SuperProbe (JEOL) microscope by means of scanning electron microscopy (SEM) observations, which also allowed to obtain the elementary composition of the worn surfaces by energy-dispersive spectroscopy (applying 15 keV), was used.

3.8. Penetration tests

Gel-like dispersions penetration indexes were determined by using a Seta Universal penetrometer, model 17000-2, with one-quarter cone geometry (Stanhope-Seta, Chertsey, UK), according to ASTM D 1403 standard. A cylindric vessel of 40 mm of diameter and 40 mm of height was used as lubricating grease container for penetration tests. The values of one-quarter scale, carried out in triplicate, were converted to full-scale penetration values in accordance with

ASTM D 217 standard, which were used to calculate the corresponding NLGI grade of each formulation.

4. References

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Chapter 4

Results & Methods

1. Article 1

Influence of epoxidation conditions on the rheological properties of gel-like dispersions of epoxidized lignin in castor oil

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Published in:

Holzforschung
Publishing company: DE GRUYTER
Editor-in-Chief: Oskar Faix
Volume 71, Issue 10, pp 777-784
Year 2017
ISSN 0018-3830
DOI 10.1515/hf-2017-0012

Category	Journal rank / Total journals	Quartile
Forestry	16/66	Q1
Materials Science, Paper & Wood	2/21	Q1
Impact Factor (2017)	2.079	

1.1. Full article

DE GRUYTER

Holzforschung 2017; 71(10): 777–784

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Influence of epoxidation conditions on the rheological properties of gel-like dispersions of epoxidized kraft lignin in castor oil

DOI 10.1515/hf-2017-0012
Received January 20, 2017; accepted April 25, 2017; previously published online June 2, 2017

Abstract: The modification of castor oil (CO) with lignin was the focus of this research to create a lubricating medium with improved gel-like properties. Namely, an alkali lignin (L) was epoxidized with epichlorohydrin (EP) and the resulting L_{EP}s were dispersed in CO. The parameters of L_{EP} synthesis were varied and the epoxidation index (EPI) of the L_{EP}s was determined. The L_{EP}s were also submitted to thermogravimetric analysis (TGA), differential scanning calorimetry (DSC) and Fourier transform infrared (FTIR) spectroscopy. Rheological responses of the L_{EP}/CO dispersions were investigated through small-amplitude oscillatory shear (SAOS) tests. Linear viscoelasticity functions are quantitatively affected by the epoxidation parameters, such as temperature, reaction time and L/EP and L/NaOH ratios. In general, lignins with higher EPI show higher values of the SAOS functions, which are indicative of better gel-strength due to a higher cross-linking density between the L_{EP}s and CO. A power-law equation describes well the evolution of the complex modulus, G*, with frequency of gel-like dispersions, where the power-law parameters were found to increase almost linearly with the EPI. The thermo-rheological characterization provides a softening temperature beyond 50°C.

Keywords: castor oil, epoxidation, functionalization, gel-like dispersion, lignin, rheology

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Introduction

In the last decades, the use of biomass as raw material for the development of consumer goods has received considerable attention because of its renewable and environmentally friendly nature (Zhang 2007; Octave and Thomas 2009). Lignins have been considered for a long time as non-commercializable by-products of pulping because of their complex structure (Lora and Glasser 2002). Lignin production is estimated to be around 40–50 M t year^{-1} and the majority of this waste is burned for chemical recovery and energy production (Carvajal et al. 2016) but their utilization as a value added product has been a matter of intensive research decades (Qiu et al. 2005; Pelaez-Samaniego et al. 2016). Nevertheless, only about 2–3% of worldwide lignin production is employed for the development of chemical, pharmaceutical, food, cosmetic or textile products (Thakur and Thakur 2015). Hydroxymethylation (Malutan et al. 2008; Yang et al. 2014), epoxidation (Gîlcă and Popa 2013), carboxymethylation (Gan et al. 2012), esterification, oxidation (Passauer et al. 2011b; Myrvold 2015) and sulfonation (Björkman 2001) are examples of lignin modification reactions to increase its reactivity. Thus, several polymers acting as gel promoters or rheological modifiers in different media were described in the context of cross-linking with lignin (Passauer et al. 2011a,b; Hong et al. 2016).

The lubricant producing industry (Bartz 1998; Wilson 1998; Boyde 2002) is also involved in the minimization of the environmental impacts of production and tries to include renewable resources into its production lines. Lubricating greases are generally highly structured colloidal dispersions, consisting of a thickener dispersed in mineral or synthetic oil. Fatty acid soaps of lithium, calcium, sodium, aluminium and barium are most commonly used as thickeners. The thickener forms an entanglement network, which traps the oil and confers the appropriate rheological and tribological behavior to the grease. Although vegetable oils are being increasingly used as lubricant base oils instead of mineral and synthetic oils, the substitution of traditional thickener agents by others derived from renewable resources, like some biopolymers, is a complicated task due to the technical efficiency of metallic soaps to impart the desired properties to the bulk system. Low-molecular weight and polymeric compatible thickeners of triacylglyceride oils are gaining special attention to produce oleogels with different applications (Sánchez et al. 2008; Laredo et al. 2011; Marangoni 2012; Satapathy et al. 2013; Lupi et al. 2015). Biomacromolecules like natural waxes, resins and polysacharides, including some cellulosic derivatives and lignocelulloses, with gelling or thickening properties in oily media (Núñez et al. 2011; 2012; Alvarez-Mitre et al. 2013; Patel et al. 2013; Zetzl et al. 2014), have a high potential in lubricating grease formulations. In particular, several isocyanate-functionalized cellulose derivatives proved to be effective gelling agents in castor oil (CO). In this case, the lubricating oil modification is aiming at the formation of cross-linking networks, in which the gel-like materials have better rheological, tribological and thermal characteristics for special applications (Gallego et al. 2013a,b, 2015).

The present work will explore the possibility to produce stable gel-like dispersions based on epoxidized alkali lignin in CO. CO is generally obtained by combining pre-pressing the seeds of the CO plant (*Ricinus communis*) and solvent extraction. It is a clear pale yellow liquid with a boiling point of 313°C and a density of 961 kg m^{-3}. Chemically, it is a triglyceride, in which ca. 90% of fatty acid chains is ricionelic acid (12-hydroxy-9-*cis*-octadecenoic acid). In focus will be the investigation of the parameters temperature (T), reaction time (t) and the ratios L/EP and L/NaOH during epoxidation on the physical stability and rheological properties of the resulting gel-like dispersions in CO.

Materials and methods

Materials: An alkali softwood lignin (L) from a Kraft process was chemically modified with epichlorohydrin (EP) (≥99% purum grade) in NaOH solution as catalyst (all reagents from Sigma-Aldrich, St. Louis, USA). CO supplied by Guinama (Valencia, Spain), served as dispersant medium. Fatty acid composition and main physical properties of CO can be found elsewhere (Quinchia et al. 2010).

Lignin epoxidation: Lignin epoxidation (Figure 1) was done according to El Mansouri et al. (2011). Basically, 10 g of lignin and the corresponding amount of NaOH solution (20% w/w) were loaded into a round-bottom flask mounted with a thermometer and dropping funnel. The mixture was stirred until complete dissolution. Then, EP was added dropwisely during 1 h under vigorous stirring at a constant

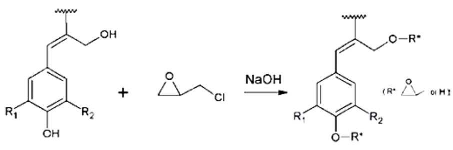

Figure 1: Lignin epoxidation reaction.

temperature (T). The reaction conditions are compiled in Table 1. The cooled down mixture to room temperature (rT) was centrifuged and was washed three times with distilled water and dried for 30 min at 80°C resulting in a brown powder.

Preparation of L_{EP} gel-like dispersions in CO: The reaction was performed in an open vessel equipped with a rotational high-speed mixing device RW 20 (Ika, Staufen, Germany) (anchor impeller). Epoxidized lignin (L_{EP}) was added to the CO until the final concentration of 35 w/w. The best L_{EP} concentration in CO was found in pre-experiments, which leads to physically stable dispersions for a wide range of epoxidation conditions. Mixing was maintained at 70 rpm for 24 h at rT, and finally, the dispersion was homogenized with an Ultra-Turrax T25 (Ika, Staufen, Germany) rotor-stator turbine at 10 000 rpm for 1 min.

Determination of the epoxy index (EPI): The L_{EP}s were hydrolyzed with HCl (0.1 N) overnight and the excess acid was neutralized with NaOH aqueous solution (0.1 N) (El Mansouri et al. 2011). The EPI expresses the moles of EP groups in 1 kg of L_{EP}.

Fourier transform infrared (FTIR) spectroscopy: A JASCO FT/IR-4200 spectrometer (Jasco Inc., Tokyo, Japan) was applied in combination with the KBr pellet methods. For gel-like dispersions, a droplet was placed between two KBr disks (32 mm×3 mm). The spectra were collected at 4 cm^{-1} resolution in the transmission mode.

Thermogravimetric analysis (TGA): The thermogravimetric analyzer, model Q-50 (TA Instruments New Castle, USA) was purged with N_2. 5–10 mg of sample were placed on a platinum pan and heated from 30°C to 600°C, at 10°C min^{-1}.

Differential scanning calorimetry (DSC): Five to 10 mg of sample was sealed in aluminum pans and placed in the Q100 (TA Instruments New Castle, USA). The sample was purged with N_2 at a flow rate of 50 ml min^{-1}. Temperature program: −80°C to 200°C at 10°C min^{-1}.

Rheological characterization: Small-amplitude oscillatory shear (SAOS) tests were carried out in the linear viscoelastic region with a Physica MCR 501 controlled-stress rheometer (Anton Paar, Graz, Austria) equipped with a Peltier temperature controller, using a serrated plate-and-plate geometry (25 mm diameter and 1 mm gap). A frequency range of 0.03–100 rad s^{-1} was applied. Generally, SAOS tests were performed at 25°C on samples taken 1 day and 1 month after their preparation. However, a few SAOS tests were also carried out at different temperatures between 5°C and 75°C. At least two replicates were performed on fresh samples. The mean percentage error in rheological measurements was always lower than 15.3%.

Table 1: Conditions of lignin (L) epoxidation reaction (T: temperature, t: reaction time), epoxidation index (EPI) of the epoxidized lignin (L_{EP}), and physical stability of L_{EP} gel-like dispersions in castor oil.

Sample code	T (°C)	t (h)	Ratios L/NaOH (w/w)	Ratios L/EP (w/w)	EPI (mol kg⁻¹)	Stability time of dispersion
L_{EP1}	120	3	1/3	1/10	0.27	1 week
L_{EP2}	100	3	1/3	1/10	0.21	1 week
L_{EP3}	60	3	1/3	1/10	0.44	5 weeks
L_{EP4}	30	3	1/3	1/10	0.95	>5 weeks
L_{EP5}	10	3	1/3	1/10	1.15	>5 weeks
L_{EP6}	30	6	1/3	1/10	0.97	>5 weeks
L_{EP7}	30	24	1/3	1/10	0.75	>5 weeks
L_{EP8}	30	3	1/3	1/20	1.36	>5 weeks
L_{EP9}	30	3	1/5	1/10	1.00	>5 weeks

Results and discussion

Lignin epoxidation performance

Lignin was successfully epoxidized under the reaction conditions presented in Table 1 resulting in L_{EP} as a brown powder. The epoxidation indices (EPIs) are also listed in Table 1 as a function of the experimental conditions employed. The EPI data are higher with decreasing temperature (T), reaction time (t) and L/NaOH and L/EP ratios. Epoxidation of lignin with epichlorohydrin, as the primary reaction, takes place at low and moderate temperatures resulting in higher EPI. In contrast, secondary reactions between the L_{EP} and the L occur at T>100°C, and this also lowers the number of EP groups in the final product (Pan et al. 2013). Short reaction times (3 and 6 h) allow a higher functionalization degree of the samples, whereas lower EPIs were observed at t>24 h. Under these conditions, crosslinking reactions may occur among the new epoxy groups and free remaining OH groups of lignin (El Mansouri et al. 2011; Pan et al. 2013). Thus, the more appropriate conditions for high EPIs are 10°C and 3 h reaction times. Moreover, when L/NaOH ratio was decreased from 1/3 down to 1/5, a slightly higher EPI was obtained. This effect may be a consequence of more lignin degradation at pH>12, which can generate more OH_{phen} groups available to react with epichlorohydrin, thus favoring the epoxydation (Pan et al. 2013). Expectedly, a decrement of the L/EP ratio leads to higher EPI values.

Main information inferred from the analysis of FTIR spectra (data not shown) of original alkali lignin and L_{EP} samples is the intensity reduction in the band at around 3400 cm⁻¹ (OH groups), together with the disappearance of the band at 1380 cm⁻¹ (OH_{phen} bending), as a consequence of epoxidation. Moreover, the band intensities around 2917 and 2850 cm⁻¹ (asym. and sym. methylene group stretching) are increasing as not otherwise expected. However, the most dominant new band is that of epoxy groups at 910 cm⁻¹ (Asada et al. 2015).

Figure 2 shows the thermograms corresponding to the second heating cycle for the original lignin and selected L_{EP} samples as well as the average values of the glass transition temperature (T_g) derived from these thermograms. As visible, T_g explicitly shifts to lower temperatures with increasing EPI, as a consequence of modified inter- and intramolecular hydrogen bondings.

TG and DTG analysis demonstrate the thermal degradation of L and L_{EP} (Figure 3a and b, respectively). The temperatures for onset (T_{onset}), maximum decomposition rate (T_{max}), the end of reaction (T_{offset}), as well as the weight loss (WL), and the final residue (%), have been estimated from the thermograms (Table 2). The original lignin degrades in a broad temperature range, because

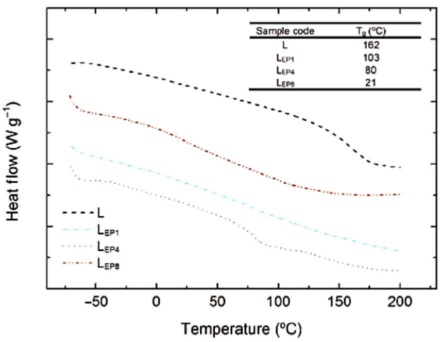

Figure 2: DSC heat flow curves for L, L_{EP1}, L_{EP4} and L_{EP8} samples and corresponding T_g values.

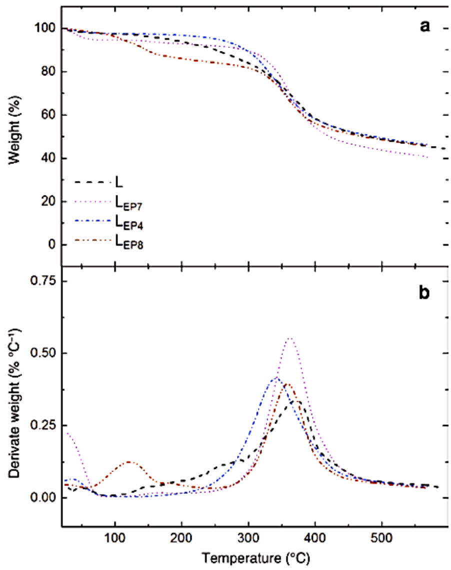

Figure 3: TG and DTG curves of L and L_{EP7}, L_{EP4} and L_{EP8}.

of the several oxygen-based functional groups with different thermal stability (Laurichesse and Avérous 2014). A relatively high amount of solid residue (44%) is left. The initial WL between 40°C and 90°C is due to water evaporation. The first decomposition stage is due to dehydration of the hydroxyl groups located in the phenyl group at around 165°C, and WL is around 4%. In the second decomposition stage between 270°C and 300°C, the aliphatic side chains start to split off from the aromatic rings via methyl C-O bond cleavage resulting in 9% WL. Finally, at 370°C–400°C the C-C-cleavage between lignin structural units takes place, which leads to a WL of around 36%. The L_{EP}s have a better thermal stability (Figure 3 and Table 2). Generally, thermal decomposition of these polymers takes place in one step in the temperature range of 300°C–400°C, except for L_{EP5} and L_{EP8}. However, as visible in Table 2, T_{onset} and T_{max} for this main degradation event slightly decrease, when the reaction temperature and the L/EP ratio are reduced. Beside this, two-step thermal decomposition profile was observed at around 90°C, when the EPI was higher than 1 (L_{EP5} and L_{EP8} samples), with a small WL (9% and 5%, respectively). This initial WL around 110–120°C observed in samples with high EPI may be attributed to a thermal degradation of epoxy rings and further dehydration of the generated OH groups.

Gel-like dispersions of L_{EPs} in CO

A simple physical blending of crude lignin in CO does not produce a stable dispersion. No matter how intense the mechanical dispersion was, a clear phase separation was seen after mixing. In analogy to cellulose derivatives (Gallego et al. 2013a), for a long-term physical stability of lignin dispersion, a lignin functionalization is required to promote a chemical interaction to the oil medium, which prevents phase separation. In L_{EP}s, the epoxy groups are able to interact with the OH groups of CO, more extensively beginning from a minimum EPI. This is the reason why L_{EP1} and L_{EP2} dispersions are stable for only 1 week after preparation (Table 1) because of the low EPI. On the other hand, L_{EP} samples with EPI > 0.5 formed stable gel-like dispersions with a long-term physical stability at least for 10 months. Even highly epoxidized lignins formed unstable dispersions

Table 2: TGA characteristic parameters for original lignin (L) and epoxidized lignins (L_{EPs}).

Sample	T_{onset} (°C)	T_{max} (°C)	T_{final} (°C)	WL (%)	Resid. (%)
L	129/249/332	164/270/373	183/286/407	4/9/38	49
L_{EP1}	324	380	412	65	35
L_{EP2}	330	380	412	67	33
L_{EP3}	310	353	389	56	44
L_{EP4}	290	342	391	54	46
L_{EP5}	87/331	110/365	160/415	9/49	42
L_{EP6}	300	341	395	58	42
L_{EP7}	321	364	398	59	41
L_{EP8}	90/326	120/360	151/394	6/46	48
L_{EP9}	294	336	389	60	40

WL is weight loss. Resid. is for residue left after thermal degradation.

with sunflower oil for lack of OH groups and the phase separation began immediately after blending the components (Figure 4).

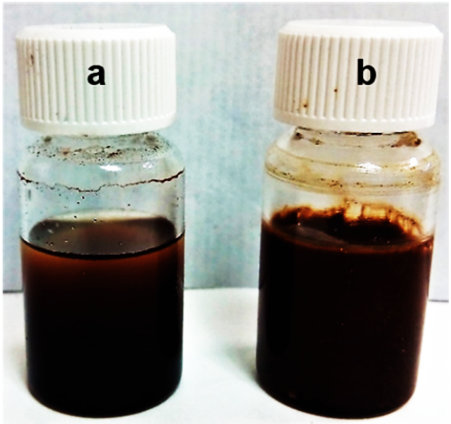

Figure 4: Visual appearance of selected epoxidized lignin dispersions. (a) Unstable dispersion of L_{EP4} sample in sunflower oil. (b) Physically stable gel-like dispersion of L_{EP4} sample in castor oil.

The SAOS response of L_{EP}/CO dispersions 24 h after their preparation is presented as a function of T (Figure 5a), t (Figure 5b), L/EP ratio (Figure 5c), and L/NaOH ratio (Figure 5d) applied in the epoxidation reaction. The storage modulus, G′, generally exhibits higher values than the loss modulus, G″, in the whole frequency range analyzed, with a relatively low slope of the G′ vs. frequency plot and with a tendency to reach a crossover between both SAOS functions at high frequencies. As is well known, this mechanical spectrum in the linear viscoelastic regime is characteristic of gel-like colloidal dispersions (Almdal et al. 1993; Gabriele et al. 2001). As can be deduced from Figure 5, the values of G′ and G″ increase with increasing EPI (Table 1), i.e. the gel strength is improved as a consequence of a high crosslinking density in the microstructural network. Thus, decreasing parameters concerning T, t, or L/EP and L/NaOH ratios lead to larger values of the linear viscoelasticity functions (Figure 5). A power-law equation describes the evolution of the complex modulus, G*, as a function of frequency according to the model of Gabriele et al. (2001):

$$G^* = \sqrt{(G')^2 + (G'')^2} = A \times \omega^{1/z} \qquad (1)$$

where z (coordination number) is related to the number of interacting rheological units within the 3D gel

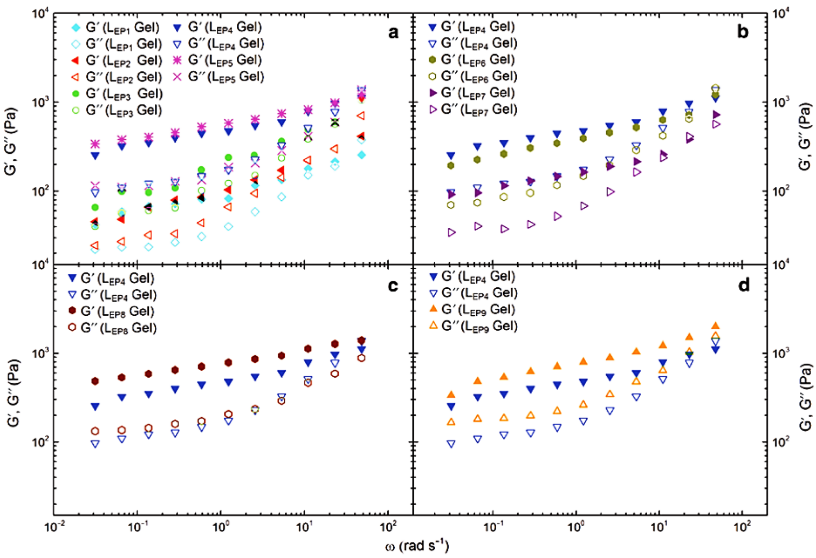

Figure 5: Frequency dependence of the storage, G′, and loss, G″, moduli for epoxidized lignin gel-like dispersions in castor oil as a function of L_{EP} synthesis parameters: (a) reaction temperature, (b) reaction time, (c) L/EP ratio and (d) L/NaOH ratio (G′, closed symbols; G″, open symbols).

network, defined as an arrangement of structural units, which are able to flow cooperatively, which may be related with the "structuration degree" by extension, whereas parameter *A* refers to the strength of interactions, which is correlated with the bulk consistency (Lupi et al. 2015). As previously reported (Lu et al. 2006), the gel strength of chemically induced gels is mainly dependent on the cross-linking density and can be quantified from the slopes of SAOS functions, i.e. the reciprocals of parameter *z*.

Figure 6 displays the evolution of these two parameters as a function of EPI. Both the logarithm of *A* and *z* increase almost linearly with the EPI. It can be concluded that the rheological response of the L_{EP} gel-like dispersions is mainly a consequence of the EPI. Thus, highly epoxidized lignin dispersions yield stronger gel networks with a higher density of cross-linking between lignin and CO.

The values of the rheological functions evolve with aging time (curing), up to around 1 month after preparation, but no longer, as a consequence of an internal curing process, where free residual epoxy groups are still reacting with the OH group of CO triglycerides. A slight time dependent intensity reduction in the EP band at 910 cm^{-1} is visible in the FTIR spectra of L_{EP} gel-like dispersions, which confirms the reaction of residual epoxy rings. The *A* values increase after 1 month of gel preparation (see Figure 6a). This increase is more important when the EPI is higher. However, the parameter *z* was independent from aging, which indicates that curing does not modify the overall microstructural pattern of the gel-like network, but curing improves the strength of interactions among structrural units. Accordingly, the cross-linking density among interacting lignin units is elevated, probably via the CO triglycerides acting as interconnection bridges.

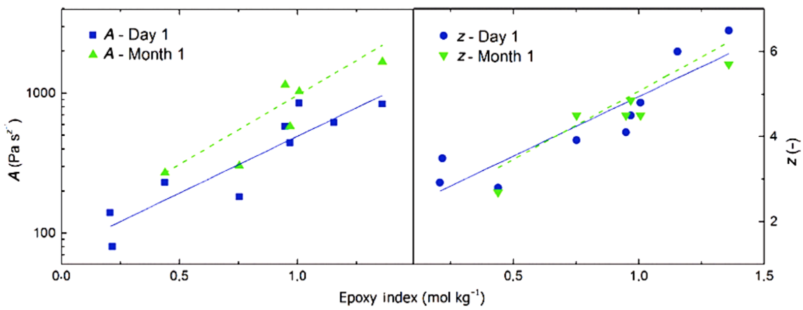

Figure 6: Evolution of Eq. (1) power-law parameters (*A*) and (*z*) with epoxy index at different aging times.

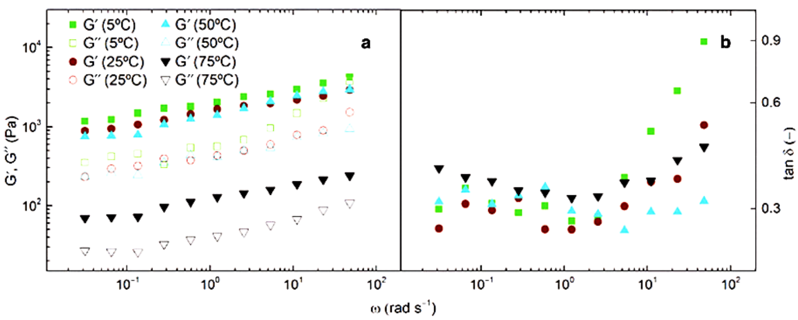

Figure 7: Frequency dependence of SAOS functions, for a selected epoxidized lignin (L_{EP8}) gel-like dispersion in castor oil, as function of temperature.
(a) Evolution of the storage, G′, and loss, G″, moduli (G′, closed symbols; G″, open symbols). (b) Evolution of the loss tangent.

The influence of the temperature on the SAOS functions was also studied for the dispersion based on the sample L_{EP8}. As seen in Figure 7a, the frequency dependence of SAOS functions was not modified by T, but G′ and G″ data decreased sharply above 50°C. Interestingly, the relative elasticity of the gel-like dispersions is not affected by T (Figure 7b), where the loss tangent (tan δ: G″/G′) is plotted for different temperatures. At T > 75°C, a significant oil separation is observable, which limits the thermo-rheological characterization.

Conclusions

An alkali lignin was successfully epoxidized with epichlorohydrin in alkaline medium leading to L_{EP} samples. L_{EP} formed stable gel-like dispersions in CO, while the stability was better at EPI > 0.5. EPI increases by performing the reaction in the temperature range of 10°C–30°C during 3–6 h reaction time. Moreover, higher EPI data were achieved by decreasing L/EP and L/NaOH ratios during L_{EP} syntheses. The linear viscoelastic response of L_{EP} gel-like dispersions in CO was essentially affected by the EPI. In general, the values of SAOS functions improve at higher EPIs, despite the fact that the frequency dependence is not much influenced. A power-law model describes the evolution of the complex modulus, G*, as a function of frequency, where the power-law parameters are increasing nearly linearly as a function of EPI. The values of the linear viscoelastic functions also increase with aging time up to around 1 month after preparation, as a consequence of an internal curing process, where remaining free epoxy groups are still reacting with CO triglycerides. The thermo-rheological characterization provides a softening temperature at around 50°C.

Acknowledgments: This work is part of two research projects (CTQ2014-56038-C3-1R and TEP-1499) sponsored by MINECO-FEDER and Junta de Andalucía programmes, respectively. One of the authors (E. Cortés-Triviño) has received a PhD Research Grant from the "Junta de Andalucía". The authors gratefully acknowledge its financial support.

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2. Article 2

Modification of Alkali Lignin with Poly(Ethylene Glycol) Diglycidyl Ether to Be Used as a Thickener in Bio-Lubricant Formulations

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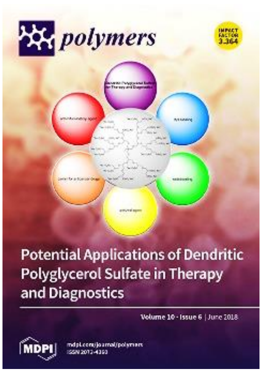
Published in:



Polymers
Publishing company: MDPI
Editor-in-Chief: Baceham Xia
Volume 10, Issue 6, pp 670
Year 2018
ISSN 2073-4360
DOI 10.3390/polym10060670

Category	**Journal rank / Total journals**	**Quartile**
Polymer Science	19/87	Q1
Impact Factor (2017)	2.935	

2.1. Full article

polymers

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Modification of Alkali Lignin with Poly(Ethylene Glycol) Diglycidyl Ether to Be Used as a Thickener in Bio-Lubricant Formulations

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Received: 14 May 2018; Accepted: 14 June 2018; Published: 16 June 2018

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Abstract: Considerable efforts are currently being made by the academic community and industry, aiming to develop environmentally friendly lubricants with suitable technical features for their performance. In this context, lignin could be considered a promising candidate to be used as a bio-sourced thickening agent to formulate eco-friendly lubricating greases. In this work, alkali lignin (AL) was chemically modified with poly(ethylene glycol) diglycidyl ether (PEGDE). Afterwards, the epoxidized lignin was properly dispersed in castor oil (CO) in order to obtain an oleogel for lubricant applications. The epoxidized lignins were characterized by means of epoxy index determination, thermogravimetric analysis (TGA) and Fourier transform infrared (FTIR) spectroscopy. The epoxide-functionalized lignin-based oleogels were analyzed from both rheological and tribological points of view. It was found that the viscosity, consistency and viscoelastic functions of these oleogels clearly increased with the epoxy index of the epoxide-modified lignin compound. Thermo-rheological characterization of these oleogels revealed a slight thermal dependence of the viscoelastic moduli below 100 °C, but a significant softening above that critical temperature. In general, these oleogels showed low values of the friction coefficient under the mixed lubrication regime as compared to the neat castor oil.

Keywords: epoxide-functionalized lignin; castor oil; lubricating greases; rheology; tribology

1. Introduction

Several million tonnes per year of used lubricants in Europe are ultimately poured into the environment as a result of leaks, spillages or other problems [1]. Consequently, this worldwide environmental concern has led to a growing interest in the use of renewable and environmentally friendly materials in lubricant formulations. Moreover, motivations to design new biodegradable materials are also induced by government incentives, public opinion, corporate programs of social and environmental responsibility, and response to marketing needs.

In the particular case of lubricating greases, the most feasible measure to be implemented by manufacturers in order to produce environmentally friendly formulations is the replacement of the mineral or synthetic lubricating oil, which comprises 70–90 wt % of grease components, as for instance established in the Blue Angel eco-label in 1978 [2]. For this purpose, it is well known that vegetable oils are gaining more importance in environmentally friendly industrial applications due to their inherent biodegradability, renewability, low ecotoxicity and low toxicity towards humans [3,4]. In particular, castor oil seems to be a good option due to the presence of hydroxyl groups in its chemical structure, which provide exceptional characteristics of lubricity [5–7].

However, the most challenging issue is the substitution of traditional thickening agents, such as lithium, aluminium, sodium and calcium soaps or polyureas, with other types of more environmentally friendly materials, in order to produce fully biodegradable lubricating greases. In this sense, Sánchez et al. [8] and Núñez et al. [9] evaluated the performance of cellulose derivatives-based oleogels and gel-like dispersions of industrial cellulose pulps, respectively. The potential use of chitin, chitosan and some acylated derivatives as biogenic thickening agents to formulate stable dispersions in vegetable oils was explored by Sánchez et al. [10]; whereas Gallego et al. [11] and Borrero-López et al. [12] reported the preparation of oleogels using NCO-functionalized lignocellulosic materials for the same use.

Lignin is one of the most abundant natural polymers present in plant biomass, and its chemical structure is characterized by phenylpropanoid units, such as *p*-hydroxyphenyl, guaiacyl and syringyl moieties, forming a complex three-dimensional network which comprises numerous inter-unit bonds, including ether and carbon-carbon linkages [13–16]. Lignin, possessing a complex and non-well defined structure, is generally considered a waste material due to its limited industrial reutilization up to now [16]. However, the existence of numerous functional groups susceptible to modification in its structure, like aliphatic and phenolic hydroxyl groups, makes possible different potential uses of lignin in several applications [17,18]. In this way, the epoxidation reaction of lignin through hydroxyl groups functionalization, among other chemical modifications, allows one to increase their chemical reactivity intensifying the lignin potential and its valorization [13,14,17–20].

In previous work, lignin was epoxidized using epichlorohydrin, and then was dispersed in castor oil thus resulting in gel-like systems stabilized by chemical crosslinking [21]. However, the toxicity of epichlorohydrin and the limited rheological properties imparted to the gel-like dispersion require another pathway for lignin epoxidation to be explored. Bearing in mind these assumptions, this work focused on finding a distinctive alternative for lignin valorization by using it as an effective thickening agent in castor oil-based lubricants through the study of the epoxidization of an alkali lignin with poly(ethylene glycol) diglycidyl ether (PEGDE). The influence of lignin/PEGDE ratio used in the epoxidation reaction and concentration of epoxide-functionalized lignin on the performance properties of the resulting oleogels, i.e., rheological, tribological and thermal characteristics, were studied.

2. Materials and Methods

2.1. Materials

Castor oil was supplied by Guinama (Valencia, Spain). Composition and main physical properties can be found elsewhere [22]. Poly(ethylene glycol) diglycidyl ether (PEGDE), with an average molecular weight (M_n) of 500 g/mol was used to chemically modify a commercial alkali softwood lignin (AL) obtained from a Kraft process. Both of them were supplied from Sigma-Aldrich (St. Louis, MO, USA).

2.2. Preparation of Epoxide-Functionalized Alkali Lignin (EAL)

In a typical facile procedure, 10 g of alkali lignin and 150 g of a 20 wt % sodium hydroxide solution were placed into a round-bottom flask mounted with a thermometer, a magnetic stir bar and dropping funnel and then stirred at 30 °C until dissolution. Then, different amounts of PEGDE (see Table 1) were added dropwise and the reaction was conducted for 3 h. Finally, the mixture was centrifuged at 4000 rpm, filtered and dried in an oven at 80 °C.

2.3. Preparation of Oleogels

EAL samples were dispersed in castor oil by mixing at 70 rpm with a RW-20 device (Ika, Staufen, Germany) using an anchor impeller. EAL concentration was varied between 2.5 and 10 wt %. This concentration range was selected based on physical stability and suitability of mechanical properties. The mixture was kept under agitation at room temperature for 24 h and then homogenized with an Ultra-Turrax T25 (Ika, Staufen, Germany) rotor-stator turbine, at 10,000 rpm. A reference system comprised of an unmodified lignin/sodium hydroxide blend and castor oil was also prepared in order to quantify the epoxide contribution on the oleogels' performance.

2.4. Epoxy Index Determination

The presence of epoxy groups in the modified lignin was determined by titration of a mixture of the epoxidized compound with chloroform, glacial acetic acid, tetraethylammonium bromide and crystal violet with perchloric acid according to ISO 3001:1999 (E).

Table 1. Input PEGDE/AL ratios applied on lignin epoxidation reaction and corresponding epoxy index values and residual NaOH amounts obtained.

Sample	AL (g)	PEGDE (g)	Epoxy index (mol/kg)	NaOH (mol/kg)
EAL1	10	2.5	0.79	5.9
EAL2	10	5	0.52	5.4
EAL3	10	10	0.37	4.7
EAL4	10	20	0.28	2.8
EAL5	10	50	0.15	1.4

2.5. NaOH Residual Analysis

The samples were washed several times with distilled water in order to quantify the amount of residual NaOH in the epoxidized lignins. The collected washing water was titrated with hydrochloric acid solution (0.1 N).

2.6. Fourier Transform Infrared (FTIR) Spectroscopy

FT/IR-4200 spectrometer (JASCO, Tokyo, Japan) was used to obtain FTIR spectra within the wavenumber range from 4000 to 400 cm^{-1}, at 4 cm^{-1} resolution, in the transmission mode. PEGDE-functionalized lignins were prepared as KBr pellets and placed into a holder.

2.7. Thermal Analysis (TG/DTA)

Thermogravimetric analysis was carried out by using an Exstar TG/DTA 6200 (Seiko, Chiba, Japan) under purging with nitrogen. 10–15 mg of each sample was placed on a platinum pan, and heated at 10 °C/min from 30 to 600 °C.

2.8. Rheological Characterization

The rheological characterization of oleogels was performed in a Physica MCR 501 (Anton Paar, Graz, Austria) rheometer, at 25 °C, using a plate-plate geometry (25 mm diameter, 1 mm gap). Small-amplitude oscillatory shear (SAOS) tests were carried out in a frequency range of 0.03 and 100 rad/s, within the linear viscoelasticity regime. The linear viscoelasticity range was previously determined by performing stress sweep tests at 1 Hz. Samples were measured after 24 h and 2 months of storage time. Moreover, SAOS tests were also performed at different temperatures (between 5 and 150 °C) for selected samples.

In addition, viscous flow tests were carried out 2 months after preparation. The viscosity of these oleogels was measured in a shear rate range of 10^{-2}–10^{2} s^{-1}, at 25 °C, using a rough surface plate-plate geometry (25 mm diameter, 1 mm gap) in order to avoid wall-slip phenomena [23]. At least two replicates of each test were done on fresh samples.

2.9. Penetration Tests

A Seta Universal penetrometer, model 17000-2, with one-quarter cone geometry (Stanhope-Seta, Chertsey, UK) was used to measure the penetration indexes of epoxidized lignin-based oleogels according to the ASTM D 1403 standard. The penetration values were converted to full-scale penetrations following the ASTM D 217 standard.

2.10. Tribological Measurements

Friction tests were performed in a ball-on-three-plates tribological cell [24] coupled to a Physica MCR 501 rheometer (Anton Paar, Graz, Austria). The tribological cell consists of a lower measuring geometry designed as a reservoir for the lubricant, with three 45° inclined steel plates (1.4301), while the upper measuring geometry keeps fixed a 6.35 mm 1.4401 grade 100 bearing ball. The ball was fixed to avoid rolling and slides on the three plates. This ball-on-three-plates configuration makes it possible to determine the friction coefficient, defined as the ratio between the applied normal force and the friction force measured by the rotational rheometer. The friction coefficient was monitored by applying a rotational speed sweep (0–1000 rpm) and 10 N of normal force, at room temperature (~25 °C). At least six replicates of each test were done on fresh sample.

3. Results and Discussion

3.1. Lignin Epoxidation with PEGDE

Epoxidation of a variety of lignins with epichlorohydrin has been previously investigated [21,25–27]. In these studies, the effects of temperature, reaction time, NaOH/lignin ratio and epoxy/lignin ratio on the chemical modification of lignin were analyzed. Cortés-Triviño et al. [21] and Malutan et al. [25] pointed out that high reaction temperatures had a negative effect on epoxidation due to the occurrence of secondary reactions. Thus, a relatively low temperature (30 °C) was selected in this research. The epoxy index decreased with reaction time, probably due to crosslinking reactions, although this effect may depend on both epoxy/lignin ratio and temperature [25]. In this sense, Ferdosian et al. [26] and Lai et al. [27] proposed the optimum reaction time range between 2.5 and 5 h. NaOH/lignin ratio tends to increase the gross weight of alkali lignin-PEGDE compound and affects the solubility of lignin. In this work, the alkali load was 20 wt % to obtain a pH value around 12–13, which is necessary for a complete dissolution of the alkali lignin powder. Consequently, a chemical lignin structure in the form of a sodium salt should be obtained, which could be of interest for the intended lubricant application, due to the use of sodium soap as thickener in the formulation of lubricating greases [28]. Therefore, taking into account that lignin/epoxy ratio is the factor exerting the most significant effect on the epoxide-modified lignin [26], several samples differing in the input PEGDE/AL weight ratio (between 0.25 and 5) were prepared by maintaining the reaction temperature at 30 °C, the reaction time at 3 h and the alkali load at 20 wt %. (see Table 1). In all cases, AL was properly epoxidized, resulting in a dark-brown powder after three hours of reaction.

Table 1 shows the epoxy index values as a function of the PEGDE/AL ratio, as well as the residual amount of NaOH in the EAL powder. Significant differences in both the epoxy index and the amount of NaOH were obtained by modifying the PEGDE/AL ratio. Thus, the lower the PEGDE/AL ratio, the higher the epoxy index and the residual sodium hydroxide. As was previously pointed out by Delmas et al. [28], two competitive reactions occur during the intermediate step of epoxidation at high pH; on the one hand, a partial etherification of lignin with the epoxy group of PEGDE and, on the other hand, the alkaline hydrolysis of PEGDE into hexahydroxy-PEG. In relation to the alkaline hydrolysis of PEGDE, it is worth pointing out that the PEGDE oxirane ring opening leads to an intermediate sodium alkoxide group that can either be converted into a hydroxyl group or attack the oxirane group of another PEGDE molecule resulting in a chain-growth polymerization [28]. Consequently, high PEGDE/AL ratios favor the alkaline hydrolysis of PEGDE, which decreases the residual amount of sodium hydroxide and prevent the epoxidation of the hydroxyl groups in the lignin to obtain the epoxide-modified lignin compound, thus resulting in lower values of the epoxy index. Therefore, the highest epoxy index was achieved in sample EAL1, which was prepared with the lowest PEGDE/AL ratio (0.25/1).

FTIR spectroscopy was employed to verify the structural changes resulted after lignin epoxidation. Figure 1 shows the spectra for both AL and a selected epoxidized sample (EAL4). As was previously reported [29], AL shows a variety of intense peaks, which can be attributed to the O–H stretching vibration

(3440 cm^{-1}), asymmetric (2917 cm^{-1}) and symmetric (2850 cm^{-1}) stretching vibration of methylene, methyl and methoxyl groups, aromatic ring vibrations of the phenyl propane skeleton (1600, 1510 and 1426 cm^{-1}), C–H deformations of asymmetric methyl and methylene groups (1459 cm^{-1}), C–O stretching vibration of guaiacyl units (1272 cm^{-1}), C–H of guaiacyl and syringyl (1130 cm^{-1}), and vibrations of C–O in secondary (1080 cm^{-1}) and primary alcohol groups (1030 cm^{-1}). However, significant differences with EAL4 spectrum can be observed within the wavenumber range of 500–2000 cm^{-1}. It is well known that the presence of NaOH significantly masks the IR absorption peaks of a given sample, especially in the range of 1300–1500 cm^{-1} [30]. Despite this fact, the epoxide modification of the alkaline lignin can be verified through the appearance of a characteristic absorption peak of the epoxy group (oxirane ring vibration) at 865 cm^{-1}. In addition, an absorption peak at 1126 cm^{-1} assigned to the stretching vibration of C–O–C in the PEGDE structure can be also observed [31,32].

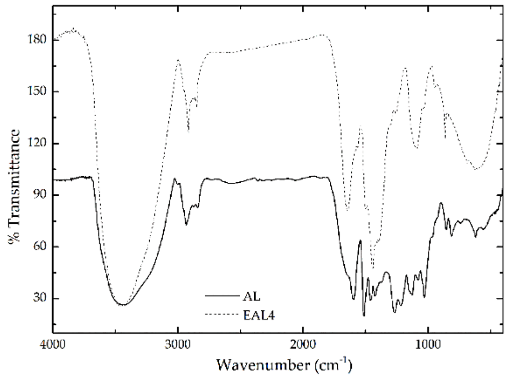

Figure 1. FTIR spectra for the original alkali lignin and a selected epoxide-modified lignin (EAL4).

TGA analysis was also applied to study the thermal decomposition of epoxidized lignins aiming to elucidate the effectiveness of functionalization. Figure 2 shows the thermogravimetric curves, in the form of both weight loss and rate of weight loss (first derivative), of the original alkali lignin (AL) and the epoxide-modified lignin samples (EALs) studied. More relevant thermal degradation data calculated from the corresponding thermogravimetric curves are collected in Table 2.

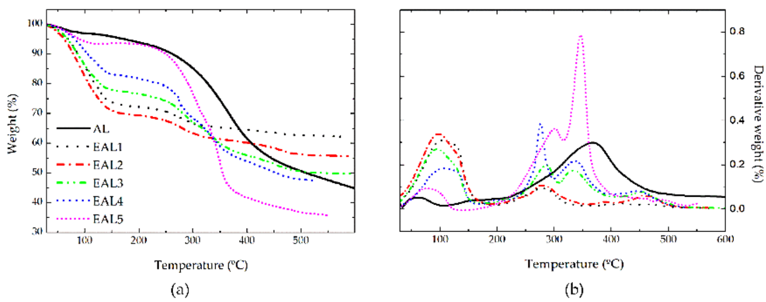

Figure 2. Loss weight (**a**) and decomposition-rates (**b**)curves during the thermal degradation for the original alkali lignin and epoxidized lignin samples.

Table 2. TGA characteristic parameters for the original alkali lignin and epoxidized lignin samples.

Sample	T_{onset} (°C)	T_{max} (°C)	T_{final} (°C)	ΔW (%)	Residue (%)
AL	130/234/335	150/277/380	221/299/423	5/8/40	47
EAL1	110/241/377	129/277/459	143/304/482	28/7/3	62
EAL2	109/261/375/442	123/277/390/464	144/301/417/489	31/6/2/4	57
EAL3	104/256/324/431	116/285/335/455	135/297/362/483	20/13/11/6	50
EAL4	115/254/322/431	120/274/339/451	142/290/361/475	17/13/15/7	48
EAL5	81/249/337/434	106/305/350/463	112/314/363/487	7/25/30/4	34

As previously described [21,26], apart from the initial weight loss of around 5% at 50–100 °C due to moisture, the thermal degradation of this alkali lignin comprises the dehydration of hydroxyl groups at around 150 °C and the cleavage of ether linkages at around 275 °C. At this temperature, volatile gases such as CO, CO_2, and CH_4 [15,33] are produced, with subsequent pyrolytic degradation, which involves the cleavage of carbon-carbon linkages at a T_{max} around 380 °C. In consequence, the complete rearrangement of the backbone at the end of the test leads to 47% char, in agreement with previous investigations [15,34].

The residual amount of NaOH also influences the thermal decomposition of epoxidized lignin samples [35]. The great weight loss displayed in all samples between 80 and 150 °C is basically the consequence of the drying process performance, which does not completely remove the moisture from the solid phase after lignin epoxidation. However, the dehydration of newly generated hydroxyl groups as a consequence of the epoxidation process may also occur at these temperatures [36]. As a consequence, higher mass losses at around 150 °C were detected for more epoxidized samples. Apart from these dehydration processes, in general, the thermal degradation of epoxide-modified lignin samples started at temperatures similar to those of alkali lignin (200–250 °C). However, additional thermal events due to both the degradation of non-lignin components (PEGDE and hexahydroxy-PEG) and the cleavage of aliphatic hydroxyl groups [26,28] are apparent in the form of sharp peaks in the derivative curve at around 270–300 °C. A weight loss of within 6–25 wt % was observed in this temperature range, increasing with the PEGDE/AL ratio. These results are in agreement with those reported by Kleen and Gellerstedt [37], who stated that the presence of Na^+ cations leads to a significant decrease in volatile pyrolysis products and facilitates the cleavage of hydroxyl and methoxyl groups. In addition to this, it was found that EAL1 and EAL2 showed the highest amount of residue, 62 and 57 wt %, respectively; while only 34 wt % char formation was achieved for EAL5. These results are also in accordance with other studies [35], which pointed out that char yield was inversely proportional to the total amount of hydroxyl and methoxyl groups in the lignin. As previously discussed, higher PEGDE/AL ratios inhibit the etherification of the hydroxyl groups in the lignin.

Alternatively, the main peak related with the pyrolytic degradation of epoxide-modified lignin was also highly affected by the PEGDE/AL ratio. In this way, changes in the distribution of functional groups and the cross-linking induced by epoxy groups may influence the carbon-carbon cleavage among lignin structural units [15,34]. Thus, the fragmentation of inter-unit linkages was shifted to temperatures higher than 400 °C for EAL1 and EAL2 samples, whereas much lower temperatures (325–350 °C) were found for EAL3, EAL4 and EAL5 samples, corroborating the lower epoxidation degree reached in these samples.

3.2. Rheological Characterization of Oleogels

The dispersion of epoxidized lignin samples in castor oil produces physically stable oleogels, except for the case of the EAL5 sample with the lower epoxy index, which shows phase separation immediately after preparation. This suggests the occurrence of chemical gelation via chemical interactions between castor oil hydroxyl groups and the remaining epoxy groups, as previously proposed for oleogels prepared with epichlorohydrin-functionalized lignins [21]. Figure 3 shows viscous flow curves of stable epoxide-functionalized lignin-based oleogels, as a function of both epoxy index (Figure 3a) and thickener concentration (Figure 3b). A power-law model (Equation (1)) satisfactorily describes the shear-thinning flow behavior observed within the shear rate range analyzed ($r^2 > 0.995$):

$$\eta = k\dot{\gamma}^{n-1} \tag{1}$$

where η is the viscosity, $\dot{\gamma}$ the shear rate and "k" and "n" are consistency and flow indexes, respectively. The values of "k" and "n" parameters are displayed in the insets in Figure 3a,b. As can be seen, extremely low values of the flow index were obtained for all samples, characteristic of the typical yielding flow shown by traditional lubricating greases [38]. The consistency index clearly increases with both the epoxy index and thickener concentration, which is in agreement with penetration values shown in Table 3. These penetration values serve to classify lubricating greases in terms of NLGI grades [39], which represent a measure of grease consistency or hardness (see Table 3). In addition, the lowest penetration value was obtained for the oleogel prepared with EAL1 sample at 10 wt % concentration. Henceforth, as can be expected, a lower PEGDE/AL ratio, i.e., higher epoxy index, favors the chemical interaction between epoxy and the hydroxyl group of ricinoleic fatty acid chain.

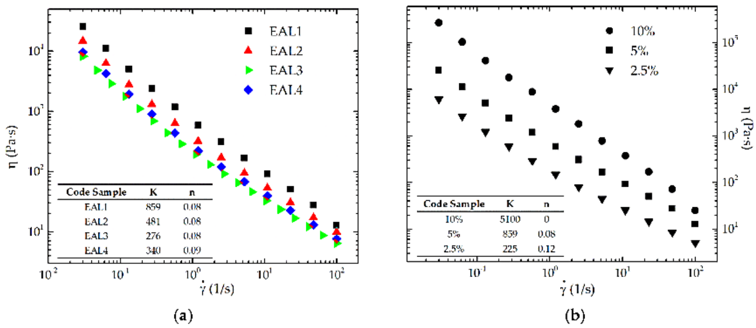

Figure 3. Viscous flow curves at 25 °C for epoxidized lignin-based oleogels as a function of (**a**) lignin epoxy index (5 wt % EAL) and (**b**) lignin concentration (EAL1 sample).

Table 3. Unworked penetration values and NLGI grade (ASTM D217) for EAL-based oleogels.

EAL Sample	EAL concentration (wt %)	Penetration (mm/10)	NLGI consistency number
EAL1	10	171	4
EAL1	2.5	350	0
EAL1	5	246	3
EAL2	5	316	1
EAL3	5	344	1
EAL4	5	328	1

Figure 4 shows the evolution of viscoelastic functions with frequency for the oleogels formulated with 5 wt % of several epoxidized lignin samples. In all cases, rheological measurements were done 24 h after oleogel preparation. These oleogels were compared with a reference prepared with non-epoxidized lignin and NaOH in the same proportion as in the oleogel containing the EAL1 sample. This reference was introduced in order to differentiate the effect of the residual NaOH in epoxidized samples on the rheological response of oleogels from the effect of lignin epoxidation.

As can be seen in Figure 4, the linear viscoelasticity response supports the idea that highly structured gels were obtained [38,40], where the values of the storage modulus, G′, were always higher than those of the loss modulus, G″, throughout the whole frequency range studied. The values of these viscoelastic moduli increased with the decrease of PEGDE/AL ratio, i.e., with the increase of the epoxy index, as a consequence of the higher density of crosslinking points induced by the reaction of epoxy and hydroxyl groups. On the other hand, the high amount of NaOH present in the highly epoxidized lignin sample brings about an additional stabilizing effect due to partial saponification of castor oil, as can be inferred from the rheological response of the reference. However, the effect of the chemical interaction between castor oil and the epoxidized lignin is well illustrated in Figure 4, where it is apparent that the oleogel prepared with the EAL1 sample showed values of both the storage and loss moduli significantly higher than the reference.

In addition, the influence of thickener concentration on the rheological behavior of these oleogels was studied for the most epoxidized lignin sample (EAL1). Figure 5 shows that the values of both storage and loss moduli increase with thickener concentration, which is also in accordance with the consistency index (Figure 3a) and penetration values (Table 3). It is worth emphasizing that the frequency dependence of SAOS functions is affected by the epoxide-functionalized lignin content. As can be seen, the minimum in the loss modulus, found at intermediate frequencies, was shifted to lower frequencies by decreasing EAL1 concentration. Moreover, a crossover between both SAOS moduli was detected at high frequencies for the 2.5 wt % concentration.

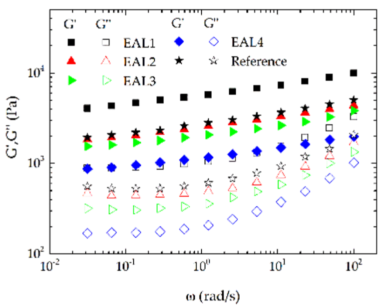

Figure 4. Evolution of the storage (G') and loss (G'') moduli with frequency for epoxidized lignin-based oleogel as a function of lignin epoxy index (5 wt % EAL). Star symbols correspond to the reference system prepared with non-epoxidized lignin and NaOH in the same proportion than sample EAL1. (G', filled symbols; G'', empty symbols).

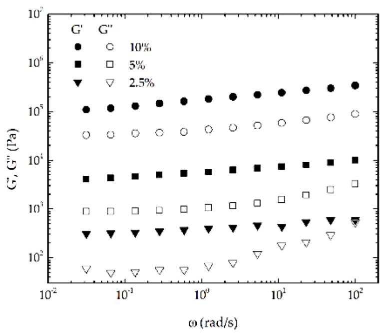

Figure 5. Evolution of the storage (G') and loss (G'') moduli with frequency for epoxidized lignin-based oleogels prepared with sample EAL1 at different concentrations (G', filled symbols; G'', empty symbols).

In order to obtain more information about the influence of functionalization degree on the rheological behavior of these epoxide-functionalized lignin-based oleogels, the plateau modulus, G_N^0, was estimated as shown elsewhere [41]. G_N^0 values for oleogels containing 5 and 10 wt % of modified lignin, as a function of epoxy index, are shown in Figure 6. G_N^0 was calculated from SAOS measurements one day and two months after oleogels preparation, resulting in quite different values as a consequence of the progress of crosslinking reaction. It is worth mentioning that, as expected, the reference system, i.e., the NaOH/non-modified lignin-based oleogel, did not show any change in the rheological response along time because of the lack of active groups. Moreover, the increase of plateau modulus with the rise of epoxy index was apparent for both thickener concentrations, following the same trend, i.e., approximately the same power-law exponent, which indicates an increase of inter-unit linkages. In addition to this, an internal curing process takes place during the 2 months after oleogel preparation, resulting in a significant increase of SAOS functions with aging time (Figure 6).

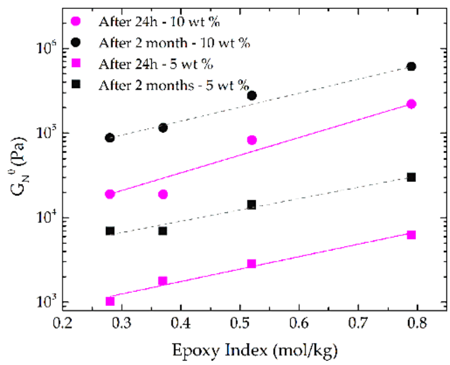

Figure 6. Evolution of G_N^0 with lignin epoxy index for EAL-based oleogels (5 and 10 wt % EAL) 24 h and 2 months after preparation.

As is well known, it is also important to evaluate the effects of temperature on the rheological behavior of semi-solid lubricants [42]. In this sense, Figure 7 shows the evolution of viscoelastic moduli with frequency for the selected oleogel over a wide range of temperature. As can be observed, the values of G' and G'' tend to decrease with the increase of temperature more dramatically above 100 °C, which is also associated with a significant increase of the loss tangent values, i.e., lower relative elasticity (Figure 7b). The effect of temperature on the plateau modulus is analyzed in Figure 8. A noticeable change in the evolution of G_N^0 versus 1/T was found at around 100 °C, which indicates a significant softening above this temperature. This result resembles the thermo-rheological behavior reported by Delgado et al. [42] for traditional lithium greases. As previously proposed [11, 43], this thermal dependence of the plateau modulus can be fitted to two different Arrhenius-type relationships in the ranges of 5 to 100 and 100 to 150 °C, respectively:

$$G_0^N = A \cdot e^{\frac{E_a}{R} \cdot \frac{1}{T}} \quad (2)$$

where Ea (J/mol) evaluates the thermal dependence in each temperature range, R is the gas constant (8.314 J/mol K), T is the absolute temperature (K), and A is the pre-exponential factor (Pa). Table 4 shows the fitting parameters of this equation in both temperature ranges for all oleogels studied. In all cases, low E_a values were obtained within the low temperature range, which indicates a very low thermal dependence of G_N^0. However, E_a values were much higher within the 100–150 °C range.

As can be expected, in this range, the thermal dependence of the viscoelastic functions was more significant on those samples which exhibited higher gel strength.

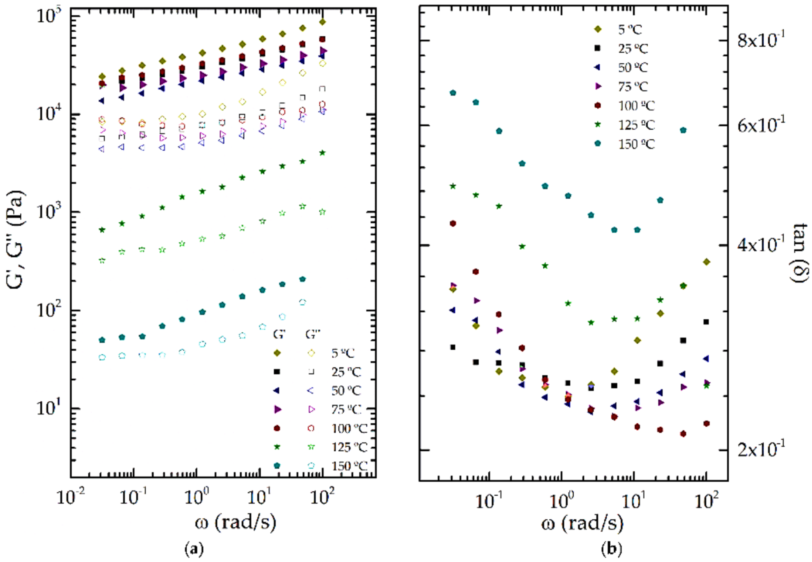

Figure 7. Frequency dependence of the storage and loss moduli (**a**) and the loss tangent (**b**) for a selected epoxidized lignin-based oleogel (EAL1 at 5 wt %) as a function of temperature (G', filled symbols; G'', empty symbols).

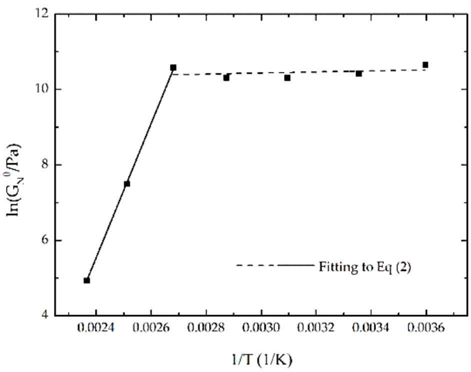

Figure 8. Evolution of $G_N{}^0$ with temperature for a selected oleogel (EAL1 at 5 wt %).

Table 4. Activation energy values for EAL-based oleogels.

EAL sample	E_a (kJ/mol)	
	5–100 °C	100–150 °C
EAL1	1.2	148
EAL2	0.1	116
EAL3	5.8	98
EAL4	7	96

3.3. Lubrication Performance of Oleogels

The lubrication performance of the epoxidized lignin-based oleogels studied was evaluated in the steel-steel ball-on-three-plates configuration of the tribological cell [24]. Figure 9 shows the friction coefficient versus rotational speed curves obtained under a normal load of 10 N for different tribological systems which include the epoxidized lignin-based oleogels as lubricants. The friction curve obtained using the neat castor oil as a lubricant was also introduced in order to assess the effect of the thickener. The influence of both epoxy index and concentration of the epoxide-modified lignin on the frictional behaviour of these oleogels was analyzed. In general, the evolution of friction coefficient with rotational speed followed the typical behavior described by the Stribeck curve. Initially, starting in the boundary film lubrication regime, the friction coefficient is relatively high and almost constant at low speed. The decrease with the increase of speed in the mixed friction lubrication regime was then detected, prior to an increase once a critical minimum value had been achieved, which preceded the hydrodynamic friction region.

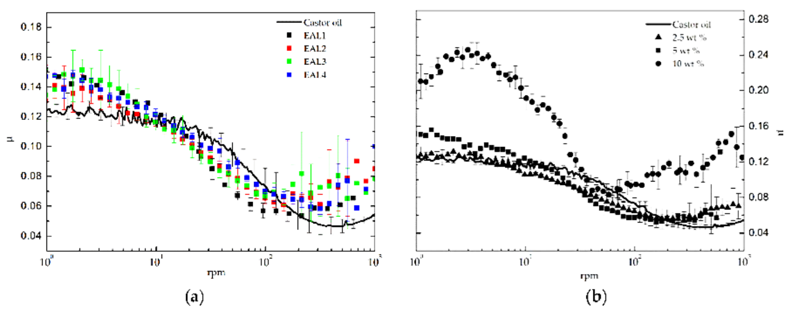

Figure 9. Friction coefficient versus rotational speed curves for epoxidized lignin-based oleogels as a function of (**a**) lignin epoxy index (5 wt % EAL) and (**b**) lignin concentration (EAL1 sample).

As can be observed in Figure 9a, in the boundary film region, the friction coefficient values for all oleogels are almost constant and are higher than the values found for the base oil, which is probably related to the reduced lubricant entrainment expected in the case of thick oleogels at low rotational speed, when the film thickness is still too narrow [44]. However, oleogels and castor oil friction curves get closer when increasing the rotational speed, finally yielding lower friction for oleogels within the mixed friction lubrication regime. This may be related to the fact that the thickener is able to penetrate into the contact area under this lubrication regime, thus increasing the film thickness and reducing friction. Finally, as expected, higher viscosity of oleogels in comparison with the base oil produces higher values of the friction coefficient along the hydrodynamic lubrication regime, where friction is essentially governed by lubricant properties. On the other hand, the lignin epoxidation degree does not exert a significant influence on the frictional behaviour, although slightly lower values of the friction coefficient were obtained for the oleogel containing the most epoxidized lignin (EAL1) in the mixed friction lubrication regime.

Regarding the thickener concentration, it was found that the oleogel prepared with 10 wt % of epoxide-functionalized lignin (EAL1) produced extremely high values of the friction coefficient within the rotational speed range studied, as a consequence of the highly viscoelastic behaviour. However, oleogels containing the same epoxidized lignin at concentrations lower than 5 wt % generally provide much lower values of the friction coefficient, similar to those provided by the neat castor oil.

4. Conclusions

Suitable thickeners for castor oil were obtained by means of chemical modification of alkali lignin (AL) with poly(ethylene glycol) diglycidyl ether (PEGDE) with the aim of developing environmentally friendly lubricating greases. The variation of the input PEGDE/AL ratio in the epoxidation reaction resulted in lignin compounds with different epoxy index and residual NaOH amounts, as a consequence of the two competitive reactions occurring during the synthesis process. Low PEGDE/AL ratios yielded lower consumption of NaOH but favored the etherification of the hydroxyl groups in lignin. Lignins epoxidized at different degrees showed different thermal degradation profiles. The higher the epoxy index, the higher the amount of char, as a consequence of higher etherification of lignin hydroxyl groups.

Epoxidized lignin-based oleogels are highly structured systems, which exhibited the typical viscoelastic response of solid-like gels and the typical yielding flow found in traditional lubricating greases. Moreover, an internal curing process, which promotes the evolution of the rheological properties with time, took place for two months. The values of viscosity, consistency and storage and loss moduli noticeably increased along with both epoxy index and thickener concentration. In addition to this, a power-law increase of the plateau modulus with the epoxy index was found for all thickener concentrations studied, which indicates that a higher epoxy index favors the inter-molecular linkages between lignin and the ricinoleic fatty acid of castor oil. The thermo-rheological characterization of these oleogels revealed a slight thermal dependence of the viscoelastic moduli below 100 °C but a significant softening above this critical temperature. This thermal dependence above 100 °C was more important on those samples with higher crosslinking density. From a tribological point of view, it is worth pointing out that oleogels containing 2.5 and 5 wt % of epoxidized lignin as thickener brought about low friction coefficient values when they were used as lubricants in a steel-steel ball-on-three plates tribocontact, lower than those obtained with the base oil alone within the mixed friction lubrication regime.

Author Contributions: All the authors have contributed equally to this work.

Funding: This research was funded by two research projects (CTQ2014-56038-C3-1R and TEP-1499) sponsored by MINECO-FEDER and Junta de Andalucía programs, respectively.

Acknowledgments: One of the authors (E. Cortés-Triviño) has received a Ph.D. Research Grant from the "Junta de Andalucía". The authors gratefully acknowledge its financial support.

Conflicts of Interest: The authors declare no conflict of interest.

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3. Article 3

Rheology of epoxidized cellulose pulp gel-like dispersions in castor oil: Influence of epoxidation degree and the epoxide chemical structure

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Published in:

Carbohydrate Polymers
Publishing company: Elsevier
Editor-in-Chief: Tatiana Budtova
Volume 199, pp 536-571
Year 2018
ISSN 0144-8617
DOI 10.1016/J.CARBPOL.2018.07.058

Category	**Journal rank / Total journals**	**Quartile**
Chemistry, applied	2/72	Q1
Chemistry, organic	6/57	Q1
Polymer Science	7/87	Q1
Impact Factor (2017)	5.158	

4. Article 4

Thermo-rheological and tribological properties of novel bio-lubricating greases thickened with epoxidized lignocellulosic materials

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Submitted in:

Journal of Industrial and Engineering Chemistry
Publishing company: Elsevier
Editor-in-Chief: Bok Ryul Yoo
ISSN 1226-086X

Category	Journal rank / Total journals	Quartile
Chemistry, Multidisciplinary	39/171	Q1
Engineering, Chemical	14/137	Q1
Impact Factor (2017)	4.841	

Chapter 5

General conclusions

The experimental research comprising this PhD has allowed to obtain several major highlights and conclusions which are described hereinafter:

- Several lignocellulosic materials, such as alkali lignin and cellulose pulp from *Eucalyptus globulus*, have been auspiciously modified through epoxidation reactions by using different (mono-, di- or tri-) functional epoxides, thus improving their compatibility with castor oil and promoting chemical gelification in this medium. Epoxidation reaction conditions (temperature, time and proportion of reagents) determine the epoxidation degree of the lignocellulosic materials. In addition, the chemical structure of the epoxy compound affects the thickening properties of these chemically modified biopolymers.

- Physically stable gel-like systems can be obtained by dispersing the epoxy-functionalized lignocellulosic materials in castor oil, as a result of the chemical crosslinking between free epoxy groups and hydroxyl groups of medium oil. These chemical interactions are responsible for the bulk properties of these oleogels. The use of aromatic epoxides as modifying agents provides a more extensive cross-linked network in the chemical oleogels, in comparison with aliphatic ones, at the same functionalization degree.

- The epoxidation of lignin and cellulose pulp was confirmed via determination of epoxy index (through titration according to standard norms), or by means of fundamental analysis, such as infrared spectroscopy (FTIR), thermogravimetric analysis (TGA) or differential scanning calorimetry (DSC). Thus, the appearance of new absorption bands in the infrared spectra of modified biopolymers, more specifically at around 910 cm^{-1}, corroborates the presence of free epoxy groups in the chemical structure of these lignocellulosic materials. Moreover, thermograms reveal the appearance of a new thermal decomposition step in the modified lignocellulosic materials, related to the dehydration of oxirane rings. Finally, lower glass transition temperatures are usually obtained in epoxidized lignocellulosic materials.

- ♣ The rheological behaviour of resulting gel-like dispersions is strongly affected by the epoxidation degree of lignin and cellulose pulp. Higher values of the viscoelastic functions, G' and G", were obtained with the increase in the epoxy index of modified lignin. On the contrary, when using cellulose pulp as raw material, the reverse effect was observed due to the rise of compatibility with the oily medium. An evolution of these rheological functions with the ageing time was also noticeable, as a consequence of an internal curing process.

- ♣ Rheological properties are also influenced by the thickener concentration, yielding an increase in the viscoelastic moduli with the increment of concentration.

- ♣ Most of the bio-lubricating greases developed by using epoxidized lignocellulosic materials and castor oil show a solid-like particle gels behaviour, exhibiting the typical viscoelastic response of commercial lubricating greases, especially samples EAL1 (5 % wt.), OECPN-2-5, OECPN-5-5, OECPB-4, and OECPR-4.

- ♣ The influence of temperature on the rheological properties of gel-like dispersions generally results in a decrease in viscoelastic functions, especially in lignin-based oleogels (at around 50 and 100 ºC for epichlorohydrin- and PEGDGE-modified lignin, respectively). On the other hand, cellulose pulp-based gel-like dispersions exhibit an excellent thermal stability, without showing significant changes in the rheological functions up to 150 ºC.

- ♣ The friction coefficient of oleogels based on epoxidized lignocellulosic materials and castor oil follows the typical evolution described by the Stribeck curve. Moreover, the introduction of the epoxidized cellulosic materials gives rise to a significant reduction in the friction coefficient in the mixed lubrication regime, with respect to that attained when only using castor oil as lubricant.

- ♣ In the mixed lubrication region, the friction coefficient slightly decreases by increasing the epoxidation degree of lignin. On the other hand, a low epoxy index and/or the use of aromatic epoxides in the preparation of cellulose pulp-based oleogels lead to a decrease in the friction coefficient.

- ♣ The effect of temperature on the tribological properties of chemically modified cellulose pulp gel-like dispersions in castor oil reveals a temperature-induced softening in all formulations, regardless of the modification degree, prevailing the tribological behaviour of the base oil at high temperatures.

- ♣ The use of epoxidized cellulose pulp as thickener substantially reduces wear in a tribological contact, in comparison to that obtained with castor oil alone. Wear scar diameters obtained by using bio-greases containing cellulose pulp with low epoxy indexes or epoxidized with aromatic epoxy compounds were smaller. At high temperatures (i.e. 95 ºC), however, wear results were quite similar for all samples as a consequence of softening and significant oil bleeding.

- ♣ Overall, epoxy-modified lignocellulosic materials have proven to be excellent thickening agents in castor oil, producing renewable and eco-friendly gel-like formulations, whose properties can be modulated by controlling the extent of epoxidation, giving rise to promising alternatives to conventional greases.

Conclusiones generales

La investigación experimental que conforma esta Tesis Doctoral ha permitido obtener una serie de hallazgos relevantes y conclusiones que se describen a continuación:

- ♣ Diversos materiales lignocelulósicos, tales como lignina álcali y pasta de celulosa procedente de *Eucalyptus globulus*, han sido favorablemente modificados mediante epoxidación con diferentes reactivos epóxidos (con uno, dos o tres grupos epóxidos terminales), mejorando su compatibilidad con el aceite de ricino y promoviendo una gelificación química en este medio. Las condiciones de la reacción de epoxidación (temperatura, tiempo y proporción de reactivos utilizados) determinan el grado de epoxidación de estos materiales lignocelulósicos. Además, la estructura química del compuesto epoxídico influencian en gran medida las propiedades espesantes de estos biopolímeros químicamente modificados.

- ♣ Oleogeles físicamente estables pueden obtenerse dispersando estos materiales lignocelulósicos químicamente modificados con grupos epóxidos en aceite de ricino, como resultado del entrecruzamiento químico producido entre los grupos epóxidos libres y los grupos hidroxilos del aceite de ricino. Estas interacciones químicas son las responsables de las propiedades finales de estos oleogeles. El uso de epóxidos aromáticos como agentes modificadores proporcionan un mayor nivel de entrecruzamiento en la red tridimensional de los oleogeles químicos comparados con los epóxidos alifáticos, para el mismo grado de funcionalización.

- ♣ La epoxidación de la lignina y de la pasta de celulosa se puede confirmar determinando su índice de epóxido (mediante técnicas volumétricas, de acuerdo a normas estándar), o mediante análisis fundamental como espectroscopia infrarroja, análisis termogravimétrico o calorimetría diferencial de barrido. Así, la aparición de nuevas bandas de vibración en los espectros de infrarrojo de los biopolímeros modificados, específicamente en torno a 910 cm^{-1}, ratifica la presencia de grupos epóxidos libres en la estructura química de los materiales lignocelulósicos funcionalizados. Además, los termogramas revelan la existencia de una nueva etapa de descomposición térmica en los materiales lignocelulósicos modificados, la cual está relacionada con la deshidratación del anillo oxirano. Finalmente, se obtienen temperaturas de transición vítrea más bajas en los materiales lignocelulósicos modificados con grupos epoxídicos.

♣ El comportamiento reológico de las dispersiones tipo gel resultantes depende, en gran medida, del grado de epoxidación de la lignina o de la pasta de celulosa. Así, valores más elevados de las funciones viscoelásticas, G’ y G”, se obtienen al aumentar el índice de epóxido de la lignina. Sin embargo, el efecto contrario se detecta cuando se usa pasta de celulosa como materia prima, lo que se atribuye a un aumento de compatibilidad con el medio oleoso. Por otro lado, las funciones viscoelásticas evolucionan con el tiempo de envejecimiento como consecuencia de un proceso de curado interno.

♣ Las propiedades reológicas dependen además de la concentración del bio-espesante, dando lugar a un aumento de los módulos viscoelásticos con el incremento de ésta.

♣ La mayoría de las grasas bio-lubricantes desarrolladas con materiales lignocelulósicos epoxidados y aceite de ricino muestran propiedades reológicas de geles particulados, exhibiendo además una respuesta viscoelástica característica de grasas lubricantes comerciales, en especial las formulaciones EAL1 (5% de concentración), OECPN-2-5, OECPN-5-5, OECPB-4 y OECPR-4.

- ♣ La influencia de la temperatura sobre las propiedades reológicas de las dispersiones tipo gel da como resultado, generalmente, una reducción de los valores de las funciones viscoelásticas, particularmente en oleogeles basados en lignina (a partir de alrededor de 50 y 100 ºC para los sistemas modificados con epiclorhidrina y PEGDGE, respectivamente). Sin embargo, las dispersiones de pasta de celulosa epoxidada muestran una excelente estabilidad térmica, sin cambios significativos de las propiedades reológicas hasta 150 ºC.

- ♣ El coeficiente de fricción de los oleogeles basados en materiales lignocelulósicos epoxidados y aceite de ricino sigue la evolución típica descrita por las curvas de Stribeck. Además, el uso de bio-espesantes epoxidados permite una reducción de los valores del coeficiente de fricción, en el régimen de lubricación mixta, comparados con el aceite de ricino como único lubricante.

- ♣ El coeficiente de fricción, en el régimen de lubricación mixta, disminuye ligeramente con el aumento del grado de epoxidación la lignina. Por otra parte, un bajo índice de epóxido y/o el uso de epóxidos aromáticos en el proceso de modificación de la pasta de celulosa da lugar a una disminución del coeficiente de fricción.

- ♣ La influencia de la temperatura sobre las propiedades tribológicas de las dispersiones tipo gel producidas con pasta de celulosa modificada y aceite de ricino es el resultado de un reblandecimiento inducido por la temperatura, independientemente de su grado de modificación, predominando el comportamiento tribológico del aceite de ricino a altas temperaturas.

- ♣ El análisis de los diámetros de las huellas de desgaste corrobora el sangrado del aceite en el contacto tribológico a altas temperaturas, mientras que el efecto del bio-espesante, es decir, un bajo grado de modificación o el uso de epóxidos aromáticos en biopolímeros de pasta de celulosa, reduce el desgaste a temperatura ambiente.

- ♣ El uso de pasta de celulosa epoxidada como espesante reduce sustancialmente el desgaste en un contacto tribológico, en comparación con el que se obtiene sólo con el aceite de ricino. Los diámetros de las huellas de desgaste obtenidos con el uso de bio-grasas que contienen pasta de celulosa con bajo índice de epóxido o epoxidadas con compuestos epoxídicos aromáticos fueron menores. Sin embargo, a altas temperaturas (i.e., 95 ºC), los resultados de desgaste fueron bastante similares para todas las muestras como consecuencia del ablandamiento y del efecto de 2sangrado” del aceite.

- ♣ En general, los materiales lignocelulósicos modificados mediante epoxidación han demostrado ser excelentes agentes espesantes en aceite de ricino, produciendo formulaciones tipo gel renovables y amigables con el medioambiente cuyas propiedades pueden ser moduladas controlando el grado de epoxidación, dando como resultado alternativas prometedoras a las grasas lubricantes tradicionales.

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