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Functionalization of biopolymers with reactive groups to be used as thickeners in oil media

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Bajo la dirección de los doctores:

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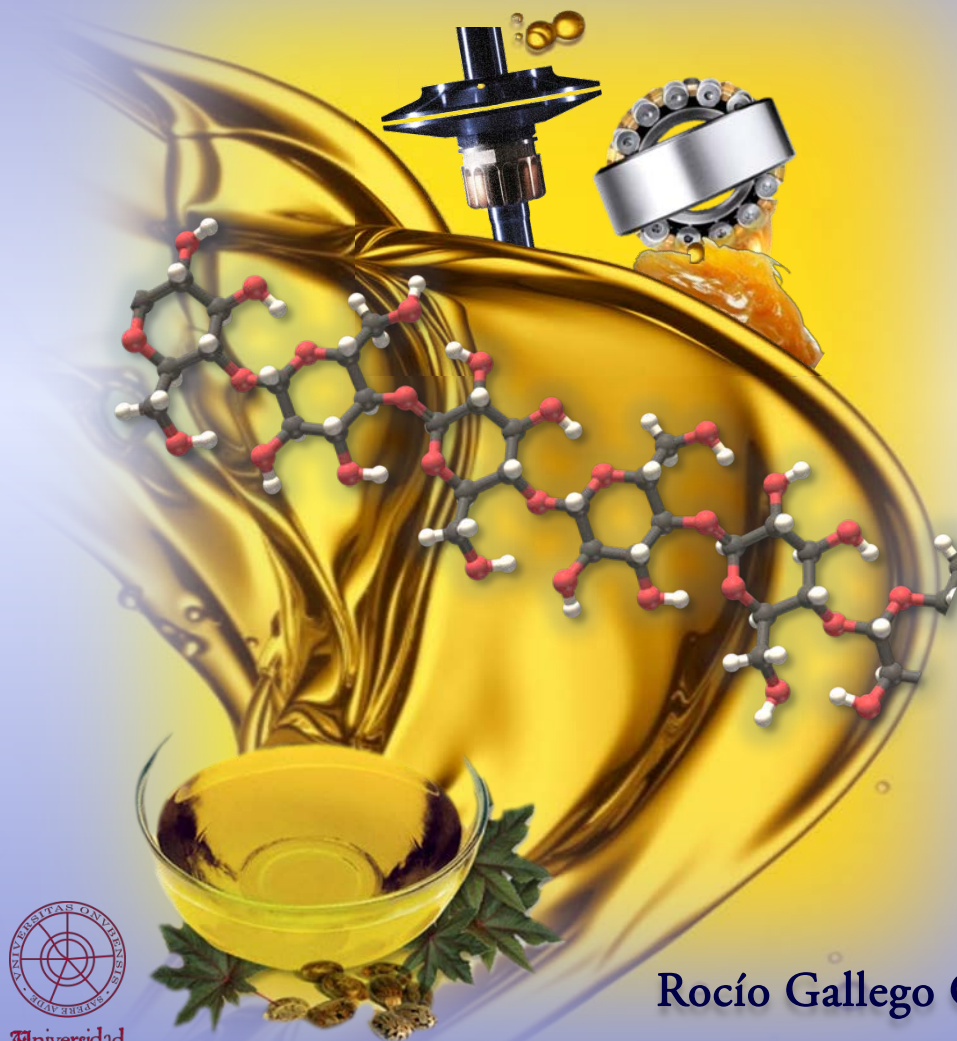
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FUNCTIONALIZATION OF BIOPOLYMERS WITH REACTIVE GROUPS TO BE USED AS THICKENERS IN OIL MEDIA

PhD Thesis



Rocío Gallego Calvo

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Department of Chemical Engineering, Physical Chemistry and Organic
Chemistry



FUNCTIONALIZATION OF BIOPOLYMERS WITH REACTIVE GROUPS TO BE USED AS THICKENERS IN OIL MEDIA

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FUNCIONALIZACIÓN DE BIOPOLÍMEROS CON GRUPOS REACTIVOS PARA SU USO COMO ESPESANTES EN MEDIOS OLEOSOS

Tesis Doctoral

Programa de Doctorado de Procesos y Productos Químicos

ROCÍO GALLEGO CALVO

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Rocío Gallego Calvo

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Contents

Chapter 1: Introduction	19
Resumen	21
1. Summary	22
2. Justification	23
3. Objectives	25
4. Structure	25
Chapter 2: State of the art	27
1. Biodegradable lubricating greases: Concept, importance and properties	29
1.1. Definition of lubricating grease	29
1.2. Rheology of lubricating greases	31
1.3. Tribological response of lubricating greases	40
1.4. Biodegradable greases	43
2. Oleogels	46
2.1. Organogels: Fundamentals	46
2.2. Biodegradable oleogels for lubricant applications	51
3. Biopolymers used as thickening agents	57
3.1. Cellulose and derivatives	57
3.2. Chitin and chitosan	60
3.2.1. Chitin	60
3.2.2. Chitosan	62
3.3. Lignocellulosic materials	64
4. Chemistry of isocyanates	75
5. References	80
Chapter 3: Materials and methods	105
1. Relevant materials	107
1.1. Starting materials for thickeners	107
1.1.1. α -cellulose and cellulose derivatives	107
1.1.2. Chitin and chitosan	109
1.1.3. Lignocellulosic materials	110
1.1.4. 1,6-hexamethylene diisocyanate (HMDI)	112

1.2. Castor oil	112
1.3. Other common reagents and solvents	114
2. Experimental procedures	114
2.1. Functionalization reaction of biopolymers	114
2.2. Crosslinking reaction in lignocellulosic materials	115
2.3. Processing of oleogels	115
3. Characterization techniques and equipment	116
3.1. Chemical characterization	116
3.1.1. Fourier transform infrared spectroscopy (FTIR)	116
3.1.2. ^1H -Nuclear magnetic resonance (^1H -NMR)	117
3.2. Thermogravimetric analysis (TGA)	118
3.3. Microstructural characterization	118
3.4. Rheological characterization	119
3.5. Tribological characterization	122
3.6. Standard mechanical tests	123
4. References	125
Chapter 4: Results and discussion	127
1. Compendium of publications	129
2. Block 1	131
2.1. Article 1	131
2.1.1. Resumen en español/summary in Spanish	132
2.1.2. Full article	135
2.2. Article 2	149
2.2.1. Resumen en español/summary in Spanish	150
2.2.2. Full article	153
2.3. Article 3	163
2.3.1. Resumen en español/summary in Spanish	164
2.3.2. Full article	167
3. Block 2	177
3.1. Article 4	177

3.1.1. Resumen en español/summary in Spanish	178
3.1.2. Full article	181
3.2. Article 5	199
3.2.1. Resumen en español/summary in Spanish	200
3.2.2. Full article	202
4. Block 3	221
4.1. Article 6	221
4.1.1. Resumen en español/summary in Spanish	222
4.1.2. Full article	226
5. Block 4	239
5.1. Article7	239
5.1.1. Resumen en español/summary in Spanish	240
5.1.2. Full article	242
Chapter 5: General conclusions	273
Conclusiones generales	279
List of Tables	285
List of Figures	291
List of Publications	303

Chapter 1:

Introduction

Resumen

Durante los últimos años, se ha desarrollado un creciente interés por el uso de componentes naturales en una gran variedad de productos manufacturados debido a la tendencia general existente que aboga por la sustitución de materias primas no renovables por aquellas provenientes de fuentes renovables. La industria de lubricantes está especialmente involucrada en la minimización del impacto ambiental de sus productos debido al grave problema que supone su liberación al medioambiente. Con este propósito, los aceites vegetales, candidatos prometedores para ser usados como bases lubricantes biodegradables y sustitutos potenciales de los aceites minerales, están siendo cada vez más considerados en el mercado. Sin embargo, la producción de una grasa lubricante completamente basada en materias primas renovables es una tarea mucho más compleja debido a la dificultad que supone la sustitución de los agentes espesantes tradicionales, tales como jabones metálicos o poliureas, que presentan una alta eficacia como espesantes de medios oleosos y confieren propiedades muy específicas al producto final. Así pues, este trabajo tiene como objetivo la producción de oleogeles químicos biodegradables, con propiedades lubricantes, compuestos por un aceite base vegetal, como es el aceite de ricino, y polímeros naturales modificados químicamente como agentes espesantes.

Para tal fin, se han seleccionado varias materias primas renovables, tales como la celulosa, el polímero más abundante en la naturaleza; derivados del mismo, como la metilcelulosa, entre otros; la quitina, segundo polímero más abundante después de la celulosa; el quitosano, el derivado desacetilado de la quitina; y pastas lignocelulósicas, de diferentes orígenes, sometidas a distintos tratamientos; las cuales han sido modificadas con grupos isocianato en diferente grado y, posteriormente, dispersadas en aceite de ricino para formar oleogeles cuya estabilidad se sustenta, principalmente, en interacciones químicas. Además, las propiedades funcionales de cada uno de los productos obtenidos fueron estudiadas empleando diversas técnicas y comparadas con estándares comerciales. Así, se ha evaluado la estabilidad térmica de los espesantes y de las correspondientes dispersiones en aceite de ricino, la respuesta reológica y tribológica de los oleogeles, conjuntamente con su estabilidad mecánica, así como la

estructura química de los biopolímeros modificados y la microestructura de los oleogeles. Como resultado de esta investigación, se han desarrollado una serie de formulaciones basadas completamente en materias primas renovables con propiedades funcionales (térmicas, reológicas y tribológicas) adecuadas para que puedan proponerse como sustitutos potenciales de las actuales grasas lubricantes comerciales.

1. Summary

During the last decades, there has been an increasing interest in the use of natural components in a wide variety of manufactured products, due to the general tendency to promote the replacement of non-renewable raw materials by renewable resources. The lubricant industry is especially involved in the minimization of the environmental impact caused by their products due to the serious consequences of their discharge to the environment. With this aim, vegetable oils, promising candidates to biodegradable lubricants and potential substitutes of the currently used mineral oils, are being more strongly considered in the market. However, the manufacture of lubricating greases completely based on renewable raw materials is a much more complicated task due to the difficulty of replacing the traditional thickening agents, such as metallic soaps and poliureas, which exhibit high technical efficiency and confer several specific properties to the final product. In this sense, the target of this work is the production of biodegradable chemical oleogels with lubricating applicability consisting of a vegetable oil, like castor oil, and chemically modified natural polymers that play the role of thickeners.

With this aim, some renewable raw materials have been selected, such as cellulose, which is the most abundant polymer in nature; some cellulose derivatives, like methylcellulose, among others; chitin, the second more important biopolymer after cellulose; chitosan, the deacetylated derivative of chitin; and some lignocellulosic materials that differ in their origins and pulping treatments. All of them have been NCO-functionalized, in some cases in different degrees, and subsequently dispersed in castor oil, promoting a chemical reaction between them that is the responsible of their physical stability. Furthermore, the specific functional properties of each of the

obtained products were studied through different techniques and they were also compared to commercial benchmarks. Therefore, the thermal stability of modified polymers and the corresponding dispersions in castor oil was explored, oleogels were rheologically and tribologically characterized, the mechanical stability evaluated as well as the possible chemical structure of the modified biopolymers and oleogel microstructures. As a result, a number of formulations completely based on renewable raw materials with suitable functional properties (thermal, rheological and tribological) to be proposed as potential substitutes of the current commercial lubricating greases were developed.

2. Justification

Nowadays, the society is increasingly aware of the importance of the preservation of the environment and, what is more, the corresponding governmental directives in numerous countries are promoting the introduction of renewable raw materials in different industrial applications. The lubricating sector is especially interested in the minimization of the environmental impact caused by these materials. In this sense, every year millions of tonnes of engine, industrial and hydraulic oils leak into the ground or waterways, or are disposed of in the environment, apart from the accidental oil spills, in which cleaning large amounts of money are spent. Moreover, mineral-based oils can contaminate groundwater for up to 100 years, which may inhibit the growth of trees and be toxic to aquatic life.

Consequently, the lubricating industry straightaway needs to include in the market new products completely based on renewable raw materials with adequate thermal, rheological, mechanical and tribological properties that help to overcome the former social and economic shortcomings. The importance of this target is reflected in the extent bibliography that precedes this work in which different attempts searching for the formulation that accomplish the desired conditions are reported. Most of the existing literature deals with the replacement of traditional liquid lubricants by vegetable and vegetable-derived base oils. On the other hand, it has also been reported the preparation of oleogels consisting of vegetable oils and cellulosic materials or their

chemical derivatives, fundamentally methyl- and ethylcellulose, which may be potentially applicable as lubricants. Despite the fact that promising results were obtained, especially when using methylcellulose together with ethylcellulose as thickeners and castor oil as lubricating base, for the moment, a number of fundamental problems hinder the consideration of these gels as real alternatives to conventional lubricating greases:

- Firstly, oleogels physical stability is limited, presenting problems of syneresis and oil bleeding after a short period of ageing. This instability can be minimized by incrementing the viscosity of the base oil or the biopolymer concentration. However, the availability of a wide range of viscosities in vegetable oils is much more limited than in the case of mineral oils. The option of incrementing the biopolymer concentration improves the physical stability of the suspension, but, on the contrary, provides it with rheological characteristics typically found in strong gels, different from those presented by lubricating greases.
- Secondly, the mechanical stability under severe operation conditions, evaluated by means of standardized tests, is not comparable to those showed by conventional formulations, especially at high temperatures. This behaviour is probably due to a poor physical interaction, traditionally named as “solvency” in the lubricant industry, between the oil and the biopolymer used as thickener.

A possible way of solving these problems is the chemical modification of the biopolymers proposed as thickening agents, so the solvency between them and the oil used as lubricating base increases. This work proposes the chemical modification of the most abundant natural polymers, such as cellulose and chitin, in order to increase the degree of interaction with the lubricating oil, once the oleogel is formed, both physically, reducing the polarity of the biopolymers, or chemically, through functionalization with reactive groups.

3. Objectives

The main objective of this Doctoral Thesis is the development of new thickeners for oil media by means of functionalization of biopolymers with reactive isocyanate groups with the aim of formulating oleogels with lubricating properties.

Regarding the specific targets of this research, on one hand, some natural polymers with certain organic groups in their structures, such as hydroxyl and amino, are selected to be chemically modified with a diisocyanate compound and subsequently dispersed in castor oil. The degree of functionalization with –NCO groups of the biopolymers and the concentration at which they are added to the oil are considered crucial points in the consecution of oleogels with different properties, so their control is one of the most important goals in this work. Therefore, the characterization of the resulting biopolymers and oleogels composes the next purpose of this investigation. Thus, the spectroscopic, thermal and microstructural characterization of both the thickeners and the corresponding formulations is performed. Moreover, the rheological and tribological behaviour of the oleogels, together with the mechanical stability, is also explored. Finally, the analysis of the applicability of the formulations as lubricating greases is made through the comparison of them with commercial benchmarks.

4. Structure

This Doctoral Thesis is divided in five chapters. Apart from the present introductory chapter, in chapter 2, a general description of lubricating greases, their typical rheological and tribological behaviour and the particular characteristics that biodegradable greases should possess is reported. In addition to this, fundamentals of organogels, focusing on oleogels, and the ultimate findings related to biodegradable oleogels for lubricant applications are stated. Moreover, the biopolymers that have been selected to be used as thickening agents, such as cellulose and some derivatives, chitin and chitosan and lignocellulosic materials, are described. With the aim of completing the information that is necessary for the understanding of this investigation, an overview on the chemistry of isocyanates, used as crosslinking agents, is also included. Afterwards, chapter 3 consists of the materials that have been used and the description

of the general methodology followed for the chemical modification of the natural substrates, the manufacture of the corresponding dispersions in castor oil and the characterization of both the thickening agents and the oleogels. Chapter 4 constitutes the main part of this manuscript, containing the obtained results and their discussion and is divided in 4 blocks, which are structurally connected. Each block comprises a number of articles, published or pendant of acceptance in several well reputed scientific journals, which are interrelated. Thus, the first three blocks are referred to the development of new thickeners based on different biopolymers and the resulting oleogels whilst the last one exposes the tribological behaviour of some selected formulations from each of the former blocks. Finally, chapter 5 collects the most relevant general conclusions that can be deduced from the results experimentally obtained.

Chapter 2:

State of the art

1. Biodegradable lubricating greases: Concept, importance and properties

1.1. Definition of lubricating grease

Lubrication is the improvement of the smoothness of movement of one surface over another by the use of a material called lubricant [Lansdown, 2004]. The use of the appropriate lubricant in any given application may reduce the demand for the necessary energy to drive the equipment and the machinery can give a higher reliability. In this way, less standstill time for maintenance may be needed and unexpected breakdowns avoided so the lifetime of the equipment will be appreciably extended and effective output increased [Hamnelid, 2000]. Most lubricants are fluids, such as oils; however, there are some applications in which liquids do not work properly and factors like fluctuations with temperature, loads, vibrations and surrounding environment conditions, within reasonable limits, can be all handled by using lubricating greases. In this sense, they can prevent the loss of lubricant under operating conditions, being especially indicated to decrease dripping, spattering and frequency of lubrication, and they can also act as seals, avoiding the penetration of contaminants.

Lubricating greases are generally described as structured colloidal suspensions where a solid thickener and/or gelling agent are dispersed in a lubricating oil [Hamnelid, 2000]. Some additional components, called additives, are normally included in order to improve specific properties and functions, like mechanical and thermal stability, corrosion and oxidation resistance, consistency or colour, among others. The most common composition of lubricating greases considers the use of mineral or synthetic oils and thickening agents based on fatty acid soaps of lithium, calcium, sodium, aluminium or barium, silica and bentonite particles or polyurea derivatives.

As detected by electron and atomic force microscopy, the thickener forms an entanglement network that traps the oil and confers the typical rheological properties of the lubricating grease (Figure 1) [Mas and Magnin, 1994; Sánchez et al., 2011a; Shuff and Clarke, 1991].

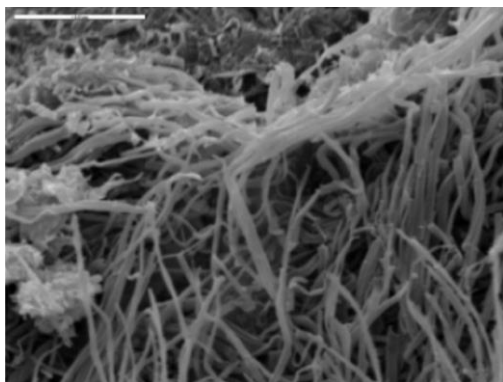


Figure 1. Lithium-based lubricating grease microstructure image obtained through scanning electron microscopy (SEM) at 3500x [Delgado et al., 2006a]

Different types of microstructure may be achieved by crystallization of the thickening agent forming fibers, rods or platelets with different configurations and characteristic sizes [NLGI, 2006]. The study of fiber growth and their network structure in grease matrix is required to relate base oil holding capacity and oil release by shear degradation of soap thickener during operation to additive compatibility, bleed resistance, viscosity, thermal stability, texture and appearance. Generally, the importance of the understanding of the microstructure resides in its significant contribution to several functional properties of lubricating greases. Many of these functional properties are dependent on their ability to flow under force, have shear stability, resist viscosity changes with temperature and pressure, show water resistance, seal out contaminants, decrease dripping and spattering, etc. Thus, the reliability of lubricating greases depends on their physical properties that are structurally related, which is obtained by the proper selection of the ingredients and processing protocol [Adhvaryu et al., 2005; Franco et al., 2005].

Lubricating greases should resist high and low temperatures, high pressures, and adverse atmospheres with high levels of moisture, powder concentration, or oxidative media, where their properties can be modified drastically while still retaining appropriate lubrication [Jhon and Choi, 2010; Jhon et al., 2003]. Moreover, as previously mentioned, the matrix of the bulk lubricating grease can absorb contaminants, such as particles and water, in relatively large amounts, without

reduction in its lubricating properties, as well. This is due to the fact that only a limited part of the lubricating grease is used for actual lubrication, the remaining acting as a seal [Hamnelid, 2000].

1.2. Rheology of lubricating greases

The main difference between lubricating greases and other lubricants is their characteristic rheological behaviour, frequently referred as consistency in the lubricant industry, which results from the addition of the thickener. Suitable rheological properties make possible the use of lubricating greases in applications where liquids do not work properly, acting as a solid or semisolid body at low stresses. The rheological behaviour and related functional properties of lubricating greases depend on both its composition and the manufacturing process used [Delgado et al., 2005a, 2006a; Franco et al., 2005]. There is a growing interest in the rheological characterization of lubricating greases [Gallegos et al., 1995; Whittingstall and Shah, 1998]; in fact, the lubricating industry is more frequently using rheological tests, not only as complementary information, but also as an alternative to the traditional technological ones. This importance arises, on one hand, from the manifest pseudoplastic behaviour of lubricating greases, characterized by the decrease of the apparent viscosity with the increase of the shear rate (Figure 2), and, on the other hand, from the strong dependence on time of their properties.

Thus, for instance, the evolution of the shear stress with time (Figure 3) exhibits a non-linear viscoelastic response with two distinct regions: the first one comprised between the onset of the transient test and the maximum shear stress, the so-called stress overshoot ($\tau_{\max}$), and the second one ranging between this maximum and the equilibrium or steady-state shear stress (τ_{eq}). The first part of these curves is mainly result of the well-known viscoelastic response of greases, being the elastic deformation the prevailing component. Once the stress overshoot is reached, the structural breakdown due to the shear flow process takes the main role. As a result, the shear stress monotonically decreases in this region until the steady-state level is reached,

which indicates that the time-dependent shear-induced microstructure become stable for the shear rate applied [Delgado et al., 2009].

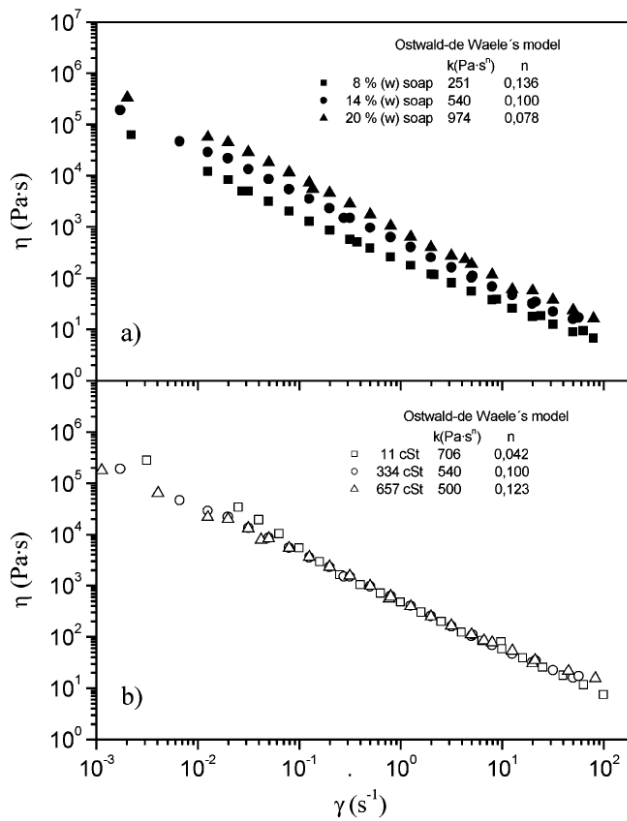


Figure 2. Pseudoplastic behaviour of lubricating greases (a) with different concentration of thickener and (b) based on oils with different viscosities [Delgado et al., 2006a]

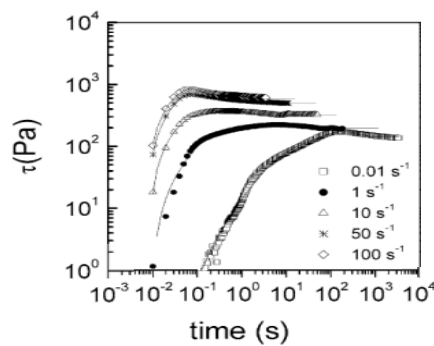


Figure 3. Evolution of the shear stress with time at different constant shear rates for a specific lubricating grease [Delgado et al., 2009]

Lubricating greases exhibit mechanical properties similar to gels at low strains, not flowing spontaneously, but after overcoming a certain yield stress, which decreases with the growth of temperature [Balan, 2000]. This effect controls the rheological performance of lubricating greases. Under the yield stress, elasticity and plasticity dictate the rheological behaviour of greases, the deformation process is extremely slow, yielding very low strain rates (10^{-5} s^{-1}), and therefore, the associated time observation scale is quite large. Over the yield stress value, the pseudoplastic character of lubricating greases is dominant.

Several flow problems that complicate the rheological characterization are usually observed in lubricating greases (Figure 4).

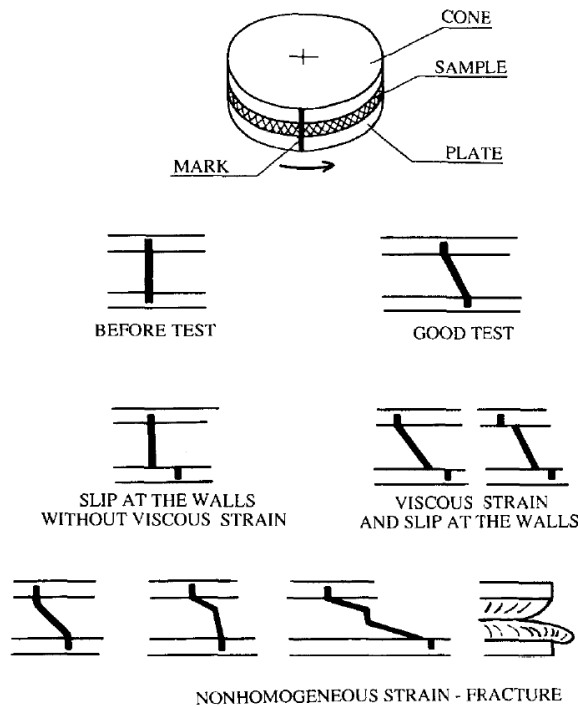


Figure 4. Schematic representation of common problems observed in viscous flow tests of greases such as wall slip, shear banding and fracture [Magnin and Piau, 1990]

Both, the effects of wall-depletion, caused by the presence of a thin layer of more easily deformable material than the bulk, next to the solid surface of the sensor, and shear-banding, which considers the existence of differently deformable zones within the

grease, originate non-homogeneous velocity gradients during viscous flow of lubricating greases [Balan and Franco, 2001]. This phenomenon favours the fracture of the grease microstructure at certain shear rates, hindering the clear observation of the real flow behaviour at high velocities.

Sample expulsion from the measuring system at high shear rates due to the centrifugal force was also observed in rotational viscometers. This fact implies the diminution of the contact surface between the sample and the sensor system, thus provoking measuring errors [Dobson and Tompsett, 1973]. Sample fracture and expulsion need to be considered in the interpretation of steady-state flow results, because of a sudden unreal reduction of the apparent viscosity [Bramhall and Hutton, 1960; Sacchettini et al., 1985]. Both effects usually appear in viscous flow test carried out in rotational rheometers at relatively high strain rates, up to $50\text{--}100\text{ s}^{-1}$ [Moreno et al., 2010].

The use of serrated geometries generates more representative rheological results because of the elimination of the wall slip effect, although favouring fracture. Apart from it, the dimensions of the geometry used in viscous flow tests influence the extent of the wall slip effect over the sample. The importance of the gap and the geometry of the sensor system increases in a certain strain rate range, being the viscosity measurements strongly influenced from 10^{-3} to 10^{-1} s^{-1} [Balan and Franco, 2001].

Regarding SAOS measurements, figure 5 shows the evolution of the storage (G') and loss (G'') moduli with frequency within the linear viscoelastic range for a typical lithium lubricating grease. As can be observed, this mechanical spectrum is quite similar to that exhibited by gel-like colloidal structures and highly entangled polymeric systems [Ferry, 1980] and is typically found in most of commercial lubricating greases [Sánchez et al., 2011a], confirming the fact that lubricating greases are highly entangled systems, as detected by electronic microscopy. On the other hand, the non-linear viscoelastic behaviour of lubricating greases has been modelled through the use of factorable constitutive equations, such as K-BKZ [Madedo et al., 2000].

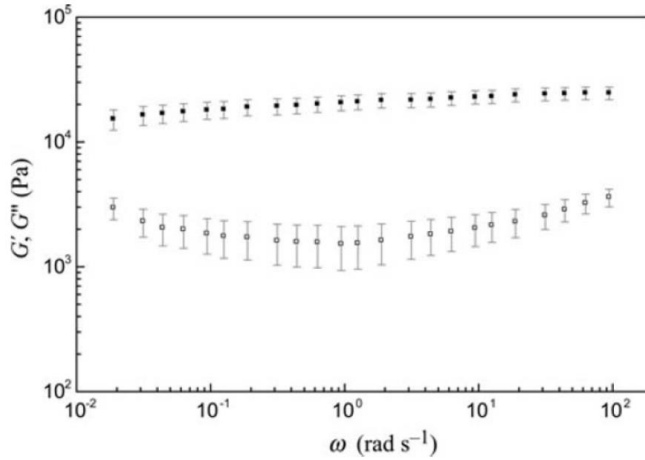


Figure 5. Lubricating grease mechanical spectrum [Delgado et al., 2005a]

Balan (2000) tried to make a compilation of possible relationships between microstructure and rheological behaviour of lubricating greases to justify the importance of Rheology on the characterization of these materials. However, as previously mentioned, certain difficulties derived from the assessment of the shear-induced microstructure complicate the rheological characterization of lubricating greases hindering the interpretation of the obtained results [Balan, 2000]. The elimination of the flow problems exhibited by lubricating greases is interesting from both the engineering [Delgado et al., 2005b; Dobson and Tompsett, 1973; Larson and Larson, 1968; Ruiz-Viera et al., 2006a, 2006b] and basic rheological [Delgado et al., 2006b] points of view. Previous knowledge of the rheological properties of lubricating greases provides with important information in order to predict their flow behaviour under processing, pumping or working conditions. Therefore, it is required the study of the flow and deformation of lubricating greases, in relation to their composition and structure. Accordingly, Delgado et al. (2006a) studied the effects that both soap concentration and base oil viscosity exert on the rheology of lubricating greases and its relationship with grease microstructure. As a result, the viscoelastic moduli increase with the thickener concentration, which is indicative of a stronger microstructural network, while the loss tangent remains almost unaffected (Figure 6).

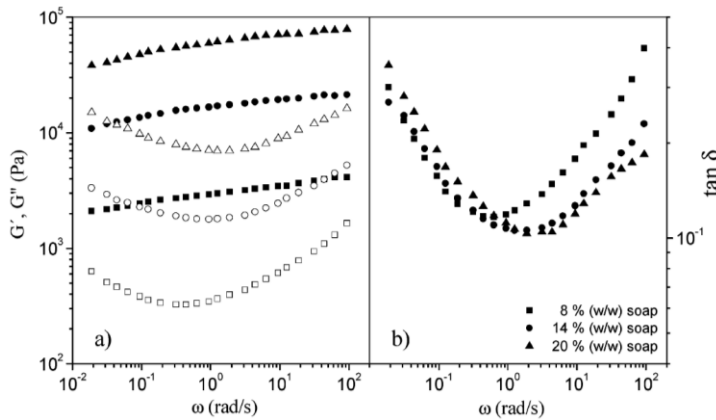


Figure 6. Influence of the thickener concentration on (a) the viscoelastic moduli and (b) the loss tangent [Delgado et al., 2006a]

The linear viscoelastic behaviour of lubricating greases is highly affected by oil viscosity, as well, obtaining that G' and G'' values noticeably decrease as the viscosity of the base oil increases (Figure 7a) whereas the loss tangent values increase by increasing oil viscosity (Figure 7b), indicating that the relative elastic characteristics of a lubricating grease increase by decreasing oil viscosity.

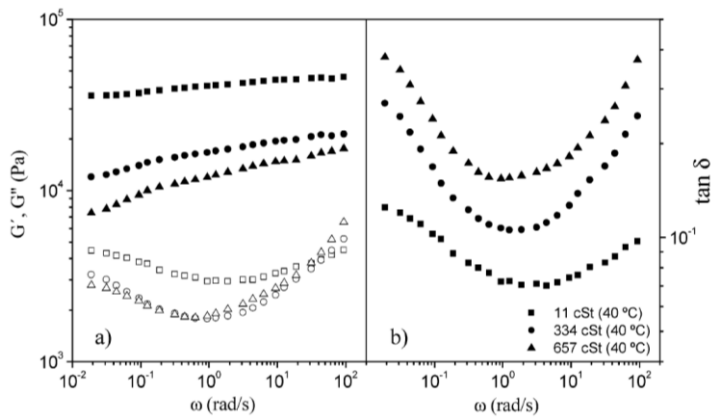


Figure 7. Influence of the oil viscosity on (a) the viscoelastic moduli and (b) the loss tangent [Delgado et al., 2006a]

In relation to the viscosity of the lubricating grease, it clearly increases with soap concentration (Figure 2a). However, the base oil viscosity does not exert a significant influence on it, although an opposite tendency has been observed at sufficiently high

shear rates, which indicates that the viscous flow behaviour is mainly governed by the base oil viscosity when the grease microstructure has been sufficiently destroyed. (Figure 2b).

Regarding the microstructure (Figure 1), it is highly influenced by the base oil viscosity and the thickener concentration. Consequently, large particles in form of platelets have been found at low soap concentration, while a high density of physical entanglements among fibers has been clearly observed at high concentrations. What is more, the oil viscosity not only affects the development and size of fibers, but also the size of hollow spaces among fibers where oil is trapped. So that, large fibers, but a weaker structure and lower density of entanglements, are obtained for greases prepared with high-viscosity base oil.

As well known, the rheological behaviour of lubricating greases can be modified with polymeric additives. In this sense, recycled [Martín-Alfonso, 2010; Martín-Alfonso et al., 2007, 2008, 2009a, 2009b] and reactive polymers [Moreno, 2012; Moreno et al., 2006, 2008a, 2008b] have been successfully introduced as rheology modifiers. Hence, the effect that different waste and virgin polymers, such as HDPE, LDPE, PP and EVA exert on the rheological properties of standard lithium lubricating greases has been evaluated, resulting in recycled polymers generally inducing a more important rheological modification than virgin polymers of the same nature [Martín-Alfonso et al., 2009a].

For instance, in the case of LDPE, the values of the plateau modulus (G_N^0) obtained for recycled LDPE-based lubricating greases are, in general, higher than those obtained for virgin LDPE-based grease formulations, as observed in figure 8. The increase in G_N^0 does not seem to be influenced by soap concentration (Figure 8a). On the contrary, larger differences between G_N^0 values of greases containing virgin or recycled LDPE are noticed as polymer concentration increases (Figure 8b). These results can be explained taking into account that recycled LDPE consists of a blend of polymers that improves the mechanical properties and resistance of the polymer, i.e. increased viscosity and elasticity [Martín-Alfonso et al., 2008].

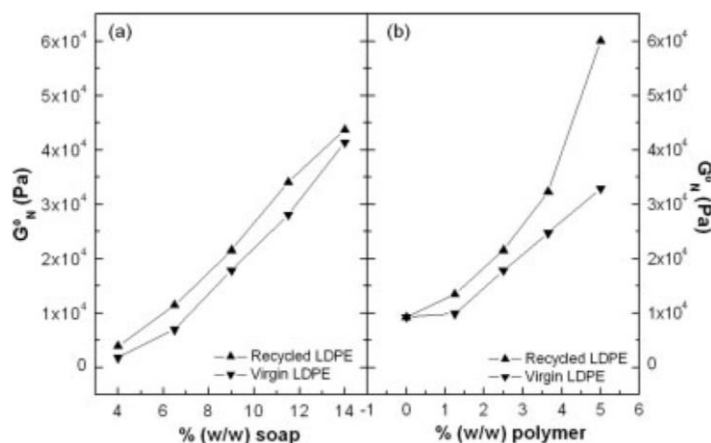


Figure 8. Values of the plateau modulus for lubricating greases modified studied as a function of (a) soap and (b) LDPE concentrations [Martin-Alfonso et al., 2008]

Alternatively, reactive diisocyanate-terminated polymeric materials were also tested as rheology modifiers of lubricating greases. In view of that, the influences that free –NCO content, molecular weight and functionality of the reactive prepolymers exert on the rheological response and microstructure of lubricating greases were analysed. Figure 9 shows the values of G_N^0 plotted versus –NCO content/prepolymer M_n ratio, both 24 h after grease manufacture and after 70–80 days ageing.

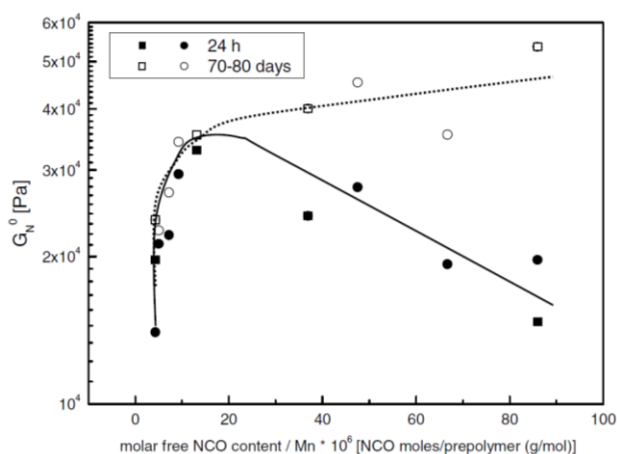


Figure 9. Evolution of the plateau modulus with the –NCO content/prepolymer molecular weight ratio, as a function of grease ageing, for greases containing either 3% w/w of reactive polymer (squares) or variable polymer concentration (circles) [Moreno et al., 2008b]

As can be observed, after 24 h ageing, the largest rheological modification is achieved at intermediate values of this ratio (around 15–25). Thus, low –NCO contents and high polymer molecular weights, and also high –NCO contents and low molecular weights should not be selected to yield a large rheological modification, at least just right after grease manufacture. However, this tendency changes with grease ageing. After 70–80 days ageing, due to the slow reactivity of the functional groups, the most effective modification is achieved for the highest values of the –NCO content/ M_n ratio studied. In addition, it is worth pointing out that ageing does not exert a significant influence on grease rheology below a certain threshold ratio (around 15) [Moreno et al., 2008b].

The influence of the addition protocol of the reactive diisocyanate-terminated polymer, i.e., poly(1,4-butanediol) tolylene 2,4 diisocyanate terminated prepolymer (PBTDI), to lithium lubricating greases on their rheological and morphological characteristics was also studied. The different processing phases and thermal protocol followed, as well as the different stages in which the PBTDI was added, are shown in figure 10 [Moreno et al., 2008a].

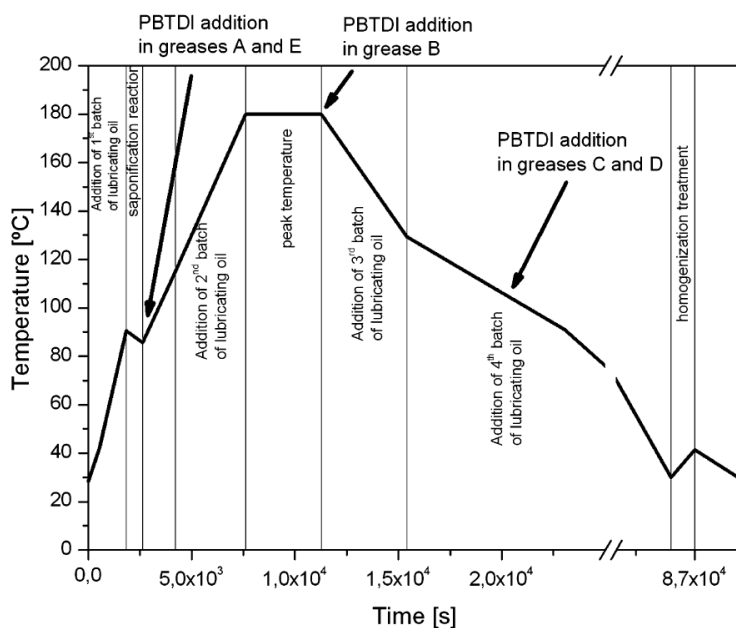


Figure 10. Processing stages and thermal protocol followed during the manufacture of lubricating greases [Moreno et al., 2008a]

Thus, the addition of PBTDI significantly increases the values of the linear viscoelastic functions of the lubricating grease with respect to the values found for the corresponding additive-free when it was added during the final cooling step of the manufacturing process. This occurs when the PBTDI is able to interact chemically with the soap network. Some competitive reactions due to either the presence of water or the high temperatures applied, which produce different amino or urea derivatives, are proposed to explain the loss of PBTDI effectiveness depending on the processing stage at which it is added to the lubricating grease [Moreno et al., 2008a].

1.3. Tribological response of lubricating greases

The lubrication process of greases in tribological systems (Figure 11) is not completely understood up to now. In a lubricated contact, lubricating greases are subjected to highly severe working conditions that produce structural and functional changes. This fact together with the lack of satisfactory relationships between the mechanism of film formation and the bulk properties of the grease, makes the prediction of the lubricating performance of specific grease for any given application [Cann, 1996] highly complicated. There is general knowledge based on the consistency (NLGI grade), the type of thickener, the nature and viscosity of the base oil and the mechanical stability of greases, simulated through different standardized technological tests [Baker, 1958], that help to understand the tribological behaviour of lubricating greases in a lubricated contact (lubrication process).

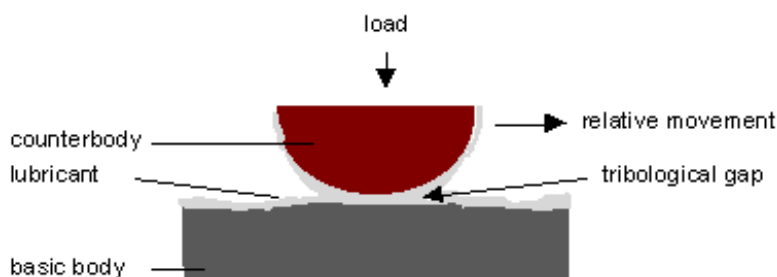


Figure 11. Scheme of a tribological system [Adelhelm, 2015]

Some decades ago, the lubricating capacity has been attributed only to the base oil. However, accurate microscopy techniques have demonstrated the presence of soap

particles in the contact surface [Astrom and Venner, 1994; Cann and Hurley, 2002; Hurley and Cann, 2000; Kauzlarich and Greenwood, 1972], giving importance to the role played by the thickener, as well. The entrance of soap particles into the contact zone causes an increase in viscosity of the elastohydrodynamic lubrication film, generating a thicker film than those found for the base oil alone, which produces a significant reduction in the friction factor [Hurley and Cann, 1999; Palacios et al., 1981; Rong-Hua, 1985]. Lubrication performance is also affected by the supply mechanisms of lubricant from the sides of the contact, which evidently depends on the flow properties of the grease.

The characterization of the frictional behaviour in lubricated systems is often carried out through the Stribeck curve. It relates the friction coefficient (μ) with the Sommerfeld number, which is defined as the product of dynamic viscosity (η) and tangential speed (U) divided by the normal contact load (F_N). This parameter influences the fluid film formation between the two surfaces in a tribo-contact and discriminates the regime of lubrication as boundary, elastohydrodynamic (EHL) or hydrodynamic (Figure 12) [Hutchings, 1992].

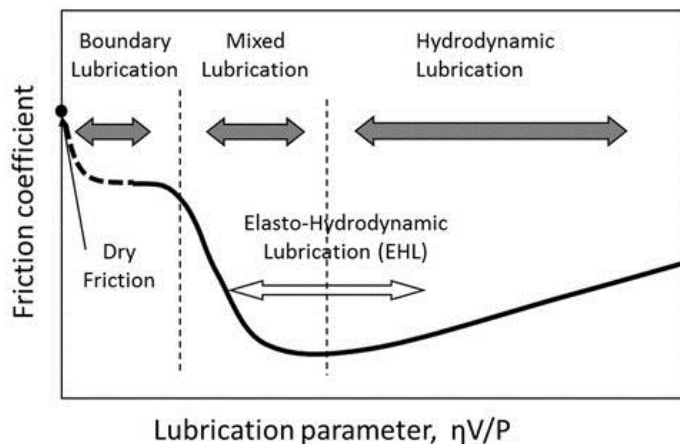


Figure 12. Lubrication regimes of the Stribeck curve [Kondo et al., 2013]

Despite the fact that the Sommerfeld number can be frequently used for oils (Figure 13) [Galda et al., 2009; Kalin et al., 2009; Sulek et al., 2010], it is not a common practice for lubricating greases because of their non-Newtonian behaviour.

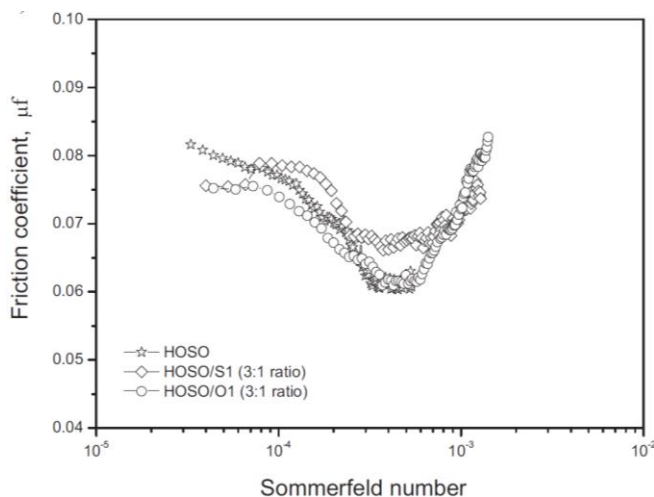


Figure 13. Stribeck curves of blends of high oleic sunflower oil (HOSO) and different estolides
[García-Zapateiro et al., 2013a]

Nevertheless, some authors utilize the Sommerfeld number with lubricating greases, but including the viscosity value of the corresponding base oil [Lu and Khonsari, 2007]. On the other hand, as an alternative to fulfil the tribological characterization of lubricating greases, instead of the Stribeck curve, it can be displayed the evolution of the friction coefficient with the velocity of the relative movement, i.e., sliding speed [Heyer and Läger, 2009]. In addition to this, in the way of completely knowing the tribological behaviour of lubricating greases, it is also interesting the obtaining of the stationary friction coefficient and the examination of the wear marks on the surfaces of the tribological contact.

As lubrication is mainly a deformation and flow phenomenon, a rheological characterisation of greases may contribute to elucidate some unresolved questions in Tribology, as for instance the effect of viscoelasticity on the lubrication process [Williamson et al., 1997]. Thus, the rheological characterization of lubricating greases may give interesting information susceptible of being empirically correlated with some tribological parameters, such as the friction coefficient [Couronné et al., 2003]. In general, both rheological and tribological behaviours of greases are related to the physico-chemical properties of the base oil (i.e. polarity and viscosity), the thickener concentration and the characteristics of the three-dimensional network resulting from

interactions between the soap particles and the base oil. Couronne' et al. (2003) found a significant influence of the soap-base oil interaction and proposed an interesting relationship among the storage modulus, the film thickness in the elastohydrodynamic lubrication contact and the friction coefficient. Similarly, the influence of some rheological parameters on the friction coefficient was also investigated by isolating the effect of composition in greases obtained with different processing protocols [Delgado et al., 2008]. Consequently, it can be assumed that the rheological parameters highly influence the tribological behaviour of lubricating greases [Delgado et al., 2009].

1.4. Biodegradable greases

Nowadays, there is a growing interest in the introduction of renewable raw materials in different industrial applications, especially in the lubricant industry [Hinman, 2003]. The development of biodegradable lubricating greases is mainly due to the new social environmental awareness and the corresponding governmental directives. The ideal aim is the generation of 100% biodegradable lubricants, which is not completely conceived yet. The next target is the design of a product with as much biodegradability potential as possible. For the regulation of the attainment degree of these environmental objectives, there are some labelling systems and classifications in different countries, such as the "Blue Angel" in Germany. An attempt of standardization of the different national ecolabels was made by the European Union, in 2005, creating the well-known "European Ecolabel for Lubricants" (EEL), directed to every lubricant that could be discharged in the environment during its use.

Until now, there is not any universal definition for biolubricants; however, it is generally assumed that they are products based on renewable raw materials with low or non-existent toxicity [Bremmer and Plonsker, 2008; Lathi and Mattiason, 2007; Theodori et al., 2004]. Moreover, the lubricating properties should not be negatively affected by the insertion of biodegradability [Loderer, 1995]. In this sense, biolubricants can be defined as ecological and non-toxic lubricants that meet the technical requirements imposed by national and international regulations and satisfy consumers' necessities [Krop and Oijen, 2010].

In the case of liquid lubricants, the use of vegetable oils is widely spread [Asadauskas et al., 1996; Randles and Wright, 1992; Wu et al., 2000] due to a number of valuable characteristics like high lubricity, easy adhesion to metal surfaces, weak viscosity-temperature dependence, low volatility, solvency for lubricant additives, easy miscibility with other fluids, low toxicity and high biodegradability, originated in renewable resources which depend on crops and higher flash point that make them safer for human use despite the fact that they are inflammable [Adhvaryu and Erhan, 2002; Erhan and Asadauskas, 2000; Lea, 2002; Maleque et al., 2003].

On the other hand, they also show certain limitations that restrict their applicability like poor thermo-oxidative stability, deficient low temperature flow properties because of crystallization, small range of viscosities, rather variable chemical compositions, higher insaturation degree so less oxidation resistance, higher costs associated to crops and transformation, prone to foam and less filterability [Lea, 2002; Maleque et al, 2003].

Nonetheless, previous studies demonstrated that these disadvantages can be easily overcome by using proper additives, as happen to the low oxidative stability [Alias et al., 2009; Becker and Knorr, 1996] and pour point [Asadauskas and Erhan, 1999; Kasturi and Carrick, 1994]. With this aim, Erhan et al. (2006) presents a systematic approach to improve both the oxidation behaviour and low temperature fluidity of vegetable oil derivatives based on the combination of chemical additives, diluent (polyalphaolefin) and high-oleic vegetable oils. Superior oxidation stability was also achieved through a series of structural modifications of vegetable oils using anhydrides of different chain lengths [Sharma et al., 2006]. In addition to this, blends of high-oleic sunflower oil (HOSO) and polymeric additives, such as ethylene vinyl acetate (EVA) and styrene-butadiene-styrene (SBS) copolymers resulted in an improvement of the low viscosity values of this oil with the only drawback of the increase of viscosity thermal susceptibility [Quinchia et al., 2009]. Moreover, EVA demonstrated to be a successful viscosity modifier, not only for HOSO, but also for vegetable oils like sunflower oil (SO) and soybean oil (SYO), at moderate temperatures [Quinchia et al., 2010]. Furthermore, the use of estolides or blends of various ratios of estolides obtained from different origins with vegetable oils of different viscosities, such as high-oleic

sunflower (HOSO) and castor oils (CO), issues a wider viscosity range [Biresaw et al., 2007; García-Zapateiro et al., 2013a, 2013b; Salimon et al., 2011]. Besides, the use of multifunctional biodegradable additives has been reported; not only to improve the properties of vegetable oils [Shui et al., 2012], but also as bio-additives of lubricating greases [Chen et al., 2012, 2014].

With respect to semisolid biolubricants, currently commercialized biodegradable greases have the same composition as the non-biodegradable ones excepting for the base oil. Mineral oils, that are non-biodegradable, are being substituted by biodegradable synthetic and vegetable oils like soybean, castor and rapeseed oils [Terradillos and Bilbao, 2004], but they usually maintain metallic soaps as thickening agents, i.e. calcium soaps. Thus, these lubricating greases based on vegetable oils keep on being semi-solid colloidal dispersions of a thickening agent, generally a metallic soap, in a matrix of biodegradable lubricating liquid [Adhvaryu et al., 2005]. Lubricating greases considered as biodegradable at this moment may have the following composition [Stempfel, 1998]:

- Base fluid (75-95%):
 - Vegetable oils
 - Synthetic esters
 - Glycols
- Thickener (5-20%):
 - Metallic soaps (preferably calcium)
 - Bentonite / silica / clays
 - Aluminium complex soaps
- Additives (1-8%):
 - Antioxidants
 - Corrosion inhibitors
 - Antiwear additives

- Additives to improve adhesive properties
- Antifoam additives
- Dyes

The excellent affinity between vegetable oils and metallic surfaces provides with intrinsic anticorrosion properties so it is not common the use of anticorrosion additives. If necessary, the amount of additive required to obtain the same anticorrosion properties offered by non-biodegradable lubricating greases is quite few [Stempfel, 1998]. Some previous modifications of the vegetable oil used in the formulation may impart even better properties like better oxidative stability [Adhvaryu et al., 2000]. Nevertheless, some limitations, mainly referred to the optimal working temperature ($-20 - 80\text{ }^{\circ}\text{C}$) [Adhvaryu et al., 2005; Loderer, 1995; Stempfel, 1998] and the limited range of viscosities available [Quinchia et al., 2009, 2010], were found.

In the case of fully biodegradable lubricating greases, their production requires not only the replacement of the mineral oil by a suitable vegetable one [Stempfel, 1998], but also the selection of an appropriate thickening agent obtained from renewable resources. As exposed above, oil substitution has been satisfactorily addressed [Dresel, 1994], but the replacement of the thickener is a much more complex task to solve due to the high technical efficiency of traditional metallic soaps imparting the desired rheological, thermal and tribological properties to the bulk system. However, different molecules and biopolymers derived from natural resources are being investigated as thickening agents in the formulation of biologically and environmentally acceptable lubricating greases. A more extensive review of the existing literature on the use of bio-thickeners is provided in section 2.2.

2. Oleogels

2.1. Organogels: Fundamentals

As well known, organogels are reversible liquid-like or solid-like viscoelastic materials comprised of an organic liquid and low concentrations (typically $<2\text{ wt } \%$) of relatively low molecular mass molecules, i.e., gelators. Gels are at the interface between

“complex fluids” [Gelbart and Ben-Shaul, 1996] and phase-separated states of matter, demonstrating physical properties that range from those of surfactants in solution [Hoffmann, 1990], such as micellization, lyotropism or crystallization, to those of polymer solutions [De Gennes, 1979], like swelling or microscopic mass motion. Organogels should meet two loosely defined criteria, one structural and the other rheological:

- They have a continuous structure with macroscopic dimensions that is permanent on the time scale of an analytical experiment, due to they are composed predominantly of a liquid at the microscopic scale.
- They are solid-like in their rheological behaviour, so that, they return to their original form when relieved of an applied stress, below a certain limit.

The macroscopic recognition of a gel state is somewhat ambiguous, and various classifications have been proposed based on either morphology, consistency or chemical and mechanistic considerations [Ferry, 1980; Hermans, 1949; Russo, 1987]. Nevertheless, rheological properties seem to be the best diagnostics to follow the changes in gelator aggregation during the sol-to-gel and gel-to-sol phase transitions [Almdal et al., 1993] (Figure 14).

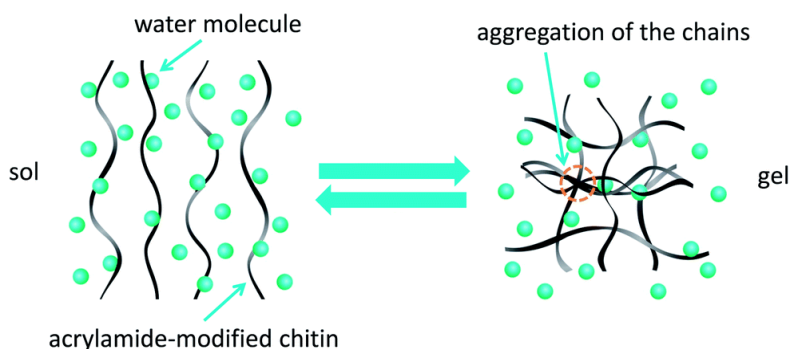


Figure 14. Schematic example of sol-to-gel and gel-to-sol phase transition [Ding et al., 2014]

Gelator molecules self-assemble through highly specific interactions, allowing preferentially one dimensional growth, usually to form fibers, strands or tapes, which are frequently crystalline. The elongated objects join in three-dimensional networks that

encapsulate the liquid component and inhibit its flow. The junction zones among these structural units provide rigidity to the microstructure [Murata et al., 1996; Shinkai and Murata, 1998; Terech, 1997, 1998; Terech and Weiss, 1997, 1999]. Gelation occurs when the individual colloidal units interact physically while pervading the liquid volume. A highly porous superstructure of elongated objects can immobilize efficiently a large volume of liquid via surface tension and related forces [Van der Schoot, 1999]. The most efficient mode for the immobilization of a large volume of liquid by a small quantity of gelator is for the elementary assemblies to be rod-like. The structure of linear aggregates in the gel is determined by the direction and strength of the binding forces associated with the aggregation process. Although it is generally assumed that strong intermolecular forces such as H-bonding, electrostatic attractions or $\pi\pm\pi$ stacking interactions are necessary to stabilize gelator assemblies [Bhattacharya and Acharya, 1999; De Vries and Kellogg, 1993; Hanabusa et al., 1999; Kimura et al., 1999; Sobna and Fages, 1997], recent observations [Abdallah and Weiss, 2000] have demonstrated that London dispersion forces alone can be sufficient. They must balance the free energy increase that accompanies reductions in translational and rotational freedom of motion. The physical gelation process is thermally reversible, so that, a sample can be heated above and cooled below the gel transition temperature, T_{gel} , (or vice versa, depending on the sample) many times to transform a gel into a sol and then back into a gel unless there is thermal decomposition (Figure 15).

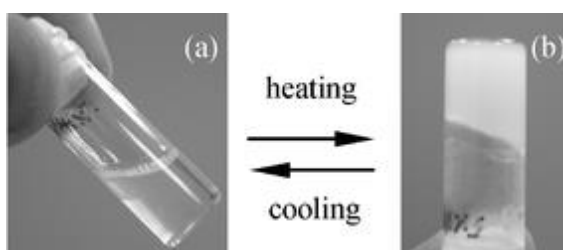


Figure 15. Appearance of a specific sample in the different phases of the reversible sol-gel process
[Kidowaki et al., 2006]

The gelator-gelator interaction energy determines the aggregation threshold and the size distribution of the aggregates. The size distribution of the chain-like aggregates is

usually very broad and depends strongly on gelator concentration and temperature. It can also depend on the (very small) concentration and structure of cosurfactants that have a strong affinity for the gelator and function as “chain terminators” or “chain growth inhibitors” by interrupting gelator-gelator interactions. For this reason, the composition and the method of preparation of the gelling mixtures must be controlled carefully, as well as factors affecting the aggregation process, such as solvent nature, polarity, conformational lability and molecular shape of the gelator and temperature.

Two different types of 3D networks and viscoelastic materials can be obtained in organogels systems (Figure 16).

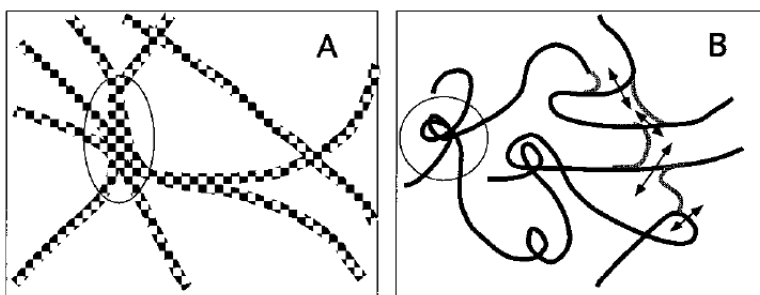


Figure 16. Nature of (a) strong and (b) weak gels network [Terech and Weiss, 1997]

On one hand, strong gel-like systems (Figure 16a) are materials exhibiting a solid-like, viscoelastic, mechanical behaviour and which are made of permanent networks obtained through a sharp solution- or sol-to-gel phase transition at a specific temperature. On the other hand, weak gel-like systems are materials exhibiting liquid-like viscoelastic behaviour which are made of transient networks obtained through a much smoother threshold somewhat analogous to the glass transition of polymers. They usually exhibit enhanced elasticity on short time scales. Both types of networks are thermally reversible, therefore, on heating, the supramolecular architecture is melted and individual molecules (or separated strands of aggregated molecules) are redispersed in the bulk solution. On the contrary, chemical gels arise as a result of a chemical reaction and, generally, the network is permanent and non-thermally reversible.

An efficient methodology to elucidate the nature of an organogel is to begin with a characterization of its rheological and thermodynamic properties. Rheology offers a convenient method to measure the flow and viscoelastic properties of gel-like materials and facilitates the classification between “strong” and “weak” gel types [Ferry, 1980]. Mechanical parameters indicate the nature of the aggregate networks which, successively, suggest the nature of the interactions responsible for their cohesion. Procedures such as steady-state shear, oscillation, stress relaxation and creep experiments can probe the mechanical properties of soft viscoelastic materials. Regarding the thermal behaviour, characterization of the phase diagram and determination of the T_{gel} are necessary. The methods used for this purpose include differential scanning calorimetry (DSC), temperature sweep rheological experiments, and different spectroscopies (fluorescence, IR, EPR, NMR, etc.) using the amplitude variation of a spectral feature with temperature to trace the aggregation phenomenon during which gelation occurs. It is also useful to investigate the structures of the unidirectional aggregates whose interactions are responsible for viscoelasticity. Electron micrographs are informative but should be combined with complementary methods, like scattering techniques, such as small angle neutron scattering (SANS) or small angle X-ray scattering (SAXS). Electron microscopy (EM) provides structural information in direct space whereas scattering data are reported in reciprocal distance space, necessitating a mathematical analysis and transformation to extract structural information.

Gels have numerous industrial applications due to the great diversity of the structures that may be achieved on microscopic and mesoscopic scales [Prost and Rondelez, 1991]. Their thermoreversibility, chemical sensitivity and diversity of nanostructures are intrinsic characteristics of organogels which make them excellent candidates for future industrial developments. Up to now, gels can be applied in duties like recovery of spilled oil, drug delivery, aviation fuels, explosive technologies and acoustic applications through aerogels, among others, being important in areas such as hydrometallurgy, cosmetics, food processing and lubrication [Haering and Luisi, 1986].

2.2. Biodegradable oleogels for lubricant applications

Oleogels are a specific kind of organogel in which the organic liquid composing the continuous media has oily nature. It is well-known that substituted fatty acid and monovalent metal salts, such as 12-hydroxystearic acid (Figure 17a) and its related salts (Figure 17b), create hardened materials from organic liquids [Polishuk, 1977; Uzu, 1975]. In fact, semisolid dispersions of the lithium salt of 12-hydroxystearic acid in oils have been used in the lubrication industry over decades [Boner, 1960; Fiero, 1940].

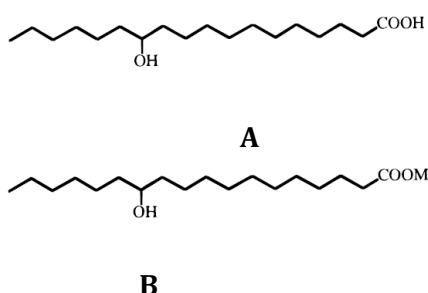


Figure 17. (a) 12-hydroxystearic acid and (b) corresponding salt

The 3D networks of aggregated fatty acid molecules act as a “sponge”, maintaining the oil component in lubricating greases [Boner, 1960] close to the friction regions of metallic surfaces [Georges, 1982] in various mechanical systems. In addition to this, divalent or trivalent metal salts of fatty acids, like $C_{16}DP-Al$ (Figure 18), have been used in lubricating applications for many years due to their thickening properties, as well.

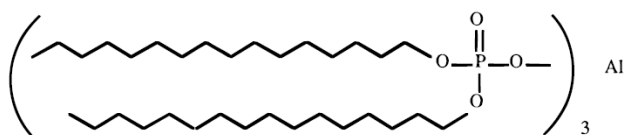


Figure 18. $C_{16}DP-Al$ molecular structure

However, metallic soaps exert noticeably negative impact on nature. This, together with the fact that every year millions of tonnes of oil are leaked into the environment,

promoted a slow but steady movement toward the use of environmentally-friendly or more readily biodegradable lubricants during the last decade. Oleogels have not been still widely explored for lubricating applications. Nevertheless, it is obvious that the lubricants industry and its customers are interested in new products that do not diminish the world finite resources of mineral hydrocarbons and, on the other hand, have a minimal adverse impact on the environment. It is worth remembering that fatty acid-based products from vegetable and animal origins were used as lubricants in the past until mineral oils began to become available in large volumes with competitive prices. Now, it is time to come back to vegetable oils to act as liquid lubricants and introduce biodegradable semisolid lubricants based on vegetable oils and biopolymers playing the role of thickeners. As mentioned before, the use of vegetable oils is widely accepted in the industry; however, the satisfactory performance of biopolymers as thickening agents is, up to now, a difficult goal to reach. Apart from providing suitable rheological characteristics, alternative eco-friendly thickeners need to impart additional properties like thermal and mechanical stability. This means that gel-like properties must be preserved at temperatures of around 100-150 °C and recovered after working in a lubricated contact. These conditions cannot be achieved by the previously described organogels due to their T_{gel} , which is excessively low. In this sense, gel-like colloidal dispersions may accomplish the required characteristics better than pure gels.

In previous research, some oleogels containing sorbitan monostearate as gelling agent showed viscoelastic properties and tribological characteristics similar to those found in standard lithium greases. Nonetheless, some weaknesses were observed regarding their mechanical stability and properties thermal dependence [Sánchez et al., 2008]. On the contrary, an improved thermal resistance was found in formulations thickened with cellulose derivatives, even better than that found for standard lubricating greases. That happened to both α -cellulose and methylcellulose-based oleogels which, presenting an evolution of the viscoelastic functions similar to that found in traditional lubricating greases, showed higher thermal stability, being methylcellulose-based oleogels even more thermally resistant than α -cellulose-based ones. However, these formulations behaved as strong gels exhibiting SAOS functions one decade higher than traditional

lubricating greases, due to the high content of thickener necessary to achieve physical stability, and low mechanical stability. Conversely, when ethyl cellulose is dispersed in castor oil a very homogeneous gel-like oily phase is achieved, even more viscous than castor oil, and lower amounts of thickener are necessary to inhibit oil separation, even under severe working conditions. Consequently, lower values for the SAOS functions were obtained, maintaining similar thermal resistance, although a high level of leakage appeared as the main drawback. Furthermore, mechanical stability values comparable to that found for commercial greases were provided by blends of ethyl and methyl cellulose (i.e. 2% and 30%wt., respectively) [Sánchez et al, 2009]. In addition to this, the influence that ethyl cellulose molecular weight exerts on the final properties of oleogels formulated with castor oil and α -cellulose/ethyl cellulose or methylcellulose/ethyl cellulose blends was investigated (Figure 19).

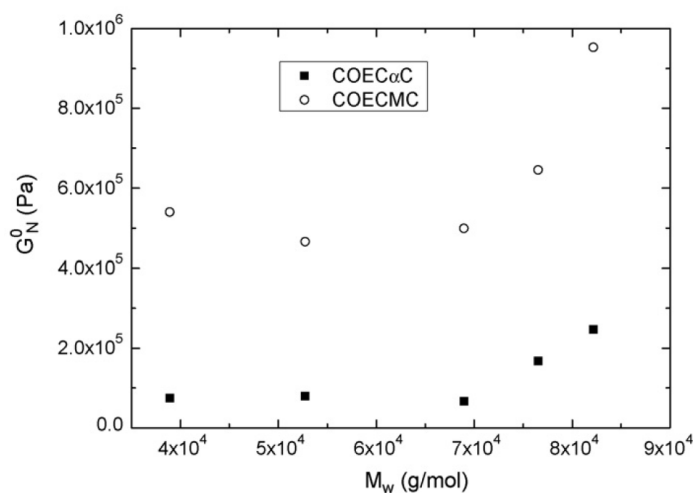


Figure 19. Influence of the ethyl cellulose molecular weight on G'_N of both α -cellulose and methylcellulose-based oleogels [Sánchez et al., 2011b]

As a result, it can be concluded that oleogels SAOS functions are influenced by ethyl cellulose molecular weight only above a critical value ($M_w < 70,000$ g/mol). Moreover, the improved mechanical stability demonstrated by oleogels containing methylcellulose/ethyl cellulose blends is enhanced by increasing ethyl cellulose molecular weight [Sánchez et al., 2011b].

The effect of cellulosic derivatives concentration ratio on the properties of these oleogels composed of α -cellulose/ethyl cellulose and methylcellulose/ethyl cellulose blends was also studied (Figure 20).

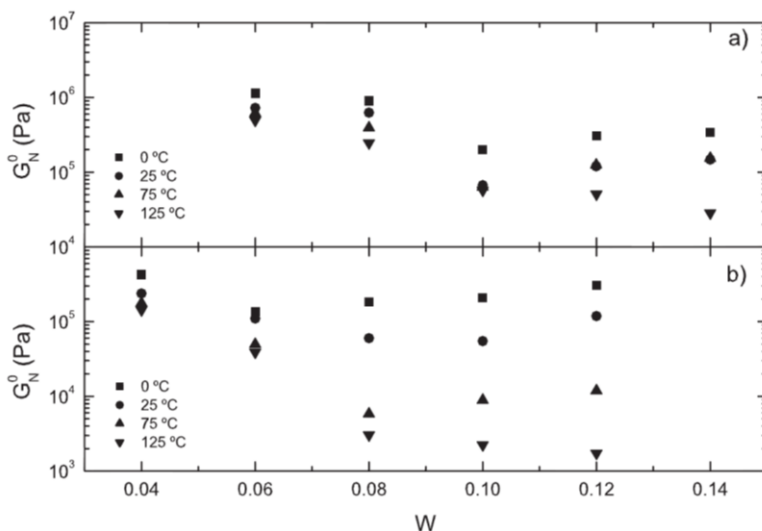


Figure 20. Evolution of the G_N^0 with W , at different temperatures, for oleogels formulated with (a) α -cellulose/ethyl cellulose blends and (b) methylcellulose/ethyl cellulose blends [Sánchez et al., 2011c]

In these sense, an important decrease in the values of the linear viscoelasticity functions down to a minimum value was found by increasing ethyl cellulose/ α -cellulose or ethyl cellulose/methyl cellulose weight ratio (W) up to a critical value, which depends on both nature of the cellulosic derivatives employed and temperature. Above this critical value, the viscoelastic functions increase with W , at temperatures ranging from 0 to 75 °C. However, at higher temperatures, i.e. 125 °C, a continuous decrease in the values of SAOS viscoelastic moduli with W has been always observed, which is related to the sol-gel transition of ethyl cellulose in castor oil. Above this transition temperature, ethyl cellulose concentration is not relevant and the concentration of the other cellulosic derivative is the only responsible for oleogel bulk rheology [Sánchez et al., 2011c].

Chitin and chitosan were also chemically modified by acylation in order to reduce the polarity and enhance the affinity between thickener and oil for bio-lubricant applications with the main drawback of poor mechanical stability [Sánchez et al.,

2011d]. What is more, lignocellulosic materials were dispersed in castor oil with the aim of producing competent formulations that avoid the use of the traditional thickeners based on metallic soaps. Núñez et al. (2011) employed cellulosic pulps from different raw materials and submitted to different pulping processes and/or several acidic treatments as biothickening agents to formulate gel-like dispersions. Different rheological responses which cover the wide spectrum found in traditional lubricating greases of NLGI grades 00–3 were obtained. The rheological behaviour was found to be mainly a consequence of the balance between the polymerization degree and lignin and α -cellulose weight fractions achieved depending on the selected raw material and the pulping treatment applied. An empirical linear correlation between G_N^0 and a power function of these three variables was proposed to predict the rheological response of the resulting gel-like dispersions, independently on the nature or processing of the cellulosic materials employed as thickener (Figure 21).

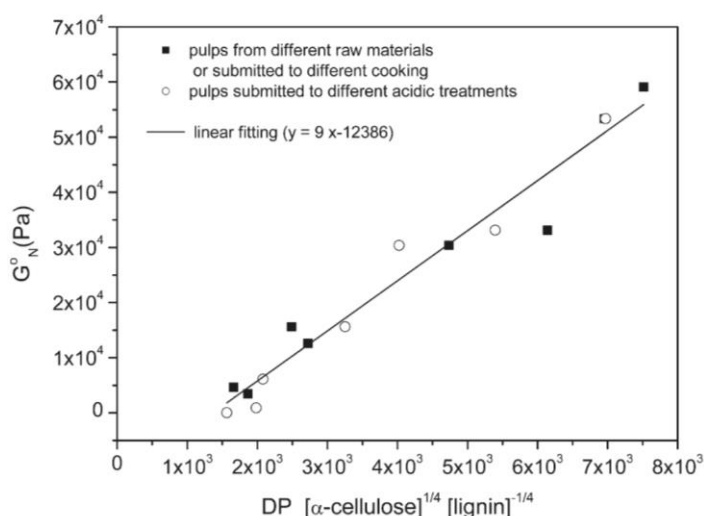


Figure 21. Correlation between G_N^0 of gel-like dispersions and a power series of cellulose polymerization degree and α -cellulose and lignin weight fractions [Núñez et al., 2011]

In addition to this, these formulations display much higher decomposition temperatures than standard lubricating greases, independently of the cellulose pulp employed. However, in general, cellulosic pulp-based dispersions in castor oil present either a poor mechanical stability or low consistency indexes, especially those prepared with

cellulose pulps submitted to drastic acid treatments or processed using a mechanical cooking [Núñez et al., 2011]. Conversely, acceptable mechanical stability was achieved with formulations prepared dispersing an industrial eucalyptus cellulose pulp in ethyl cellulose/castor oil medium, although the dispersions of its methylated derivative in the same medium resulted in poor mechanical resistance [Núñez et al., 2012a]. Additionally, the effect that Kraft cellulosic pulp cooking conditions exerts on the rheological properties and mechanical stability of cellulose pulp gel-like dispersions in castor oil was analyzed. With this aim, Eucalyptus globulus cellulosic pulps were obtained by increasing the pulping time at the maximum temperature, yielding different H factors. Cellulose pulps submitted to different H factors exhibit different polymerization degree (DP) and α -cellulose and lignin contents, yielding highly different structural morphology (Figure 22) and providing oleogels with linear viscoelastic functions that increase with the H factor.

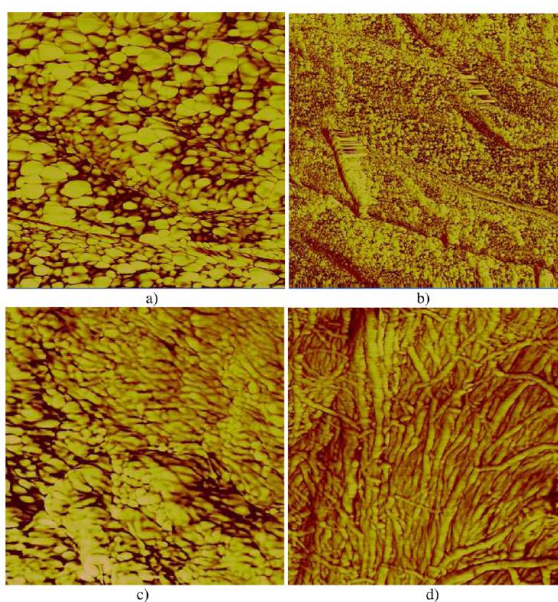


Figure 22. AFM micrographs of cellulosic pulp samples submitted to different H factor treatments:
(a) H = 150 (window size: 2 μm), (b) H= 150 (window size: 10 μm), (c) H = 300 (window size: 2 μm),
and (d) H = 500 (window size: 2 μm) [Núñez et al., 2012b]

Regarding the mechanical stability of the cellulosic pulp-based dispersions, it was obtained that penetration values decrease by increasing cooking time in the pulping treatment, i.e. the H factor [Núñez et al., 2012b].

As can be deduced, despite the fact that several attempts have been made with the intention of replacing current commercial lubricating greases by biodegradable physical oleogels, resulting in some promising findings, none of the developed formulations accomplishes the whole set of requirements and technical performance to be considered as an efficient and competitive green substitute.

3. Biopolymers used as thickening agents

The natural polymers selected to be chemically modified and subsequently used as thickeners are described below.

3.1. Cellulose and derivatives

Cellulose is the most abundant biopolymer in nature. It is a polydisperse linear homopolymer consisting of regio- and enantio- selective β -1,4-glycosidic linked D-glucose units (Figure 23). The polymer contains three reactive hydroxyl groups at the C-2, C-3 and C-6 atoms, which are, in general, accessible to the typical conversions of primary and secondary alcoholic groups.

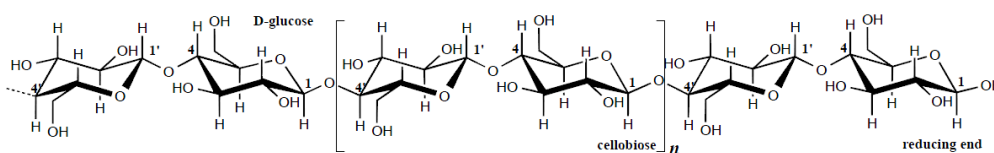


Figure 23. Cellulose structure [Ten and Vermerris, 2013]

Cellulose can adopt various types of supramolecular semicrystalline structures formed by ordered hydrogen bond systems derived from characteristics of its molecular structure such as the tacticity and the uniform distribution of the hydroxyl groups [Krässig, 1993; Salmon and Hudson, 1997]. Obviously, not only the crystallinity but

also the hydrogen bonding patterns has strong influence on the whole chemical behaviour of cellulose [Lai, 1996].

Thus, this supramolecular structure leads to the insolubility of the macromolecule in water as well as in common organic liquids, being soluble only in hydrogen-bond breaking solvents such as N-methylmorpholine-N-oxide. In all forms, apart from insoluble, cellulose is infusible and highly crystalline and presents high molecular weight. It also demonstrates promising chemical properties that increase the interest of this polysaccharide as starting material such as hydrophobicity, biocompatibility, stereoregularity, multichirality, reactive hydroxyl groups (polyfunctionality) and the ability to form superstructures [Heinze and Liebert, 2001].

The properties of cellulose are also highly dependent on the characteristics of their sources of origin (Table 1). Commercial cellulose production concentrates on easily harvested sources, i.e. wood, or highly pure ones, like cotton. However, as a naturally occurring material, cellulose may contain by-products that are likely to produce application problems and difficulties in chemical modifications.

Table 1. Chemical composition of some cellulose source [Heinze and Liebert, 2001]

Source	Composition (%)			
	Cellulose	Hemicellulose	Lignin	Extract
Wheat straw	30	50	15	5
Bagasse	40	30	20	10
Softwood	40-44	25-29	25-31	1-5
Hardwood	43-47	25-35	16-24	2-8
Flax (retted)	71.2	20.6	2.2	6.0
Jute	71.5	13.6	13.1	1.8
Henequen	77.6	4-8	13.1	3.6
Ramie	76.2	16.7	0.7	6.4
Cotton	95	2	0.9	0.4

For this reason, the most popular and commercially important step is the isolation of cellulose from plants to remove side products such as lignin and hemicellulose. Anyway, up to date, cellulose isolation and purification yield materials of high purity and variability. In addition to this, pure cellulose can be obtained using alternative pathways like bacteria, such as *Acetobacter xylinum* and *Acanthamoeba castellanii*, or algae, i.e. *Valonia ventricosa*, and enzymatic *in vitro* synthesis.

Frequently, the insolubility and infusibility of cellulose complicate its processing and possible applications, being necessary the conversion into cellulose derivatives. Actually, chemical modifications on cellulose were extensively carried out even before its polymeric nature was determined and well understood. Thus, cellulose nitrate of higher nitrogen-content was one of the most important explosives and its partially nitrated ester was among the first polymeric materials used as a “plastic”, well-known under the trade name of Celluloid. Today, cellulose nitrate is the only inorganic cellulose ester of commercial interest [Balser et al., 1986]. Further cellulose products like methyl-, ethyl-, hydroxyalkyl ethers or cellulose acetate; products with combinations of various functional groups, i.e. ethylhydroxyethyl- and hydroxypropylmethyl cellulose or cellulose acetopropionates and acetobutyrate; and ionic cellulose derivatives, such as carboxymethylcellulose, are still important, long time after their discovery. The type of functional group determines the physical properties of the cellulose derivatives, although they can be modified by the adjustment of the degree of functionalization and polymerization of the polymer backbone. New polymers based on cellulose are being the centre of interest of recent research, particularly polymers with more than one functional group, combinations of rather different functional groups, new functionalities, redox active groups, substituents with special magnetic and optical properties or biological activity combined with a controlled pre-set functionalization pattern. In this sense, potential fields of application are, in particular, liquid crystalline polymers, well-defined multilayered assemblies, selective membranes, sensor matrices, recognition devices, and bioactive and biocompatible materials. However, due to the intrinsic properties of α -cellulose, it

cannot act as a good oil thickener and chemical modifications are necessary to increase its affinity for the oil.

3.2. Chitin and chitosan

3.2.1. Chitin

Chitin, or poly (β -(1 $\rightarrow$ 4)-N-acetyl-D-glucosamine), (Figure 24) is the second most abundant polymer in nature, after cellulose.

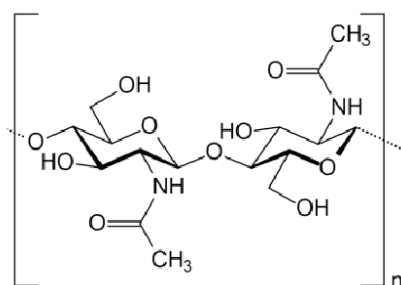


Figure 24. Chemical structure of chitin [Younes and Rinaudo, 2015]

It has a crystalline structure constituting a network of organized fibers that confers rigidity and resistance to the organisms that contain it [Roberts, 1992]. One of its most important features is the ability (flexibility) to be shaped into different forms such as fibers, hydrogels, beads, sponges and membranes [Mano et al., 2007]. It is a tough semitransparent horny substance that is the main component of arthropod exoskeletons, tendons and the linings of their respiratory, excretory and digestive systems [Clark and Smith, 1936; Herring, 1979]. It is also found in the reflective material of the epidermis and the eyes of arthropods and cephalopods [Herring, 1979] and it is an important component of the cell walls of certain fungi [Blumenthal and Roseman, 1957]. This dense substance is forming the indigestible outer skeleton of insects and the material from which the walls of the mycelia are made. It can be found in crustaceans, such as crabs, lobsters and shrimps, as well as in insects, worms, and fungus or mushrooms. Moreover, chitin is not only an essential component of invertebrates but may also be present in vertebrates, i.e. the epidermal cuticle of a vertebrate fish named

Paralipophrys trigloides is chitinous [Wagner et al., 1993]. Depending on the place of origin, chitin is found in different percentages in the same species. The origin of chitin affects its crystallinity, purity and polymer chain arrangement and dictates its properties, as well [Rinaudo, 2006].

Thus, depending on its source, chitin can exist as different allomorphic forms in nature, which vary in terms of their polymer chain structure and crystallinity [Jang et al., 2004]. There are three forms of chitin: α , β , and γ chitin that can be differentiated through techniques such as infrared and solid-state NMR spectroscopies together with X-ray diffraction.

- α -chitin: It is by far the most abundant isomorph, found in fungal and yeast cell walls, in krill, lobster and crab tendons and in shrimp shells, as well as in insect cuticle. The α -chitin chains are aligned in anti-parallel fashion which gives rise to strong hydrogen bonding and consequently makes it more stable [Sikorski et al., 2009].
- β -chitin: It is mainly found in mollusks, i.e. in squid pens, where it is in association with proteins [Rudall, 1969; Rudall and Kenchington, 1973], in the tubes synthesized by pogonophoran and vestimetiferan worms [Blackwell et al., 1965; Gaill et al., 1992] and in some diatoms. Its structure is arranged in parallel with weaker hydrogen bonding that may account for its higher chemical reactivity [Atkins, 1985; Kurita et al., 2005], which is important for enzymatic and chemical transformations [Kurita et al., 1993].
- γ -chitin: This isomorph contains two parallel and one anti-parallel strands of chitin [Atkins, 1985].

In both α and β chitin, which are commercially available, the chains are organized in sheets and held by intra-sheet hydrogen bonds. In addition, in α -chitin, inter-sheet hydrogen bonds prevent diffusion of small molecules into the crystalline phase while no inter-sheet hydrogen bonds are found in the crystal structure of β -chitin. This may explain its swelling in the presence of polar guest molecules (ranging from water to

alcohol and amines) which penetrate the crystal lattice without disturbing the sheet organization and the crystallinity of the sample. For this reason, β -chitin is more easily hydrated and soluble in water, thus improving its processability. Conversion from the β -form to the α -form is possible, but not the reverse [Lavall et al., 2007; Mazeau et al., 2002; Schiffman and Schauer, 2009], whereas γ chitin can be converted to α chitin by treatment with lithium thiocyanate [Rudall and Kenchington, 1973].

Crystalline chitin is insoluble in ordinary solvents, such as acetone or alcohol, dilute acid and concentrated alkalis [Austin et al., 1981; Muzzarelli, 1977], although it can be solved in concentrated HCl, H₂SO₄, H₃PO₄ and anhydrous formic acid [Desphande, 1986]. Due to its intermolecular bonds, chitin is also insoluble in water [Minke and Blackwell, 1978]. In this sense, an obvious method to enhance the water-solubility of chitin would be to functionalize it with hydrophilic groups or those containing moieties capable of hydrogen bonding. Mainly towards that end, carboxymethyl, hydroxypropyl, glycol, phosphoryl and sulfuryl derivatives of chitin have been synthesized [Hirano, 1988; Nishi et al., 1986; Nishimura et al., 1984; Park, and Park, 2001; Tokura et al., 1994; Trujillo, 1968]. On the other hand, while chitin is insoluble in pure organic solvents such as N-methyl pyrrolidone or dimethylacetamide, the addition of a small percentage of salt such as lithium chloride enhances its solubility dramatically [Austin, 1988; Austin et al., 1981]. In any case, insolubility is a major problem in the view of the development of processing and applications of chitin. However, the good film-forming properties and good stability promoted by the establishment of a hydrogen bond network between extended chains, together with the biocompatibility, biodegradability, non-toxicity, antimicrobial activity and low immunogenicity, make chitin a fascinating raw material.

3.2.2. Chitosan

Chitosan or poly [β (1 $\rightarrow$ 4)-2-amino-2-deoxy-D-glucopyranose] is a natural biopolymer obtained from chitin (Figure 25). In fact, both are copolymers found together in nature being environmentally friendly and easily degradable. Chitosan is obtained by alkaline deacetylation of chitin removing enough acetyl groups (CH₃-CO-) for the molecule to

be soluble in most diluted acids. This process releases amine groups ($-NH$) and gives chitosan cationic characteristics. It should be taken into account that, during deacetylation, acetyl groups are removed but also depolymerization reaction occurs, yielding changes in the molecular weight of chitosan. Chitin can be converted to chitosan by enzymatic preparations [Aiba, 1994; Kafetzopoulos et al., 1993; Tatarinova and Varlamov, 1999; Tokuyasu et al., 2000] or chemical processes [Kurita et al., 1977; No and Meyers, 1995]. The last ones are extensively used for commercial purpose because of their low cost and suitability to mass production [No and Meyers, 1995]. The typical commercial chitosan has approximately 85% degree of deacetylation (85% DD). Despite the fact that chitin is the main source of chitosan, it can also occur naturally in some fungi but its occurrence is much less widespread than that of chitin.

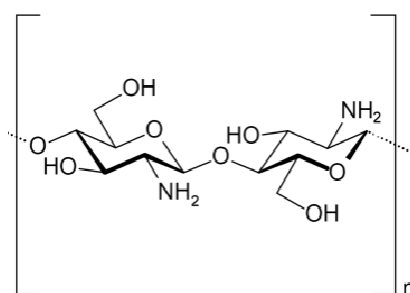


Figure 25. Chemical structure of chitosan [Younes and Rinaudo, 2015]

Chitosan has three reactive groups: one primary (C-6) and one secondary (C-3) hydroxyl groups on each repeat unit and the amino (C-2) group on each deacetylated unit. These reactive groups are readily subject to chemical modifications so mechanical and physical properties of chitosan may be easily altered. The typical reactions involving the hydroxyl groups are etherifications and esterifications. Moreover, selective O-substitution can be achieved by protecting the amino groups during the reaction. In addition to this, the presence of a nucleophilic amino group allows for selective N-substitution, such as N-alkylation and N-acylation by reacting chitosan with alkyl halides and acid chlorides, respectively.

In terms of characterization, the first step is the determination of the molecular weight (after dissolution), then the degree of acetylation and eventually the distribution of acetyl group along the chain by NMR. The determination of the degree of acetylation can be performed through different techniques such as infrared spectroscopy [Brugnerotto et al., 2001], elementary analysis and potentiometric titration, but ^1H liquid state [Kono, 2004] and solid state ^{13}C -NMR [Heux et al., 2000; Raymond et al., 1993; Saito et al., 1987] are preferred.

The primary reason for chitosan's vastly higher usage may be its ease of solubilization, what allows the processing into various forms. Although it is insoluble in water, concentrated acid, alkali and in any common organic solvent, like alcohol or acetone, it can be dissolved in dilute nitric acid, acetic acid and formic acid. As such, chitosan can be easily cast into membranes, formed into fibers or capsules by precipitation in a coagulating bath, subjected to homogenous functionalization reactions [Rafat et al., 2008] or even applied directly in solution [Campos et al., 2006] or gel [Alemdaroglu et al., 2006] forms. Consequently, chitosan, as a natural, biodegradable, biocompatible, non-toxic and anti-bacterial poly-saccharide available in different physical forms such as solution, powder, flake, fiber and film, is able to perform applications in different fields [El-hefian et al., 2011].

3.3. Lignocellulosic materials

The use of lignocellulosic fibers is being considered a scientific and technological innovation in the area of new materials, pointing out the importance of agro-waste application, especially, the use of vegetal fibers as raw material [Satyanarayana et al., 2009]. These fibers have properties such as low cost, low density, biodegradability, recyclability and low abrasiveness, specific mechanical properties capable of improving the mechanical properties of polymeric matrices, flexibility in processing and the possibility of easily changing its properties through surface treatments [Arrakhiz et al., 2012; Ghali et al., 2011; Ku et al., 2011; Le Duc et al., 2011; Tita et al., 2002]. Another important advantage of vegetal fibers is that they can be obtained from industrial waste or simply vegetation considered as invasive with no useful application, demonstrating

strong ecological appeal [Ishizaki et al., 2006]. Moreover, the growth of the use of composite based on plant fibers may increase the commercialization of such products so their production turn into industrial scale, thus provoking the reduction of the final cost of the material and favouring the definitive replacement of synthetic fibers by vegetable ones [Araujo et al., 2010]. Nowadays, lignocellulosic materials are major feedstock for the pulp and paper industry, composite industry and packaging materials, but vegetal fibers can be used in a wider range of application, i.e. filters for heavy metals retention, crafts and as reinforcement to produce polymer matrix composites [Greil, 2001; Mulinari et al., 2007; Pereira et al., 2013].

Lignocellulosic biomass results from plant photosynthesis which converts solar energy to organic material with the benefits of biodegradability and renewability [Dey and Brinson, 1984]. Renewable sources of lignocellulosic biomass are [Hoadley, 2000; U.S. Department of Energy Biomass Program, 2009]:

- Natural fibers: flax, hemp, sisal, bamboo, ramie, curauá, cotton, jute.
- Agricultural residues: wheat straw, corn stover, sugarcane bagasse, switchgrass, salix and others from the cultivation of rice, pineapple, banana and coconut.
- Forest products: hardwood and softwood.

These agricultural wastes and forest feedstock are sufficiently abundant and generate very low net greenhouse emissions. The composition as well as morphology and properties of fibers are dependent on the plant species, crop production, place of extraction, plant age, plant part chosen and soil conditions where they were grown [Faruk et al., 2014; Mohanty et al., 2005; Ogeda and Petri, 2010; Wallenberger and Weston, 2004]. In this sense, characteristics such as fiber strength, dimensions, defects, variability, crystallinity and structure must be taken into consideration when selecting a natural fiber for a specific application.

Lignocellulose is the primary building block of the plant cell walls and cellulose is their main constituent [Kumar et al., 2009]. Lignocellulosic fibers are characterized by their

cellular structures composed by cells that contains crystalline (highly ordered) and amorphous (disordered) regions of cellulose chains interconnected through lignin and hemicellulose fragments [Klemm et al., 2005]. Cellulose, hemicellulose and lignin are the three main constituents of vegetable fibers, constituting more than 75% of the lignocellulosic material, and are composed of organic polymers of high molecular weight [Abril and Abril, 2009]. However, apart from the former, this complex structure is defined by a wide variety of organic compounds such as waxes, fatty acids, fats and pectins, and some inorganic components that turn into ash following combustion [Wiselogel et al., 1996]. The proportion of these components in a fiber depends on the age, source and the extraction conditions used to obtain the fibers (Table 2).

Table 2. Chemical constituents and crystallinity index (CI) for a wide variety of fiber types [Fernandes et al., 2015]

Fiber type		Density (g/cm ³)	Cellulose (wt. %)	Hemicellulose (wt. %)	Lignin (wt. %)	Ashes (wt. %)	CI (%)
Bast, bark or stem fibers	Jute	1.3-1.4	60	22.1	15.9	1.0	58
	Ramie	1.5	80-85	3-4	0.5	-	62.9
	Kenaf	1.5	72	20.3	9	4.0	72.1
	Flax	1.5	71	18.6-20.6	2.2	-	86.1
	Hemp	1.5	72	10	3	2.3	79.9
	Sisal	1.5	74-75	10-13.9	7.6-7.9	0.4	72.2
	Banana	1.5	60-65	6-8	5-10	1.2	39
	Abaca	1.5	56-63	20-25	7.9	-	68.7
	Raffia	-	44.6	13.5	2.7	-	64
	Pineapple	0.8-1.6	83	-	12	-	38
Leaf	Curauá	1.4	70.7	21.1	7.5	0.8	75.6
	Piassava	28.6	31.6	-	48.4	-	-
	Kapok	-	50.7	49.3	13.4	-	35.3
	Cotton stalk	1.5	50.6	28.4	23.1	-	74

Fruit/Seed	Sleeve	-	55	20.6	23.8	-	-
	Weed	-	69	-	17	-	74.1
Wood	Luffa cylindrical	0.82	62	20	11.2	0.40	59.1
	Coir	1.2	43-53	14.7	38-40	-	44
	Soft density	-	30-60	20-30	21-37	≤1	-
	Hard density	-	31-64	25-40	14-34	≤1	71.6
Talus	Rice straw	-	43.2	31.7	16.9	9.9	77
	Wheat straw	-	43.2	34.1	22	4.99	54.4
	Barley	-	31-45	14-15	24-29	-	-
	Corn straw	-	39.82	23.19	11.98	-	50.3
Reed	Bamboo	0.6-1.1	33-45	30	20-25	-	59.7
	Bagasse	1.25	69.4	21	4.4	0.6	45.2

Cellulose, described in detail in section 3.1, presents a long-chain polysaccharide structure composed by repeated units of D-glucose linked together by β -1,4-glycosidic bonds (Figure 23). Neighbouring glucose residues are rotated 180° relative to each other, both named cellobiose, which is considered the repeating unit of cellulose. In lignocellulosic materials cellulose chains are packed through hydrogen bonds and Van der Waals forces, generally in bundles of 36, forming fibrous structures called microfibrils of just a few nanometres of diameter. These microfibrils are further attached to each other by hemicelluloses and amorphous polymers of different sugars as well as other polymers, such as pectin, and covered by lignin. The cellulose microfibrils, which are embedded in the hemicellulose–lignin matrix, are often associated in the form of packages of macrofibrils [Menon and Rao, 2012]. The microfibrils present highly ordered regions, i.e. the crystalline phase, which comprises the major portion of cellulose, whereas some parts of the microfibrils have a less ordered and non-crystalline structure, known as the amorphous region [Arantes and Saddler, 2010].

Hemicelluloses or hemicellulosic polysaccharides are comprised of heteropolymers including hexoses (D-glucose, D-galactose and D-mannose) as well as pentoses (D-xylose and L-arabinose) and may contain sugar acids (uronic acids), i.e. D-glucuronic, D-galacturonic and methylgalacturonic acids [McMillan, 1993; Saha, 2003]. The main hemicellulosic polysaccharide is xyloglucan (Figure 26), which contains a linear backbone of β -1,4-linked D-glucopyranose residues, with substitutions of α -D-xylose on the O-6 position of the glucose, typically the first three out of four adjacent glucose residues. The cell walls of softwood species contain other example of hemicellulose, galactoglucomannans (Figure 27). This polymer consists of a backbone containing both β -1,4-linked D-mannosyl and D-glucosyl residues, substituted with α -(1,6)-linked D-galactosyl residues. Approximately 50% of the mannosyl residues are acetylated on C2 or C3. Another example of hemicellulose can be found as the main crosslinking polysaccharide in grasses, glucuronoarabinoxylan (Figure 28), which consists of a backbone of β -1,4-linked D-xylopyranosyl residues with arabinose substitutions on the O-3 position of the xylose.

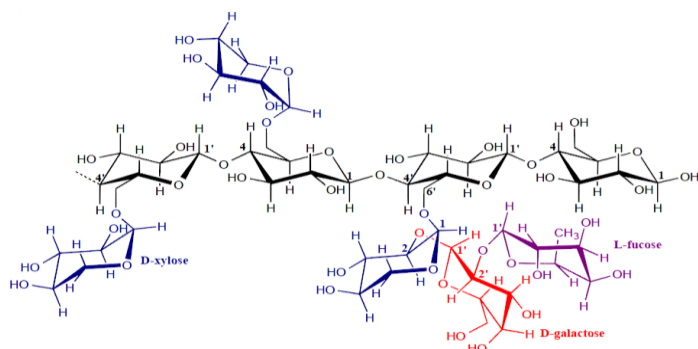


Figure 26. Xyloglucan structure [Ten and Vermerris, 2013]

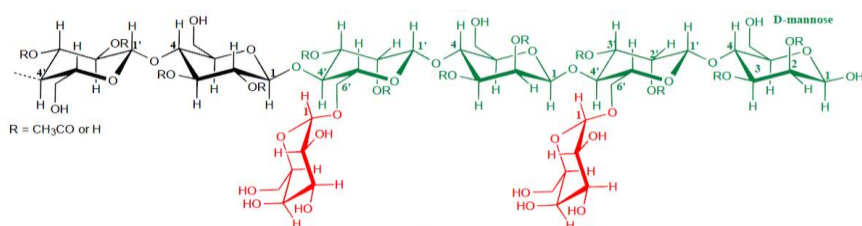


Figure 27. Galactoglucomannans structure [Ten and Vermerris, 2013]

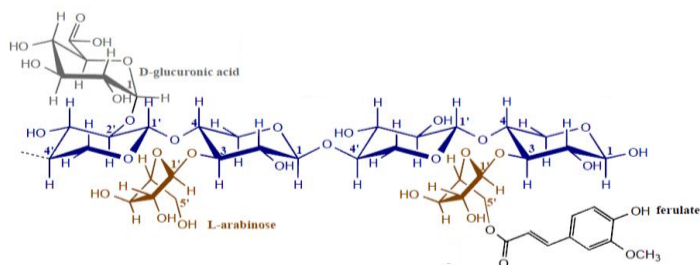


Figure 28. Glucuronoarabinoxylan [Ten and Vermerris, 2013]

As cellulose and hemicelluloses contain free hydroxyl groups that confer to the wood its inherent hygroscopic character [Stokke and Gardner, 2003], hydrogels using these materials have applications within different fields [Gabrielii et al., 2000; Karaaslan et al., 2011].

Lignin, as an amorphous aromatic polymer, shows chemical and physical properties that are fundamentally different from those of cellulose and hemicellulose. It plays a

major role in woody plants, adding strength and structure to the cell walls, controlling fluid flow and protecting against biochemical stresses by inhibiting enzymatic degradation of other components [Boerjan et al., 2003]. Its chemical structure consists of phenylpropane units, originating from three aromatic alcohol precursors (monolignols), p-coumaryl, coniferyl and sinapyl alcohols [Dorrestijn et al., 2000]. The phenolic substructures that originate from these monolignols are called p-hydroxyphenyl (H, from coumaryl alcohol), guaiacyl (G, from coniferyl alcohol) and syringyl (S, from sinapylalcohol) moieties (Figure 29).

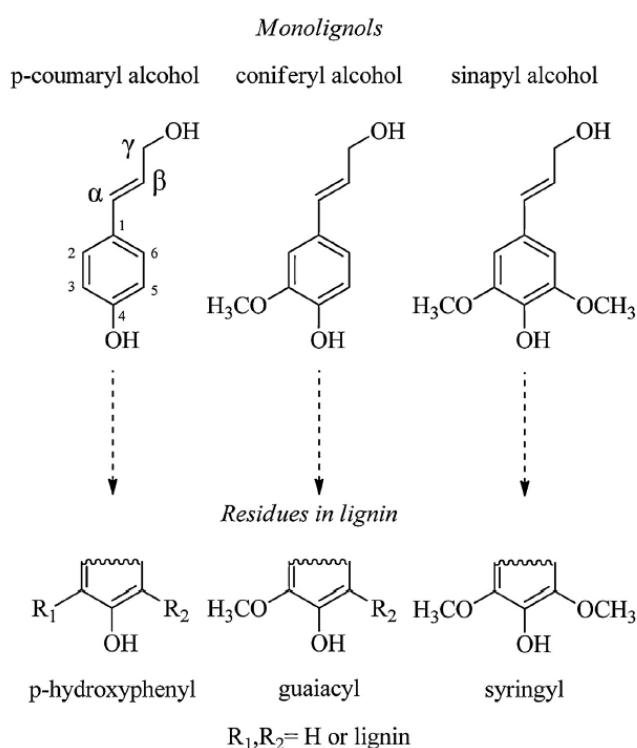


Figure 29. The three main precursors of lignin (monolignols) and their corresponding structures in lignin polymers [Laurichesse and Avérous, 2014]

During the biological lignification process, the monolignols units are linked together via radical coupling reactions [Freudenberg, 1959; Freudenberg and Nash, 1968] to form a complex three-dimensional molecular architecture that contains a great variety of bonds with typically around 50% β -O-4 ether linkages [Chen and Sarkanen, 2003; Dorrestijn et al., 2000; Ralph et al., 2004] (Figure 30). Lignin composition and content

are influenced by the species and also by the environment. Thus, softwood barks have the highest level of lignin (30–60%) followed by the hardwoodbarks (30–55%). Grasses and agricultural residues contain the lowest level of lignin i.e. 10–30% and 3–15%, respectively [Demirbas, 2005; Limayem and Steven, 2012; Pettersen, 1984].

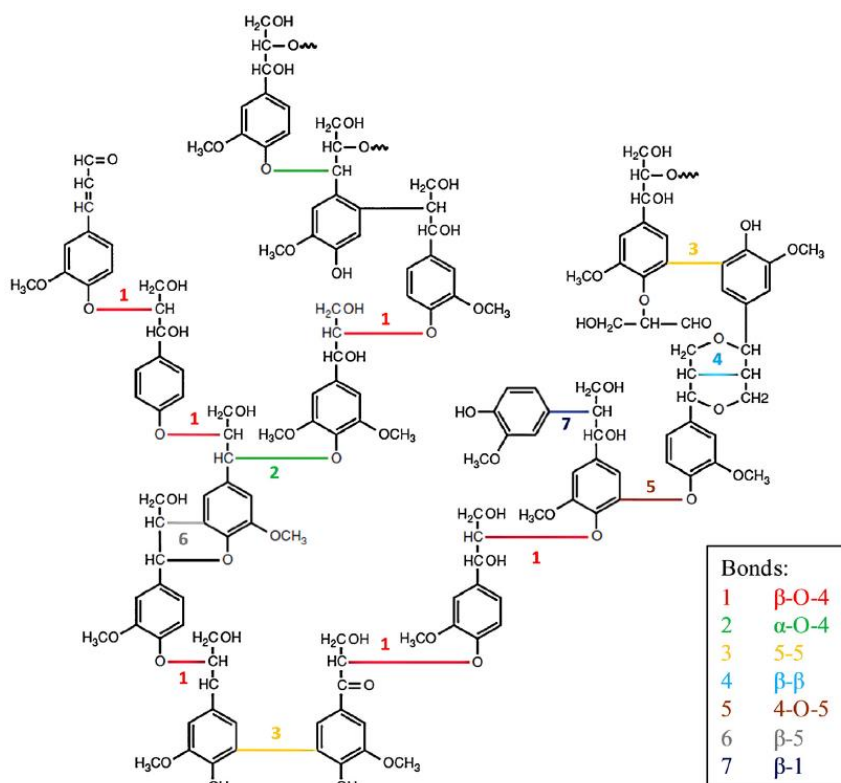


Figure 30. Main linkages in a softwood lignin [Laurichesse and Avérous, 2014]

Lignin is recognized as a highly branched polymer with a variety of functional groups: aliphatic and phenolic hydroxyls, carboxylic, carbonyl and methoxyl groups. The abundance of chemical sites offers different possibilities for chemical modification. The chemical modification of lignin can be:

- Fragmentation or lignin depolymerization to use lignin as carbon source or to cleave lignin structure into aromatic macromers: Pyrolysis and oxidation.

- Modification by creating new chemical active sites: Alkylation/dealkylation, hydroxyalkylation and amination.
- Chemical modification of hydroxyl groups: Esterification, phenolation, etherification and urethanization.

Lignin has demonstrated antioxidant capacity, strong antiviral activity against human immunodeficiency virus and other antimicrobial activities [Cazacu et al., 2004; Raschip et al., 2011], opening a wide range of possible applications.

The ease of functionalization, biocompatibility and biodegradability of cellulose, hemicellulose and lignin enable these polymers to be used in agricultural, biomedical, pharmaceutical and electro-mechanical industries. The improvement of fiber strength, fiber fitness and fiber-matrix adhesion in natural fiber composites has been achieved by different natural modifications of the natural fibers such as alkali, acetylation, silane or peroxide treatment with various coupling agents. Some chemical modifications and the corresponding specific application of these materials in the biomedical field can be seen in table 3.

Table 3. Modified cellulosic and lignin based materials and references that exploit them in the medical field

[Fernandes et al., 2013]

Modified material	Processing strategy	Biomedical application
Cellulose		
Cellulose acetate	Chemical substitution	Bone TE; Cartilage TE; Bone cements; Drug-delivery systems
Cellulose acetate phthalate	Chemical substitution	Drug-delivery systems
Hydroxypropyl cellulose	Chemical substitution	Drug-delivery systems; Periodontal TE; Bone cements
Hydroxyethyl cellulose	Chemical substitution	Bone TE
Silanized-hydroxyethyl cellulose	Chemical substitution	Bone TE
Hydroxypropylmethyl cellulose	Chemical substitution	Drug-delivery systems; Bone TE; Bone cements
Silanized-hydroxypropylmethyl cellulose	Chemical substitution	Bone TE; Bone cements; Cartilage TE
Carboxymethyl cellulose	Chemical substitution	Bone TE
Methylcellulose	Chemical substitution	Bone TE; Cartilage TE
BSA modified or PEGylated cellulose	Click chemistry	-
Lignin		
Kraft lignin	Alkali treatment	Bone TE
Acid hydrolysis lignin	Acid hydrolysis	Bone TE; Drug-delivery systems

4. Chemistry of isocyanates

Isocyanates are compounds containing the highly reactive group —N=C=O , so they are able to interact with a wide range of chemical groups, even with themselves. The reactions and reactivity of isocyanates can be best understood by considering the electronic structure of the isocyanate group (Figure 31).

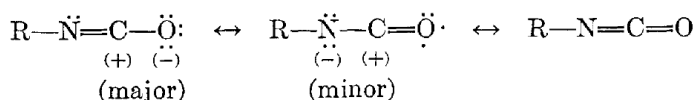
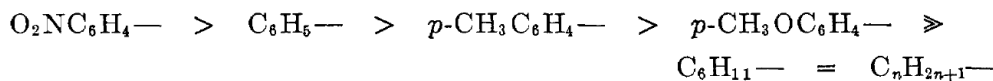
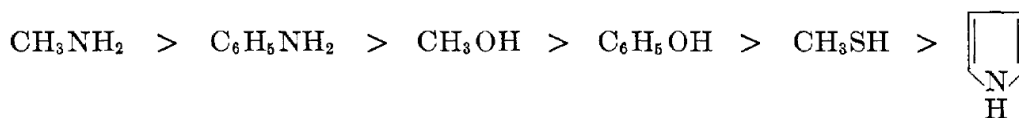


Figure 31. —NCO group possible resonant structures [Arnold et al., 1957]

It can be observed that the electronic density is greatest on the oxygen (highest negative charge) and least on the carbon (highest positive charge), the nitrogen atom being intermediate with negative charge. In addition to this, the effect on the former structure of the group attached to the nitrogen atom may be considered. For instance, in those reactions of isocyanates with active hydrogen compounds, a nucleophilic centre attacks the electrophilic carbon of the isocyanate. Therefore, if steric factor are neglected, any electron-withdrawing group attached to the —NCO moiety will increase the positive charge on the carbon atom, thereby increasing the reactivity of the isocyanate towards nucleophilic attack. Conversely, electron-donating groups will reduce the reactivity of the —NCO group:



Likewise, the reactivity of the agent attacking the electrophilic carbon of the —NCO group will increase as its nucleophilicity increases [Arnold et al., 1957]:



Consequently, there is a huge variety of different possible reactions in which isocyanates are involved, as can be summarized elsewhere [Ozaki, 1972].

Alcohols are the most reactive compounds for isocyanates and their reactivity depends on the structure and the position of the hydroxyl group. Thus, primary hydroxyl groups are more reactive than secondary and, finally, than tertiary, due to the steric hindrance of the neighbouring groups. The reaction between alcohols and isocyanates (Figure 32) produces urethane linkages, also known as carbamates.

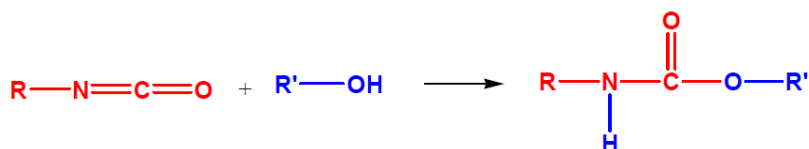


Figure 32. Chemical reaction between OH and –NCO groups [Moreno, 2012]

Polyurethanes conform and extensive family of polymers with different properties and the presence of urethane groups in their structure as the common characteristic. Structure and functionality of the reagents used in the polyurethane formation definitively influence the properties of the final product. Polyurethanes result from the reaction between di- or poly- alcohols of moderate molecular weight and di- or poly- isocyanates (Figure 33).

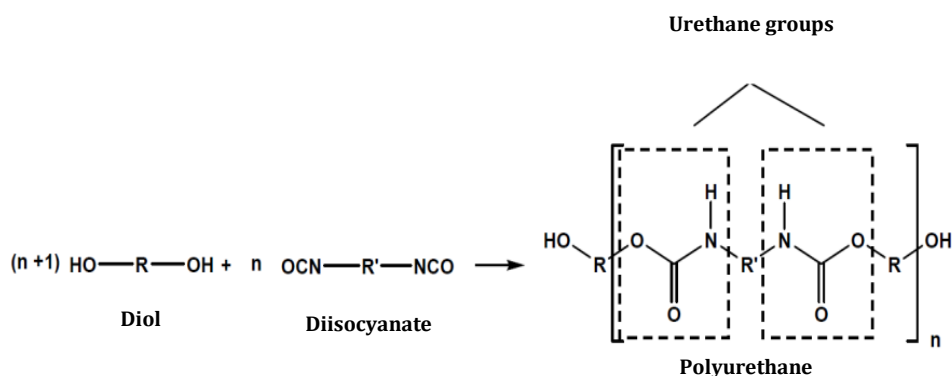
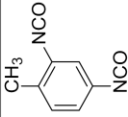
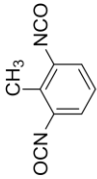
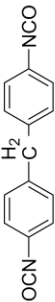
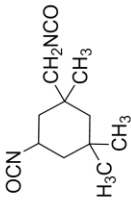
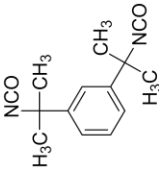


Figure 33. Synthesis of polyurethanes [Moreno, 2012]

Currently, a wide range of polyurethanes can be provided due to the huge variety of commercial diisocyanates available, which can be divided into aliphatic and aromatic. Aliphatic isocyanates are considerably less reactive and more expensive than aromatic but the resulting products from their reactions are more resistant to oxidation produced by UV radiation exposure, so they are usually employed in colour preservation. Most commonly used aliphatic diisocyanates are 1,6-hexamethylene diisocyanate (HMDI), isophorone diisocyanate (IPDI) and tetramethylxylene diisocyanate (TMXDI). On the other hand, more frequently used aromatic diisocyanates are tolylene-2,4-diisocyanate (TDI) and 4,4'-methylenediphenyl diisocyanate (MDI). TDI is commercially available as a mixture of two isomers (2,4-TDI and 2,6-TDI) or pure, whereas there are three kinds of MDI: monomeric or pure, polymeric and modified.

Table 4 shows the chemical structure and physical properties of some commercial diisocyanate compounds.

Table 4. Properties of comercial isocyanates [Moreno, 2012]

Name	Formula	Structure	Molecular weight (g/mol)	Melting point (°C)	Boiling point (°C)	Density (g/l)
Tolylene-2,4-diisocyanate (TDI)	$C_9H_6O_2N_2$		174.2	21.8	121 (10 mmHg)	1.061 (20 °C)
Tolylene-2,6-diisocyanate (TDI)	$C_9H_6O_2N_2$		174.2	18.2	120 (10 mmHg)	1.2271 (20 °C)
4,4'-methylene diphenyl diisocyanate (MDI)	$C_{15}H_{10}O_2N_2$		250.3	39.5	208 (10 mmHg)	1.183 (50 °C)
1,6-hexamethylene diisocyanate (HMDI)	$C_8H_{12}O_2N_2$		168.2	-67	127 (10 mmHg)	1.047 (20 °C)
Isophorone diisocyanate (IPDI)	$C_{12}H_{18}O_2N_2$		222.3	-60	158 (10 mmHg)	1.061 (20 °C)
Meta-tetramethylxylene diisocyanate (TMXDI)	$C_{14}H_{16}O_2N_2$		244.3	-	150 (50 mmHg)	1.05 (20 °C)

Rigid crosslinked, linear and flexible chain elastomeric polymers are possible molecular structures that polyurethanes can acquire depending on the reactants and the conditions of the synthesis reaction (Figure 34).

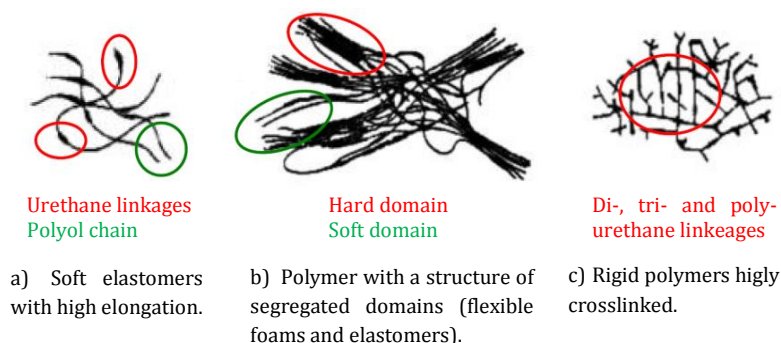


Figure 34. Possible molecular structures of polyurethanes [Moreno, 2012]

The crosslinking can have physical or chemical nature. Physical crosslinking is based on hydrogen bonds while chemical crosslinking results from the reaction between tri- or poly- functional constituents. The chemical crosslinking demonstrate higher thermal resistance with respect to the physical crosslinking that is easily destroyed.

Regarding the application of isocyanates, the high level of reactivity of them is one of the main reasons of their vast range of applicability [Arnold et al., 1957]:

- Linear polyurethanes derived from diols such as 1,4-butanediol and hexamethylene diisocyanate are of interest as plastics and fibers because of their tensile strength, low water absorption, good electrical properties and good resistance to outdoor exposure and acid.
- Relatively high-molecular-weight , linear, low-melting glycols and diamines, when polymerized with diisocyanates, are the basic intermediates for elastomeric products of an extensive interest.

- Low-molecular-weight or highly crystalline, higher-molecular weight difunctional alcohols, amines, carboxylic acids, etc., and polyfunctional reagents with di- and polyisocyanates, are the basis for plastics, coatings, films, and fibers.
- Foams, rigid or elastic, with excellent structure and almost any desired density can be obtained when isocyanates react with water and carboxylic acids, producing carbon dioxide as by-product that blow up the polymerizing material.
- In polymer modification, alkyl resins, cellulose ethers or esters, polyamides, and polyurethanes have been crosslinked with isocyanates in order to modify their properties.
- Isocyanates have been useful in the formulation of adhesives, i.e. rubber may be bonded to polar substrates with the aid of isocyanates. Condensation products of isocyanates with polymers bearing carboxyl or other groups which will react with isocyanates have been employed as adhesives.
- Other uses for isocyanates or polymers derived from them include the leading pigments on textile and paper, the joining together or coating of fibers and the preparation of cements. In addition to this, varnish treatment, tanning of leather or production of electrical insulators are also considered.

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Chapter 3:

Materials and methods

1. Relevant materials

1.1. Starting materials for thickeners

1.1.1. α -cellulose and cellulose derivatives

Partially microcrystalline α -cellulose provided by Sigma-Aldrich [Park et al., 2009] was used as a thickener precursor (Figure 35).

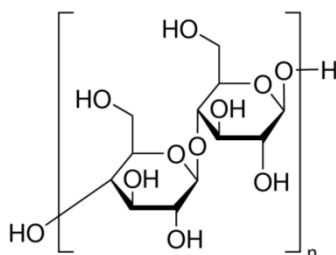


Figure 35. Molecular structure of α -cellulose

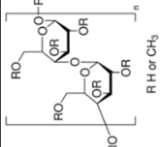
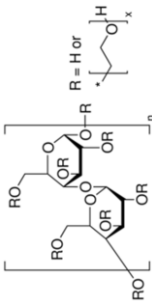
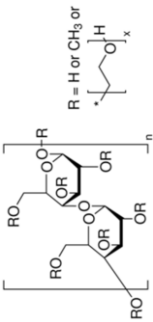
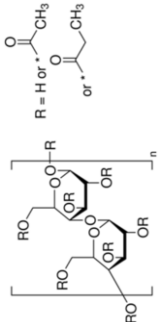
The degree of polymerization (DP) of this biopolymer was determined according to the standard method SCAN-C15, resulting a value of $DP = 1011$, which was obtained inserting the value of the intrinsic viscosity ($[\eta] = 438 \text{ cm}^3/\text{g}$) in the following equation [Gericke et al., 2009]:

$$DP^{0.76} = \frac{[\eta]}{2.28} \quad [1]$$

The average molecular weight of α -cellulose was also obtained using the degree of polymerization resulting in $M_n = 1.64 \cdot 10^5 \text{ g/mol}$.

The inclusion of protective groups in the cellulose structure allows the enhancement of the selectivity of the crosslinking reaction. Moreover, certain parameters of the protective groups, i.e., polarity and size, may influence the resulting product. Due to these reasons, several commercially available cellulose derivatives, all of them purchased by Sigma-Aldrich, differing in the type of substituent and substitution degree, have been employed as thickeners precursors as well (Table 5).

Table 5. Molecular formula, degree of substitution and average molecular weight of cellulose derivatives

Cellulose derivative	Molecular formula	Degree of substitution ^a	Average molecular weight ^a
Methyl cellulose		DS (methoxy) = 1.6-1.9	$M_n \sim 40000$
2-hydroxyethyl cellulose		MS (hydroxyethyl) = 2.5	$M_v \sim 90000$
Methyl 2-hydroxyethyl cellulose		MS (hydroxyethyl) = 0.06-0.50 DS (methyl) = 1.3-2.2	-
Cellulose acetate propionate		DS (acetyl) = 0.03 DS (propionyl) = 2.09	$M_n \sim 15000$

^a Data from supplier

1.1.2. Chitin and chitosan

Chitin, also used as thickener precursor, exhibits a molecular structure similar to cellulose, with the only difference of the presence of an acetylated amino group instead of a secondary hydroxyl group (Figure 36).

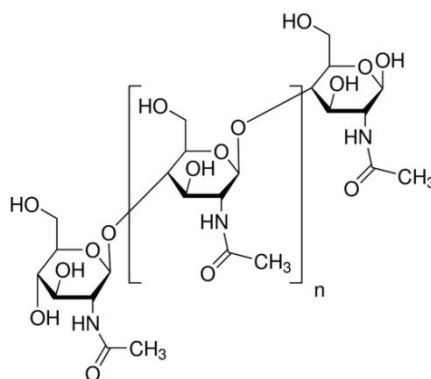


Figure 36. Chitin molecular structure

The sample of chitin employed in this work was kindly supplied by Qingdao Fraken (China), with a molecular weight of $5.4 \cdot 10^5$ g/mol and a degree of deacetylation of 7.3%, calculated through FTIR spectroscopy, according to the method described elsewhere [Baxter et al., 1992].

Chitosan, obtained by deacetylation, shows the same molecular structure as chitin, only differing in the number of deacetylated units (Figure 37).

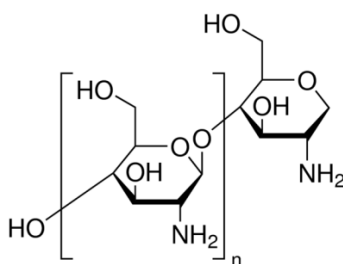


Figure 37. Molecular structure of chitosan

The type of chitosan used in this research, also purchased from Qingdao Fraken (China), has an average molecular weight of $2.3 \cdot 10^5$ g/mol and a degree of deacetylation of 86.3%.

1.1.3. Lignocellulosic materials

Lignocellulose pulps, where cellulose coexists mainly with lignin and hemicelluloses, among others, were also functionalized to act as thickeners. The selected samples (Figure 38) were a commercial grade Kraft cellulose pulp from *Eucalyptus globulus*, kindly supplied by ENCE, S.A. (Huelva factory, Spain), and other cellulose pulps produced in the laboratory from *Pinus radiata* and *Eucalyptus globulus* by applying a classical Kraft cooking with an associate H factor of 940 and a semi-mechanical treatment, respectively [Nuñez et al., 2011].

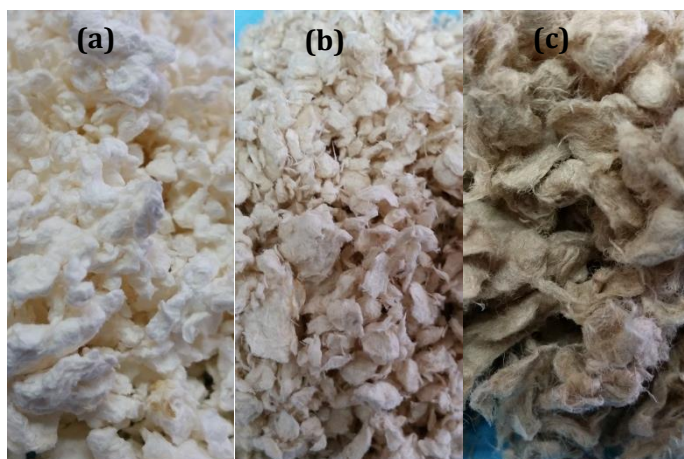


Figure 38. Cellulose pulps from (a) *Eucalyptus globulus* and (b) *Pinus radiata* after a classical Kraft cooking and (c) *Eucalyptus globulus* after a semi-mechanical treatment

The kind of wood selected and the specific pulping treatment applied determine the composition and properties of the cellulose pulp (Table 6).

Table 6. Cellulose pulps composition [Nuñez et al., 2011]

Cellulose pulp (Processing)	α -cellulose ^a (% w/w)	Hemicellulose ^b (% w/w)	Lignin ^c (% w/w)	Intrinsic viscosity ^d (cm ³ /g)	Degree of polymerization ^e
<i>Eucalyptus globulus</i> (Kraft cooking commercial grade)	85.1±1.5	13.1±1.4	0.3±0.1	688±14	1831
<i>Pinus radiata</i> (Kraft cooking)	80.5±2.7	13.8±1.6	4.5±0.1	819±16	2303
<i>Eucalyptus globulus</i> (Semi-mechanical cooking)	49.7±0.7	30.2±0.2	18.4±0.2	770±11	2123

^a Tappi T-203-05-61. ^b Wise et al., (1946). ^c Tappi T-222. ^d Tappi T-230. ^e Eq. 1.

1.1.4. 1,6-hexamethylene diisocyanate (HMDI)

The former substrates were functionalized with 1,6-hexamethylene diisocyanate (purum grade, $\geq 98.0\%$), which was purchased from Sigma-Aldrich (Figure 39). The objective was the induction of the reaction between the free hydroxyl groups of the biopolymers, as well as chitin and chitosan amino group, and one of the $-NCO$ groups of the diisocyanate. Thus, NCO-functionalized biopolymers would contain hexamethylene chains with pendant isocyanate moieties, which can later react with the hydroxyl groups of the castor oil. In this way, the diisocyanate acts as a chemical bridge between the polymer and the oil to form a chemical oleogel.

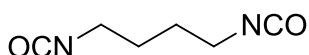


Figure 39. Molecular structure of 1,6-hexamethylene diisocyanate

1.2. Castor oil

Castor oil, as a vegetable oil, is mainly composed of triacylglycerols (98%), which consist of one molecule of glycerol esterified by different fatty acids (Figure 40), and minor quantities of diacylglycerols (0.5%), free fatty acids (0.1%), sterols (0.3%) and tocopherols (0.1%) [Dwivedi and Sapre, 2002].

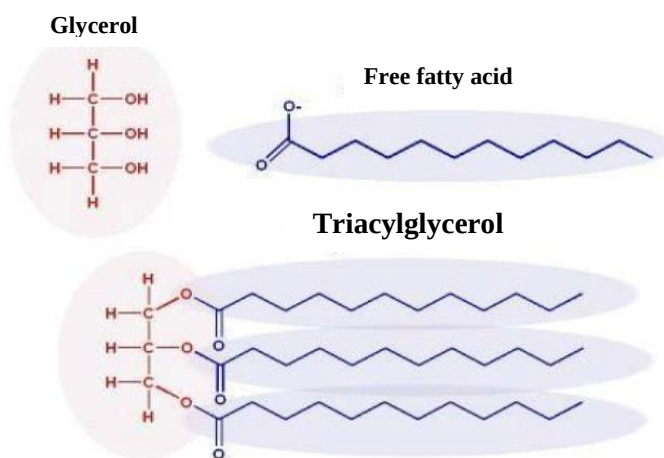


Figure 40. Basic chemical components of a vegetable oil

Castor oil used in this work was provided by Guinama (Spain). Its peculiar composition (Table 7) confers castor oil higher viscosity, lower friction coefficient in a tribological contact, lower solubility in hexane and higher in ethanol than other vegetable oils [Boyde, 2002; Conceição et al., 2007, Hua and Bin, 2004; Maleque et al., 2003]. Consequently, this oil is considered as a suitable base for biolubricant formulations [Gunstone, 2005; Lea, 2002; Maleque et al., 2003]. However, it is the high number of hydroxyl groups present in its structure what make castor oil interesting to be selected as lubricant base oil in this work.

Table 7. Fatty acids composition and viscosity at different temperatures of castor oil

Castor Oil		
Fatty Acids composition	Myristic acid (C14:0) (%)	Traces
	Palmitic acid (16:0) (%)	2.58
	Palmitoleic acid (C16:1) (%)	Traces
	Margaric acid (C17:0) (%)	Traces
	Margaroleic acid (C17:1) (%)	Traces
	Stearic acid (C18:0) (%)	2.73
	Oleic acid (C18:1) (%)	6.31
	Linoleic acid (C18:2) (%)	10.83
	Ricinoleic acid (12- hydroxy C18:1)	77.55
	Linolenic acid (C18:3) (%)	Traces
	Arachidonic acid (C20:0) (%)	Traces
	Gadoleic acid (C20:1) (%)	Traces
	Behenic acid (C22:0) (%)	Traces
	Lignoceric acid (C24:0) (%)	Traces
Dynamic viscosity (Pa·s)	40 °C	0.2293
	100 °C	0.0187
Kinematic viscosity (cSt)	40 °C	211.05
	100 °C	21.00

1.3. Other common reagents and solvents

Other common reagents and solvents were purchased from Sigma-Aldrich. A commercial model lithium lubricating grease (Castrol Optipit, Germany) and a semi-biodegradable one based on castor oil and a calcium thickener (kindly supplied by Verkol, Spain) were successfully tested as benchmarks.

2. Experimental procedures

2.1. Functionalization reaction of biopolymers

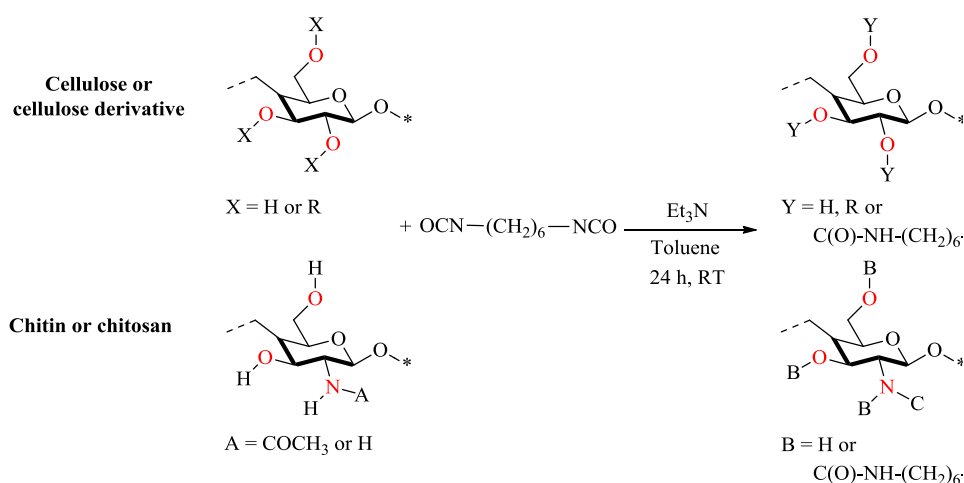


Figure 41. Functionalization reaction with HMDI of the biopolymers

The NCO-functionalization reaction of biopolymers such as α -cellulose, cellulose derivatives, chitin and chitosan (Figure 41) was carried out based on previous studies [Moreno et al., 2008]. The procedure begins with the addition of the substrate to a bottom round flask with toluene while stirring at room temperature, becoming a suspension. Then triethylamine (Et₃N) and HMDI were also added to the system, the last one drop wisely. The solution was kept at room temperature for 24 h while vigorously stirring. The synthesis was conducted under inert atmosphere of argon. Afterwards, the mixture was vacuum filtered resulting in the desired product, which is not stored but immediately used.

The relative amount of HMDI, Et_3N and toluene with respect to the substrate in every case was selected with the aim of controlling the ratio of functionalized $-\text{OH}$ groups in the polymer synthesized, from fully functionalized to a certain number of free $-\text{OH}$ groups. Moreover, reaction conditions selected avoid excessive crosslinking of $-\text{NCO}$ groups present either in the unreacted HMDI or in HMDI moieties attached to the biopolymer chains. A variety of functionalized biopolymers were obtained. Details of composition can be seen in section 3.

2.2. Crosslinking reaction in lignocellulosic materials

In the case of lignocellulosic pulps, a similar approach was followed; however, materials were not only functionalized but totally crosslinked, i.e. negligible free $-\text{NCO}$ groups remained. Previously, a mercerization treatment was applied on lignocellulose pulps in order to deshield and make more accessible the groups susceptible to chemical modification. Typically, 5 g of pulp were soaked into 125 g of 50% NaOH solution under gentle agitation during 3 h at room temperature, and then the resulting pulp was filtered and pressed to achieve a pulp/alkali ratio around 1/9 w/w. Finally, the product was washed twice with water and acetone. Afterwards, the mercerized pulp was added to a bottom round flask with toluene while stirring at room temperature becoming a suspension and then, Et_3N and HMDI were also added to the system in different proportions, the last one dropwisely. The solution was vigorously stirred at room temperature for 24 h. Finally, the mixture was filtered, obtaining the HMDI-crosslinked lignocellulose paste.

2.3. Processing of oleogels

Oleogel samples were prepared in an open vessel, using a controlled-rotational speed mixing device RW 20 (Ika), equipped with an anchor impeller to disperse the thickener in the oil (Figure 42). The thickening agent was slowly added to the oil at the required concentration depending on the desired formulation. The mixing process was maintained at 70 rpm for 24 h at room temperature.



Figure 42. Controlled-rotational speed mixing device, anchor impeller and open vessel used in the processing of oleogels

Finally, the resulting dispersion was homogenized with an Ultra-Turrax T50 (Ika) rotor–stator turbine, at 8800 rpm (Figure 43). NCO-functionalized biopolymer-based oleogels were prepared in batches of 60 g and the homogenization process was maintained for 1 min, whereas formulations based on HMDI-crosslinked cellulosic pulps were prepared in batches of 600 g and homogenized for 5 min.



Figure 43. Rotor–stator turbine and corresponding disperser used in the homogenization of oleogels

3. Characterization techniques and equipment

3.1. Chemical characterization

3.1.1. Fourier transform infrared spectroscopy (FTIR)

FTIR spectra of starting materials, developed thickeners and oleogels were obtained with a Digilab FTS 3500 ARX (Varian, USA) apparatus (Figure 44). Biopolymer

samples were prepared as KBr pellets, whereas a small drop of oleogels was placed between two KBr disks (32 mm $\times$ 3 mm). Then, in both cases, the set was placed into an appropriate sample holder. The spectra were obtained in a wavenumber range of 400–4000 cm^{-1} , at 4 cm^{-1} resolution, in the transmission mode.



Figure 44. Digilab FTS 3500 ARX (Varian, USA) infrared spectrometer

3.1.2. ^1H -Nuclear magnetic resonance (^1H -NMR)

The ^1H -NMR spectra of certain thickening agents were recorded with a Varian Direct-Drive 500 (^1H 500 MHz) spectrometer (Figure 45) using DMSO- d_6 as solvent.



Figure 45. Varian Direct-Drive 500 (^1H 500 MHz) spectrometer

3.2. Thermogravimetric analysis (TGA)

The thermogravimetric characterization was carried out through a thermogravimetric analyser, model Q-50 (TA Instruments Waters, USA) (Figure 46), which measures the mass loss of the sample with temperature. Tests were performed in a temperature range of 30-600 °C, at a heating rate of 10 °C/min, using nitrogen as purge gas, over 5-10 mg of sample placed on a platinum pan.



Figure 46. Thermogravimetric analyser model Q-50 (TA Instruments Waters, USA)

3.3. Microstructural characterization

Morphological characterization of selected functionalized cellulose derivatives and crosslinked lignocellulose gel-like dispersions in castor oil was made by means of atomic force microscopy (AFM), with a Multimode apparatus connected to a Nanoscope-IV scanning probe microscope controller (Digital Instruments, Veeco Metrology Group Inc., USA) (Figure 47). All images were acquired in the tapping mode, using Veeco Nanoprobe™ tips, in phase imaging, where the cantilever oscillates at its resonant frequency. The amplitude was used as a feedback signal. Samples were not submitted to any physical modification or partial oil extraction but previously heated at around 100-110°C by placing the AFM sample holder in an external heating plate for 20-30 s and, then, cooled down to room temperature to obtain smooth film surfaces.

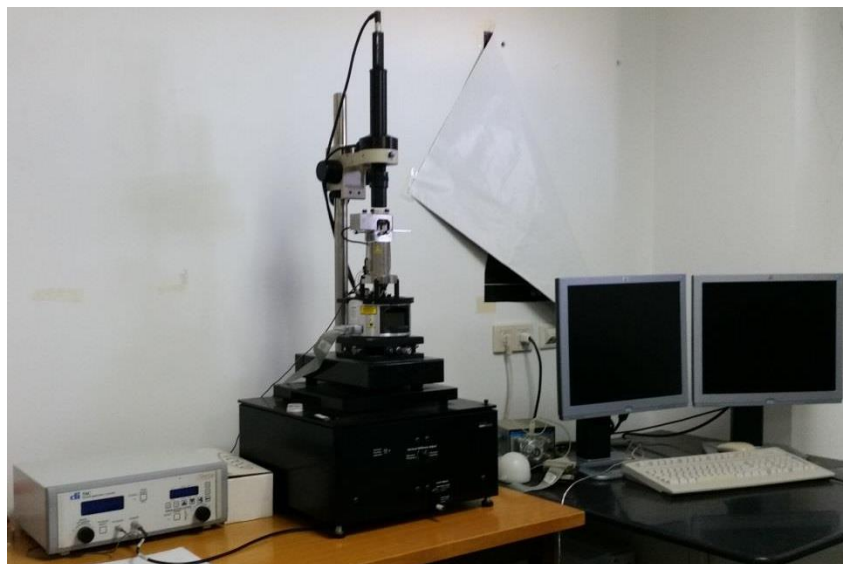


Figure 47. Atomic force microscope with a Multimode apparatus connected to a Nanoscope-IV scanning probe microscope controller (Digital Instruments, Veeco Metrology Group Inc., USA)

3.4. Rheological characterization

Small-amplitude oscillatory shear (SAOS) tests were performed inside the linear viscoelastic region in a frequency range of 10^{-2} – 10^2 rad/s to obtain the mechanical spectra of oleogels. The extension of the linear viscoelastic range was previously determined by performing stress sweep tests at 1 Hz, typically ranging from 0.01 to 1000 Pa. Additionally, viscous flow tests were carried out by applying a stepped shear rate ramp (5 min per point) in a shear rate range of 10^{-2} – 10^2 s⁻¹. Roughened plate-plate geometries of 20, 25 and 35 mm of diameter, with 1 mm of gap, were used for the measurements. The use of plate-plate geometries with grooved surfaces is especially determinant in viscous flow measurements, so that, wall slip phenomena, usually observed in lubricating greases [Balan and Franco, 2001], may be overcome. Generally, rheological measurements were performed at 25 °C; however, different temperatures in the range of 5–150 °C were occasionally applied with the aim of analysing the influence of temperature on the rheological behaviour of some specific formulations. The effect of ageing on the evolution of the viscoelastic moduli was also studied by testing the oleogels one day, one week, one month and four months after their manufacture. At

least two replicates of each test were performed on fresh samples without previous shear and structurally relaxed, and perfectly thermostated.

Three different controlled-stress rheometers were used for the rheological characterization:

- Gemini 150 (Bohlin, Malvern Instruments Ltd., Worcestershire, United Kingdom) (Figure 48).

It has a torque range of $5 \cdot 10^{-5}$ -150 mN·m, the rate range takes from 10^{-5} to 650 rad/s and the frequency range is 10^{-6} -150 Hz. It is equipped with a Peltier temperature system (Bohlin, United Kingdom), that allows the fast modification of the temperature of the sample.



Figure 48. Controlled-stress rheometers Gemini (Bohlin, Malvern Instruments Ltd., Worcestershire, United Kingdom)

- Rheoscope (ThermoHaake, Karlsruhe, Germany) (Figure 49).

The torque of the device ranges from 0,002 to 100 mN·m and the rate range takes from 0,025 to 1200 rpm. The frequency range is 0,0001-100 Hz with an angular resolution of $1,2 \cdot 10^{-6}$ rad. It was used coupled to a thermostatic bath (Phoenix, Thermohaake, Germany).

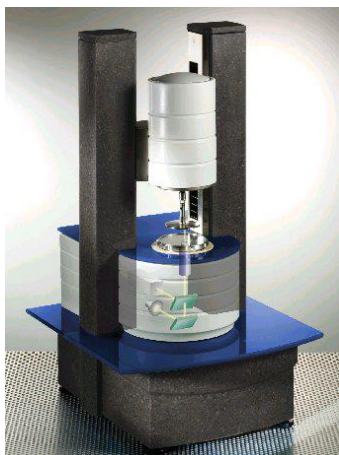


Figure 49. Controlled-stress rheometers Rheoscope (ThermoHaake, Karlsruhe, Germany)

- Physica MCR-501 (Anton Paar, Austria) (Figure 50).

This device presents a torque range between $0.01 \mu\text{N}\cdot\text{m}$ and $300 \text{ mN}\cdot\text{m}$ with a resolution of $0.1 \text{ nN}\cdot\text{m}$, and normal forces from 0.01 to 50 N with a resolution of 0.002 N . Frequencies from 10^{-5} to 628 rad/s and speeds up to 3000 1/min can be applied with a displacement resolution of $0.01 \mu\text{rad}$. It is equipped with a Peltier temperature controller.



Figure 50. Controlled-stress rheometer Physica MCR-501 (Anton Paar, Austria)

3.5. Tribological characterization

Tribological tests were performed in a tribology measuring cell coupled to the controlled-stress rheometer, Physica MCR-501 (Anton Paar, Austria) (Figure 51). The cell uses a $\frac{1}{2}$ " diameter steel ball (1.4401 grade 100) rotating on three 45° inclined steel plates (1.4301).

Two different tribological tests were performed over some selected oleogels. On one hand, the evolution of the friction coefficient, μ , with the rotational speed was tested in a range of rotational velocities of 0.01-1000 rpm at constant normal load (10-40 N). On the other hand, the stationary friction coefficient was obtained by applying normal forces of 10, 20 and 40 N and setting a constant rotational speed (0.15, 10 and 400 rpm) for 10 min duration. Five repeats of each test were performed on fresh samples at 25 and 125°C.

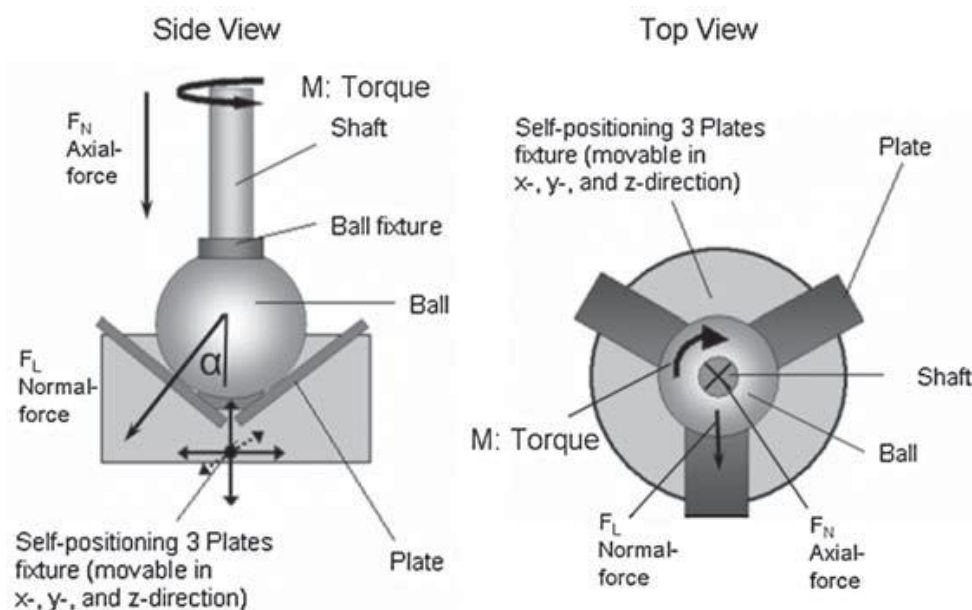


Figure 51. Schematic set-up tribology accessory in side and top view. The torque and the normal force applied by the rheometer are indicated by arrows [Heyer and Lauser, 2009]

For wear analysis, the resulting marks on the plates were examined using a scanning electronic microscope, model JSM-5410 (JEOL) (Figure 52), after every stationary friction test.



Figure 52. Scanning electronic microscope model JSM-5410 (JEOL)

3.6. Standard mechanical tests

Penetration indexes were determined according to the ASTM D 1403 standard on gel-like dispersion samples, by using a Seta Universal penetrometer, model 17000-2, with one-quarter cone geometry (Stanhope-Seta, United Kingdom) (Figure 53). The penetration device has a standard weight of 9.38 ± 0.025 g. A cylindrical container of 40 mm of diameter and 40 mm of height was used as the penetration vessel. Previously to every test, the samples were thermostated in a water bath at 25 ± 0.5 °C for an hour. The one-quarter scale penetration values were converted into equivalent full-scale cone penetration values, according to the ASTM D 127 standard:

$$P = 3.75 \cdot p + 24$$

being “P” the full-scale cone penetration value and “p” the one-quarter scale penetration value. Classical consistency NLGI grade, usually reported for conventional lubricating greases, was calculated according to the resulting penetration values.

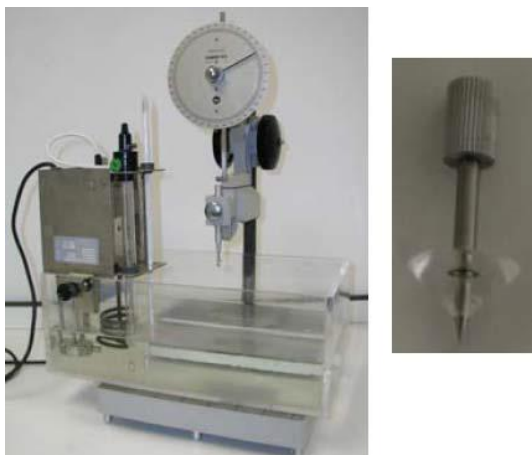


Figure 53. Seta Universal penetrometer model 17000-2 and one-quarter cone geometry (Stanhope-Seta, United Kingdom)

Selected samples were worked during 2 h in a Roll Stability Tester, model 19400-3 (Stanhope-Seta, UK), according to the ASTM D 1831 standard (Figure 54). For this test, 50 g of sample were placed in the space between the inner surface of a metallic vessel and a metallic cylinder of 5000 ± 50 g, which apply continuous shear to the sample for 2 hours. The metallic vessel spins inside the device at 165 ± 15 rpm.



Figure 54. Roll Stability Tester model 19400-3 (Stanhope-Seta, UK), the metallic vase and the metallic cylinder

Penetration measurements were performed, once again, immediately after this rolling test. The mechanical stability of gel like dispersions studied was then estimated as the difference between worked and unworked penetration values. At least three replicates of penetration measurements were performed.

4. References

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Chapter 4:

Results and discussion

CHAPTER 4: Resultats and discussion

Algunos de los artículos que forman parte del Capítulo 4 han sido retirados de la tesis debido a restricciones relativas a los derechos de autor. Dichos artículos han sido sustituido por la referencia bibliográfica, así como por el enlace al texto completo (solo miembros de la UHU), enlace a la revista y resumen.

- Gallego, R., Arteaga, J.F., Valencia, C., Franco, J.M.: "Chemical modification of methyl cellulose with HMDI to modulate the thickening properties in castor oil". Cellulose. Vol. 20, n. 1, págs. 495-507, (2013). DOI: 10.1007/s10570-012-9803-4

Enlace al texto completo del artículo (solo para miembros de la UHU):

<http://dx.doi.org/10.1007/s10570-012-9803-4>

RESUMEN:

This work deals with the selective incorporation of reactive isocyanate groups into methyl cellulose in order to be used as reactive thickening agent in castor oil. Resulting gel-like dispersions may have potential applications as green lubricating greases formulated from renewable resources. Two different isocyanate-functionalized methyl cellulose-based polymers were obtained by reaction of methyl cellulose with 1,6-hexamethylene diisocyanate. The functionalization degree, from fully functionalized to a certain number of free hydroxyl groups (58:36:6 ratio between -OMe, -NCO and free -OH groups), was controlled by modifying the reagents molar ratio. These polymers were characterized through nuclear magnetic resonance of protons (^1H -NMR), Fourier transform infrared spectroscopy and thermogravimetric analysis (TGA). Thermal and rheological responses of oleogels prepared by dispersing these polymers in castor oil were studied by means of TGA analysis and small-amplitude oscillatory shear measurements. The evolution of linear viscoelasticity functions with frequency of the oleogel containing isocyanate-functionalized methyl cellulose with lower -NCO content is quite similar to that found for traditional lithium lubricating greases. In relation to long-term stability of these oleogels, the values of viscoelastic functions significantly increase during the first 7 days of ageing and then remain almost constant.

- Gallego, R., Arteaga, J.F., Valencia, C., Franco, J.M.: "Rheology and thermal degradation of isocyanate-functionalized methyl cellulose-based oleogels". Carbohydrate Polymers. Vol. 98, n. 1, págs. 152-160, (2013). DOI: 10.1016/j.carbpol.2013.04.104

Enlace al texto completo del artículo (solo para miembros de la UHU):

<http://dx.doi.org/10.1016/j.carbpol.2013.04.104>

RESUMEN:

The —NCO-functionalization of methyl cellulose with HMDI and its application to chemically gel the castor oil is explored in this work by analyzing the influence of functionalization degree on the rheological and thermogravimetric behavior of resulting chemical oleogels. With this aim, different methyl cellulose chemical modifications were achieved by limiting the

proportion of HMDI and, subsequently, oleogels were obtained by dispersing these polymers in castor oil and promoting the reaction between those biopolymers and the hydroxyl groups located in the ricinoleic fatty acid chain. —NCO-functionalized methyl cellulose-based oleogels were characterized from thermogravimetric and rheological points of view. Suitable thermal resistance and rheological characteristics were found in order to propose these oleogels as promising bio-based alternatives to traditional lubricating greases based on non-renewable resources. In general, —NCO-functionalized methyl cellulose thermally decomposed in three main steps whereas resulting oleogels thermal decomposition takes place in one main single stage which comprises the thermal degradation of both the polymer and the castor oil. Temperature range for thermal degradation is broadened when using highly —NCO-functionalized methyl cellulose. A cross-linked viscoelastic gel was obtained with methyl cellulose functionalized in a relatively low degree (around 6% —NCO molar content). The rheological properties of highly functionalized methyl cellulose-based oleogels evolve during several months of aging, but mainly during the first week, due to the progress of the reaction between —NCO functional groups and castor oil —OH groups. SAOS functions analyzed and oleogel relative elasticity increase with the functionalization degree. Oleogel linear viscoelastic response is also extremely dependent on NCO-functionalized methyl cellulose concentration.

- Gallego, R., Arteaga, J.F., Valencia, C., Franco, J.M.: "Thickening properties of several NCO-functionalized cellulose derivatives in castor oil". Chemical Engineering Science. Vol. 134, págs. 260 -268, (2015). DOI: 10.1016/j.ces.2015.05.007

Enlace al texto completo del artículo (solo para miembros de la UHU):
<http://dx.doi.org/10.1016/j.ces.2015.05.007>

RESUMEN:

Several commercially available cellulose derivatives differing in the type of substituent and substitution degree (α -cellulose, methyl cellulose, 2-hydroxyethyl cellulose, methyl 2-hydroxyethyl cellulose and cellulose acetate propionate) have been functionalized with 1,6-hexamethylene diisocyanate (HMDI) and subsequently dispersed in castor oil to obtain chemical oleogels, which can be proposed as lubricating grease formulations completely based on renewable resources. NCO-functionalized cellulose derivatives used as thickening agents and corresponding oleogels were characterized by means of Fourier transform infrared spectroscopy (FTIR) and thermogravimetric analysis (TGA). Oleogels were also rheologically investigated and gel microstructure determined by atomic force microscope (AFM) observations. Dispersions of the different cellulosic derivatives analyzed provide oleogels with a wide variety of rheological properties, thermal stability and physical appearance. Cellulose derivatives used as thickeners exhibited a reduced thermal resistance after NCO-functionalization due to the inclusion of the HMDI segments in the cellulose structure. However, the resulting oleogels presented suitable thermal resistance. The different rheological responses obtained, from solid-like to weak gels, were found to be basically dependent on the balance between the non-polar and polar substituents molar ratio in the biopolymer structure and the size of these substituents. The presence of non-polar groups reduces cellulose polarity and, therefore, increases the affinity by the oil medium, whereas large substituents seem to hinder the development of the three-dimensional gel network. An empirical correlation between the storage modulus, G' , and a power function of both the molar ratio $[-R_{\text{polar}}/-R_{\text{non-polar}}]$ in each monomer, $-R$ being the different substituents of cellulosic

derivatives evaluated, and the ratio of average molecular weight of all substituents to cellulose monomer molecular weight has been proposed to predict the rheological behavior of resulting oleogel formulations.

- Gallego, R., Arteaga, J.F., Valencia, C., Díaz, M.J., Franco, J.M.: "Gel-like dispersions of HMDI-cross-linked lignocellulosic materials in castor oil: toward completely renewable lubricating grease formulations". Vol. 3 (9), págs. 2130–2141, (2015). DOI: 10.1021/acssuschemeng.5b00389

Enlace al artículo:

<http://dx.doi.org/10.1021/acssuschemeng.5b00389>

RESUMEN:

In this work, several lignocellulose pulps from different origins and/or submitted to different treatments were cross-linked with hexamethylene diisocyanate (HMDI) and further dispersed in castor oil in order to obtain gel-like formulations based on renewable resources, which can be potentially applicable as semisolid lubricants. The rheological and tribological properties attained as well as physical and mechanical stability were suitable to consider these gel-like dispersions as efficient alternatives to traditional lubricating greases. The rheological behavior was evaluated by means of both small-amplitude oscillatory shear tests (SAOS) and viscous flow measurements, at different temperatures. The HMDI/cellulose pulp weight ratio applied in the cross-linking reaction can be used to modify and modulate the consistency and the values of rheological functions of these gel-like dispersions. However, the rheological behavior is not qualitatively affected by the amount of HMDI used as coupling agent. The thermorheological response evidences a softening temperature of around 100 °C. Mechanical stability of HMDI-cross-linked lignocellulose-based oleogels, evaluated as the loss of consistency after submitting the sample to a working test, was significantly improved respecting the non-cross-linked lignocellulose gel-like dispersion. Microstructural morphology was examined using atomic force microscopy (AFM) and consists of long and entangled fibers, extremely similar to that found in lithium greases. Moreover, friction coefficient and resulting wear mark diameters obtained in a ball-on-disc contact lubricated with these eco-friendly formulations were, in most cases, comparable to that obtained with commercial lubricating greases. Therefore, HMDI-cross-linked lignocellulose materials are proposed as effective and promising eco-friendly thickener agents in vegetable oils.

- Gallego, R., Cidade, T., Sánchez, R., Valencia, C., Franco, J.M.: "Tribological behaviour of conventional metallic soap- and chemically modified biopolymer-thickened lubricating greases investigated in a steel-steel rotating ball-on-three plates tribological cell". Submitted for publication

1. Compendium of publications

Block 1: Development of thickening agents from cellulose derivatives

- Article 1: Chemical modification of methyl cellulose with HMDI to modulate the thickening properties in castor oil.
- Article 2: Rheology and thermal degradation of isocyanate-functionalized methyl cellulose-based oleogels.
- Article 3: Thickening properties of several NCO-functionalized cellulose derivatives in castor oil.

Block 2: Development of thickening agents from chitin and chitosan

- Article 4: Isocyanate-functionalized chitin and chitosan as gelling agents of castor oil.
- Article 5: Influence of functionalization degree on the rheological properties of isocyanate-functionalized chitin and chitosan-based chemical oleogels for lubricant applications.

Block 3: Development of thickening agents from lignocellulosic materials

- Article 6: Gel-like dispersions of HMDI-cross-linked lignocellulosic materials in castor oil: towards completely renewable lubricating grease formulations.

Block 4: Tribological characterization of biopolymer-thickened lubricating greases

- Article 7: Tribological behaviour of novel chemically modified biopolymer-thickened lubricating greases investigated in a steel-steel rotating ball-on-three plates tribology cell.

2. Block 1

2.1. Article 1

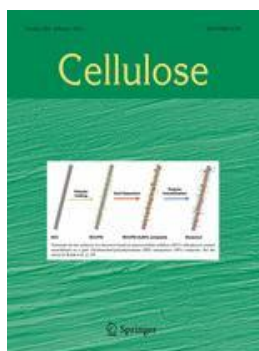
Chemical modification of methyl cellulose with HMDI to modulate the thickening properties in castor oil

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Category	Journal rank/ Total journals	Quartile
Material Science, Paper & Wood	1/21	Q1
Polymer Science	14/82	Q1
Impact factor (2013)	3.033	

2.1.1. Resumen en español/summary in spanish

En este trabajo se explora la capacidad de la metilcelulosa químicamente modificada con 1,6-hexametilendiisocianato (HMDI) como agente espesante del aceite de ricino, promoviendo la reacción química entre los grupos –NCO libres y los grupos –OH de la cadena de ácido ricinoleico. Los biopolímeros obtenidos fueron caracterizados por resonancia magnética nuclear (^1H -RMN), espectroscopía de infrarrojo (IR) y termogravimetría (TGA). La respuesta térmica y reológica de los oleogeles resultantes de la dispersión de estos polímeros en aceite de ricino fue estudiada a partir de TGA y medidas de cizalla oscilatoria.

La cantidad de grupos –NCO libres en el biopolímero funcionalizado, modificado a través de la cantidad de HMDI empleada en su preparación, es un factor determinante en la capacidad espesante del mismo. Así pues, con la intención de controlar el proceso de funcionalización, se aplicaron dos condiciones experimentales diferentes. En primer lugar, se empleó un gran exceso molar de grupos –NCO (6.8 equiv., polímero 1) y, en segundo lugar, se utilizó una menor cantidad de los mismos (2.4 equiv., polímero 2), con respecto al número de moles de grupos –OH libres presentes en la metilcelulosa (1.0 equiv.).

Los espectros de IR de los polímeros permitieron la evaluación de la modificación química de la metilcelulosa tras la reacción de funcionalización, revelando una clara reducción en la banda correspondiente a los grupos –OH (3467 cm^{-1}), las bandas propias de los enlaces uretano (3467 cm^{-1} (N–H), 1723 cm^{-1} (C=O uretano) y 1532 cm^{-1} (N–H uretano)) y la aparición de un intenso pico asociado a los grupos –NCO libres (2272 cm^{-1}). También se calculó el grado de sustitución de los polímeros a partir de los espectros de ^1H -RMN. Como resultado, el polímero 1 mostró prácticamente una completa funcionalización de los grupos –OH disponibles (–Me:–H:–NCO, 58:1:41), además de un exceso del 25% de HMDI, tanto entrecruzado como no entrecruzado; mientras que el polímero 2 mostró una relación de grupos –Me, –H y –NCO de 58:36:6. Por otro lado, mediante el análisis de los termogramas se dedujo que la inclusión de los segmentos de HMDI en el polímero de metilcelulosa produce una ostensible reducción

de su estabilidad térmica debido a la degradación de los enlaces uretano, siendo más marcada en el caso del polímero más altamente funcionalizado (polímero 1).

Posteriormente, los polímeros 1 y 2 fueron dispersados en aceite de ricino, a distintas concentraciones, dando lugar a diferentes oleogeles que demostraron patrones de degradación térmica similares, con temperaturas de inicio de descomposición térmica alrededor de 333 °C. Ésta se produce en una sola etapa que incluye la degradación térmica del polímero de metilcelulosa funcionalizado con grupos –NCO, que se emplea como agente espesante, y del aceite de ricino, que es el principal componente del oleogel. La reacción deseada entre los grupos de –NCO libres en el polímero y los grupos –OH del aceite de ricino fue monitorizada por IR, pudiéndose observar que la banda de –NCO libre (2272 cm^{-1}) se reduce hasta ser prácticamente despreciable.

La caracterización reológica de los oleogeles reveló que la dispersión del polímero 2 en aceite de ricino, a una concentración del 30%, da lugar a un gel con un comportamiento viscoelástico muy similar al de las grasas lubricantes comerciales. Así, dicha formulación exhibe valores del módulo elástico (G') más altos que los del módulo viscoso (G'') en todo el rango de frecuencias estudiado. Además, G' aumenta ligeramente con la frecuencia mientras que G'' muestra un mínimo, resultando la zona “plateau” del espectro mecánico, habitualmente observada en sistemas poliméricos altamente entrecruzados y grasas lubricantes estándar. Los valores de G' se encuentran entre 10^4 y 10^5 Pa y son aproximadamente un orden de magnitud más altos que los de G'' , lo que se corresponde con los valores encontrados en grasas lubricantes de grado NLGI 1 y 2. Asimismo, la caracterización reológica demostró que el aumento de la concentración de espesante produce un claro incremento de las funciones viscoelásticas. Respecto a la evolución de las formulaciones estudiadas con el tiempo, puede afirmarse que ambos módulos aumentan de forma significativa durante la primera semana de envejecimiento del oleogel, permaneciendo prácticamente constantes posteriormente. Esta evolución es más rápida en el polímero 1 que en el 2 debido al mayor nivel de entrecruzamiento.

Finalmente, se comprobó que la dispersión de metilcelulosa no funcionalizada en aceite de ricino o el empleo de aceites vegetales sin grupos $-OH$ en la composición de ácidos grasos, como el aceite de girasol, producen formulaciones inestables que muestran separación de aceite como consecuencia de un cierto grado de sedimentación del espesante. Este resultado confirma que la reacción química entre el biopolímero y el aceite vegetal es la responsable de la estabilidad física y de las propiedades reológicas de estos oleogeles.

2.2. Article 2

Rheology and thermal degradation of isocyanate-functionalized methyl cellulose-based oleogels

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Category	Journal rank/Total journals	Quartile
Chemistry, Applied	4/70	Q1
Polymer Science	9/82	Q1
Impact factor (2013)	3.916	

2.2.1. Resumen en español/summary in spanish

El objetivo de este trabajo es el estudio de la influencia del grado de funcionalización de metilcelulosa modificada químicamente con 1,6-hexametilendiisocianato (HMDI) en distintas proporciones sobre la respuesta termogravimétrica y reológica de las correspondientes dispersiones en aceite de ricino. Los polímeros sintetizados fueron caracterizados por resonancia magnética nuclear (^1H -RMN), espectroscopía de infrarrojo (IR) y termogravimetría (TGA), mientras que los oleogeles fueron caracterizados desde un punto de vista termogravimétrico y reológico.

El grado de sustitución de los diferentes polímeros modificados fue calculado en base los espectros de ^1H -RMN. Como resultado, se obtuvieron diferencias significativas en la proporción de grupos $-\text{OH}$ funcionalizados (en un intervalo de 1-41%), siendo proporcional a la cantidad de HMDI empleada.

La modificación química producida en la metilcelulosa tras el proceso de funcionalización con diferentes proporciones de HMDI se analizó a partir de los espectros de IR. Éstos exhiben una reducción significativa de la intensidad de la banda atribuida a los grupos $-\text{OH}$, más acusada cuanto mayor es el contenido de HMDI; la aparición de las bandas correspondientes al enlace uretano (3468 cm^{-1} ($\text{N}-\text{H}$), 1723 cm^{-1} ($\text{C}=\text{O}$ uretano) y 1561 cm^{-1} ($\text{N}-\text{H}$ uretano)) en todos los casos; y un intenso pico debido a la presencia de grupos $-\text{NCO}$ libres (2271 cm^{-1}). Esta última señal, por el contrario, es insignificante en los espectros de IR de los oleogeles, corroborando la reacción química entre los grupos $-\text{NCO}$ del polímero y los grupos $-\text{OH}$ del aceite de ricino.

El análisis termogravimétrico reveló que la inclusión de los segmentos de HMDI en el polímero de metilcelulosa reduce su estabilidad térmica. Sin embargo, la caracterización térmica de los correspondientes oleogeles demostró que éstos poseen una resistencia térmica mayor que la observada en grasas tradicionales basadas en aceites minerales. La degradación térmica de los polímeros sintetizados se produce, generalmente, en tres etapas. La primera de ellas ($82\text{-}123\text{ }^{\circ}\text{C}$) se corresponde con la descomposición térmica de los grupos $-\text{NCO}$ y da lugar a una pérdida de peso mayor cuanto mayor es el grado de funcionalización. La segunda fase ($310\text{-}336\text{ }^{\circ}\text{C}$) es debida

principalmente a la degradación de la cadena de metilcelulosa y, al contrario que la primera etapa, la pérdida de peso que se produce es mayor cuanto menor es el grado de funcionalización del polímero. Por último, la tercera etapa (443-458 °C), que sólo aparece en los polímeros altamente funcionalizados, se debe a la degradación de poliuretanos más rígidos originados por un excesivo entrecruzamiento de fracciones de metilcelulosa. Por otro lado, la degradación térmica de los oleogeles se produce en una sola etapa, la cual incluye la descomposición térmica del biopolímero modificado y del aceite. No obstante, el rango de degradación se hace mayor cuanto mayor es el grado de funcionalización del biopolímero modificado. Además, el primer pico de degradación observado en los termogramas de los biopolímeros ya no es detectable en los de los oleogeles, confirmando, una vez más, la reacción química entre biopolímero y aceite de ricino.

La caracterización reológica permitió dilucidar el espectro mecánico de los oleogeles, apareciendo, en todos los casos, la zona “plateau” del espectro, desplazada a bajas frecuencias, seguida del comienzo de la zona de transición, a altas frecuencias. Al mismo tiempo, en la mayoría de los casos, los valores de G' oscilan entre 10^4 y 10^5 Pa y son, aproximadamente, una década mayores que G'' , tal y como ocurre con grasas lubricantes convencionales de grado NLGI 2 espesadas con jabones metálicos. Por tanto, atendiendo a la respuesta reológica, estas formulaciones pueden ser propuestas como alternativas potenciales basadas en fuentes renovables.

Respecto al efecto del tiempo en las propiedades reológicas, se observó un aumento de las funciones viscoelásticas durante la primera semana, más significativo cuanto mayor es el grado de funcionalización del polímero empleado como gelificante, aumentando ligeramente o permaneciendo prácticamente constante a partir de entonces.

Finalmente, como aportación más importante, se estudió la influencia del contenido de -NCO libre en la metilcelulosa sobre la respuesta reológica de los oleogeles. Se determinó que el empleo de metilcelulosa funcionalizada en pequeña proporción (1-6 %) puede modificar en gran medida la respuesta reológica de la correspondiente dispersión en aceite de ricino, haciendo que las funciones viscoelásticas disminuyan

considerablemente respecto de la dispersión de metilcelulosa no funcionalizada en aceite. A partir de ahí, de forma general, un aumento del grado de funcionalización provoca un aumento en el valor de los módulos viscoelásticos y una disminución significativa de la tangente de pérdidas, especialmente a bajas frecuencias. Del mismo modo, un aumento en la concentración del biopolímero funcionalizado también produce un incremento en el valor de los módulos viscoelásticos y de la elasticidad relativa, permitiendo así modificar la consistencia del oleogel.

2.3. Article 3

Thickening properties of several NCO-functionalized cellulose derivatives in castor oil

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Category	Journal rank/Total journals	Quartile
Engineering, Chemical	42/134	Q2
Impact factor (2014)	2.337	

2.3.1. Resumen en español/summary in spanish

En este trabajo, varios derivados de celulosa con distintos sustituyentes y grados de sustitución (α -celulosa, metilcelulosa, 2-hidroxietilcelulosa, metil 2-hidroxietilcelulosa y acetato propionato de celulosa) fueron funcionalizados con 1,6-hexametilendiisocianato (HMDI) y, posteriormente, dispersados en aceite de ricino con el objetivo de obtener oleogeles químicos que puedan ser propuestos como grasas lubricantes completamente basadas en fuentes renovables. Los derivados de celulosa modificados con grupos –NCO y los correspondientes oleogeles fueron caracterizados a partir de espectroscopía de infrarrojo (IR) y análisis termogravimétrico (TGA). También se estudió la respuesta reológica de los oleogeles y se determinó su microestructura empleando la microscopía de fuerza atómica (AFM).

En la mayoría de los espectros de IR de los derivados de celulosa modificados se aprecia cierta reducción en la intensidad de la banda atribuida a los grupos –OH ($3341\text{--}3470\text{ cm}^{-1}$), debido a la formación de enlaces uretano tras la reacción de funcionalización con HMDI. Las señales correspondientes a estos enlaces aparecen alrededor de 1720 cm^{-1} para los grupos C=O y a unos 1570 cm^{-1} para los enlaces N–H. Además, puede observarse la señal característica de los grupos –NCO libres ($2270\text{--}2280\text{ cm}^{-1}$), la cual es prácticamente insignificante en los espectros de IR de todos los oleogeles, corroborando la reacción química entre los grupos –NCO de los polímeros y los –OH del ácido ricinoleico del aceite de ricino.

El análisis termogravimétrico mostró una reducción notable de la estabilidad térmica de los distintos derivados de celulosa tras la reacción de funcionalización con HMDI, aunque los oleogeles resultantes demostraron una adecuada resistencia térmica. Por otra parte, la etapa de degradación térmica correspondiente a los grupos –NCO ($T_{\text{max}} = 105\text{--}120\text{ }^{\circ}\text{C}$), presente en los termogramas de los diferentes biopolímeros modificados, no es apreciable en los análogos de los oleogeles, confirmando de nuevo la ocurrencia de la reacción química entre agente espesante y aceite.

La caracterización reológica de los distintos oleogeles, a pesar de estar espesados con biopolímeros funcionalizados con grupos $-NCO$ en el mismo grado ($\approx 17\%$) e incorporados al aceite de ricino en la misma concentración (30%), reveló comportamientos muy diversos, característicos tanto de geles fuertes como débiles dependiendo del derivado celulósico empleado. Así, las formulaciones basadas en metilcelulosa y metil 2-hidroxietilcelulosa exhiben un módulo elástico (G') siempre mayor que el viscoso (G'') en todo el rango de frecuencias estudiado, mostrando la conocida zona “plateau” del espectro mecánico. Como se ha dicho en capítulos anteriores, esta evolución sumada a los valores de G' y G'' obtenidos, se corresponde con la respuesta reológica de grasas lubricantes convencionales de grado NLGI 1-2. Por otro lado, los oleogeles espesados con α -celulosa, 2-hidroxietilcelulosa y acetato propionato de celulosa, previamente funcionalizados con HMDI, se comportan como geles débiles, presentando un punto de cruce entre ambas funciones viscoelásticas, que se desplaza a frecuencias menores en ese orden. En cuanto a la evolución de la tangente de pérdidas con la frecuencia, el oleogel de metil 2-hidroxietilcelulosa presenta los valores más bajos y un prominente mínimo a, aproximadamente, 1 rad/s, indicando una alta elasticidad relativa fruto de un alto nivel de entrecruzamiento. Por el contrario, los valores más altos de la tangente de pérdidas son los exhibidos por la formulación espesada con acetato propionato de celulosa, demostrando un comportamiento principalmente viscoso.

Del análisis del comportamiento reológico de las formulaciones estudiadas pueden extraerse varias conclusiones. En primer lugar, la fuerza del gel depende de la cantidad de grupos no polares presentes en el monómero de celulosa tras la reacción de funcionalización, ya que es responsable de hacer que disminuya la polaridad de la celulosa, incrementando su afinidad por el aceite. En segundo lugar, el tamaño del sustituyente puede afectar e incluso obstaculizar, la formación de la estructura tridimensional del gel. En tercer lugar, aparte del efecto adverso de la polaridad, cuando la cantidad de grupos $-OH$ en el espesante es más alta, la selectividad de la reacción disminuye, ya que aumenta el entrecruzamiento de las cadenas y se reduce la interacción de éstas con el aceite. Considerando estos factores, se estableció una

relación matemática que permite predecir las propiedades espesantes de cualquier derivado de celulosa, funcionalizado con grupos -NCO , en aceite de ricino. Así, por ejemplo, se encontró una relación potencial entre el módulo de almacenamiento, a 1 rad/s, y dos grupos adimensionales que tienen en cuenta la relación de sustituyentes polares y no polares en el monómero de celulosa y el peso molecular de los sustituyentes respecto del monómero de α -celulosa, respectivamente, resultando un exponente de -2.88 en ambos parámetros, lo que indica un debilitamiento de las propiedades espesantes al aumentar la polaridad del polímero y/o el peso molecular de los sustituyentes.

Las microfotografías obtenidas a partir de AFM de los geles de metilcelulosa y 2-hidroxietilcelulosa mostraron, en ambos casos, una estructura compuesta por fibras interconectadas formando una red tridimensional, más densa en el primero que en el segundo, lo que es coherente con la respuesta reológica observada.

3. Block 2

3.1. Article 4

Isocyanate-functionalized chitin and chitosan as gelling agents of castor oil

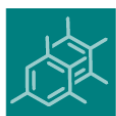
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3.1.1. Resumen en español/summary in spanish

El objetivo principal de este trabajo es la funcionalización de biopolímeros de quitina y quitosano con grupos isocianato para su utilización como espesantes reactivos en aceite de ricino, dando lugar a oleogeles que pueden ser potencialmente empleados como grasas lubricantes biodegradables. Los polímeros sintetizados fueron caracterizados a través de resonancia magnética nuclear de protones (^1H -RMN), espectroscopía de infrarrojo (IR) y análisis termogravimétrico (TGA), mientras que de las dispersiones resultantes se estudió, principalmente, su comportamiento reológico y termogravimétrico.

Quitina y quitosano fueron modificados con 1,6-hexametilendiisocianato (HMDI) con la finalidad de mejorar su capacidad espesante en aceite de ricino, para lo que la proporción de $-\text{NCO}$ resulta determinante. Así, se seleccionaron dos condiciones experimentales para el proceso de funcionalización del quitosano. Por un lado, se empleó la cantidad de grupos $-\text{NCO}$ (0.5 equiv.) necesaria para reaccionar con la mitad de los grupos $-\text{OH}$ y $-\text{NH}$ desacetilados (1.0 equiv.). Por otra parte, se usó una menor proporción de HMDI (0.25 equiv.) con la intención de funcionalizar una cuarta parte de los grupos $-\text{OH}$ y $-\text{NH}$ disponibles (1.0 equiv.), condiciones que también fueron aplicadas a la quitina. Las propiedades espesantes de los polímeros se compararon con las de quitina y quitosano no funcionalizados.

Los espectros de ^1H -RMN de los polímeros modificados resultantes mostraron que la señal atribuida al protón del grupo N-H al final de la cadena de HMDI reaccionado (5.8 ppm) y la señal originada por los dos protones del grupo $-\text{CH}_2$ unida a ésta (2.9 ppm) están presentes en proporción 1:2, de lo que se deduce que la reacción entre quitina o quitosano y el diisocianato se produce de forma satisfactoria y en la extensión deseada. Por otro lado, los espectros de IR de dichos polímeros exhibieron una notable reducción de intensidad en la banda correspondiente al grupo $-\text{OH}$ de las moléculas de quitina (3364 cm^{-1}) y quitosano (3357 cm^{-1}) tras la reacción de funcionalización que da lugar a los enlaces uretano. Las bandas correspondientes a éstos enlaces también pueden apreciarse a 3364 y 3357 cm^{-1} (N-H), 1652 y 1642 cm^{-1} (C=O de uretano) y 1559 y

1572 cm^{-1} (N–H de uretano) para quitina y quitosano, respectivamente. Además, se observa claramente el intenso pico causado por los grupos –NCO libres ($\approx 2274 \text{ cm}^{-1}$). Esta señal, por el contrario, no es apreciable en los espectros de IR de las correspondientes dispersiones de estos polímeros en aceite de ricino (al 30%) pasado un mes desde su manufactura, lo que corrobora de nuevo la ocurrencia de la reacción entre los grupos –NCO del espesante y los grupos –OH del aceite, aunque sí que puede observarse en los espectros obtenidos tan sólo un día después de la preparación del oleogel.

El análisis termogravimétrico reveló que la inserción de los segmentos de HMDI en quitina y quitosano produce una reducción de la estabilidad térmica, más acusada cuanto mayor es el grado de funcionalización. Sin embargo, los correspondientes oleogeles presentan una resistencia térmica significativamente superior a la demostrada por las grasas lubricantes tradicionales. Además, en los termogramas de las dispersiones no se observó la etapa de descomposición térmica correspondiente a los grupos –NCO (106-140 $^{\circ}\text{C}$ y 107-179 $^{\circ}\text{C}$, en referencia a quitina y quitosano, respectivamente), presente en los termogramas de los polímeros modificados. De esta forma se evidencia, una vez más, la interacción química que tiene lugar entre los grupos –NCO del polímero con los –OH del aceite.

La caracterización reológica de la mayoría de las formulaciones muestra valores del módulo de almacenamiento (G') superiores a los del módulo de pérdidas (G''), en todo el rango de frecuencias estudiado, a excepción del oleogel basado en quitina modificada, en el que puede observarse un cruce entre ambas funciones viscoelásticas a alta frecuencia. La zona “plateau” del espectro se detecta a bajas frecuencias. Las formulaciones basadas en el polímero de quitosano más altamente funcionalizado y el no modificado muestran valores de los módulos viscoelásticos similares a los de grasas lubricantes de litio de grado NLGI 2. En el caso del quitosano funcionalizado en menor grado, la respuesta reológica es más similar a grasas más blandas, con menor concentración de espesante.

En cuanto al efecto del tiempo, se observa un incremento significativo en las funciones viscoelásticas durante la primera semana tras su manufactura, aumentando ligeramente hasta el primer mes, a partir del cual permanecen prácticamente constantes. La tangente de pérdidas, sin embargo, sólo aumenta durante la primera semana, permaneciendo constante posteriormente. Esta influencia no se observa en aquellos oleogeles espesados con quitina o quitosano que no hayan sido previamente funcionalizados, ya que no se da reacción química alguna que haga que el sistema evolucione con el tiempo.

De la comparación de la respuesta reológica de los dos oleogeles basados en quitina se dedujo que una pequeña cantidad de isocianato puede producir una notable modificación en las propiedades reológicas del oleogel, observándose una disminución significativa de los elevados valores de los módulos viscoelásticos que presentan los oleogeles preparados con quitina no modificada. Por el contrario, el aumento del grado de funcionalización del polímero produce un aumento en los valores de G' y G'' , debido a un mayor grado de entrecruzamiento originado por un contenido más alto de $-NCO$ libre, como puede deducirse de la respuesta reológica mostrada por las formulaciones basadas en quitosano.

3.1.2. Full article

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Article

Isocyanate-Functionalized Chitin and Chitosan as Gelling Agents of Castor Oil

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Abstract: The main objective of this work was the incorporation of reactive isocyanate groups into chitin and chitosan in order to effectively use the products as reactive thickening agents in castor oil. The resulting gel-like dispersions could be potentially used as biodegradable lubricating greases. Three different NCO-functionalized polymers were obtained: two of them by promoting the reaction of chitosan with 1,6-hexamethylene diisocyanate (HMDI), and the other by using chitin instead of chitosan. These polymers were characterized through ¹H-NMR, FTIR and thermogravimetric analysis (TGA). Thermal and rheological behaviours of the oleogels prepared by dispersing these polymers in castor oil were studied by means of TGA and small-amplitude oscillatory shear (SAOS) measurements. The evolution and values of the linear viscoelasticity functions with frequency for –NCO-functionalized chitosan- and chitin-based oleogels are quite similar to those found for standard lubricating greases. In relation to long-term stability of these oleogels, no phase separation was observed and the values of viscoelastic functions increase significantly during the first seven days of ageing, and then remain almost constant. TGA analysis showed that the degradation temperature of the resulting oleogels is higher than that found for traditional lubricating greases.

Keywords: chitin; chitosan; castor oil; isocyanate; lubricating grease; rheology

1. Introduction

Nowadays, there is a general tendency to promote the replacement of non-renewable raw materials by renewable resources in order to avoid or minimize the impact that process technologies and industrial products cause in the environment. The lubricant industry is especially interested in reducing the environmental impact of its products [1,2]. Although vegetable oils are being increasingly used as lubricant base oils instead of mineral and synthetic oils, the substitution of traditional thickener agents, such as lithium, aluminum, sodium or calcium soaps in lubricating greases by others derived from renewable resources, like some biopolymers, is a complicated task due to the technical efficiency of these metallic soaps to impart the desired functional properties to the final product.

Chitosan is typically obtained by deacetylation under alkaline conditions of chitin, which is the second most abundant biopolymer in Nature, after cellulose. Chitin can be found as an important constituent of the exoskeleton in animals, especially in crustaceans, mollusks and insects, and it is also the principal polymer in the cell wall of certain fungi. Chitin and chitosan are linear polysaccharides composed of randomly distributed β -(1-4)-linked D-glucosamine (deacetylated unit) and N-acetyl-D-glucosamine (acetylated unit). Chitosan is available in a variety of useful forms, displays interesting properties such as biocompatibility or biodegradability [3,4] and its degradation products are non-toxic, non-immunogenic and non-carcinogenic [5,6], which make it a very attractive biomaterial. It is extensively used in many different applications such as treatment of wastewater [7], as a chromatographic support [8], in enzyme immobilization [9], as a wound-healing dressing [10], in dental applications [11], in adhesion bandages for surgery [12], and in drug-delivery systems [13–16].

Nowadays there is a growing interest in the chemical modification of chitosan in order to improve its solubility in different media and widen its applications [17–19]. Both chitin and chitosan have two types of reactive groups that can be grafted: the free amine groups on the deacetylated units and the hydroxyl groups on the C3 and C6 carbons on acetylated or deacetylated units. These reactive sites enable the linkage of a wide variety of functional reactive molecules [20–22]. One of these molecules that can be linked in those positions is the 1,6-hexamethylenediisocyanate (HMDI), which is commercially available and generally utilized as a strong cross-linker of -NH_2 or -OH groups, since it possesses two reactive isocyanate groups (-N=C=O) [23]. The -OH groups of chitin and chitosan can react with -NCO groups to form an urethane linkage (-NH-C(O)-O-) due to the transfer of protons from -OH groups to the nitrogen atoms of -NCO units. HMDI can also react with deacetylated amino groups in the biopolymers. The reaction between chitosan and HMDI has been previously promoted to use the resulting products in different applications such as molecular carriers in the biomedical and environmental fields [24], as support material for Pd catalysts used in hydrogenation reactions [25], as solid support for Cu(I) and Pd(II) catalysts used in reactions like azide/alkyne [3+2] cycloaddition and Suzuki cross-couplings [26], cholesterol absorption [23], adsorption of phenols, toxic carcinogens [27], gold sorption [28] or polyurethane elastomers [29].

The use of chitin and chitosan to thicken vegetable oil media has been previously addressed [30], but some limitations regarding physical and mechanical stabilities and rheological response were pointed out as a consequence of a certain degree of chemical incompatibility between oil and such polar biopolymers. Relatively physically stable suspensions were obtained only above the percolation threshold. Besides this, in a previous study [31], the functionalization of methylcellulose with reactive –NCO groups, and its further ability to thicken castor oil by reacting with the –OH groups of the ricinoleic fatty chain was studied. The resulting chemical oleogels may serve for different applications depending on the degree of functionalization. One of these, obtained with methylcellulose functionalized to a lower degree, presented suitable rheological properties and thermal resistance to be proposed as a biodegradable alternative to lubricating greases. Following a similar methodology, the incorporation of reactive –NCO groups into chitin and chitosan and its ability to thicken castor oil is explored in this work in order to avoid the previously mentioned problems and increase the chemical affinity between these polymers and vegetable oils. These oleogels prepared with isocyanate-functionalized chitin and chitosan polymers and castor oil were rheologically and thermally characterized.

2. Results and Discussion

2.1. Synthesis and Characterization of Isocyanate—Functionalized Chitin and Chitosan

Three different types of polymers functionalized with isocyanate groups, chitosan in two of the cases and chitin in the other one, were prepared. The introduction of the isocyanate moieties was carried out in order to improve the role of these biopolymers as thickener agents in castor oil. The amount of –NCO groups present in the final polymer will be a determining factor in the ability to act as a suitable thickener. Therefore, two experimental conditions have been selected for the preparation of the modified polymers of chitosan: the first (CSAN-1) used an amount of –NCO moieties (0.5 equiv., Table 1) required for the reaction with half of the deacetylated –OH and –NH groups present in this polymer (1.0 equiv., Table 1); and the second one (CSAN-2) using a lower amount of –NCO (0.25 equiv., Table 1) to promote the reaction with a quarter of the free –OH and –NH groups (1.0 equiv., Table 1). This last level of functionalization was the one chosen for the modification of chitin, thus affording the third isocyanate-functionalized biopolymer (CTIN-1).

Table 1. Molar ratios of chitosan, HMDI, Et₃N and toluene used in the functionalization reaction.

	Starting material [equiv.] *	HMDI [equiv.] *	Et ₃ N [equiv.] *	Toluene [mL]
CSAN-1	1.00	0.50	1.00	100
CSAN-2	1.00	0.25	0.50	100
CTIN-1	1.00	0.25	0.50	100

* Molar ratio between moles of free –OH and –NH groups present in each monomer of starting chitosan, and moles of each of the reagents employed.

The use of two different –NCO/biopolymer ratios allows the control of the functionalization process and obtaining polymers with different number of free –OH and –NCO groups. Because of HMDI's ability to act as cross-linking reagent, since it possesses a –NCO functional group at each end of the

molecule and, therefore, can react once or twice along the course of the experimental procedure, it seems necessary to control these cross-linking reactions to modulate the functional properties of the polymers synthesized. For this reason, the study of the reaction conditions, mainly the use of both reactant ratios described above, was aimed at finding the conditions under which the reaction mainly occurs only at one end of HMDI molecule, which remains linked to the biopolymer, leaving the other free -NCO group able to further interact with the corresponding -OH groups located in the ricinoleic fatty acid chain during oleogel preparation (Figure 1) [31]. Lower quantities of -NCO than that required by the reaction stoichiometric proportions are used to avoid or minimize the possible formation of compounds with a high degree of cross-linking between -NCO groups, namely polyurethanes. The structure of the chemically modified biopolymers, chitin/chitosan- $\text{O-NHC(O)-hexamethylene-NCO}$, contain a wide variety of functional groups (Figure 1) highlighting the presence of urethane linkages between the polymer and hexamethylene- NCO chain responsible for the subsequent reaction with -OH groups of castor oil fatty acids during oleogel preparation.

Figure 1. General strategy for chitin and chitosan NCO -functionalization and reaction with ricinoleic fatty acid during oleogel preparation.

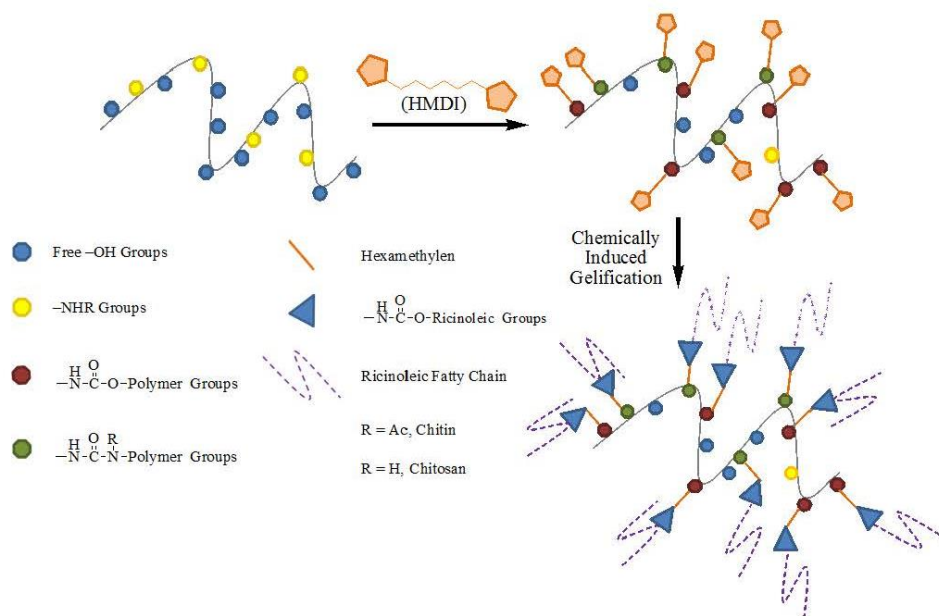
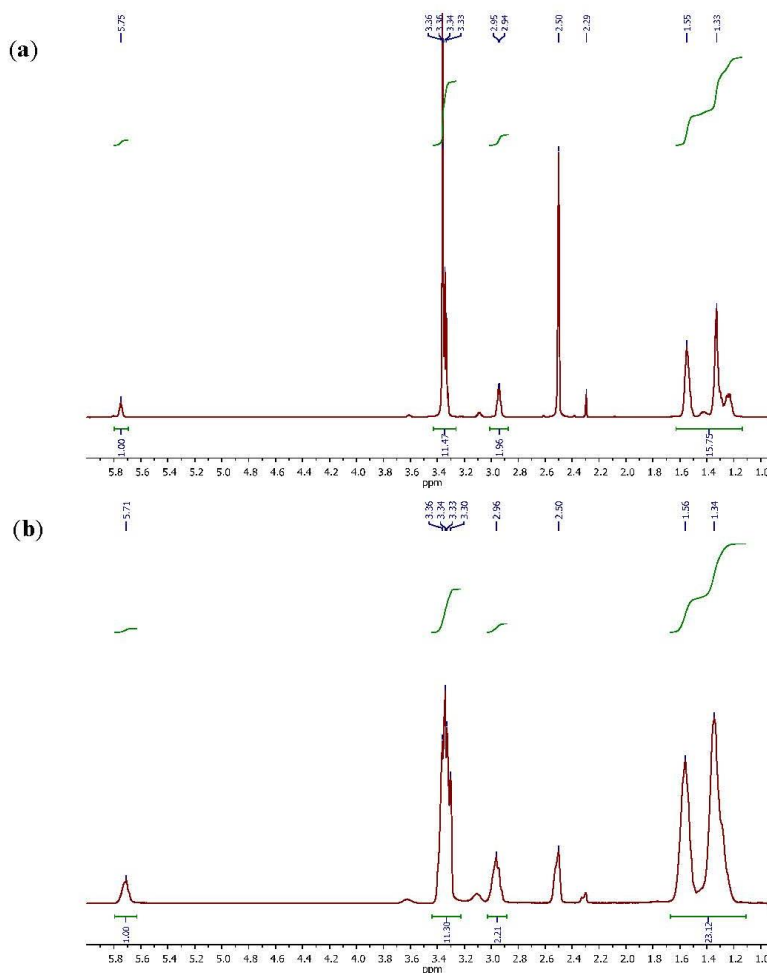


Figure 2 shows the NMR spectra of the functionalized chitosan with a higher amount of HMDI (CSAN-1) and isocyanate-functionalized chitin (CTIN-1), respectively. The main signals of both spectra are approximately the same and they are in concordance with the proposed chemical structures. The signals corresponding to the proton of the N-H group at the end of the reacted HMDI chain (5.8 ppm) and the two protons of the -CH_2 group attached to it (2.9 ppm) are present in a 1:2 ratio, which means that the reaction between chitin or chitosan and the diisocyanate was successfully accomplished. The higher amount of HMDI in CSAN-1 can be noticed by the more intense peaks corresponding to the

protons of the four $-\text{CH}_2$ groups placed in the middle of the HMDI chain (1.6–1.2 ppm). The protons of O–H, N–H, the sugar rings and the $-\text{CH}_2$ attached to non-reacted HMDI isocyanate groups appear at 3.4 ppm and they are signals corresponding to the main chitosan and chitin structure. The $-\text{CH}_3$ of the acetylated part displays a peak at 2.3 ppm and the solvent, DMSO- d_6 , shows a noticeable signal at 2.5 ppm.

Figure 2. ^1H -NMR spectra for (a) CTIN-1 and (b) CSAN-1.



Fourier transform infrared spectroscopy (FTIR) was used to evaluate the chemical modification of chitosan and chitin after the functionalization with HMDI. Figure 3 shows the FTIR spectra of chitosan, chitin and the corresponding samples once functionalized with HMDI (CSAN-2 and CTIN-1, respectively). Infrared spectra of new functionalized polymers were in concordance with the proposed chemical structures. The reduction in intensity of the bands at $3,357\text{ cm}^{-1}$ (CSAN-2) and $3,364\text{ cm}^{-1}$ (CTIN-1) attributable to the $-\text{OH}$ moieties in chitosan and chitin, once reacted with isocyanate groups of HMDI leading to urethane linkages (see Figure 4) is significant. Secondly, the urethane bands were apparent

at $3,357\text{ cm}^{-1}$ (CSAN-2) and $3,364\text{ cm}^{-1}$ (CTIN-1) for the N–H group, $1,642\text{ cm}^{-1}$ (CSAN-2) and $1,652\text{ cm}^{-1}$ (CTIN-1) for the C=O group of the urethane and $1,572\text{ cm}^{-1}$ (CSAN-2) and 1559 cm^{-1} (CTIN-1) for the N–H group in the urethane linkages of the modified biopolymers. Moreover, the intense peaks at $2,274\text{ cm}^{-1}$ (CSAN-2) and $2,275\text{ cm}^{-1}$ (CTIN-1) confirmed the presence of unreacted isocyanate groups, as intended.

Figure 3. FTIR spectra for (a) chitosan, (b) chitin and polymers, (c) CSAN-2 and (d) CTIN-1.

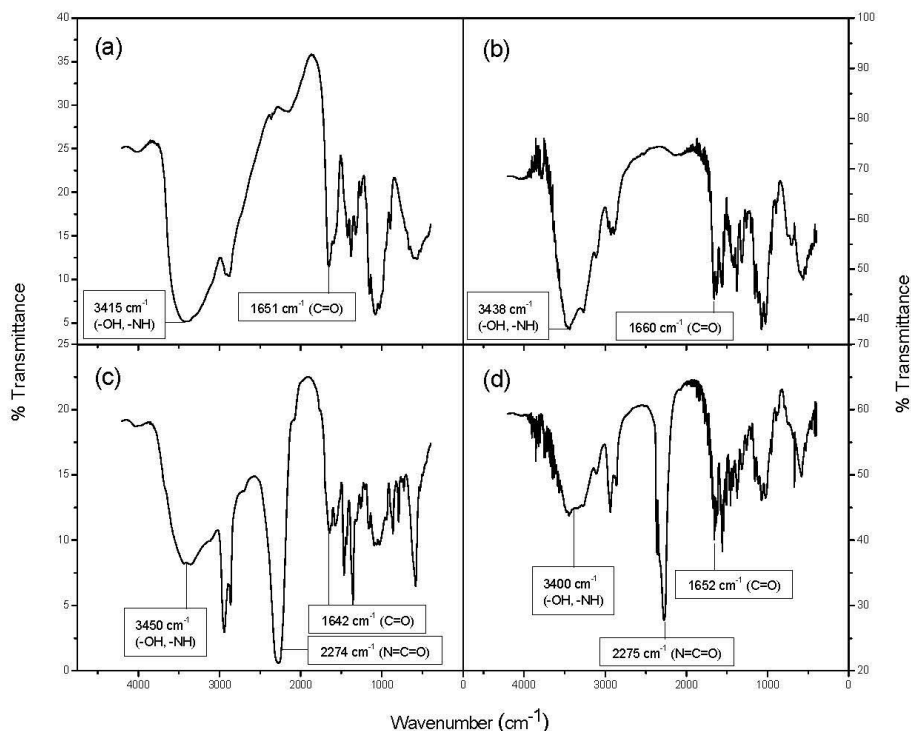
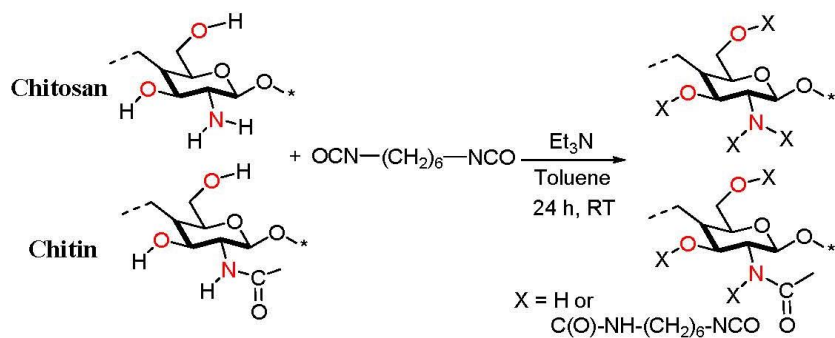


Figure 4. Reaction of chitosan and chitin with hexamethylene diisocyanate (HMDI).



2.2. Thermogravimetric Analysis of Isocyanate-Functionalized Chitosan and Chitin

Thermal decomposition of chitosan and chitin and new –NCO–functionalized chitosan (CSAN-1 and CSAN-2) and chitin compounds (CTIN-1) turned to be quite different (Figure 5). The temperature for the onset of thermal decomposition (T_{onset}), the temperature at which decomposition rate is maximum (T_{max}), the percentage of non-degraded residue and loss weight at the end of each decomposition step have been calculated from the thermograms of the samples studied (Table 2). For non-functionalized chitosan and chitin, thermal degradation under nitrogen atmosphere occurred in one main step. For chitin, this thermal event occurred in the range of 343–405 °C and was due to the degradation of the saccharide structure of the molecule, including the dehydration of saccharide rings and decomposition of both acetylated and deacetylated chitin units [32]. This decomposition step occurred for chitosan at a lower temperature, indicating lower thermal stability. The peak exhibited at 301 °C corresponds to the degradation of part of the molecule that is deacetylated. This intense peak showed an overlapped small signal at around 390 °C which could correspond to the acetylated part of the molecule. Previously, a certain mass loss, between 43 °C (chitosan)/40 °C (chitin) and 77 °C (chitosan)/79 °C (chitin), must be attributed to water evaporation. For functionalized chitin and chitosan, the inclusion of HMDI segments into the polymer structure reduced their thermal stabilities in great extent due to the –HMDI groups, with marked impact in the highest functionalized polymer, as expected (Figure 5, Table 2).

Figure 5. Thermal degradation curves, under inert atmosphere, for NCO–functionalized chitosans and chitins and starting materials.

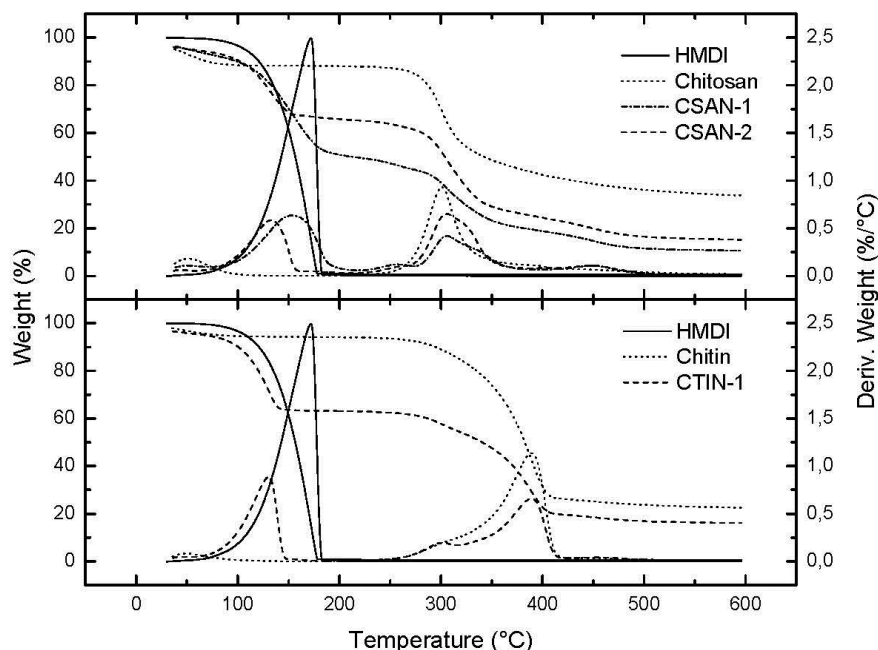


Table 2. TGA characteristic parameters for the biodegradable thickeners studied and starting materials.

Sample	T _{onset} (°C)	T _{max} (°C)	T _{final} (°C)	Residue (%)	ΔW (%)
Chitosan	43/281	51/301	77/472	34	9/57
Chitin	40/343	49/389	79/405	23	4/72
HMDI	137	172	178	1	99
CSAN-1	43/122/240/292/429	50/153/258/306/450	60/179/266/340/483	11	4/44/6/26/9
CSAN-2	40/107/283/431	43/133/306/448	50/150/335/486	15	2/30/43/9
CTIN-1	106/275/363/439	130/302/389/454	140/309/403/494	16	34/10/36/4

Apart from the loss of water, thermal decomposition of functionalized chitosan polymers exhibited two main stages: the first one takes place between 122 °C (CSAN-1)/107 °C (CSAN-2) and 179 °C (CSAN-1)/133 °C (CSAN-2) due to the loss of –NCO segments; and the second one, between 292 °C (CSAN-1)/289 °C (CSAN-2) and 340 °C (CSAN-1)/335 °C (CSAN-2), is related to the loss of the deacetylated part of the chitosan molecule. Small peaks corresponding to the degradation of the acetylated part can be also detected in the derivative curve at higher temperatures (Figure 2). For the CTIN-1 polymer, three main steps are observed: the first stage takes place from 106 °C to 140 °C and corresponds to the loss of –NCO segments, the second one, between 275 °C and 309 °C, is related to the loss of the deacetylated part of the molecule; and the third stage between 363 °C and 403 °C is due to the loss of the acetylated units. As can be deduced from Table 2, the functionalized chitosan polymer with higher –NCO content (CSAN-1) exhibited higher weight loss in the second stage and lower in the third stage. On the other hand, HMDI thermal degradation also occurs in one single stage, between 137 and 178 °C, which matches the first main degradation stage of functionalized polymers analyzed. This mass loss appears more intensively in CSAN-1 (Figure 5), due to the presence of the higher amount of inserted HMDI.

2.3. Thermal and Spectroscopic Characterization of Isocyanate-Functionalized Chitosan and Chitin Gel-Like Dispersions in Castor Oil

Different oleogels were prepared by dispersing 30% w/w of non-functionalized and –NCO–functionalized chitin and chitosan in castor oil. Figure 6 shows that chitosan and chitin derivative-based oleogels exhibit slightly different thermal tendencies. The thermal degradation of non-functionalized chitosan gel-like dispersions (CSAN-30) takes place from 278 °C to 482 °C and three different maximum peaks at 302 °C, 389 °C and 449 °C can be observed (Table 3). The first one corresponds to chitosan degradation and the second is mainly due to castor oil [33]. In the case of oleogels formed with –NCO–functionalized chitosan, the thermal degradation takes place from approximately 297 °C to 481 °C and again three maximum peaks are observed, in this case at 344 °C, 386 °C and 452 °C. The second and the third peaks are similar to those found in the non-functionalized chitosan-based oleogel (CSAN-30), whereas the first peak is delayed. Chitin-based oleogels have two clearly separated degradation steps. The onset temperature for the first one appears close to 342 °C and the final temperature at around 409 °C, with maximum degradation rate at 381 °C, which is attributable to both castor oil decomposition and the main degradation stage of chitin (see Figure 2). The second one

takes place from 425 to 595 °C with a maximum peak at 459 °C. A similar degradation pattern was obtained for the –NCO-functionalized chitin-based oleogel. Finally, it can be concluded that the disappearance of the first isocyanate-functionalized polymer degradation peak in the resulting oleogels confirms the chemical reaction promoted between the modified polymer and the castor oil. In general, thermal resistance of these oleogels is significantly higher than those previously reported for traditional lubricating greases [34–36].

Figure 6. Thermal degradation curves, under inert atmosphere, for –NCO-functionalized and non-functionalized chitosan and chitin gel-like dispersions in castor oil.

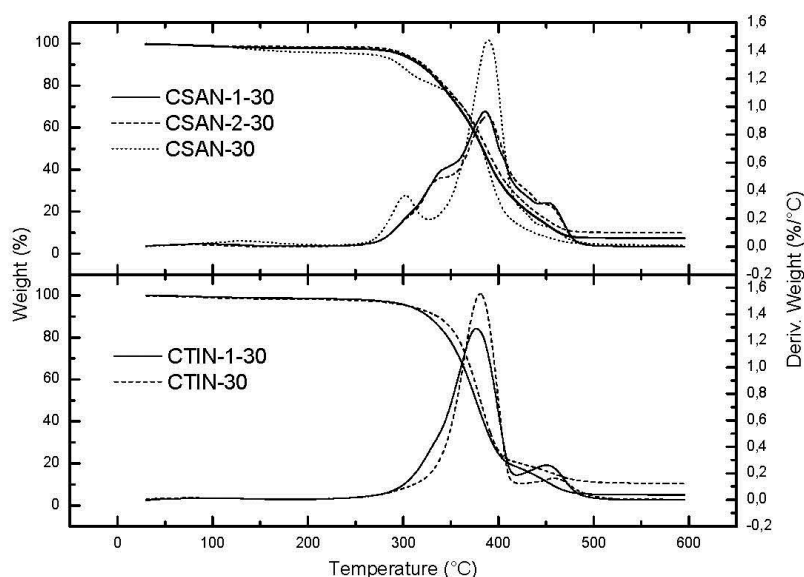
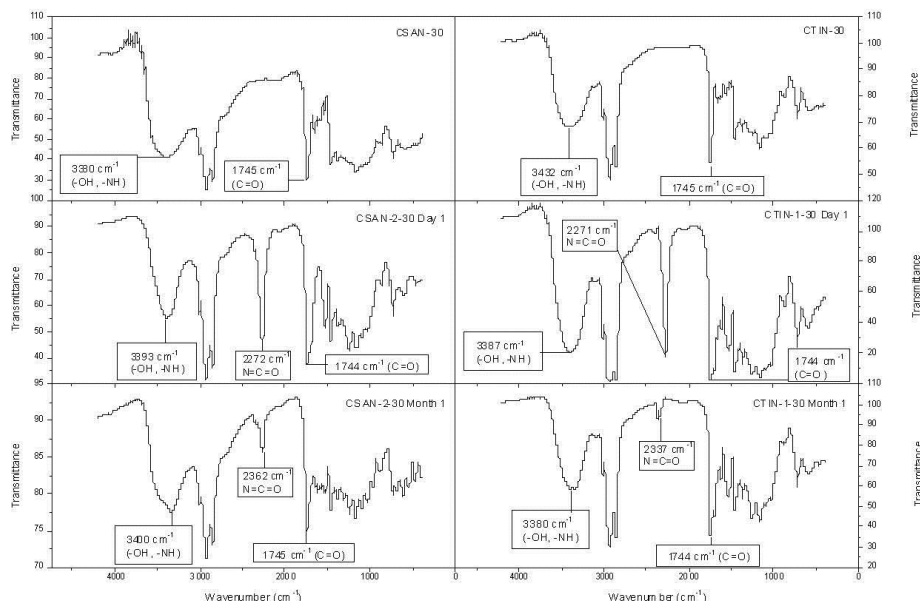


Table 3. Characteristic TGA parameters of the studied oleogel formulations.

Sample	T _{onset} (°C)	T _{max} (°C)	T _{final} (°C)	Residue (%)	ΔW (%)
CSAN-1-30	297	344/386/452	481	7.40	92
CSAN-2-30	301	339/389/451	481	9.97	90
CTIN-1-30	327/444	376/450	410/485	5.07	95
CSAN-30	278/357	302/389/449	319/482	3.89	96
CTIN-30	342/425	381/459	409/595	10.46	89

The reaction between –NCO and –OH groups of polymer and castor oil, respectively, was also studied by analyzing the FTIR spectra. Figure 7 shows the FTIR spectra of four oleogels containing different thickening agents. Chitin- and chitosan-based gel-like dispersions are compared with the corresponding –NCO-functionalized biopolymers-based oleogels, just one day after their preparation and after one month of ageing.

Figure 7. FTIR spectra for selected –NCO-functionalized and non-functionalized chitosan and chitin gel-like dispersions in castor oil.



Functionalized chitosan- and chitin-based oleogels show the same behaviour regarding the evolution with ageing (Figure 7). As can be seen, the absorption band assigned to free –NCO, at 2271 cm^{-1} is quite significant in the IR spectrum of the isocyanate-functionalized polymers-based oleogels one day after the manufacture. On the other hand, the same signal became negligible one month after oleogel preparation, which suggests a slow reaction rate for the promoted reaction. Finally, the spectra of non-functionalized polymer-based oleogels do not present any signal of free –NCO, as expected.

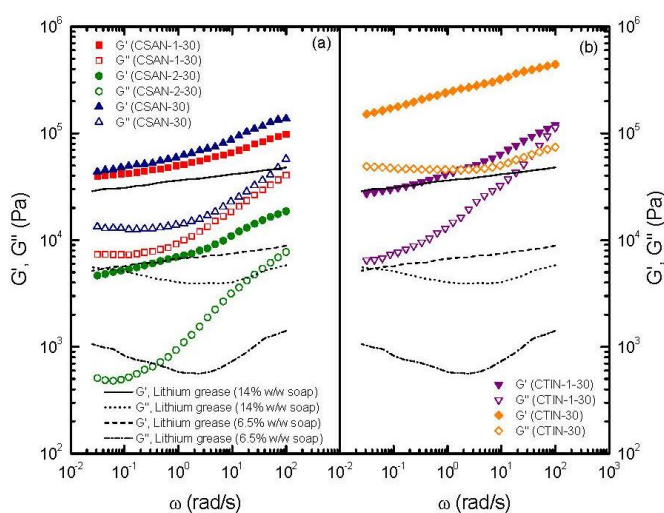
2.4. Rheological Characterization of Functionalized Chitin and Chitosan Gel-Like Dispersions in Castor Oil

Figure 8 shows the mechanical spectra, obtained from small-amplitude oscillatory shear (SAOS) measurements inside the linear viscoelastic range, for the chitosan- and chitin-based oleogels studied, one month after their preparation. The linear viscoelastic functions for chitin- and chitosan-based oleogels exhibit values of the storage modulus, G' , significantly higher than those found for the loss modulus, G'' , in the whole frequency studied. In all cases, the so-called “plateau region” was noticed, where G' slightly increases with frequency and G'' displays a minimum. This evolution is typically found in highly entangled polymeric systems [37] and is very similar to that shown by other oleogels previously studied [30,31,34,38–40] and standard lubricating greases [41]. Moreover, in the case of the isocyanate-functionalized chitin oleogel (CTIN-1-30) a tendency to achieve a crossover between both linear viscoelastic functions, at high frequencies, can be observed.

As extensively investigated [35,36,42] typical G' values in lubricating greases of NLGI grade 1–2 range from 10^4 to 10^5 Pa, around one order of magnitude higher than G'' values, depending on compositions and processing conditions.

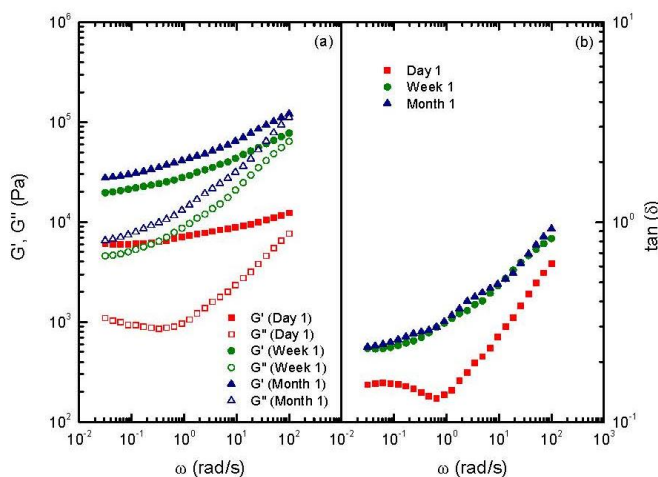
An example of mechanical spectrum for a conventional lithium grease of NLGI grade 2 (14% w/w lithium soap) is included in Figure 8. This particular evolution with frequency and similar values of the SAOS functions were obtained for the –NCO–functionalized chitosan-based oleogel with higher –NCO content (CSAN-1-30) and the non-functionalized chitosan-based gel-like dispersion (CSAN-30). However, the –NCO–functionalized chitosan with lower –NCO content (CSAN-2) produces an oleogel with significantly lower values of the viscoelastic moduli. Therefore, it is clearly noticed that the values of both SAOS functions for –NCO–functionalized chitosan-based oleogels increase with the functionalization degree, as expected attending to the higher degree of cross-linking produced by the higher –NCO content in the biopolymer. In the case of the lower functionalization, the mechanical spectrum is more similar to that exhibited by softer conventional lithium greases with lower soap concentrations (see Figure 8). Nonetheless, in general, the values of G'' at high frequencies for the chitosan-based oleogels studied increase more rapidly than found in traditional lithium greases. For chitin-based oleogels, the values of the viscoelastic functions are higher than those required for traditional lubricating greases, although chitin functionalization in a relatively low degree yields an oleogel with significantly reduced values of the SAOS functions. In this sense, NCO–functionalization may be considered a chemical tool to modulate the rheological response of chitin- and chitosan-based oleogels and design formulations comparable to traditional greases of different NLGI number.

Figure 8. Frequency dependence of the storage [G'] and loss [G''] moduli for NCO–functionalized and non–functionalized (a) chitosan and (b) chitin gel-like dispersions in castor oil (G' : full symbols, G'' : open symbols; ageing time: 1 month). Solid and dashed lines correspond to conventional lithium greases containing 14% and 6.5% soap concentration (from reference [41]).



These results can be explained attending to the physical mechanism for which these biopolymers are able to thicken castor oil. In fact, non-functionalized chitin and chitosan form physically stable gel-like dispersions in castor oil only above the percolation threshold, at around 30% w/w concentration, showing the typical rheological response of soft solid-like gels [43]. These gel-like characteristics are achieved via intermolecular hydrogen bonding and dipole-dipole interactions involving hydroxyl and amine groups of the chitin and chitosan chains and polarized groups of triglyceride molecules. However, as previously reported for methylcellulose dispersions in vegetable oils [31], below these concentration threshold the dispersions became unstable. On the contrary, the NCO-functionalization procedure induces a real chemical gelation during the biopolymer dispersion process, which allows one to obtain stable oleogels, even at a lower concentrations, also reducing the values of the viscoelastic functions as shown in Figure 8. This gelification process is promoted by the chemical interaction between –NCO functional groups and castor oil –OH groups, as previously demonstrated with FTIR results. Finally, a relatively high degree of HMDI functionalization increases the values of the SAOS functions up to level of those shown by the non-functionalized chitin or chitosan gel-like dispersion, as a consequence of an extensive cross-linking between the reactive biopolymer and the oil medium. Therefore, desired values of linear viscoelastic functions could be selected by controlling the functionalization degree of these biopolymers.

Figure 9. Frequency dependence of the (a) storage [G'] and loss [G''] moduli, and the (b) loss tangent for the NCO-functionalized chitin gel-like dispersion in castor oil (CTIN-1-30), as a function of the ageing time (G' : full symbols, G'' : open symbols).



In relation to the evolution of oleogels with time, Figure 9 shows the mechanical spectra for a selected oleogel prepared by dispersing the isocyanate-functionalized chitin in castor oil as a function of the ageing time. As can be noticed, the values of SAOS functions significantly increase during the first seven days of ageing and then slightly increase one month after oleogel preparation, remaining almost constant later on. As previously mentioned, these results can be explained on the basis of the slow reactivity of residual –NCO functional groups in a high viscous medium [44], especially during

the first week after oleogel preparation, increasing the degree of cross-linking. Obviously, since no reaction occurs when using the unmodified chitin as thickener, no ageing influence was detected in that case. Moreover, the values of the loss tangent noticeably increase during the first week, resulting almost unaffected afterwards [Figure 9(b)].

3. Experimental

3.1. Materials

Castor oil (211 cSt at 40 °C, Guinama, Valencia, Spain) was selected as lubricant base oil for oleogel formulations studied. Chitosan (degree of deacetylation = 86.3%, molecular weight = $3.0 \times 10^5 \text{ g}\cdot\text{mol}^{-1}$) and chitin (degree of deacetylation = 7.3%, molecular weight = $5.4 \times 10^5 \text{ g}\cdot\text{mol}^{-1}$), purchased from Qingdao Fraken (Qingdao, Shandong, China), were modified with 1,6-hexamethylene diisocyanate (purum grade, $\geq 98.0\%$), supplied by Sigma-Aldrich (Saint Louis, MO, USA). All other common reagents and solvents employed were purchased from Sigma-Aldrich.

3.2. General Methods

All functionalization reactions (Figure 4) were performed in flasks that were flame-dried after assembly under a positive flow of argon to eliminate surface moisture, and conducted under argon. HMDI was stored at 4 °C and handled under inert (argon) atmosphere. Solvents were purified according to standard literature techniques and stored under argon. Toluene was freshly distilled immediately prior to use from sodium/benzophenone and strictly deoxygenated for 30 min under argon. Reagents were purchased at the higher commercial quality and used without further purification, unless otherwise stated. Characterization tests were performed at least in duplicate.

3.3. Functionalization Reaction of Chitosan and Chitin with HMDI

The reactions of chitosan and chitin functionalization (Figure 4) were carried out following the methodology previously reported [31]. In the case of chitosan, the amount of HMDI, Et_3N and toluene used was modified with the aim of controlling the ratio of functionalized $-\text{OH}$ and $-\text{NH}_2$ groups in the chitosan derivative synthesized. The different ratios of HMDI, Et_3N and toluene with respect to starting material used in the reaction are listed in Table 1.

3.3.1. CSAN-1 Synthesis

Chitosan (10.0 g, 62.0 mmol) was added to a bottom round flask with toluene (100.0 mL) while stirring at room temperature becoming a suspension. Then Et_3N (35.0 mL, 250.2 mmol) and HMDI (20.0 mL, 122.4 mmol) were also added to the system, the last one dropwisely. The solution was vigorously stirred at room temperature during 24 h. The synthesis was carried out under inert atmosphere of argon. Afterwards, the mixture was vacuum filtered resulting in 35.9 g of a pale yellow powder in a yield of 87%. The product was not stored but rather used immediately.

3.3.2. CSAN-2 Synthesis

CSAN-2 was synthesized following the just described procedure above, but modifying the quantities of reagents. Chitosan (10.0 g, 62.0 mmol) was added to toluene (100.0 mL) and then Et₃N (17.0 mL, 121.5 mmol) and HMDI (10.0 mL, 61.2 mmol) were also added and stirred for 24 h. The obtained product was dried under vacuum leading to the polymer CSAN-2 (21.4 g, 52% yield).

3.3.3. CTIN-1 Synthesis

CTIN-1 was synthesized following the same procedure as for polymers CSAN-1 and CSAN-2, but using chitin as starting material and modifying the quantities of reagents. Chitin (12.0 g, 59.1 mmol) was added to toluene (100.0 mL) and then Et₃N (12.4 mL, 88.6 mmol) and HMDI (7.2 mL, 44.0 mmol) were also added and stirred for 24 h. The obtained crude was dried under vacuum leading to 22.4 g of product in a yield of 70%.

3.4. Preparation of Oleogels

Oleogel samples were prepared in an open vessel, using a controlled-rotational speed mixing device (70 rpm) RW 20 (Ika), equipped with an anchor impeller to disperse the different biopolymers in castor oil. Functionalized biopolymers were slowly added to the oil at a concentration of 30% w/w. The mixing process was maintained at 70 rpm for 24 h at room temperature. Finally, the resulting dispersion was homogenized with an Ultra-Turrax T50 (Ika) rotor-stator turbine, at 8800 rpm during 1 min. Batches of 60 g were prepared for each formulation investigated (see Table 4).

Table 4. Oleogels studied.

Thickener agent	Code applied
CSAN-1	CSAN-1-30
CSAN-2	CSAN-2-30
Chitosan	CSAN-30
CTIN-1	CTIN-1-30
Chitin	CTIN-30

3.5. Thermogravimetric Analysis (TGA)

Measurements of mass losses *versus* temperature were carried out by using a Thermogravimetric analyzer, model Q-50 (TA Instrument Waters, New Castle, DE, USA) under N₂ purge. Typically, 5–10 mg of sample were placed on a platinum pan and heated from 30 °C to 600 °C, at 10 °C/min.

3.6. Nuclear Magnetic Resonance of Protons (¹H-NMR)

NMR spectra were recorded with a Varian Direct-Drive 500 (¹H 500 MHz) spectrometer using DMSO-d₆ as solvent.

3.7. Fourier Transform Infrared Spectroscopy (FTIR)

FTIR spectra were obtained with a Digilab FTS3500ARX (Varian) apparatus. Biopolymer samples were prepared as KBr pellets, whereas a small drop of oleogels was placed between two KBr disks (32×3 mm). Then, in both cases, the set was placed into an appropriate sample holder. The spectra were obtained in a wavenumber range of $400\text{--}4,000\text{ cm}^{-1}$, at 4 cm^{-1} resolution, in the transmission mode.

3.8. Rheological Characterization

Rheological characterization of oleogels was carried out with a Gemini controlled-stress rheometer (Malvern, Worcestershire, UK). Small-amplitude oscillatory shear (SAOS) tests were performed inside the linear viscoelastic region, using plate-plate geometries (25 mm, and 1 mm gap), in a frequency range of $10^{-2}\text{--}10^2\text{ rad/s}$, at $25\text{ }^{\circ}\text{C}$. At least two replicates of each test were performed on fresh samples, one day, one week and one month after oleogel preparation. Average standard deviation for G' and G'' moduli was always lower than 4.5%.

4. Conclusions

Three new biopolymers were successfully synthesized by inducing the functionalization reaction of chitosan and chitin with 1,6-hexamethylene diisocyanate (HMDI). The introduction of the isocyanate moieties was carried out in order to improve the role of these polymers as thickener agents in a castor oil medium for lubricant applications. Two experimental conditions have been selected for the preparation of the modified polymers of chitosan: the first one using a higher amount of --NCO (0.5 equiv.) and a second one using a lower quantity (0.25 equiv.) in order to control the functionalization process and obtain polymers with different numbers of free --OH groups. Afterwards, several gel-like dispersions were prepared and rheologically characterized by dispersing these isocyanate-functionalized biopolymers in castor oil. The linear viscoelastic responses in SAOS tests of some --NCO -functionalized chitosan- and chitin-based oleogels are quite similar to those found for standard lubricating greases. The values of viscoelastic functions increase during one month of ageing, more noticeably during the first seven days, but the relative elasticity of the systems is almost unaffected after one week. From the thermogravimetry point of view, in general, thermal decomposition of functionalized biopolymers-based oleogels takes place practically in one main single stage which involves the thermal degradation of both biopolymer and castor oil, being the thermal resistance higher than that found for traditional lubricating greases. In conclusion, --NCO -functionalization of chitin and chitosan allows one to obtain more stable and homogeneous oleogels, at the same time that it serves as a powerful chemical tool to modulate the rheological response and design formulations comparable to traditional greases of different consistency.

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Conflict of Interest

The authors declare no conflict of interest.

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3.2. Article 5

Influence of functionalization degree on the rheological properties of isocyanate-functionalized chitin- and chitosan-based chemical oleogels for lubricant applications

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3.2.1. Resumen en español/summary in spanish

En este trabajo se analiza la influencia del grado de funcionalización de quitina y quitosano, una vez modificados con diferentes cantidades de 1,6-hexametilendiisocianato (HMDI), sobre las propiedades reológicas de los oleogeles resultantes de dispersar estos polímeros en aceite de ricino.

El grado de funcionalización de los biopolímeros se controló a partir de las cantidades de trietilamina (Et_3N) y HMDI empleadas en la síntesis, la temperatura ($25\text{ }^\circ\text{C}$) y el tiempo de reacción (24 h). De esta manera, se evitó un ataque rápido de los grupos -OH libres a los -NCO del HMDI y un entrecruzamiento excesivo de los grupos -NCO , tanto libres como unidos a las moléculas de quitina y quitosano.

Los espectros de infrarrojo (IR) de los polímeros modificados experimentan una reducción significativa de la banda atribuida al grupo -OH ($3200\text{-}3550\text{ cm}^{-1}$) una vez producida la reacción de funcionalización con grupos -NCO , de forma más acusada cuanto mayor es el contenido de HMDI. Los enlaces uretano que se forman en el proceso se hacen presentes en los espectros a, aproximadamente, 3400 cm^{-1} (N-H), 1740 cm^{-1} (C=O uretano) y 1580 cm^{-1} (N-H uretano). Además, la presencia de grupos -NCO libres se confirma con la aparición de una banda intensa alrededor de 2270 cm^{-1} . Esta banda, nuevamente, no se detecta en los espectros de los oleogeles, corroborando la ocurrencia de la reacción entre los grupos -NCO de los espesantes y los -OH presentes en el aceite de ricino.

La etapa de descomposición térmica de los grupos -NCO ($83\text{-}179\text{ }^\circ\text{C}$), de mayor pérdida de peso cuanto más alto es el contenido en HMDI, que se detecta en los termogramas de los polímeros funcionalizados, no aparece en los correspondientes a los oleogeles, lo que indica que el contenido de grupos -NCO libres es despreciable en los oleogeles.

La caracterización reológica reveló que la inserción de pequeñas cantidades de HMDI en las estructuras de quitina y quitosano provoca inicialmente un drástico descenso en los valores de los módulos viscoelásticos de las correspondientes dispersiones en aceite

de ricino, de forma similar a lo estudiado en los oleogel preparados con metilcelulosa funcionalizada (ver capítulo 2.2). Sin embargo, de forma general, un mayor grado de funcionalización del polímero produce un aumento de los valores de las funciones viscoelásticas. Así, la formulación basada en quitosano modificado con la menor proporción de HMDI demuestra un comportamiento similar al de un gel más débil, con valores bajos de las funciones viscoelásticas, una zona “plateau” no desarrollada completamente y un punto de cruce entre G' y G'' a alta frecuencia; mientras que los oleogel formulados con quitosano altamente funcionalizado exhiben valores de los módulos elástico (G') y viscoso (G'') superiores a los demostrados por las dispersiones de quitosano sin modificación química, como consecuencia de un alto nivel de entrecruzamiento. La funcionalización de quitina, sin embargo, siempre conduce a oleogel con valores de los módulos viscoelásticos menores a los mostrados por los análogos basados en quitina sin modificar. De forma interesante, el aumento de G' y G'' con el grado de funcionalización está asociado a una disminución de la elasticidad relativa en el caso de quitina y a un aumento en el caso de quitosano.

Asimismo, muchas de las formulaciones estudiadas presentan un espectro mecánico adecuado a lo que se requiere para aplicaciones como grasas lubricantes. El grado de funcionalización con grupos $-NCO$ de quitina y quitosano puede emplearse como herramienta química para modular el comportamiento reológico y la consistencia de los correspondientes oleogel. Además, es importante resaltar que la inserción de grupos $-NCO$ en quitina y quitosano permite superar las limitaciones de estabilidad física y mecánica encontradas en las formulaciones basadas en dichos polímeros sin modificación química previa.

Asimismo, se observó que estos geles requieren de un cierto tiempo para alcanzar propiedades reológicas estables como consecuencia de una cinética lenta de reacción de los grupos $-NCO$ del espesante y los grupos $-OH$ de las cadenas de ácido ricinoleico. En la mayoría de las formulaciones estudiadas, los valores de los módulos viscoelásticos aumentan de forma significativa durante la primera semana, creciendo ligeramente o permaneciendo constantes a partir de entonces. La tangente de pérdidas, por el contrario, no se ve apenas afectada.

3.2.2. Full article

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Article

Influence of Functionalization Degree on the Rheological Properties of Isocyanate-Functionalized Chitin- and Chitosan-Based Chemical Oleogels for Lubricant Applications

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Abstract: This work deals with the influence of functionalization degree on the thermogravimetric and rheological behaviour of NCO-functionalized chitosan- and chitin-based oleogels. Chitosan and chitin were functionalized using different proportions of 1,6-hexamethylene diisocyanate (HMDI) and subsequently dispersed in castor oil to promote the chemical reaction between the –NCO group of the modified biopolymer and the –OH group located in the ricinoleic fatty acid chain of castor oil, thus resulting in different oleogels with specific thermogravimetric and rheological characteristics. Biopolymers and oleogels were characterized through Fourier transform infrared spectroscopy (FTIR) and thermogravimetric analysis (TGA). Small-amplitude oscillatory shear (SAOS) measurements were performed on the oleogels. Oleogels presented suitable thermal resistance, despite the fact that the inclusion of HMDI moieties in the polymer structure led to a reduction in the onset temperature of thermal degradation. The insertion of low amounts of HMDI in both chitin and chitosan produces a drastic reduction in the values of oleogel viscoelastic functions but, above a critical threshold, they increase with

the functionalization degree so that isocyanate functionalization results in a chemical tool to modulate oleogel rheological response. Several NCO-functionalized chitosan- and chitin-based oleogel formulations present suitable thermal resistance and rheological characteristics to be proposed as bio-based alternatives to traditional lubricating greases.

Keywords: biopolymer; isocyanate-functionalized chitin and chitosan; oleogel; lubricating greases; rheology

1. Introduction

Organogels are generating great interest and expectation in a wide spectrum of applications such as medical and pharmaceutical [1–4], development of new materials with specific optical and mechanical properties [5–7], matrixes for food systems [8,9], art conservation [10,11], *etc.* The term organogel refers to a variety of soft materials, from viscoelastic liquid-like to solid-like, comprised of an organic liquid and some molecules, *i.e.*, organogelators, which are able to produce self-assembling and structure the organic medium [12]. In most cases, low-molecular weight amphiphilic molecules which impart thermo-reversible properties are responsible for the gelling behaviour [13–17]. However, some biomacromolecules like natural waxes, resins and biopolymers with gelling properties in oily media are gaining special attention [18–26]. Among these studies, lignocellulosic materials and cellulose derivatives have been used to obtain gel-like dispersions in vegetable oils, which may be potentially applied as environmentally friendly lubricating grease formulations [27–32].

In the frame of the general tendency to promote the replacement of non-renewable raw materials by renewable resources in order to avoid the impact that process technologies and products of different industrial sectors cause on the environment, the lubricant industry is especially involved [33,34]. In this sense, different alternatives based on modifications of vegetable oils have been proposed to replace mineral and synthetic lubricant base oils [35–40]. Although vegetable oils are being increasingly used as bio-based lubes, the substitution of traditional thickening agents, such as metallic soaps and polyureas, in lubricating greases by others derived from renewable resources is a much more complicated task. For instance, some limitations regarding physical and mechanical stabilities and thermo-rheological behaviour of previously mentioned cellulosic derivatives-based gel-like dispersions [27–29] were pointed out as a consequence of a certain degree of chemical incompatibility between oil and such polar biopolymers. Most of these problems can be overcome by inducing the formation of chemical gels, for instance by dispersing reactive isocyanate-functionalized methylcellulose in the vegetable oil medium [41,42]. Following the same procedure and based on some preliminary studies [43], the possibility of using NCO-functionalized chitin and chitosan to chemically gel castor oil is explored in this work. As well known, chitin is one of the most abundant organic materials, being second only to cellulose in the amount produced annually by biosynthesis. It is an important constituent of the exoskeleton in animals especially in crustaceans, molluscs and insects and the principal fibrillar polymer in the cell wall of certain fungi [44,45]. Chitosan is typically obtained by deacetylation of chitin under alkaline conditions in a variety of useful forms, characterized by displaying interesting properties such as biocompatibility or biodegradability [46–48], which also

produces non-toxic, non-immunogenic and non-carcinogenic degradation products [49,50]. Nowadays, there is a growing interest in the chemical modification of chitosan in order to improve its solubility or the cross-linking ability in different media and therefore widen its applications [51–54]. The reaction between chitosan and diisocyanate compounds has been previously promoted to produce bio-polyurethanes for the development of molecular carriers in the biomedical and environmental fields [55], beads for cholesterol absorption [56] or materials with controlled thermal or elastomeric properties [57,58]. As a continuation of the above mentioned research on the development of oleogels for lubricant purposes and taking into account the interest of these biopolymers, the effect of NCO-functionalization degree of chitin and chitosan on the rheological properties and thermal degradation of resulting chemical oleogels has been studied in this work.

2. Experimental Section

2.1. Materials

Castor oil (kinematic viscosity: $211 \text{ mm}^2\cdot\text{s}^{-1}$ at 40°C , Guinama, Spain) was selected as lubricant base oil to formulate the oleogel samples studied. Chitosan (degree of deacetylation: 86.3%; viscosity average molecular weight: $2.3 \times 10^5 \text{ g}\cdot\text{mol}^{-1}$) and chitin (degree of deacetylation: 7.3%; viscosity average molecular weight: $5.4 \times 10^5 \text{ g}\cdot\text{mol}^{-1}$), purchased from Fraken (Qingdao, China), were modified with 1,6-hexamethylene diisocyanate (HMDI, purum grade, $\geq 98.0\%$), supplied by Sigma-Aldrich (St. Louis, MO, USA). All other common reagents and solvents employed were purchased from Sigma-Aldrich.

2.2. General Methods

Functionalization reactions were performed in flasks that were previously flame-dried under a positive flow of argon to eliminate surface moisture. HMDI was stored at 4°C and handled under argon atmosphere. Solvents were purified according to standard literature techniques and stored under argon. Toluene was freshly distilled immediately prior to use from sodium/benzophenone and strictly deoxygenated for 30 min under argon. Reagents were purchased at the higher commercial quality and used without further purification, unless otherwise stated. Characterization tests were performed at least in duplicate.

2.3. Functionalization Reaction of Chitosan and Chitin with HMDI

The functionalization reactions of chitosan and chitin with HMDI were carried out according to the protocol described in preliminary studies [43]. Chitosan or chitin was added to a bottom round flask with toluene while stirring at room temperature until it became a suspension. Then, triethylamine (Et_3N) and HMDI were also added to the system, the last one drop-wisely. The solution was vigorously stirred at room temperature for 24 h. Afterwards, the mixture was vacuum filtered and the resulting product was immediately used to prepare the oleogels. The amount of HMDI, Et_3N and toluene was modified with the aim of achieving different functionalization degrees of $-\text{OH}$ and $-\text{NH}_2$ groups in the chitosan and chitin derivatives synthesized. The different molar ratios of HMDI, Et_3N

and toluene with respect to free $-OH$ and $-NH_2$ groups in the non-functionalized chitin and chitosan monomers are listed in Table 1.

Table 1. Molar ratios of chitin or chitosan, 1,6-hexamethylene diisocyanate (HMDI), triethylamine (Et_3N) and toluene used in each functionalization reaction.

Functionalized Polymer [*]	Starting material [equiv.] [*]	HMDI [equiv.] [*]	Et_3N [equiv.] [*]	Toluene [mL]
CSAN-1	1.00 (Chitosan)	0.50	1.00	100
CSAN-2	1.00 (Chitosan)	0.25	0.50	100
CSAN-3	1.00 (Chitosan)	0.13	0.25	100
CSAN-4	1.00 (Chitosan)	0.06	0.13	100
CTIN-1	1.00 (Chitin)	0.50	1.0	100
CTIN-2	1.00 (Chitin)	0.25	0.50	100
CTIN-3	1.00 (Chitin)	0.13	0.25	100
CTIN-4	1.00 (Chitin)	0.06	0.13	100

^{*} The acronym “CSAN” corresponds to chitosan polymers and “CTIN” to chitin polymers; the adjacent number (1–4) define a different degree of functionalization for each type of polymer. ^{*} Molar ratio between moles of free $-OH$ and $-NH_2$ groups present in each monomer of starting chitosan and chitin, and moles of each of the reagents.

2.4. Preparation of Oleogels

Oleogel samples were prepared in an open vessel (batches of 60 g), using a controlled-rotational speed mixing device (70 rpm) RW 20 (Ika, Staufen, Germany), equipped with an anchor impeller to disperse the different biopolymers in the oil. Functionalized biopolymers were slowly added to the castor oil at different concentrations (see Table 2). The mixing process was maintained at 70 rpm for 24 h at room temperature. Finally, the resulting dispersion was homogenized with an Ultra-Turrax T50 (Ika) rotor-stator turbine, at 8800 rpm for 1 min. Table 2 also shows the codes applied for each oleogel sample.

2.5. Thermogravimetric Analysis (TGA)

Measurements of mass loss versus temperature were carried out by using a Thermogravimetric analyser, model Q-50 (TA Instruments, New Castle, DE, USA) under N_2 purge. Typically, 5–10 mg of sample were placed on a platinum pan and heated from 30 °C to 600 °C, at 10 °C·min^{−1}.

2.6. Fourier Transform Infrared (FTIR) Spectroscopy

FTIR spectra were obtained with a Digilab FTS3500ARX (Varian, Palo Alto, CA, USA) apparatus. Chitin and chitosan samples were prepared as KBr pellets, whereas a small drop of oleogels was placed between two KBr disks (32 mm × 3 mm). In both cases, the set was placed into an appropriate sample holder. The spectra were obtained in a wavenumber range of 400–4000 cm^{−1}, at 4 cm^{−1} resolution, in the transmission mode. The degree of deacetylation provided in Section 2.1 for original

chitin and chitosan samples were determined by FTIR according to the method described by Baxter *et al.* [59].

Table 2. Composition of oleogel formulations studied.

Thickener agent	Concentration [%, w/w]	Code Applied *
Chitosan	30	CSAN-30
CSAN-1	30	CSAN-1-30
CSAN-2	30	CSAN-2-30
CSAN-3	30	CSAN-3-30
CSAN-4	30	CSAN-4-30
CSAN-3	15	CSAN-3-15
CSAN-3	25	CSAN-3-25
CSAN-3	35	CSAN-3-35
Chitin	30	CTIN-30
CTIN-1	30	CTIN-1-30
CTIN-2	30	CTIN-2-30
CTIN-3	30	CTIN-3-30
CTIN-4	30	CTIN-4-30
CTIN-2	15	CTIN-2-15
CTIN-2	25	CTIN-2-25

* Code Applied: polymer type (CTIN or CSAN)—different functionalization degree—concentration of the functionalized biopolymer in the oleogel prepared

2.7. Rheological Characterization

Rheological characterization of oleogels was carried out using controlled-stress rheometers (Gemini, Bohlin, Malvern Instruments Ltd., Worcestershire, United Kingdom, and Rheoscope, ThermoHaake, Karlsruhe, Germany). Small amplitude oscillatory shear (SAOS) tests were performed inside the linear viscoelastic region, using roughened plate-plate geometries (20 mm, 25 mm and 35 mm, and 1 mm gap), in a frequency range of 0.03–100 $\text{rad}\cdot\text{s}^{-1}$, at 25 °C. Measurements were done one day, one week, one month and four months after oleogel preparation. Average molecular weight of original chitin and chitosan samples were determined by means of viscosity measurements according to the methods and Mark-Houwink-Sakurada equation constants provided by Poirier and Charlet [60] and Takahashi *et al.* [61], respectively.

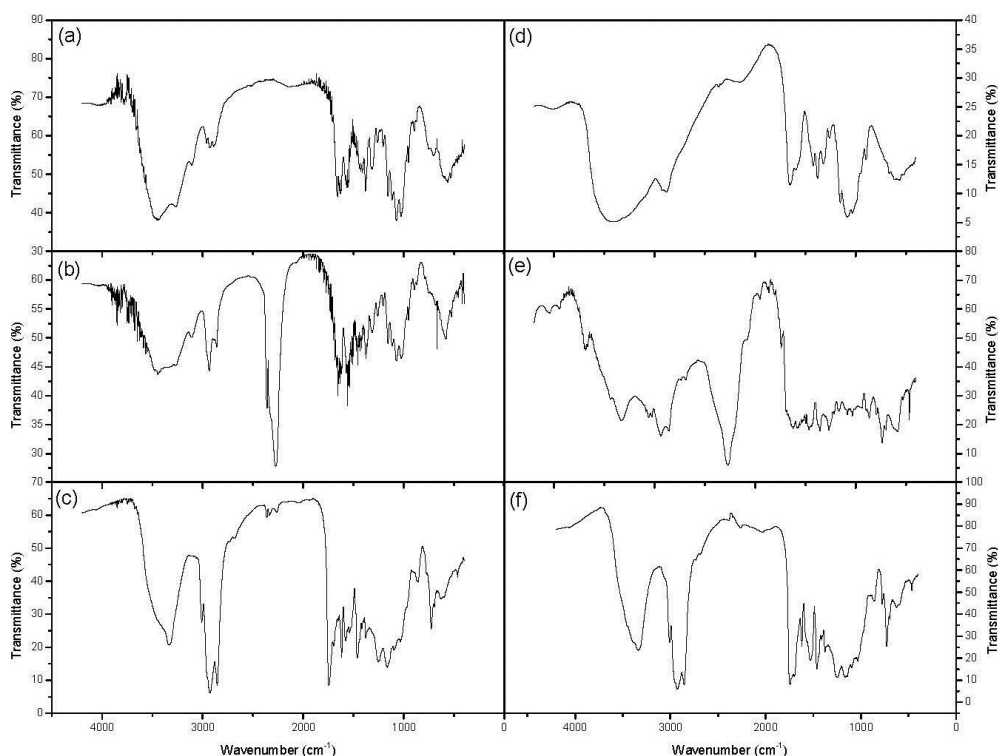
3. Results and Discussion

3.1. Spectroscopic Characterization

Chemical modification of chitin and chitosan after functionalization with different proportions of HMDI and the occurrence of further reaction with –OH groups of castor oil were evaluated by FTIR. Figure 1 shows the FTIR spectra for non-functionalized chitin (Figure 1a) and chitosan (Figure 1d), selected NCO-functionalized samples, CTIN-1 (Figure 1b) and CSAN-1 (Figure 1e), and the corresponding oleogels prepared with these biopolymers and castor oil, CTIN-1-25 (Figure 1c) and

CSAN-1-25 (Figure 1f). FTIR spectra of functionalized biopolymers were in concordance with the proposed chemical structure previously reported [43]. Table 3 lists the most relevant peaks detected in NCO-functionalized chitosan and chitin spectra. The reaction of chitin and chitosan with the -NCO groups of HMDI to form urethane linkages produces a significant reduction in the intensity of the band around $3200\text{--}3550\text{ cm}^{-1}$, corresponding to the -OH group in the molecules. The higher HMDI content, the more significant the reduction in this band is. The urethane bands (Figure 1b,e) can be detected at approximately 3400 cm^{-1} and 1740 cm^{-1} for N-H and C=O stretching vibrations in the urethane linkage, respectively, and 1580 cm^{-1} for the N-H bending vibration. Moreover, an intense peak at around 2270 cm^{-1} is noticed, confirming the presence of unreacted -NCO groups, as intended.

Figure 1. FTIR spectra for (a) chitin, (b) polymer CTIN-1; (c) oleogel CTIN-1-25; (d) chitosan; (e) polymer CSAN-1 and (f) oleogel CSAN-1-25.



The functionalization degree was controlled by means of carrying out the reaction at room temperature, the amount of HMDI and Et_3N used and the reaction time (24 h in this case). Under these conditions, both a rapid attack of free -OH to -NCO groups of HMDI and an excessive cross-linking of -NCO groups present either in the unreacted HMDI or in the HMDI segments attached to the chitin or chitosan chains are significantly dampened. Thereby, the reaction can be controlled and allows obtaining selectively polymers with different degrees of functionalization. Finally, the reaction between the -NCO group of functionalized biopolymers and the -OH group of castor oil was also

monitored by analyzing the FTIR spectra of oleogels (Figure 1c,f). As can be observed, the absorption band assigned to free -NCO groups at around 2271 cm^{-1} is negligible in the FTIR spectra of the oleogels, corroborating the occurrence of the reaction promoted.

Table 3. FTIR representative signals for selected NCO-functionalized chitin (CTIN-1) and chitosan (CSAN-1) samples.

Functional group	Signals	
	CTIN-1 (cm^{-1})	CSAN-1 (cm^{-1})
$\text{-OH} + \text{=NH}$	3338	3330
C-H aliph	2934	2936
N=C=O	2275	2271
C=O	1623	1741
N-H	1574	1580
C-N or C-OH	1259	1266
C-O or C-OC	1076	1082

3.2. Thermogravimetric Characterization

Thermal degradation of chitin, chitosan and derived NCO-functionalized compounds was studied by means of thermogravimetric analysis (TGA). Figure 2 shows TGA curves, in the form of weight loss derivative function *versus* temperature, for chitosan (Figure 2a) and chitin (Figure 2b) functionalized in different degrees, compared to those obtained with the corresponding starting materials, *i.e.*, non-functionalized biopolymers and HMDI. The onset temperature for thermally-induced weight loss (T_{onset}), the maximum weight-loss rate temperature (T_{max}), the weight loss at the end of each decomposition step (ΔW) and the percentage of non-degraded residue were calculated from the thermogram of each sample studied (Table 4). Disregarding the initial weight loss between $40\text{ }^{\circ}\text{C}$ and $80\text{ }^{\circ}\text{C}$, which is inferior to 8%, as a consequence of water evaporation, thermal degradation of non-functionalized chitosan and chitin takes place in one main stage. This main thermal event occurs in the range of $343\text{--}405\text{ }^{\circ}\text{C}$ for chitin (Figure 2b) and is due to the degradation of the saccharide structure of the molecule, including the dehydration of saccharide rings and decomposition of the acetylated and deacetylated units [62]. In the case of chitosan (Figure 2a), thermal degradation starts at lower temperature, indicating poorer thermal stability, but in a wider range ($281\text{--}472\text{ }^{\circ}\text{C}$). This thermal range corresponds to the degradation peak of the part of the molecule that is deacetylated, showing a T_{max} at $301\text{ }^{\circ}\text{C}$, and an overlapped small signal at around $390\text{ }^{\circ}\text{C}$, due to the degradation of the acetylated part of the molecule.

On the other hand, for NCO-functionalized biopolymers, the inclusion of HMDI segments in the polymer structure reduces their thermal stabilities, with marked impact in the highest functionalized polymer, as expected (Figure 2, Table 4). Thermal degradation curves of NCO-functionalized chitosans exhibit two main events. The first one at around $83\text{--}179\text{ }^{\circ}\text{C}$, with T_{max} at $116\text{--}153\text{ }^{\circ}\text{C}$, corresponds to the loss of -NCO segments, which is corroborated with HMDI thermal degradation occurring at $137\text{ }^{\circ}\text{C}$. As can be observed in Table 4, the T_{onset} and, logically, weight loss for this degradation stage increases with -NCO content. The second main degradation stage, as previously discussed for the non-functionalized sample, is related to the loss of the deacetylated part of the

molecule of chitosan and takes place between 271 °C and 340 °C, with a $T_{\max}$ at around 300 °C. The weight loss assigned to this thermal degradation process generally becomes more important as functionalization degree decreases (Table 4). A characteristic temperature corresponding to the acetylated part, expected at around 400 °C in biopolymers with lower quantity of HMDI segments in their structures (CSAN-3 and CSAN-4), also appears in the thermograms. Moreover, a final decomposition stage with $T_{\max}$ at around 450 °C was detected, which can be assigned to excessively cross-linked chitosan fractions originating more rigid polyurethanes [63]. Thermal degradation of NCO-functionalized chitin polymers (Figure 2b) is rather similar to that discussed for chitosan samples. The loss of HMDI segments was found from 83 °C to 154 °C, with maximum weight-loss rate temperatures between 119 °C and 135 °C, whereas the other main thermal degradation event takes place at around 390 °C, which corresponds to the loss of the acetylated units of the biopolymer. Finally, a third degradation stage occurs at 439–512 °C, similarly to that found in chitosan samples.

Figure 2. Thermal degradation curves, under inert atmosphere, for NCO-functionalized chitosan (a) and chitin (b) samples and starting materials.

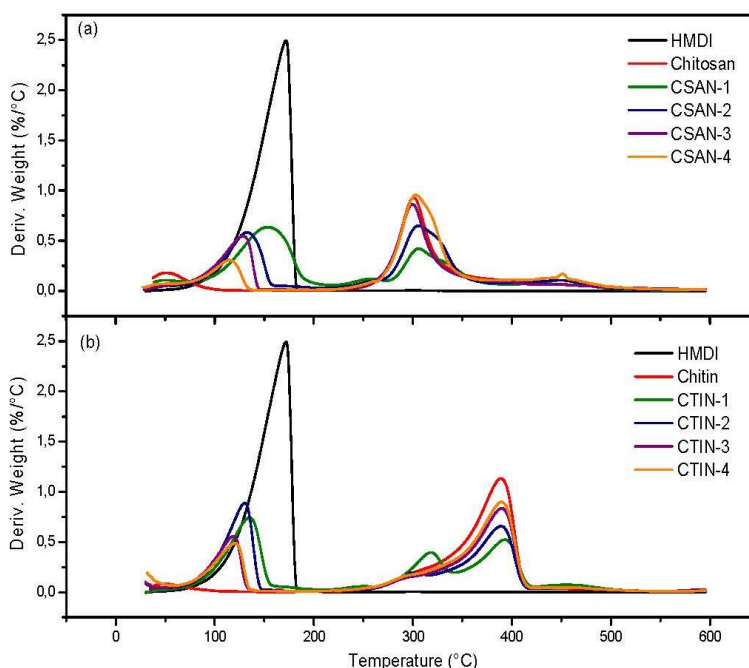


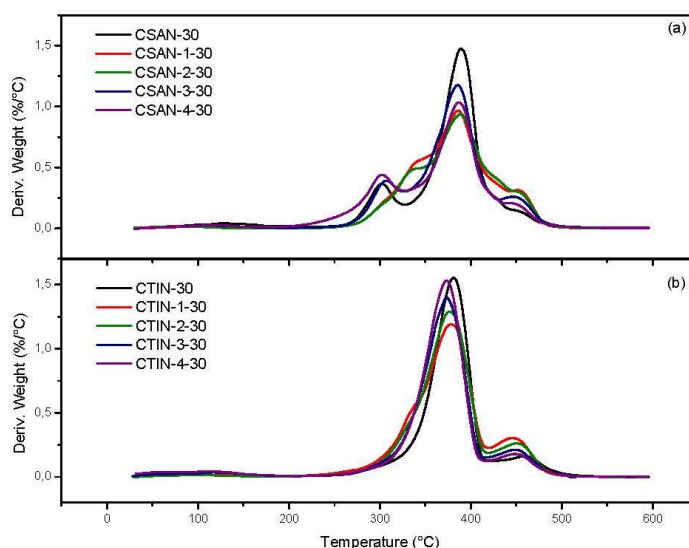
Table 4. TGA characteristic parameters for NCO-functionalized chitosan and chitin samples studied (main degradation stages in bold).

Sample	T_{onset} [°C]	T_{max} [°C]	T_{final} [°C]	ΔW [%]	Residue [%]
Chitosan	281	301	472	57	34
Chitin	343	389	405	23	72
HMDI	137	172	178	99	1
CSAN-1	122/240/292/429	153/258/ 306 /450	179/266/ 340 /483	44/6/26/9	11
CSAN-2	107 /283/431	133 / 306 /448	150 /335/486	30 /43/9	15
CSAN-3	93 /271/391/416	129 / 300 /395/443	143 / 324 /410/520	24 /41/3/7	25
CSAN-4	83 /274/388/445	116 / 303 /401/450	133 / 339 /406/464	14 /51/4/11	20
CTIN-1	93 /224/283/ 361 /444	135 /251/318/ 393 /453	154 /260/334/ 414 /512	34 /2/17/ 25 /6	16
CTIN-2	106 /275/ 363 /439	130 /302/ 389 /454	140 /309/ 403 /494	34 /10/ 36 /4	16
CTIN-3	83 / 337 /442	119 / 390 /459	132 / 411 /511	22 / 53 /4	21
CTIN-4	83 / 336 /441	121 / 390 /463	134 / 411 /512	22 / 58 /4	16

Thermal decomposition of NCO-functionalized chitosan- and chitin-based oleogels is shown in Figure 3. The thermal degradation of non-functionalized chitosan oleogel takes place from 278 °C to 482 °C and three different thermal events with T_{max} at 302 °C, 389 °C and 449 °C can be detected (Figure 3a, Table 5). The first one corresponds to chitosan degradation, the second one is mainly due to castor oil evaporation [30], the main oleogel component, and the last one refers to secondary products. For NCO-functionalized chitosan-based formulations (Figure 3a, Table 5), the thermal degradation occurs between 266 °C and 483 °C, also in three different stages. The first one, at 302–307 °C, is mainly noticed in those oleogels containing lower amounts of HMDI in their formulation (CSAN-3-30 and CSAN-4-30) and is attributed to the degradation of deacetylated chitin units. The second stage is again a consequence of castor oil evaporation. The temperature range for this event is expanded when the ratio of HMDI in the formulation increases (CSAN-1-30 and CSAN-2-30), which may be attributed to the urethane segments achieved during the reaction between functionalized chitosan and ricinoleic fatty chains. In the case of chitin-based oleogels (Figure 3b, Table 5), thermal decomposition always takes place in two clearly different stages. The main one can be observed between 324 °C and 410 °C and is a consequence of both thickener and castor oil degradations, which appear overlapped in one peak. The second minor event is observed at around 450 °C and refers to secondary products. Finally, it can be concluded that the disappearance of the first isocyanate-functionalized polymer degradation peak, due to HMDI decomposition, in the resulting oleogel confirms the chemical reaction promoted between modified polymers and the castor oil.

Table 5. TGA characteristic parameters for non-functionalized and NCO-functionalized chitosan and chitin-based oleogels studied (main degradation stages in bold).

Sample	T_{onset} [°C]	T_{max} [°C]	T_{final} [°C]	Residue [%]	ΔW [%]
CSAN-30	278/ 357	302/ 389 /449	319/ 482	4	19/77
CSAN-1-30	297	344/ 386 /452	481	8	92
CSAN-2-30	301	339/ 389 /451	481	10	90
CSAN-3-30	276/ 353 /433	307/ 386 /447	321/ 412 /483	6	17/ 66 /11
CSAN-4-30	266/ 355	302/ 387 /443	319/ 481	8	26 / 66
CTIN-30	340 /441	381 /459	409 /495	11	80 /9
CTIN-1-30	324 /439	379 /446	410 /482	3	83 /14
CTIN-2-30	327 /444	376 /450	405 /485	5	82 /13
CTIN-3-30	326 /443	374 /449	406 /462	6	83 /11
CTIN-4-30	328 /425	373 /449	404 /486	4	86 /10

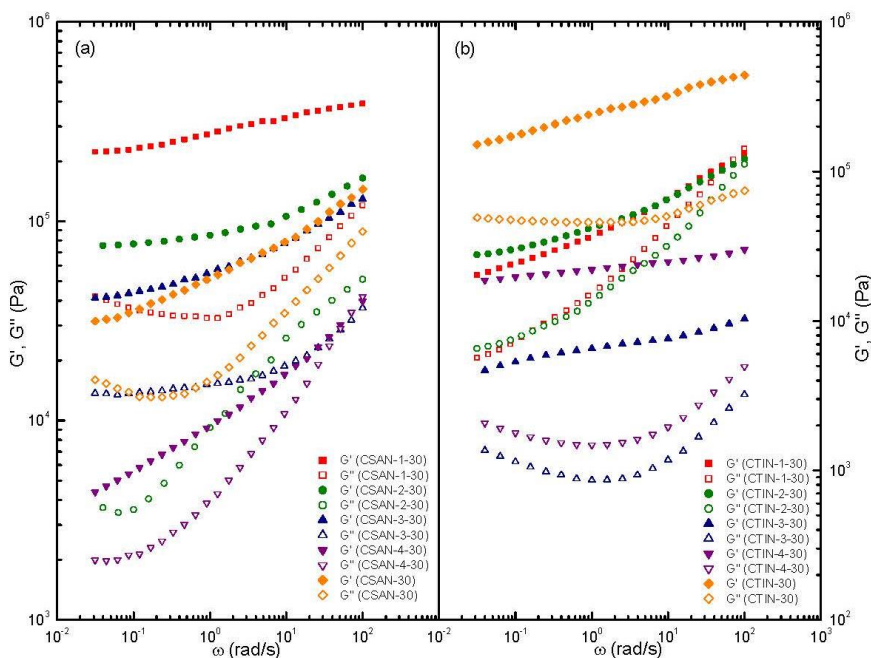
Figure 3. Thermal degradation curves, under inert atmosphere, for NCO-functionalized chitosan-(a) and chitin-(b) based oleogels.

3.3. Rheology of Chitosan- and Chitin-Based Oleogels

Figure 4 shows the SAOS response, inside the linear viscoelastic range, of NCO-functionalized and non-functionalized chitosan and chitin-based oleogels, at 30% w/w concentration, as a function of the functionalization degree. In most cases, NCO-functionalized chitosan-based oleogels exhibit values of the storage modulus, G' , significantly higher than those found for the loss modulus, G'' , in the whole frequency range studied (Figure 4a). This evolution, the so-called “plateau region”, where G' slightly increases with frequency and G'' displays a minimum, is typically found in highly entangled polymeric systems [64] and standard lubricating greases [65]. Only when using the lowest amount of HMDI (CSAN-4-30), the plateau region appears to be not well developed, indicating the consecution of a

weaker gel. The plateau region is also exhibited by some of the NCO-functionalized chitin-based oleogels such as CTIN-3-30 and CTIN-4-30 (Figure 4b). However, interestingly, a crossover between both viscoelastic functions was found at high frequency for the highly-functionalized chitin-based oleogels (CTIN-1-30 and CTIN-2-30). In these cases, this behaviour must be attributed to a higher degree of cross linking achieved during oleogel formation, resulting in a rheological response closer to the transition region of the mechanical spectrum. In general, as can be deduced from Figure 4, –NCO content in the functionalized biopolymers largely influences the values of the linear viscoelastic functions of resulting oleogels. In the case of chitosan, a high degree of functionalization (CSAN-1-30 and CSAN-2-30) increases the values of the SAOS functions with respect to those shown by the non-functionalized chitosan oleogel (CSAN-30), as a consequence of an extensive crosslinking. However, the values of the SAOS functions decrease when reducing the amount of HMDI incorporated to the biopolymer, yielding similar (CSAN-3-30) or lower (CSAN-4-30) G' and G'' values than those exhibited by the non-functionalized chitosan-based oleogel (CSAN-30).

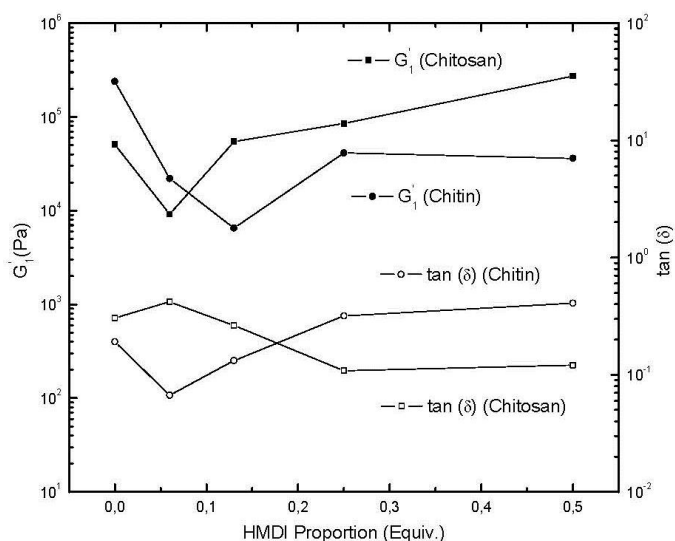
Figure 4. Frequency dependence of the storage, G' , and loss, G'' , moduli for (a) NCO-functionalized chitosan-based oleogels (aged for 4 months) and (b) chitin-based oleogels (aged for 1 month), as a function of functionalization degree.



On the contrary, for chitin-based oleogels, the most noticeable effect of HMDI segments is that they always produce lower values of the viscoelastic moduli than those shown by the non-functionalized chitin-based oleogel (CTIN-30). Apart from this, oleogels with high amounts of HMDI in their formulation (CTIN-1-30 and CTIN-2-30) exhibited the highest values of the linear viscoelastic

functions but, contrary to the expected, CTIN-3-30 showed lower values than CTIN-4-30. All these effects that functionalization degree exerts on the rheological response of chitin- and chitosan-based oleogels can be more noticeably summarized in Figure 5, where the values of G' and the loss tangent ($\tan\delta = G''/G'$), at $1 \text{ rad}\cdot\text{s}^{-1}$, are plotted *versus* the HMDI proportion applied in the functionalization of biopolymers. As can be observed, the insertion of low amounts of HMDI in both chitin and chitosan produces a drastic reduction in the values of SAOS functions, *i.e.*, G'_1 (G' at $1 \text{ rad}\cdot\text{s}^{-1}$) especially for chitosan-based oleogels. However, above a critical threshold, SAOS functions increase with the functionalization degree. Interestingly, this increase in both G' and G'' is associated to a lower relative elasticity in the case of chitin-based oleogels and higher in the case of chitosan-based ones, as can be seen in the $\tan\delta$ vs. HMDI proportion plot (Figure 5). As mentioned above, only in the case of chitosan-based oleogels a high degree of functionalization makes possible to reach values of the viscoelastic moduli higher than those displayed by the non-functionalized biopolymer-based oleogel. However, as previously reported [27,42], it must be remarked that these physically stabilized gels present some limitations regarding their physical and mechanical stability, which can be overcome by mean of functionalization.

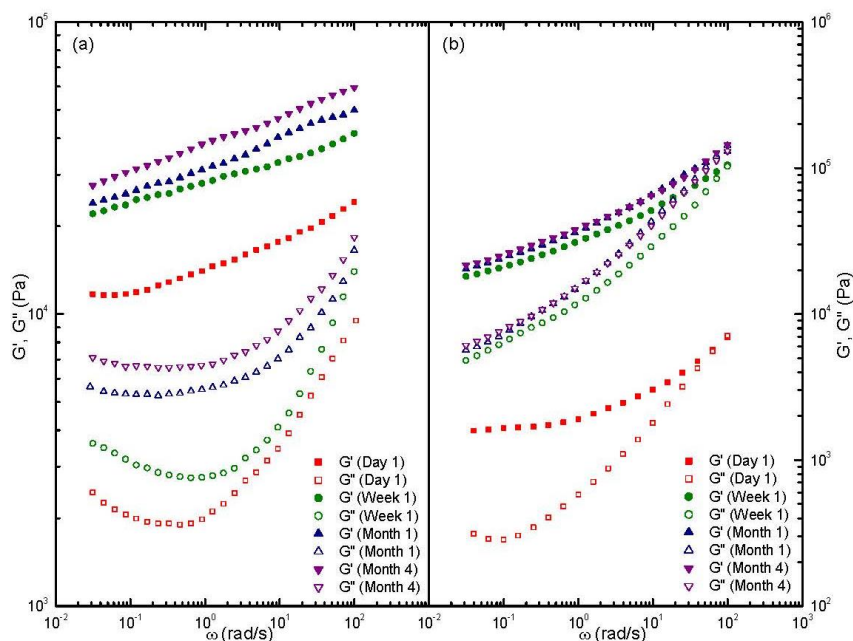
Figure 5. HMDI proportion dependence of the storage modulus, G'_1 (G' at $1 \text{ rad}\cdot\text{s}^{-1}$), and the loss tangent, $\tan\delta$, at $1 \text{ rad}\cdot\text{s}^{-1}$, for NCO-functionalized chitosan- and chitin-based oleogels.



As extensively investigated [66–68], typical G' values in conventional lubricating greases of NLGI (National Lubricating Grease Institute) grade 1–2 range from 10^4 – 10^5 Pa, around one order of magnitude higher than G'' values, depending on compositions and processing conditions. This particular rheological response has been obtained for several of the NCO-functionalized chitosan- and chitin-based oleogels studied, emphasizing that the degree of NCO-functionalization can be used as a chemical tool to modulate the rheological behaviour and consistency of these oleogels as desired.

Rheological data collected in Figure 4a,b correspond to oleogels 1 and 4 months aged, respectively. As previously reported for NCO-functionalized methyl cellulose-based oleogels [42], these chemical gels require a certain ageing time to obtain stable rheological properties. Figure 6 shows the evolution of the linear viscoelastic functions with frequency, as a function of ageing time, for selected chitosan- (CSAN-3-25) and chitin- (CTIN-1-30) based oleogels. In most of the cases studied, the values of SAOS functions significantly increase during the first seven days of ageing and then slightly increase or remain almost constant after several months of ageing. These results can be explained on the basis of the slow reactivity of residual –NCO functional groups in a high viscous medium [69]. However, interestingly, the loss tangent was almost unaffected (data not shown).

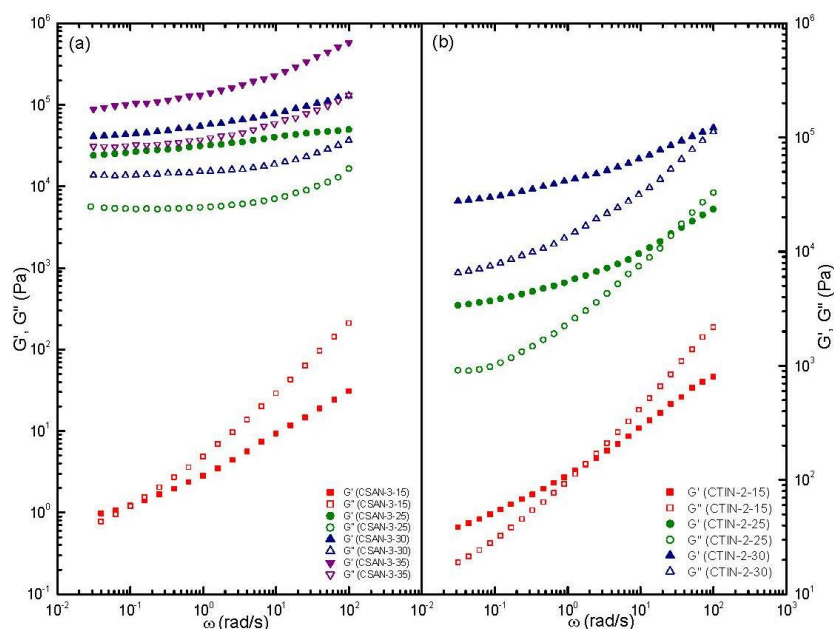
Figure 6. Frequency dependence of the storage, G' , and loss, G'' , moduli for selected NCO-functionalized chitosan- (CSAN-3-25) and chitin- (CTIN-1-30) based oleogels, as a function of ageing time.



Finally, as typically performed in conventional lubricating greases, the rheological response can be modified by changing the thickener concentration, in this case the functionalized biopolymers used as gelling agents. Figure 7 shows the mechanical spectra of functionalized chitosan- and chitin-based oleogels, containing different concentrations of the same biopolymer in their respective formulations. As can be observed, the values of the viscoelastic moduli increase with the concentration of both functionalized biopolymers. In the case of chitosan-based oleogels (Figure 7a), G' exhibits values significantly higher than those found for G'' , *i.e.*, the plateau region, for concentrations ranging from 25%–35% w/w (CSAN-3-25, CSAN-3-30 and CSAN-3-35). Nevertheless, a liquid-like weak gel was obtained with a 15% biopolymer concentration (CSAN-3-15). For chitin-based oleogels (Figure 7b),

almost three decades of both SAOS functions can be covered by modifying the thickener concentration between 15% and 30% w/w. In all cases, G' is higher than G'' at low frequencies. However, a crossover between both linear viscoelastic functions was always observed, which is shifted to lower frequencies as biopolymer concentration decreases.

Figure 7. Frequency dependence of the storage, G' , and loss, G'' , moduli for NCO-functionalized chitosan-(a) and chitin-(b) based oleogels, as a function of biopolymer concentration.



4. Conclusions

A systematic and controlled functionalization protocol for chitosan and chitin with HMDI resulted in several biopolymers functionalized in different degrees. The dispersion of these biopolymers in castor oil promoted the reaction between free $-NCO$ segments of the biopolymer and $-OH$ groups of the ricinoleic fatty acid chain thus providing different chemical oleogels with specific characteristics.

The resulting oleogels presented suitable thermal resistance despite the fact that the inclusion of HMDI segments in the polymer structure reduces their thermal stabilities. Oleogels thermal degradation basically takes place in one main stage which comprises the thermal decomposition of both the castor oil and the thickening agent.

Typical rheological behaviour found in conventional lubricating greases was achieved in different formulations studied, providing a cross-linked viscoelastic gel with a well-developed plateau region in the evolution of SAOS functions with frequency. The insertion of low amounts of HMDI in both chitin and chitosan produces a drastic reduction in the values of SAOS functions but, above a critical

threshold, viscoelastic functions increase with the functionalization degree. Therefore, isocyanate functionalization appears as a chemical tool to modulate the rheological response.

The rheological properties of functionalized chitosan- and chitin-based oleogels evolve during several months of ageing, but mainly during the first week, due to the progress of the reaction between –NCO functional groups and castor oil –OH groups. Oleogel linear viscoelastic response is also highly dependent on the concentration of NCO-functionalized biopolymers.

Several NCO-functionalized chitosan- and chitin-based oleogel formulations present suitable thermal resistance and rheological characteristics to be proposed as bio-based alternatives to traditional lubricating greases.

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Author Contributions

All the authors have contributed equally to this work.

Conflicts of Interest

The authors declare no conflict of interest.

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4. Block 3

4.1. Article 6

Gel-like dispersions of HMDI-cross-linked lignocellulosic materials in castor oil: toward completely renewable lubricating grease formulations

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Chemistry, Multidisciplinary	25/157	Q1
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Impact factor (2014)	4.642	

4.1.1. Resumen en español/summary in spanish

En este trabajo, varias pastas lignocelulósicas de orígenes diferentes (*Eucalyptus globulus* y *Pinus radiata*) y sometidas a distintos tratamientos (Kraft y semimecánico) fueron modificadas con 1,6-hexametilendiisocianato (HMDI), previa mercerización con hidróxido sódico (NaOH), y, posteriormente, dispersadas en aceite de ricino con el objetivo de obtener formulaciones tipo gel basadas en fuentes renovables que puedan ser potencialmente aplicables como lubricantes semisólidos.

La espectroscopía de infrarrojo (IR) permitió evaluar la modificación química de las diferentes pastas de lignocelulosa tras los procesos de mercerización y entrecruzamiento. Como resultado, se descubrió que el proceso de mercerización produce en la celulosa de la pasta cierta pérdida de cristalinidad, ya que la región comprendida entre 1500 y 500 cm^{-1} , particularmente sensible a cambios estructurales, muestra un patrón característico amorfo en el que las señales atribuidas a los dominios cristalinos se reducen, llegando, incluso, a desaparecer. Por otro lado, la modificación con HMDI se confirmó con el desplazamiento a longitudes de onda más altas e incremento de intensidad de las señales correspondientes a los grupos C–H (2921 – 2850 cm^{-1}). Además, los picos relacionados con los enlaces uretano pueden detectarse a 3348 cm^{-1} (N–H st), 1647 cm^{-1} (C=O st), 1612 cm^{-1} (C–N st) y 1501 cm^{-1} (N–H def). Sin embargo, no se observa la banda correspondiente a los grupos –NCO libre (2270 cm^{-1}), corroborando que la reacción de entrecruzamiento se ha completado prácticamente.

Aunque las pastas lignocelulósicas de *Eucalyptus globulus* entrecruzadas con HMDI en distintas proporciones mostraron diferencias muy leves entre sus perfiles de descomposición térmica, el análisis termogravimétrico (TGA) determinó que la modificación con grupos –NCO produce un incremento de la estabilidad térmica del esqueleto de celulosa.

Las imágenes de la microestructura de los oleogeles obtenidas empleando la microscopía de fuerza atómica (AFM) desvelaron que, independientemente del origen del material lignocelulósico empleado, en todos los casos, ésta está formada por fibras de bastante longitud, enrolladas axialmente y entrecruzadas, muy similar a la mostrada

por las grasas lubricantes de litio tradicionales. En cuanto a la influencia de los grupos –NCO en la microestructura, se observa que las fibras adquieren una disposición más densa, con un mayor grado de entrecruzamiento, especialmente en la formulación con mayor proporción de HMDI (2:1 HMDI/pulpa de celulosa), en comparación con las dispersiones de pastas lignocelulósicas no modificadas.

El comportamiento reológico de los oleogeles resultantes es prácticamente idéntico al de grasas lubricantes comerciales, independientemente del origen o tratamiento al que se haya sometido la pasta de celulosa. Así, se observa cómo, en todos los casos, el módulo elástico (G') es mayor que el módulo viscoso (G''), en todo el rango de frecuencias analizado, con valores de G' en el rango 10^4 - 10^5 Pa y, aproximadamente, una década superiores a los de G'' , además de una amplia zona “plateau” que abarca prácticamente todo el rango de frecuencias estudiado.

Si bien, origen y tratamiento de la pasta de celulosa no ejercen un efecto significativo en el valor de los módulos viscoelásticos, la proporción de HMDI utilizada en la reacción de entrecruzamiento, no obstante, sí que ejerce una influencia importante. De esta manera, la adición de una pequeña cantidad de HMDI (0.5:1 HMDI/pasta de celulosa) produce una drástica disminución de las funciones viscoelásticas respecto de los excesivamente elevados valores mostrados por la dispersión de pasta de celulosa no funcionalizada (sólo mercerizada). Tal reducción de G' y G'' continúa produciéndose con la adición de una cantidad ligeramente superior de agente entrecruzante (1:1 HMDI/pulpa de celulosa). Por el contrario, cuando la proporción de HMDI aumenta (2:1 HMDI/pulpa de celulosa), la tendencia observada es totalmente opuesta y los valores de los módulos viscoelásticos se ven incrementados. Por otra parte, la cantidad de grupos –NCO que intervienen en la reacción de entrecruzamiento no afecta ni a la evolución de las funciones viscoelásticas con la frecuencia ni a la elasticidad relativa, por lo que puede emplearse como herramienta para modular a conveniencia los valores de G' y G'' , resultando además posible la normalización de las funciones viscoelásticas, simplemente relativizándolas mediante el módulo plateau, G_N^0 .

La influencia de la temperatura en la respuesta reológica se traduce en una tendencia a disminuir el valor de las funciones viscoelásticas con la temperatura, siendo más acusada a partir de los 100 °C, lo que implica una mayor susceptibilidad térmica a partir de dicha temperatura. Este comportamiento es nuevamente muy similar al observado en grasas lubricantes de litio, en las que esta temperatura crítica es de 110 °C. Esta mayor influencia de la temperatura a partir de 100 °C puede explicarse por degradación térmica de los enlaces uretano.

El estudio de las curvas de flujo viscoso determinó que no existen diferencias notables entre los valores de viscosidad obtenidos para oleogeles basados en pastas de celulosa entrecruzadas con HMDI de orígenes distintos o a las que se haya aplicado un tratamiento diferente, mientras que la influencia de la proporción de –NCO en los valores de viscosidad sigue la misma tendencia que para los módulos viscoelásticos. Por otro lado, la temperatura ejerce un efecto idéntico al exhibido por grasas lubricantes espesadas con jabones metálicos, dando lugar a un predominante flujo no homogéneo que se hace aparente en forma de un mínimo en la evolución del esfuerzo con la velocidad de cizalla, de forma más predominante a partir de 50 °C. Esta falta de homogeneidad en el gradiente de velocidades es la causante de la fractura observada en todas las muestras, que finalmente induce la expulsión de la grasa del sensor de medida o de un contacto a lubricar.

La estabilidad mecánica de los oleogeles basados en pastas lignocelulósicas entrecruzadas con HMDI se ve significativamente mejorada respecto de las formulaciones basadas en pastas de celulosa no modificadas. Las propiedades lubricantes de las muestras en un contacto tribológico bola-placas también se estudiaron analizando los valores de los coeficientes de fricción, que resultaron ser razonablemente bajos, aunque ligeramente superiores a los mostrados por las grasas lubricantes comerciales. El diámetro de las marcas de desgaste en las placas fue, en la mayoría de los casos, comparable al obtenido con la grasa comercial de referencia espesada con jabón de calcio, aunque superiores a los obtenidos con la grasa de litio.

En general, las dispersiones de pasta lignocelulósica entrecruzada con HMDI en aceite de ricino poseen propiedades térmicas, reológicas y tribológicas adecuadas para ser propuestas como alternativas ecológicas a las grasas lubricantes convencionales.

5. Block 4

5.1. Article 7

Tribological behaviour of conventional metallic soap- and chemically modified biopolymer-thickened lubricating greases investigated in a steel-steel rotating ball-on-three plates tribological cell

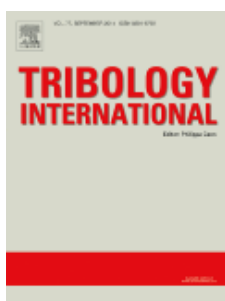
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5.1.1. Resumen en español/summary in spanish

En este trabajo, se han caracterizado tribológicamente algunas grasas lubricantes biodegradables basadas en aceite de ricino y polímeros naturales (metilcelulosa, quitina y pasta lignocelulósica) químicamente modificados con grupos –NCO, empleando una célula tribológica de tipo bola-sobre-placas, conectada a un reómetro de esfuerzo controlado. Los resultados se compararon con los obtenidos al emplear dos grasas convencionales basadas en jabones de litio y calcio como lubricantes. Se realizaron ensayos de flujo viscoso, barridos de velocidad de deslizamiento y ensayos transitorios de fricción, evaluando el desgaste originado en las placas por microscopía de barrido electrónico (SEM).

Las curvas de flujo de las grasas lubricantes estudiadas están limitadas por la aparición de fractura a altas velocidades de cizalla. Para todas las grasas se encontraron valores de viscosidad muy similares, exceptuando la formulación basada en quitina, la cual muestra viscosidades superiores en todo el rango de velocidades de cizalla estudiado. Las curvas resultantes se ajustaron de forma satisfactoria al modelo potencial. Los oleogeles basados en quitina y metilcelulosa funcionalizada con grupos –NCO exhibieron índices de consistencia más altos a 25 °C, mientras que este parámetro es mayor para las grasas de jabón de litio y quitina a 125 °C, indicando que se trata de microestructuras con una resistencia térmica superior.

La evolución del coeficiente de fricción con la velocidad de rotación en la célula tribológica muestra, a 25 °C, la progresión general desde el régimen de lubricación límite hasta el hidrodinámico. Esto se cumple en todos los casos excepto con la formulación de quitina, en la que solamente se observa la transición desde la zona de lubricación mixta a la hidrodinámica. Por otro lado, un aumento de la temperatura hasta 125 °C hace que sean necesarios valores de velocidad de rotación más altos para poder detectar la zona hidrodinámica, de manera que deja de ser visible en las grasas lubricantes comerciales, aunque no en las formulaciones biodegradables. Sólo las grasas lubricantes espesadas con jabón de calcio y metilcelulosa muestran un comportamiento tribológico simple que puede ser descrito mediante una única curva de

Stribeck, resultado de la superposición de las curvas de fricción obtenidas a diferentes temperaturas y cargas normales, usando la viscosidad del aceite base en el número de Sommerfeld. Este hecho sugiere que el aceite base es el que gobierna la formación del film. En el resto de los casos, para los que no se produce tal superposición o sólo tiene lugar en la zona hidrodinámica, como ocurre con el oleogel espesado con pasta lignocelulósica, el papel del espesante en la formación del film parece ser más evidente, afectando la respuesta tribológica.

La evolución del coeficiente de fricción con el tiempo proporciona valores constantes a los 5–6 minutos cuando el contacto se lubrica con grasas lubricantes biodegradables y a los 8-10 minutos para las formulaciones comerciales. De forma general, a 25 °C, el coeficiente de fricción disminuye con la carga normal, tendencia que se mantiene a 125 °C para las grasas de litio y quitina, aunque con coeficientes de fricción más bajos. Sin embargo, a 125 °C, se observa la progresión opuesta para el resto de formulaciones. Estos resultados dependen del equilibrio entre la resistencia reológica ofrecida por la grasa y la dependencia de la microestructura a la cizalla y la temperatura. Por otra parte, se observa que, a 25 °C, el coeficiente de fricción disminuye con la velocidad de rotación al emplear formulaciones basadas en jabones de litio y calcio y pasta lignocelulósica como lubricantes, al contrario que ocurre con la grasa de quitina. A 125 °C todas las formulaciones analizadas, excepto aquella espesadas con pasta lignocelulósica, muestran la misma tendencia, en la que se produce un aumento del coeficiente de fricción de 0.15 a 10 rpm y una disminución del mismo de 10 a 400 rpm. Estos resultados están completamente justificados con la evolución del coeficiente de fricción con la velocidad de rotación y reflejan los distintos regímenes de lubricación.

La evolución de la huella de desgaste indica, de forma general, que cuanto mayor es la carga normal aplicada o la velocidad de rotación, más grande es la marca producida en la placa, tanto a 25 como a 125 °C. Sin embargo, el desgaste ocasionado cuando se usan las grasas de metilcelulosa y quitina como lubricantes es despreciable, excepto bajo condiciones extremas de carga normal y velocidad de rotación, mientras que los oleogeles de pasta de celulosa producen marcas de desgaste comparables a las grasas lubricantes comerciales de litio y calcio.

Chapter 5:

General conclusions

- ◆ α -Cellulose and some derivatives (methylcellulose, 2-hydroxyethyl cellulose, methyl 2-hydroxyethyl cellulose and cellulose acetate propionate), chitin and chitosan and several lignocellulosic pulps from different origins (*Pinus radiata* and *Eucalyptus globulus*) and/or submitted to different treatments (Kraft or semimechanic) have been successfully modified with 1,6-hexamethylen diisocyanate (HMDI), thus enhancing their roles as chemical thickeners in a castor oil medium. Moreover, different functionalization degrees can be achieved with methylcellulose, chitin, chitosan and *Eucalyptus globulus*-based lignocellulosic pulp by controlling temperature, the amount of HMDI and Et₃N used and the reaction time (24 h).
- ◆ Physically stable chemical oleogels with specific characteristics can be obtained by dispersing the former polymers, at different concentrations, in castor oil; so that, promoting the reaction between free –NCO segments of the functionalized biopolymer and –OH groups of the ricinoleic fatty acid chain. This chemical interaction is responsible for the physical stability and rheological properties of the resulting oleogels; consequently, unstable oleogels are obtained when a non-functionalized biopolymer is used or castor oil is replaced by sunflower oil, with no available –OH groups in the fatty acid composition.
- ◆ In general, thermogravimetric analysis (TGA) reveals that the inclusion of HMDI segments into the biopolymers structure reduces their thermal stabilities in some extent, with marked impact in the highest functionalized polymers. On the contrary, thermal stability of cellulose skeleton in crosslinked lignocellulosic materials is increased with HMDI modification because of a higher amount of coupling agent which induces a more regular rearrangement. However, resulting NCO-functionalized biopolymer-based oleogels presents suitable thermal resistance, even higher than that commonly exhibited by mineral oil-based traditional greases. Thermal decomposition of these oleogels generally occurs in one single stage that comprises the thermal degradation of both the NCO-functionalized biopolymer and the castor oil. The degradation temperature range is broadened when using highly functionalized thickeners.

- ◆ Regarding the rheological response, chemical gels require certain ageing time to obtain stable rheological properties due to the progress of the chemical reaction. Thus, the viscoelastic functions significantly increase during the first seven days after the manufacture and then slightly increase or remain almost constant after several months. Moreover, higher values of free –NCO content provoke more noticeable rheological modification. Oppositely, in most cases, no significant influence over the relative elasticity is perceived.
- ◆ A very low functionalization degree of the thickening agent largely modifies the rheological response of the corresponding dispersions in castor oil, significantly lowering the values of the linear viscoelastic functions respecting those found when using the non-functionalized biopolymer, although G' and G'' values further increase with the functionalization degree.
- ◆ As expected, the increment of the thickener concentration in the formulation results in an increase in the viscoelastic moduli, as well, which can be used to adjust the consistency and rheological properties of oleogels.
- ◆ Most formulations studied exhibit a rheological behaviour similar to the exhibited by conventional lubricating greases with NLGI grades 1-3; i.e., MMC2-30, MC-NCO-2-30, MC-2, CSAN-1-30, CSAN-3-30, CTIN-3-30, CTIN-4-30 or any based on crosslinked-lignocellulosic pulps, such as GPK, GES or GEK1.
- ◆ Different NCO-functionalized cellulose derivatives provide oleogels with rheological responses ranging from weak to solid-like gels. The prediction of the thickening properties of any NCO-functionalized cellulose derivative in castor oil is possible by means of a mathematic relationship that takes into account the influence of the amount of polar and non-polar groups, as well as the size of substituents present in the cellulose monomer after NCO-functionalization.
- ◆ Origin and pulping treatment of lignocellulosic materials significantly affect neither, the SAOS functions nor viscosity. However, the amount of HMDI added in the

crosslinking reaction increases the values of the linear viscoelastic functions and viscosity.

- ◆ The influence of temperature on the rheological response of crosslinked lignocellulosic pulp-based oleogels results in a general decrease of the linear viscoelastic moduli with temperature, much more sharply above 100 °C, thus reflecting a much higher thermal susceptibility above this critical temperature, as similarly reported by traditional metallic soap-based lubricating greases, with a critical temperature of around 110 °C.
- ◆ Shear banding, or non-homogeneous flow, is apparent in the viscous flow curves of the oleogels based on crosslinked lignocellulosic pulps, yielding a clear minimum in the evolution of the stress with shear rate, which was favoured by temperature, similarly to that shown by conventional lubricating greases thickened with metallic soaps.
- ◆ The oleogels based on HMDI-crosslinked lignocellulosic materials present acceptable mechanical stability values, significantly improved respecting non-crosslinked lignocellulose gel-like dispersions.
- ◆ AFM micrographs for different oleogels prepared using HMDI crosslinked lignocellulosic materials from different sources of origin and/or submitted to different pulping treatments show a microstructure consisting of rather long, twisted and entangled fibers, which very much resemble the morphology of traditional lithium greases. With respect to the influence of HMDI/cellulose pulp weight ratio on oleogel microstructure morphology, more entangled and densely arranged fibers are obtained when using highly HMDI-crosslinked lignocellulose as thickening agent.
- ◆ The tribological characterization of selected oleogels thickened with NCO-functionalized methylcellulose, chitin and lignocellulosic pulp results in different responses depending on the balance between the rheological resistance offered by the grease and the microstructure shear and temperature dependence. Thus,

reasonable low friction coefficient values are obtained for most of the cellulosic pulp dispersions analysed but still higher than those obtained with commercial greases. However, methylcellulose and chitin-based formulations generally provide lower values of the friction coefficient.

- ◆ The study of the wear marks reveals that the stronger normal load or higher rotational speed is applied, the wider scratch is detected. Thus, excepting for severe conditions, wear is negligible when using chemically modified chitin and methylcellulose-based greases as lubricants, whereas cellulosic pulp-based grease provides wear scratches comparable, although still higher, to those found with conventional lithium and calcium greases.
- ◆ The friction coefficient vs. sliding velocity curves, at 25 °C, show the general progression from boundary to hydrodynamic lubrication regimes for most samples, although higher values of rotational speed are generally needed to detect the hydrodynamic regime at higher temperature. Methylcellulose-based samples display a simple tribological behaviour which leads to a unique Stribeck master curve by superimposing the frictional curves obtained at different temperatures and normal loads, using the base oil viscosity in the Sommerfeld number, suggesting that, in this case, the base oil governs film formation.
- ◆ NCO-functionalization of biopolymers may be considered a way of overcoming the limitations regarding the physical and mechanical stability of only physically stabilized oleogels based of non-functionalized polymers and a chemical tool to modulate the rheological behaviour and consistency in order to design novel and ecological formulations completely based on renewable resources as promising alternatives to traditional greases of different NLGI number.

Conclusiones generales

- ◆ α -Celulosa y algunos de sus derivados (metilcelulosa, 2-hidroxietilcelulosa, metil 2-hidroxietilcelulosa y acetato propionato de celulosa), quitina y quitosano y varias pastas lignocelulósicas de orígenes diferentes (*Pinus radiata* y *Eucalyptus globulus*) y/o sometidas a tratamientos diferentes (Kraft o semimecánico) han sido químicamente modificadas con 1,6-hexametilen diisocianato (HMDI) de forma exitosa, mejorando así su papel como espesantes químicos de medios oleosos. Además, se han alcanzado diferentes grados de funcionalización con metilcelulosa, quitina, quitosano y la pasta de celulosa procedente de *Eucalyptus globulus* sometida al tratamiento Kraft mediante el control de la temperatura, la cantidad de HMDI y Et_3N empleada y el tiempo de reacción (24 h).
- ◆ Se han obtenido oleogeles químicos físicamente estables con características específicas dispersando los polímeros anteriores, a diferentes concentraciones, en aceite de ricino, promoviendo así la reacción entre los grupos $-\text{NCO}$ de los biopolímeros funcionalizados y los grupos $-\text{OH}$ de las cadenas del ácido ricinoleico. Esta interacción química es la responsable de la estabilidad física y propiedades reológicas de los oleogeles resultantes. Como consecuencia, cuando se han empleado polímeros no funcionalizados o el aceite de ricino se ha reemplazado por aceite de girasol, sin grupos $-\text{OH}$ disponibles en su composición, se han obtenido oleogeles inestables físicamente.
- ◆ En general, el análisis termogravimétrico (TGA) revela que la inserción de segmentos de HMDI en la estructura de los biopolímeros reduce su estabilidad térmica en cierto grado, con un mayor impacto en los polímeros altamente funcionalizados. Por el contrario, la estabilidad térmica del esqueleto de celulosa en material lignocelulósico entrecruzado se ve incrementada con la modificación con HMDI debido a una mayor cantidad de agente de acoplamiento que induce un reordenamiento más regular. Por otro lado, los oleogeles correspondientes presentan una resistencia térmica adecuada, incluso mayor que la exhibida comúnmente por las grasas tradicionales basadas en aceite mineral. La descomposición térmica de

estos oleogeles generalmente ocurre en un solo paso que incluye la degradación térmica del biopolímero funcionalizado con grupos –NCO y del aceite de ricino. El rango de temperaturas de degradación se ve ampliado cuando se usan espesantes altamente funcionalizados.

- ◆ Respecto a la respuesta reológica, los geles químicos requieren de cierto tiempo de envejecimiento para obtener propiedades reológicas estables debido al progreso de la reacción química. Así, las funciones viscoelásticas aumentan de forma significativa durante los primeros siete días tras la manufactura, aumentando ligeramente o manteniéndose prácticamente constantes varios meses después. Además, un mayor contenido de grupos –NCO libre provoca una modificación reológica más notable. Por el contrario, en muchos casos, no se percibe influencia significativa sobre la elasticidad relativa.
- ◆ Un bajo grado de funcionalización del agente espesante modifica ampliamente la respuesta reológica de la correspondiente dispersión en aceite de ricino, disminuyendo significativamente los valores de las funciones viscoelásticas lineales respecto de las obtenidas empleando biopolímero sin funcionalizar. A partir de entonces, los valores de G' y G'' continúan aumentando con el grado de funcionalización.
- ◆ El incremento de la concentración de agente espesante en la formulación resulta en un aumento de los módulos viscoelásticos de los oleogeles, lo cual puede ser empleado para ajustar la consistencia y las propiedades reológicas de los mismos.
- ◆ Muchas de las formulaciones estudiadas muestran un comportamiento reológico similar al exhibido por grasas lubricantes convencionales con grados NLGI entre 1 y 3, como por ejemplo: MMC2-30, MC-NCO-2-30, MC-2, CSAN-1-30, CSAN-3-30, CTIN-3-30, CTIN-4-30 o cualquiera basada en pulpa lignocelulósica entrecruzada, como son GPK, GES o GEK1.
- ◆ Los diferentes derivados de celulosa funcionalizados con grupos –NCO dan lugar a oleogeles con respuestas reológicas que oscilan entre las correspondientes a geles

débiles y fuertes. La predicción de las propiedades espesantes de cualquier derivado de celulosa funcionalizado con grupos –NCO en aceite de ricino es posible mediante una relación matemática que tiene en cuenta la influencia de la cantidad de grupos polares y no polares, así como el tamaño de los sustituyentes presentes en el monómero de celulosa tras la funcionalización con grupos –NCO.

- ◆ Ni el origen ni el tratamiento al que se ha sometido el material lignocelulósico afectan de forma significativa a las funciones viscoelásticas o a la viscosidad de los oleogeles resultantes. Sin embargo, la cantidad de HMDI añadida durante la reacción de entrecruzamiento aumenta los valores de las funciones viscoelásticas lineales y la viscosidad.
- ◆ La influencia de la temperatura en la respuesta reológica de los oleogeles basados en pulpa lignocelulósica entrecruzada resulta en un descenso general de los módulos viscoelásticos con la temperatura, de forma más acusada por encima de los 100 °C, reflejando, de esta forma, una mayor susceptibilidad térmica por encima de dicha temperatura crítica, de forma similar a las grasas tradicionales basadas en jabones metálicos que tienen su temperatura crítica alrededor de los 110 °C.
- ◆ Los oleogeles basados en pulpa lignocelulósica entrecruzada muestran un flujo no homogéneo que genera un mínimo en la evolución del esfuerzo con la velocidad de cizalla, el cual se ve favorecido con la temperatura, igualmente similar a la encontrada en grasas lubricantes espesadas con jabones metálicos.
- ◆ Los oleogeles basados en pulpa lignocelulósica entrecruzada presentan valores de estabilidad mecánica aceptables, significativamente mejorados con respecto a las dispersiones tipo gel de lignocelulosa no entrecruzada.
- ◆ Las imágenes de AFM obtenidas de oleogeles preparados con material lignocelulósico entrecruzado con HMDI de origen diferente y/o sometido a tratamientos distintos muestran una microestructura que consiste en fibras largas, retorcidas y entrecruzadas, la cual se asemeja a la morfología de grasas de litio tradicionales. Con respecto a la influencia de la proporción en peso de HMDI/pulpa

de celulosa en la morfología de la microestructura del oleogel, el uso como agente espesante de lignocelulosa entrecruzada en mayor medida da lugar a una mayor densidad de fibras altamente entrecruzadas.

- ◆ La caracterización tribológica de algunos oleogeles seleccionados que ha sido espesados con metilcelulosa, quitina y pulpa de celulosa funcionalizados con grupos –NCO resulta en diferentes respuestas dependiendo del balance entre la resistencia reológica ofrecida por la grasa y la cizalla sufrida por la microestructura y la dependencia con la temperatura. Así, la mayoría de las dispersiones de pulpa de celulosa producen coeficientes de fricción razonablemente bajos, aunque todavía superiores a los obtenidos con grasas comerciales. Sin embargo, las formulaciones basadas en metilcelulosa y quitina generalmente proporcionan valores bajos del coeficiente de fricción.
- ◆ El estudio de las huellas de desgaste revela que una mayor carga normal o velocidad de rotación aplicada produce marcas más anchas. Así, excepto en condiciones severas, el desgaste es despreciable cuando se usan grasas de metilcelulosa y quitina químicamente modificadas como lubricante; mientras que las grasas de pulpa de celulosa originan marcas de desgaste comparables, aunque aún mayores, a las obtenidas con grasas convencionales de litio y calcio.
- ◆ Las curvas de la evolución del coeficiente de fricción con la velocidad de deslizamiento a 25 °C muestran una progresión general que va desde la zona de lubricación límite hasta la hidrodinámica para la mayoría de las muestras, aunque, generalmente, se necesitan valores de velocidad de rotación más altos para la detección de la zona de lubricación hidrodinámica a mayor temperatura. Las muestras basadas en metilcelulosa muestran un comportamiento tribológico simple que lleva a una única curva maestra de Stribeck mediante la superposición de las curvas de fricción obtenidas a diferentes temperaturas y fuerzas normales, usando la viscosidad del aceite base en el número de Sommerfeld, sugiriendo que, en este caso, el aceite base gobierna la formación del film.

- ◆ La funcionalización de biopolímeros con grupos –NCO puede considerarse una forma de superar las limitaciones en cuanto a estabilidad física y mecánica de oleogeles basados en polímeros no funcionalizados estabilizados únicamente de forma física y una herramienta química para modular el comportamiento reológico y la consistencia con vistas a diseñar formulaciones novedosas y ecológicas completamente basadas en fuentes renovables, como alternativas prometedoras a las grasas tradicionales de diferente grado NLGI.

List of Tables

Chapter 1: Introduction	19
Chapter 2: State of the art	27
Table 1. Chemical composition of some cellulose source [Heinze and Liebert, 2001]	58
Table 2. Chemical constituents and crystallinity index (CI) for a wide variety of fiber types [Fernandes et al., 2015]	67
Table 3. Modified cellulosic and lignin based materials and references that exploit them in the medical field [Fernandes et al., 2013]	74
Table 4. Properties of comercial isocyanates [Moreno, 2012]	78
Chapter 3: Materials and methods	105
Table 5. Molecular formula, degree of substitution and average molecular weight of cellulose derivatives	108
Table 6. Cellulose pulps composition [Nuñez et al., 2011]	111
Table 7. Fatty acids composition and viscosity at different temperatures of castor oil	113
Chapter 4: Results and discussion	127
Table (2.1.2.) 1. Molar ratios of methyl cellulose, hexamethylene diisocyanate (HMDI), Et ₃ N and toluene used in the functionalization reaction	137
Table (2.1.2.) 2. Substitution degree of modified methyl cellulose polymers	138
Table (2.1.2.) 3. Composition of oleogel formulations studied	138
Table (2.1.2.) 4. TGA characteristic parameters for polymers and oleogel formulations studied	143
Table (2.2.2.) 1. Proportion of methyl cellulose, hexamethylene diisocyanate (HMDI), triethylamine (Et ₃ N) and toluene used in the functionalization reactions	154
Table (2.2.2.) 2. Substitution degree over –OH groups of modified methyl cellulose polymers	155
Table (2.2.2.) 3. ¹ H NMR representative signals (chemical shift and relative peak areas) for a selected polymer (MC–NCO-4)	155
Table (2.2.2.) 4. IR representative signals for a selected NCO-functionalized methyl cellulose sample (MC–NCO-4)	155

Table (2.2.2.) 5. TGA characteristic parameters for NCO-functionalized methyl cellulose samples studied	156
Table (2.2.2.) 6. TGA characteristic parameters for NCO-functionalized methyl cellulose-based oleogels	157
Table (2.3.2.) 1. Codes applied to cellulose derivative samples and corresponding oleogels	168
Table (2.3.2.) 2. Degree of substitution of NCO-functionalized cellulose derivatives	169
Table (2.3.2.) 3. TGA characteristic parameters for non-functionalized and NCO-functionalized biopolymers and corresponding oleogels	171
Table (3.1.2.) 1. Molar ratios of chitosan, HMDI, Et ₃ N and toluene used in the functionalization reaction	183
Table (3.1.2.) 2. TGA characteristic parameters for the biodegradable thickeners studied and starting materials	188
Table (3.1.2.) 3. Characteristic TGA parameters of the studied oleogel formulations	189
Table (3.1.2.) 4. Oleogels studied	194
Table (3.2.2.) 1. Molar ratios of chitin or chitosan, 1,6-hexamethylene diisocyanate (HMDI), triethylamine (Et ₃ N) and toluene used in each functionalization reaction	204
Table (3.2.2.) 2. Composition of oleogel formulations studied	206
Table (3.2.2.) 3. FTIR representative signals for selected NCO-functionalized chitin (CTIN-1) and chitosan (CSAN-1) samples	208
Table (3.2.2.) 4. TGA characteristic parameters for NCO-functionalized chitosan and chitin samples studied (main degradation stages in bold)	210
Table (3.2.2.) 5. TGA characteristic parameters for non-functionalized and NCO-functionalized chitosan and chitin-based oleogels studied (main degradation stages in bold)	211
Table (4.1.2.) 1. Composition and intrinsic viscosity of mercerized lignocellulose samples	227

Table (4.1.2.) 2. Proportions of lignocellulose pulp, hexamethylene diisocyanate (HMDI), triethylamine (Et_3N), and toluene applied in the cross-linking reaction and codes of each sample	227
Table (4.1.2.) 3. Activation energy values, from eq 1 for the different gel-like dispersions studied	233
Table (4.1.2.) 4. Penetration and mechanical roll stability values for the different gel-like dispersions studied	234
Table (4.1.2.) 5. Friction coefficient values and average diameter of wear marks on plates obtained in a ball-on-plates configuration when using the HMDI-cross-linked lignocellulose gel-like dispersions and standard lubricating greases as lubricants	235
Table (5.1.2.) 1. Formulation details of model biodegradable and conventional lubricating greases studied	261
Table (5.1.2.) 2. Power-law model fitting parameters of the viscous flow curves of biodegradable (CP, MC and CH) and commercial lubricating greases (LI and CA) studied at 25 and 125 °C	262
Table (5.1.2.) 3. SEM images and corresponding average diameter of wear marks on plates for samples CP, LI and CA obtained at 25 and 125 °C, constant rotational speed (10 rpm) and different normal loads (10, 20 and 40 N)	263
Chapter 5: General conclusions	273

List of Figures

Chapter 1: Introduction	19
Chapter 2: State of the art	27
Figure 1. Lithium-based lubricating grease microstructure image obtained through scanning electron microscopy (SEM) at 3500x [Delgado et al., 2006a]	30
Figure 2. Pseudoplastic behaviour of lubricating greases (a) with different concentration of thickener and (b) based on oils with different viscosities [Delgado et al., 2006a]	32
Figure 3. Evolution of the shear stress with time at different constant shear rates for a specific lubricating grease [Delgado et al., 2009]	32
Figure 4. Schematic representation of common problems observed in viscous flow tests of greases such as wall slip, shear banding and fracture [Magnin and Piau, 1990]	33
Figure 5. Lubricating grease mechanical spectrum [Delgado et al., 2005a]	35
Figure 6. Influence of the thickener concentration on (a) the viscoelastic moduli and (b) the loss tangent [Delgado et al., 2006a]	36
Figure 7. Influence of the oil viscosity on (a) the viscoelastic moduli and (b) the loss tangent [Delgado et al., 2006a]	36
Figure 8. Values of the plateau modulus for lubricating greases modified studied as a function of (a) soap and (b) LDPE concentrations [Martin-Alfonso et al., 2008]	38
Figure 9. Evolution of the plateau modulus with the –NCO content/prepolymer molecular weight ratio, as a function of grease ageing, for greases containing either 3% w/w of reactive polymer (squares) or variable polymer concentration (circles) [Moreno et al., 2008b]	38
Figure 10. Processing stages and thermal protocol followed during the manufacture of lubricating greases [Moreno et al., 2008a]	39
Figure 11. Scheme of a tribological system [Adelhelm, 2015]	40
Figure 12. Lubrication regimes of the Stribeck curve [Kondo et al., 2013]	41
Figure 13. Stribeck curves of blends of high oleic sunflower oil (HOSO) and different estolides [García-Zapateiro et al., 2013a]	42

Figure 14. Schematic example of sol-to-gel and gel-to-sol phase transition [Ding et al., 2014]	47
Figure 15. Appearance of a specific sample in the different phases of the reversible sol-gel process [Kidowaki et al., 2006]	48
Figure 16. Nature of (a) strong and (b) weak gels network [Terech and Weiss, 1997]	49
Figure 17. (a) 12-hydroxystearic acid and (b) corresponding salt	51
Figure 18. C ₁₆ DP-Al molecular structure	51
Figure 19. Influence of the ethyl cellulose molecular weight on G_N^0 of both α -cellulose and methylcellulose-based oleogels [Sánchez et al., 2011b]	53
Figure 20. Evolution of the G_N^0 with W, at different temperatures, for oleogels formulated with (a) α -cellulose/ethyl cellulose blends and (b) methylcellulose/ethyl cellulose blends [Sánchez et al., 2011c]	54
Figure 21. Correlation between G_N^0 of gel-like dispersions and a power series of cellulose polymerization degree and α -cellulose and lignin weight fractions [Núñez et al., 2011]	55
Figure 22. AFM micrographs of cellulosic pulp samples submitted to different H factor treatments: (a) H = 150 (window size: 2 μ m), (b) H= 150 (window size: 10 μ m), (c) H = 300 (window size: 2 μ m), and (d) H = 500 (window size: 2 μ m) [Núñez et al., 2012b]	56
Figure 23. Cellulose structure [Ten and Vermerris, 2013]	57
Figure 24. Chemical structure of chitin [Younes and Rinaudo, 2015]	60
Figure 25. Chemical structure of chitosan [Younes and Rinaudo, 2015]	63
Figure 26. Xyloglucan structure [Ten and Vermerris, 2013]	70
Figure 27. Galactoglucomannans structure [Ten and Vermerris, 2013]	70
Figure 28. Glucuronoarabinoxylan [Ten and Vermerris, 2013]	70
Figure 29. The three main precursors of lignin (monolignols) and their corresponding structures in lignin polymers [Laurichesse and Avérous, 2014]	71
Figure 30. Main linkages in a softwood lignin [Laurichesse and Avérous, 2014]	72

Figure 31. –NCO group possible resonant structures [Arnold et al., 1957]	75
Figure 32. Chemical reaction between OH and –NCO groups [Moreno, 2012]	76
Figure 33. Synthesis of polyurethanes [Moreno, 2012]	76
Figure 34. Possible molecular structures of polyurethanes [Moreno, 2012]	79
Chapter 3: Materials and methods	105
Figure 35. Molecular structure of α -cellulose.	107
Figure 36. Chitin molecular structure	109
Figure 37. Molecular structure of chitosan	109
Figure 38. Cellulose pulps from (a) <i>Eucalyptus globulus</i> and (b) <i>Pinus radiata</i> after a classical Kraft cooking and (c) <i>Eucalyptus globulus</i> after a semi-mechanical treatment	110
Figure 39. Molecular structure of 1,6-hexamethylene diisocyanate	112
Figure 40. Basic chemical components of a vegetable oil	112
Figure 41. Functionalization reaction with HMDI of the biopolymers	114
Figure 42. Controlled-rotational speed mixing device, anchor impeller and open vessel used in the processing of oleogels	116
Figure 43. Rotor–stator turbine and corresponding disperser used in the homogenization of oleogels	116
Figure 44. Digilab FTS 3500 ARX (Varian, USA) infrared spectrometer	117
Figure 45. Varian Direct-Drive 500 (^1H 500 MHz) spectrometer	117
Figure 46. Thermogravimetric analyser model Q-50 (TA Instruments Waters, USA)	118
Figure 47. Atomic force microscope with a Multimode apparatus connected to a Nanoscope-IV scanning probe microscope controller (Digital Instruments, Veeco Metrology Group Inc., USA)	119
Figure 48. Controlled-stress rheometers Gemini (Bohlin, Malvern Instruments Ltd., Worcestershire, United Kingdom)	120
Figure 49. Controlled-stress rheometers Rheoscope (ThermoHaake, Karlsruhe, Germany)	121
Figure 50. Controlled-stress rheometer Physica MCR-501 (Anton Paar,	121

Austria)

Figure 51. Schematic set-up tribology accessory in side and top view. The torque and the normal force applied by the rheometer are indicated by arrows [Heyer and Lauser, 2009]	122
Figure 52. Scanning electronic microscope model JSM-5410 (JEOL)	123
Figure 53. Seta Universal penetrometer model 17000-2 and one-quarter cone geometry (Stanhope-Seta, United Kingdom)	124
Figure 54. Roll Stability Tester model 19400-3 (Stanhope-Seta, UK), the metallic vase and the metallic cylinder	124
Chapter 4: Results and discussion	127
Figure (2.1.2.) 1. General strategy for methyl cellulose NCO-functionalization and reaction with ricinoleic fatty acid during oleogel preparation	140
Figure (2.1.2.) 2. H-NMR spectra for a polymer 1 and b polymer 2	141
Figure (2.1.2.) 3. FTIR spectra for a methyl cellulose and b polymer 2	142
Figure (2.1.2.) 4. Thermal degradation curves, under inert atmosphere, for NCO-functionalized methyl celluloses and starting materials	142
Figure (2.1.2.) 5. Thermal degradation curves, under inert atmosphere, for NCO-functionalized methyl cellulose gel-like dispersions in castor oil	143
Figure (2.1.2.) 6. FTIR spectra for a selected NCO-functionalized methyl cellulose gel-like dispersions in castor oil (MMC2-25)	143
Figure (2.1.2.) 7. Frequency dependence of a the storage, G' , and loss, G'' , moduli and b the loss tangent, for NCO-functionalized methyl cellulose gel-like dispersions in castor oil 1 day after their preparation (G' : full symbols, G'' : open symbols)	144
Figure (2.1.2.) 8. Frequency dependence of a the storage, G' , and loss, G'' , moduli and b the loss tangent, for NCO-functionalized methyl cellulose gel-like dispersions in castor oil 1 week after their preparation (G' : full symbols, G'' : open symbols)	144
Figure (2.1.2.) 9. Frequency dependence of the storage, G' , and loss, G'' , moduli for a selected NCO-functionalized methyl cellulose gel-like dispersion	145

in castor oil (MMC2-25) as a function of the ageing time (G' : full symbols, G'' : open symbols)	
Figure (2.1.2.) 10. Visual appearance of a unstable non-functionalized methyl cellulose dispersion in castor oil, b unstable NCO-functionalized methyl cellulose dispersion in sunflower oil and c physically stable NCO-functionalized methyl cellulose gel-like dispersion in castor oil	145
Figure (2.2.2.) 1. FTIR spectra for (a) methyl cellulose, (b) polymer MC–NCO-4 and (c) oleogel MC–NCO-4-30	156
Figure (2.2.2.) 2. Thermal degradation curves, under inert atmosphere, for the NCO-functionalized methyl cellulose polymers studied and starting materials used in the functionalization	156
Figure (2.2.2.) 3. Thermal degradation curves, under inert atmosphere, for the NCO-functionalized methyl cellulose-based oleogels studied	157
Figure (2.2.2.) 4. Frequency dependence of (a) the storage, G' , and loss, G'' , moduli and (b) the loss tangent, for a selected NCO-functionalized methyl cellulose oleogel (MC–NCO-4-30) as a function of the aging time (G' full symbols, G'' : open symbols)	157
Figure (2.2.2.) 5. Frequency dependence of (a) the storage, G' , and loss, G'' , moduli and (b) the loss tangent, for NCO-functionalized methyl cellulose oleogels, as a function of functionalization degree, 1 week after their preparation (G' : full symbols, G'' : open symbols)	158
Figure (2.2.2.) 6. Polymer molar –NCO content dependence of (a) the storage modulus, G'_1 , and (b) the loss tangent, at 1 rad/s, for NCO-functionalized methyl cellulose-based oleogels, as a function of aging (G' : full symbols, G'' : open symbols)	159
Figure (2.2.2.) 7. Frequency dependence of (a) the storage, G' , and loss, G'' , moduli, and (b) the loss tangent, for NCO-functionalized methyl cellulose-based oleogels, as a function of polymer concentration, 1 week after their preparation (G' : full symbols, G'' : open symbols)	159
Figure (2.3.2.) 1. FTIR spectra of non-functionalized (C-0, MC-0, HEC-0,	169

MHEC-0 and CAP-0),and NCO-functionalized cellulose derivatives (C-1, MC-1, HEC-1, MHEC-1 and CAP-1) and corresponding dispersions in castor oil (C-2, MC-2, HEC-2, MHEC-2 and CAP-2)	
Figure (2.3.2.) 2. Weight-loss thermogravimetric curves for (a) non-functionalized cellulose derivatives, (b) NCO-functionalized cellulose derivatives and (c) corresponding oleogels	170
Figure (2.3.2.) 3. Frequency dependence of (a) the storage, G' , and loss, G'' , moduli and (b) the loss tangent for NCO-functionalized cellulose derivatives-based oleogels	171
Figure (2.3.2.) 4. Physical appearance of the different NCO-functionalized cellulose derivatives-based oleogels: (a) cellulose,(b) methylcellulose,(c) 2-hydroxyethyl cellulose, (d) methyl 2-hydroxyethyl cellulose and (e) cellulose acetate propionate dispersions in castor oil	172
Figure (2.3.2.) 5. Correlation between the storage modulus at 1rad/s, G'_1 , and the product of $[-R_{\text{polar}}/-R_{\text{non-polar}}]$ molar ratio and average molecular weight of all substituents to cellulose monomer molecular weight ratio	173
Figure (2.3.2.) 6. AFM micrographs for selected oleogel microstructures: (a) MC-2; (b) HEC-2 (image width: 10 μm)	174
Figure (3.1.2.) 1. General strategy for chitin and chitosan NCO-functionalization and reaction with ricinoleic fatty acid during oleogel preparation	184
Figure (3.1.2.) 2. ^1H -NMR spectra for (a) CTIN-1 and (b) CSAN-1	185
Figure (3.1.2.) 3. FTIR spectra for (a) chitosan, (b) chitin and polymers, (c) CSAN-2 and (d) CTIN-1	186
Figure (3.1.2.) 4. Reaction of chitosan and chitin with hexamethylene diisocyanate (HMDI)	186
Figure (3.1.2.) 5. Thermal degradation curves, under inert atmosphere, for NCO-functionalized chitosans and chitins and starting materials	187
Figure (3.1.2.) 6. Thermal degradation curves, under inert atmosphere, for NCO-functionalized and non-functionalized chitosan and chitin gel-like	189

dispersions in castor oil

Figure (3.1.2.) 7. FTIR spectra for selected NCO-functionalized and non-functionalized chitosan and chitin gel-like dispersions in castor oil 190

Figure (3.1.2.) 8. Frequency dependence of the storage [G'] and loss [G''] moduli for NCO-functionalized and non-functionalized (a) chitosan and (b) chitin gel-like dispersions in castor oil (G' : full symbols, G'' : open symbols; ageing time: 1 month). Solid and dashed lines correspond to conventional lithium greases containing 14% and 6.5% soap concentration (from reference [41]) 191

Figure (3.1.2.) 9. Frequency dependence of the (a) storage [G'] and loss [G''] moduli, and the (b) loss tangent for the NCO-functionalized chitin gel-like dispersion in castor oil (CTIN-1-30), as a function of the ageing time (G' : full symbols, G'' : open symbols) 192

Figure (3.2.2.) 1. FTIR spectra for (a) chitin, (b) polymer CTIN-1; (c) oleogel CTIN-1-25; (d) chitosan; (e) polymer CSAN-1 and (f) oleogel CSAN-1-25. 207

Figure (3.2.2.) 2. Thermal degradation curves, under inert atmosphere, for NCO-functionalized chitosan (a) and chitin (b) samples and starting materials 209

Figure (3.2.2.) 3. Thermal degradation curves, under inert atmosphere, for NCO-functionalized chitosan-(a) and chitin-(b) based oleogels 211

Figure (3.2.2.) 4. Frequency dependence of the storage, G' , and loss, G'' , moduli for (a) NCO-functionalized chitosan-based oleogels (aged for 4 months) and (b) chitin-based oleogels (aged for 1 month), as a function of functionalization degree 212

Figure (3.2.2.) 5. HMDI proportion dependence of the storage modulus, G'_1 (G' at $1 \text{ rad} \cdot \text{s}^{-1}$), and the loss tangent, $\tan \delta$, at $1 \text{ rad} \cdot \text{s}^{-1}$, for NCO-functionalized chitosan- and chitin-based oleogels 213

Figure (3.2.2.) 6. Frequency dependence of the storage, G' , and loss, G'' , moduli for selected NCO-functionalized chitosan- (CSAN-3-25) and chitin- (CTIN-1-30) based oleogels, as a function of ageing time 214

Figure (3.2.2.) 7. Frequency dependence of the storage, G' , and loss, G'' , 215

moduli for NCO-functionalized chitosan-(a) and chitin-(b) based oleogels, as a function of biopolymer concentration	
Figure (4.1.2.) 1. FTIR spectra for different lignocellulosic materials: (a) original commercial grade Kraft pulp, (b) mercerized pulp (sample EK0), and (c) HMDI-cross-linked lignocellulosic material (sample EK2)	228
Figure (4.1.2.) 2. Thermal degradation curves, under inert atmosphere, for HMDI-cross-linked lignocellulosic materials, as a function of HMDI/cellulose pulp weight ratio. (a) weight loss curve and (b) derivative curve	229
Figure (4.1.2.) 3. AFM micrographs (window size 20 μm) for selected HMDI-cross-linked lignocellulose gel-like dispersions: (a) GPK; (b) GEK1; (c) GES	230
Figure (4.1.2.) 4. AFM micrographs (window size 10 μm) for selected HMDI-cross-linked lignocellulose gel-like dispersions: (a) GEK0; (b) GEK1; (c) GEK2	230
Figure (4.1.2.) 5. Frequency dependence of the storage, G' , and loss, G'' , moduli for the HMDI-cross-linked lignocellulose gel-like dispersions studied as a function of (a) source of origin of lignocellulose material and (b) HMDI/cellulose pulp weight ratio (G' , closed symbols; G'' , open symbols)	231
Figure (4.1.2.) 6. Normalized viscoelasticity functions and values of the plateau modulus as a function of the HMDI/cellulose pulp weight ratio. (G' , closed symbols; G'' , open symbols)	232
Figure (4.1.2.) 7. Evolution of (a) the storage, G' , and loss, G'' , moduli and (b) the loss tangent with the frequency at different temperatures for sample GEK1. (G , closed symbols; G'' , open symbols)	232
Figure (4.1.2.) 8. Evolution of the plateau modulus with temperature and Arrhenius' fitting (solid line) for sample GEK1	232
Figure (4.1.2.) 9. Viscous flow curves for the HMDI-cross-linked lignocellulose gel-like dispersions studied, at 25 $^{\circ}\text{C}$, as a function of (a) source of origin of lignocellulose material and (b) HMDI/cellulose pulp weight ratio	233
Figure (4.1.2.) 10. Influence of temperature on (a) shear rate dependence of viscosity and (b) evolution of the shear stress with shear rate for sample GEK1	234

Figure (5.1.2.) 1. Viscous flow curves at 25 °C for commercial and biodegradable lubricating greases studied	265
Figure (5.1.2.) 2. Evolution of the friction coefficient with the sliding velocity, at 20 N for the different lubricating grease samples: LI ((a) and (b)), CA ((c) and (d)), CP ((e) and (f)), MC ((h) and (i)) and CH ((j) and (k)), at 25 and 125 °C, respectively	266
Figure (5.1.2.) 3. Stribeck curves for lubricating grease samples CA (a), MC (b) and CH (c)	267
Figure (5.1.2.) 4. Evolution of the friction coefficient with time, at 25 °C and a constant rotational speed (10 rpm) as a function of (a) lubricating greases (normal load: 10 N), and (b) normal force (sample MC)	268
Figure (5.1.2.) 5. Stationary friction coefficient values obtained by applying a constant rotational speed (10 rpm) and different normal loads (10, 20 and 40 N), at 25 and 125 °C, for the different lubricating greases studied	269
Figure (5.1.2.) 6. Stationary friction coefficient values obtained by applying 20 N constant normal load and different rotational speeds (0.15, 10 and 400 rpm), at 25 and 125 °C, for the different lubricating greases studied	270
Figure (5.1.2.) 7. Average diameter of wear marks on plates obtained by applying a constant rotational speed (10 rpm) and different normal loads (10, 20 and 40 N), at 25 and 125 °C, for the different lubricating greases studied	271
Figure (5.1.2.) 8. Average diameter of wear marks on plates obtained by applying 20 N constant normal load and different rotational speeds (0.15, 10 and 400 rpm), at 25 and 125 °C, for the different lubricating greases studied	272
Chapter 5: General conclusions	273

List of Publications

1. Articles in journals

1. Gallego, R.; Arteaga, J.F.; Valencia, C. and Franco, J.M. (2013) Chemical modification of methyl cellulose with HMDI to modulate the thickening properties in castor oil, *Cellulose*, 20, 495-507.
2. Gallego, R.; Arteaga, J.F.; Valencia, C. and Franco, J.M. (2013) Rheology and thermal degradation of isocyanate-functionalized methyl cellulose-based oleogels, *Carbohydr. Polym.*, 98, 152-160.
3. Gallego, R.; Arteaga, J.F.; Valencia, C. and Franco, J.M. (2013) Isocyanate-functionalized chitin and chitosan as gelling agents of castor oil, *Molecules*, 18, 6532-6549.
4. Gallego, R.; González, M.; Arteaga, J.F.; Valencia, C. and Franco, J.M. (2014) Influence of functionalization degree on the rheological properties of isocyanate-functionalized chitin- and chitosan-based chemical oleogels for lubricant applications, *Polymers*, 6, 1929-1947.
5. Gallego, R.; Arteaga, J.F.; Valencia, C. and Franco, J.M. (2015) Thickening properties of several NCO-functionalized cellulose derivatives in castor oil, *Chem. Eng. Sci.*, 134, 260-268.
6. Gallego, R.; Arteaga, J.F.; Valencia, C.; Díaz, M.J. and Franco, J.M. (2015) Gel-like dispersions of HMDI-cross-linked lignocellulosic materials in castor oil: toward completely renewable lubricating grease formulations, *ACS Sus. Chem. Eng.*, Published ASAP.
7. Gallego, R.; Cidade, T.; Arteaga, J.F.; Valencia, C. and Franco, J.M. (2015) Tribological behaviour of conventional metallic soap- and chemically modified biopolymer-thickened lubricating greases investigated in a steel-steel rotating ball-on-three plates tribological cell, *Tribol. Int.*, sent.

2. Participations in congresses.

1. R. Gallego, J. F. Arteaga, C. Valencia and J. M. Franco. Formulación de nuevos oleogeles biodegradables basados en aceite de ricino y metilcelulosa modificada con hexameten diisocianato. VI Congreso de Jóvenes Investigadores en Polímeros. Islantilla, Huelva, Spain. 22-26 April 2012. Oral communication.
2. R. Gallego, J. F. Arteaga, C. Valencia and J. M. Franco. Chemical modification of methylcellulose with hexamethylen diisocyanate for their use in the manufacture of biodegradable lubricants. 8th Arnold Tross Colloquium. Hamburg, Germany. 8 June 2012. Oral communication.
3. R. Gallego, J. F. Arteaga, C. Valencia and J. M. Franco. Rheological characterization of oleogels containing isocyanate-functionalized methylcellulose-based polymers as gelling agent. XVI International Congress on Rheology – ICR 2012. Lisbon, Portugal. 5-10 August 2012. Poster.
4. R. Gallego, J. F. Arteaga, C. Valencia and J. M. Franco. Formulation and characterization of isocyanate-functionalized methyl cellulose-based oleogels with different functionalization degree. VII Congreso Nacional de Jóvenes Investigadores en Polímeros, JIP 2013. Cala Galdana, Menorca, Spain. 26-30 May 2013. Oral communication.
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