

Universidad de Huelva

**Departamento de Ingeniería Química, Química Física y
Química Orgánica**



**Formulación y procesado de oleogeles para el desarrollo
de nuevas grasas lubricantes biodegradables**

**Formulation and processing of oleogels for the
development of new biodegradable lubricating greases**

**Memoria para optar al grado de doctor
presentada por:**

Rubén Sánchez Martínez

Fecha de lectura: 18 de marzo de 2011

Bajo la dirección de los doctores:

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Huelva, 2011

ISBN: 978-84-15147-59-6

D.L.: H 142- 2011

FORMULACIÓN Y PROCESADO DE
OLEOGELES PARA EL
DESARROLLO DE NUEVAS
GRASAS LUBRICANTES
BIODEGRADABLES

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OF OLEOGELS FOR THE
DEVELOPMENT OF NEW
BIODEGRADABLE LUBRICATING
GREASES

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de Huelva**

FORMULACIÓN Y PROCESADO DE OLEOGELES PARA EL DESARROLLO DE NUEVAS GRASAS LUBRICANTES BIODEGRADABLES

Tesis Doctoral

Presentada por: Rubén Sánchez Martínez

Dirigida por: Dr. José María Franco Gómez

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Huelva, Marzo de 2011

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*Memoria presentada por Rubén Sánchez Martínez para aspirar al
Grado de Doctor en Ingeniería Química con Mención Europea por la
Universidad de Huelva.*

Rubén Sánchez Martínez

*La presente Tesis ha sido realizada en el Departamento de
Ingeniería Química, Química Física y Química Orgánica de la Universidad
de Huelva bajo la dirección del Dr. José María Franco Gómez y Dr.
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Huelva, Marzo de 2011



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TÍTULO DE LA TESIS

Formulación y procesado de oleogeles para el desarrollo de nuevas grasas lubricantes
biodegradables

ÁREA/S DE CONOCIMIENTO DE LA TESIS

Ingeniería Química

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Agradecimientos

Deseo expresar mi agradecimiento a todas las personas que me han ayudado en la realización del presente trabajo, pertenecientes al Laboratorio de Ingeniería de Fluidos Complejos de la Universidad de Huelva.

A mis Directores de Tesis, el Dr. José María Franco Gómez por su valioso apoyo profesional y personal ofrecidos desde los inicios de este trabajo y la ilusión transmitida constantemente que me ha ayudado a seguir hacia delante, y al Dr. Crispulo Gallegos Montes por la confianza depositada en mí y por sus continuas correcciones que han mejorado la calidad del trabajo elaborado. Gracias a ellos he podido involucrarme en el gratificante mundo de la investigación a través de sus conocimientos y experiencias.

A la Dra. Concepción Valencia Barragán por la ayuda que siempre me ha ofrecido convirtiéndose en uno de los soportes fundamentales de esta Tesis y sobre todo por comprenderme y conseguir transmitirme los ánimos necesarios en los inevitables momentos difíciles.

Finalmente quiero agradecer al Dr. Erik Kuhn y a todo su grupo del Laboratorio de Tribología de la Universidad de Ciencias Aplicadas de Hamburgo el apoyo brindado y la extraordinaria acogida recibida durante mi estancia en esa maravillosa ciudad que me permitió descubrir el complejo mundo de la Tribología y muchas cosas más.

Gracias a la aportación de todas estas personas esta Tesis Doctoral ha podido ver la luz, por lo que siempre estaré en deuda con todos ellos.



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CAPÍTULO 1

INTRODUCCIÓN

Abstract

This work deals with the use of renewable raw materials to develop new completely biodegradable lubricating grease formulations. Different vegetable oils have been used as base oil and several polymers and/or biodegradable gelling agents have been tested as thickeners, e.g. sorbitan and glyceryl monoestearates and the two most abundant biopolymers, cellulose and chitin, or some chemical derivatives. A comprehensive rheological and mechanical characterization of the resulting formulations as well as a thermal analysis, evaluating the influence of the different biodegradable polymers used as thickeners, were carried out. Moreover, a series of tribological tests were performed to evaluate the frictional behavior of these new greases in simulated conditions of lubrication. As a result of this investigation, a number of formulations, which could be potentially used as biodegradable greases, have been proposed.

1.1 Resumen

Durante los últimos años, las pérdidas de lubricantes liberadas al medioambiente se han convertido en un grave problema medioambiental. Teniendo en cuenta que las grasas lubricantes están formadas mayoritariamente por aceites minerales y jabones metálicos no biodegradables, existe una preocupación generalizada en el sector por sustituir estos componentes de las grasas por otros biodegradables en un corto periodo de tiempo.

De esta forma, están aumentado el número de iniciativas públicas y privadas que promocionan la sustitución de recursos no renovables por otros renovables y la disminución del impacto ambiental de los residuos de los procesos industriales, por lo que el gran reto de esta investigación es la utilización de materias primas renovables como base para el desarrollo sostenible de espesantes medioambientalmente amigables y susceptibles de ser utilizados en la fabricación de grasas

lubricantes totalmente biodegradables. Así pues, se ha pretendido incorporar a la formulación de las grasas lubricantes diversos polímeros o agentes gelificantes biodegradables, por lo general de origen natural (celulosa, quitina y derivados químicos de éstos, entre otros), para intentar sustituir a los clásicos espesantes basados en jabones metálicos. Como aceites bases biodegradables se han estudiado diversos aceites vegetales (ricino, soja, colza y girasol) con el fin de sustituir a los aceites minerales tradicionales.

En general, en este trabajo se plantea la optimización tanto del proceso de fabricación de las nuevas grasas manufacturadas con estos nuevos materiales como de la formulación. Para ello, se ha efectuado una caracterización fundamentalmente reológica y mecánica de las grasas lubricantes resultantes de dicho proceso, así como un análisis térmico, evaluando, especialmente, la influencia que puedan tener los polímeros biodegradables utilizados como espesantes. Además, en función de las diferentes formulaciones y condiciones de procesado seleccionadas como óptimas, se han realizado una serie de ensayos tribológicos, con el fin de modelizar el comportamiento de estas nuevas grasas biodegradables en condiciones simuladas de lubricación. Como resultado de esta investigación, finalmente, se proponen una serie de formulaciones que podrían ser potencialmente utilizadas como grasas 100 % biodegradables.

1.2 Justificación

La presente investigación se puede justificar atendiendo a dos hechos fundamentales: la sustitución de materiales convencionales por otros biodegradables y la inclusión en el mercado de nuevos productos altamente demandados y actualmente no ofertados.

Por un lado, existe una preocupación creciente por el desarrollo sostenible, que puede dividirse conceptualmente en ambiental, económico y social. Por lo tanto, la generación de una grasa lubricante

totalmente biodegradable estaría plenamente enmarcada en el desarrollo ambiental que actualmente es perseguido en todos los campos de la industria moderna. Por otro lado, atendiendo a este desarrollo ambiental, la industria está demandando productos que cumplan con este requisito pero, a su vez, sean tecnológicamente eficaces y competitivos. Materiales que cumplan totalmente estas características no han sido ofertados hasta el momento. Así pues, existe un nuevo mercado dispuesto a incorporar este tipo de nuevos productos.

1.3 Objetivos

El objetivo principal de esta Tesis Doctoral es el desarrollo de nuevas formulaciones de grasas lubricantes biodegradables, haciendo uso de materias primas renovables.

En cuanto a los objetivos específicos de la investigación, se plantea, por un lado, estudiar diversos polímeros y/o agentes gelificantes biodegradables susceptibles de ser utilizados como agentes espesantes en la fabricación de grasas lubricantes, como por ejemplo diversos monoestearatos, así como los dos polímeros más abundantes en la naturaleza, celulosa y quitina, o modificaciones químicas de éstos. Por otro lado, se han estudiado algunos aceites vegetales que pueden ser empleados como base lubricante. Todos estos tipos de agentes espesantes o mezclas de ellos, deben presentar cierta afinidad (tradicionalmente definida como “solvencia”) con el aceite base que se utilice, que confiera la microestructura y las propiedades adecuadas a la nueva grasa lubricante biodegradable a desarrollar.

1.4 Estructura

Esta Tesis Doctoral está dividida en diez capítulos. En el Capítulo 2, se exponen una serie de generalidades sobre grasas lubricantes, biodegradabilidad y su importancia en la sociedad actual, así como

algunos conceptos sobre Reología, Tribología y Análisis Térmico, necesarios para el desarrollo de la investigación. En el Capítulo 3, se describen todos aquellos materiales que se han utilizado para el desarrollo de las grasas lubricantes biodegradables manufacturadas, así como su procesado y aquella metodología experimental empleada para la caracterización de estos nuevos materiales. Cada uno de los siguientes capítulos, desde el 4 al 7, está constituido por uno o varios artículos (publicados, aceptados para su publicación o bien sometidos a evaluación en revistas científicas), cada uno de los cuales es autónomo respecto a los demás, aunque todos están estructuralmente relacionados. En el Capítulo 4, se presentan una serie de resultados experimentales obtenidos con oleogeles formulados con diferentes tipos de aceites vegetales y dos agentes gelificantes de bajo peso molecular, como son el monoestearato de sorbitano y el monoestearato de glicerilo. En el Capítulo 5, se muestran aquellos resultados obtenidos con la formulación de oleogeles con celulosas y derivados de ésta como espesantes, mientras que, en el Capítulo 6, se analiza el uso de quitina, quitosano y derivados químicos de éstos como espesantes, utilizando de nuevo, en ambos casos, aceites vegetales de diferente naturaleza. En los Capítulos 4, 5 y 6, se ha puesto mayor énfasis en las propiedades reológicas, térmicas y mecánicas de las diferentes formulaciones estudiadas, mientras que, en el Capítulo 7, se presenta una caracterización desde un punto de vista tribológico de una serie de oleogeles seleccionados. En el Capítulo 8, se propone un grupo de formulaciones óptimas y se exponen las conclusiones más relevantes que se pueden deducir de los resultados experimentalmente obtenidos. En el Capítulo 9, se recoge la bibliografía utilizada para llevar a cabo esta investigación. Por último, en el Capítulo 10, se hace referencia al estado de difusión de los resultados de este trabajo, así como los proyectos de trabajo futuros derivados de esta investigación.



CAPÍTULO 2

CONCEPTOS Y GENERALIDADES

2.1 Concepto de grasa lubricante

La *American Society for Testing and Materials* (ASTM) define una grasa lubricante como un material sólido, o semi-fluido, constituido por un agente espesante disperso en un líquido lubricante, donde pueden ser incluidos otros ingredientes o aditivos, en pequeñas cantidades, que mejoran ciertas propiedades específicas tales como su estabilidad mecánica, resistencia a la corrosión u oxidación, consistencia, color, resistencia al calor, etc [García-Morales et al., 2004]. Así, las grasas lubricantes se pueden considerar suspensiones coloidales en las que un agente espesante sólido, normalmente un jabón metálico (Figura 2.1), se encuentra disperso en una matriz líquida, por lo general un aceite mineral, formando un entramado tridimensional tipo gel. La consistencia de la grasa es determinada, fundamentalmente, por la estructura base que forma el espesante cristalizado, normalmente formando entrelazamientos, y que da lugar a una estructura fibrosa donde el aceite se encuentra atrapado. La forma de este esqueleto base es controlada mediante tratamientos termo-mecánicos durante la preparación de la grasa lubricante.

Las grasas lubricantes presentan una serie de ventajas y propiedades en comparación con los fluidos lubricantes convencionales, así, por ejemplo, la alta consistencia que la grasa lubricante posee permite que pueda permanecer “in situ” durante un largo periodo de tiempo, reduciéndose sensiblemente su pérdida bajo condiciones de operación normales [García-Morales et al., 2004; Sharma et al., 2005].

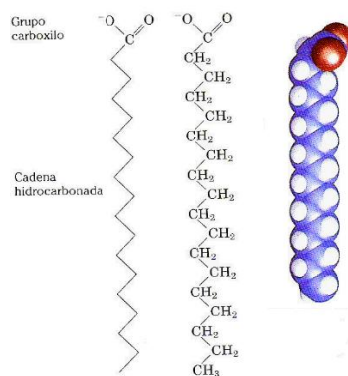


Figura 2.1. Estructura de los jabones

Los jabones metálicos de litio, calcio, sodio, aluminio y bario son los más usados como espesantes, aunque otros espesantes como poliureas o arcillas están siendo usados progresivamente bajo condiciones especiales. En 2008 se produjeron en todo el mundo 1,02 billones de kilos de grasas lubricantes, mostrándose en la Figura 2.2 la distribución de producción en función del tipo de espesante usado [Lubes'n'Greases, 2009]. Tal y como se puede observar, mayoritariamente el espesante que se selecciona en la formulación de una grasa lubricante es el jabón metálico de litio.

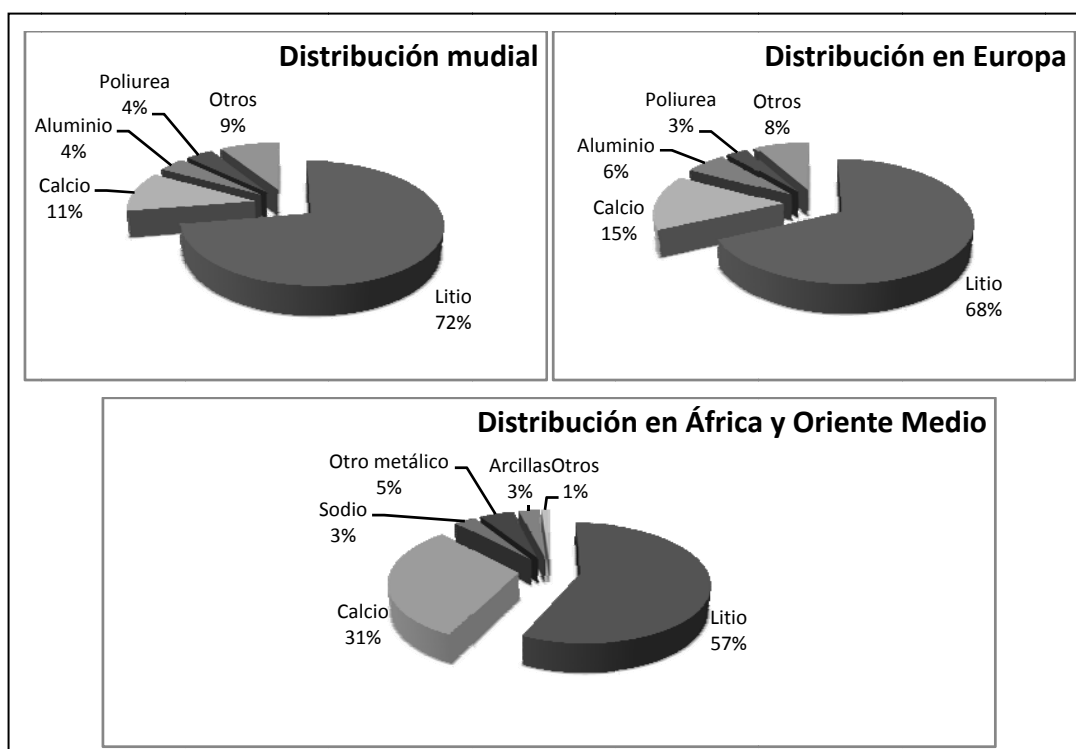


Figura 2.2. Distribución de la producción de grasas lubricantes por espesante en 2008

Como ha sido observado por microscopía electrónica (Figura 2.3), el espesante puede formar una red tridimensional entrecruzada que determina las propiedades reológicas de la grasa lubricante. Diferentes tipos de microestructuras pueden ser conseguidas con la cristalización del jabón metálico formando fibras, bastoncillos o plaquetas con configuraciones y tamaños característicos [García-Morales et al, 2004].

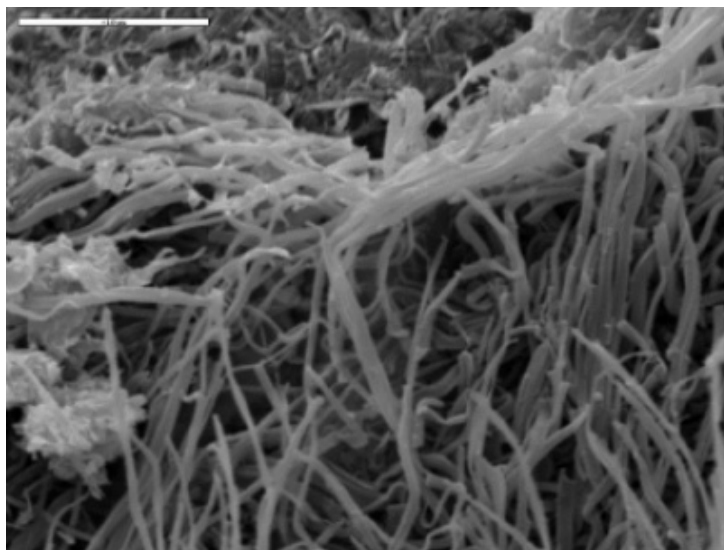


Figura 2.3. Microestructura obtenida con un microscopio de barrido electrónico (SEM) a 3500 aumentos de una grasa lubricante de litio [Delgado et al., 2006a]

El comportamiento que tiene una grasa lubricante cuando se pone en servicio depende de los materiales usados en su formulación y de las condiciones impuestas en su proceso de manufactura. El aceite se queda retenido en la microestructura que genera el espesante a través de una combinación de fuerzas de tipo físico y químico. Muchas de las propiedades de las grasas lubricantes dependen de su comportamiento reológico, el cual está relacionado con la microestructura que resulta del proceso de manufactura [Delgado et al., 2006a]. En resumen, las características de las grasas lubricantes están relacionadas con sus propiedades físicas que, a su vez, están relacionadas con su estructura obtenida en función de una adecuada selección de los ingredientes y de las variables de procesado [Adhvaryu et al., 2005a; Franco et al., 2005].

La consistencia de una grasa está altamente relacionada con la estructura que forman las partículas de espesante, generalmente fibrosa, y su distribución en el medio. Las propiedades lubricantes que una grasa exhibe dependen en gran medida de su habilidad para liberar aceite lubricante a las partes móviles de un mecanismo, formando una pequeña capa que separa las superficies metálicas, eliminando el calor y desgaste de la zona de fricción [Adhvaryu et al., 2005a].

La composición más común de una grasa lubricante es 12-hidroxiestearato de litio disperso en aceite mineral, con antioxidantes, anticorrosivos u otros aditivos [Lundberg y Berg, 2000]. Como ya se ha comentado anteriormente, otros cationes metálicos como el calcio, aluminio, sodio y bario, pueden ser usados en sustitución del litio [Hamnelid, 2000], así como diferentes combinaciones de ácidos grasos y ácidos de cadena corta con el mismo catión para formar las grasas complejas. La Tabla 2.1 muestra la composición típica y porcentaje de los componentes más comunes en las grasas lubricantes [Lubes'n'Greases, 2009].

Componente	Composición (%)	Función básica
Aceite (mineral/sintético)	65 – 95	Lubricante
Agente espesante	5 – 35	Portador de aceite / aditivo
Aditivos	0 – 10	Mejora de propiedades específicas

Tabla 2.1. Composición aproximada de una grasa lubricante

Para conseguir un producto sólido o semifluido, la afinidad entre aceite y espesante debe ser moderada; una elevada solubilidad del jabón no producirá un espesamiento de la grasa, mientras que una mala “solvencia” del aceite no es deseable por cuanto puede generar una excesiva separación de aceite además de dificultar el espesamiento de la grasa.

2.2 Propiedades mecánicas y físico-químicas

Las propiedades de grasas y aceites lubricantes suelen definirse y medirse mediante un gran número de ensayos tecnológicos normalizados por varias organizaciones como la “American Society for Testing and Materials” (ASTM) en Estados Unidos, o la “Deusches Institut für Normung” (DIN) en Alemania. Además de éstas, existen otras normas como las AFNOR en Francia, las IP en Inglaterra o las JIS en Japón. De carácter internacional existe la “International Organization for Standardizations” (ISO). En la Tabla 2.2 se presentan los principales métodos y ensayos normalizados para caracterizar grasas lubricantes según algunas de estas normas.

Propiedades	Ensayos	Normas ASTM	Normas DIN	Normas IP
Consistencia	Ensayos de penetración con cono (de 1, ½ y ¼ de escala) y ensayos de golpeo Ensayo de estabilidad al laminado Determinación de la consistencia a altas temperaturas	ASTM D-217 / ASTM D-1403 ASTM D-1831 ASTM D-3232	DIN ISO 2137 - -	- - -
Viscosidad aparente	Determinación de la viscosidad aparente	ASTM D-1092	-	-
Resistencia a la temperatura	Ensayo para la determinación del punto de gota Ensayo de separación de aceite durante su almacenamiento Ensayo de pérdida de grasa lubricante por evaporación	ASTM D-566 / ASTM D-2265 ASTM D-1742 / ASTM D-6184 ASTM D-972 / ASTM D-2595	DIN ISO 2176 - DIN ISO 51821-2	- IP-121 -
Resistencia a la oxidación	Ensayo de estabilidad a la oxidación por el método de bomba de oxígeno Ensayo de tiempo inducido de oxidación	ASTM D-942 ASTM D-5483	DIN 51808 -	- -
Resistencia a la corrosión	Ensayo para la determinación de las propiedades inhibidoras de la corrosión Ensayo para el control de las características inhibidoras de la corrosión bajo humedad Ensayo para la detección de la corrosión del cobre	ASTM D-1743 ASTM D-6138 ASTM D-4048	- - DIN 51811	- - -
Composición (jabón, alcalinidad, insolubles, agua, ácidos grasos,...)	Análisis de grasas lubricantes	ASTM D-128	-	-
Resistencia al agua	Ensayo para evaluar la acción del lavado con agua Ensayo para determinar la resistencia al agua pulverizada	ASTM D-1264 ASTM D-4049	- -	- -
Estabilidad mecánica	Determinación de la funcionalidad en rodamientos de bola a altas temperaturas Ensayo de cizalla en cojinetes	ASTM D-3336 ASTM D-3527	- -	- -
Presión Extrema (EP)	Medición de las propiedades de presión extrema en ensayo de cuatro bolas Medición de las propiedades de presión extrema por el método Timken	ASTM D-2596 ASTM D-2509	DIN 51350-4 -	IP-239 -
Propiedades antidesgaste	Determinación de las características preventivas del desgaste en ensayo de cuatro bolas Evaluación de la protección ante el desgaste corrosivo	ASTM D-2266 ASTM D-4170	DIN 51350-5 -	- -
Funcionalidad de grasas lubricantes en rodamientos	Ensayo para evaluar las pérdidas de grasa en rodamientos de ruedas de automóviles	ASTM D-1263	-	-
Clasificación y especificaciones de grasas para automoción	Clasificación estándar y especificaciones de grasas para automoción	ASTM D-4950	-	-

Tabla 2.2. Principales métodos y ensayos normalizados para grasas lubricantes

La consistencia de una grasa lubricante da una idea de la firmeza de la grasa y depende básicamente de la relación entre el espesante y el aceite base. La consistencia de una grasa debe ser apropiada para su aplicación en cada caso. Así, una grasa demasiado dura puede tener problemas a la hora de acceder a algunas zonas que necesiten ser lubricadas, mientras que una grasa demasiado blanda puede que no permanezca en la zona de lubricación. La consistencia aumenta proporcionalmente con la cantidad de espesante añadido. Dependiendo de la viscosidad del aceite base, se necesita una mayor o menor cantidad de espesante. En el caso en el que se tenga un aceite de baja viscosidad, la cantidad de espesante necesaria para una buena lubricación será mayor para disminuir el efecto de separación de fases. En cambio, con aceites más viscosos es necesaria una menor cantidad de agente espesante. Dentro del mismo tipo de grasas (con igual viscosidad y tipo de aceite base), se seleccionará la grasa de menor consistencia para los casos de lubricación centralizada y la de mayor consistencia para aquellos casos en que se quiera sellar o evitar la contaminación por elementos extraños, agua, polvo, productos de proceso, etc.

El “National Lubricating Grease Institute” (NLGI), estableció una clasificación de las grasas en función de su consistencia. El sistema para clasificar la consistencia de las grasas se define por la penetración producida por la caída de un cono estándar en una muestra de grasa (ASTM D-217). Dependiendo del valor obtenido en esta prueba se clasifica la grasa. Estos valores de penetración se convierten en grados NLGI que varían desde el 000 para las grasas más fluidas, hasta el 6 para las de mayor consistencia (Tabla 2.3). El grado NLGI de consistencia más comúnmente empleado es el NLGI 2. Menores grados, especialmente el 0 y el 1 se utilizan con frecuencia para mejorar la bombeabilidad o para servicios a bajas temperaturas. Grasas con grados NLGI mayores se usan para ciertos cojinetes de alta velocidad.

Grado NLGI	Clasificación según ASTM D-217 (dmm) 25 °C	
000	445-475	Semi-fluida
00	400-430	
0	355-385	
1	310-340	Suave
2	265-295	
3	220-250	
4	175-205	
5	130-160	
6	85-115	Dura

Tabla 2.3. Clasificación NLGI de las grasas en función de su consistencia

A altas temperaturas, el comportamiento de una grasa lubricante dependerá en gran medida de la naturaleza del aceite lubricante y del tipo de espesante que componga la grasa, pero, por lo general, un aumento de temperatura provocará una disminución progresiva de la consistencia hasta alcanzar un punto en el que la estructura del espesante se destruye, liberando el aceite por completo. Variaciones de temperatura ambiente no van a tener un efecto apreciable sobre la consistencia de una grasa en particular.

2.3 La lubricación y su problemática

El propósito de la lubricación es la separación de dos superficies con deslizamiento relativo entre sí de tal manera que se produzca el menor desgaste posible o daño en ellas. Lo que se pretende es que el rozamiento en el proceso de deslizamiento sea lo más pequeño posible. Para conseguir esto se intenta, siempre que sea posible, que haya una película de lubricante de espesor suficiente entre las dos superficies en contacto para evitar dicho desgaste [Terradillos y Bilbao, 2004].

La fricción seca es la resistencia al movimiento que existe cuando un objeto sólido y seco es movido sobre la superficie de otro objeto, también seco y sólido. Hace más de 4.000 años, los egipcios intentaron minimizar la fricción seca usando trineos y rodillos, algunas veces suplementados con lubricantes líquidos primitivos como los aceites

vegetales y animales, para transportar objetos pesados tales como piedras [Rohr, 2002].

La evaluación científica de la fricción es sin embargo mucho más reciente. La fricción cinética (fricción entre cuerpos en movimiento) ha sido estudiada desde finales de los años 70. La importancia de la fricción puede ser vista también por el hecho de que, como ha sido estimado, una sustancial parte del consumo total de energía es debido a la fricción entre partes en movimiento relativo. La reducción de la fricción mediante el uso de mejores sustancias lubricantes, como las grasas o líquidos lubricantes, es un problema de extrema importancia relacionado con la ingeniería moderna [Rohr, 2002].

La lubricación entre superficies metálicas en movimiento relativo actúa de dos formas diferentes dependiendo de dos mecanismos como son la adsorción física y la química. En la adsorción física las moléculas adsorbidas de lubricante ayudan a mantener las superficies separadas entre sí, pero estas moléculas están débilmente fijadas a la superficie metálica a través de fuerzas tipo Van der Waal's, que son interacciones totalmente reversibles, de tal forma que la capa lubricante es continuamente destruida por el calor generado en la fricción. Así, la concentración de moléculas adsorbidas disminuye con la temperatura. Las moléculas polares se orientan a lo largo de las superficies metálicas de una forma mucho más efectiva que las no polares. En la adsorción química se forman una serie de estructuras químicas generando una serie de interacciones no totalmente reversibles. Frecuentemente, la adsorción química parece ser una adsorción física a bajas temperaturas y cambia a adsorción química a mayores temperaturas, generalmente, debido a electrones de valencia que son intercambiados. Por último, un tercer fenómeno puede producirse cuando una reacción química tiene lugar. Esto puede ocurrir cuando hay intercambio de los electrones de valencia entre superficie y lubricante, formando un nuevo compuesto y resultando una reacción totalmente irreversible. Un ejemplo es cuando el azufre contenido en un lubricante reacciona con la superficie de un

metal formando sulfuro de hierro. Para producir este fenómeno, es necesario sobrepasar una elevada energía de activación, normalmente suministrada por el calor de fricción, actuando este sulfuro de hierro como una capa lubricante [Rohr, 2002].

Los componentes de una maquinaria industrial que necesitan habitualmente lubricación con grasas son [Terradillos y Bilbao, 2004]:

- ✓ Cojinetes
- ✓ Rodamientos
- ✓ Engranajes
- ✓ Otras partes en movimiento de difícil acceso

Dependiendo de si la película de lubricante es capaz de separar suficientemente las superficies a lubricar, la lubricación podrá ser de dos tipos [Terradillos y Bilbao, 2004]:

- ✓ Lubricación de película mixta: cuando no se forma una película de espesor suficiente y las superficies no están completamente separadas, existiendo algún tipo de contacto metal-metal.
- ✓ Lubricación hidrodinámica: se forma una capa de lubricante con una consistencia suficiente como para poder separar las dos superficies a lubricar.

Algunas de las propiedades más importantes necesarias para una lubricación satisfactoria son las siguientes [Maleque et al., 2003]:

- ✓ *Baja volatilidad bajo las condiciones de operación:* la viscosidad es un indicador de la volatilidad de un lubricante, en general, cuanto menor es la viscosidad mayor es el grado de volatilidad.
- ✓ *Valores de viscosidad adecuados en el rango de temperaturas usado:* los aditivos químicos, contaminantes, oxidaciones, volatilizaciones, etc... pueden afectar a la viscosidad de forma positiva o negativa.
- ✓ *Buena estabilidad o habilidad para mantener las características apropiadas durante un periodo de tiempo razonable:* la

temperatura, el oxígeno, la presencia de contaminantes, agua, ácidos corrosivos, etc... pueden limitar la vida útil de un lubricante. Todos los aceites lubricantes reaccionan con el oxígeno del aire formando ácidos o sedimentos, pudiendo provocar la corrosión de las superficies o el bloqueo de las líneas de flujo de aceite.

✓ *Compatibilidad con los materiales a lubricar.*

La elección entre una grasa y un aceite líquido depende de la relación entre la velocidad de la zona a lubricar y la viscosidad. Los cojinetes que trabajan a bajas velocidades utilizan aceites de viscosidad alta o grasas, mientras que los que van a altas velocidades necesitan aceites ligeros. La grasa o aceite elegido debe tener la suficiente viscosidad como para mantener una capa de fluido continua [Terradillos y Bilbao, 2004]. Teóricamente se podría lubricar todos los puntos sometidos a fricción de una maquinaria con aceite, pero el gasto que se generaría en lubricante sería muy elevado, por eso es preferible el uso de grasa lubricante por razones de economía. Sin embargo, las grasas no son solamente usadas de forma generalizada por razones económicas sino también por razones técnicas, ya que poseen ciertas propiedades no encontradas en líquidos lubricantes [Stempfel, 1998]:

- ✓ Son lubricantes y reservorios de lubricantes a la misma vez.
- ✓ No fluyen desde el punto de adición a otros puntos lejanos pero pueden encontrar el camino hacia la zona a lubricar con suficiente cantidad como para renovarse de forma continuada.
- ✓ Son indispensables cuando es necesario evitar el contacto con agua o suciedad del punto a lubricar (propiedades sellantes).
- ✓ Poseen una mejor capacidad de lubricación que los aceites en las regiones de fricción mixta.
- ✓ Las grasas son capaces de absorber más efectivamente los impactos por carga en los rodamientos, amortiguan las vibraciones de las partes de las máquinas expuestas a fricción y por tanto reducen el molesto ruido que éstas pueden producir.

Dependiendo de la aplicación suele ser más apropiado utilizar un aceite o una grasa. Las grasas lubricantes suelen ser más convenientes en las siguientes aplicaciones [Terradillos y Bilbao, 2004]:

- ✓ Equipos que funcionan de manera intermitente o están largos periodos de tiempo parados.
- ✓ Condiciones de funcionamiento extremas (altas temperaturas, presión, cargas por impacto, bajas velocidades).
- ✓ Zonas de difícil acceso (frecuencia de lubricación).

Puesto que la lubricación es fundamentalmente un problema de flujo y deformación, el conocimiento de las propiedades reológicas de las grasas lubricantes puede contribuir a elucidar uno de los problemas no resueltos en tribología: el efecto de la viscoelasticidad sobre las propiedades de lubricación y, por tanto, la manera en la cual una grasa lubricante se comporta bajo las condiciones de operación.

Las condiciones de operación de los nuevos equipos desarrollados imponen una serie de severas demandas que deben ser cubiertas por los lubricantes, incluyendo a las grasas, cuando son puestos en funcionamiento. Uno de estos requerimientos hace referencia a la habilidad que deben de poseer dichos lubricantes a prestar sus servicios en un amplio rango de temperaturas. La mayoría de las propiedades de las grasas lubricantes están relacionadas con su capacidad para fluir bajo la acción de un esfuerzo mecánico, cambiar su viscosidad por la acción de cambios en la temperatura y presión, ejercer de barrera física al paso de contaminantes o agua, etc. Sin embargo, estas propiedades generalmente se ven limitadas cuando la grasa lubricante está sometida a altas temperaturas de operación. Unas condiciones térmicas y mecánicas extremas pueden conllevar cambios físicos y químicos en la grasa lubricante que contribuyen finalmente a fallos de lubricación [Delgado et al., 2006b].

Entre las modificaciones físicas que una grasa lubricante puede sufrir se encuentra el deterioro de la microestructura del espesante,

aumentando el grado de separación de aceite y cambios en su viscosidad, mientras que las modificaciones químicas que se pueden encontrar corresponden a procesos oxidativos en sus componentes. Las grasas lubricantes no pueden disipar fácilmente el calor por convección, por lo que las altas temperaturas que pueden soportar aceleran los procesos de oxidación e incluso de carbonización [Delgado et al., 2006b].

De cualquier forma, el mercado de grasas lubricantes no queda exento de cambios, apareciendo necesidades de lubricación más exigentes y requiriendo grasas de mayor calidad para períodos de lubricación más largos [Terradillos y Bilbao, 2004].

2.4 Biodegradabilidad en grasas lubricantes

Una de las áreas en las cuales se está trabajando más hoy en día es la de mejorar las formulaciones de grasas lubricantes para optimizar el proceso de degradación, de forma que sea lo más natural posible [Terradillos y Bilbao, 2004].

La búsqueda de un material basado en productos naturales para usos industriales se ha acelerado en los últimos años. Los motivos por los cuales se ha promovido el desarrollo de lubricantes biodegradables incluyen incentivos gubernamentales, cambios en la opinión pública sobre preservación del medioambiente, programas corporativos de responsabilidad social y medioambiental y respuestas corporativas a las necesidades de marketing. El objetivo final es generar lubricantes, en última instancia 100% biodegradables, pero, si no es posible, el siguiente objetivo a cumplir consistiría en diseñar un producto con el máximo potencial biodegradable posible, frecuentemente denominados medioambientalmente “amigables”. Para normalizar el grado de consecución de estos objetivos medioambientales, han aparecido sistemas de etiquetado y clasificaciones en diferentes países, siendo la primera en aparecer (en el año 1998 para lubricantes de sierras

mecánicas [Lea, 2002]) y actualmente con mayor prestigio a nivel mundial en cuanto a exigencias de criterios se refiere, la etiqueta “Blue Angel”, en Alemania. Éstas etiquetas, fundamentalmente, imponen entre un 70 – 80% de degradabilidad de la sustancia lubricante con una obtención del 60% del CO₂ teórico [Flynn, 2000]. Regulaciones y legislaciones sobre el uso de lubricantes se han desarrollado también en otros países como Austria, Canadá, Hungría, Japón, Polonia, Escandinavia, Suiza, Estados Unidos, etc. También han surgido clasificaciones sobre impacto ambiental de las sustancias, siendo una de ellas la clasificación de peligrosidad en agua (ver Tabla 2.4) [Bartz, 1998].

Código	Comentario
0	Generalmente no pone en peligro el agua
1	Pone en peligro el agua ligeramente
2	Pone en peligro el agua
3	Pone en peligro el agua severamente

Tabla 2.4. Clasificación del peligro sobre el agua

En 2005, la Comisión Europea estableció oficialmente lo que se denomina “European Ecolabel for Lubricants” (EEL), siendo aplicable a diferentes tipos de lubricantes como los aceites hidráulicos, grasas lubricantes, aceites para sierras mecánicas, aceites para motores de dos tiempos y, en general, todos los lubricantes que pueden ser liberados al medioambiente durante su uso. De esta manera, la EEL fue especialmente diseñada para aquellas aplicaciones donde hay una cierta probabilidad o peligro de que los lubricantes lleguen al medioambiente. Por otra parte, la EEL fue una consecuencia lógica del deseo de unificar las diferentes ecoetiquetas nacionales, proponiéndose como objetivo intentar incorporar el mayor número posible de lubricantes dentro de sus productos. Muchos lubricantes podrían optar por esta ecoetiqueta pero eso supone la realización de ensayos adicionales y, por tanto, una mayor inversión de dinero. Por ello, la EEL intenta simplificar y ayudar a los fabricantes, facilitando la incorporación de estos productos [Krop y Oijen, 2010].

En general, el término biodegradabilidad significa la tendencia que un lubricante posee a ser ingerido y metabolizado por microorganismos, mientras que ecotoxicidad representa el efecto tóxico de un lubricante en plantas y animales (pero no en humanos) [Bartz, 1998]. Además, el objetivo de desarrollar lubricantes biodegradables o medioambientalmente compatibles incluye un número de requerimientos adicionales, como son los de ser clasificados dentro de la categoría 0 de peligrosidad en agua y no contener metales pesados, hidrocarburos halogenados o nitratos. Todo ello, sin olvidar que las propiedades que hacen ser a una grasa óptima para resolver los problemas de lubricación no se deben afectar negativamente al generar un producto biodegradable [Loderer, 1995]. De esta forma, se podría definir un biolubricante como aquel lubricante ecológico y no tóxico que, además, cumpla aquellos requisitos técnicos impuestos por las normas nacionales e internacionales y que satisfaga las expectativas del consumidor [Krop y Oijen, 2010].

En la manufactura de productos de comida y bebida a nivel industrial, se han venido usando productos derivados del petróleo para lubricar los equipos de las diferentes plantas y líneas de procesado. Antes de 1999, el Departamento de Agricultura de los Estados Unidos, en las inspecciones federales de las plantas de procesado alimentarias, clasificó los lubricantes usados en dos categorías, H1 y H2. Los lubricantes usados en aplicaciones donde hay posibilidad de un contacto accidental con los alimentos son clasificados como H1, mientras que los lubricantes usados en aplicaciones donde no hay posibilidad de contacto con los alimentos se clasifican como H2. Las condiciones en las que tiene que operar un lubricante en la industria alimentaria pueden ser muy diversas, por ejemplo, es relativamente frecuente tener que usar un lubricante para elementos móviles que pasan por un horno que trabaja a más de 200 °C, para terminar pasando por un congelador que somete al lubricante a temperaturas extremadamente bajas (incluso por debajo de 0 °C). Además, los

lubricantes deben resistir la degradación química y proteger a los equipos de corrosión. Por otra parte, atmósferas pulverulentas, particularmente procedentes de la harina en la industria panadera, conllevan la contaminación del lubricante. El polvo, al ponerse en contacto con el lubricante, puede espesar y formar residuos adhesivos que puede afectar negativamente al funcionamiento del equipo. Estas condiciones, combinadas con las demandas usuales a las cuales son sometidos los equipos, como son altas cargas, golpes, cizalla, etc., requieren un lubricante capaz de desempeñar su función de forma satisfactoria [Rajewski et al., 2000].

Un cálculo basado en el consumo de lubricantes en Alemania y el vertido de diferentes tipos de lubricantes al medioambiente concluye que, anualmente, son depositadas unas 250.000 toneladas de estos materiales [Bartz, 1998]. Otros cálculos realizados [Stempf, 1998] estiman el consumo total y la pérdida de lubricantes en Estados Unidos, Europa y Suiza, cuyos resultados se pueden ver en la Tabla 2.5.

Zona	Consumo de lubricantes (toneladas / año)	Pérdida de lubricante (toneladas / año)	Porcentaje de pérdida (%)
Estados Unidos	9.000.000	1.500.000	17
Europa	4.500.000	600.000	13
Suiza	60.000	4.000	6

Tabla 2.5. Consumo y pérdida de lubricantes en diferentes zonas del mundo

Estos datos demuestran que grandes cantidades de lubricante terminan depositadas directamente en la naturaleza cada año, de ahí que, cada vez, se estén haciendo mayores esfuerzos para encontrar lubricantes alternativos que sean más neutros para el medioambiente.

Evidentemente, en el pasado, el consumo de lubricantes era mucho menor al actual y, por lo tanto, la cantidad que llegaba al medioambiente era muy reducida. Sin embargo, con las cifras que se han comentado, se concluye que el daño que se provoca al

medioambiente es bastante elevado. Por ello, debe volverse a formular lubricantes similares en composición a los que se usaban antiguamente en la historia de la tribología, puesto que eran totalmente naturales, con la gran ventaja de partida de que la cantidad y variedad de materiales a los que tenemos acceso actualmente se ha incrementado notablemente y, hoy en día, existen muchas más opciones disponibles [Stempfel, 1998].

En la actualidad, existen diferentes puntos de vista sobre qué características podrían hacer a un lubricante ser mejor para el medioambiente [Krop y Oijen, 2010]:

- ✓ Que se biodegrade rápidamente sin efectos tóxicos
- ✓ Que su formulación se base en productos renovables
- ✓ Que se reduzca su pérdida o la frecuencia de lubricación
- ✓ Que se reduzcan los ingredientes o procesos peligrosos en la etapa de manufactura

Evidentemente, estas características pueden incrementar el precio del producto final. Sin embargo, se estima que el mercado de biolubricantes pueda crecer desde las 120.000 toneladas manufacturadas en el año 2006 hasta las 180.000 en 2013 [Krop y Oijen, 2010]. Así, hoy en día, ya no tienen tanta importancia los problemas de coste en la formulación y fabricación de las grasas, sino que se empiezan a tener en cuenta otros factores [Terradillos y Bilbao, 2004]:

- ✓ Restricciones ambientales
- ✓ Biodegradabilidad
- ✓ Aumento de la conciencia de impacto ambiental a través del ciclo de vida del producto, desde la formulación y fabricación hasta su uso final
- ✓ Mayor información del producto respecto al manejo, uso, eliminación y riesgo potencial

En la selección de las materias primas y la formulación de los productos terminados, los siguientes aspectos son actualmente importantes [Stempfel, 1998]:

- ✓ Biodegradabilidad
- ✓ Bioacumulación
- ✓ Toxicidad (humanos)
- ✓ Ecotoxicidad (peces, plantas y bacterias)
- ✓ Emisiones (gases de escape)
- ✓ Manufactura del producto (condiciones de procesado)

De todas formas, en muchas partes de Europa, una vez que los biolubricantes son usados, deben ser depositados en contenedores especiales. Esto no significa que estos nuevos lubricantes sean innecesarios, sino que, en comparación con los productos basados en aceites minerales, éstos representan un menor impacto sobre el medioambiente y, en caso de accidente, el producto disminuirá el efecto negativo que se produciría si el lubricante vertido fuese el tradicional [Stempfel, 1998].

Las aplicaciones o sectores industriales que tienen un alto impacto medioambiental son entre otros [Terradillos y Bilbao, 2004]:

- ✓ Trenes (grasa de reborde y curva)
- ✓ Minería (grasa de engranaje abierto)
- ✓ Acería (lubricantes de laminación)
- ✓ Agricultura (lubricantes para la industria transformadora de algodón)
- ✓ Construcción (lubricantes para máquinas de perforar)
- ✓ Marina
- ✓ Selvicultura
- ✓ Eólicas

En el caso de los lubricantes líquidos, ya se han introducido comercialmente productos biodegradables. Por ejemplo, hace unos

cuarenta años que los autobuses de Londres y otras compañías de vehículos usan aceite de ricino en los ejes traseros, obteniendo grandes beneficios en cuanto a consumo de combustible, junto con excelentemente bajos coeficientes de fricción [Lea, 2002]. Otro caso lo componen los aceites para motores fueraborda, a finales de los años 70, y los avances, a principios de los 80, en el área de las sierras mecánicas. Sin embargo, para el caso de las grasas lubricantes, los productos biodegradables han empezado a ponerse en un primer plano a principios de los 90, en aplicaciones como la lubricación central de los chasis de camiones, maquinaria agrícola, plantas purificadoras de aguas residuales, plantas hidroeléctricas y para la lubricación de vías, ruedas y agujas de ferrocarriles [Stempfel, 1998].

Las grasas “biodegradables” actuales están compuestas esencialmente por los mismos componentes que las no biodegradables. La principal diferencia es el aceite base utilizado para la fabricación. Se están empezando a introducir cada vez más aceites vegetales y sintéticos biodegradables en sustitución de los minerales, que no son biodegradables [Terradillos y Bilbao, 2004], pero se sigue usando el espesante metálico no biodegradable en su formulación. Estas grasas lubricantes basadas en aceites vegetales siguen siendo, por lo general, dispersiones coloidales semi-sólidas de un agente espesante (generalmente un jabón metálico) en una matriz de líquido lubricante biodegradable [Adhvaryu et al., 2005a].

Por tanto, los primeros pasos que se han dado para lograr una grasa biodegradable han consistido en el uso de aceites vegetales, generalmente de soja, ricino y colza, como sustitutos de los aceites minerales (se han encontrado mejores propiedades cuando el aceite vegetal usado ha sido modificado [Adhvaryu et al., 2000]) en la formulación de la grasa lubricante con un jabón de calcio. Las limitaciones encontradas en este tipo de grasas hacen referencia, fundamentalmente, a las temperaturas a las cuales pueden trabajar de manera óptima (-20 - +80 °C) [Adhvaryu et al., 2005a; Stempfel, 1998;

Loderer, 1995] y el rango limitado de viscosidades disponible [Quinchia 2009, 2010]. Actualmente, la mayoría de los aceites vegetales usados en Europa son el aceite de colza (tanto para aceites como grasas lubricantes) y el aceite de ricino (para grasas lubricantes) [Stempfel, 1998].

Las grasas lubricantes denominadas como biodegradables, manufacturadas actualmente, tienen la siguiente composición [Stempfel, 1998]:

- ✓ Fluido base (entre un 75 y 95%), usando comúnmente:
 - o Aceites vegetales
 - o Ésteres sintéticos
 - o Glicoles
- ✓ Espesantes (entre un 5 y 20%), usando comúnmente:
 - o Jabones metálicos (preferentemente de calcio)
 - o Bentonita / sílice / arcillas
 - o Jabones complejos de aluminio
 - o Poliureas
- ✓ Aditivos (entre un 1 y 8%), usando comúnmente:
 - o Antioxidantes
 - o Inhibidores de la corrosión
 - o Aditivos antidesgaste
 - o Aditivos para modificar la pegajosidad
 - o Antiespumantes
 - o Tintes

La excelente afinidad que los aceites vegetales tienen con las superficies metálicas dan a estos lubricantes biodegradables unas buenas propiedades naturales anti-corrosión y, en muchos casos, no es necesario ningún tipo de aditivo. De forma general, para obtener las mismas propiedades que una grasa lubricante no biodegradable exhibe con respecto a la corrosión, sólo es necesario añadir una pequeña cantidad de aditivo [Stempfel, 1998].

Teniendo en cuenta las diferentes formulaciones desarrolladas hasta ahora, los fluidos base que se están usando se dividen en dos grandes grupos, los que son miscibles con agua y los que no lo son. Aquellos que pueden ser miscibles con agua son exclusivamente los glicoles, siendo los más usados los glicoles de monopropileno y polipropileno, con un peso molecular medio de entre 200 y 1.000. La biodegradabilidad decrece notablemente con el incremento del peso molecular. Mezclas poliméricas de óxido de etileno y óxido de propileno son muy apreciadas por su viscosidad, biodegradabilidad y solubilidad en agua, encontrando grandes aplicaciones en este campo de biolubricantes. Sin embargo, este tipo de fluidos no pueden actuar como agente sellante contra el agua y son incompatibles con los aceites minerales [Stempfel, 1998].

Los fluidos base biodegradables que no se pueden mezclar con el agua, los cuales son usados principalmente en las nuevas generaciones de lubricantes, pueden ser clasificados en dos grandes grupos: aceites naturales (principalmente aceites vegetales) y ésteres sintéticos (saturados e insaturados). Químicamente, los aceites naturales y los ésteres sintéticos tienen básicamente la misma estructura por lo que sus propiedades son muy similares. Con respecto a la resistencia al envejecimiento y su comportamiento a baja temperatura, los ésteres sintéticos presentan ciertas ventajas con respecto a los aceites vegetales, pero estas ventajas se consiguen pagando un precio notablemente mayor [Stempfel, 1998].

Los dos grupos descritos anteriormente son relativamente propensos a la hidrólisis, debido a su estructura química, puesto que presentan dobles enlaces covalentes. Éstos pueden ser cuantificados con el índice de yodo, directamente relacionado con la resistencia al envejecimiento de los aceites vegetales [Stempfel, 1998].

La química de los aceites vegetales no permite su uso como fluidos base en todos los casos donde se necesita un aceite hidráulico.

Las principales razones son la proporción de dobles insaturaciones en el ácido graso, que provoca la resinificación, y las largas cadenas de grupos ésteres de los ácidos grasos, que confieren poca estabilidad a baja temperatura [Stempfel, 1998]. A estas bajas temperaturas, aparecen cristales que rápidamente se aglomeran, resultando una solidificación del aceite. Los aceites vegetales son sistemas moleculares complejos y la transición de líquido a sólido no ocurre a una temperatura determinada, sino dentro de un rango de valores. Ésto provoca las deposiciones de cera que contribuyen a un rápido incremento de la viscosidad, y, por tanto, genera una mayor dificultad para el bombeo [Adhvaryu et al., 2003; Adhvaryu et al., 2005b]. En los casos donde los aceites vegetales no pueden ser utilizados, los ésteres sintéticos sí pueden ser usados como sustitutos. Hoy en día, numerosas variantes de ésteres están disponibles, por ejemplo, el valor de yodo puede ser reducido prácticamente a cero, mejorando, de esta forma, las propiedades de envejecimiento y la estabilidad a la hidrólisis, pero, evidentemente, encareciendo el precio del producto. Por esta razón, es importante decidir qué propiedades son deseables para determinar si es necesaria una modificación química [Stempfel, 1998].

En las siguientes tablas aparecen una serie de propiedades de aceites vegetales, glicoles y ésteres sintéticos, donde se reflejan las diferencias en sus propiedades, tanto físicas como químicas, que los distinguen para su uso en ciertas aplicaciones específicas.

Tipo de aceite	Viscosidad cinemática a 40 °C (mm ² /s)	Índice de yodo (g/100 g)	“Pourpoint” (°C) ¹
Colza	34	94 / 106	-20 / -4
Soja	28	103 / 109	-18 / -8
Oliva	32	80 / 85	-6 / +4
Girasol	28	127 / 136	-18 / -16
Cacahuete	37	80 / 100	-2 / +3
Jojoba	25	82	+10
Ricino	232	82 / 90	-18 / -12

Tabla 2.6. Propiedades de algunos aceites vegetales usados como lubricantes biodegradables [Stempfel, 1998]

Propiedad	Aceite mineral	Glicol	Aceite vegetal	Éster sintético
Densidad a 20 °C (kg / m ³)	880	1100	940	930
Índice de viscosidad ²	100	100 - 200	100 - 250	120 - 220
Estabilidad a la cizalla	Buena	Buena	Buena	Buena
“Pourpoint” (°C)	-15	-40 / +20	-20 / +10	-60 / -20
Flujo a baja temperatura	Bueno	Muy bueno	Pobre	Muy bueno
Miscibilidad con aceite mineral	---	No miscible	Buena	Buena
Solubilidad en agua	No soluble	Desde muy soluble a insoluble	No soluble	No soluble
Comportamiento frente a pinturas / revestimientos metálicos	Bueno	Pobre	Bueno	Desde bueno a pobre
Biodegradabilidad (CEC) %	20 - 35	10 - 100	70 - 100	10 - 100
Estabilidad a la oxidación	Buena	Buena	Intermedia	Buena
Estabilidad hidrolítica	Buena	---	Pobre	Intermedia
Tendencia a la formación de sedimentos	Buena	---	Pobre	Intermedia
Coste en base al aceite mineral	1	2 - 4	2 - 3	4 - 20

Tabla 2.7. Comparación de las propiedades físicas y químicas de los fluidos bases biodegradables (valores medios) [Stempfel, 1998]

¹ El término “pourpoint” de un líquido se define como la menor temperatura a la cual un líquido puede fluir bajo unas condiciones estándar.

² Índice que determina la relación entre la viscosidad y la temperatura, alcanzando mayores valores conforme menor sea su dependencia con la temperatura.

En la Figura 2.4, se representa la biodegradabilidad de alguno de estos compuestos, concluyéndose que los aceites vegetales poseen las mejores prestaciones en este sentido.

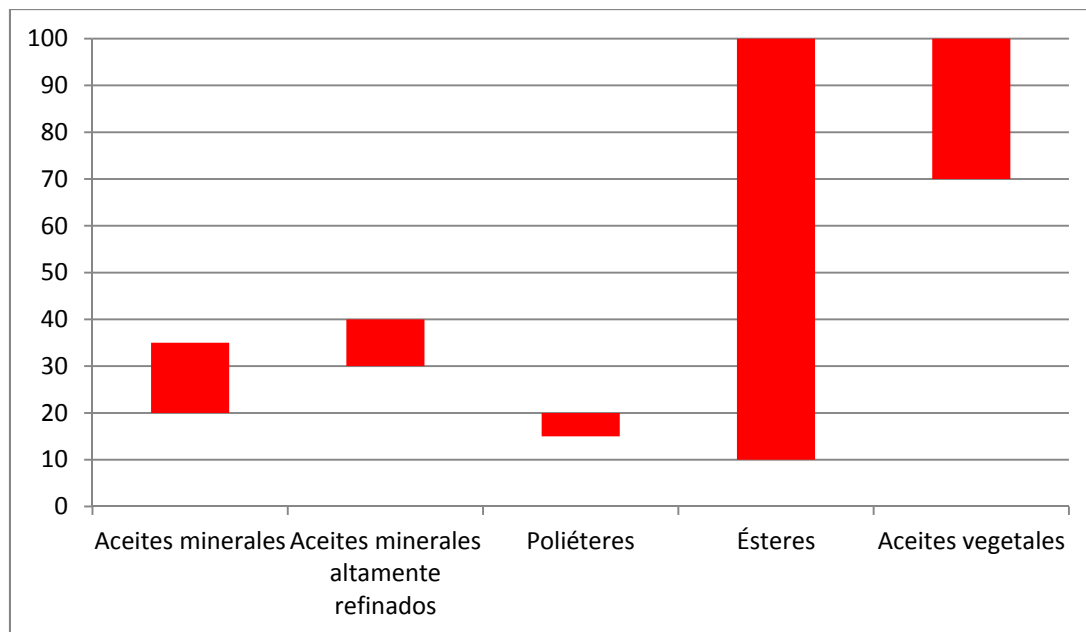


Figura 2.4. Biodegradabilidad de los fluidos base (%) según la norma CEC-L-33-A-93 (21 días) [Stempfel, 1998]

En general, las ventajas que poseen los aceites vegetales sobre los minerales son las siguientes [Maleque et al., 2003; Lea, 2002]:

- ✓ Los aceites vegetales son biodegradables y no tóxicos
- ✓ Los aceites vegetales son recursos renovables que dependen del cultivo, mientras que los aceites minerales proceden de fuentes de origen limitadas
- ✓ Los aceites vegetales tienen un “flash point”³ mayor que los aceites minerales, por lo que, al ser líquidos inflamables, son más seguros para los humanos
- ✓ Los aditivos suelen ser fácilmente solubles en ellos

Por el contrario, los inconvenientes de los aceites vegetales para ser empleados como lubricantes son [Lea, 2002]:

³ Menor temperatura a la cual se produce una ignición cuando un líquido se mezcla con aire. El vapor puede dejar de arder cuando la fuente de ignición es retirada.

- ✓ Químicamente son mezclas que pueden ser muy variables
- ✓ A muy baja o muy alta temperatura pueden no funcionar adecuadamente
- ✓ Mayor grado de insaturación
- ✓ Mayores costes (asociados al cultivo y transformación)
- ✓ Rango de viscosidad limitado

En resumen, los aceites vegetales son, generalmente, buenos lubricantes, siendo su mayor limitación el alto coste, la inestabilidad térmica y a la oxidación. La estabilidad a la oxidación de los aceites vegetales depende del nivel de insaturaciones que el producto presente. Conforme menos insaturaciones tenga el aceite vegetal mejor será su estabilidad a la oxidación pero tendrá un punto de fusión mayor. De forma general, los aceites vegetales pueden ser usados hasta una temperatura máxima de 120 °C. Sin embargo, con el uso apropiado de antioxidantes, se puede resolver este problema. Por otro lado, los aceites vegetales son más propensos a formar espumas y tienen una menor filtrabilidad comparados con los aceites minerales [Maleque et al., 2003].

La mayoría de los aceites vegetales contienen, al menos, cuatro y, algunas veces, hasta doce ácidos grasos diferentes. La proporción de cada uno de ellos depende no sólo del tipo y variedad de planta, sino también del clima, la meteorología y los sustratos disponibles para las plantas. La Tabla 2.8 muestra las fuentes de los principales tipos de aceites naturales y su producción mundial, junto con los principales ácidos grasos de su composición [Maleque et al., 2003].

Fuente	Producción mundial (millones de toneladas / año)	Tipo de ácido graso	Longitud de la cadena carbonada y número de dobles enlaces
Aceite de soja	20	Linoleico	C18:2
		Oleico	C18:1
Aceite de cacahuete	4	Linoleico	C18:2
		Oleico	C18:1
Aceite de palmera	16	Palmítico	C16:0
		Oleico	C18:1
Aceite de colza	11,5	Oleico	C18:1
Aceite de girasol	9	Linoleico	C18:2
		Oleico	C18:1
Sebo de vaca	7,5	Oleico	C18:1
		Palmítico	C16:0
		Esteárico	C18:0
Manteca	6	Oleico	C18:1
		Palmítico	C16:0
Aceite de coco	3	Láurico	C12:0
Aceite de almendra de palmera	2	Láurico	C12:0
Aceite de oliva	2	Oleico	C18:1
Aceite de pescado	1,5	Largas cadenas	C20:2 hasta 6
		Ácidos grasos	C22:2 hasta 6
Aceite de maíz	1,8	Linoleico	C18:2
		Oleico	C18:1
Aceite de ricino	0,5	Rinoleico	C18:1 – OH
Aceite de linaza	0,6	Linoleico	C18:3

Tabla 2.8. Diferentes tipos de aceites vegetales, producción mundial y tipos de ácidos grasos que contienen [Maleque et al., 2003]

De los biolubricantes modernos, se espera que exhiban una serie de propiedades que sólo se pueden conseguir añadiendo una cierta cantidad de aditivos en su formulación. Para el caso de aceites o grasas lubricantes biodegradables, los siguientes aditivos son frecuentemente empleados [Stempfel, 1998]:

- ✓ Antioxidantes:
 - o Aminas
 - o Fenoles
 - o Vitaminas
- ✓ Antidesgaste / extrema presión:
 - o Ditioposfatos (sin cenizas)
 - o Ditiocarbamatos (sin cenizas)
 - o Fosfitos
 - o Compuestos de azufre y fósforo
- ✓ Inhibidores a la corrosión
 - o Derivados de ácidos grasos
 - o Aminas
 - o Imidazolinias
 - o Triazoles
- ✓ Agentes antiespuma
 - o Siliconas
 - o Metacrilatos
- ✓ Agentes para reducir la pegajosidad
 - o Polimetacrilatos
 - o Poliisobutilenos
 - o Resinas naturales / polímeros

En la medida de lo posible, los aditivos también deben ser biodegradables, no tóxicos, puros y libres de aceites minerales y metales pesados.

Algunos especialistas consideran que la dirección que deben tomar los biolubricantes debe estar orientada hacia procesos con un menor riesgo, tanto desde un punto de vista de seguridad como de higiene industrial. De esta forma, espesantes basados en poliureas generan operaciones bastante peligrosas. Además, la manipulación de di-isocianatos y aminas puede desembocar en la necesidad de utilizar equipamiento tan especializado que muchos productores no sean capaces de obtener. Otros espesantes usados en forma de polvos, como

sílice, pueden generar nubes dañinas para el ser humano e incluso explosivas durante la manufactura de la grasa. En algunos casos, se ha pensado encapsular estos compuestos en polímeros, para evitar este tipo de problemas, y luego que estos polímeros pasen a formar parte de la formulación de la grasa. Sin embargo, el gran problema que plantea este procedimiento es encontrar un polímero que cumpla estas características y no modifique las propiedades típicas de las grasas lubricantes, como su punto de gota o fluencia, separación de aceite o estabilidad mecánica [Krop y Oijen, 2010].

De lo comentado en este capítulo, se deduce que la sustitución de los agentes espesantes tradicionales por estos biodegradables y/o basados en recursos naturales es el campo más inexplorado y el que presenta más problemas a la hora de desarrollar una grasa lubricante 100% biodegradable.

2.5 Reología de grasas lubricantes

2.5.1 Conceptos básicos de Reología

La Reología es la ciencia que estudia la deformación y el flujo de los materiales, proviniendo esta palabra del verbo griego “ $\rho\epsilon\upsilon\omega$ ”, que significa fluir. El concepto fue introducido por Eugene Bingham en 1920 [Macosko, 1994] con el fin de definir, de una forma más precisa, la mecánica de los cuerpos deformables, restringida hasta entonces a la elasticidad clásica de Hooke y a la mecánica de fluidos de Newton. El nacimiento de la Reología como ciencia diferenciada se produjo en la primera mitad del siglo XX como consecuencia del interés que suscitaron el desarrollo y utilización a nivel industrial de materiales con características de flujo especiales, tales como plásticos, pinturas, disoluciones de polímeros, fluidos biológicos, suspensiones coloidales, etc.

Así, la Reología estudia la relación existente entre las fuerzas externas que actúan sobre un cuerpo y la deformación que éstas producen [Van Wazer et al., 1963]. Dado que el movimiento de cada una de las partículas que forman un cuerpo está sometido a las leyes de la Mecánica, la Reología se basa en dicha rama de la Física.

Para entender el comportamiento reológico de los materiales es necesario definir algunos conceptos:

2.5.1.1 Tensor esfuerzo

En general, sobre un elemento material cualquiera pueden actuar dos tipos de esfuerzos, los esfuerzos normales, que se refieren a la componente en dirección perpendicular a la superficie considerada, y esfuerzos de cizalla o cortantes, que son las componentes tangenciales a dichas superficies (ver Figura 2.5) [Darby, 1976; Dealy, 1982].

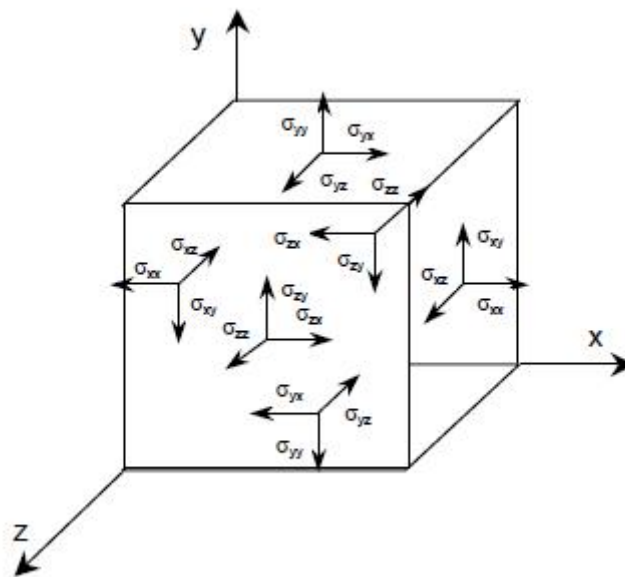


Figura 2.5. Espacio euclídeo con esfuerzos normales y de cizalla

El esfuerzo se define como la fuerza externa aplicada por unidad de área y, por tanto, tiene unidades de presión. Tanto fuerza como superficie son magnitudes direccionales que pueden ser representadas por sendos vectores con las tres componentes correspondientes al

espacio tridimensional. Por ello, para definir completamente el esfuerzo es necesario especificar nueve componentes. Es, por tanto, un tensor de segundo orden que se representa por $\bar{\sigma}_{ij}$, y se denomina tensor de tensiones. En su forma matricial presenta la siguiente forma [Darby, 1976]:

$$\bar{\sigma}_{ij} = \begin{bmatrix} \sigma_{xx} & \sigma_{xy} & \sigma_{xz} \\ \sigma_{yx} & \sigma_{yy} & \sigma_{yz} \\ \sigma_{zx} & \sigma_{zy} & \sigma_{zz} \end{bmatrix}$$

donde el primer subíndice, i , se refiere a la orientación de la cara sobre la que actúa la fuerza en el elemento material y el segundo, j , indica la dirección de la fuerza. Además, como consecuencia de la condición de equilibrio entre pares de fuerzas, el tensor es simétrico, es decir, $\sigma_{ij} = \sigma_{ji}$, con lo que sólo seis de las nueve componentes son independientes.

El tensor esfuerzo total ($\bar{\sigma}_{ij}$) puede descomponerse como la suma de una componente isotrópica (σ) y otra anisotrópica ($\bar{\tau}_{ij}$) [Dealy, 1982]

$$\bar{\sigma}_{ij} = \sigma \cdot \bar{\delta}_{ij} + \bar{\tau}_{ij}$$

donde $\bar{\delta}_{ij}$ es el tensor unitario o delta de Kronecker.

Los esfuerzos isotrópicos son perpendiculares a todas las superficies del material sobre las que actúan, y poseen idéntica magnitud en todas las direcciones, lo que puede ocasionar un cambio de volumen, pero nunca una alteración de la forma del material. Los esfuerzos anisotrópicos pueden actuar normal o tangencialmente a varias superficies del material, pudiendo provocar un cambio en la forma del material, pero no en su volumen. La expresión matemática de esta componente anisotrópica es el tensor esfuerzo desviatorio, $\bar{\tau}_{ij}$, que se anula cuando el material está en reposo, ya que en este estado el único esfuerzo que puede existir es la presión interna, P , que obedece la ley de la distribución hidrostática y es isotrópica.

No es posible medir directamente componentes aisladas del esfuerzo normal anisotrópico, pero sí es posible medir componentes del esfuerzo total:

$$\bar{\sigma}_{ij} = P \cdot \bar{\delta}_{ij} + \bar{\tau}_{ij}$$

Además considerando diferencias de esfuerzos normales es posible eliminar la contribución de la presión en las componentes del esfuerzo total:

$$\sigma_{xx} - \sigma_{yy} = (-P + \tau_{xx}) - (-P + \tau_{yy}) = \tau_{xx} - \tau_{yy}$$

$$\sigma_{yy} - \sigma_{zz} = (-P + \tau_{yy}) - (-P + \tau_{zz}) = \tau_{yy} - \tau_{zz}$$

Para los materiales incompresibles, como la mayoría de los materiales de interés reológico, sólo tiene significado los esfuerzos de cizalla y las diferencias de esfuerzos normales. Un esfuerzo isotrópico no provoca cambios en el material incompresible, ya que no puede cambiar su volumen. De esta forma, las componentes del tensor esfuerzo total, $\bar{\sigma}_{ij}$, podrán sustituirse por las del tensor esfuerzo desviatorio, $\bar{\tau}_{ij}$:

$$\sigma_{xx} - \sigma_{yy} = \tau_{xx} - \tau_{yy}$$

$$\sigma_{yy} - \sigma_{zz} = \tau_{yy} - \tau_{zz}$$

$$\sigma_{ij} = \tau_{ij} \text{ si } i \neq j$$

2.5.1.2 Tensor deformación y velocidad de deformación

La deformación, γ , y la velocidad de deformación, $\dot{\gamma}$, son las expresiones matemáticas que definen la respuesta dinámica del material al esfuerzo aplicado sobre el mismo.

Se puede considerar que una deformación tiene lugar siempre que ocurra un cambio en la separación entre dos puntos de un elemento material. Es una magnitud adimensional, ya que se expresa como el cociente entre el incremento de separación y la separación inicial entre los dos puntos. Puesto que ambas magnitudes son vectoriales, la deformación debe ser también un tensor de segundo orden, con nueve componentes. Se habla entonces de tensores deformación y velocidad de deformación.

La deformación es un tensor simétrico y puede definirse una forma isotrópica (e) y una anisotrópica ($\bar{\gamma}_{ij}$) [Dealy, 1982]:

$$\bar{e}_{ij} = e \cdot \bar{\delta}_{ij} + \bar{\gamma}_{ij}$$

Al igual que en el caso del tensor esfuerzo, la componente isotrópica indica un cambio de volumen (dilatación o compresión), sin alterar la forma, mientras que la anisotrópica refleja una modificación de la forma del material, sin alteración del volumen. La expresión matemática de esta componente anisotrópica es el tensor deformación desviatorio, $\bar{\gamma}_{ij}$. Para un material incompresible, $e = 0$, resultando $\bar{e}_{ij} = \bar{\gamma}_{ij}$.

En cuanto al tensor velocidad de deformación, se obtiene directamente por derivación con respecto al tiempo del tensor deformación:

$$\bar{\dot{\gamma}}_{ij} = \frac{d(\bar{e}_{ij})}{dt}$$

2.5.1.3 Cizalla simple

Es el tipo de deformación generada cuando un material está comprendido entre dos placas paralelas, separadas a una distancia infinitesimal, y la placa superior es sometida a una fuerza, F , que le obliga a desplazarse linealmente una distancia x , mientras que la placa inferior se mantiene en reposo. La aplicación de una fuerza constante

provoca un desplazamiento lineal de la placa superior a velocidad constante, y una respuesta en el material en forma de deformación de cizalla simple o flujo [Schramn, 1994]. Si no existe deslizamiento sobre la superficie de las placas, cada elemento del material sufrirá una deformación (ver Figura 2.6) que viene expresada como:

$$\gamma = \frac{dx}{dy}$$

y una velocidad de deformación o velocidad de cizalla simple, $\dot{\gamma}$, definida como la variación de la deformación respecto al tiempo:

$$\dot{\gamma} = \frac{d\gamma}{dt}$$

donde γ es la deformación de cizalla simple, siendo dx el desplazamiento de la superficie superior del elemento con respecto a la superficie inferior en la dirección x , y dy la altura del elemento.

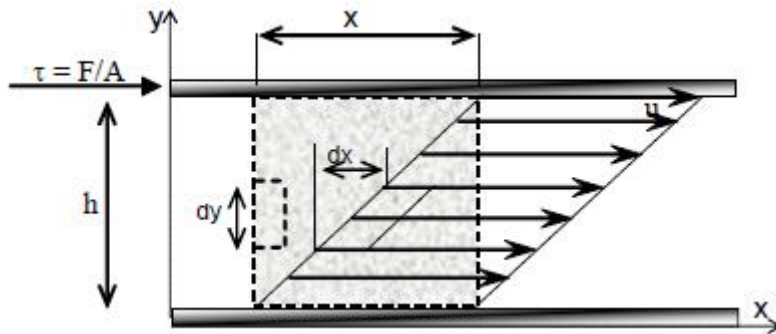


Figura 2.6. Cizalla simple entre dos placas paralelas

Como la deformación es uniforme e independiente del tamaño del elemento, puede representarse también en función de la distancia entre placas, h , y del desplazamiento de la placa superior, x :

$$\gamma = \frac{x}{h}$$

Normalmente, para el estudio de fluidos, el material se somete a una cizalla continua, alcanzándose, en estado estacionario, una

velocidad lineal constante, u . De esta forma, la velocidad de un elemento del material se expresa:

$$u = \frac{dx}{dt}$$

y la velocidad de deformación o velocidad de cizalla viene dada por:

$$\dot{\gamma} = \frac{d\gamma}{dt} = \frac{d\left(\frac{dx}{dy}\right)}{dt} = \frac{d\left(\frac{dx}{dt}\right)}{dy} = \frac{du}{dy}$$

o también como:

$$\dot{\gamma} = \frac{d\gamma}{dt} = \frac{d\left(x/h\right)}{dt} = \frac{d\left(dx/dt\right)}{h} = \frac{u}{h}$$

siendo constante a través del material.

La velocidad de deformación que puede alcanzarse para un esfuerzo aplicado, viene controlada por la resistencia interna del líquido, cuantificada por la viscosidad. Asimismo, este parámetro se puede definir como una medida de la resistencia al flujo [Macosko, 1994].

2.5.1.4 Caracterización reológica de un material

La caracterización reológica de un material consiste en encontrar la relación, en forma de ley matemática, que existe entre el esfuerzo aplicado y la respuesta dinámica del material [Darby, 1976]. Dicha expresión matemática puede relacionar todos los componentes del tensor esfuerzo con los del tensor deformación o velocidad de deformación, en tal caso se le conoce como ecuación constitutiva o ecuación reológica de estado, y define el comportamiento reológico más general posible. Por otro lado, dicha expresión puede relacionar sólo ciertas componentes parciales de los tensores anteriores, por lo que constituiría una particularización de la ecuación constitutiva, denominada función del material.

Para encontrar una función del material, en el laboratorio se recurre a flujos reales que se asemejen al de cizalla simple, ya que en esta situación idealizada tanto el esfuerzo como la deformación se distribuyen homogéneamente a lo largo de todo el material, estando relacionados de forma sencilla con fuerzas externas y desplazamientos medibles directamente. Estos ensayos de flujo semejantes a los de cizalla simple son los denominados flujos viscosimétricos. Se define flujo viscosimétrico como una corriente estacionaria en la que la velocidad tiene una sola componente en cada punto, que además depende sólo de una variable espacial. Las geometrías entre las que se coloca el material pueden ser diversas, siendo las más comunes la cono-placa, de geometría circular, en la que la superficie superior tiene una forma cónica con un ángulo muy pequeño (entre 1 y 4°), y los cilindros coaxiales, donde el flujo se establece en el espacio comprendido entre dos cilindros concéntricos de distintos diámetros. Para los dispositivos experimentales que posean estas características, la función del material vendrá definida mediante las componentes “xy” de igual forma que en cizalla simple. En lo sucesivo siempre que se omitan los subíndices se entenderá que las componentes implicadas se reducen a las “xy”.

2.5.1.5 Clasificación de los distintos comportamientos reológicos

Las teorías clásicas de la elasticidad y la hidrodinámica distinguen de forma radical entre sólido y fluidos mediante los conceptos de sólido perfectamente elástico y, en el otro extremo, el fluido puramente viscoso [Macosko, 1994; Whorlow, 1992]:

- ✓ *Sólido elástico perfecto*: según Hooke (1678), en el sólido perfectamente elástico, la aplicación de una fuerza produce una deformación permanente proporcional al esfuerzo aplicado. Esta proporcionalidad vendrá dada por el módulo elástico del material o módulo de Young (G). Cuando esta fuerza por unidad de

superficie cesa, el cuerpo recupera instantáneamente su estado inicial imperturbado.

- ✓ *Líquido viscoso puro:* según Newton (1687), si el material en consideración es un fluido de viscosidad constante, el esfuerzo aplicado es proporcional al cambio instantáneo de deformación con el tiempo o velocidad de deformación, independientemente de la deformación producida. Esta proporcionalidad viene dada por la viscosidad del material (μ).

En realidad, ambos conceptos no constituyen más que idealizaciones del comportamiento dinámico de los materiales, que se cumplen sólo en casos límite. Entre estos comportamientos extremos se engloba un gran número de materiales, definidos como materiales viscoelásticos, porque presentan tanto características de flujo viscoso como de sólido elástico. En el siguiente esquema (Figura 2.7) se presenta una clasificación típica de los materiales, desde un punto de vista reológico, atendiendo a la relación que existe entre el esfuerzo aplicado y la deformación o velocidad de deformación [Darby, 1976]. Una clasificación más correcta debería tener en cuenta que un material podría manifestar un comportamiento u otro dependiendo de la magnitud del esfuerzo o de la deformación así como del tiempo de cizalla previa.

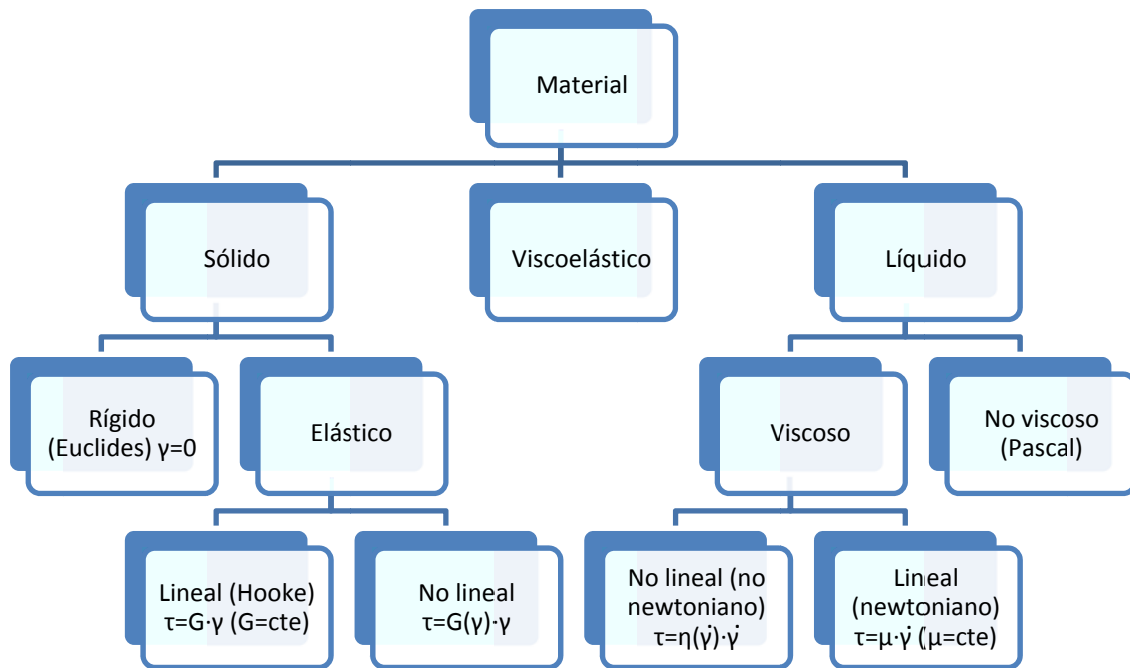


Figura 2.7. Clasificación de los materiales en función de su comportamiento frente ante la deformación (cizalla simple)

2.5.1.6 Comportamiento de flujo viscoso

En una situación de flujo estacionario, los fluidos se pueden comportar como newtonianos o no newtonianos, en función del cumplimiento de la Ley de Newton (1687). Como se ha comentado, los fluidos newtonianos son aquellos en los que los valores de esfuerzo cortante y velocidad de cizalla mantienen una relación de proporcionalidad directa. Atendiendo a la Ley de Newton de la viscosidad, dicho coeficiente de proporcionalidad, denominado viscosidad dinámica o viscosidad de Newton, μ , se define como la relación entre el esfuerzo de cizalla y la velocidad de deformación:

$$\tau = \mu \cdot \dot{\gamma}$$

Este parámetro es una propiedad del material, y es independiente del esfuerzo, siendo sólo función de la naturaleza del material, la presión y la temperatura. Presentan este comportamiento la mayoría de los fluidos con estructura sencilla y compuestos por moléculas relativamente simples en una sola fase.

Sin embargo, para los fluidos no newtonianos la relación entre el esfuerzo cortante y la velocidad de cizalla no es constante, sino que depende la magnitud de los mismos. El comportamiento de flujo viscoso de estos fluidos no puede definirse según la ecuación anterior. Aunque de forma análoga a la viscosidad de Newton, se define la viscosidad aparente para estos fluidos, η , como la relación existente entre el esfuerzo y la velocidad de deformación, para cada velocidad de cizalla:

$$\eta(\dot{\gamma}) = \frac{\tau}{\dot{\gamma}}$$

Existe una gran variedad de fluidos no newtonianos, tales como emulsiones, suspensiones concentradas, cristales líquidos, fluidos que contienen macromoléculas, etc., los cuales se pueden clasificar en función de la dependencia con la velocidad de deformación o con el tiempo de cizalla [Macosko, 1994], aunque muchos de ellos manifiestan ambos fenómenos simultáneamente.

Los tres tipos de fluidos no ideales más comunes, dependientes de la velocidad de cizalla, son los pseudoplásticos, los dilatantes y los plásticos.

El comportamiento de flujo pseudoplástico (“shear-thinning”) es el más frecuente, exhibido por las grasas lubricantes, disoluciones de polímeros, emulsiones y suspensiones, etc. Se caracteriza por una disminución de la viscosidad aparente del fluido al aumentar la velocidad de cizalla. El ejemplo más extendido de comportamiento pseudoplástico es el de los materiales estructurados, caracterizado por tres zonas bien diferenciadas [Reiner, 1960]. Estos materiales muestran una viscosidad límite a velocidad de cizalla cero, η_0 , seguida de una región no newtoniana caracterizada por un descenso potencial de la viscosidad aparente, y por último una nueva tendencia a alcanzar una viscosidad límite a altas velocidades de cizalla, η_∞ .

El origen de este fenómeno se debe a cambios en la estructura compleja de estos materiales, como consecuencia de la variación en la

velocidad de deformación. Estas estructuras están distribuidas al azar manteniendo un estado altamente desordenado que origina una gran resistencia interna al flujo. La aplicación de un gradiente de velocidad de cizalla creciente genera una deformación y orientación de las partículas que componen la estructura en la dirección del esfuerzo aplicado, lo cual se traduce en un descenso de la resistencia al flujo y, por tanto, de la viscosidad aparente. En el caso extremo de velocidades de cizalla elevadas, la estructura del material está totalmente destruida y/o reorientada con respecto a su estado inicial, tal que no existe interacciones entre las partículas dispersas, lo que origina un valor constante de viscosidad [Macosko, 1994; Schramn, 1994].

Los fluidos dilatantes muestran un comportamiento menos frecuente que el pseudoplástico y consiste en un aumento de la viscosidad aparente al elevarse la velocidad de cizalla (“shear-thickening”). Dicho comportamiento se puede encontrar en algunas suspensiones concentradas de sólidos, proteínas y ciertas disoluciones de polímeros y detergentes.

Los materiales plásticos presentan un comportamiento viscoso caracterizado por un valor de esfuerzo cortante, definido como esfuerzo umbral, τ_0 , por debajo del cual se comporta como un sólido elástico, pero fluye como un fluido cuando supera este esfuerzo. Ello se puede asociar a la destrucción de un entramado estructural sólo cuando un esfuerzo externo aplicado supera el valor de las fuerzas atractivas que mantienen el esqueleto estructural. Tradicionalmente, las grasas lubricantes han sido consideradas como ejemplo clásico de fluidos con esfuerzo umbral. No obstante, el concepto de esfuerzo umbral es ciertamente polémico, ya que en principio todo material distinto a un sólido rígido puede fluir al ser sometido a un esfuerzo, siempre que el tiempo de observación sea suficiente [Barnes y Walters, 1985]. Sin embargo, se debe destacar que el esfuerzo umbral es un parámetro reológico de gran utilidad a nivel industrial [Astarita, 1990].

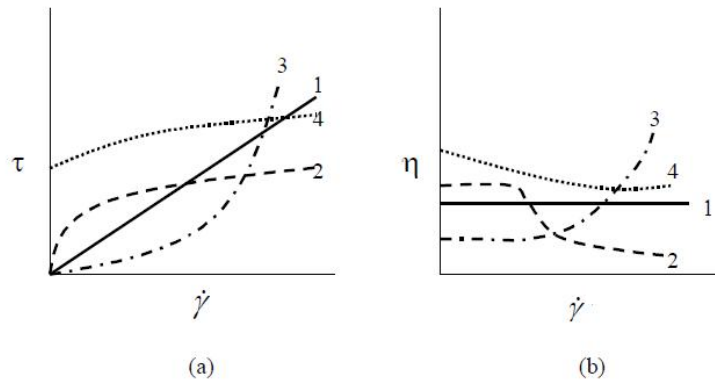


Figura 2.8. Curvas de flujo (a) y viscosidad (b) para fluidos: [1] newtonianos, [2] pseudoplásticos, [3] dilatante y [4] plástico

Cuando la estructura de un fluido necesita un período de tiempo significativo para adaptarse a cambios en la velocidad de cizalla, la viscosidad medida en un experimento de cizalla simple no varía sólo con la velocidad de cizalla, sino también con el tiempo [Quemada et al., 1984].

Si la viscosidad alcanza progresivamente su valor inicial una vez que cesa la deformación, debido a una recuperación estructural, el proceso es reversible. En este caso, el fluido se denomina tixotrópico cuando, a velocidades de cizalla constante, la viscosidad aparente descende con el tiempo, y antitixotrópico o reopéctico cuando lo que se produce es un aumento de viscosidad con el tiempo [Groves y Ahmad, 1976]. Cuando no se produzca una recuperación estructural completa debe aplicarse el término “destrucción estructural” y no el de tixotropía.

2.5.1.7 Comportamiento viscoelástico

Los materiales viscoelásticos presentan un comportamiento viscoso y elástico simultáneamente. En un material elástico lineal o sólido de Hooke, toda la energía mecánica aplicada al material es almacenada y, posteriormente, recuperada como energía mecánica una vez se retira la fuerza aplicada (no hay pérdidas de energía). Por otro lado, en un material puramente viscoso lineal, parte de la energía es

almacenada como energía mecánica dentro del mismo, y parte de la energía es disipada en forma de calor. En este caso, la respuesta de estos materiales ante una fuerza externa puede estar condicionada por la historia de la deformación a la que haya podido estar sometido previamente, por no haber recuperado completamente su estado original.

El estudio de la viscoelasticidad implica establecer relaciones entre el esfuerzo, la deformación y el tiempo. En este tipo de comportamientos es posible encontrar dos situaciones diferentes. En el caso en el que tanto el esfuerzo como la deformación sean relativamente pequeños, de manera que la estructura del material se conserva en estado prácticamente imperturbado, las relaciones entre ambas magnitudes y el tiempo se pueden describir mediante ecuaciones diferenciales lineales de coeficientes constantes y el comportamiento se denomina viscoelástico lineal. Esto implica que la relación entre la deformación y el esfuerzo es sólo función del tiempo y no de la magnitud del esfuerzo [Darby, 1976; Dealy, 1982]. En el caso contrario, en el que la cizalla aplicada sea suficientemente elevada como para producir destrucción estructural, a dicho comportamiento se le denominará viscoelástico no lineal.

Los criterios para caracterizar los materiales viscoelásticos son relativos, y depende del tiempo característico requerido por el material para responder a un cambio en esfuerzo o deformación en comparación con la escala de tiempo de observación, además de la magnitud del esfuerzo o de la deformación. Esta escala de tiempo se cuantifica a través del número de Deborah [Reiner, 1960]; cuando $D_N \rightarrow 0$, los materiales tienen un comportamiento puramente viscoso, mientras que cuando $D_N \rightarrow \infty$ se comportan como sólidos, siendo la definición más común de este parámetro:

$$D_N = \frac{\text{Tiempo de relajación característico del material}}{\text{Tiempo de observación}}$$

El estudio del comportamiento viscoelástico lineal es especialmente útil a la hora de obtener información sobre la microestructura del material [Forster y Kolfenbach, 1958; Ferry, 1980], estudiar el comportamiento de un material durante su almacenamiento, detectar posibles separaciones de componentes, etc.

Clásicamente las respuestas de los materiales viscosos y elásticos han sido descritas mediante analogías con la respuesta de ciertos elementos mecánicos [Darby, 1976; Ferry, 1980; Tschoegl, 1989]. La descripción de los materiales viscoelásticos se realiza, entonces, por combinación lineal de elementos viscosos y elásticos, por tanto, estos modelos son aplicables solamente a comportamientos viscoelásticos lineales. El elemento puramente elástico se representa mediante un muelle ideal, ya que éste almacena toda la energía aplicada, mientras que el elemento puramente viscoso se representa mediante un amortiguador hidráulico en el que el pistón se mueve holgadamente dentro de un líquido newtoniano, disipándose en forma de calor toda la energía aplicada. Para el caso del muelle ideal, el factor de proporcionalidad entre esfuerzo y deformación es el módulo de Young, G , mientras que para el amortiguador el factor de proporcionalidad es la viscosidad dinámica, μ . Combinaciones simples de estos dos elementos en serie y paralelo son los modelos de Maxwell y Voigt, respectivamente.

2.5.1.8 Funciones viscoelásticas lineales

Por lo general, el comportamiento viscoelástico de un material es más complejo que el que definen los módulos analógicos por lo que hay que recurrir al análisis de diversas funciones viscoelásticas continuas, en función del tiempo y la deformación o esfuerzo.

Un material viscoelástico puede ser caracterizado por ciertas funciones respuesta de éste, ante la aplicación de determinadas condiciones experimentales. Los ensayos más utilizados para caracterizar las propiedades reológicas de materiales viscoelásticos son

los de fluencia (“creep”) y recuperación, relajación del esfuerzo y oscilatorios [Whorlow, 1992]. En la Figura 2.9 pueden observarse comparativamente las respuestas características de materiales viscosos lineales, elásticos lineales y viscoelásticos lineales en estos ensayos reológicos.

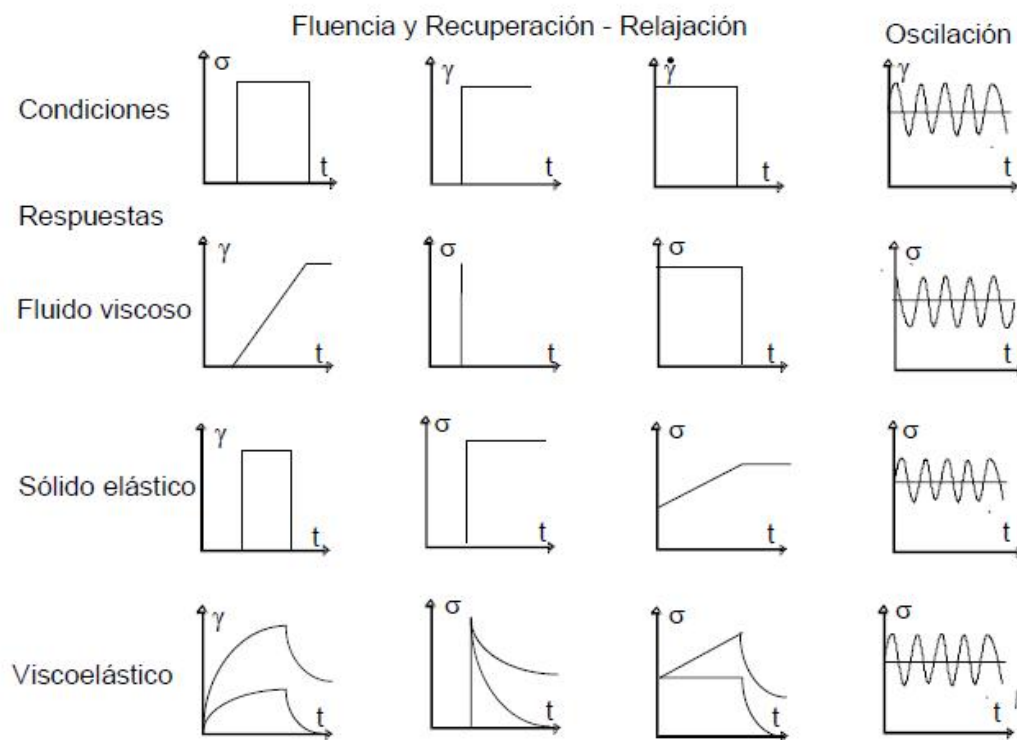


Figura 2.9. Excitación y respuesta de los distintos tipos de materiales

Ensayos de fluencia (“creep”) y recuperación

Consiste en aplicar un esfuerzo constante a tiempo cero, σ , y medir la deformación resultante en función del tiempo. Los ensayos de fluencia suelen ir acompañado de un ensayo de recuperación, a través del cual se estudia la respuesta del material tras el cese del esfuerzo de cizalla [Schramn, 1994]. La función respuesta que se define en este ensayo es la capacitancia lineal, $J(t)$:

$$J(t) = \frac{\gamma(t)}{\sigma}$$

Los sólidos elásticos perfectos alcanzan rápidamente una situación en la que $J(t)$ deja de variar con el tiempo. Este valor constante se define como capacitancia de equilibrio, J_e , y es característico de cada material. Los líquidos viscosos puros dan lugar a una función lineal creciente cuya pendiente es la inversa de la viscosidad dinámica. Los materiales viscoelásticos presentan un comportamiento intermedio, cuadrático, a tiempos pequeños, y lineal, a tiempos altos.

Ensayos de relajación del esfuerzo

En este tipo de experimento se aplica una deformación constante sobre el material y se mide la variación del esfuerzo resultante en función del tiempo. La función característica del material que se define es el módulo de relajación lineal, $G(t)$:

$$G(t) = \frac{\sigma(t)}{\gamma}$$

En el caso de un sólido elástico perfecto se alcanza una situación de equilibrio, que permite definir el módulo de rigidez de equilibrio, G_e , mientras que, en el caso de líquidos viscosos puros, el material relaja rápidamente a valores de esfuerzo nulos. De nuevo, los materiales viscoelásticos presentan un comportamiento intermedio [Schramn, 1994].

Ensayos dinámicos de cizalla oscilatoria

Los ensayos oscilatorios consisten básicamente en someter al material objeto de estudio a una deformación periódica, que generalmente se trata de una cizalla simple sinusoidal. Desde un punto de vista práctico, el movimiento oscilatorio se genera en reómetros rotatorios convencionales, operando bajo el principio de velocidad o de esfuerzo de cizallas controlados, haciendo que el rotor no gire continuamente en una dirección sino que se desplace un pequeño ángulo alternativamente en el sentido de las agujas del reloj y en el

contrario, siguiendo una función sinusoidal del tiempo [Schramm, 1994].

La deformación por cizalla aplicada sobre el material se puede expresar en función del tiempo según:

$$\gamma = \gamma_0 \operatorname{sen} \omega t$$

siendo γ la deformación por cizalla, γ_0 la deformación por cizalla máxima o amplitud de la onda correspondiente al movimiento armónico simple, ω la frecuencia y t el tiempo de aplicación del ensayo.

La velocidad de deformación por cizalla es también una función periódica:

$$\dot{\gamma} = \frac{d\gamma}{dt} = \gamma_0 \omega \cos \omega t = \dot{\gamma}_0 \cos \omega t$$

Un material sometido a una deformación sinusoidal pequeña, que garantice una respuesta viscoelástica lineal, responde tras un cierto número de ciclos con un esfuerzo de cizalla que sigue también una función sinusoidal respecto al tiempo a la misma frecuencia pero con una amplitud característica de la naturaleza de dicho material.

Si el material se comportara como un sólido ideal, la respuesta sería puramente elástica por lo que el esfuerzo de cizalla dependería linealmente de la deformación ($\sigma = G\gamma$; G es el módulo de cizalla) y por tanto las ondas de deformación por cizalla y esfuerzo de cizalla estarían en fase:

$$\sigma = G\gamma_0 \operatorname{sen} \omega t$$

Si el material fuera un fluido ideal viscoso, se cumpliría la ley de Newton ($\sigma = \eta[d\gamma/dt]$) por lo que la onda correspondiente al esfuerzo de cizalla estaría desfasada 90° respecto a la onda de deformación de cizalla:

$$\sigma = \eta\gamma_0\omega \cos \omega t = \sigma_0 \cos \omega t = \sigma_0 \operatorname{sen}(\omega t + 90)$$

Un material viscoelástico muestra un comportamiento intermedio entre el viscoso y el elástico puro, de ahí que la onda del esfuerzo de cizalla presente un ángulo de desfase respecto a la onda de deformación, comprendido entre 0° y 90° . El esfuerzo de cizalla se puede expresar matemáticamente como:

$$\sigma = \sigma_0 \text{sen}(\omega t + \delta)$$

donde σ_0 es la amplitud de la onda correspondiente al esfuerzo de cizalla (máximo valor del mismo) y δ el ángulo de desfase respecto a la onda de deformación, en ocasiones denominado “ángulo de pérdidas mecánicas” [Dealy, 1982].

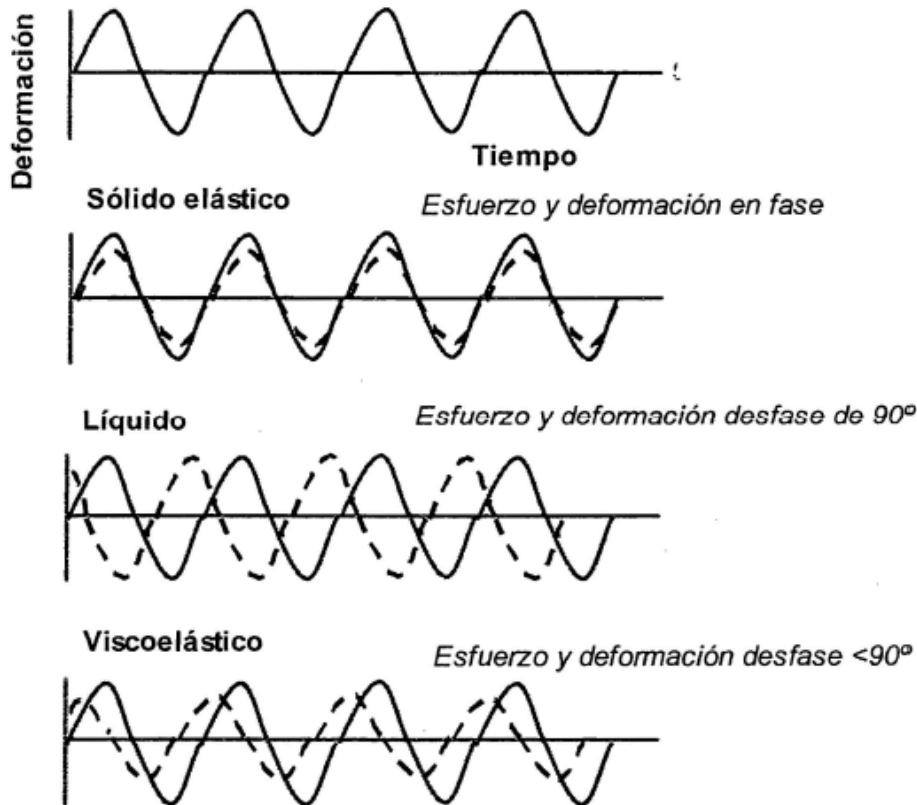


Figura 2.10. Ensayos dinámicos en un reómetro de deformación controlada para un sólido ideal, un fluido ideal y un material viscoelástico

Si se dividen ambos miembros de la expresión anterior por γ_0 :

$$\left(\frac{\sigma}{\gamma_0}\right) = \left(\frac{\sigma_0}{\gamma_0}\right) \text{sen}(\omega t + \delta)$$

En el dominio viscoelástico lineal, tanto la relación de amplitudes (σ_0/γ_0) como el ángulo de desfase δ son independientes de la amplitud de la deformación. En consecuencia, los resultados de un ensayo de cizalla oscilatoria de baja amplitud se podrían presentar en forma de gráficas de (σ_0/γ_0) y δ frente a la frecuencia. No obstante, en la práctica, no se suelen usar dichas funciones sino que se usan para calcular valores de funciones del material con un significado físico más claro.

Si se desarrolla trigonómicamente la expresión del esfuerzo de cizalla para un material viscoelástico se tiene que:

$$\sigma = \sigma_0(\text{sen}\omega t \cos\delta + \text{sen}\delta \cos\omega t)$$

Un análisis de la ecuación anterior sugiere que la onda correspondiente al esfuerzo de cizalla se puede descomponer en dos ondas de la misma frecuencia, una en fase con la onda de la deformación por cizalla $(\text{sen}\omega t)$ y otra con un desfase de 90° $(\cos\omega t)$. De esta forma, esta ecuación se puede presentar de la siguiente forma:

$$\sigma = \sigma' + \sigma'' = \sigma'_0 \text{sen}\omega t + \sigma''_0 \cos\omega t$$

de donde se deduce que:

$$\sigma'_0 = \sigma_0 \cos\delta$$

$$\sigma''_0 = \sigma_0 \text{sen}\delta$$

Esta descomposición permite la definición de dos módulos dinámicos:

$$G' = \left(\frac{\sigma'_0}{\gamma_0}\right) = \left(\frac{\sigma_0}{\gamma_0}\right) \cos\delta$$

$$G'' = \left(\frac{\sigma''_0}{\gamma_0}\right) = \left(\frac{\sigma_0}{\gamma_0}\right) \text{sen}\delta$$

G' y G'' se denominan módulo de almacenamiento y módulo de pérdidas, respectivamente y en general son funciones de la frecuencia.

G' se corresponde con la componente en fase con la onda de la deformación por cizalla y G'' con la componente desfasada, asociándose a las respuestas elásticas y viscosas del material. De hecho, G' es directamente proporcional a la energía media almacenada en un ciclo de deformación por unidad de volumen y G'' lo es a la energía disipada en un ciclo de deformación por unidad de volumen [Macosko, 1994].

Las ecuaciones anteriores sugieren que G' y G'' se pueden analizar como las componentes real e imaginaria de un número complejo, que se denomina módulo complejo, G^* , y cuya forma trigonométrica sería:

$$G^* = \left(\frac{\sigma_0}{\gamma_0}\right) \cos\delta + i \left(\frac{\sigma_0}{\gamma_0}\right) \sin\delta = G' + iG''$$

El módulo del número complejo G^* sería:

$$|G^*| = \sqrt{G'^2 + G''^2} = \frac{\sigma_0}{\gamma_0}$$

Por otro lado, se deduce que:

$$\tan\delta = \left(\frac{G''}{G'}\right)$$

La tangente del ángulo de desfase, también denominada tangente de pérdidas, es una función viscoelástica dinámica, generalmente dependiente de la frecuencia, que indica la razón entre componente viscosa y elástica presentada por el material. Así, el valor 1 de la tangente de pérdidas indica que en estas condiciones el material responde con componentes viscosa y elástica del mismo valor. Es decir, como sería esperable un ángulo de desfase de 45° significa que no se da una preponderancia de la componente elástica sobre la viscosa ni de la viscosa sobre la elástica.

Otra forma de analizar los resultados dinámicos, consiste en definir una función del material denominada viscosidad dinámica. Esta

metodología suele ser más adecuada para materiales viscoelásticos de carácter predominantemente fluido. Se puede definir una viscosidad dinámica en función de la componente del esfuerzo desfasada respecto a la onda de la deformación por cizalla, σ''_0 , que está relacionada con la componente viscosa de la respuesta viscoelástica, G'' .

$$\eta' = \frac{\sigma''_0}{\dot{\gamma}_0} = \frac{\sigma_0 \sin \delta}{\gamma_0 \omega} = \frac{G''}{\omega}$$

También se puede definir una componente de la viscosidad en función de σ'_0 , es decir, relacionada con G' :

$$\eta'' = \frac{\sigma'_0}{\dot{\gamma}_0} = \frac{\sigma_0 \cos \delta}{\gamma_0 \omega} = \frac{G'}{\omega}$$

η' , denominada viscosidad dinámica, y η'' son las componentes de un número complejo η^* , denominado viscosidad compleja, cuyo módulo es:

$$|\eta^*| = \sqrt{\eta'^2 + \eta''^2} = \sqrt{\left(\frac{G''}{\omega}\right)^2 + \left(\frac{G'}{\omega}\right)^2} = \frac{|G^*|}{\omega}$$

Un sólido elástico perfecto se caracteriza por un ángulo de desfase δ nulo, lo cual implicaría que:

$$G' = \frac{\sigma_0}{\gamma_0}; \quad G'' = 0; \quad \eta' = 0$$

Un líquido viscoso ideal se caracteriza por un ángulo de desfase de 90° , por tanto:

$$G' = 0; \quad G'' = \frac{\sigma_0}{\gamma_0}; \quad \eta' = \frac{\sigma_0}{\dot{\gamma}_0}$$

En la Figura 2.11 se muestra a modo de ejemplo un espectro mecánico completo característico de un material viscoelástico, por ejemplo de un polímero una vez aplicado el principio de superposición tiempo-temperatura, en el que se pueden observar los diversos

comportamientos viscoelásticos más característicos de los materiales [Ferry, 1980]. Se observa que en la zona de bajas frecuencias o región de flujo terminal, por debajo del punto de corte entre las funciones viscoelásticas G' y G'' , el material presenta un comportamiento típico de líquido ($G'' > G'$) con variaciones potenciales de ambos módulos con la frecuencia, caracterizadas por pendientes 2 y 1, respectivamente, en escalas logarítmicas. En la zona de frecuencias intermedias, denominada zona de comportamiento cauchoso o región “plateau”, la respuesta es predominantemente elástica, siendo el coeficiente de almacenamiento superior al de pérdida ($G' > G''$). En esta región se establece el módulo “plateau”, G_N^0 , el cual se define en el campo de polímeros como una extrapolación de la contribución del grado de entrecruzamientos sobre G' a altas frecuencias [Baumgaertel et al., 1992]. En el caso de sistemas coloidales y, en concreto, para grasas lubricantes se considera como una medida del número de interacciones entre el agente espesante y el aceite lubricante, relacionado con la fortaleza y consistencia del esqueleto estructural de la grasa lubricante. La representación gráfica de la tangente de delta con la frecuencia, para sistemas altamente estructurados, se caracteriza por la existencia de un mínimo a frecuencias intermedias. De esta manera, se puede definir el estado de gel tipo sólido como aquél que poseen los sistemas formados por dos o más componentes de los cuales uno de ellos es un líquido presente en una proporción substancial siendo blandos, sólidos o materiales asimilables al comportamiento sólido. Según Almdal et al. (1993), la definición del término gel tipo sólido se debe de realizar a través de las propiedades mecánicas dinámicas, de tal manera que este tipo de materiales deben mostrar un módulo de almacenamiento, $G'(\omega)$, con una pronunciada zona “plateau” que se extiende en el tiempo al menos en el orden de segundos y un módulo de pérdidas, $G''(\omega)$, considerablemente menor que el módulo de almacenamiento en la región “plateau”.

En la zona de altas frecuencias se encuentra la región de transición vítrea donde de nuevo $G'' > G'$, y finalmente, la región vítrea, donde el material se comporta como un sólido, mostrando un valor de G' elevado e independiente de la frecuencia.

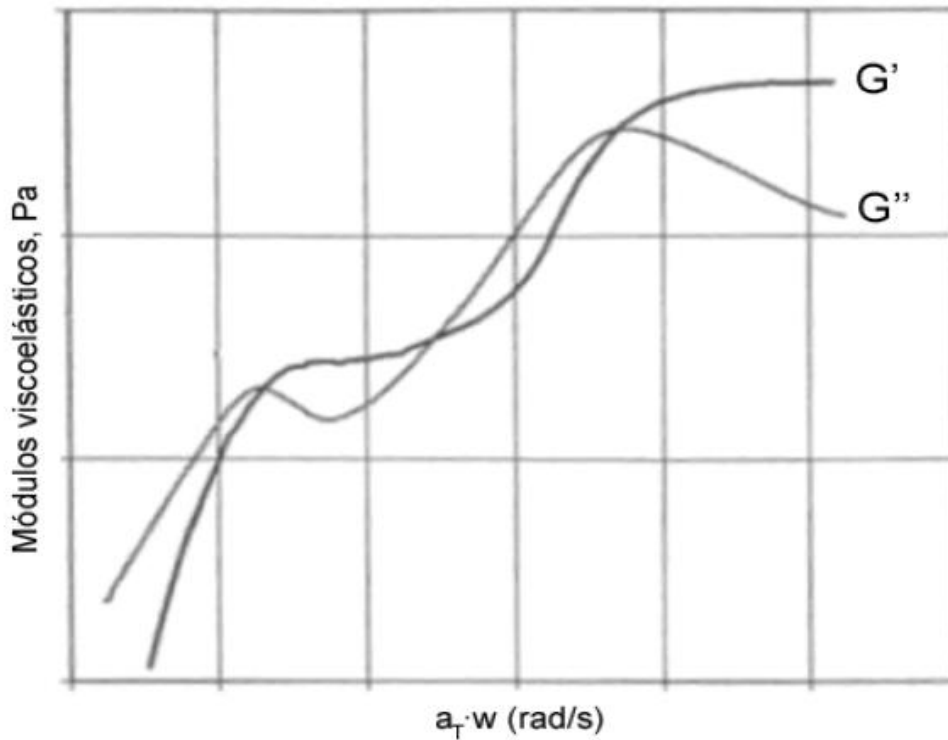


Figura 2.11. Espectro mecánico completo de un polímero de alto peso molecular no reticulado

La obtención del espectro mecánico completo sólo es posible si el intervalo de frecuencias estudiado es lo suficientemente amplio o bien si el material permite la aplicación del principio de superposición tiempo-temperatura.

2.5.2 Comportamiento reológico de grasas lubricantes

El estudio reológico de las grasas lubricantes está aumentando en los últimos años debido al marcado carácter pseudoplástico (Figura 2.12) y la fuerte dependencia que tienen las propiedades de las grasas con el tiempo. Además, se ha incrementado el interés de los fabricantes

de grasas lubricantes por la caracterización reológica de éstas como complemento o sustitución de los ensayos tecnológicos tradicionales.

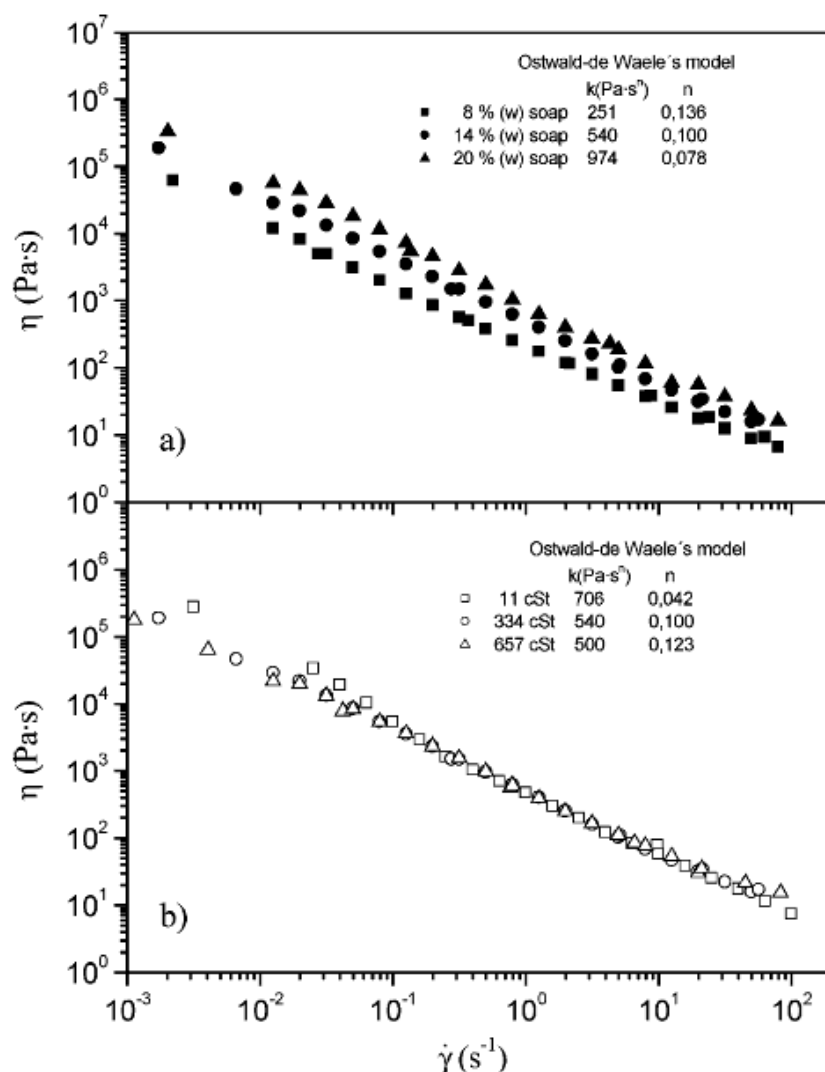


Figura 2.12. Carácter pseudoplástico de varias grasas lubricantes manufacturadas con diferentes concentraciones de espesantes y viscosidades de aceites base [Delgado et al., 2006a]

Balan (2000), intentó recopilar en una serie de capítulos relaciones entre la microestructura de grasas lubricantes y su comportamiento reológico y justificar la importancia de la Reología en la caracterización de estos materiales. La reología de grasas lubricantes presenta ciertas dificultades debidas a su microestructura [Balan, 2000]. Así, ensayos reológicos sobre estos materiales pueden inducir a errores en la interpretación de los resultados. El efecto de deslizamiento

en la pared o “wall depletion”, causado por la presencia de una fina capa de material más fácilmente deformable que la propia grasa, entre la superficie sólida de la geometría de medida y ésta (Figura 2.13a), y la existencia de zonas en el seno de la grasa con distinto nivel de deformación (“shear banding”), originan gradientes de velocidades no homogéneos durante el flujo viscosimétrico de las grasas lubricantes (Figura 2.13b) [Balan y Franco, 2001]. Estas irregularidades en el gradiente de velocidades favorecen la fractura de la grasa a altas velocidades de cizalla, impidiendo observar claramente el comportamiento de flujo a estas velocidades.

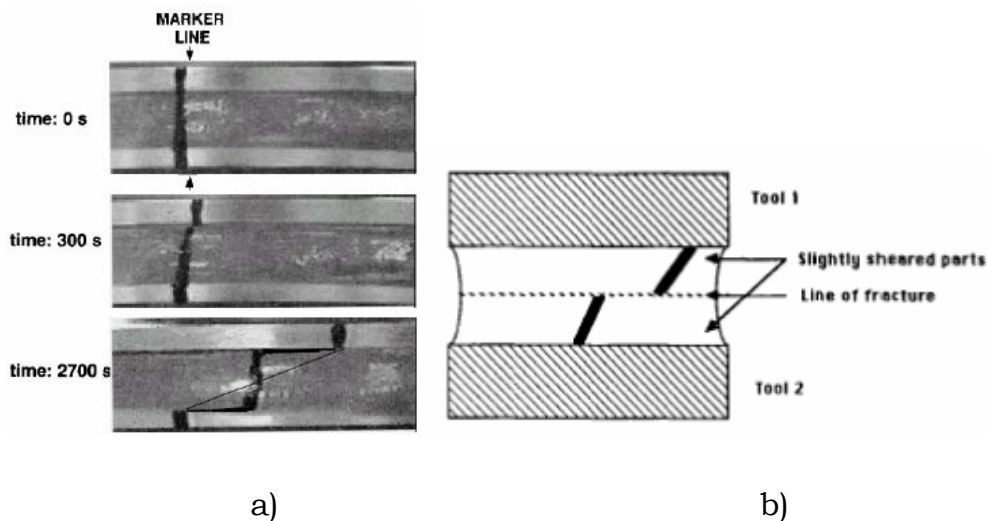


Figura 2.13. Fenómenos de a) “wall depletion” y b) “shear banding” en grasas lubricantes

En viscosímetros de rotación, se ha observado la expulsión de muestra del sistema sensor a altas velocidades debido a los efectos de la fuerza centrífuga. Este fenómeno implica que la superficie de contacto de la muestra con las paredes del sistema sensor disminuye, provocando errores en la medida [Dobson y Tompsett, 1973]. Los efectos de fractura y expulsión de muestra también han de ser tenidos en cuenta a la hora de interpretar el comportamiento de flujo en estado estacionario, ya que dan lugar a una repentina reducción irreal de la viscosidad aparente [Bramhall y Hutton, 1960; Sacchetti et al., 1985]. Estos fenómenos suelen aparecer en los ensayos de flujo realizados con

reómetros de rotación a relativamente altas velocidades de deformación, mayores de $50\text{-}100\text{ s}^{-1}$.

La utilización de sensores rugosos ayuda a la obtención de resultados más representativos del comportamiento reológico real en estado estacionario de la grasa lubricante eliminando el deslizamiento en la pared, aunque favoreciendo la fractura. También las dimensiones de la geometría utilizada en ensayos de flujo son importantes en cuanto a la magnitud del efecto de deslizamiento sobre la medida. La importancia de la separación entre las superficies así como de la geometría del sistema sensor se hace mayor cuanto más baja sea la velocidad de deformación, observándose una fuerte influencia entre 10^{-3} y 10^{-1} s^{-1} [Balan y Franco, 2001].

La Figura 2.14 muestra la evolución del módulo de almacenamiento (G') y el módulo de pérdidas (G'') con respecto a la frecuencia dentro del rango viscoelástico lineal. Este espectro mecánico es bastante similar al mostrado por sistemas poliméricos altamente estructurados [Ferry, 1980] y normalmente encontrado en grasas lubricantes comerciales [Madieto et al., 2000], confirmando el concepto de que las grasas lubricantes son sistemas altamente estructurados tal y como se detecta por microscopía electrónica.

La modelización del comportamiento viscoelástico no lineal de grasas lubricantes mediante el uso de ecuaciones constitutivas factorizables, como la K-BKZ, se llevó a cabo igualmente por Madieto et al. (2000).

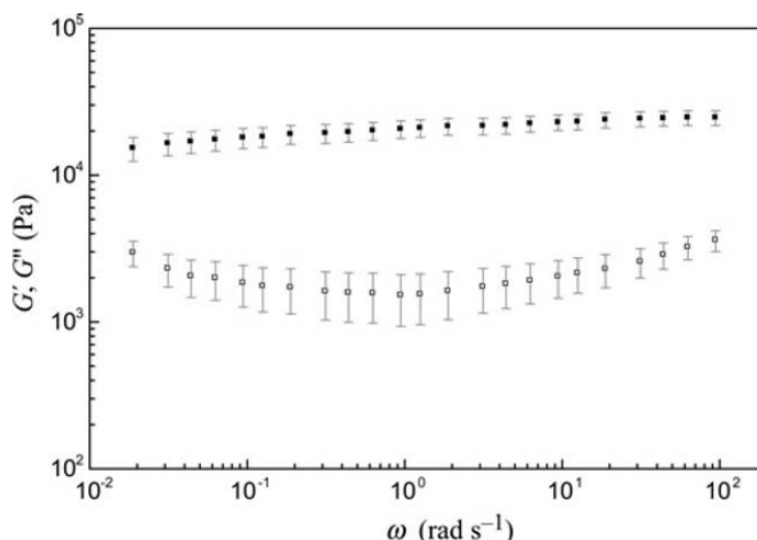


Figura 2.14. Espectro mecánico de una grasa lubricante [Delgado et al., 2005]

Recientemente, se ha estudiado el efecto que ejercen una serie de aditivos poliméricos sobre el comportamiento reológico de grasas tradicionales de litio, evaluando la efectividad que como modificadores de la reología tiene la adición de, por un lado, polímeros reciclados [Martín-Alfonso et al., 2009a] y, por otro, de polímeros reactivos con grupos di-isocianato terminales [Moreno et al., 2006], entre otros.

2.6 Conceptos básicos de Tribología

La Tribología es un nuevo campo de la ciencia definido en 1967 por un comité de la Organización para la Cooperación Económica y Desarrollo, que se centra en la fricción, desgaste y lubricación de superficies en movimiento relativo que interaccionan entre sí. La palabra “Tribología” es una derivación de la palabra griega “tribos” que significa fricción o deslizamiento.

El desgaste es la mayor causa de la pérdida de rendimiento de un mecanismo por lo que cualquier reducción en el desgaste podría resultar en considerables beneficios. La fricción es la principal causa de desgaste y disipación de energía. Se estima que un tercio de la energía que se usa en todo el mundo es invertida en superar la fricción entre superficies, por lo que resulta de vital importancia la mejora del proceso

de fricción. La lubricación es la manera más efectiva de controlar y reducir tanto el desgaste como la fricción.

Las superficies en movimiento relativo que se encuentran en contacto controlan el funcionamiento o forman parte de prácticamente todos los sistemas, maquinarias o utensilios desarrollados por el hombre. Un análisis de las roturas en máquinas muestra que, en la mayoría de los casos, los fallos y las paradas son debidos a las superficies en movimiento y en contacto. De esta forma, la interacción entre superficies en movimiento relativo es un aspecto bastante importante en la economía, que afecta a casi todos los sectores productivos.

De forma general, el objetivo práctico de la Tribología es la minimización de las dos desventajas principales que genera el contacto sólido-sólido: fricción y desgaste. Sin embargo, no siempre es interesante reducir ambos puesto que existen aplicaciones donde es necesario reducir uno de ellos. Por ejemplo, la reducción del desgaste, pero no de la fricción es deseable para los frenos de un automóvil, o una reducción de la fricción, pero no del desgaste, es deseable en lápices. Incluso un incremento tanto en la fricción como en el desgaste es deseable en gomas de borrar [Stachowiak y Batchelor, 1993].

2.6.1 Lubricación

Desde la antigüedad, delgadas capas de gases, líquidos y sólidos son interpuestas entre dos superficies para mejorar el movimiento de una sobre otra y, así, evitar daños sobre éstas. En general, el espesor de estas capas suele ser de entre 1 a 100 μm , aunque pueden ser encontradas otras de mayor o menor tamaño. El conocimiento relacionado con el diagnóstico de la efectividad de estas capas para la prevención de daños en contactos entre sólidos se denomina lubricación. Aunque no hay restricciones en el tipo de materiales requeridos para formar esta capa lubricante, el tipo de lubricante

influye sobre su efectividad. Por ejemplo, una capa gaseosa es adecuada para contactos sometidos a baja carga mientras que las capas sólidas se aplican normalmente para movimientos de baja velocidad. El análisis detallado de capas gaseosas y líquidas se suele denominar “lubricación hidrodinámica”, mientras que la lubricación mediante sólidos se denomina “lubricación sólida”. Una forma especial de lubricación hidrodinámica, la cual involucra interacciones físicas entre los cuerpos en contacto y el líquido lubricante, se denomina “lubricación elastohidrodinámica” siendo el tipo de lubricación más común en la práctica. Otra forma de lubricación tiene en cuenta las interacciones químicas entre los cuerpos en contacto y el líquido lubricante, denominándose “lubricación límite” o “de extrema presión”. En el caso de ausencia total de capa lubricante, para mantener un buen movimiento relativo entre cuerpos, se debe acudir a campos de fuerzas externas para mantener una distancia de separación entre las superficies. Esto puede ser conseguido aplicando fuerzas magnéticas. La levitación magnética es, sin embargo, una tecnología altamente especializada que todavía está en etapa de experimentación [Stachowiak y Batchelor, 1993].

2.6.2 Fricción

La fricción se define como la pérdida de energía mecánica durante un movimiento relativo de materiales que están en contacto a través de una superficie determinada. Se puede hablar de diferentes tipos de fricción que se caracterizan en función del tipo de movimiento relativo:

- ✓ Fricción de rodamiento
- ✓ Fricción de deslizamiento
- ✓ Fricción de rodamiento y deslizamiento de forma simultánea

El proceso de fricción está caracterizado por el conjunto de características de las superficies de los materiales en contacto. De esta manera podemos definir:

- ✓ Fricción de cuerpos sólidos: cuando se ponen en contacto dos materiales directamente. En este caso el área que sufre los esfuerzos es el área de contacto.
- ✓ Fricción fluida: entre los dos sólidos se incluye una gran capa de lubricante que evita el contacto entre las dos superficies, siendo este material el que sufre los esfuerzos.
- ✓ Fricción mixta: existe fricción debido a la presencia de una capa de lubricante pero también entre los cuerpos sólidos. Este tipo de fricción es la más común.

Existen dos leyes fundamentales para el estudio de la fricción:

- ✓ La fricción es proporcional a la fuerza normal entre dos superficies
- ✓ La fricción es independiente del área aparente de contacto entre dos superficies

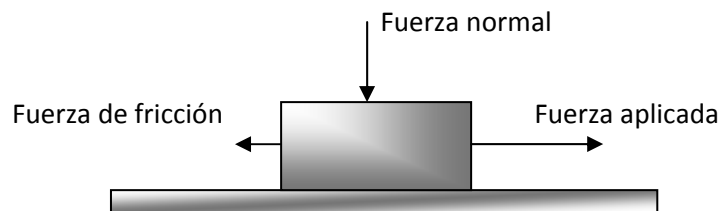


Figura 2.15. Fuerzas mecánicas existentes durante el movimiento entre dos superficies en contacto

Estas leyes dan origen a la fórmula básica de la fricción:

$$F_R = f \cdot F_N$$

de donde se deduce que el coeficiente de fricción, f , se define como la relación entre la fuerza de fricción, F_R , y la fuerza normal a la superficie, F_N . El coeficiente de fricción depende principalmente de las características de las superficies y de la existencia o no de lubricante entre las mismas, de tal manera que su obtención suele ser experimental para cada caso en concreto [Kuhn, 2009].

2.6.3 Desgaste

Cuando se producen fallos en la capa lubricante que separa a cuerpos sólidos en contacto y en movimiento relativo, de forma inevitable, se producen daños en las superficies en contacto y, como consecuencia, se origina un severo desgaste. El desgaste en estas circunstancias es el resultado de la adhesión entre cuerpos en contacto y se denomina “desgaste adhesivo”. Cuando las capas de lubricante que intervienen son parcialmente efectivas dentro del contacto entre los cuerpos también ocurre un ligero desgaste como consecuencia de procesos de fatiga debido a la aplicación de un esfuerzo de forma repetitiva, denominándose “desgaste por fatiga”. Por otro lado, si la capa de lubricante contiene partículas duras o, simplemente, un fluido impacta contra un cuerpo, entonces se produce una forma de desgaste, que algunas veces puede ser muy rápido, conocido como “desgaste abrasivo”. Otras dos formas de desgaste son el “desgaste erosivo” (debido al impacto de partículas) y el “desgaste de cavitación” cuya causa es el flujo rápido de líquidos. En algunas situaciones particulares, la capa de material lubricante se forma por ataque químico de alguna superficie en contacto y, aun cuando esto puede provocar algo de lubricación, es inevitable un desgaste asociado. Este tipo de desgaste se denomina “desgaste corrosivo” y cuando el oxígeno atmosférico es el agente que corroe se denomina “desgaste oxidativo”. Cuando la amplitud del movimiento entre los cuerpos en contacto es restringida sólo a unos pocos micrómetros, la capa de lubricante es atrapada dentro del contacto y puede ser finalmente destructiva, generándose bajo estas condiciones un “desgaste de agitación”. Hay otras muchas formas o mecanismos de desgaste, ya que casi cualquier interacción entre sólidos generará desgaste. Ejemplos típicos son el “desgaste por impacto” causado por el impacto entre sólidos, el “desgaste por fusión”, que ocurre cuando las cargas y velocidades que soporta el contacto son suficientemente altas como para permitir que

las superficies lleguen a fundirse totalmente, y el “desgaste difusivo” que ocurre a altas temperaturas [Stachowiak y Batchelor, 1993].

Además, puede añadirse un nuevo concepto referido al desgaste del lubricante (también denominado como “desgaste reológico”), definido a través del cambio irreversible de las propiedades del lubricante (viscosidad, estructura...) debido a la fricción [Kuhn, 2009].

2.6.4 Modelo tribológico

Una abstracción del contacto tribológico real se hace a través del modelo tribológico. Este modelo consta de cuatro elementos: dos superficies sólidas en contacto, la interfase entre ambas superficies y las condiciones ambientales.

Los procesos tribológicos suelen ocurrir en el área de contacto entre las superficies sólidas, los cuales pueden tener una naturaleza física, fisico-química (adsorción, desorción) o química. La obtención del consumo energético, desde un punto de vista tribológico, depende del área y la geometría de la superficie de contacto, la carga aplicada en esa superficie y el espesor de la película de lubricante [Kuhn, 2009].

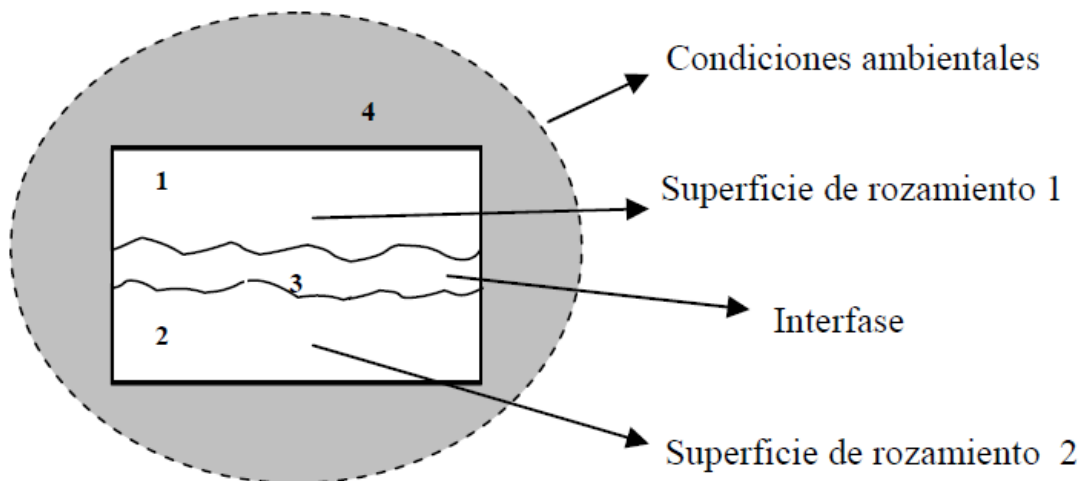


Figura 2.16. Modelo tribológico

2.6.5 Enfoque energético del proceso tribológico

La energía en el proceso de fricción se invierte en producir dos tipos de modificaciones en el sistema tribológico [Kuhn, 2009]:

- ✓ Deformaciones, que pueden ser:
 - o Elásticas
 - o Plásticas
 - o Reológicas (del lubricante utilizado)
- ✓ Adhesiones: este proceso consiste en invertir la energía consumida en la fricción para separar aquellos microporos que se fusionan como consecuencia del proceso tribológico. Para que se produzcan estas adhesiones es necesario un contacto directo entre ambas superficies.

Existe un algoritmo para investigar un problema tribológico desde un punto de vista energético desarrollado por Fleischer (1982) y Kuhn (2000) y utilizado para el diseño de rodamientos, contactos con fricción, análisis de desgaste y estimación de fiabilidad entre otras aplicaciones. Este algoritmo se define siguiendo una serie de pasos:

- ✓ Describir la geometría de contacto: como resultado de esta etapa se define un área de contacto real y el número de contactos
- ✓ Cálculo de la energía requerida en el proceso de fricción (pérdida de energía): en esta etapa se determina la energía de fricción ya sea elástica, plástica o para cizallar el lubricante
- ✓ Cálculo de la densidad de energía crítica: a partir de esta etapa se cuantifica la densidad de energía de fricción aparente y la intensidad lineal de desgaste

2.6.5.1 Geometría de contacto

Para describir la geometría de contacto son necesarios estudios a escala macro, micro y nanométricos. Esto es necesario debido a que aunque visualmente muchas superficies tienen un aspecto liso, a escala

microscópica (o menor) se pueden diferenciar una serie de rugosidades que afectan al proceso de fricción.

De forma general, existen diferentes formas para enfocar el estudio de la superficie de los cuerpos en contacto:

- ✓ Modelizando las rugosidades con determinadas formas geométricas (generalmente esferas) donde se definen una serie de variables aleatorias.
- ✓ Mediante un perfil que caracterice la superficie a través de un proceso estocástico. Generalmente se necesita invertir una gran cantidad de tiempo con la ayuda de un software para generar un resultado.
- ✓ Describiendo la superficie con la ayuda de campos estocásticos. Esta opción es la más compleja pero la que da una mayor aproximación a la realidad.

Cuando no es necesario un estudio muy profundo sobre la descripción de la geometría de contacto, es preferible usar la modelización a través de formas geométricas, siendo el modelo más usado el esférico, de tal forma que la superficie se representa a través de una serie de esferas caracterizadas por su radio y la altura relativa con respecto a la posición de referencia. Tanto los radios como las alturas se pueden caracterizar a través de una distribución gaussiana [Kuhn, 2009].

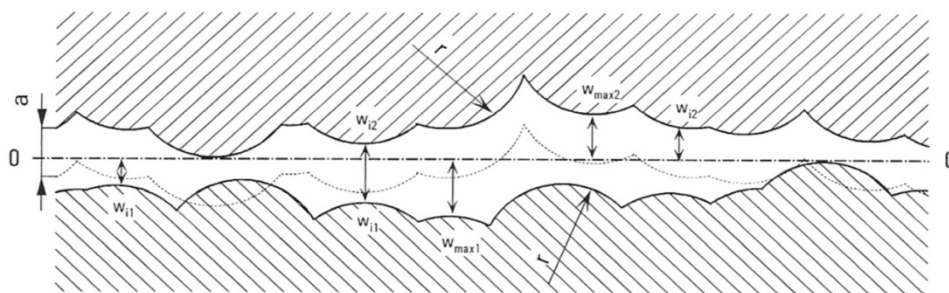


Figura 2.17. Contacto entre dos superficies sólidas modelizado a través de esferas
[Kuhn, 2009]

2.6.5.2 Determinación de la energía consumida en el proceso de fricción

La energía de fricción se cuantifica a través de la siguiente expresión:

$$W_R = e \cdot V \cdot n$$

donde “ W_R ” es la energía consumida en la fricción, “ e ” es la densidad de energía, “ V ” es el volumen de las rugosidades y “ n ” el número de contactos.

En un proceso de fricción mixta, la energía de fricción debida a la adhesión se puede despreciar, siendo la deformación de las asperezas (causante del desgaste de la superficie) y la del lubricante los mecanismos principales a estudiar. La energía puesta en juego durante este proceso se determina como la suma de las energías necesarias para producir cada una de las deformaciones existentes:

$$W_R = \sum e_i \cdot V_i \cdot n_i = e_{el} \cdot V_{el} \cdot n_{el} + e_{pl} \cdot V_{pl} \cdot n_{pl} + e_{reo} \cdot V_{reo} \cdot n_{reo}$$

donde los subíndices “el” y “pl” hacen referencia a las deformaciones elásticas y plásticas, respectivamente, en el sólido y “reo” a las deformaciones reológicas en el lubricante, siendo generalmente $e_{pl} > e_{el} > e_{reo}$ [Kuhn, 2009].

2.7 Análisis térmico

Dada la importancia que presenta el comportamiento térmico de los materiales poliméricos, resulta interesante profundizar en un conjunto de técnicas que aportan gran cantidad de información sobre los fenómenos y procesos térmicos que se producen en estos materiales y que aportan gran cantidad de información sobre sus prestaciones.

El análisis térmico engloba una serie de técnicas que permiten evaluar determinadas propiedades físicas y químicas de una muestra cuando se somete a un programa de temperatura.

Actualmente, las áreas de aplicación de estas técnicas incluyen mediciones ambientales, análisis de composiciones, estudio de reacciones químicas, determinación de propiedades dinámicas, etc. Un equipo integrado de análisis térmico, puede aportar gran cantidad de información sobre un material: temperaturas de transición vítrea, pérdidas de peso, energías de activación, cambios dimensionales, propiedades viscoelásticas, etc [Balart et al., 2003].

2.7.1 Técnicas de análisis térmico

El análisis térmico puede emplearse con fines cualitativos y/o cuantitativos. Las muestras pueden ser identificadas y caracterizadas mediante investigación cualitativa de su comportamiento térmico. Los resultados cuantitativos se obtienen a través de los cambios de peso y de entalpía a medida que la muestra es calentada.

Las técnicas más importantes de análisis térmico empleadas en la caracterización de materiales poliméricos se muestran en la Tabla 2.9.

Técnica	Variable medida	Aplicaciones
Calorimetría Diferencial de Barrido (DSC)	Calor y temperaturas de transiciones y reacciones	Cinéticas de reacción, análisis de purezas, curado de polímeros...
Análisis Térmico Diferencial (DTA)	Temperaturas de transiciones y reacciones	Diagramas de fase, estabilidad térmica
Análisis Termogravimétrico (TGA)	Cambios de masa	Estabilidad térmica, análisis cualitativo
Análisis Termomecánico (TMA)	Cambios de viscosidad y dimensiones	Temperaturas de reblandecimiento, coeficientes de expansión
Análisis Mecánico Dinámico (DMA)	Módulos, humedad y comportamiento viscoelástico	Resistencia al impacto, estabilidad mecánica
Análisis de gases desprendidos (EGA)	Cantidad de gases producidos en reacciones inducidas por la temperatura	Análisis de componentes orgánicos volátiles

Tabla 2.9. Técnicas de análisis térmico empleadas en la caracterización de materiales poliméricos [Balart et al., 2003]

Además de las técnicas reseñadas en la tabla anterior, el análisis térmico engloba otras tantas técnicas que, si bien no tienen una utilización masiva, pueden ser útiles en algunas ocasiones. Como las anteriores, también se basan en la medición de una propiedad física o química en función de un programa controlado de temperatura. Algunas de estas técnicas son:

- ✓ Termodilatometría (variaciones dimensionales)
- ✓ Termosonometría (variaciones de los sonidos)
- ✓ Termooptometría (propiedades ópticas)
- ✓ Termoelectrometría (propiedades eléctricas)
- ✓ Termomagnetometría (propiedades magnéticas)

De entre todas las técnicas mencionadas, las más relevantes son la Calorimetría Diferencial de Barrido (DSC), el Análisis Termogravimétrico (TGA), el Análisis Termomecánico (TMA), y el Análisis

Mecánico Dinámico (DMA) [Balart et al., 2003], siendo las dos primeras las utilizadas en el presente trabajo.

2.7.1.1 Calorimetría diferencial de barrido

Un calorímetro diferencial de barrido mide la diferencia entre el flujo de calor suministrado a una muestra objeto de estudio y una referencia, expuestas ambas al mismo programa de temperaturas.

El flujo de calor se corresponde a una potencia transmitida y por lo tanto, se mide en Watios. Con la integración de la potencia con respecto al tiempo se obtiene una cantidad de energía. La energía transmitida corresponde a un cambio exactamente igual a la entalpía de la muestra. Cuando la muestra absorbe energía, el cambio de entalpía se denomina endotérmico. Cuando la muestra desprende energía, el proceso se denomina exotérmico.

La Figura 2.18 muestra, a modo de ejemplo, las transiciones térmicas más relevantes de un termoplástico semicristalino, el polietileno tereftalato (PET) en una curva de DSC típica.

La transición vítrea (cambio de comportamiento dúctil a frágil) se identifica por un salto de la línea base ya que no hay ningún calor latente asociado a esta transición relacionada con la movilidad de las cadenas poliméricas. Un proceso de cristalización se identifica con un pico exotérmico que lleva asociado un calor de cristalización, mientras que un proceso de fusión aparece como un proceso endotérmico que requiere un aporte de calor (entalpía de fusión). Los procesos de degradación se pueden identificar teniendo en cuenta que al tratarse de materiales de naturaleza orgánica, su exposición a altas temperaturas da lugar a reacciones de oxidación (combustión) de naturaleza exotérmica [Balart et al., 2003].

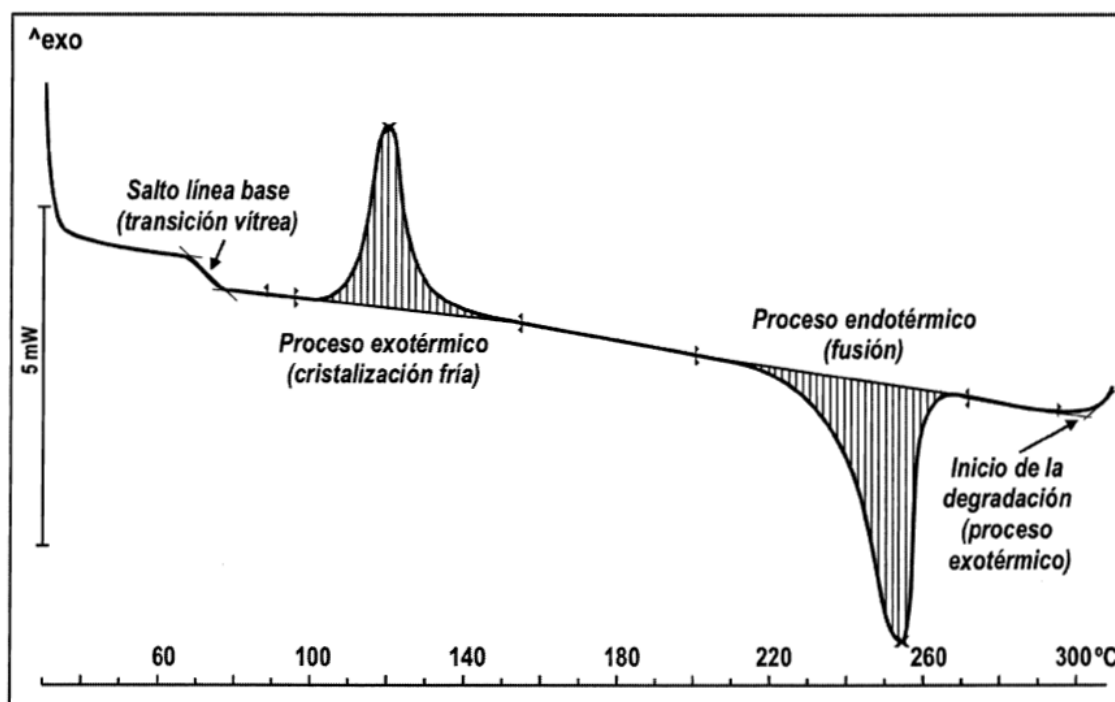


Figura 2.18. Curva calorimétrica de un termoplástico semicristalino con sus diferentes transiciones térmicas [Balart et al., 2003]

2.7.1.2 Análisis termogravimétrico

En el análisis termogravimétrico, se mide la masa de una muestra cuando se somete a un determinado programa de temperaturas. La medición se lleva a cabo en atmósferas perfectamente definidas, habitualmente nitrógeno (condiciones inertes) o bien en aire u oxígeno (condiciones oxidativas). La masa de la muestra en cada instante del programa de temperaturas queda registrada por una balanza de alta sensibilidad.

Al mismo tiempo, los gases que se desprenden durante el desarrollo de la termogravimetría pueden ser analizados por técnicas como EGA. De forma general, esta técnica aporta información sobre las temperaturas y el curso de los procesos de descomposición/degradación en atmósferas inertes.

La Figura 2.19 muestra un ejemplo típico de termograma junto con los fenómenos más habituales que se pueden interpretar en este tipo de gráficos.

La información de las temperaturas y cantidades de masa que se pierden en cada uno de los saltos pueden ayudar, no sólo a la identificación cualitativa del proceso que provoca dicha pérdida de masa, sino también a cuantificar la extensión del proceso.

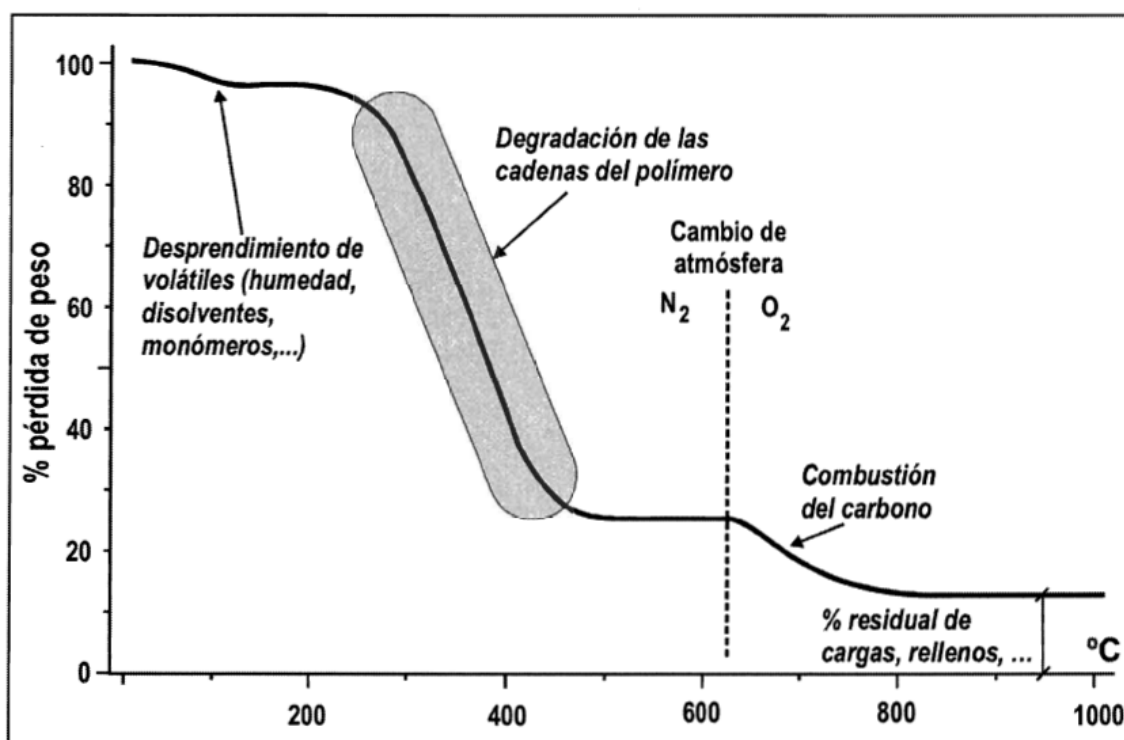


Figura 2.19. Termograma característico con los fenómenos más frecuentemente encontrados [Balart et al., 2003]

2.7.2 Análisis térmico en grasas lubricantes

Las técnicas de análisis térmico son muy útiles para la caracterización de grasas lubricantes puesto que es posible detectar sus componentes, por ejemplo, a través de DSC. En investigaciones previas [Martín-Alfonso et al., 2009a], se han modificado grasas lubricantes mediante la adición de polímeros vírgenes y reciclados registrándose en las curvas de DSC los puntos de fusión de estos aditivos, aunque con ciertas desviaciones como consecuencia de la su inclusión en la matriz

de la grasa lubricante, así como del espesante de litio usado en su formulación (Figura 2.20).

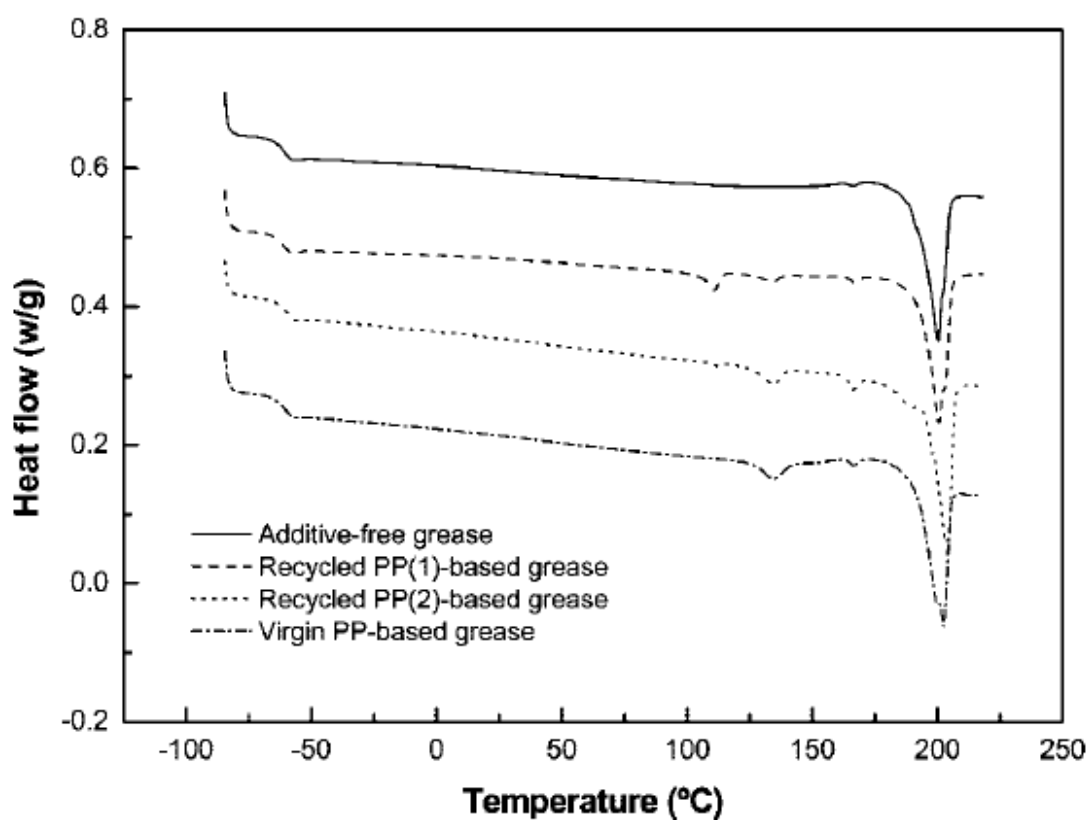


Figura 2.20. Curvas de DSC de grasas lubricantes modificadas con polímeros [Martín-Alfonso et al., 2009a]

Por otro lado, el análisis termogravimétrico se puede usar para estudiar la descomposición térmica de las grasas lubricantes [Martín-Alfonso et al., 2009a] así como para determinar la humedad y el contenido de ciertos aditivos. Las curvas termogravimétricas pueden mostrar diferentes caídas correspondientes a diferentes componentes de las grasas lubricantes aunque en ocasiones varios de ellos se solapan en un único proceso de pérdida de masa.



CAPÍTULO 3

MATERIALES Y MÉTODOS

3.1 Materias primas

3.1.1 Aceites

Como ya se ha comentado en el Capítulo 2, los aceites vegetales son buenos candidatos para ser usados en la manufactura de formulaciones lubricantes debido a su excelente lubricidad, biodegradabilidad, la constante viscosidad con la temperatura (alto índice de viscosidad) y su baja volatilidad, aunque siempre teniendo en cuenta las restricciones que presentan por su baja estabilidad a la oxidación y al flujo a baja temperatura. Para la manufactura de los oleogeles estudiados, se utilizaron distintos tipos de aceites vegetales como el aceite de ricino (Guinama), girasol (Fresenius-Kabi), soja (Fresenius-Kabi) y colza (Verkol S.A.). En la Tabla 3.1 se muestran las composiciones de ácidos grasos de los aceites y sus viscosidades a diferentes temperaturas:

		Aceite ricino	Aceite girasol	Aceite soja	Aceite colza
Composición de ácidos grasos	Ácido mirístico (C14:0) (%)	Trazas	Trazas	Trazas	Trazas
	Ácido palmítico (16:0) (%)	2,58	6,19	10,70	4,56
	Ácido palmitoleico (C16:1) (%)	Trazas	Trazas	Trazas	Trazas
	Ácido margárico (C17:0) (%)	Trazas	Trazas	Trazas	Trazas
	Ácido margaroleico (C17:1) (%)	Trazas	Trazas	Trazas	Trazas
	Ácido esterárico (C18:0) (%)	2,73	3,43	3,44	Trazas
	Ácido oleico (C18:1) (%)	6,31	25,83	24,14	65,99
	Ácido linoleico (C18:2) (%)	10,83	64,80	54,70	21,13
	Ácido ricinoleico (12- hidroxi C18:1)	77,55	Trazas	Trazas	Trazas
	Ácido linolénico (C18:3) (%)	Trazas	Trazas	6,04	8,16
	Ácido araquídico (C20:0) (%)	Trazas	Trazas	Trazas	Trazas
	Ácido gadoleico (C20:1) (%)	Trazas	Trazas	Trazas	Trazas
	Ácido behénico (C22:0) (%)	Trazas	Trazas	Trazas	Trazas
	Ácido lignocérico (C24:0) (%)	Trazas	Trazas	Trazas	Trazas
Viscosidad dinámica (Pa·s)	40 °C	0,2293	0,0359	0,0321	0,0341
	100 °C	0,0187	0,0087	0,0072	0,0080
Viscosidad cinemática (cSt)	40 °C	211,05	38,55	35,37	36,86
	100 °C	21,00	9,99	8,24	9,02

Tabla 3.1. Composición de ácidos grasos y viscosidades de los aceites vegetales empleados para la formulación de oleogeles

3.1.2 Espesantes

Los espesantes usados para las distintas formulaciones de grasas biodegradables se pueden clasificar en tres grupos. Por un lado, se utilizaron moléculas anfifílicas de bajo peso molecular como el monoestearato de sorbitano, SMS, (Panreac) y el monoestearato de glicerilo, GMS, (Guinama). Por otro lado, se han empleado celulosas y derivados como α -celulosa, etil celulosa, metil celulosa y acetato de celulosa, todos ellos suministrados por Sigma-Adrich. Finalmente, se han usado quitinas, procedentes de dos suministradores diferentes (Sigma-Adrich y Qingdao Fraken), quitosano de diferentes pesos moleculares (Sigma-Aldrich) y quitosanos acilados (con diferentes grados de acilación) sintetizados a partir de los anteriores. A continuación se detallan algunas características de cada uno de ellos.

3.1.2.1 Monoestearato de sorbitano

Se produce a partir de sorbitol y ácido esteárico tanto de origen animal como vegetal, ya que desde un punto de vista químico son idénticos, siendo también comercialmente conocido como Span 60 o E491. Entre sus aplicaciones se puede mencionar que es ampliamente usado en la industria alimentaria como emulsificante y estabilizante puesto que se metaboliza hasta sorbitol y ácido esteárico sin ningún efecto colateral. Se suele comercializar en forma de esferas de aspecto ceroso de color crema [Food-info.net, 2006].

Su fórmula molecular es $C_{24}H_{46}O_6$ con un peso molecular de 430,70 g/mol. El punto de fusión es de 54 °C – 57 °C, siendo soluble en etanol, isopropanol, aceite mineral y aceite vegetal e insoluble en agua fría y propilenglicol. El balance hidrofílico-lipofílico (HLB) es de 4,7 [Panreac.es, 2006].

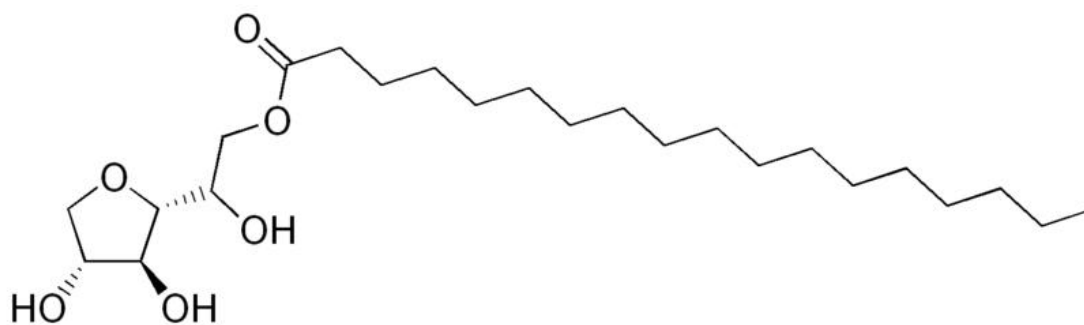


Figura 3.1. Estructura molecular del monoestearato de sorbitano

3.1.2.2 Monoestearato de glicerilo

Se obtiene por alcoholólisis del ácido esteárico con glicerina. Se usa como agente espesante y emulsionante para margarina, manteca y otros productos alimenticios. También es usado como aromatizante, emulsionante para aceites, ceras y disolventes, cosméticos, protectores solares y otros usos diversos.

Su fórmula molecular es $C_{21}H_{42}O_4$ con un peso molecular de 358,57 g/mol. Su densidad es de 0,97 g/mL y su punto de fusión está en torno a 58 – 59 °C. Es soluble en etanol caliente, dietil éter, benceno, acetona, aceites e insoluble en agua. El balance hidrofílico-lipofílico (HLB) es de 4,2 [Ciacomeqltda.com, 2006].

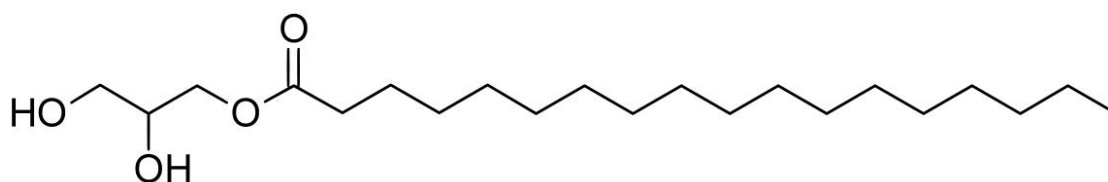


Figura 3.2. Estructura molecular del monoestearato de glicerilo

3.1.2.3 Celulosas

La celulosa es la biomolécula orgánica más abundante en la naturaleza. Es un homopolímero lineal polidisperso que contiene tres grupos hidroxilos reactivos (átomos C2, C3 y C6) que son, en general, accesibles a la conversión típica de grupos alcohólicos primarios y

secundarios. Debido a su estructura molecular y a la distribución uniforme de grupos hidroxilos se pueden formar varios tipos de estructuras semicristalinas. Aunque es ampliamente conocida su insolubilidad en agua y líquidos orgánicos comunes, todavía se investiga su solubilidad en disolventes no convencionales.

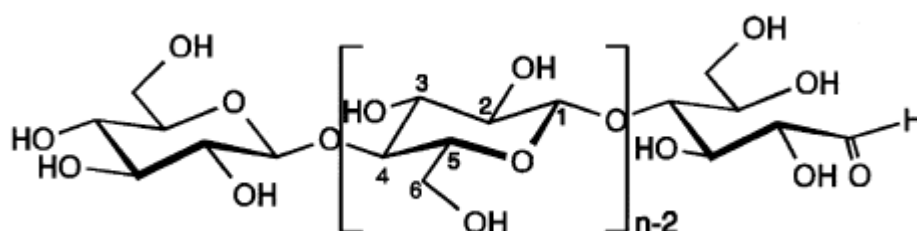


Figura 3.3. Estructura química de la celulosa

La producción de celulosa comercial se concentra fundamentalmente en las cosechas de plantas madereras de fácil crecimiento, como el eucalipto, o en fuentes que tengan una alta pureza en celulosa, como el algodón. La celulosa puede contener otros productos que para ciertas aplicaciones o modificaciones químicas pueden presentar problemas o inconvenientes. Sin embargo, hoy en día los procedimientos de aislamiento y purificación permiten obtener materiales de una alta pureza y variabilidad (por ejemplo en el grado de polimerización).

Además, las aplicaciones de la celulosa como precursor de modificaciones químicas han sido estudiadas extensivamente incluso antes de que su naturaleza polimérica fuese determinada y totalmente comprendida. Así, por ejemplo, el nitrato de celulosa de alto contenido en nitrógeno fue uno de los explosivos más importantes. Su éster parcialmente nitrado fue uno de los primeros materiales poliméricos usado como plástico bajo el nombre comercial de Celuloide. Hoy en día, el nitrato de celulosa es el único éster de celulosa inorgánico de interés comercial. Además, productos derivados de la celulosa como metil-, etil- o hidroxialquil- éteres, acetato de celulosa y productos con combinaciones de varios grupos funcionales, como por ejemplo

hidroxietil celulosa, hidroxipropil metil celulosa, acetopropionatos de celulosa y acetobutiratos de celulosa son todavía importantes después de muchas décadas desde su descubrimiento. Derivados iónicos de la celulosa son conocidos desde hace mucho tiempo. La carboximetil celulosa, hasta ahora el éter de celulosa iónico más importante, fue por primera vez preparado en 1918 y comercializado en los años 20 en Alemania.

Las propiedades de los distintos derivados de la celulosa vienen determinadas generalmente por el tipo de grupo funcional. Sin embargo, esto puede ser modificado significativamente ajustando el grado de funcionalización y el grado de polimerización del esqueleto del polímero.

El creciente interés por la celulosa y sus derivados es, en parte, consecuencia de que procede de las paredes leñosas de las plantas, siendo por tanto un material renovable. Desde un punto de vista químico, la celulosa tiene una serie de propiedades muy deseadas, como son [Heinze y Liebert, 2001]:

- ✓ Biocompatibilidad
- ✓ Estereoregularidad
- ✓ Multiquiralidad
- ✓ Grupos hidroxilos reactivos
- ✓ Habilidad para formar superestructuras

Los productos procedentes de la celulosa que se han probado como espesantes biodegradables en el presente trabajo son los siguientes:

α -celulosa

Se ha utilizado α -celulosa parcialmente microcristalina procedente de Sigma-Aldrich (Park et al., 2009). El grado de polimerización (DP) de esta α -celulosa se determinó de acuerdo con el método oficial SCAN-C15 resultando un valor de DP = 1011, el cual se obtuvo insertando la viscosidad intrínseca ($[\eta] = 438 \text{ cm}^3/\text{g}$) en la siguiente ecuación (Gericke et al., 2009):

$$DP^{0,76} = \frac{[\eta]}{2,28}$$

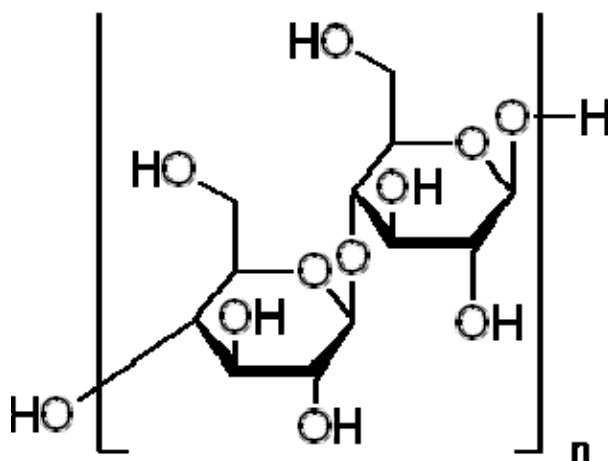


Figura 3.4. Estructura molecular de la α -celulosa

Metil celulosa

Se usa como espesante en sistemas acuosos y no acuosos, como ayudante para la retención de agua y aglutinante. El peso molecular promedio en número de la metil celulosa utilizada en la formulación de los oleogeles estudiados es de 40.000 g/mol con un grado de sustitución de grupos metoxi comprendido entre 1,60 y 1,90 [Sigma-Aldrich.com, 2007].

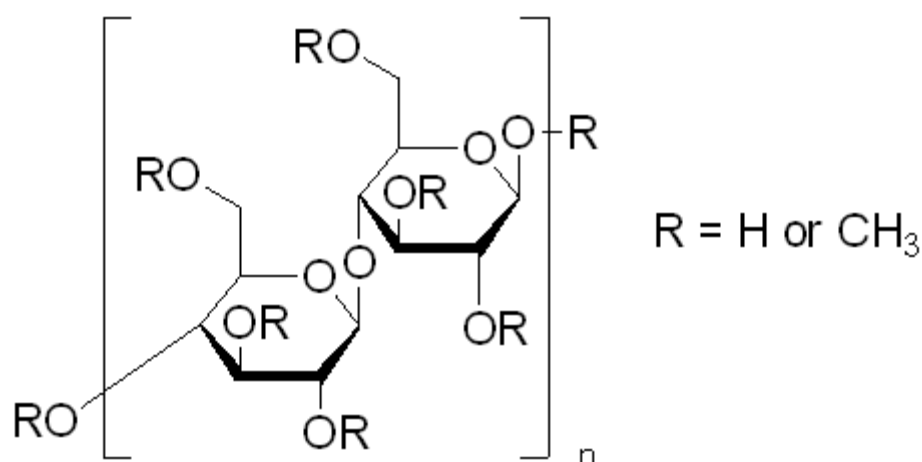


Figura 3.5. Estructura molecular de la metil celulosa

Etil celulosa

Se han usado cinco tipos de etil celulosa con una densidad de 1,14 g/mL y un 48% de grupos etoxi, diferenciadas comercialmente por su viscosidad en disolución al 5% en un disolvente consistente en tolueno/etanol (80:20) [Sigma-Adrich.com, 2007]. En la siguiente tabla se muestran los diferentes pesos moleculares promedios determinados experimentalmente a través de cromatografía de permeación en gel (GPC) así como su índice de polidispersidad.

Viscosidad (cP)	M_w (g/mol)	M_n (g/mol)	M_w / M_n
4	38.908	24.376	1,60
10	52.742	36.187	1,46
45	68.960	59.803	1,15
100	76.528	68.629	1,12
300	82.166	75.399	1,09

Tabla 3.1. Pesos moleculares promedios en peso y en número e índice de polidispersidad de los diferentes tipos de etil celulosa usados como espesantes (obtenidos a partir de GPC)

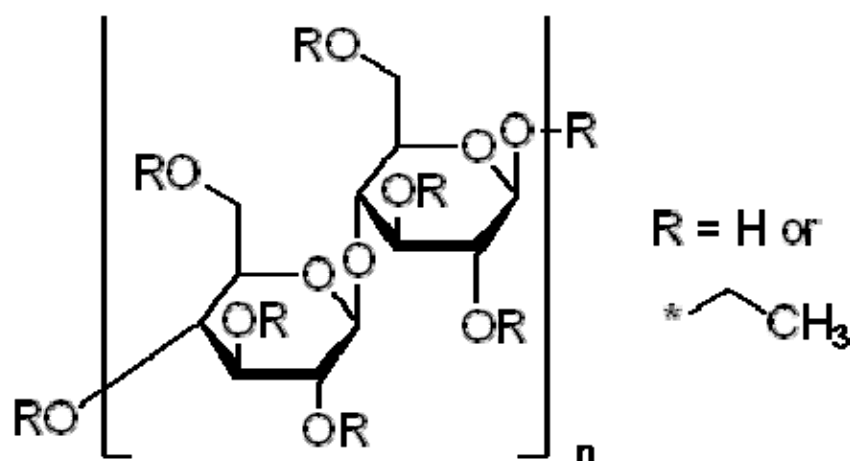


Figura 3.6. Estructura molecular de la etil celulosa

Acetato de celulosa

El acetato de celulosa empleado en la manufactura de los oleogeles estudiados posee un peso molecular promedio en número de 50.000 g/mol y un 39,7% en peso de grupos acetilos, teniendo una densidad de 1,3 g/mL [Sigma-Adrich.com, 2007].

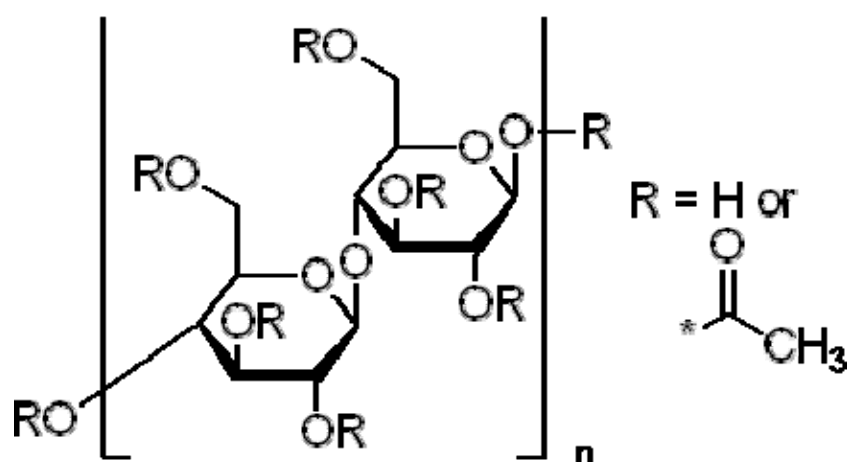


Figura 3.7. Estructura molecular del acetato de celulosa

3.1.2.4 Quitina y quitosano

Quitina

La quitina es un polisacárido natural de gran importancia en la naturaleza, identificado por primera vez en 1884. Este biopolímero es sintetizado por un gran número de organismos y considerado el

polímero más abundante en la naturaleza después de la celulosa. La quitina se presenta como microfibras cristalinas ordenadas siendo uno de los componentes del esqueleto de artrópodos o de las paredes celulares de hongos y levaduras. Sin embargo, hasta ahora las principales fuentes para la obtención de quitina comercial son las cáscaras de gambas y los caparazones de cangrejos. Desde un punto de vista industrial, la quitina se extrae de los crustáceos a través de un tratamiento ácido para disolver el carbonato de calcio, seguido de una extracción alcalina para solubilizar las proteínas. Por último, normalmente se realiza una decoloración para eliminar posibles pigmentos y obtener de esta manera un producto sin color [Rinaudo, 2006].

La quitina se encuentra de forma natural parcialmente desacetilada siendo insoluble en los disolventes más usuales. La insolubilidad es el mayor problema para desarrollar aplicaciones o usos de la quitina. Sin embargo, debido a su biodegradabilidad, no toxicidad, propiedades antibacterianas, fisiología inerte, propiedades para formar geles y afinidad a las proteínas, se han encontrado aplicaciones en muchas áreas. En la industria alimentaria, por ejemplo, la quitina se usa para inmovilizar enzimas en la clarificación de zumos de fruta y procesado de leche [Krajewska, 2004]. La quitina también puede ser obtenida en forma de films y fibras para su uso en la fabricación de papel con mayor resistencia a la rotura [Tokura y Nishi, 1982] o en aplicaciones médicas y farmacéuticas como material de recubrimiento para heridas y para controlar la liberación de medicamentos [Kanke et al., 1989; Yusof et al., 2003]. También se puede usar como excipiente o en tratamientos de regeneración de huesos como material de relleno [Ito et al., 1998].

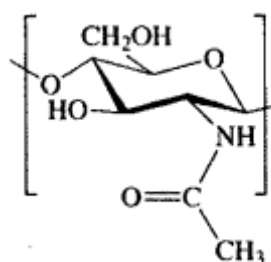


Figura 3.8. Estructura química de la quitina

Para formular oleogeles, en este trabajo, se han utilizado dos muestras de quitina, una procedente de Sigma-Aldrich con un peso molecular medio de $4,0 \cdot 10^5$ g/mol y otra procedente de Qingdao Fraken (China) con un peso molecular de $5,4 \cdot 10^5$ g/mol y un grado de desacetilación del 7,3%, determinado a través de análisis de infrarrojos.

Quitosano

Cuando el grado de desacetilación de la quitina alcanza un valor cercano al 50% se vuelve soluble en medios ácidos acuosos y se denomina quitosano. Sin embargo, la solubilidad del quitosano no depende sólo del grado de desacetilación medio sino de la distribución de los grupos acetil a lo largo de la cadena y de su peso molecular [Rinaudo, 2006].

El quitosano se usa para preparar geles, films, fibras y esponjas. El campo más importante de aplicación se encuentra en la cosmética (especialmente para el cuidado del cabello), farmacia y biomedicina [Thanou y Junginger, 2005]. El quitosano es mucho más fácil de procesar que la quitina, sin embargo la estabilidad de los materiales basados en quitosano es generalmente menor debido a su carácter hidrofílico y especialmente su susceptibilidad al pH [Rinaudo, 2006].

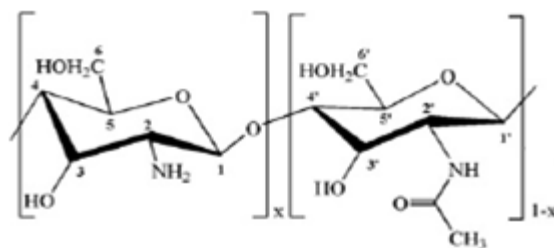


Figura 3.9. Estructura química del quitosano

Se han empleado dos tipos de quitosano como agentes espesantes de los oleogeles estudiados con pesos moleculares de $3,9 \cdot 10^5$ g/mol y $5,6 \cdot 10^5$ g/mol (según datos proporcionados por Takahashi et al, 2005) y grados de desacetilación del 87,6% y 82,1%, respectivamente, determinados por análisis de infrarrojos.

Quitosano acilado

La reacción de acilación del quitosano se realizó siguiendo el método descrito por Ma et al., 2009. De esta forma, 24 gramos de quitosano se mezcló con trietilamina (250 mL) y acetona (250 mL) durante 24 horas a 50 °C para, posteriormente, enfriar y agitar la mezcla durante una hora a 0 °C. Por otro lado, 48 gramos de cloruro de estearilo se disolvió en acetona (300 mL) y se añadió gota a gota a la mezcla anterior durante una hora. Transcurrido este tiempo, la temperatura se incrementó de forma gradual hasta 90 °C durante 4 horas, manteniéndola una hora más. Por último, la disolución resultante se enfrió hasta temperatura ambiente sin agitación para finalmente moler el producto obtenido.

Esta síntesis se llevó a cabo utilizando los quitosanos de medio y alto peso molecular descritos anteriormente, resultando dos productos diferentes de quitosano acilado. Además, el mismo procedimiento se realizó cambiando la proporción de cloruro de estearilo y quitosano de 2:1 a 3:1, con ambos tipos de quitosano, por lo que se generaron otros dos tipos más de quitosano acilado.

La determinación del grado de sustitución conseguido se llevó a cabo a través del método descrito por Klemm et al., 1998, expresado sobre la máxima posible sustitución del monómero. Con el quitosano de peso molecular medio se consiguió un grado de acilación de 0,3 cuando la proporción usada de cloruro de estearilo y quitosano fue de 2:1 y 0,7 para una proporción 3:1. En el caso del quitosano de bajo peso molecular los grados de acilación fueron de 0,8 y 1,0 respectivamente.

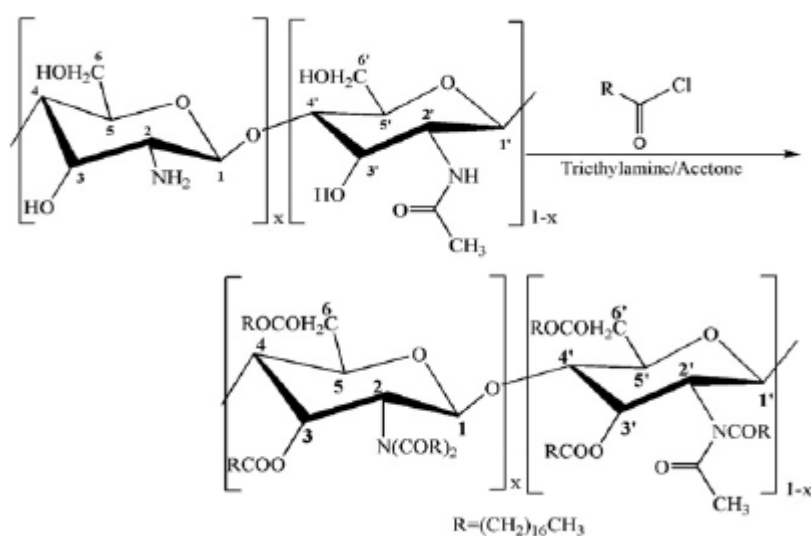


Figura 3.10. Síntesis del quitosano acilado

3.2 Procesado de oleogeles

El procesado de la mayoría de los oleogeles estudiados se llevó a cabo con un agitador modelo RW 20 (Ika, Alemania) al cual se le acoplan dos tipos de agitadores, uno de ellos tipo ancla, de dimensiones 90x110 mm, y otro tipo lazo helicoidal, de 90x90 mm (ver Figura 3.11). El tanque de procesado tiene unas dimensiones de 100 mm de diámetro y 145 mm de altura. Dicho tanque se introduce en un baño con polietilenglicol acoplado a un termostato de inmersión, modelo Tectron-L (Selecta, Alemania), con capacidad de calentamiento hasta 300 °C, capacidad de circulación máxima de 12 L/min y presión máxima de bombeo de 150 mbar.

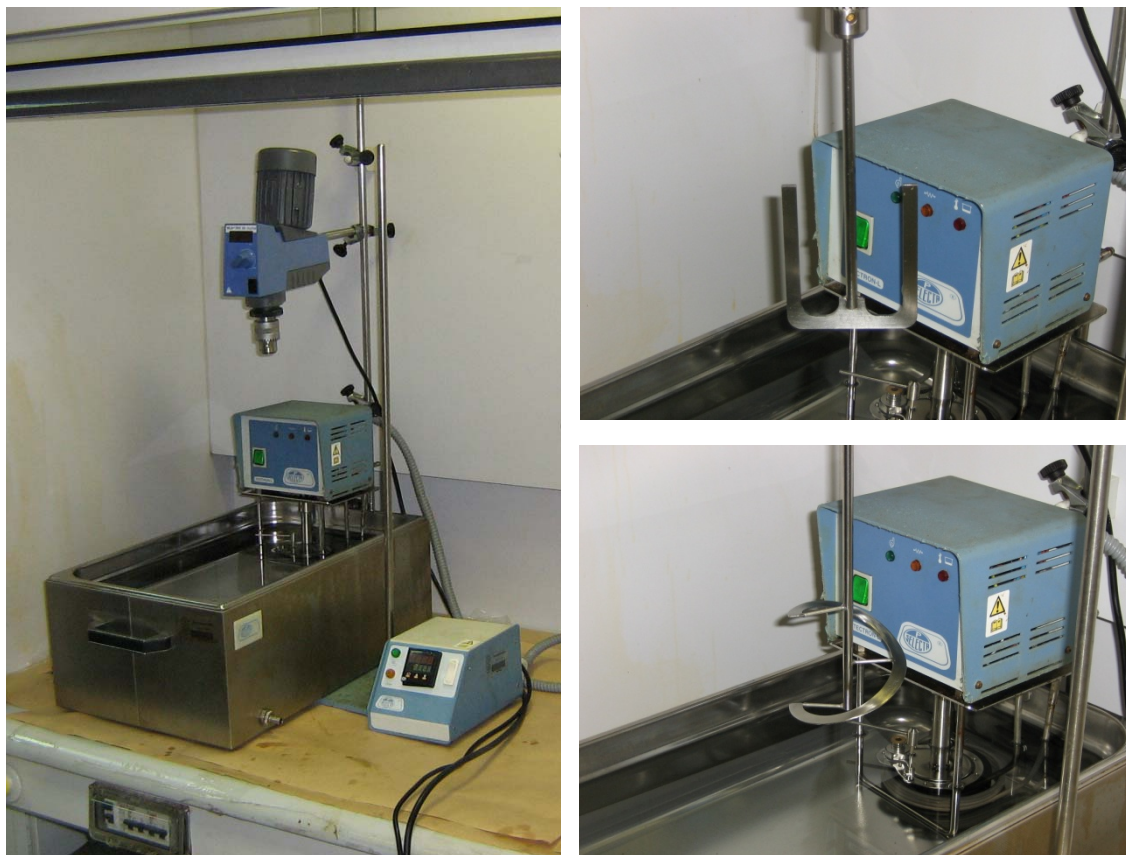


Figura 3.11. Agitador RW 20 (Ika, Alemania), baño termostático Tectron-L (Selecta, Alemania) y geometrías usados en el procesamiento de oleogeles

Una serie de oleogeles fueron procesados usando una mezcladora/amasadora Polylab con medida “in situ” del par de torsión (Rheocord, modelo 300p, Thermohaake, Alemania). Puede alcanzar una velocidad máxima de 250 rpm, con medidas del par de torsión máximo de 300 N·m. La temperatura máxima que se puede establecer es de 450 °C a través de un control eléctrico. Se utilizaron como geometría de mezclado los “roller-rotors” (ver Figura 3.12), en una cámara de 310 cm³ que se llena aproximadamente al 80%.



Figura 3.12. Polylab y geometría de mezclado seleccionada (roller-rotors)
(Thermohaaake, Alemania)

3.3 Caracterización reológica de oleogeles

Se han realizado ensayos en cizalla oscilatoria generalmente al día siguiente de haber completado el proceso de fabricación de cada oleogel. De esta manera, se efectuaron barridos de esfuerzo a una frecuencia de 1 Hz, aplicando una serie ascendente de valores de esfuerzo de 1 a 1000 Pa, para la determinación del intervalo de viscoelasticidad lineal. Posteriormente, se realizaron barridos de frecuencia, para obtener el espectro mecánico, aplicando un valor del esfuerzo dentro del intervalo viscoelástico lineal, en un intervalo de frecuencias comprendido entre 10^{-2} y 10^2 rad/s.

Esta caracterización reológica de los oleogeles se llevó a cabo sobre muestras sin historia previa de cizalla y a una temperatura constante de 25 °C (excepto en aquellos ensayos donde se estudió la influencia de la temperatura en la reología), realizándose al menos dos replicados por cada ensayo. Después de colocar la muestra en el sistema sensor, en todos los casos, se esperó un tiempo de 30 minutos, asegurándose con ello una termostatización adecuada de toda la muestra y que todas presentaran un proceso de relajación estructural similar. Transcurrido ese tiempo, se procedió a realizar la medida correspondiente.

Otros ensayos reológicos más específicos se han realizado puntualmente en determinadas muestras o componentes tales como ensayos de flujo viscoso, rampas de temperatura o monitorización “in situ” de las propiedades reológicas durante el procesado de oleogeles.

Los reómetros utilizados para la caracterización reológica de los oleogeles fueron los siguientes:

- ✓ Reómetro de esfuerzo controlado Rheoscope (Thermohaake, Alemania), utilizando una geometría de medida placa – placa de superficie rugosa (20 ó 35 mm de diámetro, 1 mm de separación). El rango de par de torsión del equipo es de 0,002 a 100 mN·m y el de velocidades de 0,025 a 1200 rpm. El rango de frecuencias es de 0,0001 a 100 Hz con una resolución angular de $1,2 \cdot 10^{-6}$ rad.



Figura 3.13. Reómetro de esfuerzo controlado Rheoscope (Thermohaake, Alemania)

- ✓ Reómetro de esfuerzo controlado RS-150 (Thermohaake, Alemania), utilizando como sistema sensor placa – placa de superficie rugosa (35 mm de diámetro, 1 mm de separación). El rango de par de torsión del equipo es de 0,0005 a 150 mN·m y el de velocidades de 10^{-7} a 1200 rpm. El rango de frecuencias es de 0,0001 a 100 Hz con una resolución angular de $6 \cdot 10^{-7}$ rad.



Figura 3.14. Reómetro de esfuerzo controlado RS-150 (Thermohaake, Alemania)

- ✓ Reómetro de esfuerzo controlado Gemini 150 (Bohlin, Inglaterra), utilizando una geometría de medida placa – placa de superficie rugosa (25 mm de diámetro, 1 mm de separación). El rango de par de torsión del equipo es de $5 \cdot 10^{-5}$ a 150 mN·m y el de velocidades de 10^{-5} a 650 rad/s. El rango de frecuencias es de $1 \cdot 10^{-6}$ a 150 Hz.



Figura 3.15. Reómetro de esfuerzo controlado Gemini 150 (Bohlin, Inglaterra)

- ✓ Reómetro de deformación controlada ARES (Reometric Scientific, EE.UU.), empleando geometrías de medida placa-placa de superficie rugosa (25 mm de diámetro, 1 mm de separación) y un reo-reactor cilíndrico de 40 mm de diámetro y 48 mm de altura con una geometría de mezclado tipo ancla de 38 mm de diámetro acoplada al transductor del reómetro. Este equipo presenta un intervalo de velocidades de rotación de 0,00125-100 rad/s, siendo el mínimo ángulo de desplazamiento que puede ser medido de 0,01 rad.



Figura 3.16. Reómetro de deformación controlada ARES (Reometric Scientific, EE.UU.)

Para la termostatización de las muestras, el reómetro Rheoscope incorpora un baño termostático (Phoenix, Thermohaake, Alemania), el reómetro RS-150 un horno eléctrico (TC 501, Thermohaake, Alemania) que permite alcanzar altas temperaturas, el reómetro Gemini 150 un sistema peltier (Bohlin, Inglaterra) con el que se puede modificar rápidamente la temperatura de la muestra y el reómetro ARES un horno de inyección de aire (Reometric Scientific, EE.UU.).

3.4 Ensayos mecánicos estándar

Los ensayos mecánicos están ampliamente implantados en la industria de las grasas lubricantes convirtiéndose de esta manera en ensayos que se realizan de forma rutinaria sobre estos lubricantes. Se realizaron ensayos de penetración, de acuerdo con la norma ASTM D1403, a cada una de las muestras, trabajadas y no trabajadas. Para ello se empleó un penetrómetro modelo Seta Universal Penetrometer 17000-2 (Stanhope-Seta, Gran Bretaña) equipado con un cono de $\frac{1}{4}$ escala. El dispositivo de penetración tiene un peso normalizado de $9,38 \pm 0,025$ g. Como vaso de penetración se utilizó un recipiente cilíndrico de 40 mm de diámetro y 40 mm de altura. Todas las muestras se termostataron previamente en un baño con agua a $25 \pm 0,5$ °C durante una hora. Los valores de penetración obtenidos con este cono se convirtieron a la escala completa de penetración de acuerdo a la norma ASTM D217:

$$P = 3,75 \cdot p + 24$$

donde “P” es la penetración a escala completa y “p” la penetración con el cono de ¼ de escala.

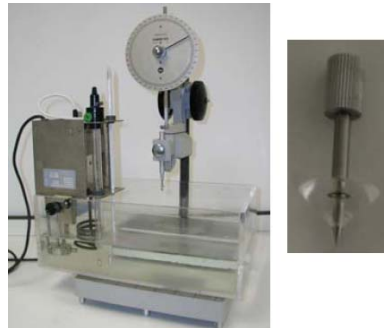


Figura 3.17. Penetrómetro Seta Universal Penetrometer 17000-2 y cono de ¼ de escala (Stanhope-Seta, Gran Bretaña)

Para trabajar las muestras se empleó un equipo para evaluar la estabilidad de grasas lubricantes frente al laminado (“Roll Stability Tester”), modelo 1940-3 (Stanhope-Seta, Gran Bretaña), de acuerdo a la norma ASTM D1831. En estos ensayos se introdujeron 50 gramos de muestra en el espacio comprendido entre la carcasa cilíndrica y el cilindro interno de 5.000 ± 50 gramos, que cizalla la muestra de forma continua durante 2 horas (excepto para aquellos oleogeles que presentaron una baja estabilidad mecánica en los que se estableció un tiempo de 30 minutos). La carcasa cilíndrica gira en el interior del equipo a 165 ± 15 rpm.



Figura 3.18. Roll stability tester modelo 1940-3 (Stanhope-Seta, Gran Bretaña)

En algunas muestras seleccionadas se determinó la tendencia a expulsión en rodamientos mediante un equipo Petrotest, modelo 17-0450 (Petrotest, Alemania) siguiendo la norma ASTM D1263. Con este método se evalúa la tendencia a la expulsión de grasas lubricantes cuando son sometidas a determinadas condiciones. En estos ensayos se depositan 85 gramos de muestra en la cavidad interna de una rueda metálica que gira sobre un eje mediante dos rodamientos de diferentes tamaños, 3 gramos de la misma muestra se aplica sobre la superficie externa del rodamiento mayor y 2 gramos sobre la superficie del rodamiento menor. En el eje se coloca un colector que recoge la muestra expulsada durante el ensayo y, posteriormente, se introduce el rodamiento mayor, sobre el cual se fija la rueda metálica que contiene la muestra. Finalmente, se introduce el rodamiento menor y se fija el sistema mediante una arandela, una tuerca, aplicando sobre ésta una presión de $6,8 \pm 0,1 \text{ N}\cdot\text{m}$ y volviendo hacia atrás un sexto de vuelta, y una contratuerca. Por último se enrosca una pieza metálica en forma de tapadera que sella este lado del eje. El sistema se hace gira a una velocidad de $660 \pm 30 \text{ rpm}$ durante $6 \text{ horas} \pm 5 \text{ minutos}$ llegando a una temperatura de $105 \pm 1,4 \text{ }^{\circ}\text{C}$ en el eje del sistema en aproximadamente $60 \pm 10 \text{ minutos}$, que se mantiene durante el resto del ensayo. Debido a la alta velocidad, temperatura y forma de la cavidad de la rueda metálica, parte de la muestra fluye hacia el colector atravesando el

rodamiento mayor. Al final del ensayo se pesa el colector y se determina así la cantidad de muestra perdida durante el ensayo.

Ocasionalmente se realizó el mismo ensayo pero sin calentar el sistema (aproximadamente a 25 °C), para determinar el efecto que tiene la temperatura sobre la expulsión de muestra en el ensayo.



Figura 3.19. Equipo para la determinación de expulsión Petrotest, modelo 17-0450
(Petrotest, Alemania)

3.5 Caracterización tribológica

Se realizaron ensayos de caracterización tribológica en dos tribómetros diferentes, ambos de geometría bola – disco.

La primera serie de medidas fueron realizadas en un tribómetro diseñado por el Laboratorio de Tribología de la Universidad de Ciencias Aplicadas de Hamburgo. Este equipo trabaja en un intervalo de fuerzas normales de 3 a 20 N, usando un diámetro de bola de 1/2". Durante la medición, la fuerza de fricción se detecta con una celda de carga, siendo esta señal amplificada para, posteriormente, ser monitorizada y, a continuación, se convierte en el coeficiente de fricción. En los ensayos se aplicó una fuerza normal de 11,91 N sobre una bola de acero (100Cr6) en contacto con un disco (1,2210/115CrV3) que gira a 120 rpm durante 15 minutos, tiempo necesario para obtener un coeficiente

de fricción estacionario, repitiendo dicho ensayo tres veces para promediar el valor final obtenido.



Figura 3.20. Tribómetro del Laboratorio de Tribología en la Universidad de Ciencias Aplicadas de Hamburgo, Alemania

La segunda serie de mediciones fueron realizadas en un nanotribómetro (CSM Instruments, Suiza) capaz de registrar de forma continua el coeficiente de fricción, fuerza de fricción, fuerza normal, profundidad de la hendidura sobre el plato y datos ambientales tales como la temperatura y la humedad. Las fuerzas se miden por medio de la detección óptica del desplazamiento de un “cantilever”. Para las mediciones de fricción se puede usar un rango de fuerzas normales de 0,02 – 1000 mN, dependiendo del “cantilever” instalado. La fuerza de fricción se detecta con una resolución de 0,01 mN y los valores de la huella pueden detectarse con una resolución de 50 nm. Este equipo puede funcionar tanto en modo rotacional como oscilatorio pudiendo registrar en ambos modos la profundidad de la huella en la zona de fricción. Para el caso de test oscilatorios, se estableció una fuerza normal de 50 mN, una velocidad lineal máxima de 0,5 mm/s y una amplitud de 1 mm utilizando una bola de zafiro de 1,5 mm de diámetro y un disco de acero (115CrV3) con una rugosidad máxima de 3 μm . Para el caso de test rotacionales, se estableció una fuerza normal de 50 mN, un radio de la pista de fricción de 7 mm y una velocidad lineal de 10 mm/s. En este caso se probaron dos tipos de contactos, la bola de zafiro usada en los ensayos oscilatorios sobre un disco de zafiro o sobre un disco de acero (115CrV3). En todos los casos se realizaron tres

repeticiones de 15 minutos cada una, para posteriormente ser promediadas.

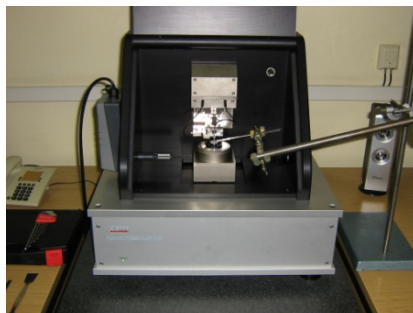


Figura 3.21. Nanotribómetro (CSM Instruments, Suiza)

3.6 Análisis térmico

Calorimetría diferencial de barrido (DSC)

El análisis térmico mediante la técnica de calorimetría diferencial de barrido permite medir los efectos térmicos asociados a cambios físicos o químicos que sufre una sustancia al aumentar o disminuir la temperatura a una velocidad constante. Mediante esta técnica se registra, en función del tiempo, la diferencia de flujo de calor que hay que suministrar a la muestra y a una referencia, para mantenerlas a la misma temperatura. Esta diferencia de energía es equivalente a la energía térmica absorbida o desprendida por el material objeto de estudio [Pohlen, 1998].

Los ensayos de calorimetría diferencial de barrido se llevaron a cabo en un calorímetro modelo Q-100 (TA Instruments Waters, EE.UU.). Este equipo incorpora un sistema de refrigeración tipo (RCS) para realizar medidas en un intervalo de temperatura de -90 a 550 °C. Como medio inerte se utilizó un flujo de nitrógeno de 50 mL/min. Las muestras se colocaron en el interior de una cápsula de aluminio hermética, la cual se sella con ayuda de una prensa. Como sistema de referencia se utilizó una cápsula de aluminio similar vacía.

Todas las muestras fueron sometidas al mismo protocolo de medida consistente en un doble calentamiento para evitar, por una parte, la influencia de la historia térmica, y por otra, suprimir los posibles efectos de reorganizaciones estructurales o cristalizaciones durante el almacenamiento de las muestras. Se colocaron cantidades de muestra comprendidas entre 5 y 10 mg en el interior de las cápsulas de aluminio selladas sometidas a una rampa de temperatura desde -75 hasta 250 °C.



Figura 3.22. Calorímetro diferencial de barrido, modelo Q-100 (TA Instruments Waters, EE.UU.)

Análisis termogravimétrico

El análisis termogravimétrico se realizó en una microbalanza termogravimétrica, modelo Q50 (TA Instruments Waters, EE.UU.), donde se registran pérdidas de masa al modificar la temperatura. Los ensayos se realizaron desde temperatura ambiente hasta 500 °C, a una velocidad de calentamiento de 10 °C/min, usando nitrógeno como gas de purga. Alternativamente, también se utilizó como gas de purga aire sintético para determinar el efecto que tiene el oxígeno en el proceso de pérdida de masa con el calentamiento.



Figura 3.23. Analizador termogravimétrico modelo Q-50 (TA Instruments Waters, EE.UU.)

3.7 Caracterización microestructural

La caracterización microestructural de algunos oleogel se llevó a cabo a través de microscopía de fuerza atómica (AFM), con un equipo Multimode conectado a un controlador de microscopía tipo sonda Nanoscope-IV (Digital Instruments, Veeco Metrology Group Inc., EE.UU.). Todas las imágenes fueron tomadas en el modo “tapping” usando puntas Veeco Nanoprobe™.



Figura 3.24. Microscopio de fuerza atómica Nanoscope-IV (Digital Instruments, Veeco Metrology Group Inc., EE.UU.)

3.8 Caracterización química

Cromatografía gaseosa (GC)

Se realizaron análisis de cromatografía gaseosa con un cromatógrafo Agilent, modelo 6890 (HP, EE.UU.), equipado con un detector de ionización de llama a fin de determinar el contenido de ácidos grasos en los diferentes tipos de aceites vegetales estudiados. Se utilizaron ésteres metílicos de ácidos grasos comprendidos entre C14-C24 como patrones.



Figura 3.25. Cromatógrafo Agilent 6890 (HP, EE.UU.)

Cromatografía de permeación en gel (GPC)

El peso molecular de los diferentes tipos de etil celulosas empleados, se determinaron por medio de la técnica de GPC, usando un equipo de Waters (EE.UU.), equipado con una columna de styragel HR 4E (7,8 x 300 mm), a 35 °C, y tetrahidrofurano como eluyente. Se utilizó un detector de índice de refracción de Waters 2414. El flujo empleado fue 1,0 mL/min. Se calculó el peso molecular medio en número (M_n), el peso molecular medio en masa (M_w) y el índice de polidispersidad (M_w/M_n) tomando como referencia estándares de poliestireno.



Figura 3.26. Cromatógrafo de permeación en gel (Waters, EE.UU)

Espectroscopia de infrarrojos por transformada de Fourier (FTIR)

Para obtener los espectros de infrarrojo de algunos biopolímeros se utilizó un equipo Digilab FTS3500ARX (Varian, EE.UU.) Las muestras de biopolímeros se prepararon formando pastillas con bromuro potásico, las cuales fueron ubicadas en un receptáculo adecuado. Los espectros se obtuvieron en un rango de número de onda entre $400\text{-}4000\text{ cm}^{-1}$ con una resolución de 4 cm^{-1} en el modo de transmisión.



Figura 3.27. Espectrómetro de infrarrojos Digilab FTS3500ARX (Varian, EE.UU.)



CAPÍTULO 4

OLEOGELES FORMULADOS CON MONOESTEARATO DE SORBITANO Y MONOESTERATO DE GLICERILO

4.1 Effect of thermo-mechanical processing on the rheology of oleogels potentially applicable as biodegradable lubricating greases

4.1.1 Introduction

Oleogels are complex microstructured systems composed of an organic hydrophobic solvent and a substance, frequently an amphiphilic molecule, able to form a three-dimensional network which immobilizes the continuous medium. Nowadays, the main applications of oleogels are found in the field of pharmaceuticals and cosmetics [Hinze et al., 1996]. In particular, sorbitan esters have been successfully tested as organogelators [Murdan et al., 2005; Almeida and Bahia, 2006]. However, these studies have been mainly focused on the physical stability and microstructure of oleogels. Thus, little attention has been paid to the optimization of the processing protocol necessary to form these oleogels.

On the other hand, up to now, other potential applications of oleogels have not been explored. Nowadays, one of the main problems of very different industrial sectors concerns the impact that process technologies and products cause in the environment. In this sense, there is a general tendency to promote both the replacement of non-renewable raw materials by renewable resources, and the minimization of the environmental impact caused by industrial waste materials. Concerning the impact that lubricants exert on the environment, every year millions of tonnes of engine, industrial and hydraulic oils are leaked into the ground or motorways, or are poured in the environment. Even small amounts of these products can inhibit the growth of trees and can be toxic to aquatic life [Wilson, 1998]. In this sense, a slow but steady movement toward the use of “environmentally-friendly” or more readily biodegradable lubricants has been noticed during the last decade. Erhan and co-workers [Erhan and Asadauskas, 2000;

Adhvaryu and Erhan, 2002; Adhvaryu et al., 2004; Erhan et al., 2006] and Dicken, 1994, have reported the advantages and disadvantages of using vegetable oils and organic esters as liquid lubricants. As they pointed out, the main disadvantage of vegetable oils is their poor oxidative stability, in comparison to some of the mineral oils traditionally employed. However, they also present good lubricity and ability for adhering to metal surfaces, low volatility, small viscosity-temperature dependence and, of course, non-toxicity and high biodegradability.

The development of environmentally-friendly lubricating grease formulations based on 100% biodegradable raw materials seems to present much more difficulty. Greases may be considered gel-like colloidal suspensions in which a suitable thickener is dispersed in a lubricating liquid, traditionally a mineral or synthetic oil [NLGI, 1994]. As Adhvaryu and co-workers reported [Adhvaryu et al., 2005a], a more biodegradable formulation can be obtained just replacing the mineral oil by a vegetable one. However, the substitution of the thickener agents traditionally used (metallic soaps, phyllosilicates or polyurea compounds) by others more environmentally acceptable has not yet been considered. The traditional thickeners, especially metallic soaps, confer to greases their main functional properties, among others gel-like characteristics and suitable rheological properties, but cannot be considered as biodegradable materials. Obviously, finding a biodegradable thickener agent with suitable properties may create a new market niche with interesting perspectives for the future [Fessenbecker, 2003]. In this sense, although some limitations, especially related to maximum working temperature (which otherwise depends on the solvent [Murdan et al., 2005]), are apparent, oleogel formulations based in vegetable oils may offer some benefits as a biodegradable alternative to greases, at least for specific applications.

As previously reported [Delgado et al., 2005; Franco et al., 2005], the manufacturing process of traditional lubricating greases is highly

complex, with many thermo-mechanical variables affecting the final properties of this product, i.e. rheological behaviour and mechanical stability among others. Basically, the manufacture of lubricating greases, with generation “in situ” of the soap thickener during the mixing process, consists of the saponification reaction of fatty acids, followed by dehydration, heating up to near the phase transition temperature of soap crystallites and cooling down to crystallize the soap [Hamnelid, 2000]. Similarly, it is well-known that the gel formation mechanism is also affected by the processing variables, especially by the thermal protocol selected [Moros et al., 2003; Nunes et al., 2006; Zhong et al., 2004]. The aim of this work was focused on the development of some oleogels, potentially useful as biodegradable lubricating greases, by studying the effect that some thermo-mechanical processing variables exert on the rheological properties and microstructure of oleogels. In addition to this, some mechanical and tribological tests, usually employed to confirm the lubrication performance and stability of greases, have been carried out with oleogels formulations, in order to test their suitability as lubricants.

4.1.2 Materials and methods

Materials

Castor oil (Guinama, Spain) was used as the biodegradable raw material to prepare oleogel formulations. Sorbitan monostearate (SMS) of HLB = 4.7 (Panreac, Spain) was used as the gelling agent. Standard lithium 12-hydroxystearate lubricating greases were used as reference systems. 12-hydroxystearic acid, hydrated lithium hydroxide, and paraffinic and naphthenic mineral oils were kindly supplied by Verkol Lubricantes S. A. (Spain). Values of kinematic viscosities, at 40 °C, of the different oils used in these grease formulations are listed in Table 4.1.

Oil	Kinematic viscosity (cSt)
Naphthenic	110
Paraffinic 1	334
Paraffinic 2	105
Castor	211

Table 4.1. Kinematic viscosity values, at 40 °C, for the different oils used

Manufacture of oleogel formulations

Processing of oleogels was performed in an open vessel, using an anchor impeller geometry (D=90 mm; H=110 mm) to disperse the gelling agent. Batches of 600 g were prepared, employing in all cases a SMS concentration of 20% w/w. SMS was dispersed in the vegetable oil under agitation (60-150 rpm) at different temperatures, comprised between SMS melting point (≈ 58 °C) and 80 °C, and for different mixing times, ranging from 15 to 60 min. It is worth pointing out that the application of temperatures lower than the SMS melting point does not yield a homogeneous gel. Then, the solution was cooled down to room temperature in order to induce gelification. Cooling was carried out either by switching off the thermostatic device, or placing the vessel into a large quenching system of water at 0, 5 or 25 °C, under mild agitation. In addition, several oleogel agitation speeds (0-150 rpm) during cooling were tested.

Rheological characterization

Rheological characterization of oleogels was carried out with both a Rheoscope controlled-stress rheometer (TermoHaake, Germany), and an ARES controlled-strain rheometer (Rheometrics Scientific, UK). Small-amplitude oscillatory shear (SAOS) tests were performed inside the linear viscoelastic region, using a rough plate-plate geometry (20 mm, 1 mm gap, relative roughness 0.4), in a frequency range of 10^{-2} - 10^2 rad/s. At least two replicates of each test were performed on fresh samples. Figure 4.1 illustrates the sample-to-sample variability in SAOS functions for a selected system. Rheological tests were always carried out at 25 °C.

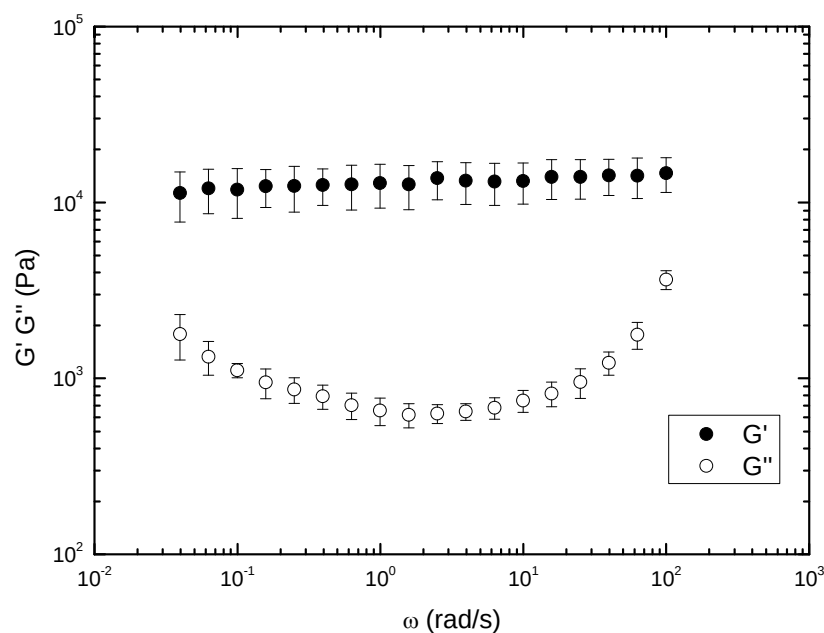


Figure 4.1. Standard deviation of SAOS functions for a selected oleogel (processing conditions: 60 °C during 60 min and 60 rpm and cooling with water at 25 °C)

Occasionally, “in situ” viscosity measurements during processing were monitored using the ARES rheometer equipped with a cylindrical rheo-reactor (40 mm diameter, 48 mm height) and an anchor mixing geometry (38 mm diameter) coupled with the transducer of the rheometer. This tool allows one to monitor the evolution of viscosity with time during processing, as well as to accomplish further rheological measurements after the mixing process [Nachbaur et al., 2001]. This geometry was calibrated according to the Couette analogy, as described elsewhere [Aït-Kadi et al., 2002].

Morphological observations

Morphological characterization of greases was carried out 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). All images were acquired in the tapping mode, using Veeco Nanoprobe™ tips.

Penetration and mechanical stability tests

Both unworked and worked penetrations were determined by using a Seta Universal penetrometer, model 17000-2, with one-quarter cone geometry (Stanhope-Seta, UK). The one-quarter scale penetration values were converted into the equivalent full-scale cone penetration values, according to the ASTM D 217 standard. Samples were worked during 30 minutes in a Roll Stability Tester, model 19400-3 (Stanhope-Seta, UK) and penetration measurements were carried out, once again, immediately after the rolling test and after 5 hours, in order to evaluate its mechanical stability and structural recovery.

Measurements of the friction coefficient

A classical ball-disc tribometer was used to determine the friction factor, which is defined as the relationship between the load applied (normal force) and the friction force, under flooded flow lubrication, i.e. under the assumption that the lubricant is supplied to the film inlet at a sufficient flow rate. Original bearing balls, made of 100Cr6 (12.7 mm diameter), were employed. All of them had the same roughness and hardness. Steel plates were made of 9SMn28. In this device, the plate rotated while the ball was kept fixed. The lubricant was spread homogeneously on the steel plate, and the ball was supported by a holder on the sample. This arm was also put in contact with a force sensor, which directly measured the friction force. The friction coefficient was obtained under specific conditions where the lubricant film is not complete and the asperities of the solid bodies may still come into contact, hereafter called mixed friction conditions. The friction force was measured, during 600 s, at room temperature (24 ± 1 °C). This test was repeated ten times, to obtain a quite accurate average friction factor. Taking into account sampling and measurement errors, the friction factor values had an average standard deviation of ± 0.01 . For each test, a new contact area on the ball surface was used, and all specimens were cleaned with ethanol.

4.1.3 Results and discussion

Monitoring “in situ” rheological properties during processing

The evolution of the degree of dispersion of the thickener in the oil, and the consequent formation of the oleogel can be easily followed in Figure 4.2, which shows the temperature profile and the viscosity values monitored “in situ” during processing, using the rheo-reactor device coupled with the ARES rheometer. This procedure simulates the manufacturing process of the oleogels in a stirred tank. In this case, a maximum temperature of 60 °C was selected to disperse the thickener (SMS). Later on, a controlled cooling profile (1.2 °C/min) was applied, as it is shown in Figure 4.2. Taking into account the evolution of viscosity and the thermal protocol applied, the oleogel formation may be divided in two different steps. First, the monitored viscosity values correspond to that of the castor oil used, at 60 °C, which is around 0.06 Pa·s. When SMS is added, a sudden increase in viscosity is noticed. However, once the thickener is totally melted and well dispersed, the viscosity values reach constant values (around 0.07 Pa·s) once again. Afterwards, in the second stage, a sudden rise in viscosity is monitored, due to a cooling-induced gelification process. Finally, viscosity tends to a constant value once temperature is kept constant at 25 °C. The resulting gel shows a non-Newtonian behaviour. This experimental protocol has been repeated at different agitation speeds (or shear rates). As can be observed in Figure 4.2, the viscosity values of the final gels are larger as agitation speed during processing decreases. However, this is not the only consequence of the characteristic shear-thinning behaviour of the resulting gel. As will be discussed below, the intensity of sample agitation during cooling significantly affects the strength of the gel and, therefore, the oleogels processed in the rheo-reactor at different agitation speeds may show different rheological properties.

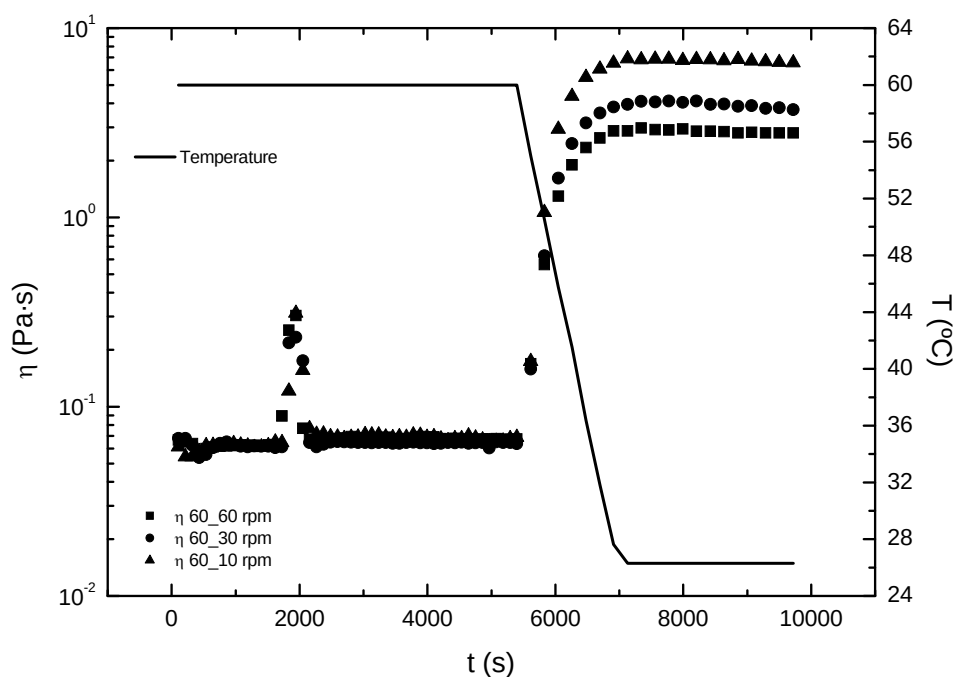


Figure 4.2. “*In situ*” monitoring of viscosity evolution during oleogel processing in a rheo-reactor

Influence of different thermo-mechanical processing variables

a) Influence of maximum processing temperature. The maximum temperature applied during the first stage of the processing protocol was varied between 60 °C, close to the SMS melting point (≈ 58 °C) and 80 °C. Oleogels were prepared by heating the sample at the selected temperature for one hour, and then cooling it down to room temperature by natural convection in the same heating device. Figure 4.3 shows the evolution of different SAOS functions with frequency, within the linear viscoelasticity range and at 25 °C, for oleogels processed by applying different maximum temperatures. The evolutions of the storage (G') and loss (G'') moduli with frequency are quite similar to those found for standard lithium lubricating greases [Delgado et al., 2005; Franco et al., 2005; Madiedo et al., 2000; Martín-Alfonso et al., 2007]. As can be observed, G' is always higher than G'' in the whole frequency range studied. The presence of a plateau region in this mechanical spectrum, showing a clear minimum in G'' and a power-law

relationship, with G' versus frequency slope of around 0.1, is typical of entangled polymeric systems and weak gels [Moros et al., 2003; Nunes et al., 2006; Ferry, 1980].

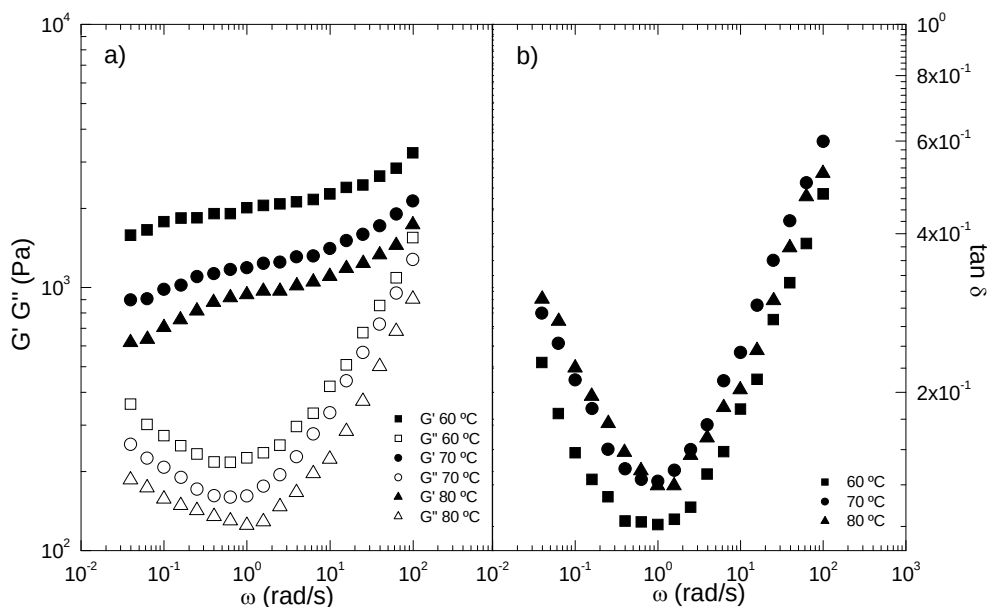


Figure 4.3. Frequency dependence of (a) the storage and loss moduli and (b) the loss tangent for oleogels processed at different maximum temperatures. Other conditions: 60 rpm for 1 hour (first process stage), and cooling by natural convection in the same processing device

The maximum processing temperature applied does not seem to influence qualitatively the above mentioned mechanical spectrum. Thus, although an increase in this temperature clearly reduces the values of both SAOS functions, the loss tangent, defined as the ratio between G'' and G' , presents quite similar values in the whole frequency range studied for the samples processed at 70 and 80 °C (Figure 4.3b). However, the oleogel sample processed at the lowest temperature (60 °C) shows slightly lower values of the loss tangent, that is, a more marked elastic behaviour. Consequently, these results indicate that the strength of the resulting gel is reinforced by applying a maximum temperature (to disperse the gelling agent) only slightly higher to its melting point.

b) Influence of heating time. Figure 4.4 shows the influence of heating time (60, 30, and 15 min), at the maximum temperature, during the first process stage, on the SAOS response of the oleogel samples studied. Oleogels were processed by dispersing SMS at 60 °C. It is apparent that the oleogel sample processed at a temperature of 60 °C, during 60 min, shows the lowest values of G' and G'' . It is worth mentioning that this sample was more homogeneous and, as a result, a higher relative elasticity was achieved (see Figure 4.4b). Moreover, it was proved that, after 15 minutes, the thickener was not totally well dispersed in the oil medium. In this sense, Figure 4.5, which shows the microstructure of selected oleogel samples obtained with the AFM technique, supports this statement. As can be deduced from these pictures, the morphology of these oleogels consists of multilayer aggregates, which seem to be swollen by some oil components in the case of the oleogel sample obtained after heating during 60 minutes (see Figure 4.5a). On the contrary, some not well dispersed granules appear in the oleogel sample obtained after heating the sample during 15 minutes (Figure 4.5b).

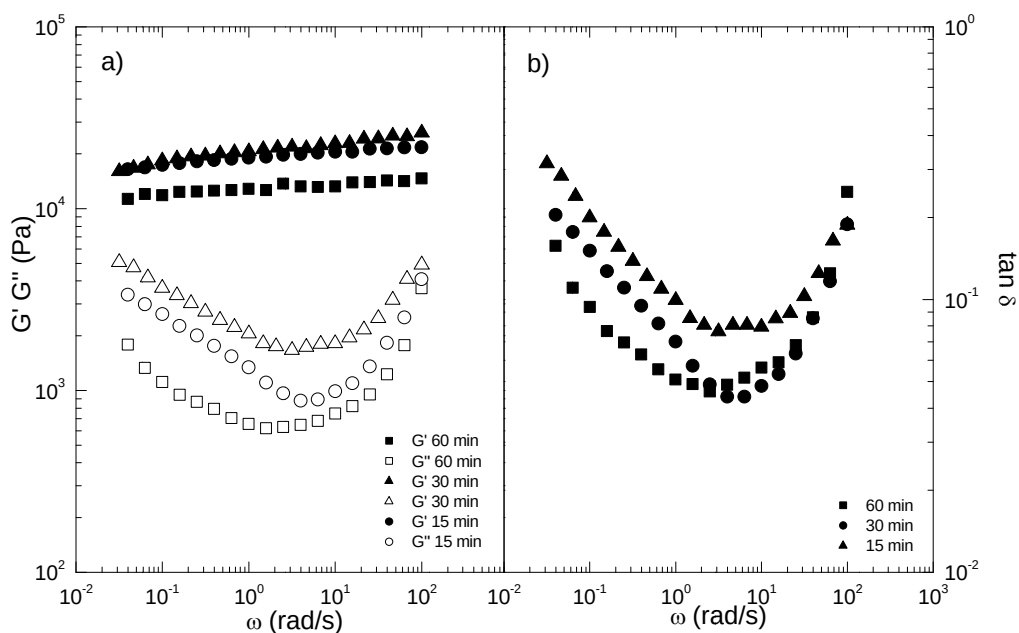


Figure 4.4. Frequency dependence of (a) the storage and loss moduli and (b) the loss tangent for oleogels processed during different heating times. Other conditions: 60 °C (first stage temperature), 60 rpm (first process stage), and cooling with water at 25 °C

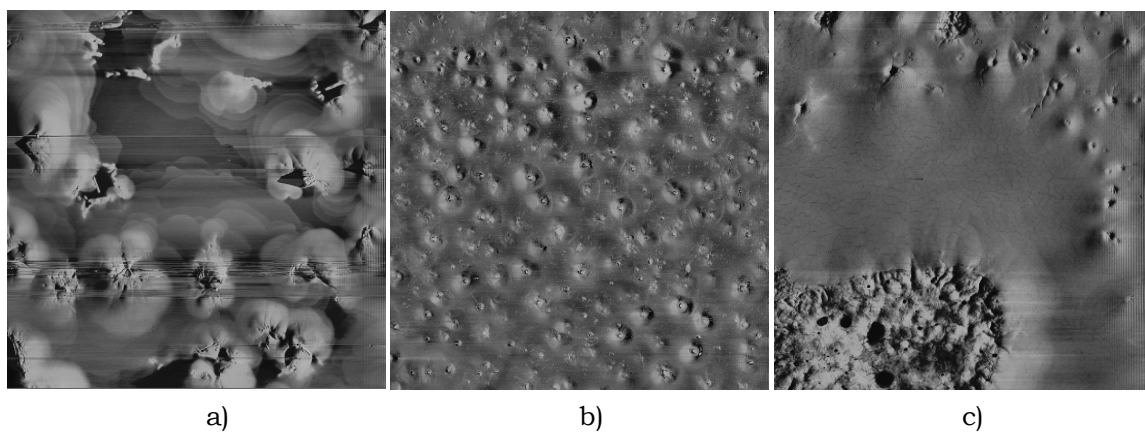


Figure 4.5. AFM photomicrographs for oleogels prepared under different processing conditions: a) 60 °C during 1h (first process stage), and cooling with water at 25 °C; b) 60 °C during 15 min (first process stage), and cooling with water at 25 °C; c) 60 °C during 1h (first process stage), and cooling with water at 0 °C (window size corresponds to 20 μm)

c) *Influence of the agitation speed.* Figure 4.6 shows the mechanical spectra of oleogels processed at different agitation speeds during the first stage of their manufacture (dispersion of the gelling agent in castor oil). An increase in G' and G'' values was found when the rotational speed was increased from 60 to 100 rpm. It is apparent that an increase in rotational speed should induce a better dispersion due to an improved mixing efficiency. However, a further increase in the rotational speed up to 150 rpm yields an opposite effect. This can be attributed to larger and more frequent air entrainments, which are also apparent in the final gel. It must be then emphasized that oleogels are not manufactured properly at large rotational speeds. This effect can be observed in Figure 4.6a, which clearly shows a decrease in the values of G' and G'' when the rotational speed was increased from 100 rpm to 150 rpm.

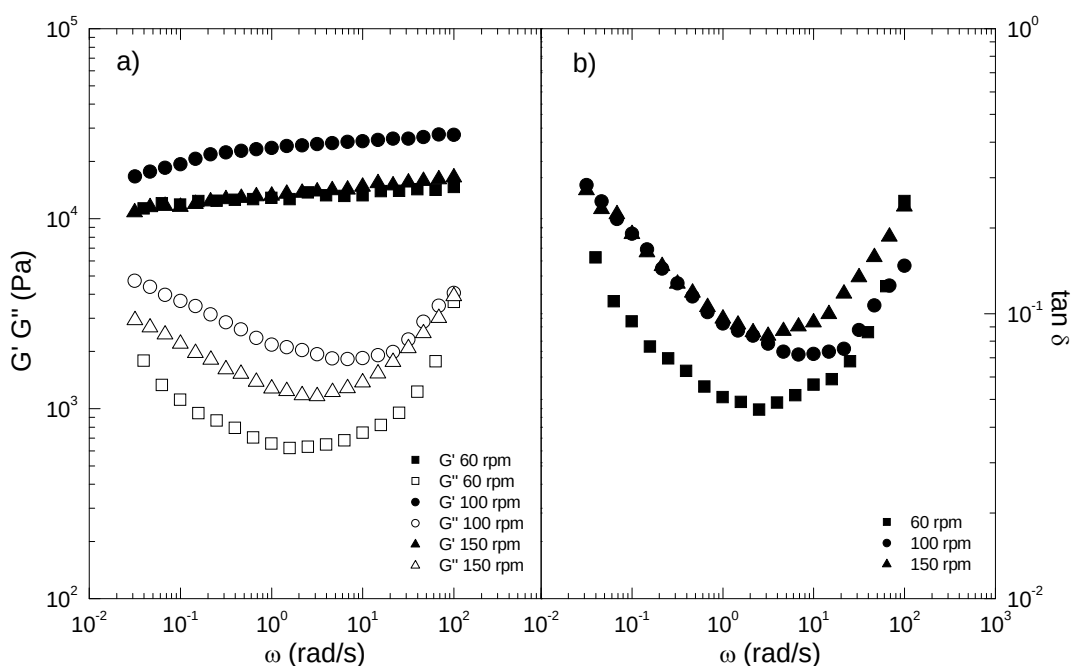


Figure 4.6. Frequency dependence of (a) the storage and loss moduli and (b) the loss tangent for oleogels processed at different rotational speeds. Other conditions: 60 °C (first stage temperature), 1 hour (first process stage), and cooling with water at 25 °C

Thus, the oleogel sample processed at 150 rpm shows similar G' values to those corresponding to the sample processed at 60 rpm, although larger G'' values. In addition, the sample processed at 60 rpm, in spite of showing the lowest viscoelastic moduli values, presents the higher relative elasticity, i.e. lower values of the loss tangent (Figure 4.6b). On the other hand, the oleogel prepared at 100 rpm presents values of the loss tangent very similar to those shown by the oleogel prepared at 150 rpm, although the minimum found in the frequency evolution of this function is slightly shifted to higher frequencies.

d) Influence of cooling profile. Cooling rate in a gelification process is frequently an important influencing variable [Nunes et al., 2006; Zhong et al., 2004]. The effect of the cooling profile in the manufacture of the oleogel samples studied is shown in Figures 4.7 and 4.8, for oleogels samples not submitted (Figure 4.7) or submitted (Figure 4.8) to agitation (60 rpm) during cooling. In order to study this processing variable, four different cooling conditions were tested: either allowing the dispersion to cool until room temperature in the same heating tank used to disperse the thickener (thermal fluid cooling by natural convection, which provides the slower cooling rate), or introducing the incipient gel in a stirred device containing water at 25, 5 or 0 °C. In addition, the influence of oleogel agitation during this cooling process was also studied.

As expected, the cooling profile is the processing parameter that affects more dramatically the rheological properties of oleogels. As can be observed in Figures 4.7a and 4.8a, an increase in cooling rate always produces an important increase in the values of the linear viscoelastic functions. Thus, differences of more than one decade are found for oleogels processed by applying external natural convection cooling and those cooled in water at 0 and 5 °C. In some cases, differences of almost two decades can be observed, depending on frequency (see, for instance, G'' values at low frequencies in Figure 4.8a). In this sense, some authors [Toro-Vazquez et al., 2007; Lescanne et al 2003; 2004]

proposed for other organogel systems some microstructural changes induced by a modification in the cooling rate. For instance, Toro-Vazquez et al., 2007, found microplatelet-based networks for oleogels developed with waxes, which exhibited a greater hardness when the organogel was formed by setting a lower temperature, as it was observed for the SMS-based oleogels studied in this work. This fact was attributed to smaller microplatelet unit sizes in the three-dimensional network, observed by polarizing microscopy, with a more dense organization. Similarly, Lescanne et al., 2003; 2004, in the case of gels formed with several low-molecular-weight organogelators, proposed a dendritic structure with an increasing density of junctions in the interconnected aggregates detected by using light and X-ray scattering.

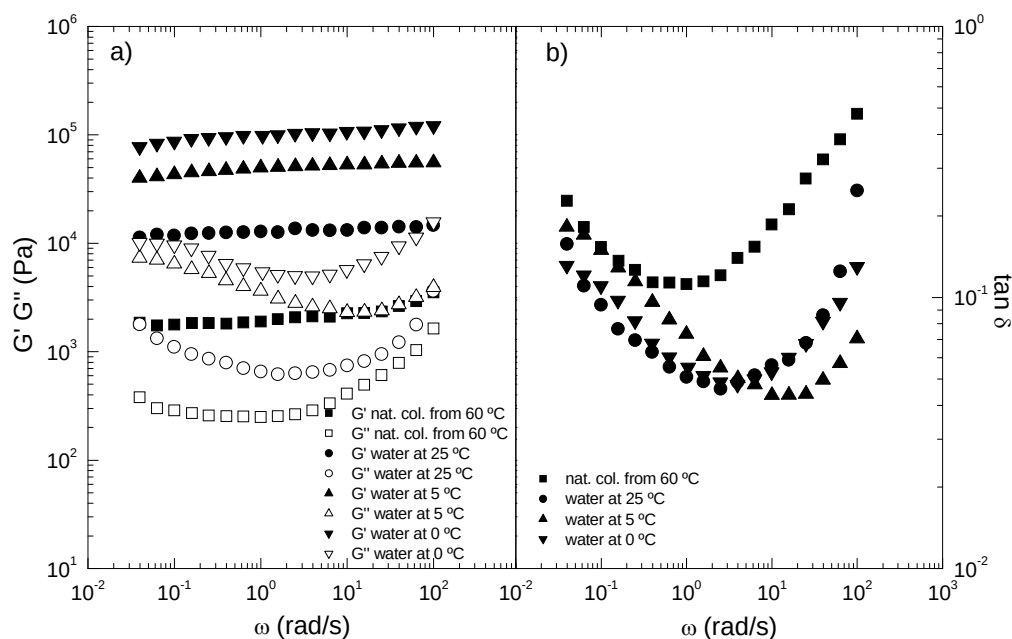


Figure 4.7. Frequency dependence of (a) the storage moduli and loss moduli and (b) the loss tangent for oleogels processed with different cooling profile protocols. Other conditions: 60 °C (first stage temperature), 60 rpm for 1 hour (first process stage), no sample agitation during cooling

When cooling was carried out by placing the sample in water at 0 °C without sample agitation, a very important temperature gradient between the centre and the wall of the vessel containing the oleogel was

detected during the first cooling stages (down to ≈ 25 °C), yielding a highly heterogeneous gel. This is illustrated in Figure 4.5c, where some crystals can be observed in the AFM image. Consequently, the rheological information obtained using this thermal protocol is not very relevant. As expected, the application of an agitation speed to the oleogel sample during cooling significantly reduces this temperature gradient, although this yields lower values of both moduli. Thus, mixing seems to affect negatively gel strength. The influence of oleogel agitation during cooling will be briefly commented in the next subsection.

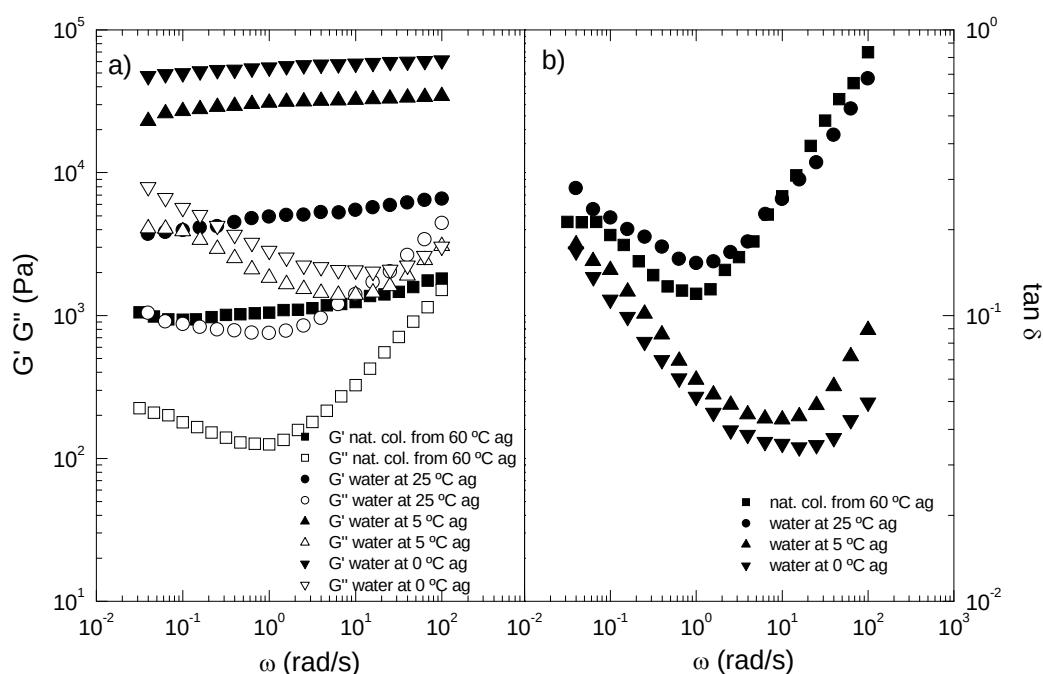


Figure 4.8. Frequency dependence of (a) the storage and loss moduli and (b) the loss tangent for oleogels processed with different cooling profile protocols. Other conditions: 60 °C (first stage temperature), 60 rpm for 1 hour (first process stage), sample agitated at 60 rpm during cooling

In addition, the cooling protocol selected affects the relative elasticity of gels. As can be observed in Figures 4.7b and 4.8b, the values of the loss tangent significantly decrease with cooling rate, especially at high frequencies. This relative increase in elasticity is more evident for stirred oleogels samples cooled in water at 0 and 5 °C (Figure

4.8b). Moreover, the minimum found in the evolution of the loss tangent with frequency is generally shifted to higher frequencies when cooling is performed at these low temperatures. In any case, the values of the loss tangent tend to be very similar at low frequencies for all the cooling conditions studied. This characteristic behaviour is also clearly displayed in Figure 4.8b.

The resulting cooling profiles, consequence of the different experimental protocols previously described, are shown in Figure 4.9. Temperature was always measured in the centre of the vessel. Obviously, the decrease in temperature is slightly accelerated when the sample is agitated during the cooling step. The dependency of temperature with time has been fitted successfully ($R^2 \geq 0.999$) to a double-exponential equation:

$$\frac{T - T_{\infty}}{T_0 - T_{\infty}} = \alpha \cdot e^{-t/\lambda_1} + (1 - \alpha) \cdot e^{-t/\lambda_2} \quad (4.1)$$

where t is the time expressed in minutes, T is the instantaneous temperature measured in the centre of the vessel, T_0 is the initial temperature (≈ 62 °C in this case), T_{∞} is the temperature of the cooling medium and α , λ_1 , λ_2 are fitting parameters. The values of these fitting parameters are listed in Table 4.2. When the thermal fluid used is cooling by natural convection (from 60 °C down to room temperature), temperature decay is much slower, and only one exponential term in equation (4.1) is necessary, being λ_1 significantly higher. However, it must be noticed that values shown in Table 4.2 are only useful from a comparative point of view and, since equation (4.1) is purely empirical, may be affected by the mixing geometry and stirring conditions used to cool the sample.

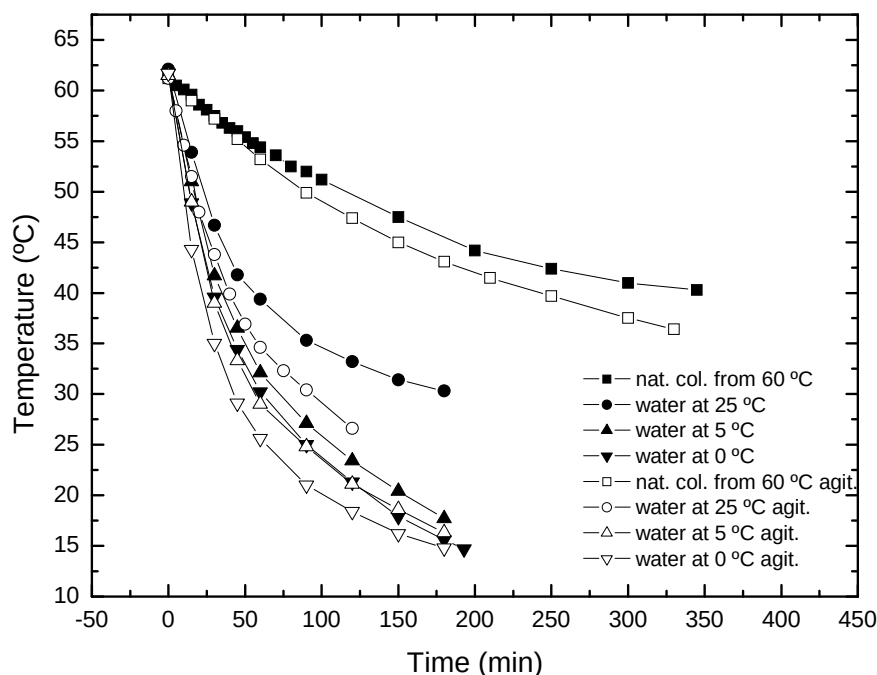


Figure 4.9. Temperature profiles for oleogels samples during cooling (with and without sample agitation)

External cooling conditions	Sample agitation (60 rpm)	α	λ_1 (min)	λ_2 (min)
Thermal fluid cooling by natural convection (from 60 °C down to room temperature)	NO	0.69	177.6	---
	YES	0.84	199.7	---
Stirred device with water at 25 °C	NO	0.71	39.6	251.8
	YES	0.96	43.3	200.5
Stirred device with water at 5 °C	NO	0.44	32.8	201.0
	YES	0.52	30.0	208.1
Stirred device with water at 0 °C	NO	0.40	26.6	208.7
	YES	0.54	23.5	266.5

Table 4.2. Equation 4.1 fitting parameters for samples submitted to different cooling conditions

In order to quantify the influence of cooling rate on the rheological response of the oleogel samples studied (sample cooling with 60 rpm or without agitation), the plateau modulus has been plotted versus λ_1 (Figure 4.10). The values of this parameter are closely related to the

initial temperature decay. The “plateau” modulus, G_N^0 , is a characteristic parameter for the plateau region of the mechanical spectrum [Baumgaertel et al., 1992], exhibited in all cases by the oleogels studied. As shown in Figure 4.10, an increase in cooling rate (lower λ_1) strongly affects the rheological properties of oleogels, more important when the cooling process is performed without sample agitation, in spite of a certain degree of heterogeneity due to a higher temperature gradient.

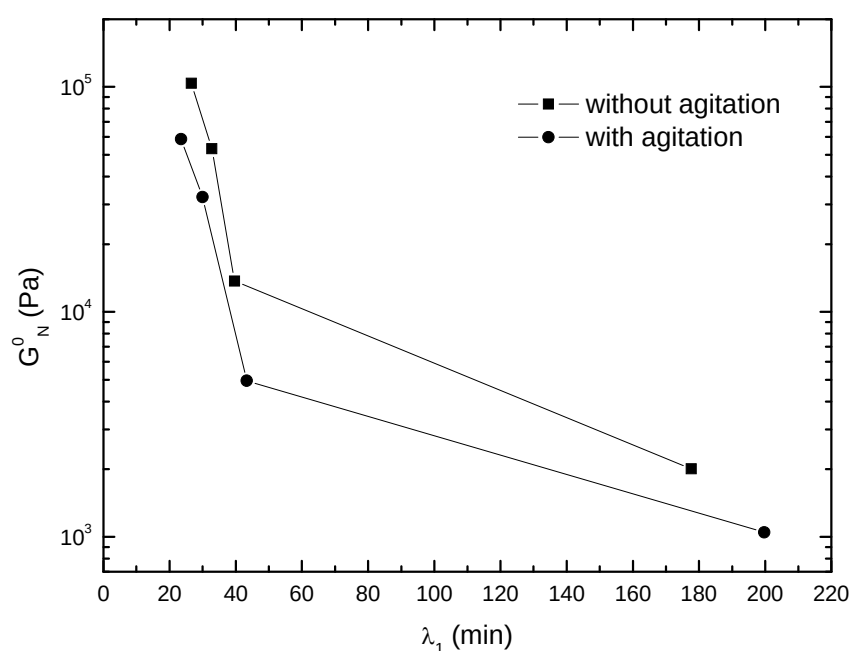


Figure 4.10. Evolution of G_N^0 with λ_1 (equation (4.1)) for sample cooling with (60 rpm) or without agitation

e) Influence of agitation speed during cooling. As it has been previously commented, stirring during cooling reduces gel strength. Figure 4.11 shows the mechanical spectra of several oleogels processed at different agitation speeds during the cooling step. It can be observed that an increase in agitation speed yields lower values of both linear viscoelasticity moduli. This effect is especially dramatic when rotational speeds of 100 and 150 rpm are applied. Thus, G' and G'' values are more than one decade lower than the oleogel sample processed without agitation during cooling.

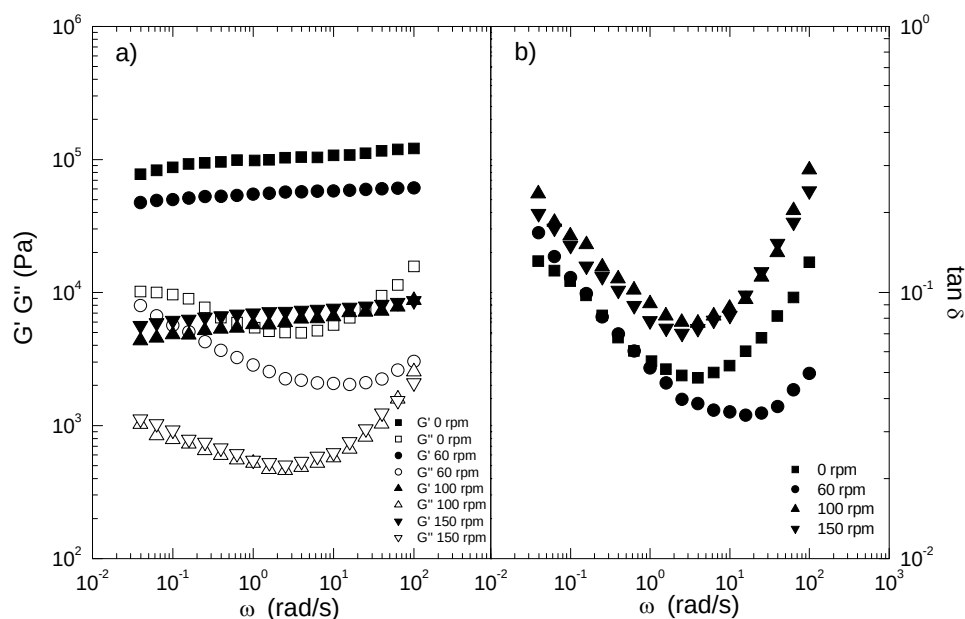


Figure 4.11. Frequency dependence of (a) the storage and loss moduli and (b) the loss tangent for oleogels submitted at different agitation speeds during the gelification (cooling) process. Other conditions: 60 °C (first stage temperature); 60 rpm during 1 hour (first process stage); cooling with water at 0 °C

Lubrication properties of oleogels

Lubrication properties of oleogels have been tested according to mechanical stability and tribological experiments, and compared with those shown by model mineral oil-based lithium lubricating greases containing oils of similar kinematic viscosity (see Table 4.1). As it is well known, the mechanical stability of lubricating greases is traditionally determined as the difference between penetration indexes after and before submitting the grease to a standard working test (in this case, a shear rolling test). Greases with good mechanical stability characteristics must exhibit penetration increments after working close to zero. Table 4.3 shows the penetration values of oleogels before and after submitting the grease to the rolling test, in comparison to both mineral and castor oil-based lithium greases. As can be observed, the penetration values of selected unworked oleogel samples, which otherwise determine the NLGI grade, are comparable to those obtained

with model mineral oil-based greases, but higher than that obtained with a lithium grease prepared with the same castor oil. However, penetration values obtained after working are much higher than those shown by model lithium greases (>500 dmm), which indicate a poor mechanical stability (penetration increments comprised between 60-140 dmm). On the other hand, Table 4.3 also lists the penetration values after 5 hours ageing at rest, in order to show sample consistency recovery after working. As can be observed, oleogel samples recover their un-worked consistency, showing a similar behaviour to that found with model lithium greases.

Concerning the tribological response, the values of the friction coefficient obtained in a ball-disc tribometer are also reported (see Table 4.3). Oleogel samples studied in this work show lower friction coefficient values than model mineral oil-based lithium greases and quite close to that obtained with model castor oil-based lithium greases. This seems to indicate that these frictional forces are mainly determined by the base-oil employed. As was previously pointed out [Adhvaryu et al., 2004], vegetable oils present optimum lubricity, lowering more effectively the frictional forces in comparison to other mineral oils of similar kinematic viscosities. This fact was confirmed by ball-disc tribological tests carried out with oleogel samples studied.

Grease			Friction coefficient	Unworked penetration (dnm)	NLGI grade	Worked penetration (dnm)	Penetration recovery (dnm)
Oil	Thickener	Processing conditions					
Naphthenic	Lithium 12-hydroxystearate (14%)	See Delgado et al., 2005	0.110	325	1	302	290
Paraffinic 1	Lithium 12-hydroxystearate (14%)		0.110	409	00	384	380
Paraffinic 2	Lithium 12-hydroxystearate (9.75%)		0.099	437	00-000	461	450
Castor	Lithium 12-hydroxystearate (14%)		0.085	242	3	260	245
Castor	Sorbitan monostearate (20%)	Cooled at 25 °C with agitation (Figure 4.7)	-	449	000	> 500	380
		Cooled at 5 °C with agitation (Figure 4.7)	-	367	0	> 500	249
		Cooled at 0 °C without agitation (Figure 4.6)	0.086	415	00	> 500	437

Table 4.3. Friction coefficient and penetration values for model lithium lubricating greases and selected oleogel formulations

4.2 Rheology of oleogels based on sorbitan and glyceryl monostearates and vegetable oils for lubricating applications

4.2.1. Introduction

Oleogels, also referred as organogels or lipogels, are semisolid materials composed of an amphiphilic molecule, usually known as organogelator, and a hydrophobic liquid. Oleogels microstructure is characterised by either permanent rigid networks or transient semiflexible meshes, both of them thermo-reversible. Examples of oleogels are those containing, for instance, ethylcellulose, cholesterol, sorbitan monostearate or lanolin alcohols, as organogelators, dispersed in vegetable oils, as organic solvents [Almeida and Bahia, 2005]. Different oleogels applications have been investigated over the past few years. It is worth mentioning their potential use in the area of environmental chemistry, and in the pharmaceutical and cosmetic industries [Hinze et al., 1996], sometimes related to the discovery of new gel-forming molecules in organic solvents. These hydrophobic gel materials do require neither new nor extensive manufacturing knowledge to be produced, and can be formulated in a wide viscosity range [Almeida and Bahia, 2006].

Up to now, oleogels have not been widely explored for lubricating applications. However, 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. Inside the field of lubricants, oleochemicals are the natural alternative to mineral oils [Adhvaryu and Erhan, 2002]. 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. However, every year worldwide

millions of tonnes of engine, industrial and hydraulic oils leak into the ground or waterways or are disposed of in the environment, with the well-known adverse effect to the aquatic life. In order to minimise the contamination damage that petroleum-based products cause in the environment, there has been an increasing demand for environmentally acceptable products suitable to be used as lubricants [Wilson, 1998]. In this sense, a slow, but steady, movement toward the use of “environmentally friendly” or more readily biodegradable lubricants has been noticed during the last decade.

Erhan and co-workers [Erhan and Asadauskas, 2000; Adhvaryu and Erhan, 2002; Adhvaryu et al., 2004; Erhan et al., 2006] have reported some advantages and disadvantages concerning the use of vegetable oils and organic esters as liquid lubricants. As they pointed out, the main disadvantage of vegetable oils is their poor oxidative stability, in comparison to some of the mineral oils traditionally employed. However, they present good lubricity and ability for adhering to metal surfaces, low volatility, small viscosity-temperature dependence and, of course, non-toxicity and high biodegradability. Some solutions to overcome problems related to the low viscosity of vegetable oils, for different lubricating applications, has also been previously reported [Quinchia et al., 2009; Garcia-Zapateiro et., 2010]. Nevertheless, the development of environmentally friendly lubricating grease formulations, based on 100% biodegradable raw materials, seems to be a much more difficult task. Greases may be considered gel-like colloidal suspensions in which a suitable thickener, generally a metallic soap, is dispersed in a lubricating liquid, traditionally a mineral or synthetic oil [NLGI, 1994]. The replacement of the base oil for a biodegradable material is possible using vegetable oils, as it has been previously mentioned. However, the use of a “green thickener”, able to replace metallic soaps and yield a formulation with proper characteristics to be used as lubricating grease, is a not completely solved problem at present. In this framework, some rheological and

technological (related to their performance as lubricants) properties of several oleogels, containing sorbitan and glyceryl monostearates as organogelators and different types of vegetable oils, have been studied and related to their potential use as a biodegradable alternative to traditional lubricating greases.

4.2.2 Materials and methods

Materials

Castor oil, purchased from Guinama (Spain), and rapeseed and soybean oils, kindly supplied by Fresenius-Kabi Deutschland GmbH, were used to prepare oleogel formulations. Fatty acid composition and kinematic viscosity values, at 40 °C, of the different vegetable oils are listed in Table 4.4. Sorbitan monostearate (SMS) of HLB= 4.7 and glyceryl monostearate (GMS) of HLB=4.2, from Panreac and Guinama respectively, were used as gelling agents. Some standard lithium 12-hydroxystearate lubricating greases were used as reference systems. They were prepared, as described elsewhere [Franco et al., 2005; Delgado et al., 2005], using 12-hydroxystearic acid, hydrated lithium hydroxide, and paraffinic and naphthenic mineral oils, all of them supplied by Verkol Lubricantes S. A. (Spain).

	Castor oil	Rapessed oil	Soybean oil
Kinematic viscosity at 40 °C (cSt)	211	36	33
Fatty acid composition (%):			
Palmitic acid (C16:0)	2.6	4.6	10.7
Stearic acid (C18:0)	2.7	-	3.4
Oleic acid (C18:1)	6.3	66.0	24.1
Linoleic acid (C18:2)	10.8	21.1	54.7
Linolenic acid (C18:3)	-	8.2	6.0
Ricinoleic acid (12OH-C18:1)	77.6	-	-

Table 4.4. Fatty acid compositions and kinematic viscosities of the vegetable oil samples used in this study

Oleogel preparation

Processing of oleogels was performed in an open vessel, using an anchor impeller (D=90 mm; H=110 mm) to disperse the gelling agent.

Batches of 600 g were prepared, employing SMS and GMS concentrations between 10 and 20% w/w. SMS and GMS were dispersed in the vegetable oil under agitation (60 rpm), during 60 min, at around 60 °C, a temperature slightly higher than their melting points to favour the dispersion. Afterwards, the solution was cooled down to room temperature in order to induce gelification. Cooling was carried out either by natural convection, switching off the thermostatic device, or placing the vessel into a large quenching system of water at 0 °C under mild agitation.

Rheological characterization

The rheological characterization of oleogels was performed in both controlled-stress (Rheoscope, ThermoHaake, Germany) and controlled-strain (ARES, Rheometric Scientific, UK) rheometers, in a temperature range comprised between -10 and 50 °C. Small amplitude oscillatory shear (SAOS) tests, inside the linear viscoelasticity regime, were carried out in a frequency range comprised between 0.01 and 100 rad/s. A profiled plate-and-plate geometry (25 mm diameter, 1 mm gap and 0.4 relative roughness) was used. Stress or strain sweep tests, at the frequency of 1 Hz, were previously carried out on each sample to determine the linear viscoelasticity region. A bath heating unit fitted to the static plate of the tool and a convection oven that encloses the sample were used to control the temperature in the controlled-stress and controlled-strain rheometers, respectively. At least two replicates of each test were carried out on fresh samples.

Penetration and mechanical stability tests

Both unworked and worked penetrations were determined by using a Seta Universal penetrometer, model 17000-2, with one-quarter cone geometry (Stanhope-Seta, UK). The one-quarter scale penetration values were converted into the equivalent full-scale cone penetration values, according to the ASTM D 217 standard. Classical consistency NLGI grade was established according to these penetration values

(NLGI, 1994). Samples were worked during 30 minutes in a Roll Stability Tester, model 19400-3 (Stanhope-Seta, UK), and penetration measurements were carried out, once again, immediately after the rolling test and after 5 hours, in order to evaluate their mechanical stability and consistency recovery.

Measurements of the friction coefficient

A classical ball-disc tribometer was used to determine the friction coefficient, which is defined as the relationship between the applied load (normal force) and the friction force, under flooded flow lubrication, i.e. under the assumption that the lubricant is supplied to the film inlet at a sufficient flow rate. Original bearing balls made of 100Cr6 (12.7 mm diameter) were employed, all of them with the same roughness and hardness. Steel plates were made of 9SMn28. In this device, the plate rotated while the ball was kept fixed. The lubricant was spread homogeneously on the steel plate, and the ball was supported by a holder on the sample. This arm was also put in contact with a force sensor, which directly measured the friction force. The friction force was measured, during 900 s, at room temperature (25 ± 1 °C). This test was repeated three times, to obtain a quite accurate average friction factor. Taking into account sampling and measurement errors, the friction factor values had an average standard deviation of ± 0.01 . For each test, a new contact area on the ball surface was used and all surfaces were cleaned with ethanol.

4.2.3 Results and discussion

Linear viscoelasticity

a) Influence of processing thermal protocol

It is well-known that the manufacturing process of standard lithium soap-based lubricating greases is highly complex, with many thermo-mechanical variables affecting the final properties of this gel-

like dispersion, i.e. rheological behaviour and mechanical stability among others [Delgado et al., 2005; Franco et al., 2005]. On the other hand, it has been reported that the mechanism of gelification in aqueous systems is highly affected by the thermal protocol selected [Nunes et al., 2006; Zhong et al., 2004]. In the case of SMS/castor oil gels [see Sanchez, et al., 2008], the rheological behaviour is influenced by the thermo-mechanical protocol selected to induce gelification, and, especially, by the cooling profile. This effect is clearly illustrated in Figure 4.12a, where the SAOS functions, storage (G') and loss (G'') moduli, are plotted versus frequency. As can be observed, differences of around one decade are found in the values of both viscoelastic functions for SMS-based oleogels cooled under natural convection mechanism (room temperature, around 25 °C) or in water at 0 °C. On the contrary, the cooling profile applied during gelification does not significantly affect the rheological response of GMS-based oleogels, as can be seen in Figure 4.12b. Only a slight increase in the relative elastic characteristics of the sample is noticed by cooling the incipient oleogel in water at 0 °C. Thus, the influence of the thermo-mechanical processing protocol is a distinctive variable to take into account in both types of organogelators studied.

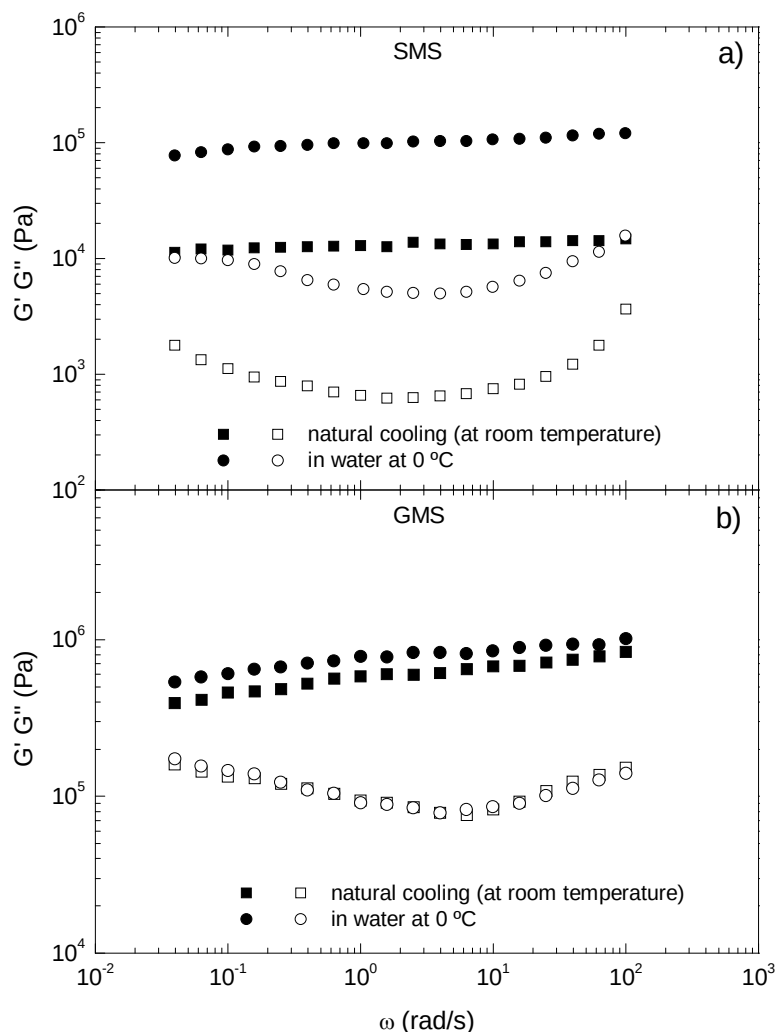


Figure 4.12. Frequency dependence of the storage and loss moduli, at 25 °C, for a) SMS/castor oil, and b) GMS/castor oil oleogels processed under different cooling profiles (G' full symbols, G'' open symbols; organogelator concentration: 20% w/w)

b) Influence of gelling agent concentration

Figure 4.13 shows the influence of gelling agent concentration on SAOS response of both SMS/castor oil and GMS/castor oil gels. As expected, the values of G' and G'' always increase with gelling agent concentration, more dramatically in the case of SMS-based gels. In addition, some qualitative differences in the rheological behaviour can be also observed. Thus, in the case of GMS-based oleogels, G' is always

larger than G'' in the whole frequency range studied, and a well-developed plateau region in the mechanical spectrum is noticed, that is an apparent minimum in G'' and a power-law relationship for G' with slopes of around 0.1-0.2. This behaviour is typical of entangled polymers [Ferry, 1980] and gel-like disperse systems [Mewis and Spaul, 1976; Franco et al., 1995; Gallegos et al., 2004; Ruiz-Márquez et al., 2010], such as standard lubricating greases [Delgado et al., 2006a; Martín-Alfonso et al., 2007, 2009]. This minimum in G'' is shifted to high frequencies for the lowest SMS concentration, yielding slightly lower values of the loss tangent ($\tan \delta = G''/G'$) (Figure 4.13d). On the contrary, for SMS-based oleogels, an extensive plateau region is only apparent for the oleogel containing the highest SMS concentration evaluated (20% w/w). At lower concentrations, a crossover between both SAOS functions (which is shifted to lower frequencies as SMS concentration decreases), and much similar values of both linear viscoelasticity functions, indicative of weak gels [Lizaso et al., 1999; Heng et al., 2005], are observed (Figure 4.13a). As a consequence, relatively high values of the loss tangent are obtained for 10% and 15% w/w SMS concentrations (Figure 4.13b).

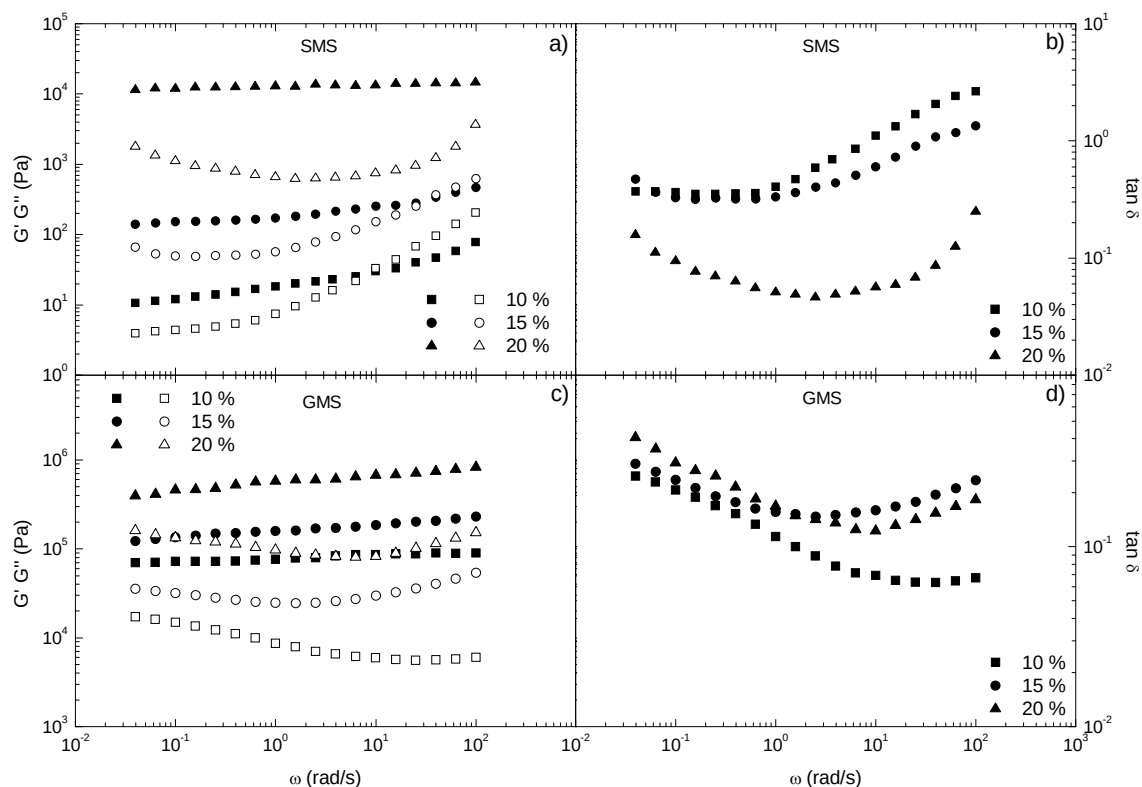


Figure 4.13. Frequency dependence of (a, c) the storage and loss moduli, and (b, d) the loss tangent, at 25 °C, for oleogels prepared with different SMS and GMS concentrations (G' full symbols, G'' open symbols)

c) Influence of temperature

Figure 4.14 shows the evolution of SAOS functions with frequency, as a function of temperature, for selected SMS- and GMS-based oleogels. No linear viscoelasticity range was detected at temperatures higher than those indicated in Figure 4.14, as a consequence of the proximity to oleogel sol-gel transition (55-60 °C). As can be expected, the values of both SAOS functions generally decrease with temperature. In addition, an evolution from the plateau to the terminal region of the mechanical spectrum can be noticed at the highest temperatures, mainly for SMS-based oleogels. On the other hand, the frequency dependence of both moduli is not highly influenced by temperature for GMS-based oleogels thus exhibiting a well-developed

plateau region even at high temperatures. Moreover, the values of SAOS viscoelastic functions are almost identical up to around 35 °C and then decrease with temperature. More surprisingly, the loss tangent is not greatly affected (data not shown), which indicates that the relative elastic characteristics of the oleogels are not influenced by temperature either.

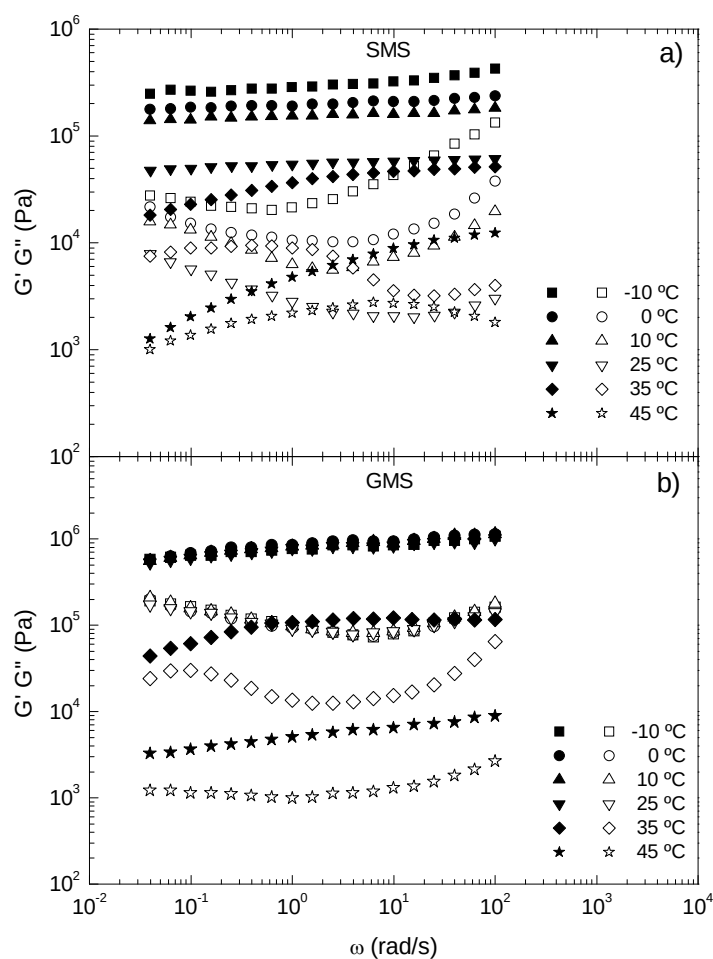


Figure 4.14. Frequency dependence of the storage and loss moduli, at different temperatures, for a) SMS/castor oil, and b) GMS/castor oil oleogels (G' full symbols, G'' open symbols; organogelator concentration: 20% w/w)

As previously reported for standard and biodegradable greases [Delgado et al., 2006b, Sánchez et al., 2008, 2011], the plateau

modulus, the characteristic viscoelastic parameter associated to the plateau region [Ferry, 1980], can be used to quantify the influence of temperature on the linear viscoelastic properties of these oleogels. An Arrhenius-type equation fit the evolution of this viscoelastic parameter with temperature fairly well:

$$G_N^0 = A \cdot e^{\frac{E_a}{R} \left(\frac{1}{T} \right)} \quad (4.2)$$

where E_a is a parameter that evaluates oleogel thermal susceptibility, similar to the activation energy (J/mol), R is the gas constant (8.314 J/mol K), T is the absolute temperature (K), and A is the pre-exponential factor (Pa).

Once again, as may be deduced from the previous discussion, different behaviour was found depending on the type of thickener used. In the case of the SMS-based oleogel, equation 4.2 fits the G_N^0 values, in the whole temperature range studied, fairly well, as can be observed in Figure 4.15. This behaviour, in a much wider temperature range, was observed in biodegradable greases manufactured with castor oil and cellulosic derivatives [Sánchez et al., 2008, 2011]. On the contrary, two different Arrhenius-type equations are necessary to fit the evolution of the GMS-based oleogel. Thus, the thermal susceptibility of this oleogel is very low (SAOS viscoelastic functions values almost constant) below a critical temperature, whilst oleogel thermal susceptibility is much more dramatic above it. This last behaviour is quite similar to that shown by standard lithium lubricating greases [Delgado et al., 2006b]. In this sense, the E_a value (Figure 4.15) found for the GMS-based gel in the low-temperature range is similar to those obtained for lithium lubricating greases up to around 110 °C. Above this temperature, the thermal dependence of lithium greases is more similar to that shown by the SMS-based oleogel. Evidently, in any case, the sol-gel transition temperature of these oleogels limits their potential use as biodegradable grease formulations to low temperature in-service applications.

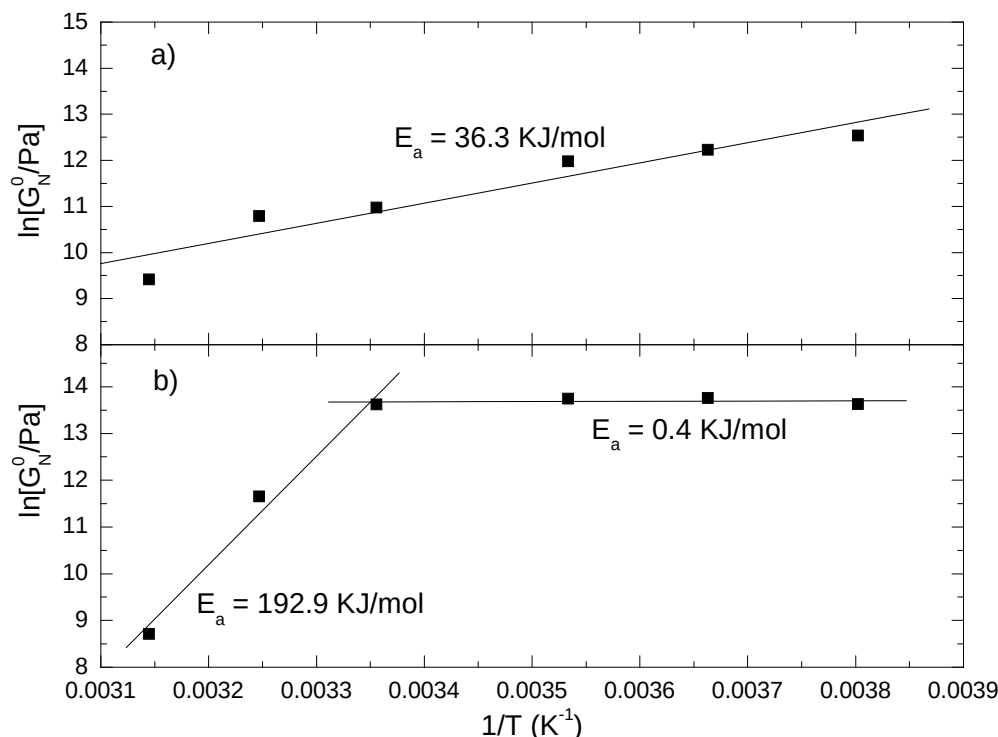


Figure 4.15. Evolution of the plateau modulus with temperature, and equation 4.2 fitting, for a) SMS/castor oil, and b) GMS/castor oil oleogels (organogelator concentration: 20% w/w)

d) Influence of vegetable oil nature

As discussed elsewhere [Quinchia et al., 2010], castor oil is much more viscous than the rest of conventional vegetable oils, which represent an important advantage for lubricating purposes. However, its high content in ricinoleic acid (see Table 4.4) yields a poor stability to oxidation. Figure 4.16 shows the evolution of SAOS viscoelastic functions with frequency for oleogels prepared with SMS or GMS and different vegetable oils. Some unexpected experimental result can be observed. The lowest G' and G'' values were obtained for oleogels prepared with the most viscous oil, i.e. castor oil, both for SMS- and GMS-based oleogels. On the contrary, significantly higher values of the linear viscoelastic functions were found for gels prepared with low-viscosity oils, like rapeseed and soybean oils. However, an extensive

plateau region, with almost identical relative elastic characteristics in a wide frequency range (Figures 4.16b and 4.16d), was noticed in all cases. Only at the highest frequencies, lower values of the loss tangent can be observed for oleogels prepared with low-viscosity oils, especially in the case of those containing soybean oil, as a consequence of the displacement of the minimum in G'' to higher frequencies. Similar results were previously found with standard lithium soap-based lubricating greases manufactured with paraffinic oils of different viscosities (Delgado et al., 2006a). Larger gel strength, associated to enhanced elastic properties, was found in greases prepared with low-viscosity paraffinic oils. This fact was attributed to a higher solvency between the base oil and the thickener agent, which reinforces the gel network.

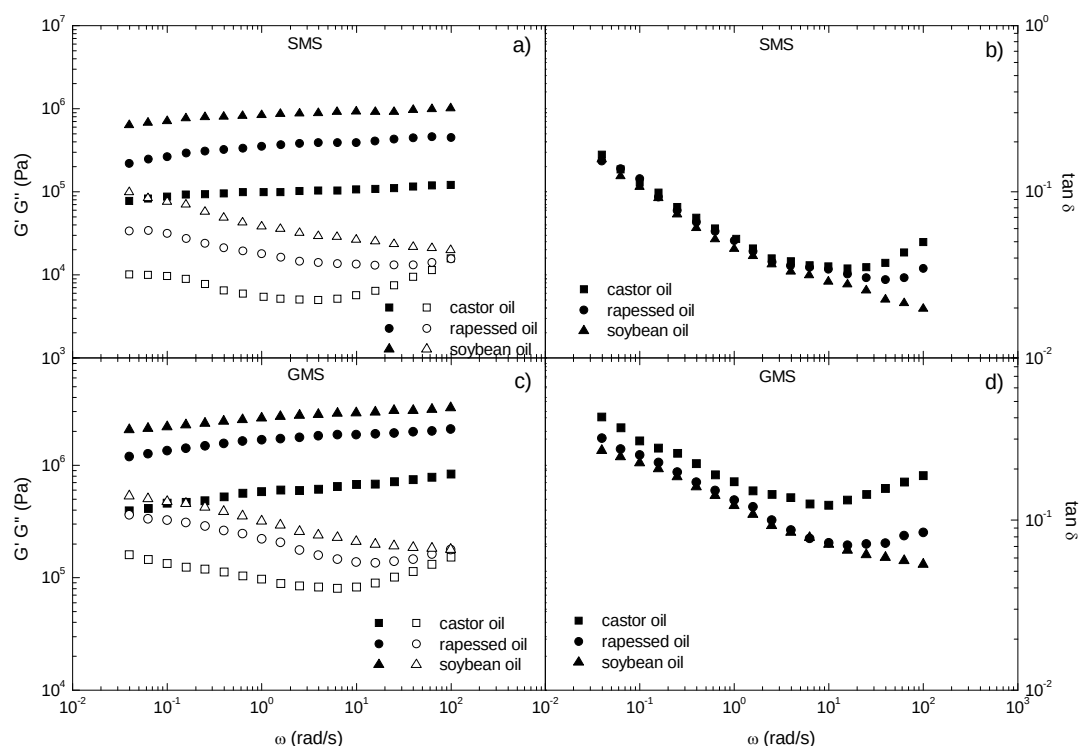


Figure 4.16. Frequency dependence of (a, c) the storage and loss moduli, and (b, d) the loss tangent, at 25 °C, for SMS- and GMS-based oleogels containing different vegetable oils (G' full symbols, G'' open symbols; organogelator concentration: 20% w/w)

Lubrication performance-related properties

Some lubrication performance-related properties of the oleogels studied have been analyzed according to standard mechanical stability tests and tribological experiments, and compared with those shown by two target lithium lubricating greases, based on paraffinic and naphthenic oils, respectively (Table 4.5). Consistency is a widely-accepted technological parameter for lubricating greases, obviously related to the rheological behaviour, which is usually evaluated in the industry of lubricants through standard penetration tests. Penetration values of unworked samples are traditionally converted to NLGI grades, in order to classify greases according to their consistency degree (between 000 and 6). The most commonly used greases are those with NLGI grade 2. Softer grades, especially 0 and 1, are sometimes used for improved pumpability or low-temperature applications, while higher consistency indexes are used for certain high-speed bearings [NLGI, 1994]. Table 4.5 collects unworked penetration values for the different oleogels studied. As can be seen, SMS-based oleogels show lower consistency values than GMS-based oleogels, being the NLGI grades of the later comparable to those displayed by mineral oil-based greases. Table 4.5 also includes information about the mechanical stability of the samples analyzed, determined as the difference between penetration indexes after and before submitting the grease to a standard working test, in this case a shear rolling test. Greases having appropriate mechanical stability must exhibit penetration increments after working close to zero. As can be observed in Table 4.5, oleogels penetration values obtained after working are generally much higher than those shown by model lithium greases, especially for SMS-based samples (>900 dmm), which indicate a very poor mechanical stability. GMS-based oleogels exhibit much lower penetration values after working, but only the GMS/castor oil gel shows a suitable mechanical stability (penetration increment of 37 dmm). However, the oleogels studied present a high level of consistency recovery, during sample storage, after working test cessation. Thus, as can be observed in Table 4.5,

oleogels penetration values, after 5 hours ageing at rest, are similar to the unworked penetration values, especially in the case of GMS-based gels.

Lubricating Grease			Unworked penetration (dmm)	NLGI grade	Worked penetration (dmm)	Penetration variation (dmm)	Recovery penetration, after 5 h at rest (dmm)
Oil	Thickener	Thickener concentration (% w/w)					
Castor	SMS	20	415	00	>1000	>551	380
	GMS		265	2	302	37	264
Rapessed	SMS		313	1	929	616	823
	GMS		259	2	391	132	290
Soybean	SMS		325	1	903	578	489
	GMS		249	3	339	90	275
Naphthenic (*)	Lithium soap	14	274	2	289	15	-
Paraffinic (**)	Lithium soap	20	303	1-2	305	2	-

(*) data from Martin-Alfonso et al. (2009)

(**) data from Delgado et al. (2006a)

Table 4.5. Penetration values and mechanical stability for oleogel formulations and some reference lithium lubricating greases

Finally, the potential applicability of these oleogels as biodegradable lubricating greases has been also investigated in a tribological contact. Table 4.6 shows the friction coefficient values, obtained in a ball-disc tribometer, for selected castor oil-based oleogel samples compared to those found for model lithium greases. As can be observed, the oleogel samples studied in this work show lower friction coefficient values than model mineral oil-based lithium greases. As previously discussed [Sánchez et al., 2008], this suitable tribological response is mainly determined by the base oil employed. In this sense, Adhvaryu and co-workers (2004) pointed out that vegetable oils present optimum lubricity, lowering, more effectively, the frictional forces in comparison to other mineral oils of similar kinematic viscosities.

Sample	Friction coefficient
Castor oil/SMS (20% w/w)	0.063
Castor oil/GMS (20% w/w)	0.057
Naphthenic oil/lithium soap (14% w/w)	0.090
Paraffinic /lithium soap (20% w/w)	0.105

Table 4.6. Friction coefficient values for selected oleogels and reference lithium lubricating greases



CAPÍTULO 5

OLEOGELES FORMULADOS CON CELULOSA Y ALGUNOS DERIVADOS QUÍMICOS

5.1 Preliminary evaluations

5.1.1 Introduction

In this section, some preliminary studies on the formulation of oleogels containing α -cellulose and ethyl cellulose as thickeners agents are presented. In particular, some processing conditions and thickener concentrations have been evaluated, in order to select the best ones to formulate and manufacture this type of oleogels. In all cases, castor oil was used as base oil.

5.1.2 Influence of processing conditions

In order to study how processing variables affect the SAOS response and mechanical stability of this type of oleogels, different samples were manufactured by modifying the geometry used during the mixing process, processing time, temperature and agitation speed of the impeller either during the mixing step, in the case of those oleogels manufactured only with α -cellulose, or during the cooling step for oleogels manufactured with both ethyl cellulose and α -cellulose.

Influence of mixing geometry

Firstly, three oleogels containing castor oil and 25% (w/w) α -cellulose were manufactured using three different mixing tools: a helical ribbon, an anchor impeller and the Polylab roller-blades system (described in Chapter 3). The agitation speed was set at 60 rpm for both, helical ribbon and anchor impeller, while, in the case of Polylab, a roller agitation speed of 50 rpm was established. The mixing process was performed, at room temperature, for 30 minutes.

As can be seen in Figure 5.1, these oleogels show, in all cases, qualitatively similar mechanical spectra with the storage modulus always higher than the loss modulus in the whole frequency range studied. The “plateau” region of the mechanical spectrum is always

apparent having both moduli a similar evolution than those found in standard lubricating greases [Delgado et al., 2005; Franco et al., 2005; Madiedo et al., 2000; Martín-Alfonso et al., 2007], with the difference that their values are around one decade higher than the typical values obtained for commercial lubricating greases.

Oleogels manufactured with helical ribbon and anchor impeller show almost identical rheological response. However higher values of G' and slightly lower values of G'' , and, consequently, a decrease in the loss tangent were obtained in the case of the oleogel manufactured with the Polylab system.

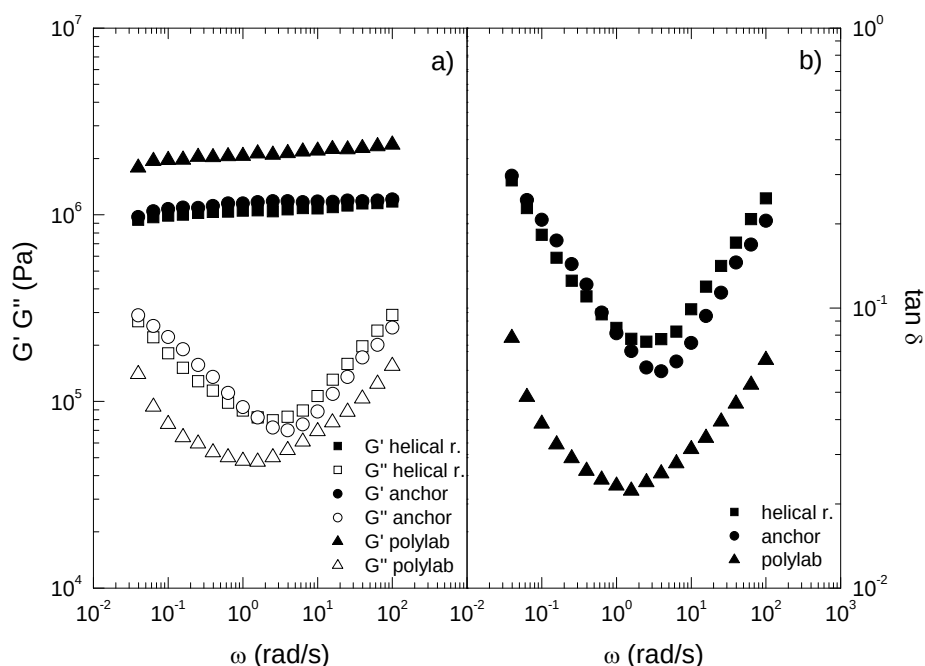


Figure 5.1. Evolution of the storage and loss moduli (a) and loss tangent (b) with frequency for α -cellulose based-oleogels manufactured with different types of mixing geometries (25% w/w α -cellulose in castor oil mixed at 50-60 rpm during 30 minutes at room temperature)

In spite of these differences in SAOS response, almost identical penetration values, before and after sample working, in the mechanical stability test, have been found in all cases (see Table 5.1).

Mixing geometry	Unworked penetration (dmm)	NLGI grade	Worked penetration (dmm)	Penetration variation (dmm)
Helical ribbon	324	1	354	30
Anchor	320	1	354	34
Polylab	324	1	354	30

Table 5.1. Penetration values of oleogels manufactured with different types of mixing geometries (25% w/w α -cellulose in castor oil mixed, at 50-60 rpm and during 30 minutes, at room temperature)

Influence of processing temperature

In order to study the effect that processing temperature exerts on the final characteristic of this type of oleogels, three new oleogel samples were processed using the helical ribbon as mixing geometry, by applying an agitation speed of 60 rpm, for 30 minutes, and at temperatures of 50, 100 and 150 °C, respectively. In Figure 5.2, the mechanical spectra of these oleogels have been compared with that processed at room temperature. As can be observed, a slight decrease in G' and no significant differences in G'' were found by increasing processing temperature. Moreover, the minimum in G'' is shifted to higher frequencies when the processing temperature is raised to 100 or 150 °C. The loss tangent shows a slight increase with processing temperature at low frequencies, but tends to similar values at high frequencies.

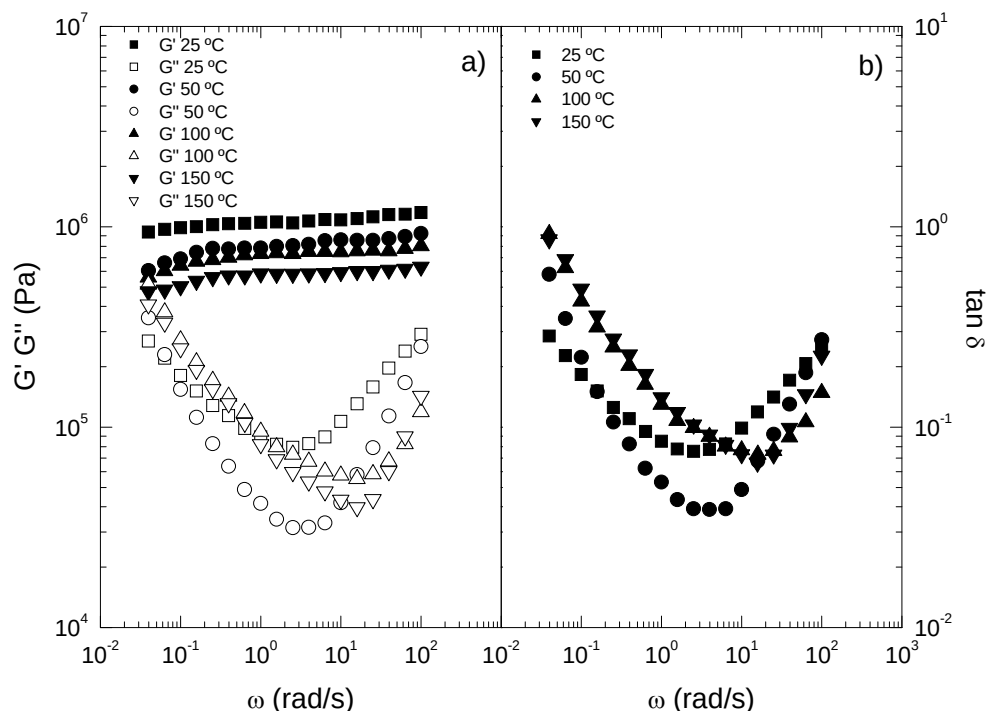


Figure 5.2. Evolution of the storage and loss moduli (a) and loss tangent (b) with frequency for oleogels manufactured at different processing temperatures (25% w/w α -cellulose in castor oil mixed with the helical ribbon geometry, at 60 rpm, during 30 minutes)

Table 5.2 shows the penetration values of oleogels processed at different temperatures. Unworked and worked penetration values as well as the penetration increment, increase with processing temperature.

Processing temperature (°C)	Unworked penetration (dmm)	NLGI grade	Worked penetration (dmm)	Penetration variation (dmm)
25	324	1	354	30
50	354	0-1	403	49
100	358	0	437	79
150	362	0	459	98

Table 5.2. Penetration values of oleogels manufactured at different processing temperatures (25% w/w α -cellulose in castor oil mixed with the helical ribbon geometry at 60 rpm during 30 minutes)

Influence of processing time

Three oleogel samples were processed with the helical ribbon geometry, at 60 rpm and room temperature, modifying the mixing time (15, 30 and 60 minutes, respectively). As can be seen in Figure 5.3, this processing variable does not affect the SAOS response of the oleogels studied. Furthermore, the consistency and mechanical stability of the oleogels are not influenced by processing time (Table 5.3). Therefore, 15 minutes is enough time to obtain homogeneous gels using α -cellulose as thickener.

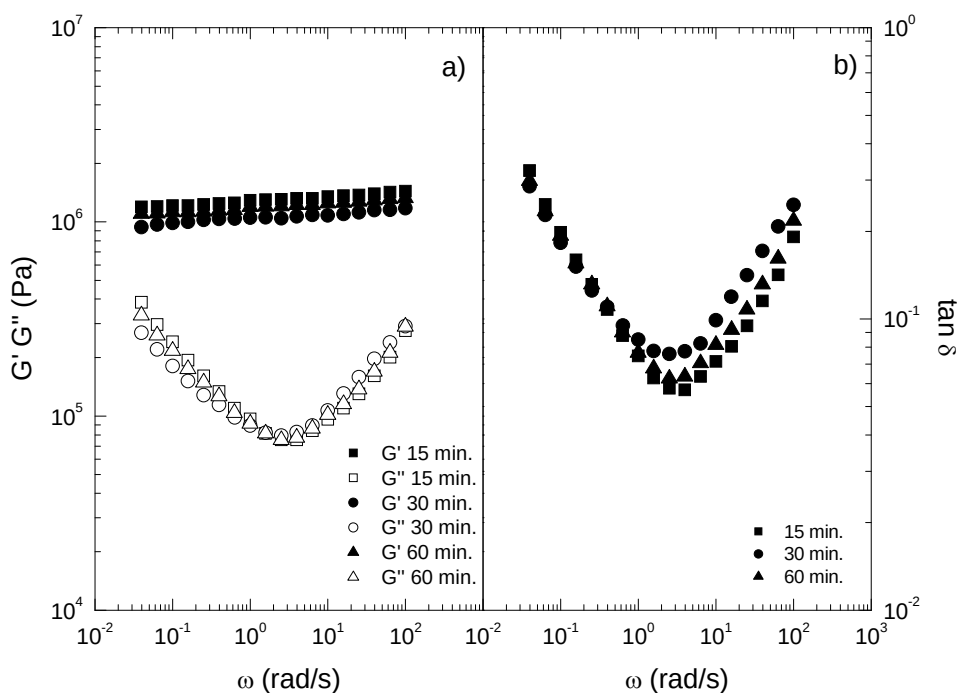


Figure 5.3. Evolution of the storage and loss moduli (a) and loss tangent (b) with frequency for oleogels manufactured applying different processing times (25% w/w α -cellulose in castor oil mixed with the helical ribbon geometry, at 60 rpm, at room temperature)

Processing time (minutes)	Unworked penetration (dmm)	NLGI grade	Worked penetration (dmm)	Penetration variation (dmm)
15	320	1	350	30
30	324	1	354	30
60	320	1	350	30

Table 5.3. Penetration values of oleogels manufactured applying different processing time (25% w/w α -cellulose in castor oil mixed with the helical ribbon geometry, at 60 rpm, at room temperature)

Influence of agitation speed

Three oleogel samples were processed using the helical ribbon geometry, by applying agitation speeds of 60, 100 and 150 rpm for 30 minutes at room temperature. Once again, this processing variable does neither significantly affect the rheological response (Figure 5.4) nor the mechanical stability (Table 5.4) of these oleogels.

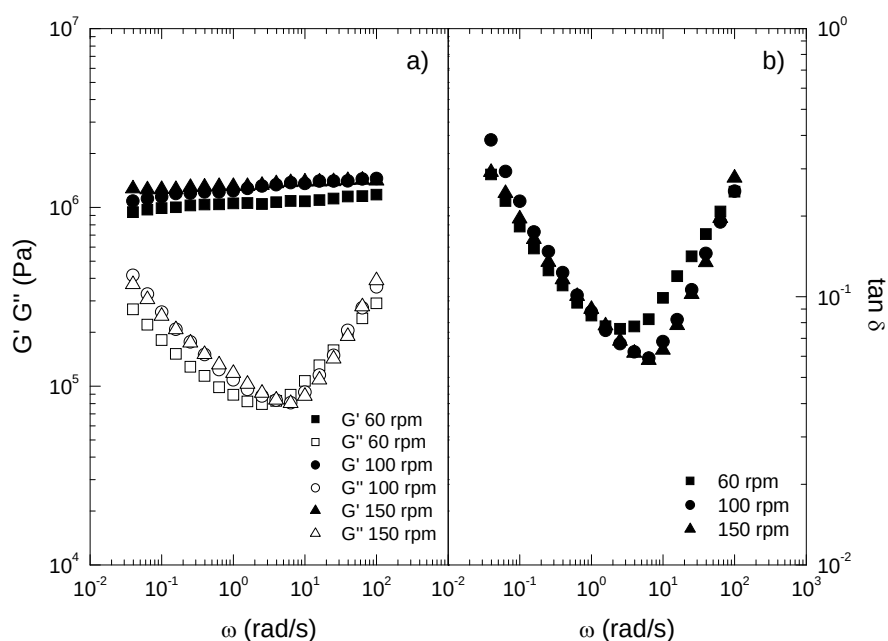


Figure 5.4. Evolution of the storage and loss moduli (a) and loss tangent (b) with frequency for oleogels manufactured applying different agitation speeds (25% w/w α -cellulose in castor oil mixed with the helical ribbon geometry during 30 minutes at room temperature)

Agitation speed (rpm)	Unworked penetration (dmm)	NLGI grade	Worked penetration (dmm)	Penetration variation (dmm)
60	324	1	354	30
100	320	1	358	38
150	317	1	347	30

Table 5.4. Penetration values of oleogels manufactured applying different agitation speed (25% w/w α -cellulose in castor oil mixed with the helical ribbon geometry during 30 minutes at room temperature)

Influence of cooling profile

Oleogels processed with a single thickener display values of the storage and loss moduli much higher than conventional lubricating greases. It has been experimentally verified that increasing the viscosity of the oil used in the manufacture of the oleogels generates more desirable properties. In particular, the use of ethyl cellulose at low concentration in the formulation of the oleogels is proposed in this work to yield a significant viscosity modification in the vegetable oil, which confers better physical stability and mechanical properties to the final product. Since it is necessary to reach a temperature of around 150 °C to dissolve the ethyl cellulose in the vegetable oil, it is interesting to know the effect that cooling rate exerts on the final properties of oleogels. With this purpose, three oleogels were manufactured using castor oil, 2% (w/w) ethyl cellulose and 20% (w/w) α -cellulose. The manufacturing process was carried out by heating the total amount of castor oil and ethyl cellulose up to 150 °C under agitation, using the helical ribbon geometry, at 60 rpm. These conditions were kept until the entire amount of ethyl cellulose was completely dissolved in the vegetable oil. In this moment, α -cellulose was added and the agitation variables kept constant for other 30 minutes to get an effective homogenization. Afterwards, three different cooling profiles were applied on the sample by placing the vessel into a bath with water at either 25 °C, with (60 rpm) or without agitation, or 0 °C, without agitation.

As shown in Figure 5.5, oleogels that were submitted to agitation during the cooling step display a well-developed plateau region and the storage and loss moduli increase with cooling rate under static conditions. Moreover, increasing the cooling rate by means of agitation produces a significant softening of this material, lowering the storage modulus, which also show a tendency to a crossover with G'' at low frequencies. As a consequence, higher values of the loss tangent were obtained for this system.

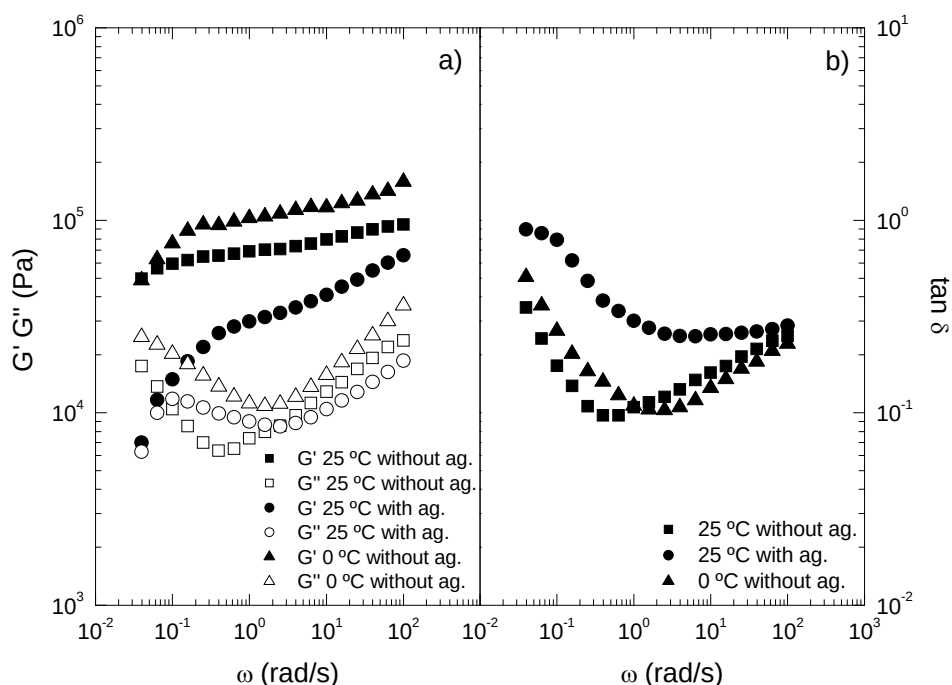


Figure 5.5. Evolution of the storage and loss moduli (a) and loss tangent (b) with frequency for oleogels manufactured applying different cooling profiles (2% w/w ethyl cellulose and 20% w/w α -cellulose in castor oil mixed with the helical ribbon geometry, at 60 rpm during 30 minutes, at 150 °C)

Moreover, penetration values increase with cooling rate, especially when agitation was introduced (Table 5.5). Optimum mechanical stability (lower penetration variation) was obtained by applying the lower cooling rate, i.e. placing the vessel in a bath with water at 25 °C without agitation.

Cooling conditions (rpm)	Unworked penetration (dmm)	NLGI grade	Worked penetration (dmm)	Penetration variation (dmm)
25 °C without agitation	324	1	354	30
25 °C with agitation	418	00	463	45
0 °C without agitation	369	0	440	71

Table 5.5. Penetration values of oleogels manufactured applying different cooling profiles (2% w/w ethyl cellulose and 20% w/w α -cellulose in castor oil mixed with the helical ribbon geometry, at 60 rpm during 30 minutes, at 150 °C)

5.1.3 Influence of α -cellulose concentration

The rheological response of olegels containing 20, 25 and 30% (w/w) α -cellulose, processed under the same conditions, has been compared (see Figure 5.6). As may be observed, an increase in α -cellulose concentration yields an important increase in both SAOS moduli (Figure 5.6a) but no significant changes in the relative elastic characteristics (Figure 5.6b).

The lower α -cellulose concentration used results in G' and G'' values much more similar than those obtained for standard lubricating greases. However, this concentration is not sufficient to avoid oil separation, usually known as “oil bleeding”. On the contrary, the oleogel containing 30% (w/w) α -cellulose is highly stable, although the SAOS moduli are much higher than those required for lubricating greases.

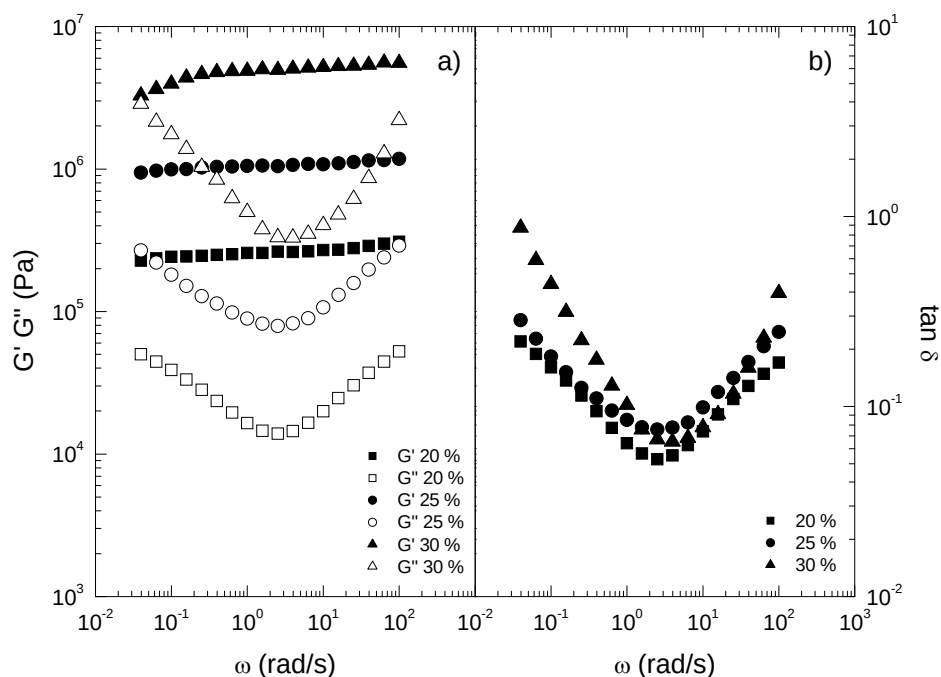


Figure 5.6. Evolution of the storage and loss moduli (a) and loss tangent (b) with frequency for oleogels manufactured using different α -cellulose concentration (α -cellulose in castor oil mixed with the helical ribbon geometry, at 60 rpm during 30 minutes, at room temperature)

Moreover, as can be seen in Table 5.6, an increase in α -cellulose concentration produces a decrease in both, unworked and worked penetration values and, consequently, the NLGI degree increases drastically in the case of oleogel containing 30% (w/w) α -cellulose. However, optimum mechanical stability was obtained by adding 25% (w/w) α -cellulose.

α -cellulose concentration (%)	Unworked penetration (dmm)	NLGI grade	Worked penetration (dmm)	Penetration variation (dmm)
20	380	0	482	102
25	324	1	354	30
30	170	4-5	272	101

Table 5.6. Penetration values of oleogels manufactured using different α -cellulose concentration (α -cellulose in castor oil mixed with the helical ribbon geometry, at 60 rpm during 30 minutes, at room temperature)

5.1.4 Selection of processing parameters

Taking into account these preliminary studies, it can be concluded that:

- ✓ The best geometry to manufacture these oleogels is the helical ribbon, since it generates oleogels with lower relative elasticity than those processed using the Polylab mixing device. Moreover, processing with helical ribbon does not present any type of overload, frequently registered with the anchor geometry.
- ✓ It has been proved that 15 minutes mixing time is sufficient to obtain a proper oleogel. However, when the viscosity of castor oil is modified by adding ethyl cellulose, 30 minutes is set as the best mixing time.
- ✓ Agitation speed has not a significant effect on the rheological properties of the final oleogel. In this sense, the lowest agitation speed (60 rpm) has been selected as standard speed during oleogel manufacture.
- ✓ Although the values of oleogel linear viscoelastic moduli decrease as processing temperature increases, this reduction is rather slight. As a consequence, 25 °C was selected as very convenient processing temperature. Obviously, when ethyl cellulose is added to the oleogel formulation, it is necessary to reach 150 °C to solve this cellulose derivative in the oil medium.
- ✓ Oleogels containing ethyl cellulose in their formulations (processing temperature 150 °C) must be cooled down without agitation by placing the vessel in a bath with water at 25 °C.
- ✓ The optimum α -cellulose concentration is 25% taking into account the penetration values obtained. However, the addition of ethyl cellulose allows a reduction in this concentration and improves oleogel rheological behaviour, decreasing both SAOS moduli and increasing its physical stability.

5.2 Development of new green lubricating grease formulations based on cellulosic derivatives and castor oil

5.2.1 Introduction

It is well known that the use of renewable resources for different industrial applications has a remarkable importance in our society, due to its positive effect on the environment. Among these renewable resources, cellulose derivatives and vegetable oils are increasingly taken into account. Thus, for instance, cellulose has been used in biocomposites for packaging applications [Kumar and Singh, 2008], whilst vegetable oils have been employed as biodegradable raw material in a wide range of new applications [Gryglewicz et al., 2003; Honary, 1996; Dmytryshyn et al., 2004].

From a general perspective, there is a marked tendency to increase the use of eco-friendly consumer products, as a result of government regulations, or due to increasing public concern for a pollution-free environment [Adhvaryu and Erhan, 2002]. More particularly, the lubricant industry and its customers are keen on products that do not diminish the world finite resources of mineral hydrocarbons, and/or exert minimal adverse impact on the environment [Wilson, 1998; Nurun Nabi et al., 2006; Boyde, 2002]. 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. Mineral-based oils can contaminate groundwater for up to 100 years, which may inhibit trees' growth and be toxic to aquatic life [Wilson, 1998]. In addition to this, large amounts of money have been spent to clean up accidental oil spills [Adhvaryu and Erhan, 2002; Adesodun and Mbagwu, 2008]. To minimise the contamination damage that petroleum-based products cause in the environment, there has been an increasing demand for green products suitable to be used as

lubricants [Wilson, 1998], where cellulose-based oleogels may play an important role as environmentally friendly substitutes.

Oleogels are gel systems obtained with a gelling agent and a hydrophobic liquid. In previous studies [Almeida and Bahia, 2005; Almeida and Bahia, 2006], organogelators like ethylcellulose, cholesterol, sorbitan monostearate and lanolin alcohols were tested with several organic solvents, including vegetable oils. The main advantages of these gels are that they do not require extensive manufacturing expertise to be produced [Almeida and Bahia, 2006], in contrast to traditional soap-based lubricating greases which require a particular and rather sophisticated technology with several processing stages [Ishchuk, 2005; Delgado et al., 2005; Franco et al., 2005], and they can exhibit permanent rigid networks or transient thermoreversible semiflexible meshes [Almeida and Bahia, 2005].

Over the last fifteen years, there has been an increasing interest on these oleogels [Almeida and Bahia, 2006; Ruíz Martínez et al., 2003; Bot et al., 2009]. Among their potential applications, biodegradable oleogels could be used as lubricating greases. In a previous work [Sánchez et al., 2008], the possibility of using oleogels based on sorbitan monostearate (SMS) and castor oil for lubricating purposes was explored. However, in spite of the promising rheological characteristics found, the use of SMS as organogellator confers to the final product some limitations, mainly related to the maximum working temperature that can be reached and to its rather poor mechanical stability.

Although some work concerning biogreases development has been previously carried out by other authors [Adhvaryu et al., 2005a; Dresel, 1994], it has been mainly focused on the replacement of mineral oil by vegetable oil. Among the vegetable oils, the castor oil is being occasionally used for lubricant purposes due to its high viscosity and good performance characteristics at low temperatures [Asadauskas et

al., 1996]. However, the research of new biodegradable thickeners, as substitutes for metal soaps or polyurea, is up to now much less explored. In this work, the use of cellulose derivatives, aiming to obtain biodegradable lubricating greases completely based on natural products, is reported. The performance of these cellulose derivatives-based oleogels was investigated through rheological, thermal, and standard mechanical tests.

5.2.2 Materials and Methods

Materials

Castor oil (211 cSt at 40 °C, Guinama, Spain) was selected as biodegradable lubricating oil. The fatty acid composition of castor oil is shown in Table 5.7. Ethyl cellulose (Mn 66000 g/mol; 49% ethoxy content), methyl cellulose (Mn 40000 g/mol; 32% methoxy content), cellulose acetate (Mn 50000 g/mol; 39.7% acetyl content), and α -cellulose, all of them from Sigma-Adrich, were used as gelling agents to prepare different oleogel formulations. Standard lithium 12-hydroxystearate lubricating greases (14-20% lithium soap) of similar NLGI grade were used as reference systems. 12-hydroxystearic acid, lithium hydroxide, and paraffinic (334 cSt at 40 °C) and naphthenic (115 cSt at 40 °C) mineral oils were kindly supplied by Verkol Lubricantes S.A. (Spain).

Fatty acid	%
Palmitic acid (C16:0)	2.6
Estearic acid (C18:0)	2.7
Oleic acid (C18:1)	6.3
Linoleic acid (C18:2)	10.8
Ricinoleic acid (12-hidroxi C18:1)	77.6

Table 5.7. Fatty acid composition of the castor oil used to prepared oleogels

Manufacture of oleogel formulations

Castor oil and cellulose derivatives were mixed using a Polylab-Rheomix 3000p (Haake, Germany), which consists of a batch mixer fitted with two counter-rotating rollers. Specifically, the chamber (310 cm³) was first filled with the corresponding amount of oil in the blend. The cellulose derivative was then slowly added to the castor oil. Batches of 250 g oleogel were prepared. A constant rotational speed (50 rpm) was applied to this mixture, for 30 minutes, at room temperature. The mixture was previously heated, up to 150 °C, only for samples containing ethyl cellulose, and then cooled by natural convection. The reason for using this type of mixing device is due to the high viscosity of these formulations, especially during the first stages.

Specific thickener concentrations are required to obtain stable oleogels, with visual appearance similar to traditional lubricating greases, depending on the cellulose derivative employed. In the case of formulations without ethyl cellulose, stable oleogel formulations were achieved by dispersing, at room temperature, 35% w/w methyl cellulose (COMC35), 35% w/w cellulose acetate (COAC35), or 25% w/w α -cellulose (CO α C25), respectively, in castor oil. Lower cellulose derivative concentrations yield low consistency indexes (NLGI grade 000) and low physical stability, evidenced by an apparent oil separation after several days of ageing. On the other hand, higher cellulose derivative concentrations than those previously mentioned provide highly strong oleogels, with physical appearance very different to traditional lubricating greases. In the case of formulations prepared by adding 2% w/w ethyl cellulose, stable oleogel samples were obtained with 25% and 30% w/w methyl cellulose (COECMC25 and COECMC30), and 20% w/w α -cellulose (COEC α C20). Cellulose acetate does not seem to be compatible with ethyl cellulose, and does not produce a gel-like material that could be considered as lubricating grease.

Gas chromatography (GC)

GC analysis was performed with an Agilent 6890 (HP, USA) chromatograph equipped with a flame-ionization detector in order to determine the fatty acid profile in castor oil. C14-C24 FAMES provided standards were used.

Thermogravimetric analysis (TGA)

Thermogravimetric analyses were carried out by using a Q-50 (TA Instruments Waters, USA) under N₂ and O₂ purge. Approximately, 15 mg of each sample were placed on a Pt pan, and heated from 30 °C to 500 °C at 10 °C/min.

Rheological characterization

Rheological characterization of oleogels was carried out with two controlled-stress rheometers (RS-150 and Rheoscope, ThermoHaake, Germany). Small-amplitude oscillatory shear (SAOS) tests were performed inside the linear viscoelastic region, using a serrated plate-plate geometry (35 mm, 1 mm gap, relative roughness 0.4), in a frequency range of 10⁻²-10² rad/s, and temperatures comprised between 0 and 225 °C. At least two replicates of each test were performed on fresh samples.

Penetration and mechanical stability tests

Both unworked and worked penetration indexes were determined according to the ASTM D 1403 standard, by using a Seta Universal penetrometer, model 17000-2, with one-quarter cone geometry (Stanhope-Seta, UK). The one-quarter scale penetration values were converted into the equivalent full-scale cone penetration values, following the ASTM D 217 standard. Samples were worked during 2 hours in a Roll Stability Tester, model 19400-3 (Stanhope-Seta, UK) according to the ASTM D 1831 standard, and penetration

measurements were carried out, once again, immediately after this rolling test.

Leakage tendencies in wheel bearings

Oleogel leakage tendencies in wheel bearings were determined in a Petrotest equipment, model 17-0450 (Germany), according to the ASTM D 1263 standard. This test method covers the evaluation of the leakage tendencies of lubricating greases when they are tested under specific simulated wheel bearing conditions. The sample is distributed in a modified front-wheel hub and spindle assembly. The hub is rotated at a speed of 660 ± 30 rpm for 6 hours $\pm$ 5 minutes, at a spindle temperature which is raised to and then maintained at 105 ± 1.2 °C. Leakage of the sample is measured, and the condition of the bearing surface is checked at the end of the test.

5.2.3 Results and Discussion

Oleogel formulations without ethyl cellulose

Figure 5.7 shows oleogel weight loss with temperature, using N₂ flux, for a selected formulation containing α -cellulose as thickener. Its derivative function is also shown in this figure. Table 5.8 shows the most characteristic parameters obtained from this thermogravimetric analysis for all the oleogel formulations studied. In general, the thermal decomposition of the oleogels studied takes place in one single stage, comprised between 340 and 415 °C, approximately. The thermal stability of oleogels has been estimated from the onset temperature (T_{onset}), which is determined from the interception between the slope of the first region, where the sample weight is approximately constant, and the slope of the region where sample weight loss rate is maximum. The sample containing α -cellulose displays a slightly lower thermal stability (lower T_{onset}), being its maximum decomposition rate reached at lower temperature (T_{max}). The oleogel containing methyl cellulose shows the highest T_{onset} value, although the sample that exhibits the maximum

decomposition rate at a higher temperature is the oleogel prepared with acetate cellulose, which also contains a larger amount of residues. In general, oleogels based in cellulose derivatives show slightly higher T_{onset} and T_{max} values than a standard grease prepared with the same castor oil and a lithium soap (sample COLi), and much higher values than the standard grease prepared with a mineral paraffinic oil, fact that can be explained by considering the lower volatility of castor oil.

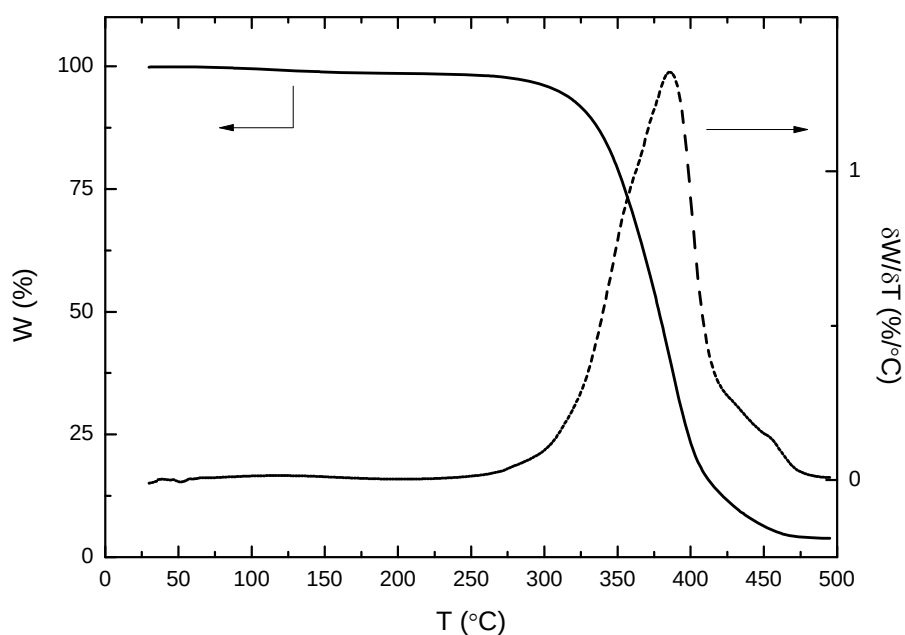


Figure 5.7. TGA thermogram for a selected oleogel (CO α C25). Test performed under nitrogen atmosphere

Sample	Atmosphere	T _{range}		T _{max} (°C)	Residue (%)
		T _{onset} (°C)	T _{final} (°C)		
COMC35	N ₂	353	401	370	3.0
	O ₂	334	---	360	5.9
COAC35	N ₂	348	412	376	4.6
	O ₂	338	---	367	10.8
CO α C25	N ₂	341	413	368	3.8
	O ₂	283	---	367	4.1
COECMC25	N ₂	354	402	377	3.0
	O ₂	348	---	368	5.4
COECMC30	N ₂	351	399	378	3.7
	O ₂	330	---	362	7.5
COEC α C20	N ₂	347	417	388	3.2
	O ₂	313	---	364	8.3
COLi	N ₂	329	403	362	0.3
	O ₂	321	---	357	14.3
Standard paraffinic oil-based grease	N ₂	188	---	245	3.8
	O ₂	181	---	245	1.3

Table 5.8. Characteristic parameters obtained from TGA measurements

Oleogel weight loss with temperature for the same samples, using oxygen flux during the thermogravimetric analysis, shows that the onset temperatures are always significantly lower than the ones obtained using nitrogen, especially in the case of the sample prepared with α -cellulose, which shows a T_{onset} even lower than COLi sample. In addition, the maximum decomposition rate is also reached at lower temperature. An increase in the residual content using an oxygen atmosphere is apparent. These effects must be attributed to different oxidative processes occurred in both the cellulose derivatives [Azambre et al., 2000; Cancellieri et al., 2005] and the castor oil [Fox and Stachowiak, 2007]. It is well known that other vegetable oils not containing hydroxyl groups in the predominant fatty acids, for instance soy or sunflower oils, are more resistant to oxidation than castor oil [Asadauskas et al., 1996]. However, the high viscosity provided by the castor oil is crucial to reduce both the oil separation and the leakage tendency of oleogels. In any case, more work is needed to find a balance between the benefits of oil viscosity and resistance to oxidation.

Figures 5.8 and 5.9 show the evolution of the linear viscoelasticity functions with frequency, as a function of temperature, for the different samples studied. This evolution is similar to those found for traditional lubricating greases [Madiedo et al., 2000; Martín-Alfonso et al., 2007]. As can be observed, G' is always higher than G'' in the whole frequency range studied, except for the formulation that contain cellulose acetate at 225 °C, which displays a crossover between both viscoelastic functions at high frequencies. The plateau region of the mechanical spectrum is always noticed, which is not qualitatively affected by temperature, oppositely to the behaviour found for most of standard greases [Delgado et al., 2006b]. Moreover, oleogel elastic network seems to resist higher temperatures than metallic soap-based greases. Thus, standard grease elastic network vanishes above the soap melting point, that is, around 200 °C in the case of lithium greases.

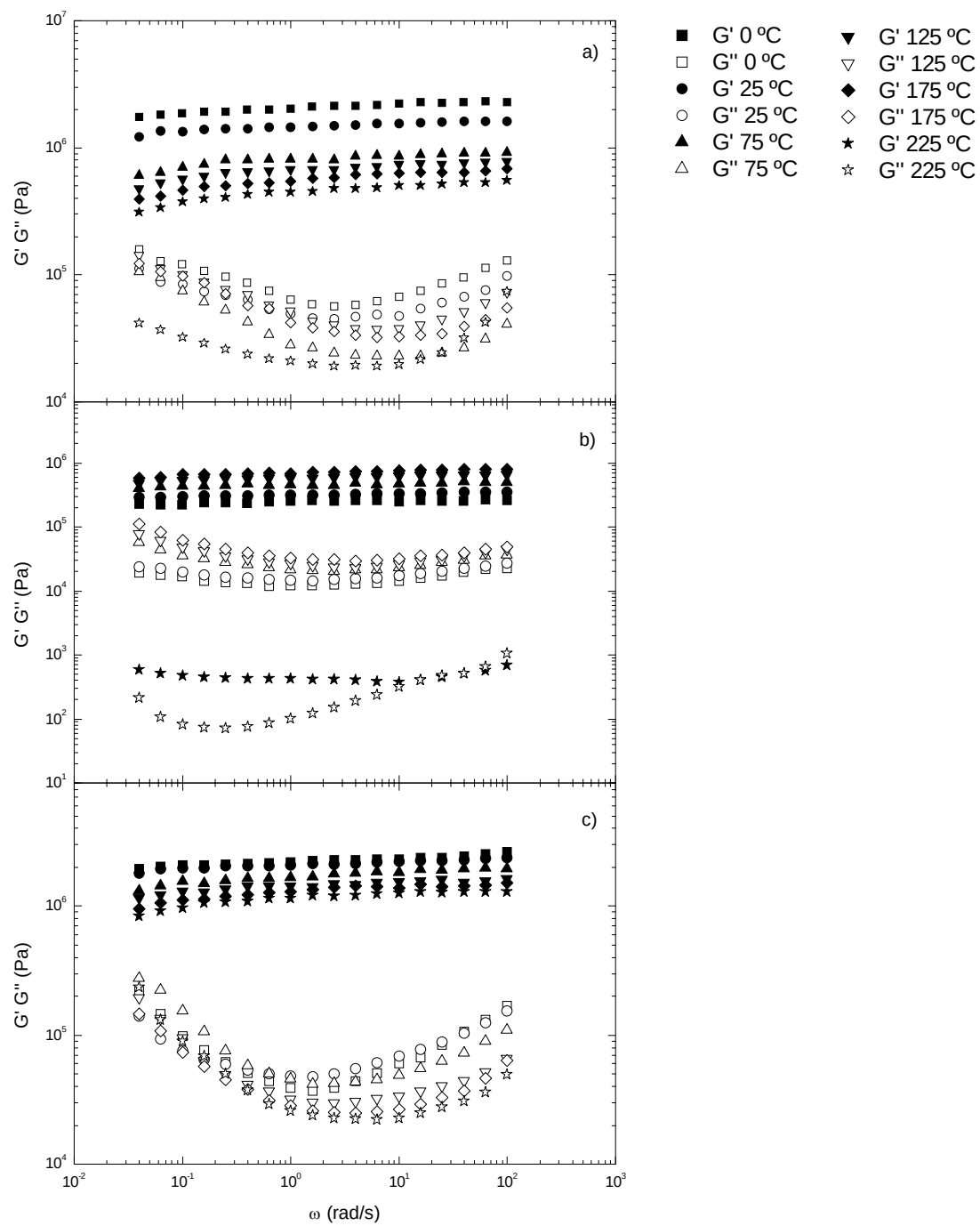


Figure 5.8. Evolution of the storage and loss moduli with frequency for a) COMC35, b); COAC35 and c) CO α C25, at different temperatures

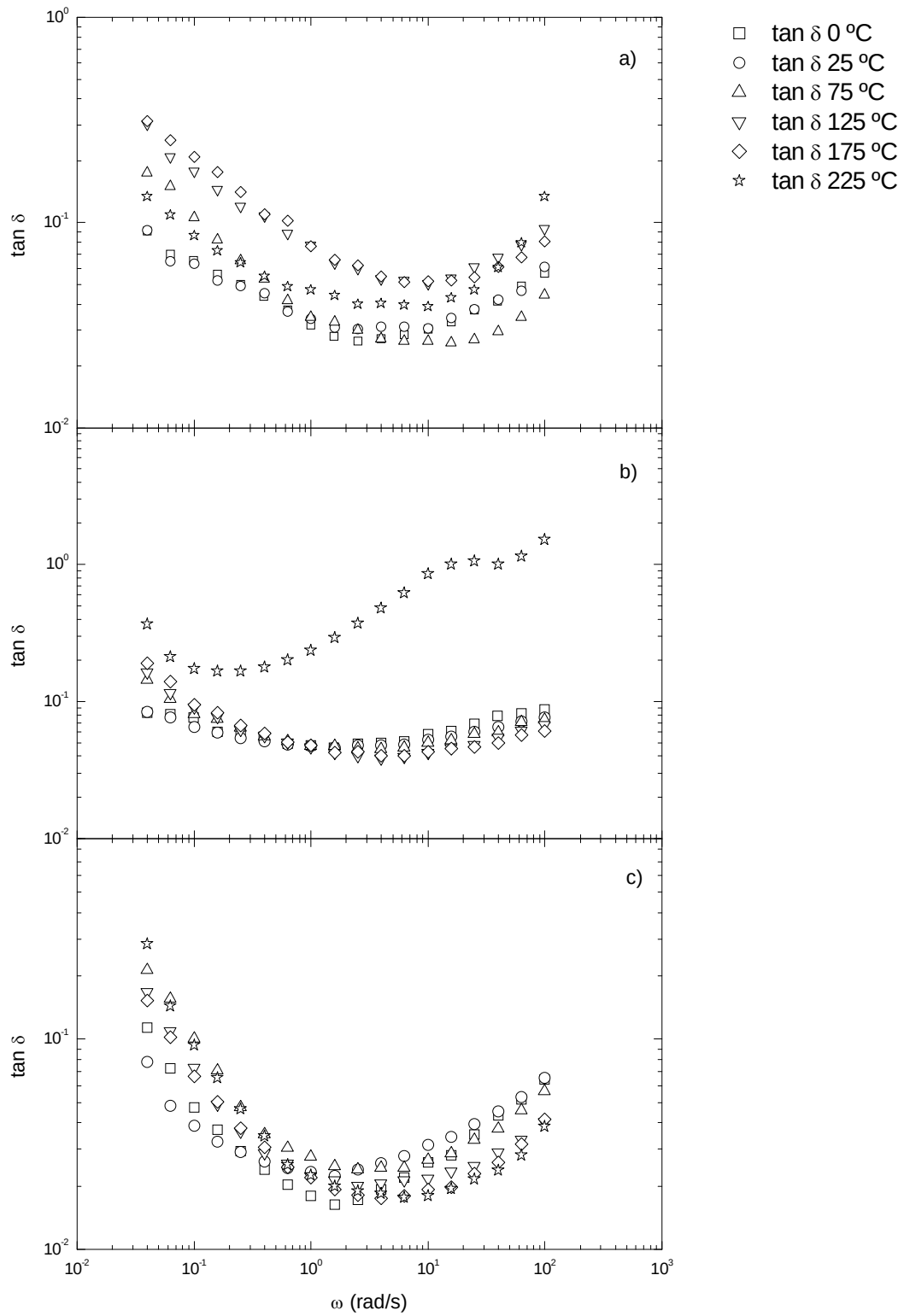


Figure 5.9. Evolution of the loss tangent with frequency for a) COMC35, b) COAC35 and c) COαC25, at different temperatures

The oleogel sample containing methyl cellulose shows a continuous decrease in G' by increasing temperature, above all in the range 25-75 °C (Figure 5.8a). The loss modulus, G'' , also decreases with temperature, but to a lesser extent. As a consequence, the loss tangent ($\tan\delta=G''/G'$) generally increases with temperature, excepting at 225 °C, due to an important decrease in G'' values (Figure 5.9a).

On the contrary, the cellulose acetate-based formulation displays a completely different behaviour. The values of both moduli slightly increase with temperature (Figure 5.8b). However, the rheological behaviour drastically changes at 225 °C, due to cellulose acetate melting [Scandola and Ceccorulli, 1985], yielding the above mentioned crossover between both viscoelastic functions. The evolution of the loss tangent with frequency is almost independent of the temperature excepting, obviously, at 225 °C (Figure 5.9b).

Finally, the oleogel sample containing α -cellulose shows a thermorheological behaviour relatively similar to that of the formulation containing methyl cellulose. However, in this case, the storage modulus is less affected by temperature (Figure 5.8c). Moreover, the loss modulus continuously decreases with temperature, although a tendency to reach similar values at low frequencies is apparent. The loss tangent is slightly influenced by temperature (Figure 5.9c). The small influence of temperature on oleogel loss tangent is, thus, rather general, and is also an important characteristic of these materials, not found in traditional lithium greases [Delgado et al., 2006b].

The plateau modulus, G_N^0 , is a characteristic parameter of the plateau region of the mechanical spectrum. For polymeric systems, it is defined as the extrapolation, at high frequencies, of the contribution of entanglements to G' [Baumgaertel et al., 1992]. Similarly to the behaviour found for traditional lubricating greases [Delgado et al., 2006b], the oleogels studied in this research are not thermorheologically simple materials and, therefore, the time-temperature

superposition principle is not applicable. This means that the value of the plateau modulus is not unique for a given system but a function of temperature. Thus, the evolution of G_N^0 with temperature has been fitted successfully (see Figure 5.10 for a selected formulation) to an Arrhenius-like equation ($R^2 > 0.988$).

$$G_N^0 = A \cdot e^{\frac{E_a}{R} \left(\frac{1}{T} \right)} \quad (4.2)$$

where E_a is the activation energy (J/mol), R is the gas constant (8.314 J/mol·K), T is the absolute temperature (K), and A is the pre-exponential factor (Pa).

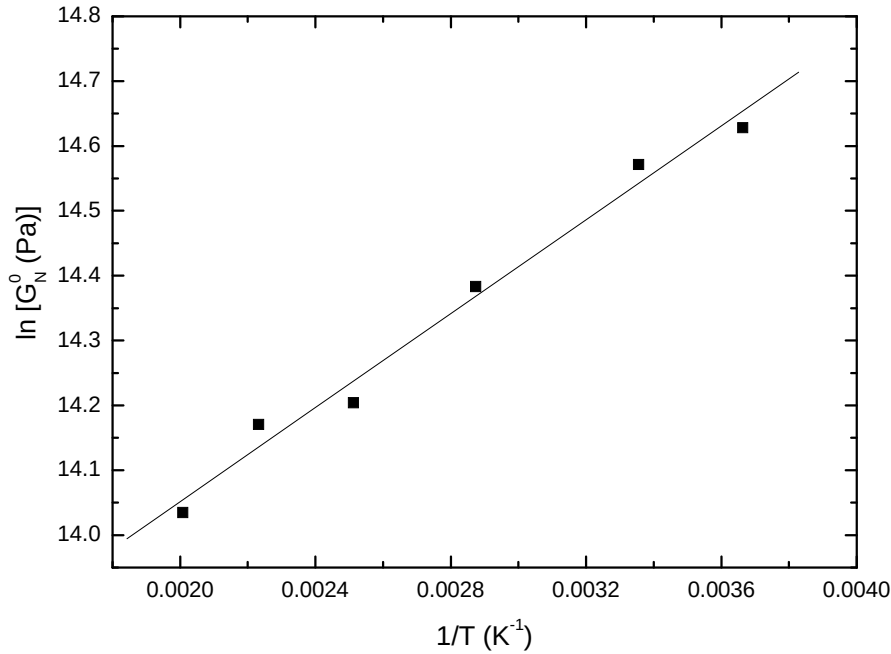


Figure 5.10. Evolution of the plateau modulus (square symbols) with temperature, and Arrhenius' fitting (solid line), for a selected oleogel (CO α C25)

Table 5.9 shows equation 4.2 fitting parameters for the oleogels studied. The sample containing methyl cellulose as thickener shows the highest activation energy, since the plateau modulus is more affected by temperature than, for instance, the oleogel prepared with α -cellulose. On the other hand, the sample prepared with acetate cellulose shows a

negative value of this activation energy, due to the fact that, as was previously mentioned, the plateau modulus increases with temperature (excluding the measurement carried out at 225 °C).

Sample	E_a (J/mol)
COMC35	6978
COAC35	-6099
CO α C25	3011
COECMC25	18655
COECMC30	4505
COEC α C20	1814

Table 5.9. Activation energy values, from equation 4.2, for the different oleogel samples studied

Oleogel formulations containing ethyl cellulose

The oleogel formulations studied in the previous section, which include just one cellulose derivative, present two important disadvantages in relation to traditional lubricating greases. First, these oleogels may be considered as strong gels, with values of the SAOS functions more than one decade higher than traditional lubricating greases [Madedo et al., 2000; Martín-Alfonso et al., 2007; Delgado et al., 2006b], which is attributed to the high thickener content required to achieve stable formulations. However, these gels are highly susceptible to shear, showing, for instance, lower mechanical stability than lithium greases, in spite of the higher values of the oleogel SAOS functions. On the other hand, a certain degree of oil phase separation is apparent (oil bleeding), especially when samples are submitted to severe working conditions, due to the rigidity of the gel network. In order to minimize these adverse effects, ethyl cellulose (2% w/w) was dispersed in castor oil, above its glass transition temperature (~150 °C). Further on, the sample was cooled. The result was a very homogeneous gel-like oil phase, much more viscous than the castor oil. Afterwards, the standard protocol was followed to mix the oil phase with the other cellulose derivative. As mentioned in the experimental section, stable oleogel samples were obtained by adding 25% and 30% w/w methyl cellulose

and 20% w/w α -cellulose when ethyl cellulose was also included in the formulation. Therefore, the use of ethyl cellulose allows us to reduce the thickener content in the oleogel, and inhibits oil phase separation, even when the sample is submitted to severe working conditions. The use of a high-viscosity vegetable oil like the castor oil reinforces the role of ethyl cellulose.

As can be seen in Table 5.8, the sample prepared with methyl cellulose has better thermal stability (i.e. higher T_{onset} than oleogel prepared with α -cellulose), and very similar to that shown by the oleogel prepared with this thickener but without ethyl cellulose. The temperature for maximum decomposition rate is, in general, much higher than for samples formulated without ethyl cellulose when using nitrogen flux during the test. This effect is probably due to the modification that the ethyl cellulose exerts in the properties of castor oil. Once again, the onset and maximum decomposition rate temperatures decrease when the test is carried under oxygen instead of N_2 atmosphere, yielding similar values to those found for COLi sample, especially in the case of the α -cellulose-containing oleogel.

Figures 5.11 and 5.12 show the evolution of the SAOS functions with frequency for oleogels including ethyl cellulose in their formulations, in a temperature range of 0–225 °C. The linear viscoelasticity range was not experimentally observed, at temperatures higher than 100 °C, for the oleogel containing 25% w/w methyl cellulose. The mechanical spectra of these oleogels are qualitatively similar to those previously shown for oleogels without ethyl cellulose, but, as intended, significantly lower values of the SAOS functions were obtained. The linear viscoelasticity functions of the sample containing 2% ethyl cellulose and 25% methyl cellulose are highly influenced by temperature (see Figures 5.11a and 5.12a). G' and G'' values decrease one decade in the whole frequency studied, whilst the loss tangent slightly increases as temperature is raised from 0 to 100 °C. On the other hand, the formulation that contains 2% ethyl cellulose and 30%

methyl cellulose is much less affected by temperature (see Figure 5.11b), a qualitatively similar behaviour to that found for the formulation which includes only methyl cellulose as thickener. Finally, the influence of temperature on the linear viscoelasticity functions of the oleogel sample containing 2% ethyl cellulose and 20% α -cellulose is more complex. Thus, although the storage modulus slightly decreases as temperature increases, the loss modulus at 0 and 25 °C shows a minimum value at low frequency, which is shifted to higher frequencies when temperature is raised above 75 °C. Above this temperature, the behaviour is quite similar to that found for the sample without ethyl cellulose, where G'' is almost independent of temperature (see Figure 5.11c).

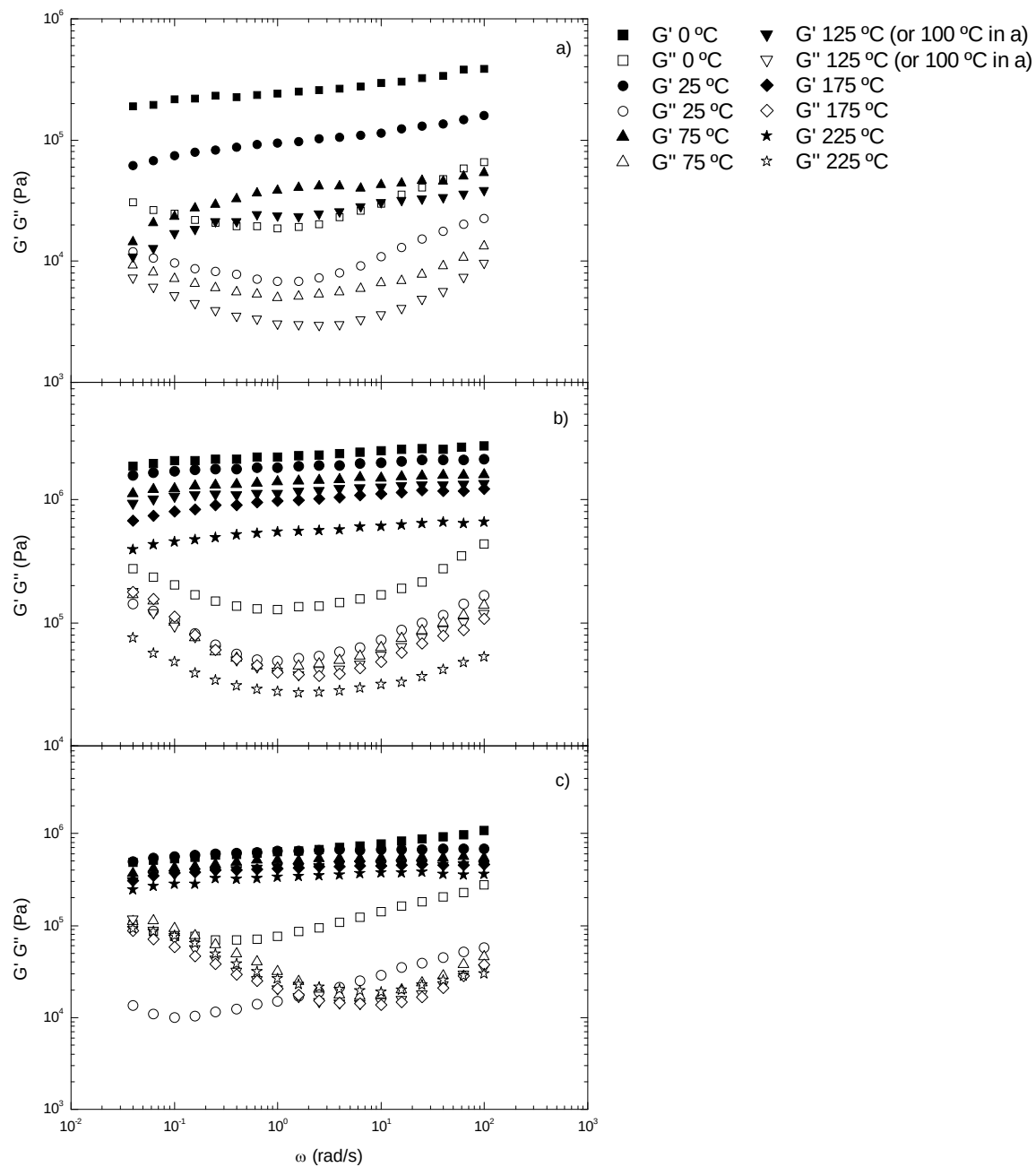


Figure 5.11. Evolution of the storage and loss moduli with frequency for a) COECMC25, b) COECMC30 and c) COEC α C20, at different temperatures

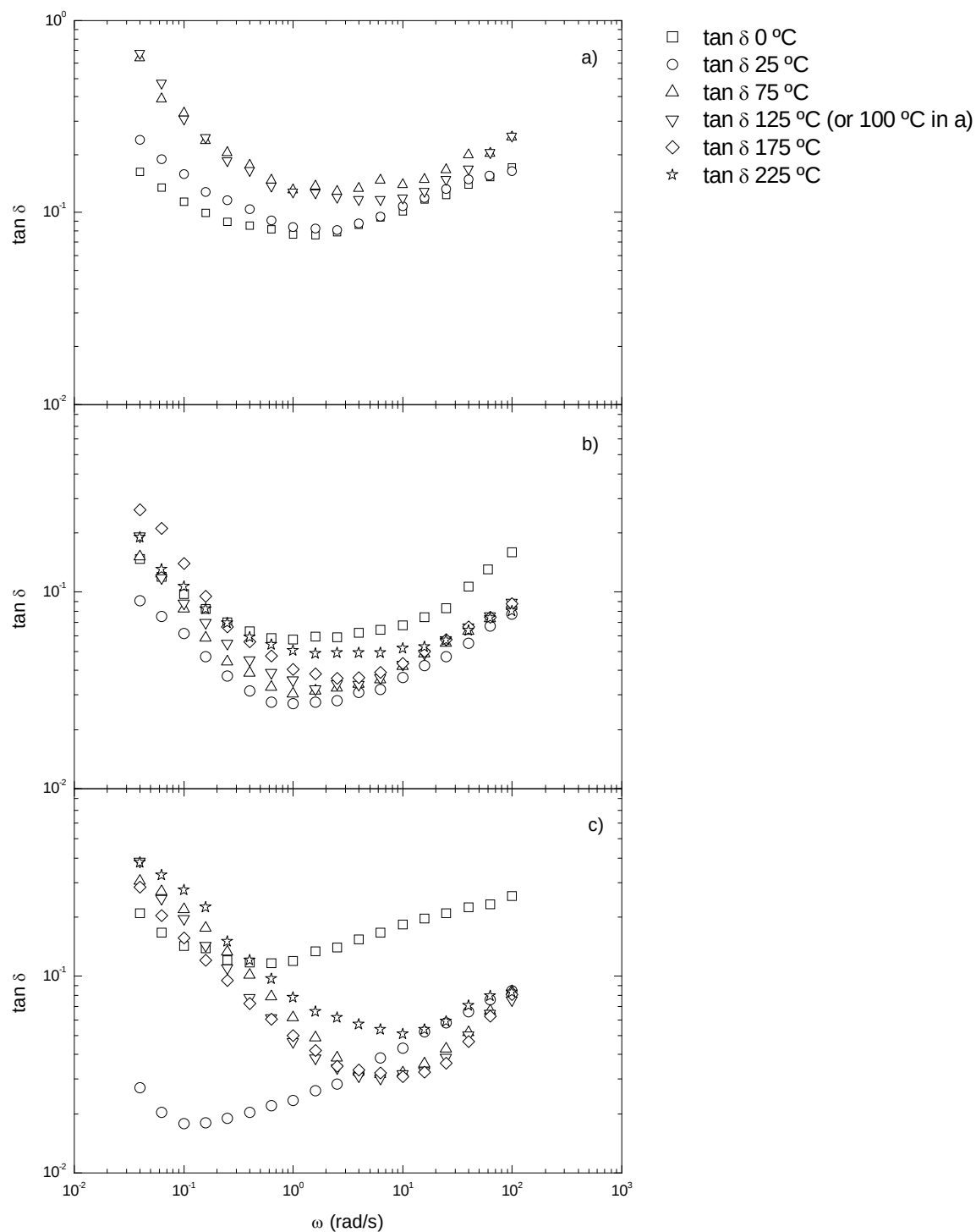


Figure 5.12. Evolution of the loss tangent with frequency for a) COECMC25, b) COECMC30 and c) COECαC20, at different temperatures

The influence of temperature on the SAOS functions of the oleogel formulations containing ethyl cellulose can also be evaluated by comparing the activation energy values obtained from equation 4.2 (see Table 5.9). In this sense, ethyl cellulose addition increases significantly

the activation energy for samples containing 25% methyl cellulose, probably related to the rather low methyl cellulose concentration in the formulation. On the contrary, an important reduction in E_a values can be observed for samples with 30% methyl cellulose or 20% α -cellulose. Therefore, it may be concluded that the presence of ethyl cellulose in the formulation dampens significantly the thermal susceptibility of these oleogels, when formulations containing similar total concentrations of cellulose derivatives are compared.

Penetration, mechanical stability and leakage tests

Penetration values of unworked samples are traditionally converted to NLGI grades, in order to classify greases according to its consistency degree (between 000 and 6). The most commonly used greases are those with NLGI grade 2 [NLGI, 1994]. Softer grades, especially 0 and 1, are sometimes used for improved pumpability or low-temperature applications, while higher consistency indexes are used for certain high-speed bearings [NLGI, 1994]. Table 5.10 collects unworked penetration values for the different oleogels studied, as well as the values obtained once the samples were submitted to the standard roll-stability test. In addition, the penetration values for selected (NLGI grades 1-3) lithium greases [Delgado et al., 2006a; Martín-Alfonso et al., 2009a], prepared with either a mineral (paraffinic or naphthenic) oil or the same castor oil used to formulate the oleogels studied in this work (sample COLi), are also included for the sake of comparison. In general, the mechanical stability of the oleogels studied, which is inversely proportional to the penetration increment after working, is slightly lower than for lithium greases. Only the blend consisting of ethyl and methyl cellulose (2 and 30%, respectively) provides low enough penetration increment values, comparable to those found for commercial greases. In addition to this, the combination of ethyl cellulose and α -cellulose increases the NLGI grade of the oleogel, but, however, reduces its mechanical stability.

Sample	Unworked penetration (dmm)	NLGI grade	Worked penetration (dmm)	Penetration variation (dmm)	Leakage (%)
COMC35	279	2	320	41	14.6
COAC35	388	00-0	459	71	26.4
CO α C25	324	1	354	30	21.7
COECMC25	380	0	422	42	49.4
COECMC30	324	1-2	347	23	37.5
COEC α C20	257	2-3	395	138	46.5
COLi	242	3	260	18	0.4
Standard paraffinic oil-based grease	303	1-2	305	2	1.2
Standard naphthenic oil-based grease	274	2	289	15	0.8

Table 5.10. Penetration and leakage values for different oleogels, lithium soap/castor oil grease, and standard lubricating greases

The main negative aspect of the oleogels containing cellulose derivatives is the high level of leakage found when they are subjected to the leakage standard test, at 105 °C (Table 5.10). The presence of ethyl cellulose in the formulation increases leakage, since the sol-gel transition of ethyl cellulose in oil is around 60 °C. However, when the same standard test was carried out by setting the spindle temperature at 25 °C, the leakage values obtained were 1.4 ± 0.2 for formulations with ethyl cellulose, which indicates that these oleogels show relatively low leakage tendencies when moderate temperature working conditions are applied.

5.3 Thermal and mechanical characterization of cellulosic derivatives-based oleogels potentially applicable as bio-lubricating greases: influence of ethyl cellulose molecular weight

5.3.1 Introduction

Nowadays, there is a continuous tendency to improve the performance of industrial processes and machineries. Concerning mechanical elements submitted to movement, friction reduction is one of the main goals. Design of more efficient lubricants is, then, necessary to reach this objective. However, the industry of lubricants is not only interested in the manufacture of new lubricants for enhanced mechanical performance, but also on improved products from an environmental point of view. In this sense, mostly in the last two decades, lubricant customers are aware of the negative effects that traditional lubricants exert on the environment and, therefore, are demanding new green products able to reduce this impact. In addition to this, the increase in the use of eco-friendly materials has been promoted as a result of strict government regulations that some countries are adding in their legislation [Adhvary and Erhan, 2002; Beran, 2008]. In fact, the use of biodegradable lubricants is not an innovative idea (i.e. 4000 B.C. natural fats were used for cart wheels lubrication). Lately, biolubricants are of increasing importance for different applications like engines, gears and transmissions [Lea, 2002].

Standard lubricating grease formulations are gel-like colloidal suspensions in which a suitable thickener, usually a metallic soap, is dispersed in a mineral or synthetic oil [NLGI, 1994], both components considered non-biodegradable materials. Obviously, the generalized use of these formulations for different applications incorporates part of these products into the environment, thus increasing pollution and destroying natural resources [Beran, 2008; Wilson, 1998]. The first step

made to produce a friendlier lubricating grease formulation was the replacement of the mineral oil, the main component (70-95% w/w), by a vegetable one [Stempfel, 1998]. Using vegetable oil in the lubricant formulations reduces environmental pollution, since it is high biodegradable [Beran, 2008; Maleque et al., 2003]. Vegetable oils have many other advantages, such as low toxicity, low evaporation, high load carrying abilities, naturally multigrade, good solvent power for additives, etc. On the contrary, these raw materials also present certain disadvantages, for instance, low temperature performance, low oxidation stability and high costs [Fox and Stachowiak, 2007; Jayadas and Prabhakaran, 2006; Lea, 2002].

However, complete biodegradable lubricating grease will imply not only the replacement of the mineral oil by a suitable vegetable one, but also using natural thickener agents, which can suitably play the role of traditional metallic soaps or polyureas. As has been mentioned before, oil substitution has been satisfactorily addressed [Dresel, 1994], and some products are being sold as biodegradable greases, although they still contain a non-biodegradable thickener agent in their formulations. Consequently, the main objective of this research was to test different natural thickeners, which combined with suitable vegetable oils would yield biodegradable greases with appropriate performance. In a previous study [Sánchez et al., 2009], different gel-like cellulosic derivatives suspensions in a castor oil medium were proposed as potential substitutes of lubricating greases for some applications. Cellulosic derivatives present some advantages as lubricating grease thickeners. They are biodegradable biopolymers obtained from the most abundant natural polymer [Rimtusit et al., 2008] and, on the other hand, they can provide suitable rheological properties to these formulations [Park and Ruckenstein, 2001]. In particular, the use of ethyl cellulose combined with other cellulose derivatives, i.e. methylcellulose or α -cellulose, yields gel-like dispersions with acceptable thermal, rheological and mechanical properties. The term “oleogel” was used according to

the definition proposed by Almdal et al., (1993) for solid-like gels attending to the dynamic rheological properties, which otherwise fits the rheological response of traditional lubricating greases. As it was previously reported [Sánchez et al., 2009], the role of ethyl cellulose, by increasing oil viscosity, is essential to impart long-term physical stability to these oleogels. In this work, the influence of ethyl cellulose molecular weight on the thermal and rheological properties of oleogels based on castor oil and different cellulosic derivatives was explored. Moreover, some standard mechanical stability tests, usually performed on lubricating greases, were carried out in order to evaluate the suitability of these oleogels for lubricant applications.

5.3.2 Materials and Methods

Materials

Castor oil (211 cSt at 40 °C, Guinama, Spain) was selected as biodegradable lubricating oil. The fatty acid composition of the castor oil used is shown in Table 5.11. Five ethyl cellulose samples (48% ethoxy content) differing in molecular weight [see Table 5.12], methyl cellulose (M_n 40000 g/mol; 32% methoxy content), and partially microcrystalline α -cellulose [Park et al., 2009], all of them from Sigma-Aldrich, were used as thickener agents to prepare different gel-like dispersions. The degree of polymerization (DP) for α -cellulose sample, determined according to the SCAN-C15 official method, was DP=1011, obtained inserting the intrinsic viscosity ($[\eta] = 438 \text{ cm}^3/\text{g}$) in the following equation [Gericke et al., 2009]:

$$DP^{0.76} = \frac{[\eta]}{2.28} \quad (5.1)$$

Standard lithium 12-hydroxystearate lubricating greases (14 and 20% lithium soap, NLGI grade 2) were used as benchmarks. 12-hydroxystearic acid, lithium hydroxide, and paraffinic (334 cSt at 40 °C) and naphthenic (115 cSt at 40 °C) oils, kindly supplied by Verkol

Lubricantes S.A. (Spain), were used to prepare the oleogels, using the methodology reported elsewhere [Delgado et al., 2005; 2006a].

Fatty acid	% (w/w)
Palmitic acid (C16:0)	2.6
Stearic acid (C18:0)	2.7
Oleic acid (C18:1)	6.3
Linoleic acid (C18:2)	10.8
Ricinoleic acid (12-hidroxi C18:1)	77.6

Table 5.11. Fatty acid composition of the castor oil used to prepare oleogels

Ethyl cellulose	M_n (g/mol)	M_w (g/mol)	M_w / M_n
EC1	$2.4 \cdot 10^4$	$3.9 \cdot 10^4$	1.60
EC2	$3.6 \cdot 10^4$	$5.3 \cdot 10^4$	1.46
EC3	$6.0 \cdot 10^4$	$6.9 \cdot 10^4$	1.15
EC4	$6.9 \cdot 10^4$	$7.7 \cdot 10^4$	1.12
EC5	$7.5 \cdot 10^4$	$8.2 \cdot 10^4$	1.09

Table 5.12. Weight average molecular weight (M_w), number average molecular weight (M_n) and polydispersity index (M_w/M_n) of the ethyl cellulose used in the manufacture of oleogels

Preparation of oleogel formulations

Oleogel batches (400 g) were processed in an open vessel, using a helical ribbon impeller geometry ($D = 90$ mm; $H = 90$ mm) to disperse the thickener agents. In the first step, the vessel was filled with the corresponding amounts of oil and ethyl cellulose. A constant rotational speed (60 rpm) was then applied to the mixture, while heating up to 150 °C. The other cellulosic derivatives employed in the formulation were added once the ethyl cellulose was completely dissolved, and blended at the same rotational speed and temperature, for 30 minutes. Finally, the mixture was cooled down to room temperature by natural convection, achieving gel-like suspensions of α -cellulose or methyl cellulose in the castor oil medium modified with the ethyl cellulose. Table 3 shows the compositions of the different formulations studied, as well as the codes used for further reference. Thickener concentration was previously optimized, taking into consideration both physical stability and

rheological properties similar to those found with standard lubricating greases [Sánchez et al., 2009].

Code	ethyl cellulose		α -cellulose (%)	methyl cellulose (%)
	(%)	M_w (g/mol)		
COEC1 α C	2	$3.9 \cdot 10^4$	20	0
COEC2 α C	2	$5.3 \cdot 10^4$	20	0
COEC3 α C	2	$6.9 \cdot 10^4$	20	0
COEC4 α C	2	$7.7 \cdot 10^4$	20	0
COEC5 α C	2	$8.2 \cdot 10^4$	20	0
COEC1MC	2	$3.9 \cdot 10^4$	0	30
COEC2MC	2	$5.3 \cdot 10^4$	0	30
COEC3MC	2	$6.9 \cdot 10^4$	0	30
COEC4MC	2	$7.7 \cdot 10^4$	0	30
COEC5MC	2	$8.2 \cdot 10^4$	0	30

Table 5.13. Formulations and codes of the processed oleogels

Gas chromatography (GC)

GC analysis was performed with an Agilent 6890 (HP, USA) chromatograph, equipped with a flame-ionization detector, in order to determine the fatty acid profile in castor oil. C14-C24 FAMES provided standards were used.

Gel permeation chromatography (GPC)

Molecular weight data of ethyl cellulose samples were determined by means of the GPC technique, using a Waters apparatus (USA), equipped with a styragel HR 4E column (7.8 x 300 mm), at 35 °C, and using THF as eluent. A Waters 2414 refractive index detector was used. The flow rate was 1.0 mL/min. The number-average molecular weight (M_n), the weight average molecular weight (M_w), and polydispersity index (M_w/M_n) were calculated relative to poly(styrene) standards.

Thermogravimetric analysis (TGA)

Thermogravimetric analysis was carried out with a Q-50 (TA Instruments Waters, USA). Approximately, 15 mg of each sample were

placed on a Pt pan, and heated from 30 °C to 600 °C, at 10 °C/min, under N₂ or O₂ total flow of 100 mL/min.

Rheological characterization

Rheological characterization of oleogels was carried out in two controlled-stress rheometers (RS-150 and Rheoscope, ThermoHaake, Germany). Small-amplitude oscillatory shear (SAOS) tests were performed inside the linear viscoelastic region, using a plate-plate geometry (35 mm, 1 mm gap), in a frequency range of 10⁻²-10² rad/s, and temperatures comprised between 0 and 225 °C. The viscous flow behaviour of ethyl cellulose/castor oil binary systems was measured in a shear rate range of 10⁻²-10² s⁻¹. At least two replicates of each test were performed on fresh samples.

Penetration and mechanical stability tests

Both unworked and worked penetration indexes were determined according to the ASTM D 1403 standard, by using a Seta Universal penetrometer, model 17000-2 (Stanhope-Seta, UK), with one-quarter cone geometry. The one-quarter scale penetration values were converted into the equivalent full-scale cone penetration values, following the ASTM D 217 standard. Classical consistency NLGI grade was established according to these penetration values [NLGI, 1994]. Samples were worked during 2 hours in a Roll Stability Tester, model 19400-3 (Stanhope-Seta, UK) according to the ASTM D 1831 standard, and penetration measurements were performed, once again, immediately after this rolling test.

Leakage tendencies in wheel bearings

Oleogel leakage tendencies were determined in a wheel bearing equipment, model 17-0450 (Petrotest, Germany), according to the ASTM D 1263 standard. This test method evaluates the leakage tendency of lubricating greases when they are tested under specific simulated wheel bearing conditions. The sample was distributed in a modified front-

wheel hub and spindle assembly. The hub rotated, at a speed of 660 ± 30 rpm for 6 hours $\pm$ 5 minutes, at a spindle temperature, which was raised to and then maintained, of 105 ± 1.2 °C. The same test was also performed at room temperature. Leakage of the sample was measured, and the condition of the bearing surface was checked at the end of the test.

5.3.3 Results and Discussion

Figure 5.13 shows the frequency dependence of the linear viscoelasticity functions for gel-like α -cellulose suspensions in castor oil media containing several ethyl celluloses with different molecular weights. This dependence is qualitatively similar to that found for other relatively concentrated colloidal suspensions like standard lubricating greases [Madieto et al., 2000; Martín-Alfonso et al., 2007]. As can be observed, G' is always higher than G'' in the whole frequency range studied. In addition, a pronounced plateau region of the mechanical spectrum is always noticed, as extensively described elsewhere for solid-like disperse systems [Douglas et al., 1971, Batchelor, 1974, Mewis and Spaul, 1976, Delgado et al., 2005, 2006a; 2006b]. This mechanical spectrum corresponds with the definition given by Almdal et al., (1993) for solid-like gels. However, both moduli show higher values than those found in standard lithium greases, being maxima for the oleogel containing ethyl cellulose with the highest molecular weight. Moreover, G' and G'' are not significantly influenced by ethyl cellulose molecular weight below a critical molecular weight ($M_w < 70000$ g/mol). On the contrary, a significant increase in both SAOS functions, and a shift of the minimum in G'' to higher frequencies, are noticed when using ethyl cellulose with M_w values higher than the critical one. The above-mentioned increase in both linear viscoelasticity functions is quite similar in the low frequency range and, consequently, the relative elastic characteristics of these gel-like dispersions are not significantly affected, as can be observed in Figure 5.13b where the loss tangent ($\tan$

$\delta=G''/G'$) is plotted versus frequency. However, these differences increase with frequency. In this sense, formulations containing high-molecular weight ethyl celluloses show minimum loss tangent values at large frequencies.

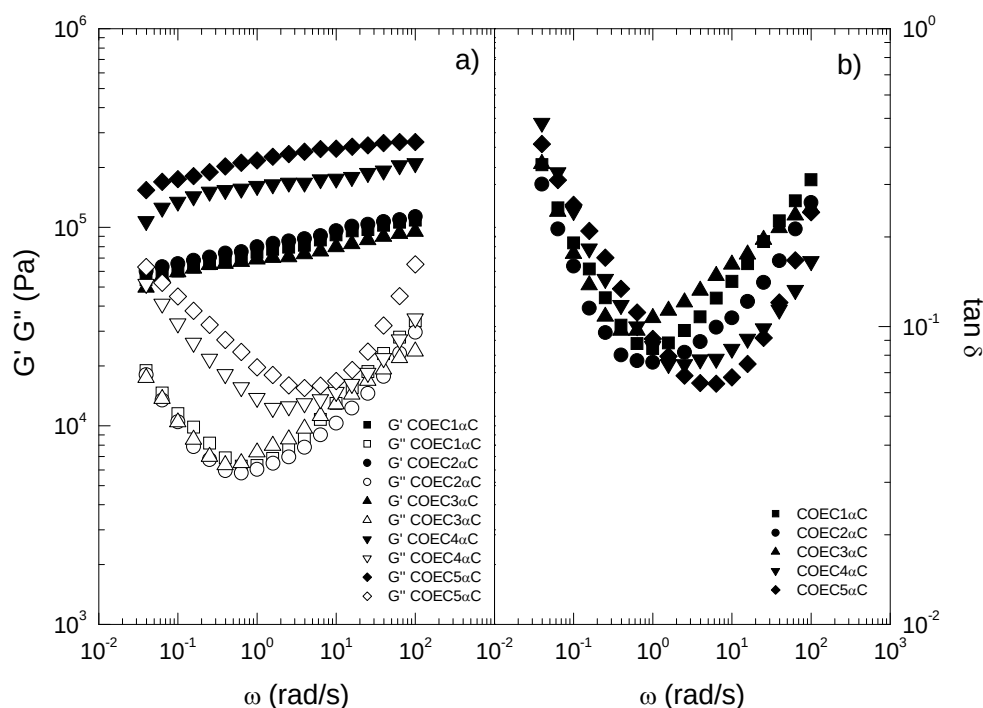


Figure 5.13. Evolution of the storage and loss moduli (a) and the loss tangent (b) with frequency for oleogels formulated with blends of α -cellulose and ethyl cellulose with different number average molecular weight (M_w)

Figure 5.14a shows the mechanical spectra for formulations containing methylcellulose instead of α -cellulose. As can be observed, the evolution of G' and G'' with frequency is qualitatively similar than that found in oleogels containing α -cellulose/ethyl cellulose blends, although the values of both moduli are now significantly higher. As before, both SAOS functions are not influenced by ethyl cellulose molecular weight, below the same critical M_w value. Moreover, a significant increase in G' is observed for the oleogel containing ethyl cellulose with the highest molecular weight, yielding a slight decrease in the loss tangent (Figure 5.14b). However, in this case, the frequency

dependence of SAOS functions is not affected by ethyl cellulose molecular weight.

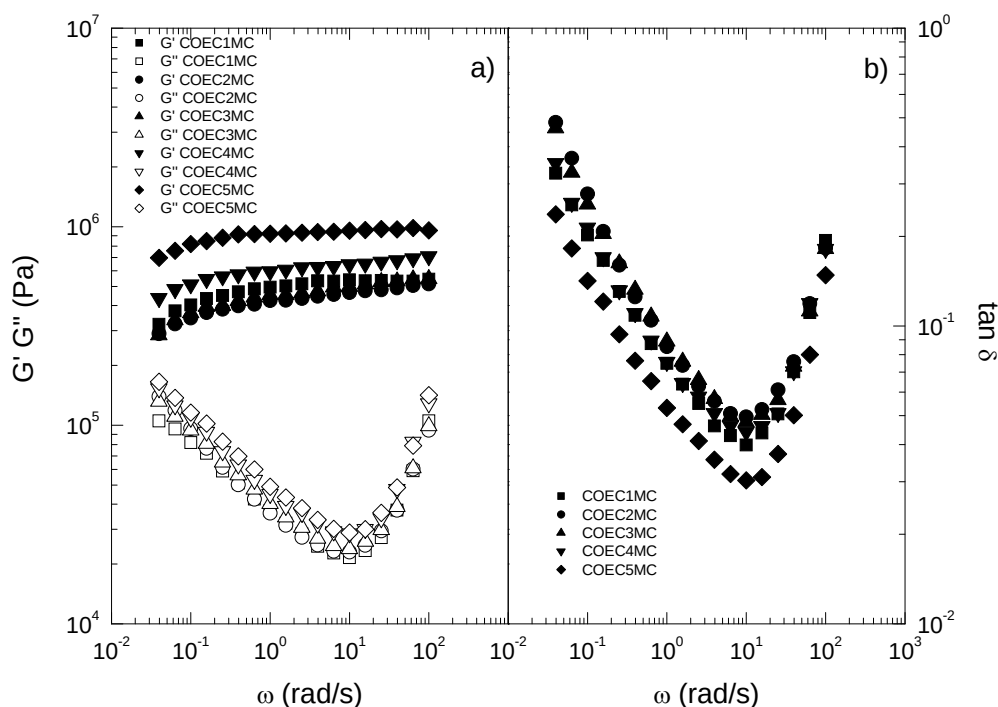


Figure 5.14. Evolution of the storage and loss moduli (a) and the loss tangent (b) with frequency for oleogels formulated with blends of methyl cellulose and ethyl cellulose with different number average molecular weight (M_w)

As previously reported [Sánchez et al., 2009], the mechanical spectra of the binary systems castor oil/ α -cellulose and castor oil/methyl cellulose are qualitatively similar to these discussed for ternary mixtures. The introduction of the ethyl cellulose in the formulation decreases the values of both G' and G'' without significant modification of the relative elastic characteristics, i.e. the values of the loss tangent. However, as shown in Figure 5.15a, the ethyl cellulose significantly increases the oil viscosity (conferring also a shear thinning behaviour), which is essential to impart long-term physical stability to these gel-like dispersions. On the contrary to that found in the above mentioned binary mixtures, no phase separation was visually detected at least during 8-9 months of ageing. As a consequence, the use of ethyl

cellulose allows to reduce the other thickener content as well as to inhibit oil phase separation (oil bleeding), even when the sample is submitted to severe working conditions [Sánchez et al., 2009]. This improvement in physical stability is not only due to the increasing oil viscosity but to the viscoelastic properties of the castor oil/ethyl cellulose binary systems, which at the concentrations employed (2.6-2.9% w/w) display a certain elastic-like character (see Figure 5.15b). The mechanical spectra of these binary systems is similar to other non-aqueous ethyl cellulose solutions or weak gels [Lizaso et al., 1999; Heng et al, 2005], although the crossover between G' and G'' observed appears at higher frequencies in the data reported in the existing literature, depending on the solvent and ethyl cellulose concentration. In the ethyl cellulose/castor oil binary systems studied, this crossover between both SAOS functions is shifted to lower frequencies when the ethyl cellulose molecular weight is increased. Moreover, G' and G'' values increase with the ethyl cellulose molecular weight, especially for $M_w > 53000$ g/mol, which contributes to the behaviour above discussed for the ternary systems. This elastic character was mainly detected at temperatures below 60-65 °C, with values of the loss tangent of 0.3-3, depending on the frequency. Above this temperature, a significant increase in the loss tangent was observed (Figure 5.15c).

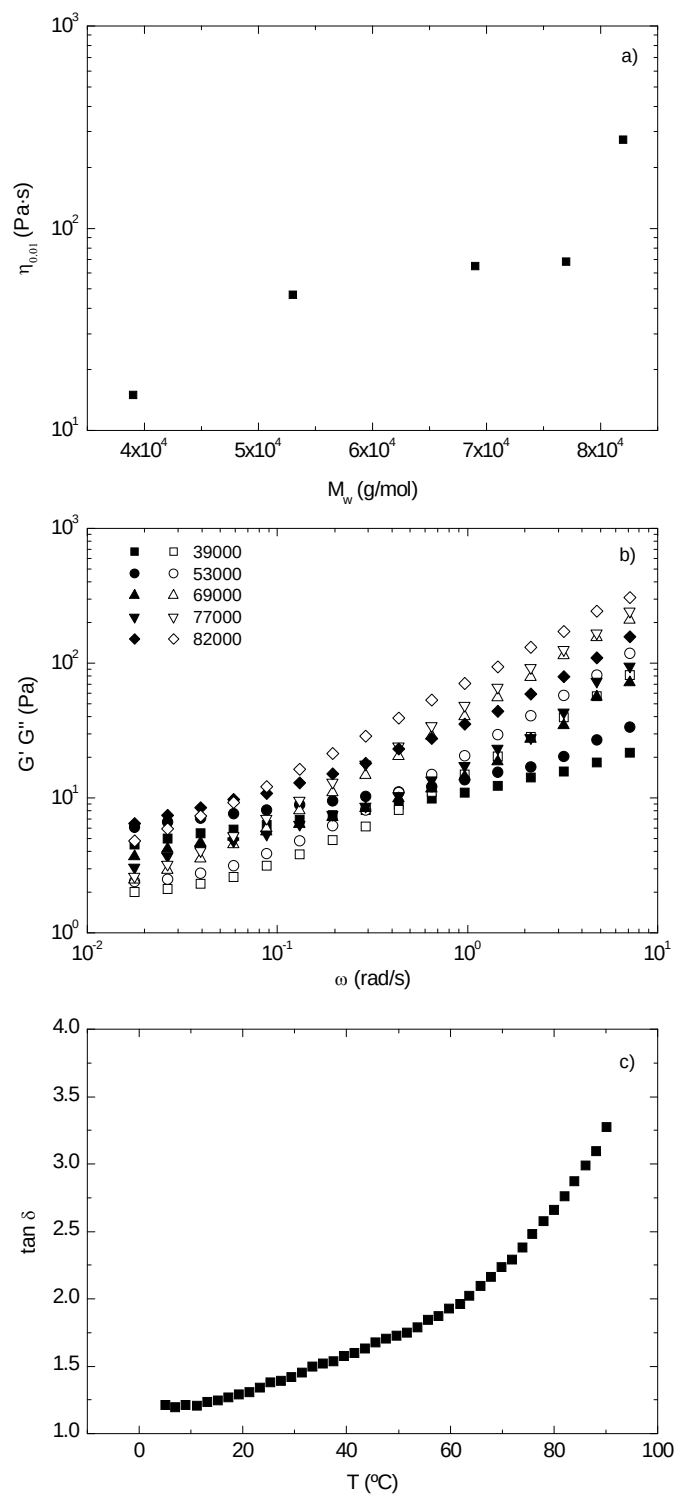


Figure 5.15. Rheological characteristics of the ethyl cellulose/castor oil binary systems: a) evolution of the apparent viscosity, at 0.01 s^{-1} , with ethyl cellulose molecular weight; b) mechanical spectrum as a function of ethyl cellulose molecular weight (G' full symbols, G'' open symbols); c) evolution of the loss tangent, at 0.1 rad/s , with temperature for a selected binary system ($M_w=69000 \text{ g/mol}$)

Figure 5.16 summarizes and compares the influence of the ethyl cellulose molecular weight on the plateau modulus of both α -cellulose and methylcellulose-based oleogels. As can be observed, the plateau modulus, G_N^0 , a characteristic parameter of the plateau region in the mechanical spectrum [Baurngaertel et al., 1992], increases above a critical ethyl cellulose molecular weight (M_w around 70000 g/mol) and remains almost constant below it. Apart from the evolution of the SAOS functions with the ethyl cellulose molecular weight (Figure 5.15b), this behaviour may be also related to the classical evolution of viscosity with molecular weight found for polymer solutions [Ferry, 1980]. As well-known, according to the Bueche theory, the viscosity of undiluted polymer solutions potentially increases with molecular weight but more rapidly above a certain molecular weight, which is illustrated in Figure 5.15a where the viscosity, at 0.01 s⁻¹, is plotted versus the ethyl cellulose molecular weight for the ethyl cellulose/castor oil binary systems.

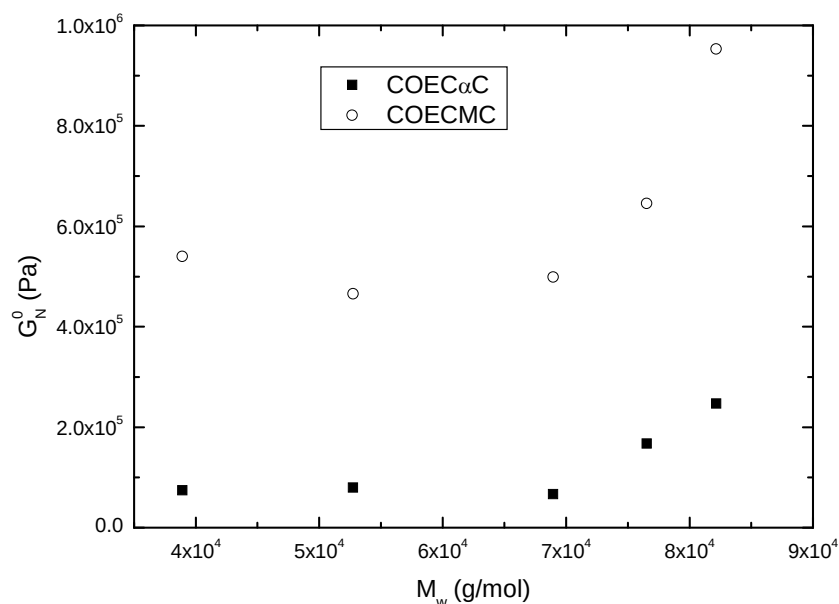


Figure 5.16. Influence of the ethyl cellulose molecular weight on the plateau modulus, G_N^0 , of both α -cellulose and methyl cellulose-based oleogels.

Figure 5.17 shows the evolution of SAOS functions with frequency, as a function of temperature, for a selected formulation (COEC5 α C). As can be expected, the values of SAOS functions decrease with temperature in the whole frequency range studied, although a well developed plateau region is always noticed. On the other hand, the frequency dependence of both moduli is not qualitatively influenced by temperature, fact that is completely opposite to the behaviour reported for many standard greases [Delgado et al., 2006b]. More surprisingly, the loss tangent is almost unaffected, which indicates that the relative elastic characteristics are not influenced by temperature either, in spite of the decrease in the relative elastic characteristics observed for the ethyl cellulose/castor oil binary systems at around 60 °C (Figure 5.15c). Therefore, these oleogels microstructures seem to resist higher temperatures than metallic soap-based greases. For those standard greases, the elastic characteristics vanish above the soap melting point, i.e. around 200 °C in the case of lithium greases.

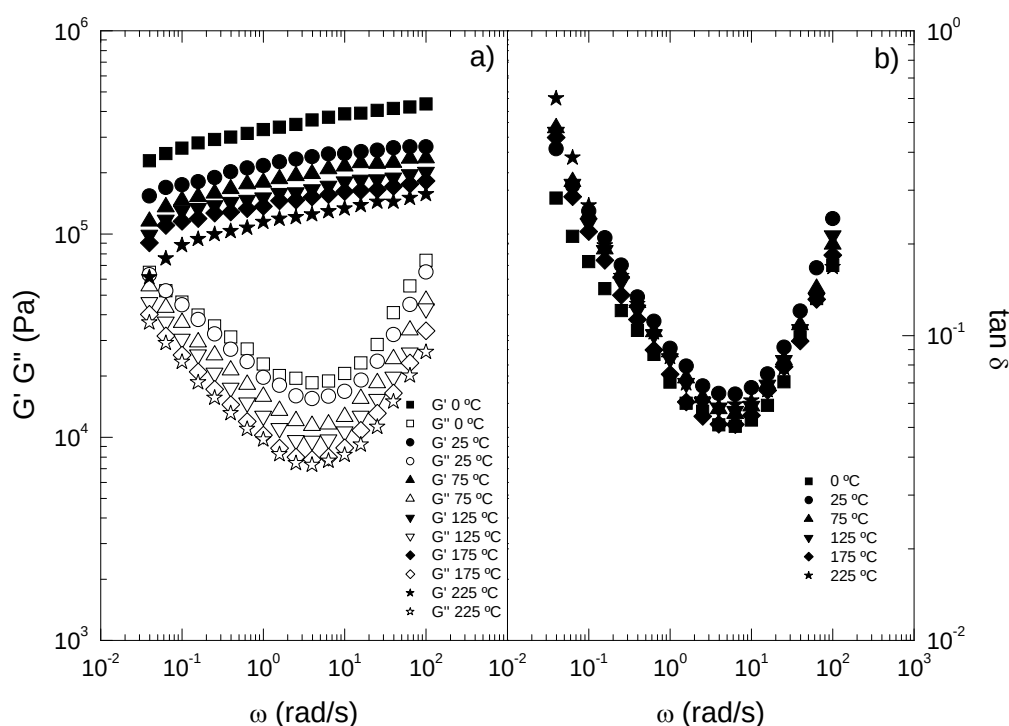


Figure 5.17. Evolution of the storage and loss moduli (a) and the loss tangent (b) with frequency for a selected oleogel, COEC5 α C, at different temperatures

As previously reported for standard lithium greases [Delgado et al., 2006b], the plateau modulus can be used to quantify the influence of temperature by using an Arrhenius-type equation:

$$G_N^0 = A \cdot e^{\frac{E_a}{R} \left(\frac{1}{T} \right)} \quad (4.2)$$

where E_a is a parameter which evaluates the thermal dependence, similar to the activation energy (J/mol), R is the gas constant (8.314 J/mol K), T is the absolute temperature (K), and A is the pre-exponential factor (Pa). Equation 4.2 fits the experimental plateau modulus values, in the whole temperature range studied, fairly well, as can be observed in Figure 5.18 for a selected oleogel (COEC2MC). This is, once again, quite different to the behaviour of standard lithium greases. Thus, two different Arrhenius-type equations are necessary to fit the evolution of standard lubricating grease plateau modulus with temperature, being the thermal dependence of SAOS functions much more dramatic above a critical temperature [Delgado et al., 2006b]. Table 5.14 gathers E_a values, obtained from equation 4.2, for all gel-like dispersions studied. As can be seen, α -cellulose suspensions display higher values of E_a than gel-like dispersions manufactured with methylcellulose. Moreover, these E_a values are higher than those obtained for standard lithium greases in the low-temperature range (1-2 kJ/mol), but much lower than those found in the high-temperature range (18-20 kJ/mol) [Delgado et al., 2006b].

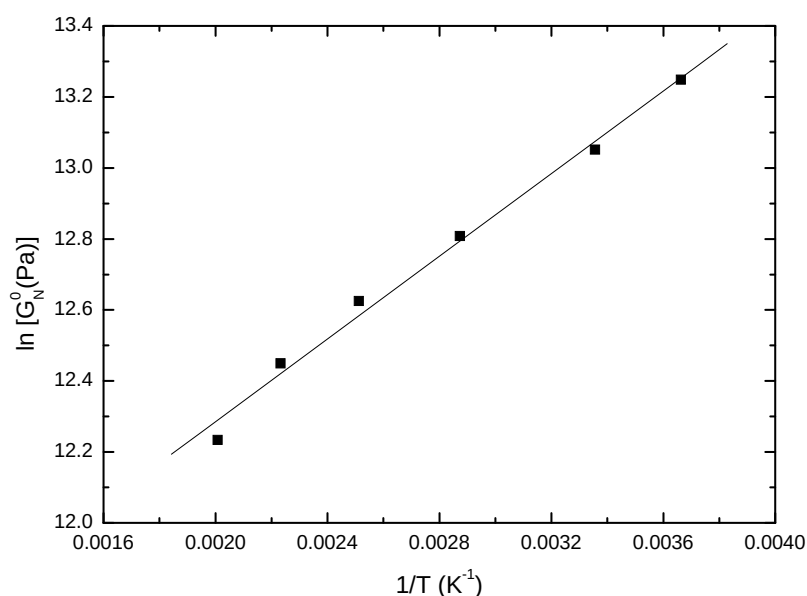


Figure 5.18. Evolution of the plateau modulus (square symbols) with temperature, and Arrhenius' fitting (solid line), for a selected oleogel (COEC2MC)

Sample	Ea (kJ/mol)
COEC1 α C	5.0
COEC2 α C	5.8
COEC3 α C	6.0
COEC4 α C	5.1
COEC5 α C	5.3
COEC1MC	3.9
COEC2MC	4.8
COEC3MC	3.5
COEC4MC	4.0
COEC5MC	4.1

Table 5.14. Activation energy values, from equation 4.2, for the different oleogels studied

One of the technical parameters more often used by lubricating grease manufacturers and customers is grease mechanical stability, obtained from penetration tests before and after working the sample. In this study, samples were worked in a roll stability tester. Mechanically stable greases display penetration increments (before and after working the sample) close to zero. Table 5.15 shows worked and unworked penetration values, and their differences (penetration variations), for all

the oleogels manufactured in this study. Furthermore, penetration values for different lithium soap-based lubricating greases containing different base oil (paraffinic, naphthenic and castor oil) have been also included. In order to classify the different types of samples studied, penetration values of unworked samples were converted to NLGI grades, according to the ASTM D 217 standard. In general, α -cellulose-based oleogels show poor mechanical stability, with penetration increments much higher than those obtained with the lithium greases selected as benchmarks. Specifically, α -cellulose-containing oleogels always show similar unworked penetration values, independently of ethyl cellulose molecular weight. However, oleogels containing ethyl cellulose with the highest molecular weights shows the highest worked penetration value, yielding the worst mechanical stability.

Sample	Unworked penetration (dmm)	NLGI grade	Worked penetration (dmm)	Penetration variation (dmm)	Leakage (%)
COEC1 α C	384	0	474	90	40.4 $\pm$ 0.7
COEC2 α C	377	0	470	94	
COEC3 α C	380	0	467	86	
COEC4 α C	377	0	485	109	
COEC5 α C	369	0	504	135	
COEC1MC	380	0	392	12	30.9 $\pm$ 1.0
COEC2MC	369	0	377	8	
COEC3MC	324	1	332	8	
COEC4MC	294	2	298	4	
COEC5MC	275	2	279	4	
COLi	242	3	260	18	0.4
Standard paraffinic oil-based grease	303	1-2	305	2	1.2
Standard naphthenic oil-based grease	274	2	289	15	0.8

Table 5.15. Penetration and leakage values for oleogels, model lithium soap/castor oil grease, and standard lubricating greases

On the other hand, both unworked and worked penetrations values clearly decrease by increasing ethyl cellulose molecular weight

for methyl cellulose-based oleogels. Moreover, the penetration values are generally lower than those found in oleogels with α -cellulose, yielding higher NLGI grades, similar to those found for lithium greases. Most remarkable is the improved mechanical stability shown by these oleogels, particularly those including ethyl cellulose with high molecular weight. Thus, the use of methyl cellulose and high-molecular weight-ethyl cellulose blends in these oleogel formulations provides a mechanical stability comparable to that obtained with standard lithium lubricating greases.

Table 5.15 also shows leakage tendency values of oleogels in wheel bearings (ASTM D 1263). As can be seen, a very high level of leakage was always obtained, independently of both nature of the cellulosic derivative and ethyl cellulose molecular weight. This high level of leakage is related to the rather high temperature (105 °C) at which these standard tests are carried out. As it was previously discussed, an important softening of the binary systems, associated to a significant decrease in the relative elastic characteristics, was detected at around 60 °C. Above this temperature, the viscosity of the oily phase is significantly reduced and, therefore, the leakage is favored. However, it is worth mentioning that the same tests performed at room temperature provide very similar leakage values to those shown by lithium greases ($1.8 \pm 0.5\%$).

In addition to mechanical stability, thermal resistance is another important issue for biolubricant formulations. Figure 5.19 shows thermogravimetric analysis curves for a selected cellulosic derivative-based oleogel, as compared with two benchmarks, a standard paraffinic oil-based lithium grease and a partially-biodegradable grease (based on lithium soap and castor oil). In general, thermal decomposition takes place in just one main single stage, which is almost identical for all the oleogels studied. As can be observed, castor-oil based formulations can resist much higher temperatures, without losing a significant amount of mass, than the paraffinic-based grease. Thus, the main factor affecting

TGA response is the volatility of the base oil used in these formulations. However, substitution of lithium soap for cellulosic derivatives also delays the onset temperature for thermal decomposition (T_{onset}) and, in general, the whole decomposition range. Table 5.16 shows the most relevant temperatures obtained from the TGA analysis, using both nitrogen and oxygen atmospheres, for all the oleogels studied and for the formulations taken as references. T_{onset} was determined from the interception between the slope of the first region, where the sample weight is approximately constant, and the slope of the region where sample weight loss rate is maximum, whereas T_{max} is the temperature which corresponds to the maximum of the weight loss derivative function. Oleogel thermal stability is not influenced by ethyl cellulose molecular weight. On the contrary, it is clearly affected by the nature of the second cellulose derivative, employed as thickener. In this sense, Table 5.16 shows the mean values of the above-mentioned characteristic temperatures, and the corresponding standard deviations, for oleogels containing α -cellulose or methyl cellulose. It is apparent that the formulation containing α -cellulose shows the best thermal stability when a nitrogen atmosphere is used. On the contrary, this oleogel displays T_{onset} values lower than the methyl cellulose-based formulation when an oxygen atmosphere is used, although a wider decomposition temperature range, that is, higher T_{final} .

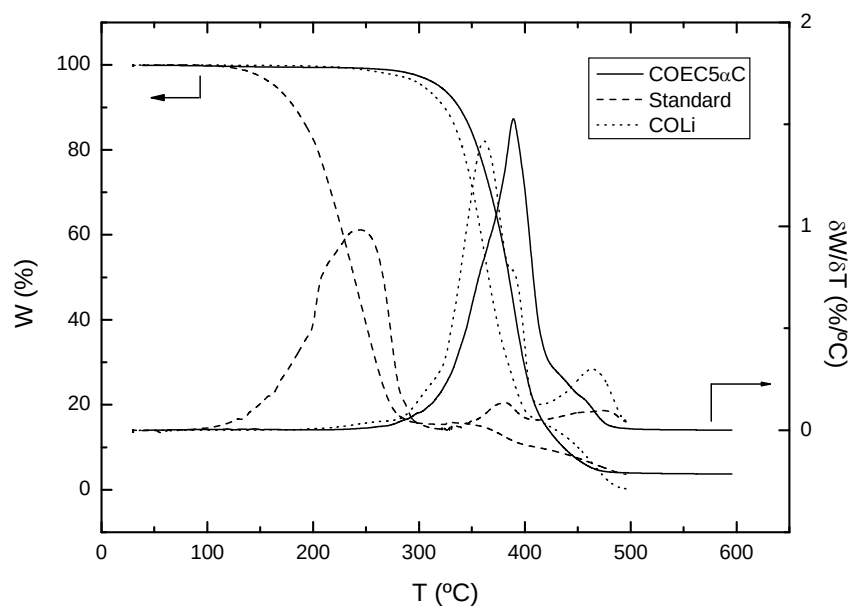


Figure 5.19. TGA thermograms for a selected oleogel, a standard lubricating grease and a partially-biodegradable material

Sample	Atmosphere	T_{range} (°C)		T_{max} (°C)
		T_{onset} (°C)	T_{final} (°C)	
COEC α C	N ₂	352.0 ± 1.4	417.2 ± 1.1	391.6 ± 2.4
	O ₂	322.4 ± 2.7	415.0 ± 0.7	369.0 ± 3.1
COECMC	N ₂	345.4 ± 1.8	396.4 ± 1.0	374.3 ± 2.4
	O ₂	338.2 ± 1.1	394.4 ± 1.5	365.4 ± 2.3
COLi	N ₂	329.2	403.0	362.4
	O ₂	321.5	-	357.2
Standard paraffinic oil-based grease	N ₂	188.3	-	245.4
	O ₂	181.6	-	245.1

Table 5.16. Characteristic decomposition temperatures, from TGA measurements, for oleogels and lubricating grease benchmarks

5.4 Rheology and mechanical stability of oleogels based on castor oil and cellulosic derivatives potentially applicable as bio-lubricating greases: influence of cellulosic derivatives concentration ratio

5.4.1 Introduction

Lubricating greases are highly structured suspensions, traditionally consisting of a thickener dispersed in mineral or synthetic oil. Fatty acid soaps of lithium, calcium, sodium, aluminium or barium are most commonly employed as thickener agents. Although the lubricating component is the base oil, the thickener is a key component, added to increase the consistency of the lubricant, in order to solve some difficulties that lubricating oils cannot cover properly in specific applications [NLGI, 1994]. With this purpose, during the manufacturing process, the thickener is induced to form a three dimensional network in the oil medium, which imparts to the lubricating grease the desired gel-like characteristics and, specifically, appropriate rheological properties [Delgado et al., 2006b]. Thus, for instance, optimal rheological properties help not only to prevent loss of lubricant under operating conditions when they are subjected to inertial forces and shear, but also to avoid the penetration of contaminants (solid particles, water...). In this sense, the grease plays the role of a seal without a significant reduction of its lubricating properties, since only a small part of grease acts as a lubricant in the contact between different mechanical parts in relative motion [Hamnelid, 2000].

Operating conditions in current technologies impose high demands on lubricating greases. For instance, they need to resist high and low temperatures, high pressures or adverse atmospheres where the properties of lubricating greases can be modified drastically. As a result, they may lose the ability to favour an appropriate lubrication. Nowadays, the lubricating market is interested not only in materials

that can be used in these conditions but it is also demanding new completely biodegradable products, or more environmentally acceptable, than the traditional lubricants, even although this new type of products will imply higher prices. The main reason for the tendency of replacing non-renewable raw materials by renewable resources in the field of lubricants is due to the high impact that they exert on the environment, since, every year, millions of tonnes of engine, industrial and hydraulic oils are leaked into the ground or poured in the environment. This is a rather problematic issue, as small amounts of these products can inhibit the growth of trees and can be toxic to aquatic life [Wilson, 1998].

On the other hand, motivations to design new biodegradable materials are also induced by government incentives, public opinion, corporate programs of social and environmental responsibility, and corporate response to marketing needs. To reach this objective, lubricants producers are looking for suitable materials to provide adequate biodegradable products. This idea is not really new, since formulations with, at least, 70-80% degradability requirements of the basic ingredient (oil) appeared in the lubricants market several decades ago (for instance, the Blue Angel eco-label in 1978) [Flynn, 1999]. However, the objective of developing environmentally compatible lubricants contains a number of additional requirements, such as classification in water hazard category “0”, and no content of heavy metals, halogenated hydrocarbons or nitrite, taking also into account that the most important requirement is that grease performance must not be affected negatively [Blackburn, 2000]. Moreover, 100% biodegradable materials are necessary to cover some specific lubrication problems, i.e. lubrication in food production, aiming to prevent any type of contamination in the manufacture of the final product. In this sense, the United States government has classified lubricants used in food processing plants into two categories: i) H1, lubricants used in applications where there is a possibility of incidental food contact; and

ii) H2, lubricants used in applications where there is not possibility of food contact [Rajewski et al., 2000]. Some biodegradable greases consisting of vegetable oils, synthetic esters or glycols as base fluids; metal soaps or polyureas as thickeners, and additives to improve the behaviour of the final material in specific conditions, have been designed to cover this goal [Stempfel, 1998]. However, this general formulation still includes highly non-biodegradable components, particularly the thickener agents, and, consequently, more efforts to find new suitable ingredients to manufacture a completely biodegradable material are needed.

In previous studies [Sánchez et al., 2009; Sánchez et al., 2011], gel-like dispersions based on castor oil and cellulosic derivatives were proposed as potential biodegradable lubricating greases. Particularly, the use of ethyl cellulose combined with other cellulosic derivatives, i.e. α -cellulose or methyl cellulose, provides an appropriate thermal and rheological behaviour of the lubricating grease. In this work, the influence of cellulosic derivatives concentration ratio on the linear viscoelasticity and mechanical stability of the resulting formulations was studied.

5.4.2 Materials and Methods

Materials

Castor oil (211 cSt at 40 °C, Guinama, Spain) was selected as biodegradable lubricating oil. Ethyl cellulose (Mn: 60000 g/mol; 48% ethoxy content), methyl cellulose (Mn: 40000 g/mol; 32% methoxy content), and α -cellulose, all of them from Sigma-Aldrich, were used as gelling agents to prepare different gel-like dispersions. Standard lithium 12-hydroxystearate lubricating greases (14-20% lithium soap) were used as reference systems. 12-hydroxystearic acid, lithium hydroxide, and paraffinic (334 cSt at 40 °C) and naphthenic (115 cSt at 40 °C) oils were kindly supplied by Verkol Lubricantes S.A. (Spain).

Manufacture of oleogel formulations

Gel-like dispersions (400 g batches) were processed in an open vessel, using a helical ribbon impeller geometry ($D = 90$ mm; $H = 90$ mm) to disperse the gelling agents. In the first step, the vessel was filled with the corresponding amount of oil and ethyl cellulose. After that, a constant rotational speed (60 rpm) was applied to the mixture, at 150°C , until ethyl cellulose was completely dissolved and, then, the other cellulosic derivative was added, keeping the same rotational speed and temperature during 30 minutes. Finally, the mixture was cooled down to room temperature by natural convection. Table 5.17 shows the composition of the different oleogel formulations studied. W values in Table 5.17 correspond to the ratios between the concentrations of ethyl cellulose and the other cellulosic derivatives used as thickeners, i.e. α -cellulose or methyl cellulose, respectively.

Castor oil (%)	Ethyl cellulose (EC) (%)	α -cellulose (α C) (%)	Methyl cellulose (MC) (%)	(EC/ α C) or (EC/MC) weight ratio (W)
78.0	1.2	20.8	—	0.06
78.0	1.6	20.4	—	0.08
78.0	2.0	20.0	—	0.10
78.0	2.4	19.6	—	0.12
78.0	2.7	19.3	—	0.14
73.0	1.0	—	26.0	0.04
73.0	1.5	—	25.5	0.06
73.0	2.0	—	25.0	0.08
73.0	2.5	—	24.5	0.10
73.0	2.9	—	24.1	0.12

Table 5.17. Chemical compositions of the oleogel formulations studied

Rheological characterization

Rheological characterization of oleogels was carried out with two controlled-stress rheometers (RS-150 and Rheoscope, ThermoHaake, Germany). Small-amplitude oscillatory shear (SAOS) tests were performed inside the linear viscoelastic region, using a plate-plate geometry (35 mm, 1 mm gap), in a frequency range of 10^{-2} - 10^2 rad/s,

and temperatures comprised between 0 and 125 °C. At least two replicates of each test were performed on fresh samples.

Penetration and mechanical stability tests

Both unworked and worked penetration indexes were determined according to the ASTM D 1403 standard, by using a Seta Universal penetrometer, model 17000-2 (Stanhope-Seta, UK), with one-quarter cone geometry. The one-quarter scale penetration values were converted into the equivalent full-scale cone penetration values, following the ASTM D 217 standard. The same samples were worked during 2 hours in a Roll Stability Tester, model 19400-3 (Stanhope-Seta, UK), according to the ASTM D 1831 standard. Penetration measurements were carried out, once again, immediately after this rolling test. Sample mechanical stability was then calculated as the difference between worked and unworked penetration values.

5.4.3 Results and Discussion

Figure 5.20 shows the evolution of the linear viscoelasticity functions with frequency, at different temperatures, for gel-like dispersions processed using castor oil and different combinations of α -cellulose and ethyl cellulose. All the formulations contain the same total amount of cellulosic derivatives but different ethyl cellulose/ α -cellulose weight ratios (W). The evolution of SAOS functions is very similar to that found for standard lubricating greases [Madieto et al., 2000; Martín-Alfonso et al., 2007]. Thus, G' values are always higher than G'' values in the whole frequency range studied, and the “plateau” region of the mechanical spectrum is always noticed, i.e. G' slightly increases with frequency and G'' displays a minimum at intermediate frequencies. This mechanical spectrum corresponds with the traditional description given for solid-like gels [Almdal et al., 1993]. As extensively investigated [Franco et al., 2005; Martín-Alfonso et al., 2009a; Martín-Alfonso et al., 2009b; Moreno et al., 2008], G' values in conventional lithium

lubricating greases typically range from 10^4 to 10^5 Pa, at 25-75 °C, around one order of magnitude higher than G'' values, depending on composition and processing conditions. As can be observed in Figure 5.20, dispersions with the lowest ethyl cellulose/ α -cellulose weight ratios ($W=0.06-0.08$) show significantly higher values of both G' and G'' and lower values of the loss tangent ($\tan\delta = G''/G'$), especially at high frequencies, indicating an enhanced relative elastic response. A dramatic decrease in both SAOS functions, but more important in G' , is noticed by slightly increasing ethyl cellulose/ α -cellulose weight ratio ($W=0.10$), in the whole temperature range studied. On the other hand, the minimum in G'' and, consequently, in the loss tangent is generally shifted to lower frequencies. However, a further increase in W produces the opposite effect, at temperatures ranging from 0 °C to 75 °C. Consequently, SAOS functions increase, although this behaviour is not associated with changes in the relative elasticity (see $\tan \delta$ in Figure 5.20). It is worth noting that this evolution of the linear viscoelasticity functions with W (0.10-0.14) is not found at 125 °C. At this temperature, a continuous decrease in the values of both moduli with ethyl cellulose/ α -cellulose weight ratio is always observed. Moreover, the relative elasticity of the samples generally decreases by increasing W .

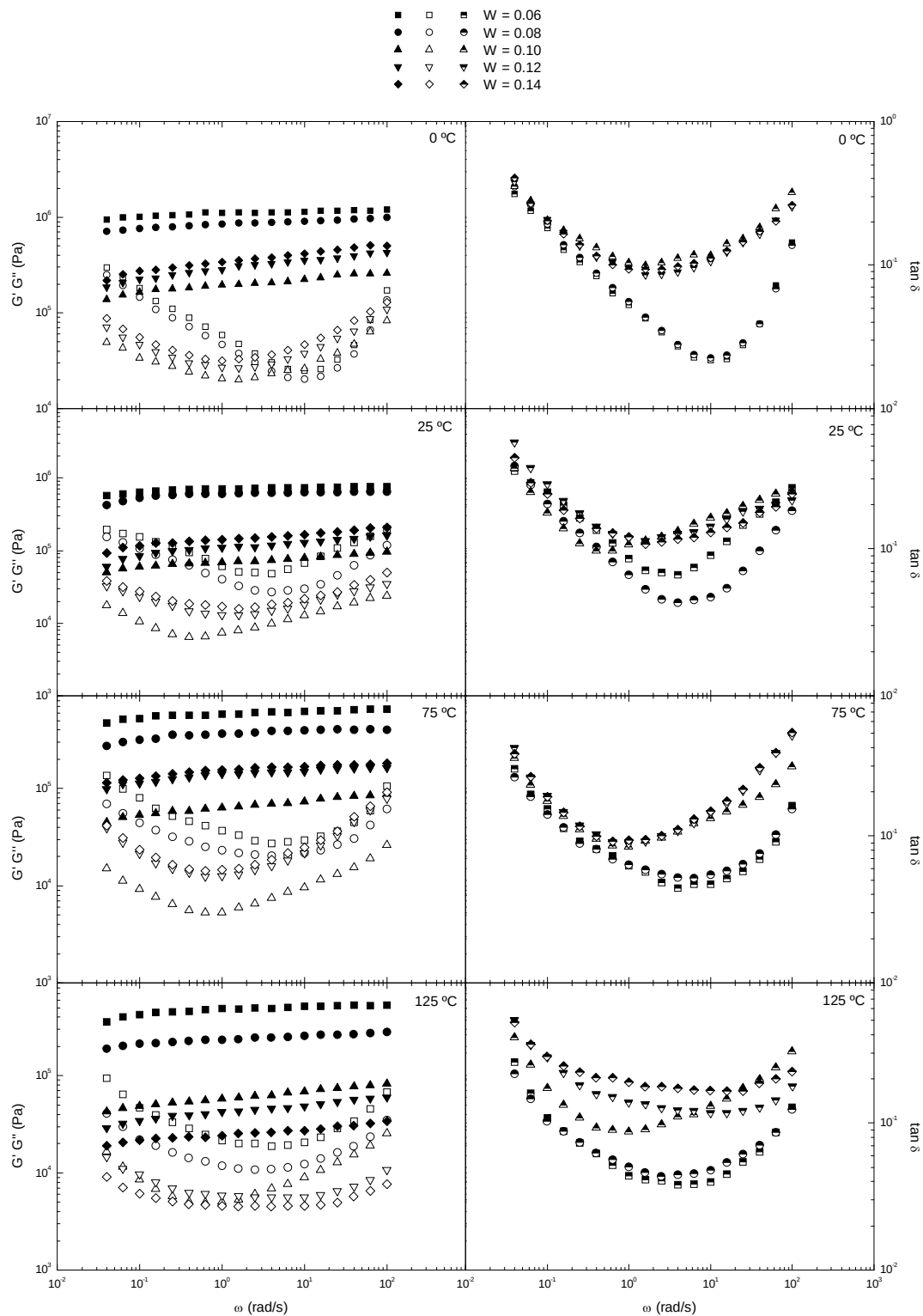


Figure 5.20. Evolution of the storage modulus (G' , filled symbols), loss modulus (G'' , open symbols) and loss tangent ($\tan \delta$, half-filled symbols) with frequency, for oleogels formulated with castor oil and ethyl cellulose/ α -cellulose blends, at different temperatures

Figure 5.21 shows the evolution of the SAOS functions with frequency for gel-like dispersions containing methyl cellulose instead of α -cellulose. The influence of ethyl cellulose/methyl cellulose weight ratio on the linear viscoelastic response of this type of dispersions is very similar to that previously shown for oleogels containing ethyl cellulose/ α -cellulose blends. Thus, minimum values in both G' and G'' were found for an intermediate ethyl cellulose/methyl cellulose weight ratio (W between 0.06 and 0.10, depending on temperature), excepting at 125 °C, where SAOS functions continuously decrease with W . Moreover, oleogel relative elasticity increases as ethyl cellulose/methyl cellulose weight ratio decreases.

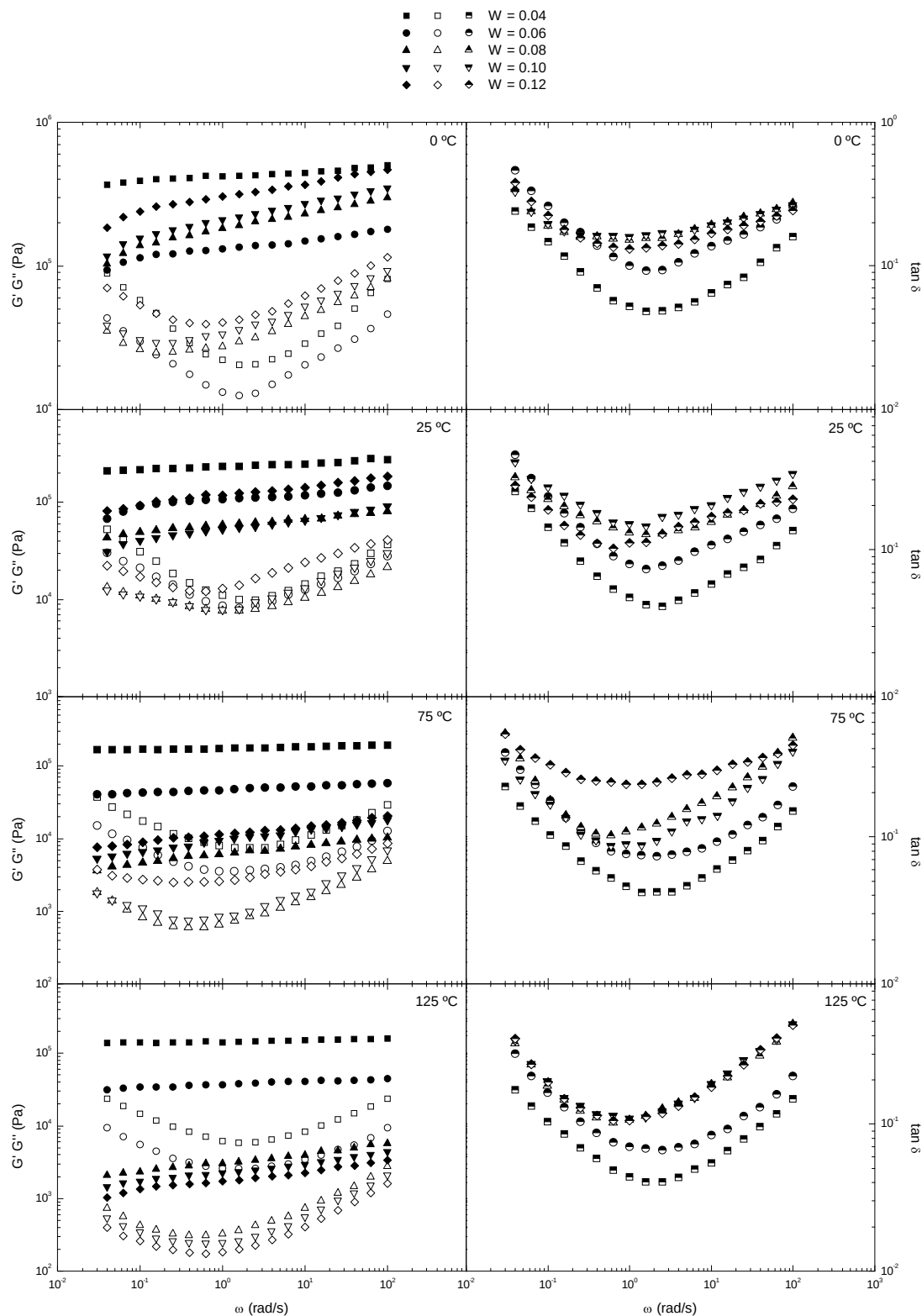


Figure 5.21. Evolution of the storage modulus (G' , filled symbols), loss modulus (G'' , open symbols) and loss tangent ($\tan \delta$, half-filled symbols) with frequency, for oleogels formulated with castor oil and ethyl cellulose/methyl cellulose blends, at different temperatures

Figure 5.22 summarizes and compares the effect of thickeners weight ratio on the linear viscoelastic response of both α -cellulose- and methyl cellulose-based oleogels. In this figure, the “plateau” modulus evolution with W is presented. The plateau modulus, G_N^0 , is a characteristic parameter of the “plateau” region in the mechanical spectrum, as described elsewhere [Ferry, 1980]. As can be observed, G_N^0 values reach minimum values at intermediate values of W , excepting at 125 °C where a continuous decrease of this viscoelastic parameter with W is clearly observed. The peculiar influence of W on SAOS functions, at 125 °C, is related to the sol-gel transition of ethyl cellulose in castor oil, which takes place around 70 °C [Sánchez et al., 2011]. As previously described [Sánchez et al., 2009], ethyl cellulose stabilizes the gel-like dispersion by significantly increasing castor oil viscosity below this critical temperature, reducing oil bleeding. Figure 5.23 illustrates the evolution of the viscosity with ethyl cellulose concentration for ethyl cellulose/castor oil binary systems corresponding to methyl cellulose dispersions, at 25 and 125 °C. An important increase in viscosity, associated to a non-Newtonian behaviour, can be clearly observed at 25 °C. This improvement in physical stability is not only due to the increasing oil viscosity but to the viscoelastic properties of the castor oil/ethyl cellulose binary systems, which at low temperatures display a certain elastic-like characteristics [Sánchez et al., 2011], similar to those extensively described for concentrated polymer solutions and weak gels [Ferry, 1980]. However, above a critical temperature of around 70-75 °C a Newtonian behaviour can be found for the ethyl cellulose/castor oil binary systems, yielding a dramatic decrease in viscosity (see Figure 5.23) and also disappearing the viscoelastic characteristics. Therefore, at these high temperatures, an increase in ethyl cellulose concentration is not relevant, being the concentration of the other cellulosic derivative the only responsible for the resulting bulk rheology of the oleogel. On the contrary, below ethyl cellulose sol-gel transition temperature, there is a joint contribution of both types of thickeners. In this case, intermediates W values, in the range studied,

provide oleogel rheological responses much more similar to those found in standard greases [Delgado et al., 2006a; Delgado et al., 2006b; Madiedo et al., 2000; Martín-Alfonso et al., 2007].

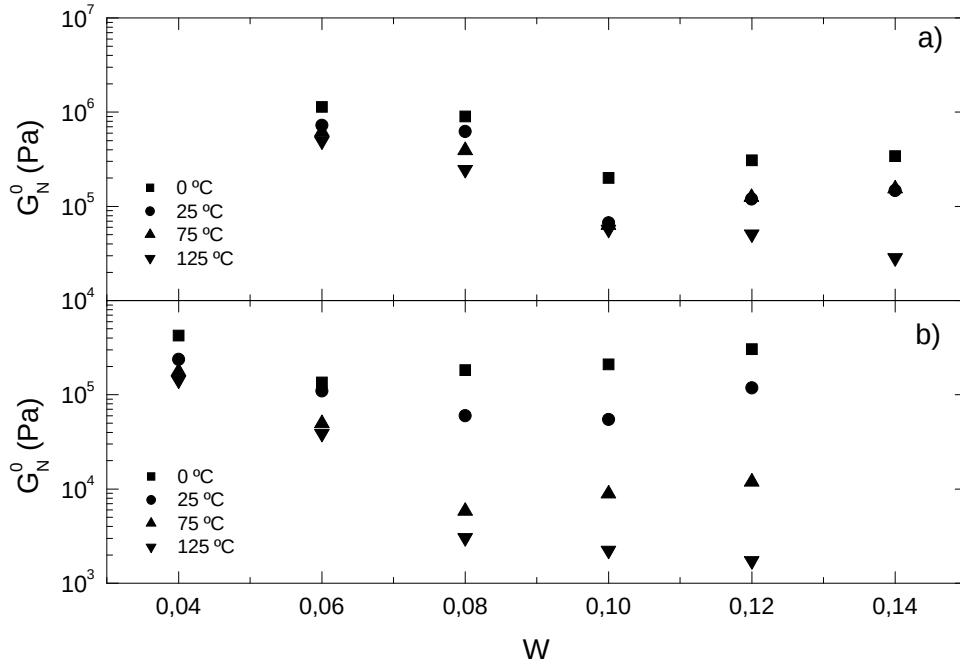


Figure 5.22. Evolution of the “plateau” modulus with cellulosic derivatives concentration ratio, at different temperatures, for oleogels formulated with: a) ethyl cellulose/ α -cellulose blends, and b) ethyl cellulose/methyl cellulose blends

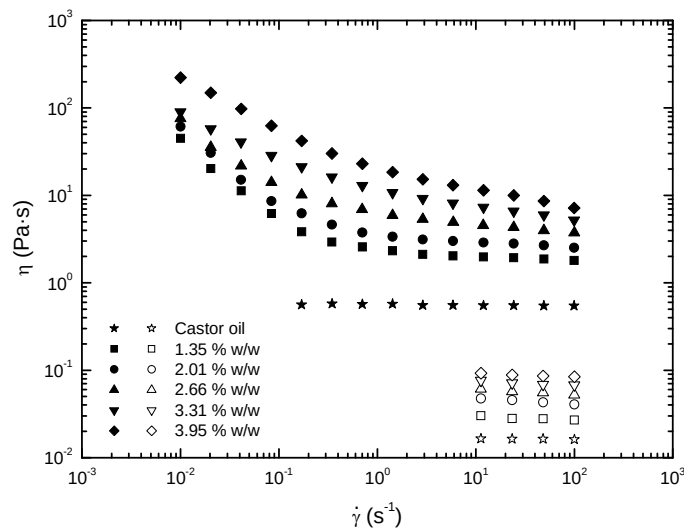


Figure 5.23. Evolution of the viscosity with shear rate for ethyl cellulose/castor oil binary systems corresponding to methyl cellulose dispersions, at 25 °C (full symbols) and 125 °C (open symbols)

On the other hand, as can be deduced from Figures 5.20 and 5.21, the values of the SAOS viscoelastic functions decrease as temperature increases in the whole frequency range studied. As can be observed in these figures, the frequency dependence of both moduli for a given oleogel is not qualitatively influenced by temperature. On the contrary, the evolution of oleogel linear viscoelastic functions with temperature largely depends on the cellulosic derivatives concentration ratio employed. Thus, SAOS viscoelastic functions thermal dependence is clearly dampened by reducing ethyl cellulose concentration in oleogels thickened with both α -cellulose/ethyl cellulose and ethyl cellulose/methyl cellulose blends. As previously reported for standard lithium greases [Delgado et al., 2006b], the “plateau” modulus can be used to quantify the influence of temperature by using an Arrhenius-type equation:

$$G_N^0 = A \cdot e^{\frac{E_a}{R} \left(\frac{1}{T} \right)} \quad (4.2)$$

where E_a is a parameter which evaluates the thermal dependence, similar to the activation energy (J/mol), R is the gas constant (8.314 J/mol K), T is the absolute temperature (K), and A is the pre-exponential factor (Pa). Equation 4.2 fits the experimental plateau modulus values, in the whole temperature range studied, fairly well ($R^2 > 0.992$, see Figure 5.24). Table 5.18 shows the activation energy values for all the oleogels studied. In general, E_a values increase with ethyl cellulose/ α -cellulose and ethyl cellulose/methyl cellulose weight ratios, although the most important changes seem to occur when cellulosic derivatives concentration ratio, W , is increased from 0.06 to 0.08 for both types of dispersions (Table 5.18). Furthermore, thermal susceptibilities are generally lower for oleogels formulated with ethyl cellulose/ α -cellulose blends. In this sense, E_a values found for gel-like dispersions formulated with low cellulosic derivatives concentration ratio are only slightly higher than those obtained for standard lithium greases in the low-temperature range [Delgado et al., 2006b]. In the

case of dispersions based on ethyl cellulose/ α -cellulose blends, at high W values, E_a values are also lower than those found for conventional lithium greases in the high temperature range (18-20 kJ/mol). On the other hand, oleogels manufactured with ethyl cellulose and methyl cellulose, using W values higher than 0.06, show much higher thermal susceptibilities than lithium greases [Delgado et al., 2006b].

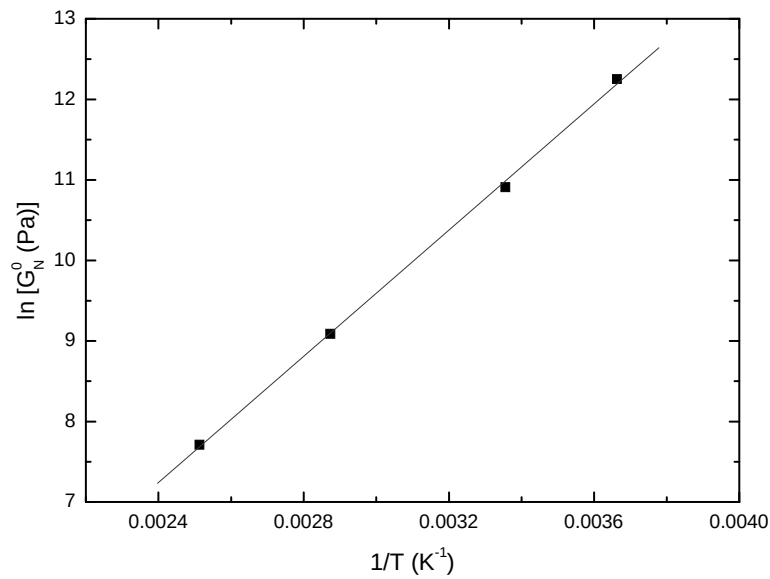


Figure 5.25. Evolution of the “plateau” modulus (square symbols) with temperature, and Arrhenius’ fitting (solid line), for a selected oleogel formulation (ethyl cellulose/methyl cellulose weight ratio: 0.10)

	W	Ea (kJ/mol)
Oleogel based on ethyl cellulose and α -cellulose	0.06	5.54
	0.08	9.16
	0.10	9.54
	0.12	11.58
	0.14	16.20
Oleogel based on ethyl cellulose and methyl cellulose	0.04	7.39
	0.06	9.69
	0.08	31.09
	0.10	32.58
	0.12	37.85

Table 5.18. Activation energy values, from equation 4.2, for the different oleogels studied

Finally, mechanical stability, traditionally determined for lubricating greases from the difference between penetration indexes after and before submitting the grease to a standardized working test, was evaluated. In this study, oleogel mechanical stability was estimated after the application of a shear rolling test. In general, greases with good mechanical stability must exhibit penetration increments after working close to zero. Worked and unworked penetration values and mechanical stability data for the oleogels studied are gathered in Table 5.19. These values are compared with those obtained for two standard lithium lubricating greases based on both paraffinic and naphthenic oil, and a model semi-biodegradable grease made from castor oil and lithium 12-hydroxystearate soap (CoLi). As can be observed, the consistency (determined from penetration values) shown by the oleogels studied is generally lower than that of standard lithium lubricating greases, especially when dispersions were formulated with ethyl cellulose/methyl cellulose blends. However, it is worth pointing out that these cellulose derivatives blends yield oleogel formulations with appropriate mechanical stability values, similar to those found for standard greases. On the contrary, the consistency of oleogels based on ethyl cellulose/ α -cellulose blends is significantly affected by the application of a severe continuous shear, like that induced by the standardized rolling elements.

Sample	W	Unworked penetration (dmm)	Worked penetration (dmm)	Penetration variation (dmm)
Oleogels based on ethyl cellulose and α -cellulose	0.06	335	407	71
	0.08	343	418	75
	0.10	380	467	86
	0.12	358	433	75
	0.14	354	433	79
Oleogels based on ethyl cellulose and methyl cellulose	0.04	429	422	-7
	0.06	440	440	0
	0.08	422	425	3
	0.10	410	410	0
	0.12	425	429	4
COLi		242	260	18
Standard paraffinic oil-based grease		303	305	2
Standard naphthenic oil-based grease		274	289	15

Table 5.19. Penetration and leakage values for oleogels, model lithium soap/castor oil grease, and standard lubricating greases

5.5 Influence of vegetable oil

In order to study how the type of vegetable oil affects the mechanical properties of oleogels thickened with α -cellulose, different oleogels containing castor, soybean, rapeseed and sunflower oil have been processed under the same processing conditions (see Figure 5.25). Very similar mechanical spectra have been found for all the oils used in oleogel formulations, excepting in the case of the castor oil based oleogel which exhibits much lower values of both SAOS moduli. Soybean, rapeseed and sunflower oils yield almost identical G' values but slightly different G'' values, reflected in different $\tan\delta$ values. Thus, the oleogel formulation containing sunflower oil shows the highest values of the loss modulus with the minimum shifted to higher frequencies, while the oleogel processed with rapeseed oil shows lower G'' values at low frequency, although the minimum in G'' is placed at lower frequency. Finally, the evolution of the loss modulus in the case of the oleogel formulated with soybean oil is similar to that formulated with rapeseed oil, although slightly lower values have been obtained in the whole frequency range studied. As previously studied with mineral oils [Delgado, 2006a], these different behaviours, especially that obtained with the castor oil, must be attributed to oil viscosity. Thus, the higher oil viscosity, the lower values of oleogel SAOS functions are obtained.

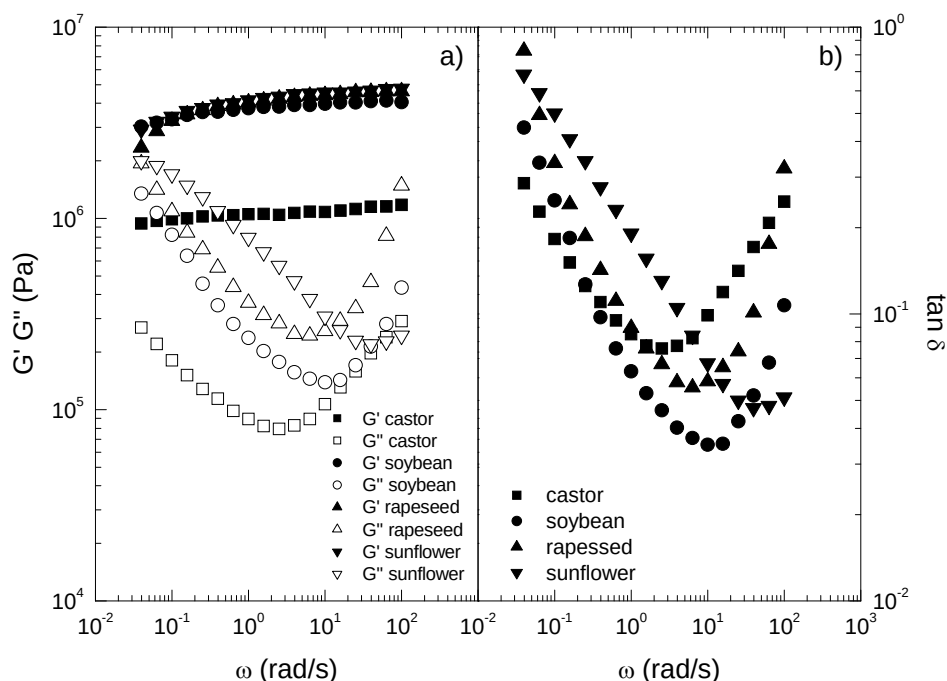


Figure 5.25. Evolution of the storage and loss moduli (a) and loss tangent (b) with frequency for oleogels manufactured using different types of vegetable oils (25% w/w α -cellulose in vegetable oils mixed with the helical ribbon geometry, at 60 rpm during 30 minutes, at room temperature)

Finally, the oleogel formulated with castor oil presents a significant higher consistency (lower penetration) and NLGI grade more similar to lubricating greases but lower mechanical stability than oleogels prepared with low-viscosity vegetable oils (see Table 5.20).

Oil	Unworked penetration (dmm)	NLGI grade	Worked penetration (dmm)	Penetration variation (dmm)
Castor	324	1	354	30
Soybean	418	00	410	-8
Rapeseed	474	000	482	8
Sunflower	474	000	482	8

Table 5.20. Penetration values of oleogels manufactured with different types of vegetable oils (25% w/w α -cellulose in vegetable oils mixed with the helical ribbon geometry, at 60 rpm during 30 minutes, at room temperature)



CAPÍTULO 6

**OLEOGELES FORMULADOS CON
QUITINA, QUITOSANO Y
ALGUNOS DERIVADOS QUÍMICOS**

6.1 Use of chitin, chitosan and acylated derivatives as thickener agents of vegetable oils for bio-lubricant applications

6.1.1 Introduction

Lubricating greases are generally described as highly structured suspensions where a thickener or gelling agent is dispersed in a lubricating oil [Hamnelid, 2000]. Some additional components, called additives, are normally included, in order to improve specific properties and functions. 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 a 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. Thus, for instance, fluctuations with temperature, loads, vibrations and surrounding environment conditions, within reasonable limits, can be all handled by using this type of product. Moreover, 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. 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]. As extensively reported, the rheological behaviour and related functional properties of a lubricating grease depend on both its composition and the manufacturing process used [Delgado et al., 2005; Franco et al., 2005; Delgado et al., 2006a]. The most common composition of lubricating greases is a mineral oil thickened with a metallic soap, although it may also contain additives, such as anti-oxidants, anti-corrosion, etc.

Nowadays, it is well-known that there is an increasing interest in the use of natural components in a wide variety of manufactured

products, due to the general tendency to promote both the replacement of non-renewable raw materials by renewable resources, and the minimization of the environmental impact caused by industrial waste materials [Lea, 2002]. In this sense, a new market based on eco-friendly products is developing quite fast, where consumers are well disposed to test new products or even pay higher prices if they receive an alternative material with reduced negative effects on the environment. Concerning the impact that lubricants exert on the environment, it is estimated that, every year, more than 10 million tons of engine, industrial and hydraulic oils are returned into the environment [Bartz, 1998]. This is a very problematic situation from an environmental point of view, since even small amounts of these products, which are accidentally spilled on ground and water, can inhibit the growth of trees and can be toxic to aquatic life [Wilson, 1998].

Vegetable oils are promising candidates to be used as eco-friendly lubricants, presenting good lubricity, ability for adhering metal surfaces, weak viscosity-temperature dependence, non-toxicity, and high biodegradability. Although raw vegetable oils present some shortcomings, like poor oxidation stability, deficient low temperature flow properties and small range of viscosities, previous studies demonstrated that these properties can be improved by using some additives [Erhan et al., 2006; Quinchia et al., 2009]. However, developing lubricating greases based on 100% biodegradable raw materials is a much more complicated task, due to the difficulty of the substitution of the thickener agents traditionally used (metallic soaps, phyllosilicates or polyurea compounds) by other environmentally friendly additives. Thus, a bio-thickener should convey to the oleogel similar or improved rheological characteristics, and thermal and mechanical stabilities to those provided by traditional metallic soaps.

Previous research carried out by some of the authors reported the use of sorbitan monostearate as gelling agent in the formulation of bio-lubricating greases. Some oleogels containing this thickener showed

viscoelastic properties and tribological characteristics similar to those found with standard lithium greases. However, some weaknesses were observed regarding their mechanical stability and properties thermal dependence [Sánchez et al., 2008]. On the other hand, an improved thermal resistance was found for formulations thickened with cellulose derivatives (even better than that found for standard lubricating greases), as well as satisfactory mechanical and physical stabilities, especially in the case of oleogels formulated with castor oil and blends of ethyl and methyl cellulose [Sánchez et al., 2011]. However, in these cases, suitable mechanical and physical stabilities were linked to values of the linear viscoelastic functions much higher than those found for standard greases. In this sense, it is necessary to investigate the performance of other natural thickeners, aiming to develop new biogreases with the whole set of relevant properties matching those of the benchmark. Finding this new biodegradable thickener agent, obtained from natural resources, may create a new market niche with interesting perspectives for the future [Fessenbecker, 2003].

In addition to cellulose derivatives, chitin and its derivatives are another interesting group of biopolymers that could be used as potential thickeners for biolubricant applications. Chitin is a natural polysaccharide, synthesized by a large number of living organisms, mostly found in the shell of crustacean, the cuticles of insects, and the cell walls of fungi [Knorr, 1984]. Chitin is considered the most abundant biopolymer in nature after cellulose. When the degree of deacetylation of chitin reaches about 50%, it becomes soluble in aqueous acidic media and is called chitosan [Rinaudo, 2006]. In this work, the potential use of chitin, chitosan and some other acylated derivatives, as bio-thickener agents to formulate stable dispersions in vegetable oils, is explored. Rheological and thermogravimetric characterizations, as well as evaluation of their tribological properties and mechanical stability, under standardized methods for lubricants, were carried out, in order to investigate the potential applicability of these gel-like dispersions as biodegradable lubricating greases.

6.1.2 Materials and methods

Materials

Castor (Guinama, Spain) and soybean (kindly supplied by Fresenius Kabi, Sweden) oils were used as base oils for the oleogel formulations studied. Moreover, three biopolymers were used as potential thickeners or gelling agents: crab shell chitin (CC), purchased from Qingdao Fraken (China), and low (LMC) and medium (MMC) molecular weight chitosan (Sigma-Aldrich, Germany). The average molecular weight and degree of deacetylation (DD) of the original biopolymers are shown in Table 6.1. In addition, acylated chitosan samples (synthesis procedure described below) were also tested. All other common reagents and solvents employed were purchased from Sigma-Aldrich.

Thickener	Mean Molecular Weight (g/mol) ⁺	DD (%) ⁺⁺	DD (%) ⁺⁺⁺
CC	$5.4 \cdot 10^5$	-	7.3
LMC	$3.9 \cdot 10^5$ *	83.4 *	87.6
MMC	$5.6 \cdot 10^5$ *	83.1 *	82.1

⁺ determined by viscometric methods

⁺⁺ determined using the titration method

⁺⁺⁺ determined from IR analysis

* values taken from Takahashi et al., 2005

Table 6.1. Mean molecular weight and degree of deacetylation (DD) of the chitin and chitosan biopolymers used

Standard lithium 12-hydroxystearate lubricating greases (14 and 20% lithium soap, NLGI grade 1-2) were used as benchmarks. 12-hydroxystearic acid, lithium hydroxide, and paraffinic (334 cSt at 40 °C) and naphthenic (115 cSt at 40 °C) oils, kindly supplied by Verkol Lubricantes S.A. (Spain), were used to prepare these traditional lubricating greases, using the methodology reported elsewhere [Delgado et al., 2005; Delgado et al., 2006a].

Acylation of Chitosan

The acylation reaction of chitosan was basically performed following the method described by Ma and co-workers [Ma et al., 2009]. Chitosan (24.0 g) was soaked in a mixed solvent of triethylamine (250 mL) and acetone (250 mL), for 24 h at 50°C, and then cooled and stirred, for 1 h at 0°C. Stearoyl chloride (48 g) dissolved in acetone (300 mL) was added drop wise into the mixed solution within 1 h and, then, the temperature was gradually increased to 90°C during 4 h, and maintained for 1 h more. Afterwards, the solution was cooled down to room temperature without stirring and, finally, grounded. This synthesis was performed using medium and low molecular weight chitosan, resulting two different products, which are referred as A2MMC and A2LMC, respectively. The same procedure was followed when the stearoyl chloride/chitosan mass ratio (3:1) was changed. In this case, the resulting products are referred as A3MMC and A3LMC for the medium and low molecular weight chitosan, respectively. The determination of the average substitution degree achieved was carried out according to the method described by Klemm et al [Klemm et al., 1998], expressed over the maximum possible substitution of the monomer (see Table 6.2).

Biopolymer	Degree of Substitution	1 st peak		2 nd peak	
		T _m (°C)	ΔH _f (J/g)	T _m (°C)	ΔH _f (J/g)
A2MMC	0.3	43	18	64 / 74	40
A3MMC	0.7	40	13	65 / 73	44
A2LMC	0.8	39	12	65 / 72	64
A3LMC	1.0	40	11	65 / 73	67

Table 6.2. Degree of substitution, melting temperature and fusion enthalpy data of the acylated chitosan samples obtained in this study

Processing of Biodegradable Lubricating Greases

Processing of biogrease samples was performed in an open vessel, using a controlled-rotational speed mixer (60 rpm), equipped with a helical ribbon impeller to disperse the different biopolymers. Thickener

concentrations were previously optimized to provide physically stable oleogels, i.e. without significant oil bleeding. Batches of 220 g were prepared for each formulation investigated (see Table 6.3). Samples were heated, up to 85-90°C, while dispersing the biopolymer, in order to decrease its viscosity and improve mixing. The mixing process was maintained during 1 h. Finally, oleogel cooling down to room temperature was carried out by external natural convection, under continuous internal stirring, in the same heating device.

Thickener Agent	Concentration (% w/w)	Vegetable Oil (up to 100% w/w)	Code Applied
CC	19	Castor	CC-19
CC	21	Castor	CC-21
CC	21	Soybean	CC-21-S
CC	23	Castor	CC-23
MMC	23	Castor	MMC-23
MMC	25	Castor	MMC-25
MMC	27	Castor	MMC-27
MMC	27	Soybean	MMC-27-S
LMC	39	Castor	LMC-39
LMC	39	Soybean	LMC-39-S
A2MMC	35	Castor	A2MMC-35
A3MMC	35	Castor	A3MMC-35
A2LMC	35	Castor	A2LMC-35
A3LMC	35	Castor	A3LMC-35

Table 6.3. Compositions of the oleogel formulations studied

Thermogravimetric Analysis (TGA)

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

Differential Scanning Calorimetry (DSC)

DSC measurements were performed with a Q-100 TA instrument, using 5-10 mg samples sealed in hermetic aluminium pans, and heated from -80 up to 200 °C. Then, a second heating ramp was performed, in order to eliminate the thermal-history and residual moisture. In all

cases, a heating rate of 10°C/min was applied, and the samples were purged with N₂, at a flow rate of 50 mL/min.

Fourier Transform Infrared Spectroscopy (FTIR)

FTIR spectra were obtained with a Digilab FTS3500ARX (Varian, USA) apparatus. Biopolymer samples were prepared as KBr pellets and 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.

Rheological Characterization

Rheological characterization was carried out with two controlled-stress rheometers, Rheoscope (ThermoHaake, Germany) and Gemini (Bohlin, UK). Small-amplitude oscillatory shear (SAOS) tests were performed inside the linear viscoelastic region, using rough plate-plate geometries (35 mm diameter and 25 mm diameter, respectively, and 1 mm gap), in a frequency range of 10⁻²-10² rad/s, at 5, 25, 50, 100 and 130°C. At least two replicates of each test were performed on fresh samples.

Penetration and Mechanical Stability Tests

Both unworked and worked penetration indexes were determined according to the ASTM D1403 standard, by using a Seta Universal penetrometer, model 17000-2, with one-quarter cone geometry (Stanhope-Seta, UK). The one-quarter scale penetration values were converted into the equivalent full-scale cone penetration values, following the ASTM D217 standard. Classical consistency NLGI grade was established according to these penetration values [NLGI, 1994]. The same samples were worked during 2h in a Roll Stability Tester, model 19400-3 (Stanhope-Seta, UK), as indicated in the ASTM D1831 standard and, then, penetration measurements were carried out, once again, after this rolling test. Sample mechanical stability was then calculated as the difference between worked and unworked penetration values.

Tribological Tests

Tribological tests were performed in a Nanotribometer (CSM Instruments, Switzerland) with a classical ball-on-disc geometrical coupling, using a ball diameter of 1.5 mm, and working in the rotational mode, by selecting a normal load of 50 mN, a track radius of 7 mm, and a linear speed of 10 mm/s. The material combination for these series of measurements was a sapphire ball on a sapphire plate, both with a maximum roughness of 1 μm . The friction coefficient was continuously measured, during 15 min, as the ratio between the resulting friction and the normal forces applied. Forces were determined by means of optically detecting the displacement of a cantilever. Frictional force was measured with a resolution of 0.01 mN. In all cases, a deflector had to be applied to re-spread the grease after each revolution. Three replicates of the friction coefficient were made, at room temperature, and the average value calculated.

6.1.3 Results and Discussion

Thermal and Spectroscopic Characterization of Biopolymers

The different chitin derivatives employed as thickeners were thermally characterized by means of DSC and TGA techniques. Figure 6.1 shows the DSC curves for selected non-acylated and acylated chitosan samples. As can be observed, samples MMC and LMC do not show any melting or glass transition event in the temperature range from -80 °C to 200 °C. In this sense, the rheological properties of the final products thickened by these biopolymers should not dramatically change with temperature. On the other hand, the acylated biopolymers heat flow curves display two main peaks, which can be related to acylated chitosan structures with different degree of substitution and, consequently, two different melting temperatures. Table 6.2 shows the melting temperatures found for all the acylated chitosan samples studied. In general, the melting temperatures are the same for all the

samples, excepting for sample A2MMC, with lower degree of substitution, which displays a first melting peak slightly shifted to higher temperatures. In this particular case, the fusion enthalpy (ΔH_f) is also slightly higher than those found for all the remaining samples studied (see Table 6.2), which indicates a larger proportion of the less acylated component, associated to this first melting peak. However, the fusion enthalpy (ΔH_f) corresponding to the second peak clearly decreases with chitosan molecular weight and increases with the substitution degree (see Table 6.2). This fact supports the X-ray diffraction results previously reported [Ma et al., 2009], which suggest that the cristallinity of acylated chitosan increases with the number of long aliphatic chain introduced. The acylated structures have been also investigated using FTIR techniques. Figure 6.2 displays selected (for the sake of clarity) FTIR spectra for CC, MMC and A2MMC samples, respectively. As expected [Guinesi and Cavalheiro, 2006], chitin and chitosan FTIR spectra are very similar (see Figures 6.2a and 6.2b), mainly differing in the intensity of the absorption bands at around 1655 cm^{-1} , corresponding to N-acetyl groups, and 3440 cm^{-1} , attributed to the inter- and intra-molecular hydrogen bonding of both $-\text{NH}_2$ and $-\text{OH}$ stretching vibration, respectively. The different intensity of both peaks can be used to determine the degree of deacetylation (DD), as previously reported [Guinesi and Cavalheiro, 2006; Baxter et al., 1992; Lee et al., 1995]. DD values, obtained from FTIR analysis, are compared in Table 6.1 with those found in the literature using the titration method [Takahashi et al., 2005]. On the other hand, the broad band at around 3440 cm^{-1} is clearly reduced in the acylated compound [Ma et al., 2009]. Moreover, a new peak appears at 1704 cm^{-1} , assigned to the $\text{C}=\text{O}$ of $-\text{N}(\text{COR})_2$ and $-\text{OCOR}$ groups, as a consequence of the acylation reaction between stearyl chloride and $-\text{NH}_2$ or $-\text{OH}$ groups of chitosan. Other new significant peaks, at 2920 and 2850 cm^{-1} (see Figure 6.2c), assigned to the asymmetrical and symmetrical bending vibrations of methylene groups, confirm the insertion of long aliphatic chains in the chitosan molecular structure.

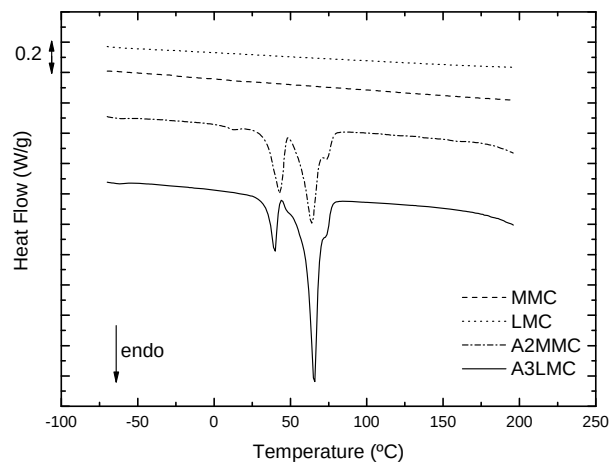


Figure 6.1. DSC heat flow curves for MMC, LMC, A2MMC and A3LMC samples

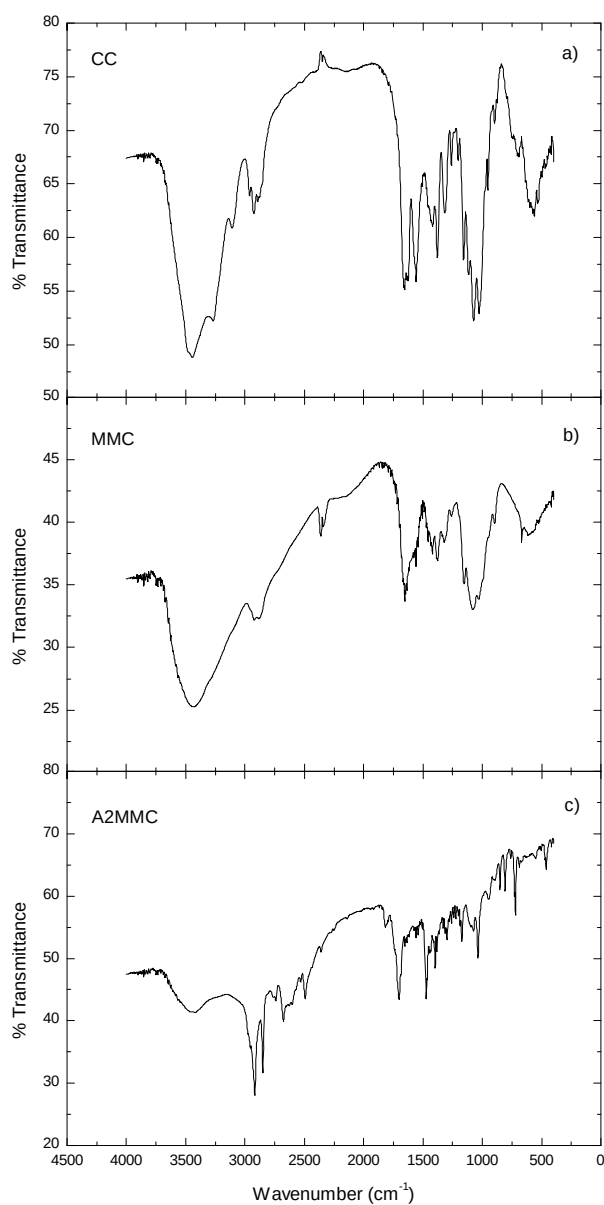


Figure 6.2. Selected IR spectra for CC, MMC and A2MMC samples

Figure 6.3a shows selected thermogravimetric curves (weight loss vs. temperature and its derivative function) for some of the biopolymers studied. On the other hand, Table 6.4 gathers the main characteristic parameters derived from this analysis (estimated as indicated elsewhere [Sánchez et al., 2009], and related to the thermal stability of the biopolymers used as thickeners. As can be seen, in general, biopolymer thermal decomposition occurs in one single stage, although the temperature decomposition range ($T_{\text{final}}-T_{\text{onset}}$) is much wider for the acylated chitosan samples, as a consequence of the different degree of acylation achieved. The highest thermal stability corresponds the chitin sample, showing values of T_{onset} and temperature for the maximum decomposition rate, T_{max} , much higher than chitosan and acylated chitosan samples, which is attributed to the decomposition of the chitin acetoamido groups [Guinesi and Cavalheiro, 2006]. On the contrary, the acylated chitosan samples present the lowest thermal stability, showing T_{onset} of around 190°C, while LMC and MMC samples show very similar characteristic degradation temperatures (Table 6.4), associated to their higher amine groups contents [Guinesi and Cavalheiro, 2006]. These results are in agreement with those found by Zong et al. [Zong et al., 2000], who concluded that the thermal stability of acylated chitosans was lower than that found for chitosan. These authors also found that the decomposition temperature increased with the length of the aliphatic chain inserted in the chitosan molecule, being, for instance, around 255 °C for the lauroyl-substituted chitosan, which is slightly lower than that obtained in this work for stearyl-substituted chitosans. However, the maximum decomposition temperature found for acylated chitosan is much lower than those obtained by Ma et al. [Ma et al., 2009], who reported values even higher than chitosan T_{max} values.

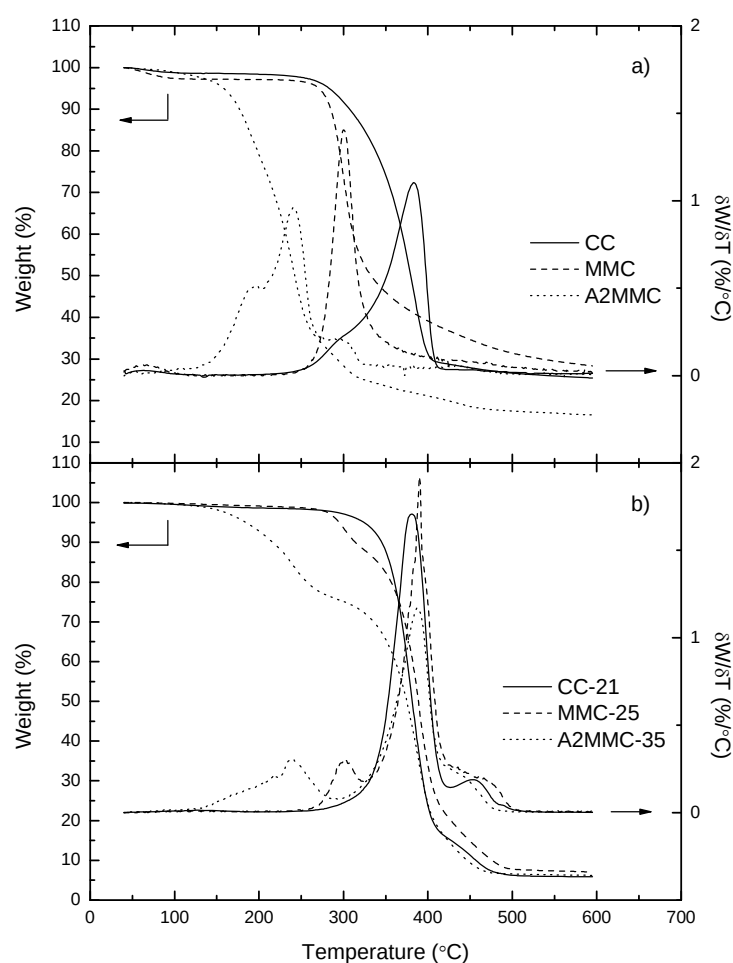


Figure 6.3. TGA thermograms for a) selected biopolymers and b) some of their corresponding oleogel formulations

Sample	T_{onset} (°C)	T_{max} (°C)	T_{final} (°C)	Residue (%)
CC	336	383	398	26.4
MMC	284	301	330	27.7
LMC	280	298	328	30.8
A2MMC	190	241	275	16.4
A3LMC	198	246	269	7.0

Table 6.4. TGA characteristic parameters for some of the biodegradable thickeners studied

Thermogravimetric Analysis of Oleogel Formulations

As can be observed in Figure 6.3b, thermal decomposition of oleogel samples containing chitin, chitosan, or acylated derivatives occurs in two main stages. The first one corresponds to the

decomposition of the biopolymer (as can be deduced from the characteristic temperatures shown in Tables 6.4 and 6.5), whilst the second one, much more remarkable, is associated to the thermal degradation of the castor oil. In the case of the chitin-based oleogel, thermal decompositions of both biopolymer and castor oil occur at similar temperatures and, consequently, only one main thermal event is clearly detected, i.e. one main peak in the weight loss vs. temperature derivative function. The characteristic temperatures obtained from TGA are listed in Table 6.5 for selected oleogel samples, which are potentially applicable as bio-lubricating greases. As expected, oleogel formulations prepared with LMC and MMC chitosan samples show almost identical thermal stabilities, otherwise much higher than formulations containing acylated chitosans as thickener (see Table 6.5). On the other hand, the chitin-based oleogel displays the highest T_{onset} and T_{max} values and, therefore, can be considered the most thermo-resistant formulation.

Table 6.5 also includes characteristics parameters for thermal decomposition of two standard lithium greases, manufactured with paraffinic and naphthenic oils, respectively, which occurs in one main single stage. As can be observed, chitin and chitosan-based dispersions tolerate much higher temperatures without losing a significant amount of mass (T_{onset}) than mineral oil-based greases. Besides this, the characteristic temperatures associated to the first thermal decomposition event of acylated chitosan-based oleogels are very similar to those found for standard lithium greases (see Table 6.5).

Sample	T _{onset} (°C)	T _{max} (°C)	T _{final} (°C)	Residue (%)
CC-21	351 / 442	379 / 459	396 / 486	5.8
MMC-25	282 / 369	300 / 390	311 / 414	7.1
LMC-39	281 / 367	300 / 389	311 / 409	14.4
A2MMC-35	203 / 358	240 / 388	262 / 414	6.2
A3MMC-35	211 / 359	234 / 393	256 / 428	3.2
Standard paraffinic oil- based grease	188	245	-	3.8
Standard naphthenic oil- based grease	229	295	326	1.3

Table 6.5. TGA characteristic temperatures for selected oleogels and some standard lithium lubricating greases

Rheological Characterization of Oleogel Formulations

Figures 6.4 and 6.5 show the mechanical spectra, obtained from SAOS measurements inside the linear viscoelastic range, for chitin- and chitosan-based oleogels, respectively. As can be observed, the so called “plateau” region of the mechanical spectrum is always noticed. In this region, the storage modulus, G' , is always higher than the loss modulus, G'' , in the whole frequency range studied. G' slightly increases with frequency, whilst G'' displays a clear minimum. This evolution is typically found in highly entangled polymeric systems [Ferry, 1980], and is very similar to that shown by standard lubricating greases [Madieto et al., 2000; Balan and Franco 2001]. As extensively investigated [Franco et al., 2005; Delgado et al., 2006a; Martín-Alfonso et al., 2007; Martín-Alfonso et al., 2009a; Martín-Alfonso et al., 2009b; Moreno et al., 2008], 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 composition and processing conditions. This range of G' and G'' values can be matched by using chitin concentrations comprised between 19 and 23% w/w (see Figure 6.4a). The relative elasticity of chitin-based oleogels is also similar to that found in standard greases, as shown in Figure 6.4b, where the values of the loss tangent ($\tan \delta = G''/G'$) are plotted versus frequency [Martín-Alfonso et al., 2009a; Martín-Alfonso et al., 2009b; Moreno et al., 2008].

As can be observed, oleogel relative elasticity increases with chitin concentration in a wide frequency range. Furthermore, a significant decrease in G' and G'' values was found when castor oil was replaced by a less viscous oil, such as soybean oil.

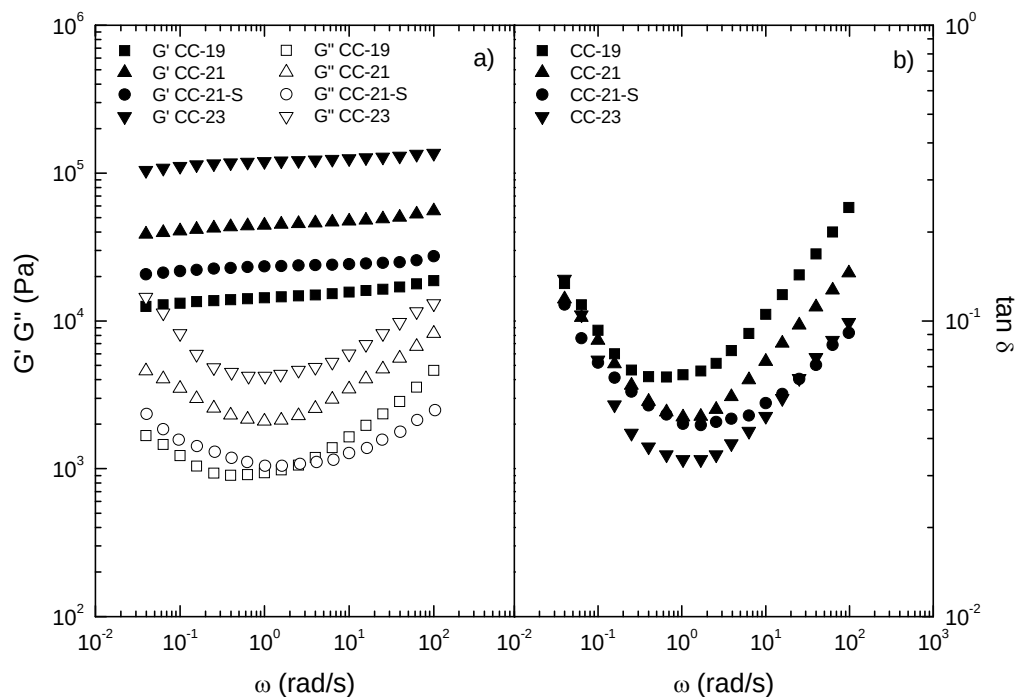


Figure 6.4. Evolution of SAOS functions with frequency for chitin-based oleogel formulations, at 25 °C

On the other hand, much higher values of the linear viscoelasticity functions are found for physically stable chitosan-based oleogels (Figure 6.5), around one decade higher than those obtained for standard lithium greases and chitin-based oleogels. As previously remarked, it is also clearly noticed that the values of both SAOS functions for MMC-based oleogels increase with thickener concentration (Figure 6.5a). Moreover, a slight decrease in G' and no significant differences in G'' are found when castor oil is replaced by soybean oil. The loss tangent is slightly affected by chitosan concentration (slight decrease as thickener concentration increases) or type of oil (slightly higher for castor oil-based oleogels). If a low-molecular weight-chitosan (LMC) is used as thickener, instead of MMC, higher concentrations of biopolymer are required to produce a stable dispersion, avoiding phase

separation and also reducing the grainy aspect of the samples, which turn to show a much more homogeneous appearance. At least, 35% w/w LMC is necessary to achieve physically stable oleogels. However, at this concentration, a rather different mechanical spectrum is obtained. Thus, no “plateau” region is observed in the mechanical spectrum of this oleogel (data not shown). This mechanical spectrum develops as thickener concentration increases. In this sense, a crossover between both linear viscoelastic functions, at low frequencies, followed by the previously mentioned “plateau” region, are noticed for castor oil oleogels containing 39% LMC. For this thickener concentration, G' values are similar to those obtained for MMC-based oleogels, whilst G'' values are even higher (Figure 6.5a). Consequently, the values of the loss tangent are higher and the relative elasticity of LMC-based castor oil oleogel decreases (Figure 6.5b). The replacement of castor oil by soybean oil significantly reduces the values of the SAOS functions, yielding a rheological behaviour much more similar to that shown by standard lubricating greases.

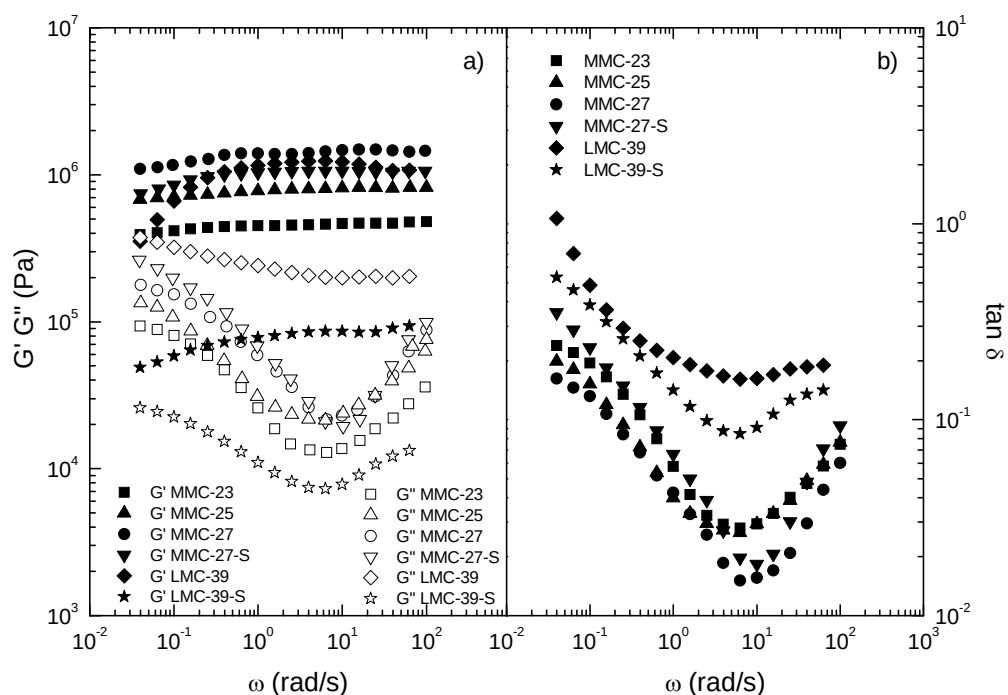


Figure 6.5. Evolution of SAOS functions with frequency for chitosan-based oleogel formulations, at 25 °C

An alternative for reducing the values of the SAOS functions is the use of acylated chitosan as thickener. Figure 6.6 shows the mechanical spectra of oleogels formulated with castor oil and different acylated chitosan thickeners. As can be observed, both linear viscoelasticity functions decrease by using acylated biopolymers. In addition, a well-developed plateau region is always noticed, excepting for A3LMC-35 oleogel, which shows rather low values of both functions. In general, SAOS functions decrease as the substitution degree achieved during the acylation reaction increases, either for low or medium molecular weight chitosans. Besides this, it is also apparent that acylated MMC-based oleogels show higher values of the linear viscoelasticity functions, and lower values of $\tan \delta$ (more elastic) than ALMC-based products. In fact, the most promising rheological response was achieved by using A2MMC, with a low degree of acylation (see Table 6.2), as thickener agent. The most important advantage of using an acylated chitosan is its increased solubility in oil, as a consequence of a lower polarity, and resulting in a more stable and homogenous oleogel. However, acylated chitosan-containing oleogels lose their gel-like behaviour at moderate temperatures, turning into very fluid materials at 50°C, as illustrated in Figure 6.7 for A2MMC-35 oleogel. This experimental evidence can be explained taking into account that part of the acylated chitosan starts to melt at 40°C, as previously discussed (see Figure 6.1). Evidently, this fact implies an important limitation for its use in a lubricating grease formulation at high in-service temperatures.

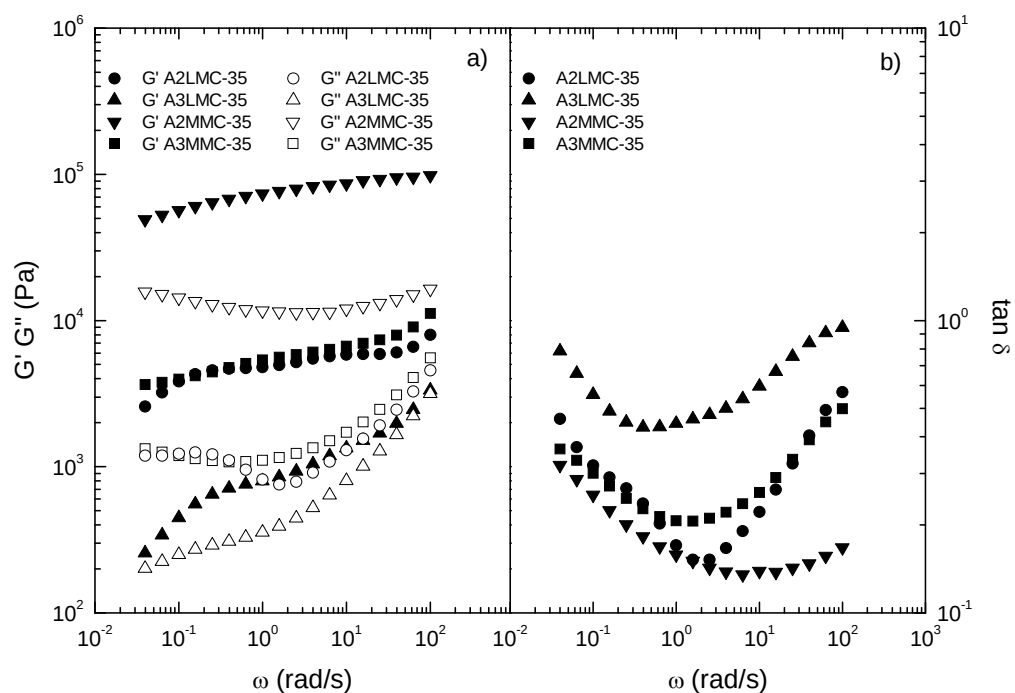


Figure 6.6. Evolution of SAOS functions with frequency for acylated chitosan-based oleogel formulations, at 25 °C

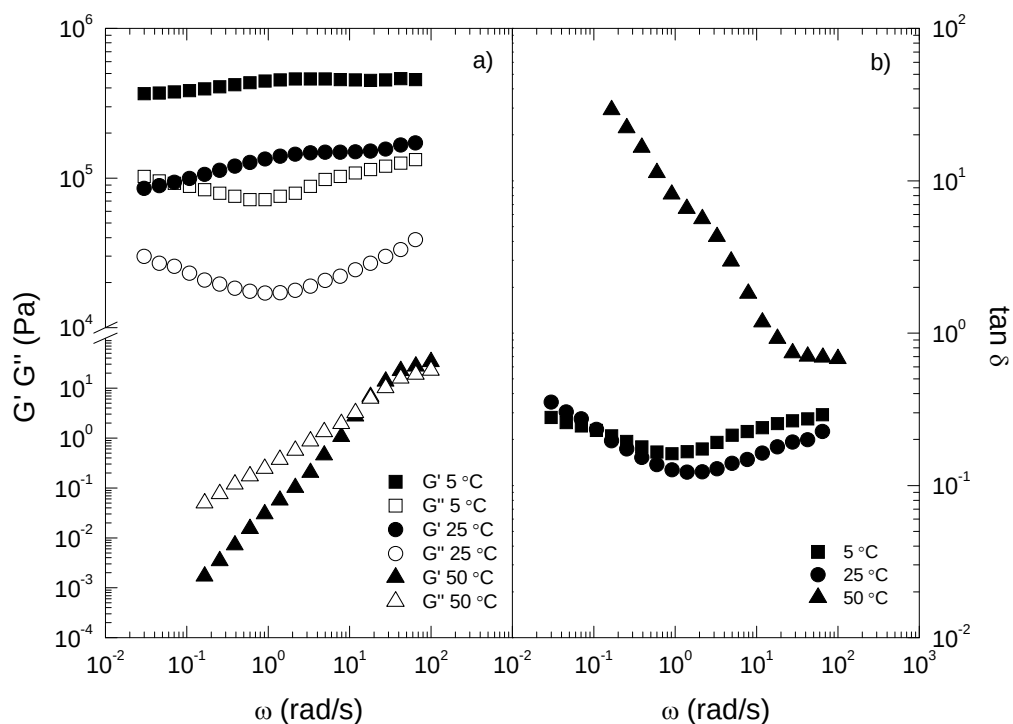


Figure 6.7. Evolution of SAOS functions with frequency for A2MMC-based oleogel formulations, at different temperatures

The influence of temperature on the SAOS functions was also analyzed for other selected samples (CC-21 and MMC-35, data not shown). For these oleogels, SAOS functions are not largely influenced by temperature (between 5 and 130 °C). In this sense, a slight decrease in both G' and G'' is observed up to around 100 °C, followed by an increase at higher temperatures. This slight increase noticed in both SAOS functions at high temperatures should be related to an apparent oil separation (oil bleeding), which increases the effective concentration of the thickener.

Below this critical temperature, the temperature dependence of the plateau modulus G_N^0 , defined elsewhere [Baumgaertel et al., 1992], can be described by means of an Arrhenius-type equation, as previously reported [Sánchez et al., 2009]:

$$G_N^0 = A \cdot e^{\frac{E_a}{R} \cdot \left(\frac{1}{T}\right)} \quad (4.2)$$

where E_a is a fitting parameter that gives information on the oleogel thermal dependence, with a physical meaning similar to an activation energy (J/mol), R is the gas constant (8.314 J/mol·K), T is the absolute temperature (K), and A is the pre-exponential factor (Pa). The activation energy values resulting from this fitting were 3701 and 424 J/mol for selected chitin- and chitosan-based formulations, respectively. These values are similar, or even lower (chitosan-based oleogel) than those obtained for standard lithium greases in the low-temperature range (1-2 kJ/mol) and much lower than those reported in the high-temperature range (18-20 kJ/mol) [Delgado et al., 2006b]. This thermal dependence is also lower than that shown by other biodegradable lubricating greases based on castor oil and cellulosic derivatives [Sánchez et al., 2009; Sánchez et al., 2011], although, in those cases, the available range of temperature where oil bleeding is not perceived was much higher.

Mechanical Stability and Tribological Behaviour

It is well known that the mechanical stability of lubricating greases is traditionally determined from the difference between penetration indexes after and before submitting the grease to a standardized working test. In this study, oleogel mechanical stability was evaluated after the application of a shear rolling test. Greases with good mechanical stability must exhibit penetration increments after working close to zero. Table 6.6 shows the penetration indexes of the samples studied, before and after applying the rolling test, as well as the corresponding NLGI grade [NLGI, 1994] referred to the non-perturbed sample. In general, the NLGI grade increases with thickener concentration and decreases when soybean oil, instead of castor oil, is used in the formulation. As can be observed, chitin-based oleogels show a negative variation of the penetration index. This means that the rolling test induces an increase in consistency, which is probably associated to the shear-induced “oil bleeding” observed in these samples after the application of the rolling test. On the contrary, chitosan-based dispersions display a significant positive variation of penetration indexes. Only a few samples with penetration variations around 30-40 dmm can be considered moderately stable and comparable to standard lithium greases. Finally, formulations containing acylated chitosan show, in general, very low consistency and poor mechanical stability.

Sample	Unworked Penetration (dmm)	NLGI Grade	Worked Penetration (dmm)	Penetration Variation (dmm)
CC-19	423	00	373	-50
CC-21	352	0-1	320	-32
CC-23	302	1-2	268	-34
MMC-23	358	0	407	49
MMC-25	295	2	325	30
MMC-27	248	3	310	62
MMC-27-S	310	1	405	95
LMC-39	339	1	385	46
LMC-39-S	598	<000	634	36
A2LMC-35	813	<000	815	2
A3LMC-35	563	<000	674	111
A2MMC-35	363	0	423	60
A3MMC-35	537	<000	474	-63
Standard paraffinic oil-based grease	303	1-2	305	2
Standard naphthenic oil-based grease	312	1	336	24

Table 6.6. Penetration and mechanical stability values for the oleogels studied, and for some standard lithium lubricating greases

The potential applicability of these oleogels as biodegradable lubricating greases has been also investigated in a tribological contact. Table 6.7 shows the friction coefficient values, obtained in a ball-disc nanotribometer, for selected oleogel samples. With the exception of the formulation containing chitin as thickener, which exhibits a much higher friction coefficient, the remaining oleogel samples studied show a satisfactory response. Thus, the friction coefficient value obtained with the chitosan-based dispersion is only slightly higher than that found for naphthenic oil-based lithium grease, whilst the use of an acylated chitosan as thickener provides a friction coefficient even lower.

Sample	Friction coefficient
CC-21	0.25
MMC-25	0.16
A2MMC-35	0.12
Standard naphthenic oil-based grease	0.14

Table 6.7. Friction coefficient values for selected oleogels and a standard lithium lubricating grease



CAPÍTULO 7

CARACTERIZACIÓN

TRIBOLÓGICA DE OLEOGELES

FORMULADOS CON DIFERENTES

ESPESANTES

7.1 Tribological characterization of green lubricating greases formulated with castor oil and different biogenic thickener agents: a comparative experimental study

7.1.1 Introduction

Lubricating greases may be considered colloidal suspensions in which a suitable thickener, generally a metal soap, is dispersed in lubricating liquids, normally mineral or synthetic oils [Sacchettini et al., 1985; NLGI, 1994; Kuhn, 2009]. Fatty acid soaps of lithium, calcium, sodium, aluminium and barium are most commonly used as thickeners [Mas and Magnin, 1994]. As it has been detected by electron microscopy, these thickeners form an entanglement network which traps the oil and confers the rheological properties of the lubricating grease [Magnin et al., 1988; Shuff & Clarke, 1991; Mas and Magnin, 1994]. The thickener is mainly added to prevent loss of lubricant under operating conditions but it must not offer a significant increase in the resistance to the motion of the rubbing surfaces [Madieto et al., 2000]. Moreover, the matrix of the bulk lubricating grease can absorb contaminants, such as particles and water, in relatively high amounts without a reduction in its lubrication properties because only a small part of the lubricating grease is taking part in the lubrication, with the larger part acting as a seal [Hamnelid, 2000]. However, the lack of satisfactory relationships between the mechanism of film formation in a lubrication process and the bulk properties of greases highly complicates the prediction of lubricating performance for any given application [Cann, 1996]. During decades, the lubricating capacity has been attributed to the base oil whereas the role of the thickener in the lubrication process has been ignored. Microscopy techniques have demonstrated the presence of small soap particles in the contact surface [Kauzlarich and Greenwood, 1972; Åstrom and Venner, 1994;

Hurley, 2000; Cann and Hurley, 2002]. Thus, the entrance of thickener particles into the contact zone causes an increase in viscosity of the EHL film, generating a thicker film than those found for the base oil alone, which produces a significant reduction in the friction factor [Palacios et al., 1981; Rong-Hua, 1985; Hurley and Cann, 1999].

Nowadays, some industrial sectors, including the lubricant industry, try to reduce the environmental impact that process technologies and products exert on the environment. As a consequence, there is a general tendency to replace non-renewable raw materials by renewable resources. It is well known that lubricants produce many environmental problems since every year millions of tonnes of engine, industrial and hydraulic oil are poured in the environment. In this sense, a movement towards the use of environmental materials has been noticed not only for a reduction of the environmental impact but also for the requirements in the current legislation of many countries, public opinion and marketing needs [Flynn, 2000]. Nowadays, customers are very interested in this type of products although the price is higher than the standard non biodegradable product.

In the case of liquid lubricants, vegetable oils seem to replace fairly well the mineral ones without significant problems. The advantages and disadvantages, as well as possible specific applications, of lubricants derived from renewable resources have been extensively discussed in previous works [Wilson, 1998, Bartz, 1998, Lea, 2002]. Vegetable oils show good lubricity and ability for adhering to metal surfaces, low volatility, small viscosity-temperature dependence and, obviously, non-toxicity and high biodegradability. On the other hand, the main disadvantages of vegetable oils are their poor oxidative stability, the low temperature flow properties and the limited range of viscosity available. However, several solutions have been proposed to reduce and overcome these problems either using some additives or inducing chemical modifications [Adhvaryu, 2002, 2004, 2005a, Quinchia et al., 2009, 2010, Garcia-Zapateiro et al., 2010].

The development of environmentally friendly lubricating greases based on completely biodegradable materials is a much more difficult task. Traditional thickeners, especially metallic soaps and polyureas, confer to greases optimum functional and performance properties but, obviously, they cannot be considered as biodegradable components. The satisfactory replacement of these traditional thickener agents by others based on renewable materials is up to now an unresolved question from a technical point of view. In fact, some greases are introduced in the market as biodegradable materials or eco-label products although they still contain a non-biodegradable thickener agent in the formulation. In previous studies [Sánchez et al., 2008, 2009, 2011], some gel-like formulations have been developed using castor oil and natural thickeners, such as sorbitan or glyceryl monostearates, cellulose, chitin and some of their chemical derivatives. Some of them showed similar or even better rheological, thermal and mechanical properties than those displayed by traditional lubricating greases. Following with these investigations, in this work some selected formulations based on castor oil and different biodegradable thickeners have been characterized from a tribological point of view and compared with some traditional lithium greases.

7.1.2 Materials and methods

Materials

Castor oil (Guinama, Spain) was used as biodegradable lubricating oil. Sorbitan monostearate (SMS) HLB = 4.7 (Panreac, Spain), glyceryl monostearate (GMS) HLB = 4.2 (Guinama, Spain), ethyl cellulose (M_n 59803 g/mol; 49% ethoxy content, Sigma-Aldrich), methyl cellulose (M_n : 40000 g/mol; 32% methoxy content, Sigma-Aldrich), α -cellulose (Sigma-Aldrich), chitosan (M_w : $5.6 \cdot 10^5$ g/mol, Sigma-Aldrich), acylated chitosan (DS = 0.3) and chitin (M_w : $5.4 \cdot 10^5$ g/mol, Qingdao Fraken) were used as thickener agents to prepare different gel-like formulations. Standard lithium 12-hydroxystearate (14% w/w) greases

were used as reference systems. 12-hydroxy stearic acid, lithium hydroxide, high-density polyethylene (M_w : $1.5 \cdot 10^5$ g/mol), polypropylene (M_w : $8.2 \cdot 10^5$ g/mol) and naphthenic mineral oil (density at 20 °C: 916 kg/m³; kinematic viscosity at 40 °C: 115 mm²/s), all of them kindly supplied by Verkol, S.A. (Spain), were used to prepare lithium lubricating greases.

Preparation of oleogel formulations

Processing of oleogels containing sorbitan or glyceryl monostearates were performed in an open vessel under agitation to disperse the gelling agent, following the protocol described by Sánchez et al. (2008). Different cooling profiles were applied to induce gelification as indicated in Table 7.1. Gel-like dispersions containing cellulose or chitin derivatives as thickeners were prepared following the methodology detailed in Sánchez et al. (2009, 2011), respectively. Finally, traditional lithium greases were manufactured according to the well-known protocol, as described elsewhere [Delgado et al., 2005; NLGI, 1994]. Table 7.1 shows the type of thickener employed and concentrations for each formulation studied, as well as the corresponding code applied.

Sample Code	Oil	Thickener concentration (w/w)	Additional information
COSMS1	Castor	Sorbitan monostearate (20%)	Cooling with water at 25 °C
COSMS2	Castor	Sorbitan monostearate (20%)	Cooling with water at 0 °C
COGMS1	Castor	Glyceryl monostearate (20%)	Cooling with water at 25 °C
COaC1	Castor	α -cellulose (25%)	
COECaC1	Castor	α -cellulose (20%) and ethyl cellulose (2%)	
COMC1	Castor	Methyl cellulose (35%)	
COECMC1	Castor	Methyl cellulose (30%) and ethyl cellulose (2%)	
COECMC2	Castor	Methyl cellulose (25%) and ethyl cellulose (2%)	
COCS1	Castor	Chitosan (25%)	
COAC1	Castor	Acylated chitosan (35%)	
COCQ1	Castor	Chitin (21%)	
REF1	Naphthenic	Lithium soap (14%)	
REF2	Naphthenic	Lithium soap (14%)	Additive: HDPE (2.5% w/w)
REF3	Naphthenic	Lithium soap (14%)	Additive: PP (2.5% w/w)

Table 7.1. Formulation details and additional information for different types of oleogels based on biogenic thickeners and reference lithium greases

Tribological characterization

Tribological characterization was performed in two different tribometers with a geometrical coupling of ball-on-disc. The first series of measurements were carried out in a tribometer designed by the MuT laboratory at the University of Applied Sciences of Hamburg, which works within a normal force range of 3-20 N. During the measurement the friction force is detected with a load cell and, using an external amplifier, the signal is grabbed by a computer and then converted into the friction coefficient. A normal force of 11.91 N and a material coupling of steel-steel (1/2" diameter 100Cr6 ball on 1.2210/115CrV3 steel plate) were used in each test at 120 rpm. Due to the texture of greases and their tendency to yield the ball, a polyurethane deflector had to be applied to the disc in order to re-spread the grease track after each disc revolution and hence grease depletion of the frictional track was avoided. The evolution of the friction coefficient with time was

followed during 5 or 15 min and each test replicated ten or three times, respectively, in order to get a representative average value.

The second and third series of tests were performed in a nanotribometer (CSM Instruments, Switzerland), able to continuously measure friction and normal forces, indentation depth and environmental data such as room temperature and humidity, in the oscillatory and rotational modes, respectively. Forces were registered by means of optically detecting the displacement of a cantilever. Frictional force is detected with a resolution of 0.01 mN and indentation values can be detected with a resolution of 50 nm. A normal load of 50 mN, maximum linear velocity of 0.5 mm/s and amplitude of 1 mm were applied during tests performed in the oscillatory mode. Materials coupling employed was 1.5 mm diameter sapphire ball on steel (115CrV3) plate, with maximum roughness of 1 and 3 μm , respectively. An average friction coefficient value was monitored at the central point of wear tracks (amplitude zero). On the other hand, a normal load of 50 mN, track radius of 7 mm and linear speed of 10 mm/s was applied in rotational mode. Material combinations used for these tests were both sapphire-sapphire and sapphire-steel ball on disc. In the rotational mode, a deflector had to be also used to re-spread the grease after each revolution. In both modes, three replicates of each test were performed during 15 min and the friction coefficient obtained averaged.

7.1.3 Results and discussion

The evolution of the friction coefficient in different tribological contacts has been analysed. Figure 7.1 shows the evolution of the friction coefficient with time using the tribometer designed in the MuT laboratory for selected oleogels studied and a reference lithium grease. As can be observed, for standard greases, a steady value of the friction coefficient is obtained after approximately five minutes; however, this time is not enough to get a stationary value in the case of oleogels prepared with castor oil and natural thickeners. For this reason, the

friction coefficient has been determined, in most cases, after 15 minutes in order to obtain a representative steady-state value of this parameter. On the other hand, in general, castor oil-based formulations exhibit similar or lower values of the friction coefficient than traditional lithium greases, depending on the type of thickener agent employed.

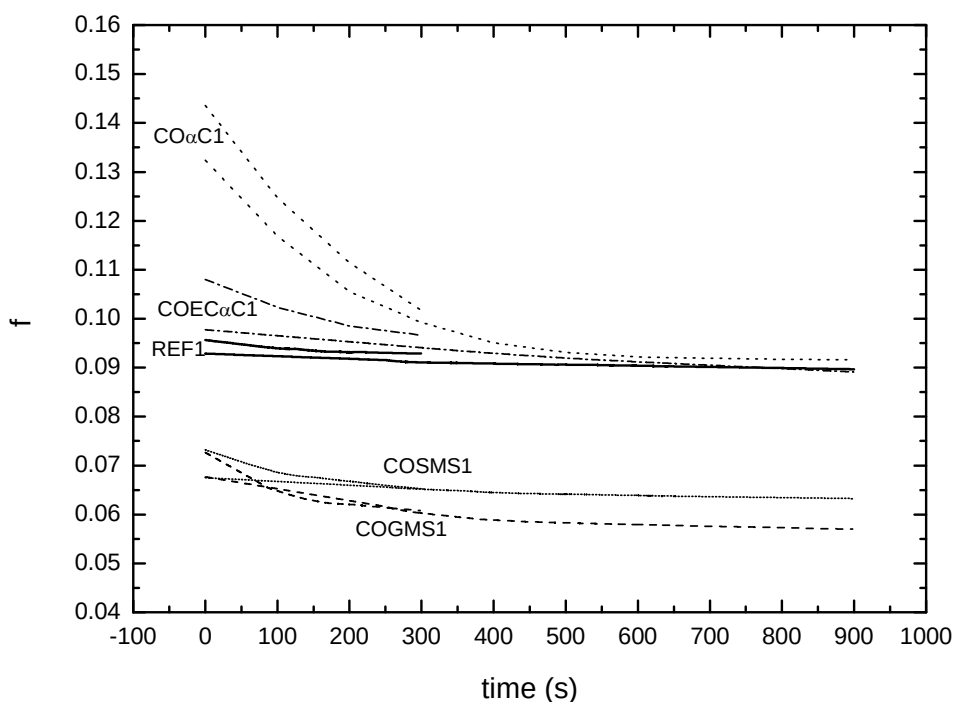


Figure 7.1. Evolution of the average friction coefficient with time for some selected oleogels based on biogenic thickeners and a reference lithium grease

Table 7.2 collects the friction coefficient values obtained with different types of tribometers, material coupling and frictional tests, with the corresponding standard deviation, for the different biodegradable lubricating greases studied. As can be seen in this table, the use of all reference samples based on naphthenic oil and a lithium soap thickener provide similar values of the friction coefficient in each configuration, excepting sample REF 3 in the oscillatory mode. This means that polymeric additives do not significantly influence the tribological behaviour of lithium greases. Only the polypropylene seems to increase the friction coefficient respecting the additive-free grease,

which is especially evident in the oscillatory mode frictional test. In addition to this, the reference lithium greases show significantly higher values in the oscillatory mode than the rest of formulations potentially applicable as biodegradable greases. In this sense, the generally higher friction coefficient values found for the reference greases are magnified in the oscillatory mode as a consequence of the direction change in the ball relative motion.

The group of oleogels thickened with monostearate derivatives shows values of the friction coefficient always much lower than those obtained with the reference greases in every type of configuration or frictional test analysed. Moreover, the friction coefficient is not highly influenced by the type of gelling agent (glyceryl or sorbitan monostearate) nor the processing conditions, in spite of the different rheological response previously reported [Sánchez et al., 2008]. Although this type of oleogels presents very poor mechanical stability [Sánchez et al., 2008], this could be considered a positive characteristic from a tribological point of view since the gel microstructure is easily destroyed inside the tribological contact turning into a more fluid material, significantly decreasing the consistency and being able to lubricate the contact more effectively. However, this mechanical behaviour evidently represents a clear disadvantage in inclined tribological contacts since this type of biogreases could be gradually ejected from the contact finally yielding lubricant starvation.

Biogrease formulations containing cellulose derivatives as thickener agents generally display higher values of the friction coefficient, which depends on the type and concentration of the cellulosic derivative and the tribological configuration. In general, in frictional tests performed in the rotational mode, oleogels containing only α -cellulose or methyl cellulose display values of the friction coefficient lower than those found in formulations also containing ethyl cellulose. As it was previously reported [Sánchez et al., 2011], the role of ethyl cellulose is to increase the oil viscosity which is essential to impart

long-term physical stability to these oleogels. In the series of tests carried out in the tribometer designed at the MuT laboratory, with a steel-steel ball-on-disc configuration, the friction coefficient values obtained with α -cellulose- or methyl cellulose-based formulations are essentially the same as those obtained with standard lithium greases and slightly lower, but not significantly different, than those measured using α -cellulose/ethyl cellulose or methyl cellulose/ethyl cellulose blends as thickener agents. However, in the series of tests performed in the nanotribometer, under rotational mode, in both sapphire-sapphire and sapphire-steel ball-on-disc configurations, significant higher values of the friction coefficient can be observed for biogreases containing ethyl cellulose, some of them very similar or even higher than those obtained with the reference greases. On the contrary, under these configurations, especially low values were found for the formulation only containing α -cellulose, comparable to those obtained with gels based on glyceryl and sorbitan monostearates. Finally, in the oscillatory mode, not very different friction coefficients were found for all biogreases containing cellulose derivatives and all of them significantly lower than those obtained with the reference systems. Nevertheless, under this frictional mode, α -cellulose-based formulations exhibit higher values of the friction coefficient than methyl cellulose-based oleogels, probably due to the higher consistency achieved with α -cellulose. The higher frictional force measured, under a rotational mode, in formulations containing ethyl cellulose is obviously a consequence of the viscosity modification exerted on the castor oil, which plays the dominant role in this type of tests. This influence is mainly detected in the rotational mode, especially when using deflectors, but however is not clearly observed in the oscillatory mode, where the structural breakdown is not so important and, therefore, the main thickener influences the friction coefficient in a higher degree.

Oleogels which have been formulated using chitin or chitosan as thickeners were completely ejected outside the tribological contact after

some revolutions in the tribometer designed at MuT laboratory. This behaviour is mainly due to the low resistance to structural breakdown and low adhesion imparted by these biopolymers. However, it was possible to get suitable data using the nanotribometer (Table 7.2). The same tendency of the friction coefficient was observed independently on the type of configuration and frictional test. Thus, the oleogel thickened with chitin always shows the highest friction coefficient and, on the contrary, the formulation containing an acylated chitosan provides, in every contact, the lowest friction coefficient. If these values are compared with those obtained using the reference greases, it may be concluded that, in rotational mode, either with sapphire-sapphire or with sapphire-steel ball-on-disc configurations, the friction coefficient values provided by the chitin-based oleogel are always significantly higher whereas the chitosan-based formulations are only slightly higher or identical to that displayed by the lithium grease containing polypropylene as additive in the sapphire-steel configuration. On the contrary, the use of acylated chitosan-based oleogel yields, in all cases, much lower friction coefficient values than those obtained with the reference greases and close to those presented by gels based on glyceryl and sorbitan monostearates. On the other hand, this tendency is not followed in the case of oscillatory tests since the reference greases exhibit friction coefficients even higher than those shown by the oleogels thickened with chitin and chitosan. In spite of the optimum tribological response exhibit by the acylated chitosan-based formulation, the chitosan acylation reaction confers to the final product poor thermal and mechanical stability [Sánchez et al., 2011], similarly to that previously discussed for gels containing glyceryl or sorbitan monostearates, which evidently limits the range of application as lubricating grease. Therefore, the tribological results obtained seems to be a consequence of the balance between the friction in the ball-on-disc contact, the friction in the lubricant film, favoured by the high viscosity induced by the ethyl cellulose, and the poor mechanical stability of

weak gels like those containing sorbitan and glyceryl monostearates or acylated chitosan.

Sample (Code)	MuT Tribometer (rotational mode - steel-steel contact)	Nanotribometer (oscillatory mode - sapphire-steel contact)	Nanotribometer (rotational mode - sapphire-sapphire contact)	Nanotribometer (rotational mode - sapphire-steel contact)
COSMS1	0.063±0.002	0.167±0.006	0.094±0.003	0.089±0.005
COSMS2	0.058±0.003	0.172±0.003	0.080±0.003	0.090±0.004
COGMS1	0.057±0.002	0.181±0.005	0.087±0.002	0.094±0.003
COaC1	0.092±0.012	0.224±0.011	0.099±0.021	0.075±0.016
COECaC1	0.089±0.011	0.197±0.002	0.170±0.015	0.112±0.012
COMC1	0.090±0.025	0.187±0.009	0.113±0.017	0.097±0.015
COECMC1	0.104±0.016	0.189±0.004	0.161±0.010	0.099±0.012
COECMC2	0.109±0.017	0.196±0.003	0.142±0.011	0.122±0.013
COCS1	---	0.158±0.014	0.164±0.011	0.143±0.014
COAC1	---	0.126±0.002	0.117±0.003	0.106±0.005
COCQ1	---	0.218±0.016	0.247±0.013	0.173±0.017
REF1	0.090±0.002	0.301±0.006	0.136±0.010	0.116±0.009
REF2	0.090±0.001	0.281±0.026	0.138±0.027	0.120±0.021
REF3	0.092±0.002	0.417±0.023	0.143±0.025	0.143±0.017

Table 7.2. Friction coefficient for different types of oleogels based on biogenic thickeners and reference lithium greases the samples obtained from different frictional tests and material coupling



CAPÍTULO 8

CONCLUSIONES GENERALES

8.1 Conclusiones

- ✓ De forma general, aquellos oleogeles formulados con aceite de ricino presentan una mayor estabilidad física a la separación de aceite (“sangrado”) debido fundamentalmente a la alta viscosidad de este aceite y un comportamiento reológico más similar a las grasas lubricantes tradicionales.
- ✓ El comportamiento reológico de los oleogeles espesados con monoestearato de sorbitano está altamente influenciado por la concentración de espesante, naturaleza del aceite vegetal y el protocolo térmico aplicado cuando se induce la gelificación, alcanzando los módulos viscoelásticos (y los grados NLGI registrados) valores similares a los encontrados en las grasas lubricantes tradicionales cuando el enfriamiento se lleva a cabo rápidamente. Sin embargo, la estabilidad mecánica es muy baja.
- ✓ En el caso de los oleogeles espesados con monoestearato de glicerilo, la respuesta viscoelástica sólo se modifica significativamente con la concentración de espesante y la naturaleza del aceite vegetal empleado en su formulación (aunque en menor grado que en los oleogeles procesados con monoestearato de sorbitano), obteniéndose con este espesante geles más fuertes que con el monoestearato de sorbitano en igualdad de condiciones.
- ✓ Aquellos oleogeles procesados empleando derivados celulósicos como espesantes (α -celulosa y metil celulosa) muestran una estabilidad térmica muy superior a la registrada en las grasas lubricantes tradicionales y un comportamiento reológico cualitativamente similar aunque con valores de las funciones viscoelásticas dinámicas aproximadamente una década superior. Los oleogeles preparados con metil celulosa presentan además una estabilidad mecánica adecuada.
- ✓ La adición de etil celulosa a algunas formulaciones de oleogeles permite reducir la concentración de los otros espesantes

celulósicos empleados y reduce la separación de aceite como consecuencia del aumento en la viscosidad de éste. Esta modificación genera una mayor influencia de las funciones viscoelásticas lineales con la temperatura, una mejora en la estabilidad mecánica y una mayor tendencia a la expulsión en rodamientos.

- ✓ Un aumento del peso molecular de la etil celulosa empleada en la manufactura de los oleogeles modifica el comportamiento reológico sólo a partir de un cierto valor crítico ($M_w < 70.000$ g/mol), induciendo además un aumento de la estabilidad mecánica cuando se usa conjuntamente con la metil celulosa.
- ✓ Las funciones viscoelásticas lineales de los oleogeles descienden inicialmente cuando se incrementa la relación de concentraciones etil celulosa / α -celulosa o etil celulosa / metil celulosa, hasta un cierto valor, a partir del cual vuelven a aumentar. A temperaturas elevadas no se observa este efecto, encontrándose un descenso continuo de los módulos dinámicos conforme se aumenta la relación de concentraciones de ambos tipos de derivados celulósicos.
- ✓ Aquellos oleogeles espesados con quitina o quitosano acilado muestran valores de los módulos viscoelásticos lineales similares a aquellos obtenidos con las grasas lubricantes estándares. Sin embargo, los oleogeles formulados con quitosano muestran valores significativamente mayores. Los oleogeles formulados con quitina y quitosano presentan escasa influencia de las funciones viscoelásticas lineales con la temperatura, aunque se detecta cierta separación de aceite a alta temperatura. Todo lo contrario se observa cuando se usa quitosano acilado como espesante. La mayoría de los oleogeles formulados con estos espesantes presentan poca estabilidad mecánica, sobre todo aquellos formulados con quitosano acilado.
- ✓ El estudio tribológico realizado sobre los diferentes oleogeles estudiados muestra que el coeficiente de fricción es similar o

incluso inferior al mostrado por las grasas lubricantes tradicionales. Para el caso de los oleogeles formulados con monoestearatos de sorbitano y glicerilo y quitosano acilado el coeficiente de fricción es menor al de las grasas de referencia. Para aquellos oleogeles formulados con celulosa, quitina y sus derivados se obtienen coeficientes de fricción comparables a los de las grasas de referencia aumentando éstos ligeramente con la inclusión de etil celulosa en su formulación como consecuencia de un incremento de la viscosidad del aceite vegetal.

8.2 Formulaciones propuestas y sus características

De todos aquellos oleogeles estudiados en el presente trabajo, las formulaciones de cada serie de espesante que poseen unas mejores características para ser empleadas como biograsas son las siguientes:

- ✓ Aceite de ricino con monoestearato de sorbitano al 20% y enfriamiento rápido (COSMS20)
- ✓ Aceite de ricino con monoestearato de glicerilo al 20% (COGMS20)
- ✓ Aceite de ricino con α -celulosa al 25% (CO α C25)
- ✓ Aceite de ricino con etil celulosa de medio peso molecular al 2% y α -celulosa al 20% (COEC2 α C20)
- ✓ Aceite de ricino con metil celulosa al 35% (COMC35)
- ✓ Aceite de ricino con etil celulosa de medio peso molecular al 2% y metil celulosa al 30% (COEC2MC30)
- ✓ Aceite de ricino con quitina al 21% (CC-21)
- ✓ Aceite de ricino con quitosano de medio peso molecular al 25% (MMC-25)
- ✓ Aceite de ricino con quitosano de medio peso molecular acilado en proporción 2:1 al 35% (A2MMC-35)

A modo de resumen, la Tabla 8.1 muestra, de forma general, las principales características termo-mecánicas de estas formulaciones y su similitud con las grasas lubricantes tradicionales. Así, se ha

comprobado el comportamiento reológico, la resistencia térmica (termoreológica y termogravimétrica), la consistencia determinada a través de los grados NLGI, la estabilidad mecánica y la respuesta tribológica obtenida.

Oleogel	Funciones viscoelast.	Termoreología	TGA	Grado NLGI	Estabilidad mecánica	Tribología
COSMS20	😊	😞	😞	😊	😞	😊
COGMS20	😐	😞	😞	😊	😞	😊
CO α C25	😞	😊	😊	😐	😊	😊
COEC2 α C20	😊	😊	😊	😐	😞	😐
COMC35	😞	😊	😊	😊	😐	😊
COEC2MC30	😐	😊	😊	😊	😊	😐
CC-21	😊	😐	😊	😊	😞	😐
MMC-25	😞	😐	😊	😊	😊	😐
A2MMC-35	😊	😞	😊	😐	😞	😊

😊 = características positivas, 😐 = características aceptables, 😞 = características negativas

Tabla 8.1. Formulaciones propuestas y sus principales características

8.1 Conclusions

- ✓ In general, those oleogels based on castor oil show better physical stability to oil separation ("oil bleeding"), mainly due to the high viscosity of this oil, and similar rheological behaviour to that obtained with traditional lubricating greases.
- ✓ The rheological behaviour of oleogels thickened with sorbitan monoestearate is highly influenced by the thickener concentration, nature of vegetable oil and cooling protocol applied to induce the gelling process, reaching values of the viscoelastic moduli and NLGI grades similar to those found in traditional lubricating greases, when applying high cooling rates during the gelling process. However, the mechanical stability is very low.
- ✓ The rheological response of oleogels thickened with glyceryl monoestearate is significantly modified with both thickener concentration and the nature of the vegetable oil used in the formulation (but with a lower impact than oleogels processed with sorbitan monoestearate), getting stronger gels than those obtained with sorbitan monoestearate under the same conditions.
- ✓ Oleogels processed using cellulosic derivatives as thickeners (α -cellulose and methyl cellulose) show much higher thermal stability than that obtained with traditional lubricating greases. They also display qualitatively similar rheological behaviour but dynamic viscoelastic rheological functions approximately one decade higher. Oleogels prepared with methyl cellulose present suitable mechanical stability.
- ✓ The addition of ethyl cellulose to some oleogel formulations can reduce the concentration of the other cellulosic thickeners and significantly avoid oil separation as a result of the increasing oil viscosity. This modification produces a higher dependence of the linear viscoelastic functions with temperature and improves both mechanical stability and leakage in ball bearings.

- ✓ From a rheological point of view, oleogels SAOS functions are influenced by ethyl cellulose molecular weight only above a critical value ($M_w < 70,000$ g/mol). Addition of low and medium molecular weight ethyl cellulose does not exert a significant influence on SAOS functions. Moreover, temperature does not influence the relative elastic characteristics of these oleogels, nor their qualitative dependence on frequency. Oleogels containing ethyl cellulose / methyl cellulose blends display improved mechanical stability, which is enhanced by increasing ethyl cellulose molecular weight, and quite similar to that found for standard lithium greases.
- ✓ An important decrease in the values of the linear viscoelasticity functions down to a minimum value has been 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.
- ✓ The evolution of the linear viscoelasticity functions with frequency, and the orders of magnitude of the linear viscoelasticity functions, for oleogels containing chitin or acylated chitosan, in a characteristic range of thickener concentration, were very similar to those obtained with standard lubricating greases. On the contrary, stable chitosan-based oleogels showed much higher values of both linear viscoelasticity moduli. Higher concentrations of biopolymer were required to produce stable

oleogels when using a low-molecular weight-chitosan. In general, SAOS functions increased with biopolymer concentration and decreased when soybean oil was used in the formulation of the oleogel. Acylated chitosans yielded much softer materials, with significantly lower values of both linear viscoelasticity functions, which also decrease with the acylation degree. Linear viscoelasticity functions were not significantly influenced by temperature in the case of chitin and chitosan-based oleogels. On the contrary, formulations containing acylated chitosans lost their gel-like behaviour at moderate temperatures, turning into very fluid materials above 40-50°C. Oleogels formulated with these thickeners exhibited poor mechanical stability especially those formulated with acylated chitosan.

- ✓ The tribological behaviour of the different studied oleogels shows that the friction coefficient is similar or even lower than those obtained with traditional lubricating greases. Weak oleogels like those thickened with glyceryl and sorbitan monostearates or acylated chitosan, provides the lowest values of the friction coefficient in every type of configuration or frictional test analysed, much lower than those obtained with the reference lithium greases. Biogrease formulations containing cellulose or chitin derivatives as thickeners agents generally yield higher values of the friction coefficient, which may be comparable to those obtained with the reference lithium greases depending on the thickener and tribological configuration. In frictional tests performed in the rotational mode, the inclusion of ethyl cellulose in addition to α -cellulose or methylcellulose provides higher values of the friction coefficient as a consequence of the oil viscosity modification exerted by this additive.

8.2 Proposed formulations and their main physical characteristics

Considering all oleogels studied in this work, selected formulations with more suitable characteristics to be used as biodegradable lubricating greases stabilized by each type of thickener are proposed:

- ✓ Castor oil and 20% sorbitan monoestearate with high cooling rate (COSMS20)
- ✓ Castor oil and 20% glyceryl monoestearate (COGMS20)
- ✓ Castor oil 25% and α -cellulose (CO α C25)
- ✓ Castor oil, 2% ethyl cellulose of medium molecular weight and 20% α -cellulose (COEC2 α C20)
- ✓ Castor oil and 35% methyl cellulose (COMC35)
- ✓ Castor oil, 2% ethyl cellulose of medium molecular weight and 30% methyl cellulose (COEC2MC30)
- ✓ Castor oil and 21% chitin (CC-21)
- ✓ Castor oil and 25% medium molecular weight chitosan (MMC-25)
- ✓ Castor oil and 35% acylated (DS = 0.3) medium molecular weight chitosan (A2MMC-35)

Table 8.1 shows, as a summary, the main thermo-mechanical characteristics of these oleogels and their similarities with traditional lubricating greases. Thus, the rheological behaviour, thermal resistance (thermorheological and thermogravimetric responses), consistency using the NLGI grades, mechanical stability and tribological response have been compared.

Oleogel	SAOS functions	Thermorheology	TGA	NLGI grade	Mechanical stability	Tribology
COSMS20	😊	😞	😞	😊	😞	😊
COGMS20	😊	😞	😞	😊	😞	😊
CO α C25	😞	😊	😊	😊	😊	😊
COEC2 α C20	😊	😊	😊	😊	😞	😊
COMC35	😞	😊	😊	😊	😊	😊
COEC2MC30	😊	😊	😊	😊	😊	😊
CC-21	😊	😊	😊	😊	😞	😊
MMC-25	😞	😊	😊	😊	😊	😊
A2MMC-35	😊	😞	😊	😊	😞	😊

😊 = positive characteristics, 😊 = acceptable characteristics, 😞 = negative characteristics

Table 8.1. Proposed formulations and their main physical characteristics



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CAPÍTULO 10

ANEXOS

10.1 Publicaciones derivadas de la Tesis Doctoral

10.1.1 Artículos científicos

Capítulo 4

Título: Effect of thermo-mechanical processing on the rheology of oleogels potentially applicable as biodegradable lubricating greases.

Situación actual: Publicado en Chemical Engineering Research and Design 86 (2008) 1073–1082.

Capítulo 4

Título: Rheology of oleogels based on sorbitan and glyceryl monostearates and vegetable oils for lubricating applications.

Situación actual: Aceptado para ser publicado en Grasas y Aceites.

Capítulo 5

Título: Development of new green lubricating grease formulations based on cellulosic derivatives and castor oil.

Situación actual: Publicado en Green Chemistry 11 (2009) 686–693.

Capítulo 5

Título: Thermal and mechanical characterization of cellulosic derivatives-based oleogels potentially applicable as bio-lubricating greases: Influence of ethyl cellulose molecular weight.

Situación actual: Publicado en Carbohydrate Polymers 83 (2011) 151–158.

Capítulo 5

Título: Rheological and mechanical properties of oleogels based on castor oil and cellulosic derivatives potentially applicable as bio-lubricating greases: influence of cellulosic derivatives concentration ratio.

Situación actual: Aceptado para ser publicado en Journal of Industrial Engineering Chemistry.

Capítulo 6

Título: Use of chitin, chitosan and acylated derivatives as thickener agents of vegetable oils for bio-lubricant applications.

Situación actual: Aceptado para ser publicado en Carbohydrate Polymers.

Capítulo 7

Título: Tribological characterization of green lubricating greases formulated with castor oil and different biogenic thickener agents: a comparative experimental study.

Situación actual: Aceptado para ser publicado en Industrial Lubrication and Tribology.

10.1.2 Comunicaciones a congresos

Título: Development of oleogels potentially applicable as lubricants.

Congreso: Póster en “AERC-2007. 4th Annual European Conference on Rheology”, 12-14 Abril 2007, Nápoles (Italia).

Título: Rheology and mechanical stability of bio-lubricating greases thickened with cellulosic derivatives.

Congreso: Comunicación oral en “Iberian Meeting on Rheology”, 11-12 Septiembre 2008, Madrid (España).

Título: New oleogels for biolubricant applications.

Congreso: Comunicación oral en “SASOR 2008. 2nd Southern African Conference on Rheology”, 6-8 Octubre 2008, Ciudad del Cabo (Sudáfrica).

Título: Thermo-rheological behaviour of bio-lubricating greases based on castor oil and cellulosic derivatives.

Congreso: Póster en “8th World Congress Of Chemical Engineering (WCCE8)”, 23-27 Agosto 2009, Montreal, Quebec (Canadá).

Título: Tribological and rheological characterisation of biolubricating greases.

Congreso: Comunicación oral en “6th Arnold Tross Colloquium”, 11 Junio 2010, Hamburgo (Alemania).

Título: Gel-like dispersions based on cellulosic derivatives and castor oil applicable as biodegradable lubricating greases.

Congreso: Comunicación aceptada en “The tenth International Conference on Chemical & Process Engineering”, 8-11 Mayo 2011, Florencia (Italia).

10.2 Propuestas de trabajo futuro derivadas de la Tesis Doctoral

Las formulaciones seleccionadas como posibles sustitutas de las grasas lubricantes tradicionales no biodegradables poseen ciertas propiedades que las hacen adecuadas para determinadas aplicaciones en concreto, sin embargo, ninguna de ellas posee de forma simultánea unas propiedades similares a las grasas estándares.

Por otro lado, todos los espesantes empleados en la manufactura de estos oleogeles son productos comerciales, exceptuando el caso del quitosano acilado. Debido a los resultados obtenidos con el proceso de acilación se puede plantear como acciones de trabajo futuras, el desarrollo de nuevos agentes espesantes medioambientalmente amigables a partir de modificaciones químicas de biopolímeros, como la celulosa y quitina usadas en la presente Tesis Doctoral. Con estas modificaciones químicas podrían obtenerse unos mejores espesantes donde se favorezca la interacción con el aceite biodegradable empleado para manufacturar grasas, ya sea físicamente reduciendo la polaridad del biopolímero de partida, o químicamente promoviendo reacciones químicas entre el nuevo espesante sintetizado y el aceite vegetal.

Partiendo de los resultados obtenidos por esta Tesis Doctoral como base, podría estudiarse el efecto final que se obtiene sobre las biograsas manufacturadas cuando se modifican parámetros en el proceso de síntesis de nuevos biopolímeros (grado de sustitución, tipo de sustituyente, peso molecular del polímero...), buscando de esta forma una mejora en aquellas propiedades que limitan el uso de las formulaciones estudiadas.