



Formulation of lubricating greases from renewable basestocks and thickener agents: A rheological approach



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ABSTRACT

This work deals with the development and rheological characterization of a variety of green lubricating grease formulations based on different combinations of vegetable oil-derived basestocks and biopolymers obtained from renewable resources. Castor oil, high-oleic sunflower acid oil (HOS-AO) and a ricinoleic acid-derived estolide were tested as basestocks, whereas chitosan and Kraft cellulose pulp, apart from traditional lithium soap, were selected as thickener agents. Rheological behaviour was characterized by means of small-amplitude oscillatory shear (SAOS) and viscous flow measurements. In addition to these, some standard mechanical tests were carried out in order to evaluate the suitability of these formulations for lubricant applications. The rheological response depends on the type of vegetable oil-derived basestocks and thickener agent. Higher values of the SAOS functions were obtained for chitosan-based formulations. High viscosity and consistency were particularly achieved by combining the estolide sample and lithium hydroxide. On the contrary, soft greases and generally higher flow indexes were found in cellulose pulp-based formulations. The effect of the different basestocks on the rheological response was explained attending to the influence exerted by oil viscosity and basestock-thickener polar interactions, as well as the chemical reaction between the basestock carboxylic moieties and lithium hydroxide to form different thickener structures.

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1. Introduction

It is well-known that the use of renewable resources for different industrial applications has remarkable importance in our society due to its positive effect on the environment. Nowadays, there is a marked tendency to increase the use of eco-friendly consumer products, either as a result of government regulations, or just due to the increasing public concern for a pollution-free environment (Adhvaryu and Erhan, 2002). Among these renewable resources, vegetable oils are increasingly taken into account as biodegradable raw materials, especially for biodiesel and biolubricant applications (Gryglewicz et al., 2003; Dmytryshyn et al., 2004; Garces et al., 2011). In this line, the industry of lubricants is not only interested in the development of new lubricants for enhanced mechanical performance, but also in improved products from an environmental point of view. Mostly in the last two decades, lubricant customers

are aware of the negative effects that traditional lubricants exert on the environment (Adesodun and Mbagwu, 2008a, 2008b) and, therefore, are demanding new green products able to reduce this impact (Adhvaryu and Erhan, 2002; Beran, 2008). Besides this, the lubricant industry in the European Community must fit the REACH regulation (Regulation 06/1907/EC) dealing with the registration, evaluation, authorization, and restriction of chemical substances.

Lubricating greases constitute a group of lubricants with particular properties mainly related to their gel-like characteristics, which are mainly attributed to a thickener agent. They are highly structured suspensions consisting of a thickener, usually a metal soap, dispersed in a lubricating liquid, mineral or synthetic oil (NLGI, 2006). Due to its semisolid character, lubricating greases must remain in place during operation and act as a seal, thus preventing both solid and liquid contaminants from entering the system, without the need for a sump (Gow, 1997). An effective substitution of traditional thickener agents in lubricating grease formulations (metallic soaps, phyllosilicates or polyurea compounds) by others more environmentally acceptable presents special difficulties, mainly due to the functional properties and efficiency achieved with those compounds. Operating conditions in current technologies impose high demands on lubricating greases

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and, consequently, alternative thickeners coming from natural resources must impart to the final product, apart from non-toxicity and biodegradability, gel-like characteristics, thermal resistance and efficiency to minimize friction and wear in the machinery, similar to that achieved with the traditional non-renewable thickener agents (Boyde, 2002).

An extensive literature on a great variety of vegetable oils and chemically modified derivatives proposed as biodegradable alternatives to mineral and synthetic lubricant oils has been reported in the last years (see for instance very recent publications of Abidakun and Koya, 2013; Cermak et al., 2013; Gryglewicz et al., 2013; Hashem et al., 2013; Zulkifli et al., 2013; Salih et al., 2013). Among them, castor oil (Sánchez et al., 2009), residual acid oils (García-Zapateiro et al., 2013a) and fatty acid-derived estolides (García-Zapateiro et al., 2013b) may present additional benefits as base materials for the manufacturing of lubricating greases. Acid oils are by-products of oil refining where the high amount of free fatty acids is responsible for their acidity. They have little commercial value and are sold at a fraction of the oil cost (Hayes and Kleiman, 1995). On the other hand, estolides are a class of ester resulting from the reaction between a carboxylic group in a fatty acid molecule and an unsaturation in another fatty acid molecule to form an ester linkage (Cermak and Isbell, 2011; Isbell et al., 1994, 2001). The number of these linkages determines the structure and properties of estolides. Different molecular parameters (e.g., molecular weight, branching, etc.) and physical properties (e.g. viscosity and density) are obtained by modifying the nature of the base material and reaction conditions. In previous studies (García-Zapateiro et al., 2010, 2013a,b,c), the production of estolides from both oleic and ricinoleic acids and high-oleic sunflower and olive pomace acid oils, as well as the effect of the synthesis protocol on their potential use in biolubricant applications were explored.

Besides, cellulose pulp and chitosan, which are two of the most important substances obtained from renewable resources, may represent an interesting alternative to replace non-renewable thickeners. In general, cellulose derivatives have attracted great interest in the past and have been used as thickeners in food, cosmetics, pharmaceuticals, paints and paper coatings as well as in other many applications (Klemm et al., 2005). Chitin is a natural polysaccharide, considered the most abundant biopolymer in nature after cellulose, which is synthesized by a large number of living organisms, mostly found in the shell of crustacean, cuticles of insects and cell walls of fungi (Kumar, 2000). When the degree of deacetylation of chitin reaches about 50%, it becomes soluble in aqueous acidic media and is called chitosan (Rinaudo et al., 2006). Some previous studies reported the use of chitosan and acylated derivatives (Sánchez et al., 2011a) and different cellulosic pulps (Nuñez et al., 2011, 2012) as thickener agents of vegetable oils. In this work, these biopolymers were tested as thickener agents in different vegetable oil-derived basestocks, i.e. castor oil, a residual acid oil resulting from the refining treatment of high-oleic sunflower oil (HOS-AO) and a ricinoleic acid-derived estolide, in order to formulate lubricating greases completely based on renewable resources. The traditional lithium soap was also used in these oil media as a reference. In the case of acid oils and estolides, lithium hydroxide can directly react with the oil medium carboxylic moieties to form the thickener structure.

2. Materials and methods

2.1. Materials

Castor oil (211 cSt at 40 °C, Guinama, Spain), HOS-AO (33.90 cSt at 40 °C, Coreysa, Spain) and a selected estolide sample (581.56 cSt at 40 °C, $M_w = 1832$ g/mol) obtained from the ricinoleic acid

(García-Zapateiro et al., 2013b) were used as biolubricant base-stocks. Acidity and fatty acid profile of HOS-AO can be found elsewhere (García-Zapateiro et al., 2013c). Chitosan (average molecular weight: 2.29×10^5 g/mol, degree of deacetylation: 86.3%, Qingdao Fraken, China) and Kraft cellulose pulp, produced in the laboratory from *Pinus radiata* (Nuñez et al., 2011), in combination with commercial ethyl cellulose ($M_n = 66,000$ g/mol, 49% ethoxy content, Sigma-Aldrich), were tested as biodegradable thickener agents. 12-hydroxystearic acid and anhydrous lithium hydroxide, kindly supplied by Verkol Lubricantes S.A., were used to prepare lithium soap-based greases. Table 1 shows the codes used for the different formulations prepared using these starting materials.

2.2. Manufacture of lubricating greases

2.2.1. Preparation of lithium lubricating greases

Lithium lubricating grease processed with castor oil as base oil was prepared according to details and procedure described elsewhere (Franco et al., 2005; Martín-Alfonso et al., 2012). Lithium soap concentration was fixed at 14% w/w in the final product.

Lithium lubricating greases prepared using HOS-AO or estolide basestocks were manufactured as follows: the process was performed in a stirred batch reactor (600 g) equipped with an anchor impeller geometry, by applying a rotational speed of 60 rpm. In a first step, 55% of the total amount of HOS-AO or estolide was charged into an open vessel. This was pre-heated up to 90 °C and lithium hydroxide (3.5% w/w on dry basis over the total formulation) was then slowly added in the form of aqueous solution up to neutralization. Then, part of the remaining basestock (15%) was added and a heating profile up to a maximum temperature of 180 °C was imposed. The mixture was maintained at this maximum temperature for one hour and, afterwards, a third batch of base oil (15%) was added, followed by another batch (15%), at 120 °C, during cooling the mixture. Finally, a homogenization treatment (rotational speed: 8800 rpm) during 15 min was applied using a rotor-stator turbine (Ultra Turrax T-25, Ika, Staufen, Germany).

2.2.2. Processing of chitosan-based gel-like dispersions

Processing of chitosan-based gel-like dispersions was carried out according to previous studies (Sánchez et al., 2011a). The process was performed in an open vessel, using a controlled-rotational speed mixer (60 rpm), equipped with a helical ribbon impeller to disperse chitosan (32% w/w) in the base oil. Thickener concentration was previously optimized to provide physically stable oleogels, i.e. without significant oil separation. Batches of 200 g were prepared for each formulation investigated. Chitosan was dispersed at 50–60 °C, in order to decrease the blend viscosity and enhance mixing efficiency. The mixing process was maintained during 3 h. Finally, the sample was cooled down to room temperature by external natural convection, under continuous internal stirring, in the same heating device.

2.2.3. Preparation of cellulose derivatives-based gel-like dispersions

Processing of cellulose derivatives-based formulations was basically carried out following the methodology reported to disperse cellulose pulp samples in castor oil (Nuñez et al., 2011). The process was performed in an open vessel, using an anchor impeller geometry to disperse the cellulosic pulp and ethyl cellulose. In the first step, the vessel was filled with the corresponding amount of basestock and ethyl cellulose (4% w/w). Ethyl cellulose was mainly added to modify the basestock viscosity thus preventing oil separation (Sánchez et al., 2011b). A constant rotational speed (60 rpm) was then applied to the mixture, while heating up to 150 °C. Once the ethyl cellulose was completely dissolved, this mixture was then cooled down to room temperature by natural convection and Kraft

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