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

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## H I G H L I G H T S

- NCO-functionalized cellulose derivatives as thickening agents of castor oil.
- Chemical oleogels or gel-like dispersions with unlike rheological properties.
- Rheological properties depend on the type of substituent and substitution degree.
- Gel-like dispersions proposed as bio-based alternatives to lubricating greases.

## A R T I C L E I N F O

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## A B S T R A C T

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

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## 1. Introduction

As well known, cellulose is the most abundant renewable organic material in the biosphere, produced in amounts of 100–150 billion tons each year (Brown Jr., 1982; Gilbert, 1994), being employed in many different applications such as textile, medical and industrial materials due to its renewability, low cost, and attractive physical properties. It is also considered a promising raw

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material for producing important value-added chemicals based on renewable resources, including cellulose ethanol, hydrocarbons, and starting materials for the production of other polymeric materials (Gonzalez et al., 2012; Mosier et al., 2001; Mukherjee et al., 2013; Ragauskas et al., 2006). Eco-friendly polymers from renewable resources are attracting great attention in diverse areas due to the rapidly growing concerns to environmental pollution and energy crisis (Scott, 2000). In this sense, the production of different cellulose derivatives has extensive interest worldwide, mainly because of its abundance in nature, biodegradability and lower environmental impact in comparison with other polymers obtained from fossil sources (Zhang, 2007). Cellulose derivatives have been widely used in waste treatment, oil recovery, paper manufacturing, textile finishing, food additives and pharmaceutical applications (Yan et al., 2006).

At the present time, the different industrial sectors, and the lubricant industry in particular (Bartz, 1998; Boyde, 2002; Wilson, 1998), need to face the impact on the environment of process technologies and products with the replacement of non-renewable raw materials by renewable resources. Despite the fact that vegetable oils, castor oil among them (Singh, 2011; Wu et al., 2014), are being increasingly used as lubricant base oils over mineral and synthetic oils, the substitution of traditional thickening agents in lubricating greases, such as lithium, calcium or aluminum soaps, by others derived from renewable resources, like some biopolymers, is a complicated task due to the technical efficiency of metallic soaps to impart the desired rheological, thermal and tribological properties to the bulk system.

In general, the finding of low-molecular weight and polymeric appropriated gelators or thickeners of triacylglyceride oils is gaining special attention in order to produce oleogels with different applications (Behera et al., 2012; Co and Marangoni, 2012; Laredo et al., 2011; Lupi et al., 2013; Patel et al., 2015; Sánchez et al., 2008; Satapathy et al., 2013). The use of some biomacromolecules like natural waxes, resins and polysaccharides, including some cellulosic derivatives, with gelling or thickening properties in oily media have been reported (Alvarez-Mitre et al., 2013; Gravelle et al., 2013; Patel et al., 2013a; Ruiz-Martinez et al., 2003; Toro-Vazquez et al., 2010; Zetzel et al., 2012, 2014). In particular, Patel et al. (2013b, 2014) have put special emphasis in the last years on novel protocols to achieve oleogels with targeted rheological or textural properties using water soluble cellulose derivatives, which reflects the importance of polymer polarity. Apart from suitable rheological characteristics, oleogels or gel-like dispersions potentially applicable as environmentally friendly lubricating grease formulations need to fit additional requirements like thermal and mechanical stability. This means that gel-like rheological properties must be preserved at temperatures of around 100–150 °C and recovered after working in a lubricated contact. Some attempts to achieve such proper formulations using lignocellulosic materials and cellulosic derivatives have been made in previous investigations (Núñez et al., 2011, 2012a, 2012b; Sánchez et al., 2009, 2011a, 2011b). However, some weaknesses mainly regarding physical and mechanical stabilities were pointed out. Aiming to improve the affinity of cellulosic materials by vegetable oils, the so called “solveny” in the lubricant industry, two different approaches were followed later on: on one hand, the functionalization with non-polar groups in order to reduce the polarity (Martín-Alfonso et al., 2009a, 2011) and, on the other hand, the functionalization of cellulosic derivatives with reactive isocyanate groups able to chemically interact with triacylglycerides (Gallego et al., 2013a, 2013b), resulting promising formulations. As a continuation of this investigation, the effect of biopolymer polarity, once functionalized with reactive isocyanate groups, has been explored in this work by evaluating the ability of several commercially available cellulosic derivatives differing in substituents and substitution degree to thicken castor oil. As a result, dispersions of the different cellulosic derivatives analyzed provide oleogels with a wide

variety of rheological properties, thermal stability and physical appearance.

## 2. Experimental

### 2.1. Materials

Castor oil (211 cSt at 40 °C, Guinama, Spain) was selected as vegetable oil medium to prepare oleogel formulations.  $\alpha$ -cellulose ( $M_n$ :  $1.64 \times 10^5$  g/mol (Sánchez et al., 2011a)), methylcellulose ( $M_n$ : 40,000 g/mol; DS: 1.6–1.9), 2-hydroxyethyl cellulose ( $M_n$ : 90,000, MS: 2.5), methyl 2-hydroxyethyl cellulose (MS (hydroxyethyl): 0.06–0.50; DS (methoxy): 1.3–2.2) and cellulose acetate propionate ( $M_n$ : 15,000 g/mol; DS (acetyl content): 0.03, DS (propionyl content): 2.09) were used as thickening agents after modification with 1,6-hexamethylene diisocyanate (HMDI, purum grade,  $\geq 98.0\%$ ), all of them purchased from Sigma-Aldrich. All other common reagents and solvents employed were supplied by Sigma-Aldrich too.

### 2.2. General methods

Functionalization reactions were performed in flasks that were previously flame-dried under a positive flow of argon to eliminate surface moisture. HMDI was stored at 4 °C and handled under argon atmosphere. Solvents were purified according to the standard literature techniques and stored under argon. Reagents were purchased at the higher commercial quality and used without further purification, unless otherwise stated. Characterization tests were performed at least in duplicate.

### 2.3. Functionalization reaction with HMDI

$\alpha$ -Cellulose, methylcellulose, 2-hydroxyethyl cellulose, methyl 2-hydroxyethyl cellulose and cellulose acetate propionate were NCO-functionalized using HMDI in concordance with the protocol described in previous study (Gallego et al., 2013a). Each of them (1.0 mmol) was added to a bottom round flask with toluene (100 ml) while stirring at room temperature, becoming a suspension. Then, triethylamine ( $\text{Et}_3\text{N}$ , 1.0 mmol.) and HMDI (0.5 mmol.) were also added to the system, the last one dropwisely. The solution was vigorously stirred at room temperature for 24 h. Afterwards, the mixture was vacuum filtered and the resulting products (Table 1) were immediately used to prepare the oleogels. The substitution degrees of all derivatives synthesized are collected in Table 2.

### 2.4. Preparation of oleogels

The dispersion of the different biopolymers in the base oil was carried out in an open vessel (batches of 60 g), using a

**Table 1**  
Codes applied to cellulose derivative samples and corresponding oleogels.

Substrate	Code		
	Non-functionalized biopolymer	NCO-functionalized biopolymer	Oleogel
$\alpha$ -Cellulose	C-0	C-1	C-2
Methylcellulose	MC-0	MC-1	MC-2
2-Hydroxyethyl cellulose	HEC-0	HEC-1	HEC-2
Methyl 2-hydroxyethyl cellulose	MHEC-0	MHEC-1	MHEC-2
Cellulose acetate propionate	CAP-0	CAP-1	CAP-2

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