Rheological study of acetylated lignin gel-like dispersions in vegetable oil: Influence of acetylation degree

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Introduction

Lignin is a polyphenol with a complex and amorphous three dimensional structure, found in the cell wall of plants, being the second most abundant biopolymer in the planet, constituting between 15 and 30% of the lignocellulosic biomass [1]. It is also the largest natural and renewable source of aromatic compounds, representing a sustainable alternative to petrochemicals, which makes the appreciation of lignin attractive from the point of view of the sustainable development [2]. Lignin is produced through different processes such as kraft, soda, organosolv, steam explosion, etc. The physical and chemical properties of lignin are dependent on the type of plant and its extraction method [3]. Sulfonate lignin- is one of the lignin types extracted from the sulfite process, and contains hydrophilic groups such as sulfonic, phenolic hydroxyl and alcoholic hydroxyl, and hydrophilic groups such as aromatic rings [4]. On the other hand, lignin acetylation, one of the most widespread chemical modifications used for improves the solubility of this biopolymer in organic solvents and increase polymer-lignin compatibility The main aim of this study was to investigate the influence of acetylation process on the rheological and tribological properties and microstructure of lignin based gel-like dispersions. Low-sulfonate lignin was treated with acetic anhydride and pyridine as a catalyst by modifying three different variables, i.e. reaction temperature (10-60ºC), ratio of pyridine/acetic anhydride (0:1,-1:5), reaction time (3-72 h).

Experimental

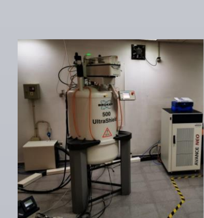
Materials and acetylation process

Softwood low sulfonate Kraft lignin (LSL, Mw: ~10,000 g/mol) was obtained from Merck Sigma-Aldrich. Acetic anhydride and pyridine were also purchased from Merck Sigma-Aldrich. All chemicals were reagent grade and used without any further purification. Castor oil (211 cSt at 40 °C, Guinama, Spain) was used as biodegradable oil media to prepare oleogel formulations with acetylated lignins. All samples were dispersed in oil, employing lignin concentrations in the range of 30-40% (w/w) at room temperature using an anchor impeller geometry (60 rpm for 60 min).

For esterification reaction, 2 g of low-sulfonate lignin sample was added to a mixture of acetic anhydride and pyridine as a catalyst by modifying three different variables, i.e. reaction temperature (10, 20, 30, 40, 50, 60ºC), ratio of pyridine/acetic anhydride (0:1, 1:1, 1:2, 1:3, 1:4, 1:5), reaction time (3, 6, 12, 24, 36, 48, 72 h). Lignin and pyridine were dissolved in a flask of 100 mL and acetic anhydride was added, then the reaction mixture was stirred at controlled temperature. Finally, 10 volumes of HCl 0,1 M were added at 0ºC, and acetylated lignin was filtered and washed with distilled water to a neutral pH, and then dried in a vacuum oven at 70°C.

Chemical Characterization

FTIR analysis were conducted in a Jasco FT-IR 4200 spectrometer in the scan range of 40 to 4000 cm^{-1},at 4 cm^{-1} resolution.

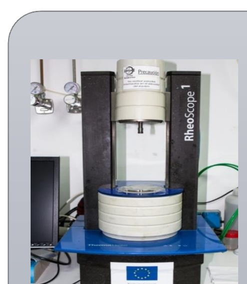


Chemical structure changes during reaction were observed by NMR ^{1}H and ^{13}C techniques (AV NEO 500 MHZ).

DSC was carried out with a TA Q-100 (TA Instruments Water, USA), in a temperature range of 30–200 °C for glass transition determination at a scan rate of 10 °C/min under a nitrogen atmosphere.

TGA was carried out using a Q-50 thermal analyzer (TA Instruments Water, USA) with a heating rate of 10 °C/min from 30 to 600 °C under a nitrogen flow of 50 mL/min.

Rheological properties

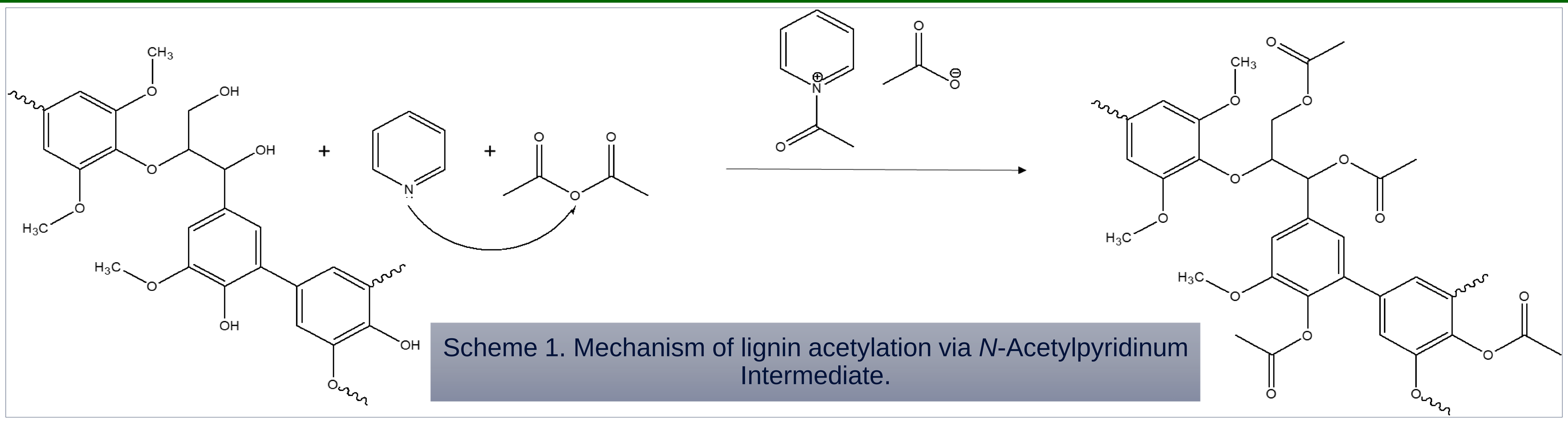


Flow curves and oscillating shear tests were obtained in a small-amplitude oscillatory shear rheometer (ThermoHaake RheoScope).

Tribological properties

Friction factor vs time at 20 N curves were performed in a controlled stress rheometer (Physica MCR-501, Anton Paar).

Results



Scheme 1. Mechanism of lignin acetylation via *N*-Acetylpyridinum Intermediate.

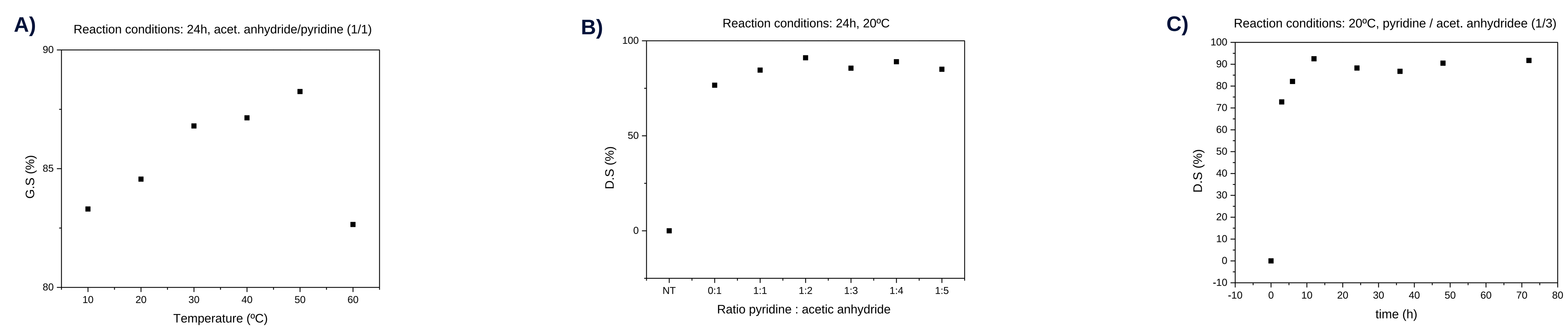


Figure 2. Evolution of the substitution degree (%) with A) ratio pyridice/acetic anhydride, B) temperature and C) reaction time of acetylation.

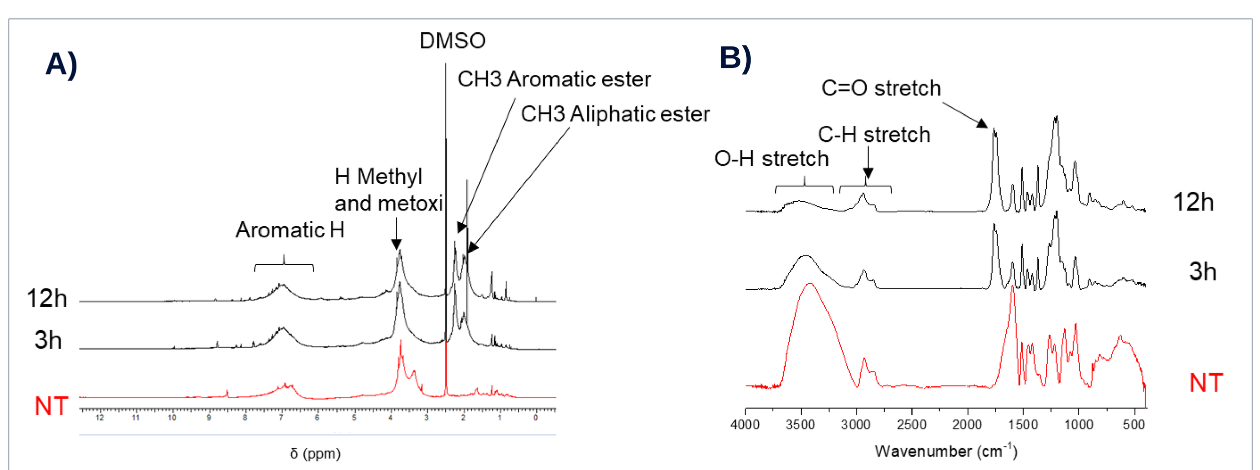


Figure 1. NMR ^{1}H recorded in DMSO-d$_6$ A) and FTIR B) spectra for Lignin L.S unprocessed Lignin (NT), Lignin acetylated during 3, 6 and12h.

t (h)	T_{onset} (ºC)	$T_{10\%}$ (ºC)	T_{max} (ºC)	T_f (ºC)	ΔW (%)	Residue to 600ºC (%)	Tg 1st cycle (ºC)
0	170/ 311	181/ 309	269/ 342	295/ 507	32.7	63.3	144.6
3	121/ 293	157/ 288	198/ 370	241/ 477	59.4	40.6	94.6
6	124/ 264	142/ 284	198/ 374	237/ 504	60.4	39.6	94.8
12	177/ 279	183/ 289	228/ 382	257/ 507	57.4	41.3	93.4
24	178/ 292	150/294	235/ 382	256/ 504	59.8	40.2	85.7
36	174/ 293	149/ 282	235/ 380	244/ 502	60.3	39.7	78.9
48	183/ 284	191/ 341	231/ 378	255/ 502	85.7	13.5	48.6
72	177/ 296	164/ 298	236/ 381	257/ 510	58.9	40.9	93.8

Table 1. Characteristic parameters obtained from TGA and DSC measurements for acetylated simples.

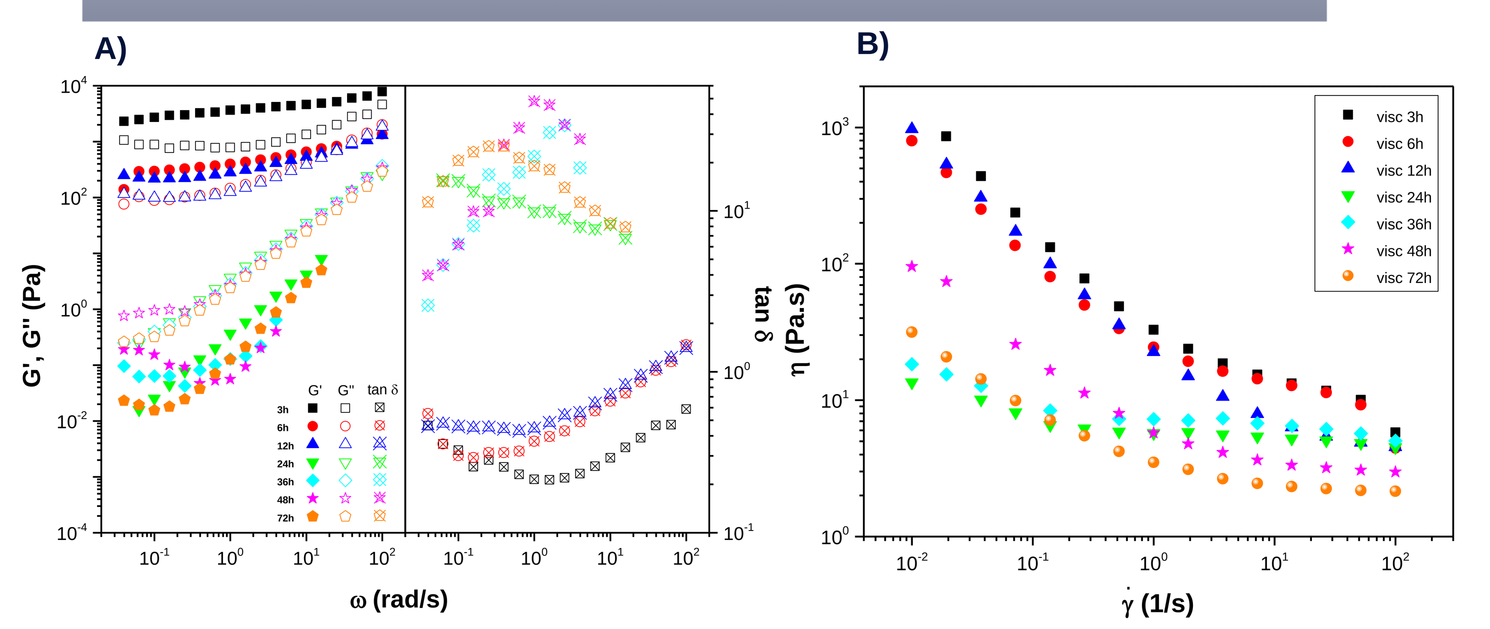


Figure 3. SAOS tests A) and viscous flow tests B) of gel-like dispersions as influence of reaction time

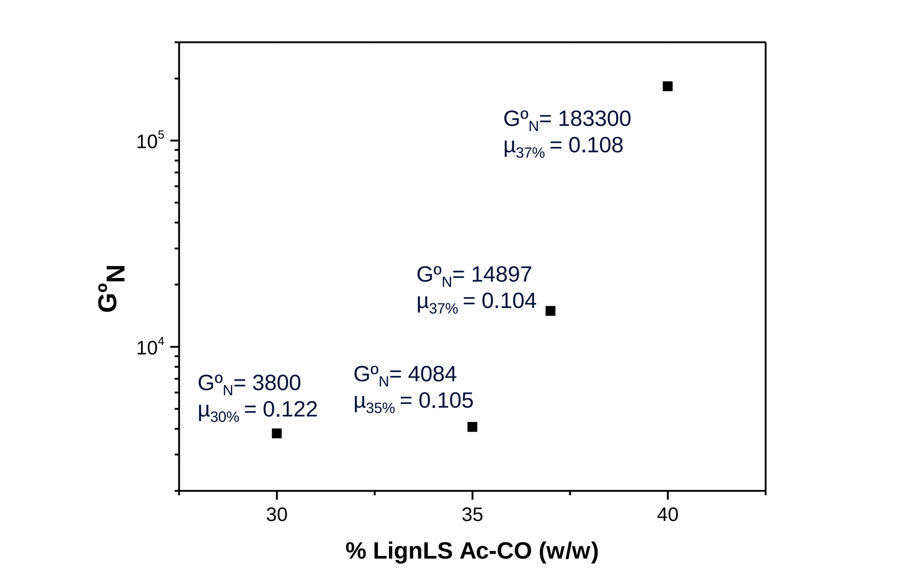


Figure 4. Evolution of the plateau modulus with acetylated lignin (3h, 30ºC, 1:3 ratio) for gel-like dispersions

Conclusions

In this work, the influence of acetylated process of low sulfonate lignin on the tribological and rheological properties of gel-like dispersions of the lignin in castor oil, which may be useful as completely bio-based lubricating greases, was investigated. The optimal values of temperature, amount of reagents and reaction time were obtained to be 30°C, 1:3 and 3 h, respectively, attending to the rheological response of oleogels. It was found that linear viscoelastic functions, determined in small-amplitude oscillatory shear (SAOS), and viscosity values of acetylated lignin gel-like dispersions decreased by increasing the acetylation index. In general, gel-like dispersions studied exhibited similar values of the friction coefficient comparable to those found for commercial lubricating greases. This work demonstrates that the optimization of the acetylation process is a key issue to achieve final desired properties of the lignin based gel-like dispersions in a vegetable oil, resulting an effective method for improving the compatibility of lignin and vegetable oil.

References

[1] Davi Rabelo de Oliveira, Francisco Avelino, Selma Elaine Mazzetto, Diego Lomonaco. Microwave- assisted selective acetylation of Kraft lignin: Acetic acid as a sustainable reactant for lignin valorization. International Journal of Biological Macromolecules, 164, (2020), 1536-1544.

[2] S. Sahoo, M. Seydibeyoğlu, A. Mohanty, M. Misra, Characterization of industrial lignins for their utilization in future value added applications, Biomass Bioenergy 35 (10) (2011) 4230–4237.

[3] T. Aro, P. Fatehi, Production and application of lignosulfonates and sulfonated lignin, ChemSusChem 10 (9) (2017) 1861–1877,

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