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Structuring natural deep eutectic solvents with epoxidised lignin-enriched residues: a green alternative to petroleum-based thickened formulations

E. Cortés-Triviño [a,*], J. Cubero-Cardoso [b], A. Tenorio-Alfonso [a], M.A. Fernández-Recamales [c], C. Valencia [a], J. Urbano [b], J.M. Franco [a]

[a] Pro2TecS-Chemical Product and Process Technology Centre, University of Huelva, 21071 Huelva, Spain
[b] Laboratory of Sustainable and Circular Technology. CIDERTA and Chemistry Department, Faculty of Experimental Sciences. Campus de "El Carmen", University of Huelva, 21071 Huelva, Spain
[c] AgriFood Laboratory, Faculty of Experimental Sciences, University of Huelva, 21007 Huelva, Spain

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ABSTRACT

Natural deep eutectic solvents (NADESs) differing in the number of hydroxyl groups in the hydrogen bond donor (HBD) compound were investigated for usage as a matrix base in reactions involving a lignin-enriched fraction. NADESs were prepared by mixing citric acid with different HBDs (glycerol, xylitol, and sucrose). In addition, waste lignocellulose was epoxidised for use as a thickening agent for NADESs by promoting chemical crosslinking between the HBD hydroxyl groups and the epoxy rings of the lignocellulosic material. Fourier transform infrared spectroscopy, nuclear magnetic resonance spectroscopy, and thermogravimetric analysis were used to verify the reaction between NADES and the epoxidised lignin-rich material. In addition, full rheological characterisation was performed to evaluate the effects of the viscosity of NADESs and lignin-enriched residue concentration. A heating process was applied to determine the influence of water on the viscoelastic properties of the final products. The chemical interaction between NADESs and epoxidised lignocellulose was successfully achieved, resulting in various rheological responses, from liquid-like to gel-like, depending on the HBD compound comprising NADESs and the lignin concentration. The higher the number of hydroxyl groups in the HBD, the higher was the viscosity of the lignin-structured NADESs. An analysis of the relative viscosity data reveals that the epoxidised ligninocellulose residue exerts a similar structuring role in the three different NADESs.

1. Introduction

Over the last century, green and sustainable chemistry has been at the forefront of providing solutions to mitigate climate change and pollution-derived problems. Traditional industries have been forced to decrease the use of petroleum-based materials and search for new eco-friendly alternatives from bio-sourced and/or biodegradable substances [1–3] to manufacture their products in compliance with green chemistry principles while preserving their fundamental properties [4]. Extensive research has been performed in recent decades to decrease the use of mineral oils in lubricant formulations, promoting their replacement by vegetable oils [5–7]; this allows for an increase in the biodegradable character and converts them into more eco-friendly alternatives. In this manner, castor oil containing distinctive ricinoleic acid in its fatty acid profile, with hydroxyl groups in its chemical structure, has been proven to be an excellent candidate for replacing mineral oils and resulting in renewable formulations with excellent properties [8–11]. Moreover, its viscosity can be modulated by adding different bio-based thickening or gelling agents, making it a promising alternative to petroleum-based liquid or gel-like lubricants. However, although vegetable oils are considered promising options for the production of bio-based lubricants, they exhibit some limitations regarding tribological properties (i.e., the ability to minimise friction and wear in a lubricated contact) and particularly chemical stability [12,13], requiring chemical modifications or the incorporation of some specific additives prior to their final use [12–14]. To address, researchers enhanced the tribological performance by combining vegetable oils with ionic liquids, thus

* Corresponding autor at: Departamento de Ingeniería Química. Campus de "El Carmen". Universidad de Huelva. 21071 Huelva. Spain.
E-mail address: esperanza.cortes@diq.uhu.es (E. Cortés-Triviño).

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resulting in effective base matrices for lubricant formulations along with an increased biodegradable character [15,16].

Natural deep eutectic solvents (NADESs), which are typically liquids at room temperature, form a supramolecular structure via intermolecular hydrogen bonding with multiple chemical sites for further reactions and have several advantages and outstanding physicochemical properties, such as adjustable viscosity, high thermal stability, and water solubility [17]. In addition, their low cost, biodegradability, non-toxicity, sustainability, and ease of preparation reinforce their potential use as raw materials for applications in different fields [18,19]. NADESs are formed by natural primary metabolites such as sugars, sugar alcohols, and organic acids, involving a hydrogen bond donor (HBD) and a hydrogen bond acceptor (HBA), from which hydrogen bonding interactions are produced, giving rise to highly viscous liquids [20]. These compounds usually contain hydroxyl groups in their chemical structures, which have proven to be feasible candidates for further reactions. Owing to their chemical nature, NADESs have received the attention of the scientific community in recent years, and they can be potentially used in different unexplored fields, where their outstanding properties could make them a promising sustainable option as functional solvents and matrices for end-use products.

In recent decades, lignocellulose has been one of the most exploited bio-renewable material on earth and, in some cases, considered as a waste bioproduct and/or inexpensive resource originating from agricultural practices [21]. This natural polymer, whose composition depends on the nature of the source, is composed of cellulose, hemicellulose, and lignin, thus comprising a wide range of functional groups in its chemical structure available for further reactions [22,23]. Among these groups, hydroxyl groups are one of the most susceptible to chemical modifications, causing an increase in the chemical reactivity of lignocellulose [24,25]. Thus, some researchers have focused their work on different chemical reactions involving the hydroxyl groups of lignocellulose [26,27], resulting in the epoxidation reaction with di-epoxy compounds as a promising alternative to encourage the use of this bio-based polymeric material as feedstock in several applications [28,29]. The epoxidation reaction is performed through a nucleophilic attack, owing to the reactive character of hydroxyl groups, while keeping the other terminal epoxy ring closed and accessible for further nucleophilic linkages [9].

Based on this functionalisation, epoxidised waste lignin could be implemented to chemically interact with hydroxyl groups contained in NADESs, thus increasing the viscosity or even achieving a certain degree of structuration and promoting thickened formulations with enhanced rheological properties. Therefore, these waste materials may represent a considerable breakthrough in the replacement of nonbiodegradable thickening agents for lubricating grease formulations. In principle, NADES structuration can result in gel-like formulations, depending on the chemical composition of both the NADES and lignocellulose and the extent of epoxidation. Finally, for industrial applications, in addition to the synthesis procedure used to develop these formulations being simple, the industrial production costs should be low. The lignin-enriched feedstock is a residue from the bioethanol production process, where major costs are incurred during pretreatment of biomass for bioethanol production. Therefore, the valorisation of lignin waste may represent a pathway to make these treatments cost-effective. In addition, the prices of citric acid, glycerol, xylitol, and sucrose are well below those of mineral or vegetable oils and traditional thickeners such as lithium 12-hydroxy-stearate. In this work, different NADES-based matrices containing a waste lignin-enriched material as a structuring agent, previously modified via epoxidation, were produced to obtain novel sustainable thickened liquids or gels with potential application as biolubricants. Three different eutectic blends comprising citric acid and glycerol, xylitol, and sucrose as hydrogen bond donors (HBD), which contain a different number of hydroxyl groups in their chemical structure, were synthesised to analyse the influence of the viscosity of NADESs. The ability of epoxidised lignin-rich waste to structure NADESs was assessed by using rheological measurements.

2. Experimental section

2.1. Materials

Waste lignin from a bioethanol production process involving pre-saccharification and simultaneous saccharification and fermentation of sugarcane bagasse, consisting of 25.8 wt.% cellulose, 3.6 wt.% hemicellulose, 56.3 wt.% lignin, and 11.4 wt.% ashes, was kindly supplied by CIEMAT (Madrid, Spain). Additional information about the production and pretreatment processes and the detailed chemical composition of this lignin-rich residue is available in literature [30]. Neopentyl glycol diglycidyl ether (NPGDGE), supplied by Merck-Sigma Aldrich (St. Louis, USA), was used to epoxidise lignocellulosic material. Different natural deep eutectic solvents (NADESs) were synthesised by mixing citric acid (CA) with several hydroxyl-containing compounds such as glycerol (Gly), xylitol (Xyl), and sucrose (Suc), all of which were purchased from Merck Sigma Aldrich (St. Louis, MO, USA).

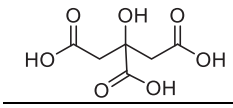
2.2. Synthesis of NADESs

NADESs were obtained by mixing a hydrogen bond acceptor (HBA) compound (citric acid) with two hydrogen bond donor (HBD) compounds, i.e. the corresponding polyalcohol and water, following a previously described synthesis method [17,31]. The desired amounts of CA and the corresponding HBD to produce 20 g of NADESs were mixed in a round-bottom flask at 56 °C for 1 h to achieve a clear and homogeneous liquid at the eutectic point. Three different compounds, glycerol, xylitol, and sucrose, comprising three, five, or eight hydroxyl groups (see Table 1), were combined with CA and water in the proportions indicated in Table 2. The HBA/HBD ratios were similar to those reported in the existing literature [17,32,33], based on the hydrogen bond connections that can occur depending on the available hydroxyl groups, whereas the water content provided the required viscosity modulation [17,31,34] to further facilitate interaction with the modified lignin.

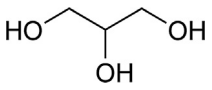
2.3. Epoxidation of lignocellulosic material

According to previous studies [9], lignin-enriched residue was chemically modified by reaction with NPGDGE, which was generally conducted in an open vessel at room temperature under stirring conditions. Typically, 40 g of lignin was dispersed in 250 g of water, and 200 g of NPGDGE was added to the mixture (1/5 lignin residue/epoxy weight ratio). The reaction mixture was agitated for 3 h, centrifuged at 4000 rpm for 10 min, washed several times with distilled water, and finally dried in a lyophiliser (Virtis Advantage) to obtain epoxidised lignocellulose (EPL). An example epoxidised monolignol is presented in Table 1. However, because of the complex composition of lignocellulosic waste material, epoxidation of other compounds such as carbohydrates is also likely to occur. The unreacted epoxy groups are available for further reactions with other hydroxyl groups, leading to enhanced extensive crosslinking in the lignocellulosic material. The epoxy index, determined using the titration method (ISO 3001:1999E), was found to be 1.8 mol/kg, which is consistent with previous work [9] and allows verification of the availability of free epoxy rings for further reactions.

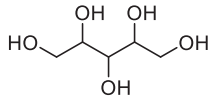
Table 1
Chemical structures of constituents of NADESs and example of epoxidized monolignol.



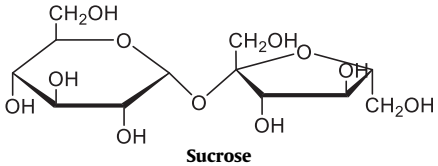
Citric acid



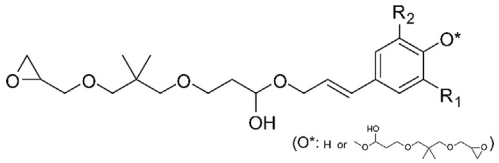
Glycerol



Xylitol



Sucrose



Example of epoxidized monolignol

Table 2
Composition of NADESs.

NADES code	Compounds			Weight Ratio (%) (HBA/HBD/W)	Molar ratio (mol) (HBA/HBD/W)
	Hydrogen bond acceptors	Hydrogen bond donors			
CA-Gly	Citric Acid	Glycerol	Water	49/43/8	~1/2/2
CA-Xyl		Xylitol		50.5/36.5/13	~1/1/3
CA-Suc		Sucrose		42/42/16	~2/1/8

2.4. Preparation of lignin-structured NADES formulations

NADES and the epoxidised lignin-enriched fraction were mixed for 3 h in an open vessel, in the proportions shown in Table 3, to promote chemical crosslinking between both components, according to the protocols employed in previous studies using castor oil instead of NADES [9,35]. The reaction was conducted at two different temperatures, viz. room temperature (RT) and 120 °C. To maintain 120 °C during the reaction, the reacting mixture was placed in an oven. Finally, the samples were homogenised for 1 min at 10 000 rpm using an Ultra-Turrax T-25 (Ika) rotor-stator turbine.

2.5. Characterization techniques

Fourier transform infrared (FTIR) spectra of NADESs, epoxidised lignin residues, and the resulting thickened formulations were acquired using an FT/IR-4200 spectrometer (JASCO, Tokyo, Japan). The epoxidised lignin-based fraction was measured by preparing KBr-based pellets and placing them in a holder, while structured NADES samples and the resulting gels were characterised using an attenuated total reflectance (ATR) accessory containing a monolithic diamond crystal. FTIR spectra were recorded in transmission mode at a resolution of 4 cm^{-1} in the wavenumber range of 400–4000 cm^{-1}.

A Q-50 thermal analyser (TA Instruments Water, USA) was used to assess the thermal degradation patterns of the raw materials and the synthetised formulations. Samples (10–20 mg) were placed in platinum pans, and mass losses were quantified by applying a temperature ramp from 30 °C to 600 °C at 10 °C min^{-1} under a nitrogen atmosphere.

Nuclear magnetic resonance (NMR) spectroscopy (^{1}H, ^{13}C, and HSQC) experiments were performed at 500 MHz using a Varian Mercury 500 spectrometer. Deuterated dimethyl sulfoxide (DMSO-d6) was used as solvent. The DMSO-d6 resonance at 2.51 and 39.8 ppm was used as chemical shift reference of ^{1}H- and ^{13}C-NMR, respectively. Diffusion-ordered spectroscopy (DOSY) NMR experiments were performed to elucidate the diffusion properties of the species.

Viscosity measurements of both the NADESs and the resulting lignin-structured formulations were performed using an ARES G2 rheometer (TA Instruments, USA) at 25 °C, equipped with a Peltier temperature controller and plate-plate geometries (25 mm and 50 mm, 1 mm gap), by applying a shear rate range of 10^{-2}–10^{2} s^{-1}. Small-amplitude oscillatory shear (SAOS) tests in the linear vis-

Table 3
Proportions used in the preparation of lignin-based-structured NADES matrices.

NADES	EPL concentration(wt.%)	Synthesis temperature(°C)	OH*/Epoxy molar ratios	Formulation Code
CA-Gly	30		0.98/0.06	Gly-EPL30
CA-Xyl		RT	0.84/0.06	Xyl-EPL30
CA-Suc			0.60/0.06	Suc-EPL30
CA-Gly	5	120	1.33/0.009	Gly-EPL5-120
	12		1.23/0.022	Gly-EPL12-120
	20		1.12/0.036	Gly-EPL20-120
	30		0.98/0.06	Gly-EPL30-120

* only considering hydroxyl groups comprising the HBD compounds

coelastic regime were performed in the same rheometer, at 25 °C, in a frequency range of 0.03–100 rad/s.

At least two replicates of each experimental measurement or analysis were performed for fresh samples.

3. Results and discussion

3.1. Synthesis and characterization of NADESs and epoxidized lignin-enriched residue

NADESs were successfully synthesised by mixing the components, according to the proportions shown in Table 2, at 56 °C [17,31,36], achieving homogeneous mixtures at their eutectic points after 60 min, which were stable at room temperature. As mentioned above, three kinds of NADES were synthesised by modifying the HBD component based on the number of hydroxyl groups (see Table 1), with the aim to explore their influence on the rheological properties of the structured systems when reacting with the epoxidised lignin waste. In general, NADES structure is influenced by the different interactions occurring between the carboxylic groups of citric acid (the HBA) and the hydroxyl groups of the HBD component, which requires different proportions of these compounds to attain the eutectic point, and specially different amounts of water (between 8 and 16 wt.%) [17]. Numerous studies have demonstrated that the addition of certain amounts of water (< 50 wt.%) is essential to obtain liquid systems at room temperature while preserving the supramolecular structure at the eutectic point [31,37]. In addition, water plays an important role in NADES properties by decreasing viscosity, synthesis time, and/or temperature, as well as providing high polarity to the blend [18]. In addition, it has been corroborated that a good combination with water prevents NADES evaporation, which is a part of the NADES structure [17,38]. However, excessive dilution can lead to the loss of existing hydrogen bonds due to their progressive breakage, resulting in a weakened supramolecular structure [39]. Molecular interactions, such as H-bonding within the eutectic mixture, van der Waals, and electrostatic interactions, are responsible for the supramolecular structure and physicochemical properties, which highly depend on the number of hydroxyl groups present in the HBD component and the amount of water. As a result, as deduced from Table 2, in order to obtain stable liquid blends at room temperature, the amount of water was varied for the three systems, and those based on sucrose (CA-Suc) required higher quantities due to the stronger interactions arising in the supramolecular network promoted by the eight available hydroxyl groups of sucrose and the hygroscopic nature of citric acid [17,38]. Therefore, the stabilisation capacity of NADESs, as well as their viscosity and polarity, may be modulated by modifying the water percentage, which will also affect the interaction of NADESs with epoxidised lignin waste and the resulting properties of the final lignin-enriched residue-structured systems.

In previous studies [33,40], the formation of the NADES supramolecular structure was verified by infrared spectroscopy tests (Figure 1), where the interaction through hydrogen bonding was related to the shift of significant FTIR bands associated with the constituents. Thus, many authors mentioned a shift from 1692 to 1714 cm^{-1}, corresponding to the C=O stretching vibration of citric acid, thereby confirming the existence of intermolecular interactions and hydrogen bonding between the carboxylic and hydroxyl groups of the HBD component, which was detected in the FTIR spectrum of the CA-Gly sample in Figure 1c.

On the other hand, the thermal decomposition of eutectic blends has been investigated by other authors [17,18,41], indicating that the first thermal degradation peak at approximately 100 °C was related to the volatilisation of water molecules, whereas the successive ones were concerned with the characteristic degradation events of the components forming the eutectic. In this case, as shown in Figure 2, the CA-Gly characteristic thermal degradation peaks correspond to CA decomposition, from approximately 170 to 310 °C, and glycerol evaporation at approximately 290 °C [33,34,42].

NADES samples were rheologically characterised to understand the effect of viscosity on the rheological properties of the generated lignin-structured matrices. These liquids usually give rise to concerns related to their viscosity, as most exhibit high values that limit their use in many applications [43]. As mentioned previously, the viscosity of these eutectic mixtures depends on the amount of water that forms the blend. Table 4 shows the viscosity values of the NADESs studied at room temperature, as well as those obtained after heating at 120 °C for 3 h to remove water. Important differences in viscosity were obtained when modifying the HBD compound used to prepare NADESs samples. As previously demonstrated by Dai et al. [18], the formation of hydrogen bonds is conditioned by the number of donors and acceptor groups, their spatial structure, and the position of these bonds, thus greatly affecting the viscosity of NADESs. Consequently, the CA-Suc sample, which contains a higher number of hydroxyl groups due to sucrose chemical structure, showed the highest viscosity value, while significantly lower values were obtained for CA-Xyl and, especially, CA-Gly blends (see Table 4). Thus, the more hydroxyl groups that are available to interact with the carboxylic groups of citric acid, the more hydrogen bonds are formed, leading to an increase in viscosity [18]. However, NADES viscosity is highly influenced by both the HBA/HBD ratio and water content. For instance, at $1 s^{-1}$, Savi et al. [17] reported viscosity values of 514 and 1456 Pa·s for NADESs with 1:1 and 1:3 CA:Suc weight ratios, respectively, and 16 wt.% water and 48 Pa·s for NADES with a 1:1 CA:Suc weight ratio and 20 wt.% water. On the other hand, Santana et al. [33] reported a viscosity value of 0.011 Pa·s for a 1:1:10 CA:Xyl:water molar ratio, which is much lower than that given in Table 4 for the same CA:Xyl molar ratio but a lower amount of water. The effect of water on the viscosity of the NADESs was analysed by subjecting the sample to heating process at 120 °C, aiming to remove the free water content. As shown in Table 4, a remarkable increase in the viscosity of NADESs was obtained after this removal. Although CA-Gly and CA-Xyl samples only exhibited increased viscosity values while keeping the liquid supramolecular structure intact, a solid mixture was observed when water was eliminated from the CA-Suc sample, preventing viscosity determination. Similar behaviour was observed by other authors [31,38], who concluded that water removal from some types of NADES is not possible due to the strong interaction in the supramolecular network, with a 16 wt.% the minimum amount of water to obtain stable eutectic mixtures based on citric acid and sucrose [31].

Regarding the structuring material, a lignin-enriched fraction from the bioethanol production of sugarcane bagasse was chemically modified by inserting epoxy groups in its chemical structure, aiming to induce chemical crosslinking between the oxirane rings and NADES hydroxyl groups. Lignocellulose epoxidation with NPGDGE was successfully achieved (epoxy index:1.8 mol/kg) under gentle conditions (3 h at room temperature), as similarly achieved in previous investigations for cellulose pulp epoxidation [9,44]. It should be noted that although lignocellulose waste comprises a higher percentage of lignin, cellulose and hemicellulose hydroxyl groups are also available for reaction with epoxy rings, possibly yielding a certain degree of crosslinking. However, an appropriate concentration of free epoxy rings is still available for subsequent reactions with NADES.

The chemical modification of the lignin-enriched residue was verified by FTIR spectroscopy. The FTIR spectra of the original lignin material, NPGDGE, and EPL are shown in Figures 1a and 1b,

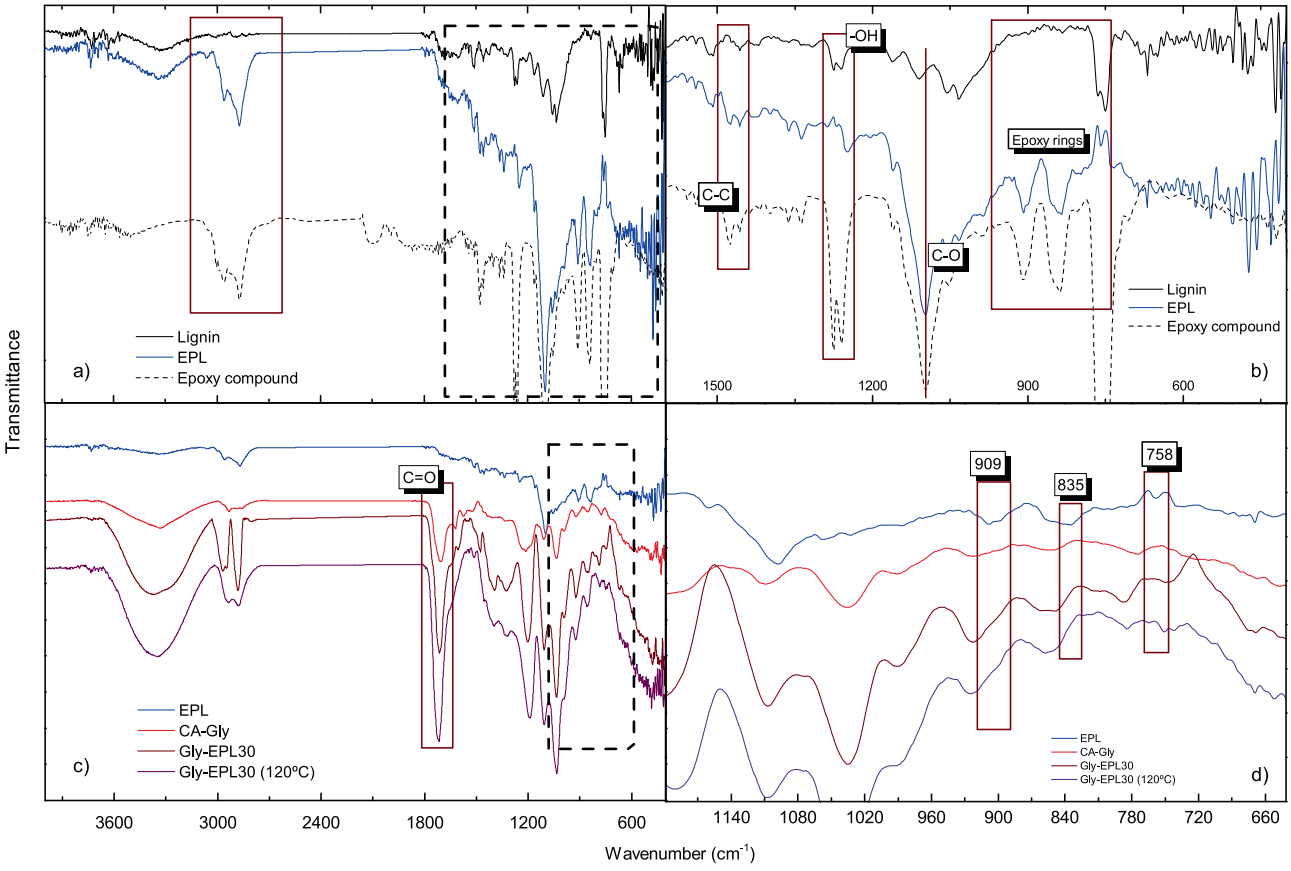


Figure 1. FTIR spectra for raw materials and synthetized structured formulations.

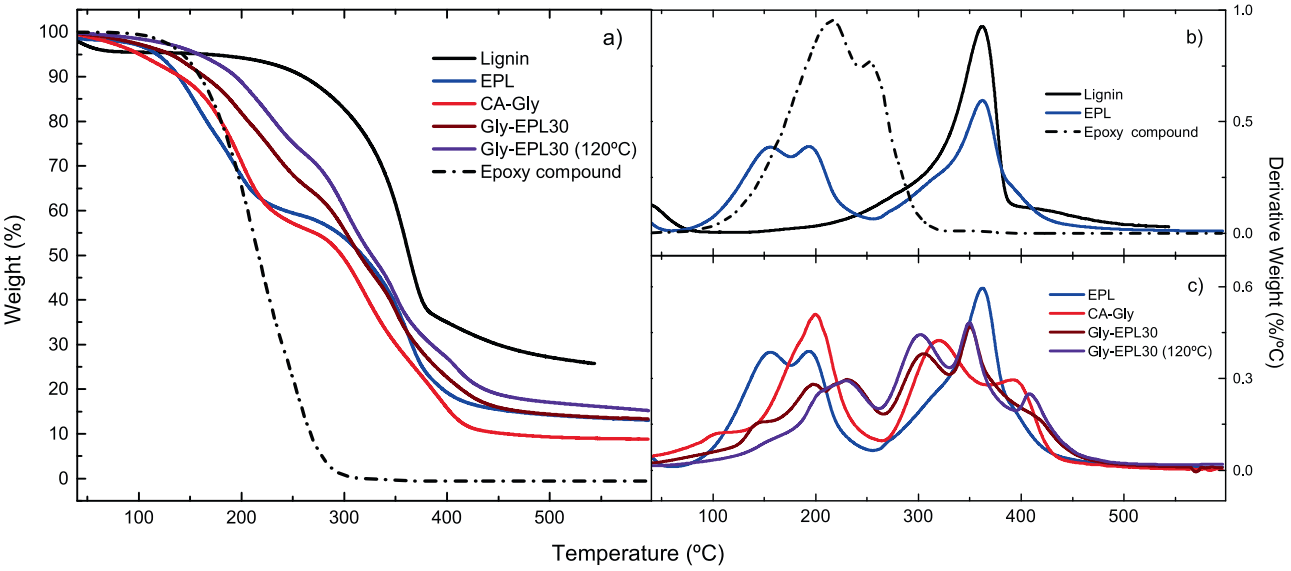


Figure 2. TGA curves for raw materials and synthetized structured formulations.

Table 4
Viscosity of NADESs at 25 °C.

NADESs	Viscosity after standard preparation (Pa·s)	Viscosity after heating process at 120 °C (Pa·s)
CA-Gly	1.19	12.10
CA-Xyl	8.97	97.60
CA-Suc	120.94	–

where remarkable differences were observed in the EPL with respect to the original lignin, especially in the wavenumber ranges of 3200–2700 cm^{-1} and 1200–600 cm^{-1}. Thus, a noticeable increase in the intensity of the asymmetric and symmetric stretching vibration bands associated with methyl and methylene groups (2871 and 2961 cm^{-1}) was detected in the spectrum of the modified lignin-enriched material owing to the introduction of the

epoxy compound into the lignocellulose structure, as well as the appearance of a new band at 3060 cm^{-1} attributable to the existence of terminal oxirane groups (C−H stretching of the epoxy ring) [45]. The grafting of epoxy rings in the chemical structure of lignin can also be verified by the disappearance of the −OH in the plane vibration band at approximately 1230 cm^{-1} [46,47]. In addition, a new peak at 1100 cm^{-1} associated with the stretching vibration of aliphatic ether groups can be detected, which can be attributed to the formation of C−O bonds resulting from the opening of the epoxy ring [48,49] (Figure 1b). This fact corroborates the chemical reaction between the epoxy rings and hydroxyl groups of lignocellulosic materials. In addition, the presence of oxirane groups in the molecular structure of lignin introduces new vibration bands in the wavenumber range of 900 to 700 cm^{-1}, corresponding to the stretching vibration of C−O−C of the newly generated epoxy groups [50,51].

Thermogravimetric analysis (TGA) also allows the verification of the chemical modification of lignocellulosic waste material. The different thermal events for the original lignin, NPGDGE, and EPL are displayed in Figure 2. Regarding the thermal degradation of the lignocellulosic raw material, a single main step with a maximum degradation rate of approximately 362 °C was detected, which is related to the cleavage of the multiple linkages forming the lignocellulose skeleton, together with a small overlapped thermal event at approximately 270 °C, typical of the soft dehydration of hydroxyl groups (Figure 2b) [52,53]. Chemical modification resulted in a decrease in its thermal stability owing to the introduction of the epoxy compound in its chemical structure. Thus, two new degradation events at lower temperatures (155 and 193 °C) were observed in the EPL, which can be related to the existence of epoxy end-rings available for further reactions and their isomerisation by means of C−O bond scission when producing the epoxy ring opening [9,54].

The NMR spectra were also helpful in verifying the chemical modification of lignin through epoxidation. Figure 3a shows the ^{1}H-NMR spectra of the waste lignin, NPGDGE, and EPL, where the appearance of new proton signals related to epoxy rings in the EPL can be appreciated in the range between 2.5 and 4 ppm. Moreover, 2D HSQC-NMR of NPGDGE (Figure 3b) was performed to identify signals related to closed epoxy rings in the NPGDGE, shown at δ_H/δ_C = 2.7/43.4 ppm (C3) and δ_H/δ_C = 3.0/51.0 ppm (C4), respectively, which were compared to those found in EPL (Figure 3c), where the same signals were detected. Similar proton NMR chemical shifts in epoxy compounds were reported by Xiao et al. [55]. Therefore, the presence of epoxy rings in the EPL, which are available for further reactions when blending this compound with NADESs, is confirmed.

3.2. Synthesis and characterization of lignin waste-structured NADES formulations

As shown in Table 3, the 30 wt.% of EPL was mixed with the different NADESs studied, at room temperature, in order to promote structuration to some extent, depending on the number of hydroxyl groups contained in the HBD component. The three types of eutectic mixtures resulted in homogeneous and physically stable structured liquids, arising from the chemical compatibility between the epoxidised lignin-enriched fraction and the eutectic mixtures. Moreover, NADES comprising citric acid and glycerol (CA-Gly) was selected to study the influence of both reaction temperature, which affects the amount of water, and the proportion of the lignocellulosic structuring agent.

The chemical interaction between the epoxidised lignocellulosic material and NADES was confirmed by FTIR spectroscopy (Figure 1). As an example, the FTIR spectrum of a selected system based on citric acid and glycerol is shown in Figures 1c and 1d, where the disappearance of the EPL epoxy ring characteristic bands (between 910 and 750 cm^{-1}) can be observed after reacting with the hydroxyl groups contained in the eutectic mixture (Figure 1d) [48], thus confirming the completion of the intended chemical reaction. Moreover, no significant differences in the FTIR spectra were observed when the EPL-structured NADESs were processed at 120 °C.

TGA also verified the interaction of EPL with NADESs (Figure 2). Thus, the disappearance of the thermal events related to the epoxy rings proved the reaction with the hydroxyl groups contained in the NADESs mixtures, leading to the formation of a new secondary hydroxyl group as a consequence of the opening of the epoxy ring [55,56]. In addition, no significant changes were observed in the degradation curves of lignin-structured NADES matrices synthesised at high temperatures, confirming the completion of the crosslinking reaction at room temperature. The small changes occurring at around 100–150 °C may be due to the volatilisation of water molecules forming the eutectic blend and the dehydration of the newly generated hydroxyl groups due to the opening of the epoxy ring.

The epoxy ring-opening reaction and the subsequent chemical crosslinking between hydroxyl and epoxy groups can also be corroborated by means of ^{13}C- and DOSY-NMR experiments. The ^{13}C-NMR spectra of the resulting structured formulations, Gly-EPL30 and Gly-EPL30 (120 °C), are shown in Figure 3c in comparison with ^{13}C-NMR spectra of CA-Gly and EPL. The opening of the epoxide ring can be verified by means of the chemical shift of C4 in EPL, at 50.9 ppm in the closed epoxy ring, which has been detected at 63.6 ppm when the epoxy ring opens (C4, CH-OH) in both Gly-EPL30 and Gly-EPL30 (120 °C) spectra. The chemical shift at low field was due to the hydroxyl groups generated in C4 by the opening of the epoxy ring. However, the peaks of CA-Gly overlapped with the epoxy peaks and were not detected in the other ^{13}C-NMR spectra. Therefore, phase-edited DOSY spectra were obtained to evaluate the stability of these new compounds, as shown for Gly-EPL30 (120 °C) (Figure 3d). In the case of a mixture of several compounds, different groups of signals should be observed because of their different diffusion properties. However, in this case, only a single cluster of signals was observed, apart from the peak corresponding to DMSO-d6, corroborating the existence of a single compound.

Figure 4 shows the viscous flow curves of lignocellulose-structured NADESs synthesised at room temperature as a function of the HBD component employed. An evaluation of the three NADESs yielded highly structured shear-thinning liquids. As expected, much higher viscosity values than those provided by NADESs (see Table 3) were obtained as a result of the chemical interactions between the epoxy groups of EPL and the hydroxyl groups of the eutectic mixture [9,35]. The power-law model (Equation (1)) was used to describe the shear-thinning characteristics of these formulations (R^2 > 0.990).

$$\eta = k\ \dot{\gamma}^{n-1} \tag{1}$$

Here, k and n are consistency and flow indices, respectively. The values of these fitting parameters are shown in the inset of Figure 4. As expected, a higher consistency index was obtained for the formulation prepared with the CA-Suc sample, which also exhibited a slightly enhanced shear-thinning character (lower n value). To elucidate the effect of NADES viscosity on the viscous flow properties of thickened matrices, the relative viscosity ($\eta_{rel} = \frac{\eta}{\eta_{NADES}}$) is plotted in Figure 4b [57,58]. Similar relative viscosity vs. shear rate plots were obtained when using the three types of eutectic mixtures. The similar values of relative viscosity found at low shear rates indicate that EPL exerts a similar structuration in the three NADESs, and the differences in viscosity are mainly due to the vis-

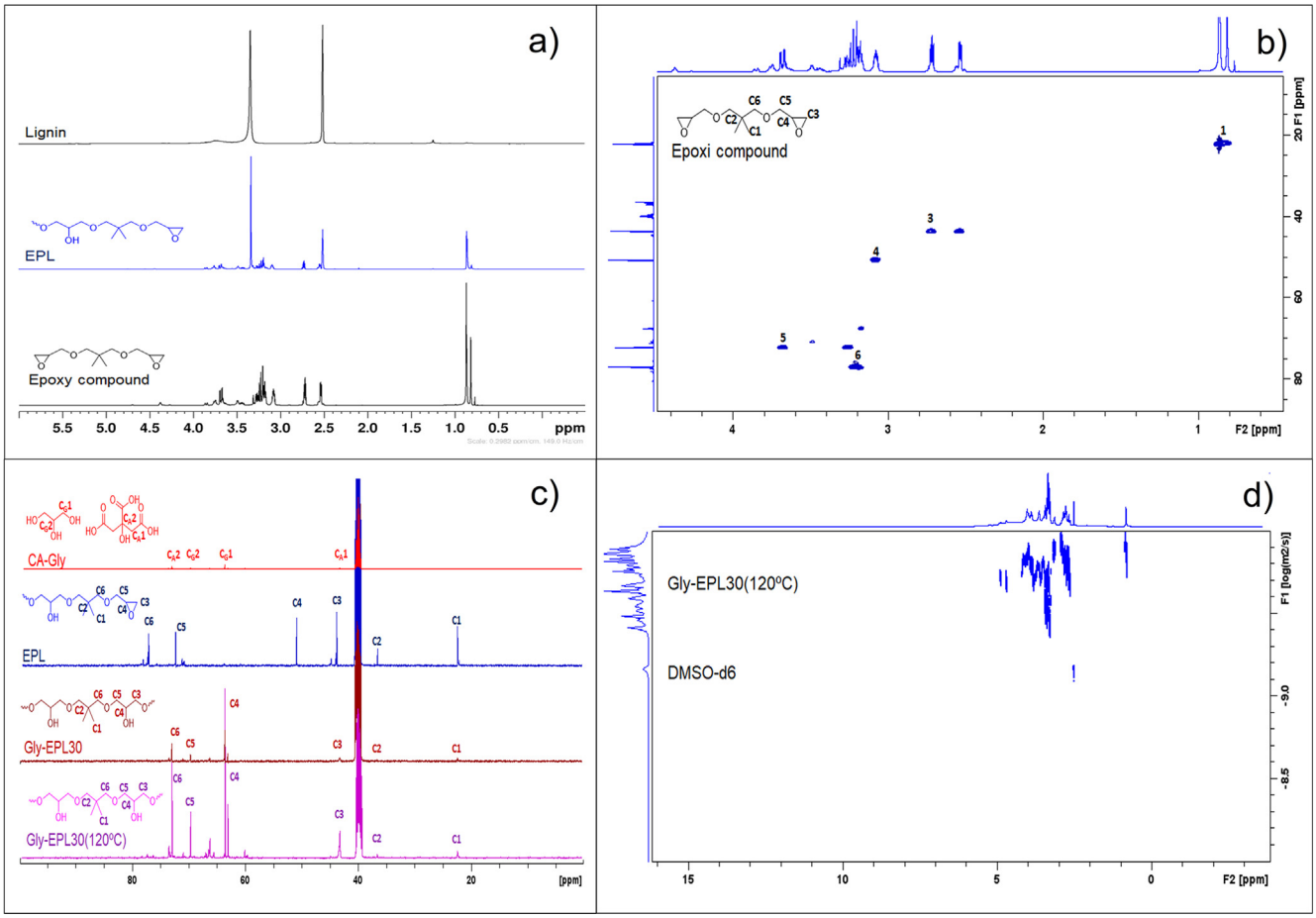


Figure 3. **(a)** ^{1}H-NMR spectra of raw materials; **(b)** representative structure of NPGDGE by HSQC; **(c)**. ^{13}C-NMR spectra of CA-Gly, EPL, Gly-EPL30, and Gly-EPL30 (120 °C); **(d)**. ^{1}H DOSY spectrum of Gly-EPL30 (120 °C). *x*-axis represents the regular ^{1}H chemical shift, and *y*-axis represents the relative diffusion rate.

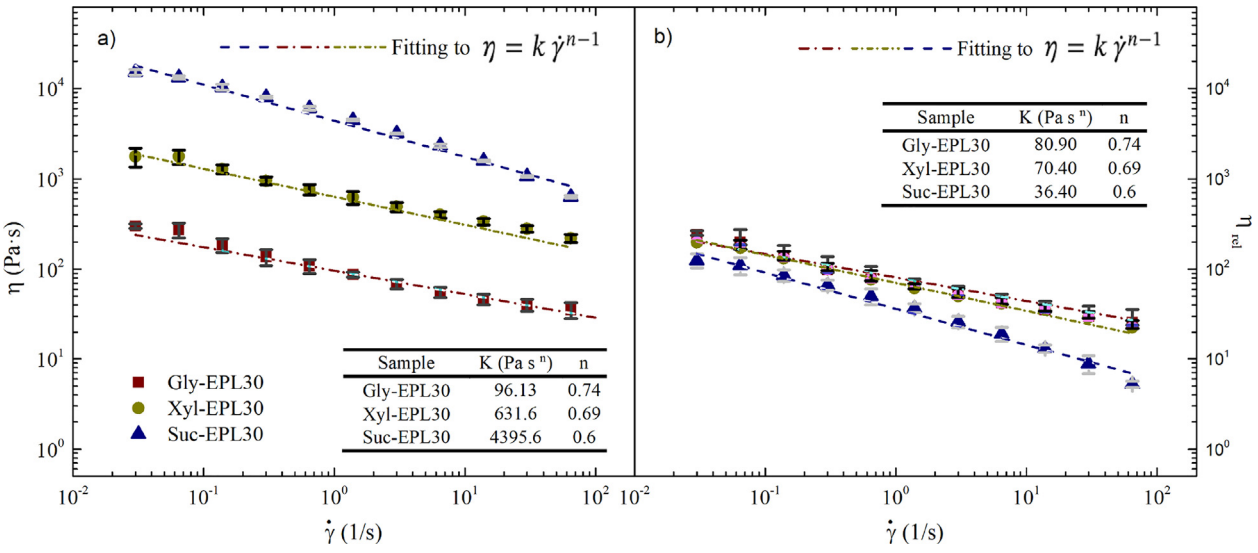


Figure 4. Viscous flow curves of lignin-based thickened formulations. a) apparent viscosity; b) relative viscosity.

cosity of the NADESs. These results are not surprising because, according to Table 2, the molar ratio of hydroxyl groups in all NADESs was always higher than that of the free epoxy groups available for crosslinking in EPL, which contributes to the total consumption of these reactive groups, as supported by the TGA, FTIR, and NMR results. However, as mentioned above, a more pronounced shear rate influence for the more structured formulation based on CA-Suc is apparent in Figure 4b. Therefore, the viscosity of eutectic mixtures appears to be crucial for achieving the desired rheological behaviour in these lignin-structured matrices.

The lignin-enriched residue-structured formulations prepared with different NADESs were also evaluated from a viscoelastic perspective. Figure 5 shows the evolution of the SAOS functions with frequency in the linear viscoelastic regime for the samples containing 30 wt.% EPL. Different viscoelastic responses were obtained depending on the type of eutectic mixture used to formulate thickened matrices. The values of both the storage (G′) and loss (G″) moduli increased with the number of hydroxyl groups in the HBD compounds, as previously discussed for viscous flow curves. For each formulation, both viscoelastic moduli presented similar values and frequency dependence characteristics of soft gels, which resembled either a viscoelastic response close to a critical gel [59] or a glass transition from a crosslinked network [60]. For example, formulations containing glycerol and xylitol as HBD compounds in eutectic mixtures showed higher G′ values than G″ values at low frequencies, which tended to achieve a plateau region. However, a crossover between the SAOS functions was identified at intermediate frequencies. On the contrary, despite the high values of both moduli, the G″ values are always slightly higher than the G′ values in the entire experimental frequency range for the formulation prepared with the CA-Suc sample, which is the typical viscoelastic response for materials achieving a glass transition. This is supported by a recent report, which indicates that gels with even larger amounts of solvent can still exhibit glass transition behaviour [61]. Moreover, different rheological properties from purely viscous to strong network gels have been identified in nanocrystalline cellulose colloidal suspensions, where the viscous and viscoelastic responses and the glass transition mainly depend on attractive interactions [62].

As mentioned earlier, water has been proven to have an important effect on the viscosity of eutectic mixtures. To evaluate the role of water in the viscoelastic properties of lignin-structured NADES matrices, CA-Gly based formulations were prepared at 120 °C. It is inferred from the comparison of the mechanical spectra in Figures 5 and 6 for the lignin-structured CA-Gly eutectic mixture, at 30 wt.% EPL concentration, that a more extensively crosslinked gel network was obtained when removing the water from the eutectic mixture. The influence of EPL concentration was also analysed by modifying the EPL percentage from 5 to 30 wt.% (Figure 6). In general, when the EPL concentration was reduced to below 20 wt.%, a predominant viscous response was obtained, resulting in higher values of G″ in the whole frequency range. However, a transition from a viscous liquid to a strong gel was clearly apparent when the concentration was increased from 20 wt.% to 30 wt.%.

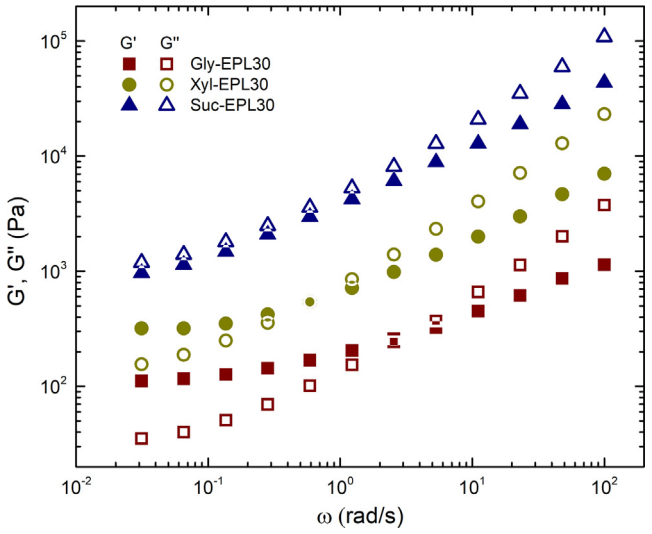


Figure 5. Frequency dependence of the storage, G′, and loss, G″, moduli for thickened formulations based on epoxidized lignocellulose fraction and NADESs.

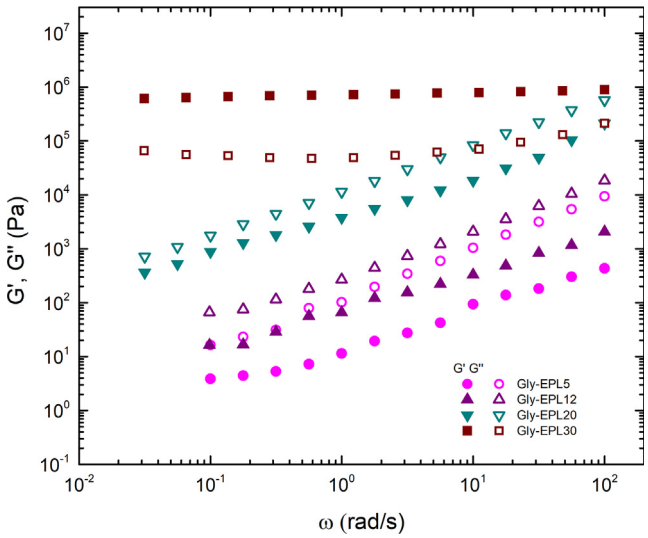


Figure 6. SAOS functions evolution for CA-Gly based thickening formulations synthetized at 120 °C as a function of the lignin concentration (G′, filled symbols; G″, empty symbols).

4. Conclusions

A lignin-enriched lignocellulosic fraction from bioethanol production of sugarcane bagasse was epoxidised and successfully applied as a thickener of different natural deep eutectic solvents (NADESs) as a result of chemical crosslinking. The resulting thickened green formulations covered a wide range of rheological responses, from liquid- to gel-like systems, with applications in different industrial sectors.

Homogeneous and stable NADESs were successfully synthesised to explore the influence of the hydrogen bond donor (HBD) used during the synthesis process as well as the amount of water comprising the mixture on the rheological properties of both the NADESs and the resulting structured systems after reaction with the epoxidised lignin-enriched fraction.

Thus, important differences in viscosity were obtained when modifying the HBD compound used to prepare NADESs samples, which was conditioned by the formed supramolecular structure. Thus, the more hydroxyl groups that are available to interact with the carboxylic groups of citric acid (CA-Suc sample), the more hydrogen bonds are formed, leading to an increase in viscosity. In addition, the removal of free water from NADESs resulted in a remarkable increase in viscosity, which was dramatic in the CA-Suc sample, for which a solid mixture was observed.

However, the chemical interaction between the epoxidised lignin-enriched fraction and these eutectic mixtures gave rise to homogeneous and physically stable structured formulations. Highly structured shear-thinning liquids with much higher viscosity values than those provided by NADESs were obtained in all cases, exhibiting a higher consistency index and more marked shear-thinning character in the formulation prepared with the CA-Suc sample. Measurements of the relative viscosity conclude that EPL exerts a very similar structuring role in the three different NADESs, with the differences in viscosity mainly due to the supramolecular properties of NADESs. Viscoelastic functions increased with the number of hydroxyl groups in the HBD compound, conforming to the NADESs mixture. Finally, a predominant

viscous response was obtained when the EPL concentration was reduced to < 20 wt.%, yielding a change from liquid-like to gel-like systems when increasing EPL concentration from 20 to 30 wt.%.

CRediT authorship contribution statement

E. Cortés-Triviño: Investigation, Methodology, Data curation, Validation, Formal analysis, Writing – original draft, Writing – review & editing. **J. Cubero-Cardoso:** Investigation, Formal analysis, Validation. **A. Tenorio-Alfonso:** Investigation, Formal analysis, Validation. **M.A. Fernández-Recamales:** Investigation, Validation. **C. Valencia:** Investigation, Supervision, Funding acquisition, Writing – review & editing. **J. Urbano:** Investigation, Conceptualization, Supervision, Writing – original draft, Writing – review & editing, Project administration, Funding acquisition. **J.M. Franco:** Conceptualization, Methodology, Investigation, Formal analysis, Writing – original draft, Writing – review & editing, Supervision, Project administration, Funding acquisition.

Declaration of Competing Interest

The authors declare that they have no known competing financial interests or personal relationships that could have appeared to influence the work reported in this paper.

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