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Production and characterization of a novel lignin-based biopolymer from *Ulex europaeus*

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Abstract

Invasive plant species are a global environmental threat since they affect native species and may modify ecosystems, which negatively impact human health and world economics. The aim of this study was to synthesize and characterize a new lignin-based biopolymer from gorse (*Ulex europaeus*), a globally widespread invasive plant. The lignin extraction was carried out through acid-base and solvent-based methodologies to compare the reaction yield. Subsequent polymerization of the extracted lignin was performed by glycine condensation in a 70% 1,4-dioxane solution with H_2O_2 and $CaCl_2$ as catalysts. The extraction and polymerization products were characterized by Fourier-transform infrared spectroscopy. Thermal and stability properties of the new biopolymer were determined by thermogravimetric analysis,

differential scanning calorimetry, and analysis of biodegradation rate. The alkaline extraction process of lignin resulted in higher yield than the one by organic solvent. In comparison to the extracted lignin, the novel biopolymer showed differently absorption bands that are characteristic of tensions and flexions of alkenes, amine, and amide groups. Additionally, thermal properties revealed peaks corresponding to decomposition and dehydration reactions, endothermic processes and a melting point of 258.71°C. Total biodegradation was reached after ten hours. A new polymeric, possibly cross-linked, thermally stable material with a potentially high degree of crystallinity was synthesized from a renewable raw material, which might contribute to the gorse management according to the concept of novel ecosystem, besides the reduction in contamination by other polymeric materials.

Keywords

Invasive species; gorse; polymers; Fourier transform infrared spectroscopy; organic chemistry

Introduction

One of the main causes of current biodiversity loss is the presence of invasive species that can compete with, prey on, and displace native species, as well as cause significant alterations to natural ecosystems [1]. Currently, the *Ulex europaeus*, also known as gorse, is one of the world's most damaging invasive species, listed in the red list of the Global Invasive Species Database of the International Union for Conservation of Nature (UICN) [2]. *Ulex europaeus* is found practically all over the world and in all types of soil, due to its easy adaptation to changes in the environment, rapid growth, high reproductive output, propagule persistence, and low vulnerability to pests [3]. In

Colombia, the Biological Resources Research Institute "Alexander Von Humboldt" has declared the *Ulex europaeus* as one of the invasive species with the greatest impact in the country [4], due to the negative effect that has been reported on the composition and structure of the vegetation, highlighting the invasion in the Andean region in the departments of Antioquia and Cundinamarca (e.g., in Bogotá it is found in ten of the fourteen wetlands declared by the district and in different parts of the city such as the eastern hills and rural areas) [5].

Actions for the eradication of this shrub are based mainly on burning, revegetation with native species and manual and/or mechanical techniques with subsequent control of sprouts and seed banks [6]; however, the different processes that have been employed have not been effective due to the competitive characteristics of the plant and the impact generated on the ecosystems. In fact, the mechanical removal or destruction of *Ulex europaeus* can induce chronic soil erosion, compaction, and structural decline, which decreases prospects for sustainable land rehabilitation [3]. Thus, a large part of the research seeks to control this invasive plant, having found important results controlling it in the seedling phase through the formation of canopies of fast growing native species or with artificial shade [7,8]. Other research on the eradication of *Ulex europaeus* focuses on strategies of ecological restoration with Pinus plantations (e.g., *Lupinus bogotensis*, *Pinus patula*, *Pinus radiata*), facilitating land clearings or taking advantage of clearings formed by the fall of trees [3,9-11]. Although the solution to this problem seems easy at first sight, many environmental and social constraints must be overcome in order to restore the natural dynamics. For example, in Bogotá, it has been indicated that recovering the forest that once existed in the lowlands of the Sumapaz Páramo (considered the largest páramo ecosystem in the world) is an arduous task, given that at present there are minimal remnants of that forest that are not progressing because of the invasion of *Ulex europaeus* and because the land is poor in its essential

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compounds [12]. Other botanical studies in mountain ecosystems have revealed a great influence of this invasive species on birds of the natural environment due to the great amount of thorns that cover the gorse [13]. In addition, the double edged effects of climate change may be linked to scenario and species specific interactions, which suggest that research in this regard should be specific for both aspects [14]. Additionally, models have been developed to assess the potential for invasion in regions such as South Africa, which has established a protocol for future modelling exercises to assess the invasion potential of other emerging invaders [15]. For example, using logistic regression for modelling the increase, decrease and permanence of *Ulex europaeus* invasion, it has been found a strong relationship between changes in land cover and the invasion process, especially connected with forest plantations of exotic species [16]. Thus, proper management for this invasive species must take into account the spatial dynamics of the landscape within the invaded area in order to address containment, control or mitigation of the invasion.

Complementary, as a control strategy, *Ulex europaeus* has been extensively studied both chemically and biologically. Phytochemical studies have shown the presence of secondary metabolites such as quinolizidine alkaloids, amino acids, glycosides, flavonoids, carotenes, hexacosanol and phytosterols in the plant stem [17]. In this sense, the physicochemical characterization and extraction of essential oils from Colombian *Ulex Europeans* has shown that it represents a very good raw material for several industrial processes due to their lignocellulosic composition (e.g., carbon fibers from lignin, cellulose whiskers, bioethanol from cellulose, and hemicellulose can be obtained), and it appears to be a suitable source for activated carbon obtention [18]. Therefore, as a natural source of raw materials, the *Ulex Europeans* might be used in processes that allow its eradication and in turn be useful to society. For instance, Núñez-Moreno et al. [19] reported in a recent study that gorse can possibly become

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an energetic crop guided towards the generation of both domestic and even industrial heat, which would not only contain and avoid the random spread of *Ulex Europeans* but also create an opportunity to turn an environmental problematic into a 100% eco-friendly energy source. Moreover, some efforts have been made to produce polymeric materials from the biomass of this invasive plant and the current literature only have feasibility or theoretical studies in this regard [20,21]. In particular, the elaboration of new materials, mainly polymers, is a field that is highly active nowadays due to the need to appease the environmental impacts generated by human activities. Lignin, as a main component of the plants, has been studied in different industrial processes with or without structural modifications to obtain new materials [22]. Given the lignin is distributed in the stem of all the plants and, therefore, it can be extracted from any of these; several extraction methodologies have been documented, although extractions based on aqueous solutions and organic solvents stand out, due to their easiness and use of common reagents [23]. Based on our literature review no study has focused on the production of lignin-based polymers from *Ulex europaeus,* which is of great interest due to the need to develop methodologies that allow the synthesis of biodegradable and/or recyclable materials that take advantage of its large accumulation in the environment. Therefore, the aim of this study was to synthesize and characterize a new lignin-based biopolymer from gorse (*Ulex europaeus*). We believe that the use of organic matter from this globally widespread invasive plant has great potential to create renewable new materials that can be biodegradable or recyclable.

Results

Lignin extraction

Table 1 shows some relevant data obtained in the extraction of lignin by alkaline and organic solvent treatment. Lignin extracted by alkali treatment was darker brown than that extracted by organic solvent treatment; in addition, the first had more penetrating odor and smaller particle size.

Table 1: Lignin extraction methodologies and yield.

Extraction Method	Stem (g)	Theoretical Yield [a] (g)	Actual yield (g)	Percentage yield (%)
Alkaline	10.0	2.25	1.575	70
Solvent-based	10.0	2.25	1.120	50

[a] Calculated according to the approximate theoretical percentage of lignin in the plant stem

In the spectra shown in Figure 1 is observed: a band at 3400 cm^{-1} corresponding to –OH group stretching; at 2900 cm^{-1} are evident the C-H stretching bands; at 2400 cm^{-1} the characteristic vibrations of the aromatic ring; between 2000 and 1750 cm^{-1} the aromatic combination bands; the peak at 1700 cm^{-1} can be due to the stretching vibration band of C=O; at 1450 cm^{-1} the CH_2-C=O the stretching band; at 1300 cm^{-1} the C–O the stretching band; between 1100 and 1150 cm^{-1} the bands for C-O stretch; and between 600 and 650 cm^{-1} the bands corresponding to the aromatic substitutions pattern.
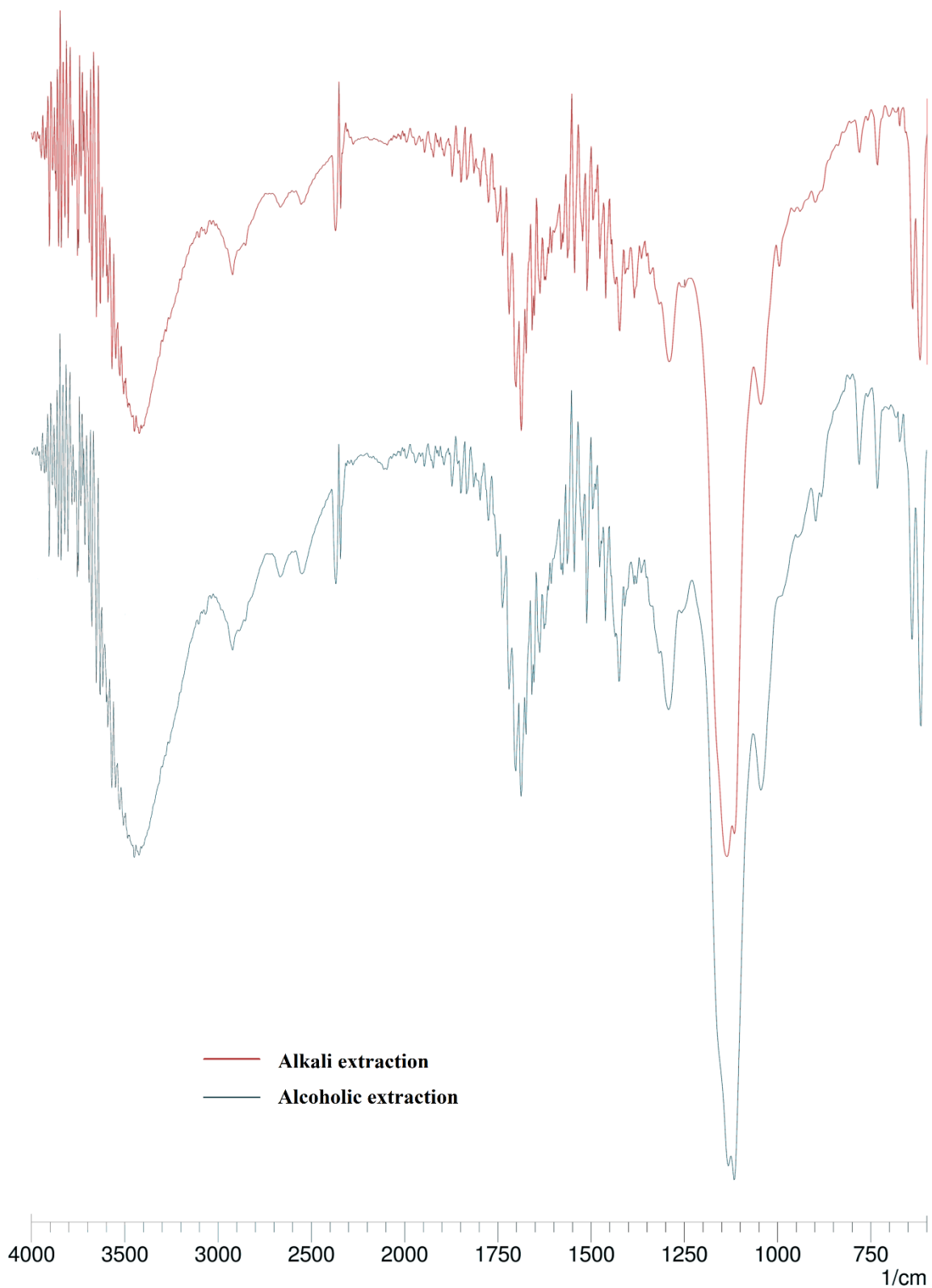
Figure 1: FT-IR spectra of lignin extractions in the wavenumber zone of 4000 - 600 cm^{-1}. FT-IR spectra of the lignin extract by alkaline treatment (red) and by organic solvent treatment (blue).

Polymerization and characterization

Table 2 shows the ratio of reagent quantities of the two solutions prepared for lignin and glycine polymerization and the amount of co-polymer obtained.

Table 2: Relevant data on lignin and glycine polymerization.

Solution	Reactants	Amount	Solvent	Product
1	Lignin*	0.5 g	20 ml of 70% Dioxane	1.2 g
	H_2O_2	5 ml		
	$CaCl_2$	0.2 g		
2	Glycine	1.5 g	30 ml of 70% Dioxane	

a Lignin extracted by alkaline treatment

When the solutions came into contact with each other, a light-yellow highly viscous mixture was formed, later a white precipitate was produced. When all the solvent evaporated, light yellow crystals were obtained, which were washed with distilled water until they became white. Figure 2 shows the IR spectrum of the obtained co-polymer.
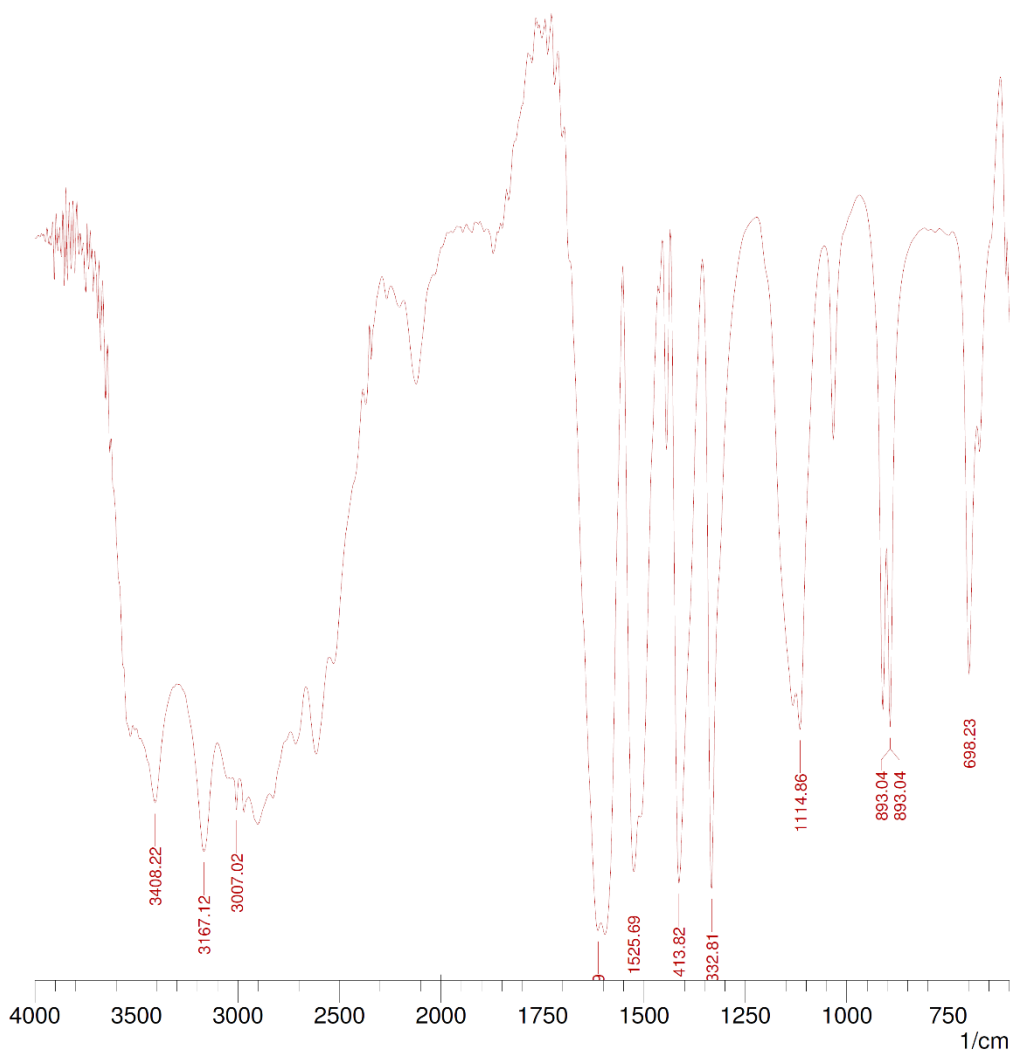
Figure 2: FT-IR spectra of obtained co-polymer in the wavenumber zone of 4000-600 cm^{-1}.

Table 3 shows the correspondence of bands in the IR spectrum of the synthesized co-polymer, where it is possible to distinguish the formation of new functional groups such as the amide group (the C–O the stretching band at 1614.42 cm^{-1}). At high wavenumbers we found the overlapping of a great amount of bands, because in that zone (>3000 cm^{-1}) the stretching bands of alcohol, amide and amine groups are presented. Around 2900 cm^{-1} the bands corresponding to methylene, ether and alkene groups are evident, which can be confirmed at lower wavenumbers. Also, it is straightforward to identify the existence of combination bands of the benzene group between 2000 and 1600 cm^{-1}. At low wavenumbers (<1650 cm^{-1}) the carbonyl group

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(C=O) of amides and other confirmation bands of amines, ethers, alcohols, aromatics and alkenes are observed. Finally, it is possible that the band located at 1612.49 cm^{-1} corresponds to imide groups (C=N stretch) formed by the reaction between ketones or aldehydes with primary amines. Similarly, due to the large number of functional groups of the obtained co-polymer, it can be found a high degree of overlap between bands, in which some of the aromatics, alkenes and amines stand out.

Table 3: Correspondence of bands of the copolymer IR spectrum.

Wavenumber (cm^{-1})	Correspondence
3529.73	O-H stretch for alcohols
3408.22	N-H stretch for amides
3026.31	=CH$_2$ asymmetrical stretch for alkenes
3007.02	=CH$_2$ symmetrical stretch for alkenes
2827.64	–OCH$_3$ stretch for ethers
2000 – 1660	Combination bands of benzene
1870.95	Out-of-plane =CH$_2$ vibrations for alkenes
1614.42	C=O stretch for amides
1612.49	C=N stretch for imines
1525.69	N-H bend for amides
1444.68	CH$_2$-C=C stretch for alkenes
1413.82	O-H bend for alcohols
1332.81	C-N stretch for amines
1116.78	C-O stretch for ethers
1114.86	C-O stretch for alcohols
1033.84	=C-O-C stretch for ethers
910.40	In-plane =CH$_2$ bend for alkenes

893.04	Out-of-plane =CH$_2$ stretch for alkenes
698.23	Out-of-plane N-H bend for amines
673.16	Out-of-plane Ar-H bend for benzene derivates

Figure 3 shows the co-polymer TGA thermogram, highlighting a loss of mass from approximately 205°C. The same figure shows the thermograph of the DSC with an endothermic peak around 258.71 °C.
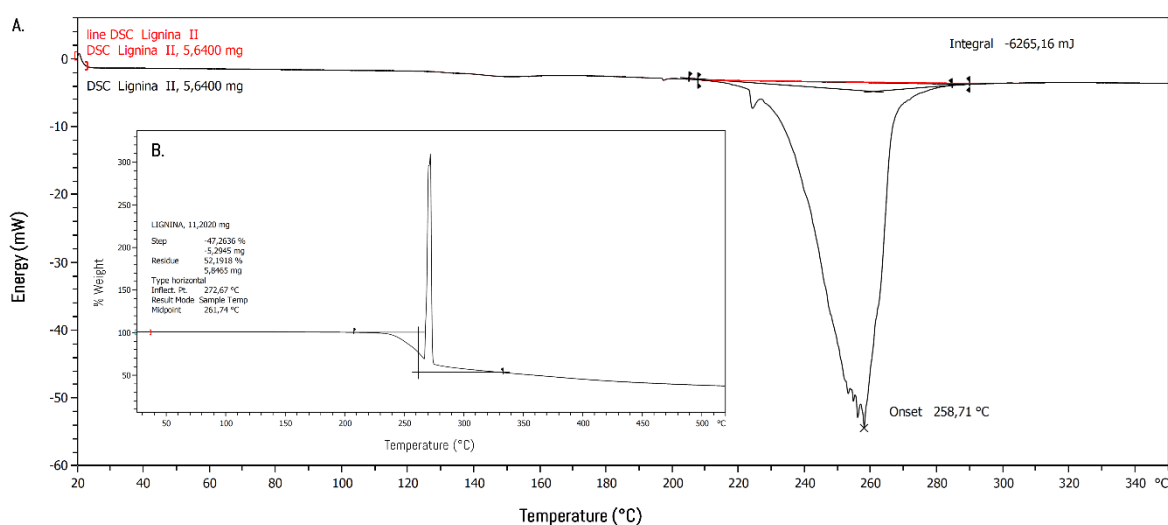

Figure 3: TGA/DSC thermogram of the obtained lignin-based co-polymer. The figure shows the DSC (A) and TGA spectrum (B) of the synthetized co-polymer.

Our biodegradability study showed a total "degradation" of the new co-polymer in 10 hours (Figure 4).
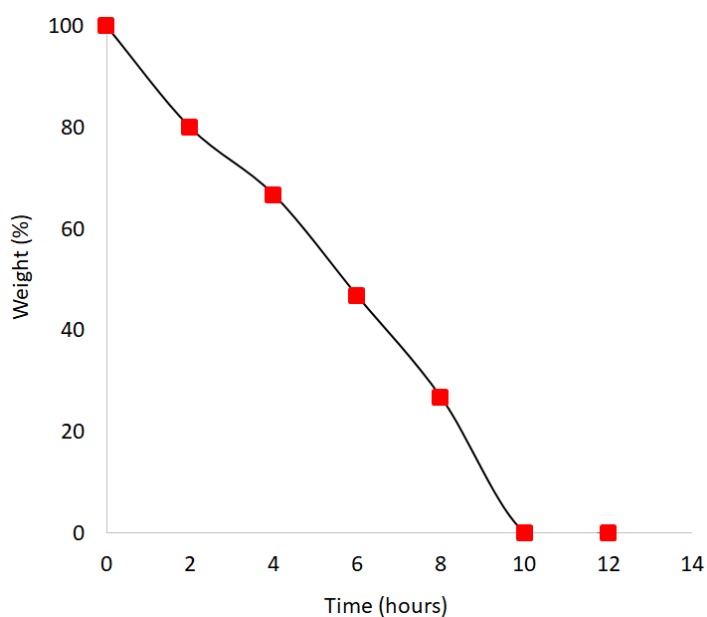
Figure 4: Biodegradation of the co-polymer in the soil of the eastern hills in Bogotá, Colombia. Percentage of mass as a function of time in hours.
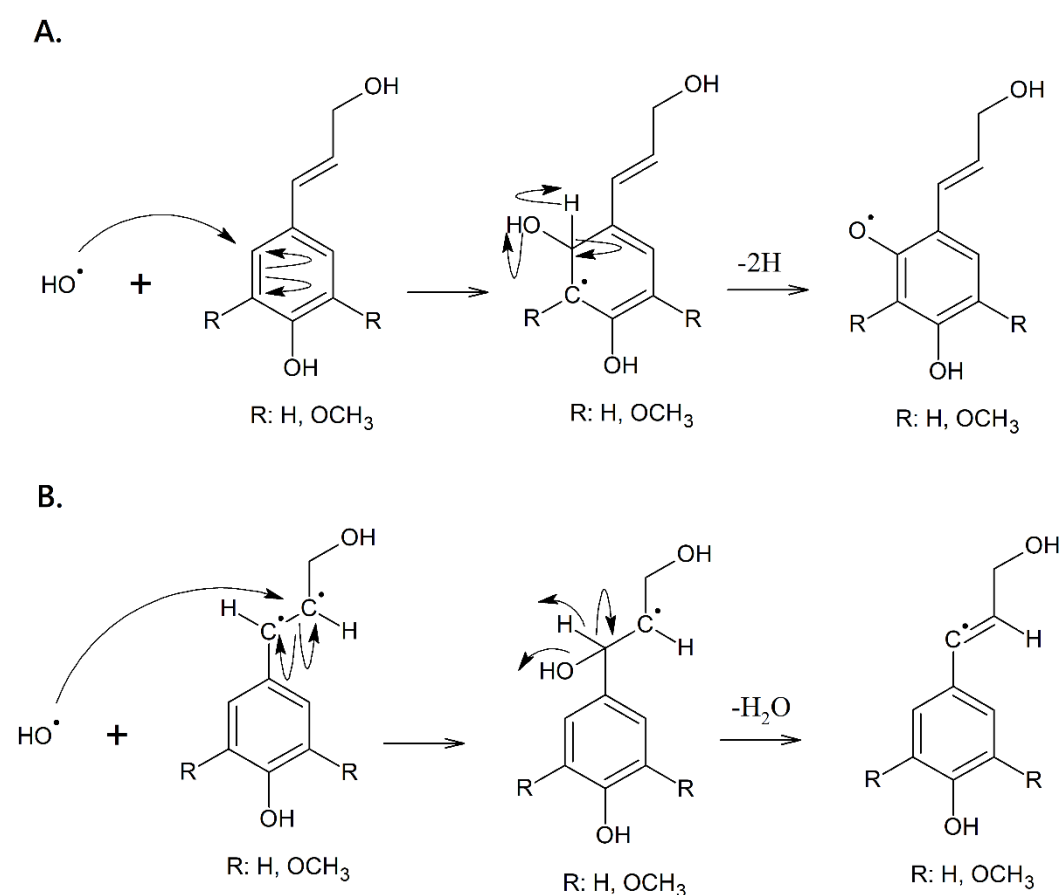
Discussion

Invasive plant species are a global environmental threat since they affect native species and may modify ecosystems, which negatively impact human health and world economics. This study aimed to synthesize and characterize a novel lignin-based biopolymer using *Ulex europaeus* as a raw material. We performed the lignin extraction based on alkali and organic solvent treatment. Considering wood consists mainly of lignin, cellulose and hemicellulose, for the extraction of lignin it is necessary to ensure the complete separation of the other substances present. Lignin has a chemical structure with many polar groups such as hydroxyl (aromatic and aliphatic), methoxyl, carbonyl and alkene, so its separation is based on its solubility. At alkaline pH lignin is easily solubilized; however, at very acidic pH (close to 2) it precipitates completely; for this reason, the second rationale for the extraction is based on its insoluble property at low pH. Given that NaOH is a strong base that releases hydroxyl groups into the

medium and, therefore, increases the pH (while ethanol act as a weak base), the higher yield after alkali treatment than using the organic solvent (15.75% vs. 11.20% of extraction yield) might be explained by the different chemical properties of the substances. As it can be noticed in Figure 1, the spectra of the extracted lignin by both methods were very similar and, actually, they highly matched with previous characterization of several types of lignin using FT-IR [24,25]. Based on this, it is possible to ensure that the dominant functional groups in our extracted lignin correspond to the aromatic, aliphatic, hydroxyl, carbonyl and ether, which are common within the phenylpropanoid compounds that characterize this organic polymer [26].

Regarding the polymerization reactions, it has been reported the use of free radicals and radiation as initiators of lignin-based polymerizations [27-31]. In fact, common methodologies include the production of lignin co-polymers and acrylic compounds, which use aqueous solution of 70% dioxane as solvent and peroxides as catalyzers. These two are part of the polycondensation reaction to obtain polyamides and polyesters, functional groups formed during the co-polymer synthesis in this study, which have also been described in other investigations using this solution polymerization method [22,32,33]. In fact, in 2001, researchers at Universidad Distrital Francisco José de Caldas synthesized biodegradable polymers from a mixture of amylose (extracted from corn starch) and polyvinyl alcohol, using the solution method and alkaline treatment [34]; nonetheless, there are other examples of solution polymerizations to obtain this type of polymers using solvents such as dimethyl sulfoxide and initiators like triethylamine [35]. As we demonstrated in this study, the solution polymerization method might be a practical and relatively easy way to produce lignin-based polymers from *Ulex europaeus*, but considering other available options that have been studied [22,32-36] further research is needed to explore/compare results between methods.
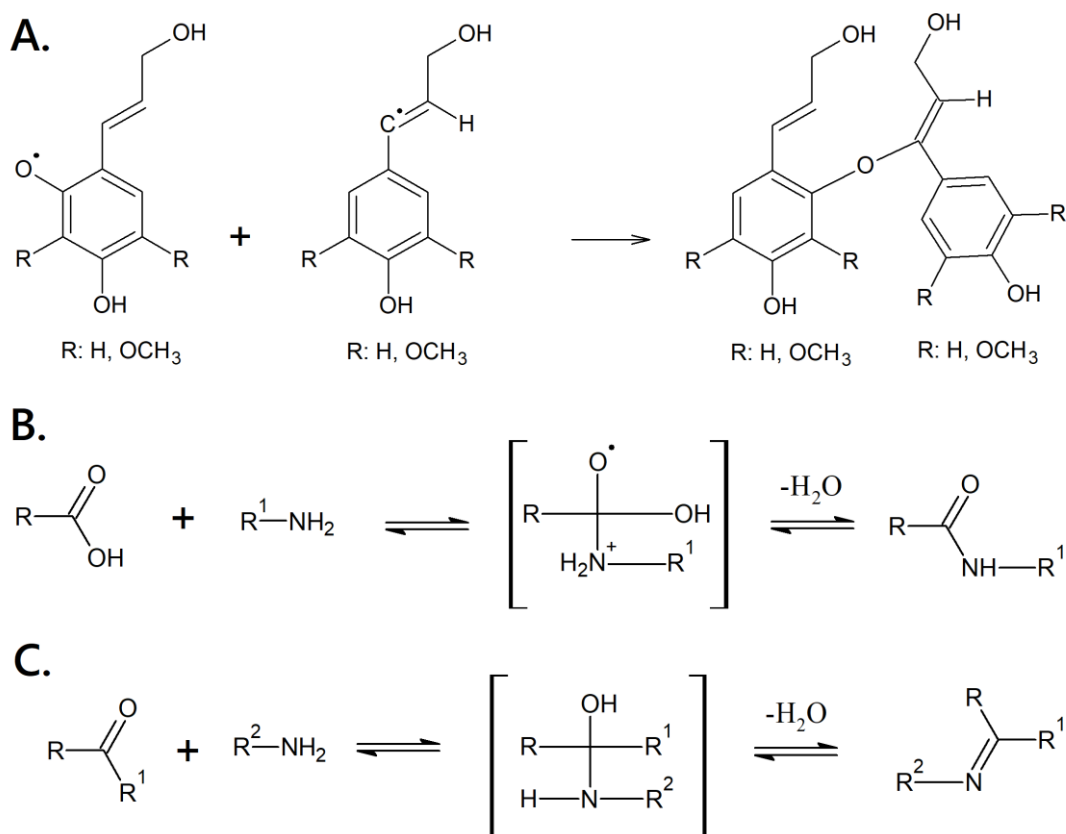
Our lignin and glycine polymerization reaction is mainly based on additions resulting from nucleophilic, electrophilic and free radical interactions. The first step of the reaction consists of the formation of radicals ·OH that later produce highly reactive lignin radicals. The radicals ·OH are obtained from the homolytic breakdown of H_2O_2, which generates highly unstable and therefore reactive species that attack the electronic cloud of the aromatic rings and alkene groups of the phenylpropanoids (Scheme 1).

A.

B.

Scheme 1: Formation of lignin radicals. Lignin radicals formed by attacking the aromatic ring (A) and by attacking the alkene group (B) have the capacity to create intramolecular interactions with other lignin radicals or intermolecular interactions with glycine.

The lignin radicals can stabilize with each other forming alkenyl aryl ethers, establishing the interactions in an intermolecular fashion (Scheme 2A). Additionally,

condensation reactions between lignin and glycine can occur, where reactive amino acid groups (carboxylic acid and amine) react with polar lignin groups (aldehydes, carboxylic acids, ketones, alcohols, etc.) and produce amides and imines through nucleophilic addition mechanisms (Scheme 2B-C). The reaction that leads to polymerization through the formation of amide groups follows a mechanism of addition followed by elimination, which is characteristic of the carbonyl group. In this case, the carbon with a high density of positive charge of the carboxyl group of the lignin is attacked by the nitrogen atom present in the amine group of the glycine, that has a high density of negative charge due to its free electronic pair, which gives rise to an intermediate of very low stability. In addition, as a weak Lewis base, the hydroxyl group fixes protons to generate oxonium ions through an acid-base balance. These oxonium ions are a good salient group (better than the hydroxyl group) and therefore are eliminated in the form of water to finally produce the amide (Scheme 2B). Another of the possible reactions that occur during polymerization consists of the formation of imines from the reaction between an aldehyde or ketone groups of the lignin with the amine group of the glycine, in which the mechanism is based on an addition to carbonyl group followed by elimination. But in this case, the carbon with positive charge density of the carbonyl group is attacked by the nitrogen atom of the amine, thus producing a carboxylamine as an intermediate, which by an acid-base balance generates oxonium ions which are subsequently eliminated in the form of water and produce the imine (Scheme 2C).

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Scheme 2: Lignin interactions and reactions between lignin and glycine. Intermolecular interactions between lignin radicals (A). Reaction mechanism in the formation of amide (B) and imine (C) groups after the reactions between lignin and glycine.

The loss of mass of the polymer from approximately 205°C is possibly due to solvent desorption or pyrolytic breaks due to polymer heating, mainly in the lignin regions. The ruptures mentioned above may correspond to the formation of small monomers of the phenylpropanoids that make up the lignin and its derivatives [37]. The decomposition of the derivatives through endothermic processes could explain the subsequent decrease in mass percentage, which involves an energy absorption that can be observed in the DSC spectrum (Figure 3A); however, it is possible that this loss of mass corresponds to processes of depolymerization of glycine units. The temperature values corresponding to the processes mentioned above are a little lower than those

reported by Caballero (1995), which may be due to the lignin-glycine interactions that decrease the inter and intramolecular forces due to the steric hindrance generated after the polymerization reaction [38]. At 200°C the thermal degradation in lignin and its derivatives are mainly due to the dehydration reactions; between 150°C and 300°C occurs the cleavage of alkyl-aryl-ether bonds; around 300°C the aliphatic side chains start splitting off from the aromatic ring [39]; and, finally, the carbon-carbon bond between the phenylpropanoid units break between 370°C and 400°C [40]. Our analysis showed that at approximately 275°C there was a peak indicating a mass gain, which was interpreted as an interference during the analysis because the procedure was done in an inert atmosphere and there was no way for the polymer to increase its mass. After the DSC analysis, an endothermic peak around 258.71°C was observed. This may correspond to several melting points of similar segments, highlighting that the monomer with the highest melting point is glycine, so this grouping of endothermic peaks may respond to melting processes of polymer segments composed by glycine chains, which would indicate that these structures have higher intermolecular forces compared to the monomer from which they are derived. This information is important to identify the new biopolymer because when comparing the theoretical melting points of lignin (158-185°C) and glycine (233°C) it is possible to affirm that the product obtained corresponds to a substance different from the reagents used.

Taking into account the aforementioned, it is very possible that the new biopolymer contains a lignin nucleus with dendrites (ramifications) product of the reaction with glycine, thus being a cross-linked polymer (in network), thermally stable and with zones susceptible to crystallization. This can be inferred considering the degree of molecular organization that has been described in other lignin-based polymers [41]; however, further studies are required to have the molecular characterization of the new product and its derivatives. Furthermore, the produced co-polymer had high solubility in water,

perhaps because of the large number of hydrophilic groups along the chains (mainly amines, amides and carboxyl groups), suggesting a potentially biodegradable material. In fact, during our biodegradability study, it was very likely that a solubilization process of the material took place; therefore, it is recommended to perform studies based on the releasing of carbon dioxide in order to evaluate the degradation by microorganisms through the process of bio-deterioration, bio-fragmentation, and assimilation [42]. Besides the environmental context, this type of material may be in interesting demand due to its potential commercial use, given its properties as a cross-linked, thermosetting and biodegradable material under controlled conditions. The present work contributes to two problems that affect the local, national and global population, that is the invasion of *Ulex europaeus* and the synthesis of biodegradable polymers, although external validation of the method is necessary.

Conclusions

The lignin extraction process by alkaline treatment was more effective than the organic solvent treatment, which increased the overall percentage yield. We were able to obtain a new polymeric network material, thermally stable, crystalline, with a melting point at 258.71°C and biodegradable. The properties of the new biopolymer make it a potential raw material for industry; however, more research is required considering that it would be possible to use another catalyst in the process to improve kinetics and have better yields. This research has a significant contribution to the development of polymeric materials through economic and reproducible methodologies that use renewable raw materials, easily affordable and that contribute to reduce the deterioration of ecosystems by the presence of invasive plants such as *Ulex europaeus*.

Experimental

Sample Preparation

A random sampling was performed from different parts of the shrub stem of *Ulex europaeus* in an area located in "*La Macarena*" neighborhood near the Faculty of Science and Education of the Universidad Distrital Francisco José de Caldas - Sede A in Bogotá D.C., Colombia (4º36'49.26'' N - 74º3'49.59'' W). Subsequently, the samples were combined to take a fraction of ¼ from the final mixture of approximately 100 g. This sample was left to dry at room temperature, cleaned (free of dust, stones and soil), ground and sieved to obtain dust particles.

Lignin extraction

The lignin extraction was carried out through acid-base and solvent-based methodologies: i) *Alkali treatment:* The sample was mixed with 7.5% w/w NaOH solution in a 1:0.6 ratio, refluxed for 90 minutes and then filtered. To the resulting supernatant, a 2M H_2SO_4 solution was added until a pH equal to 2 was obtained, then it was stirred and centrifuged at 4000 rpm for 20 minutes. Finally, the resulting solid was dried in an oven at 50 °C; ii) *Organic solvent treatment:* The sample was mixed with 60% w/w ethanol in a 1:0.6 ratio, refluxed for 90 minutes with magnetic stirring and then filtered. Two volumes of acidified H_2O at pH 2 were added to the resulting supernatant, stirred and centrifuged at 4000 rpm for 20 minutes. Finally, the resulting solid was dried in an oven at 50 °C.

Synthesis of the biopolymer

Subsequent polymerization of the extracted lignin was performed by glycine condensation in a 70% 1,4-dioxane solution with H_2O_2 and $CaCl_2$ as catalysts. 0.5 g of extracted lignin were dissolved in 20 ml of 70% dioxane in a glass reaction flask. In

parallel, 1.5 g of glycine, 5 ml of hydrogen peroxide and 0.2g of $CaCl_2$ were mixed in 20 ml of 70% dioxane. Both mixtures were added in a beaker, stirred vigorously and left to stand until the complete volatilization of the solvent.

Spectroscopic characterization

Fourier-transform infrared (FT-IR) spectroscopy was used to characterize the lignin extracts and the obtained co-polymer. The analysis was performed within a FT-IR spectrophotometer (Shimadzu IR Affinity) by the potassium bromide pellet method, which consisted of 100 mg KBr and 0.1 mg of fine powder of the sample. Scans were recorded from 600 to 4000 cm^{-1} at a resolution of 16 cm^{-1}. The procedures took place in the facilities of the Instrumental Analytical Chemistry Laboratory at the Universidad Distrital Francisco José de Caldas - La Macarena (Bogotá, Colombia).

Thermal properties and biodegradation

The thermal stability of the co-polymer was determined by Thermogravimetric Analysis (TGA) and the melting temperature was measured by Differential Scanning Calorimetry (DSC). A second-generation simultaneous TGA/DSC Q600 SDT thermal analyzer (TA Instruments, Delaware, USA) was used to obtain the TGA signal (which measures the dehydration and the onset of a higher temperature decomposition) and the DSC signal (which reveals transitions associated with the dehydration, a polymorphic phase transition and the high temperature melt). DSC heat flow data was dynamically normalized using the instantaneous sample mass at the start of each transition. The obtained data were processed within the open-software Universal Analysis® developed by the TA Instruments (Delaware, USA). The thermal analysis was performed under nitrogen inert atmosphere at the facilities of the Organic Chemistry Laboratory at Universidad Nacional de Colombia (Bogotá, Colombia). To examine for possible biodegradation, samples of the produced biopolymer were dried,

massed accurately and, buried into the soil of the Eastern Hills (*Cerros Orientales*) in Bogotá, Colombia. The samples were massed every two hours in order to determine the percentage of mass loss.

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