ISOLATION AND CHARACTERISATION OF LIGNINS FROM DIFFERENT BLACK LIQUORS

J. Labidi [1,*], A. Tejado [1], C. Peña [1], V. Angulo [2] and L. Jiménez [2]

[1] Chemical and Environmental Engineering Department, University of Basque Country, Pz. Europa 1, 20018 Donostia-San Sebastián, Spain. E-mail: jalel.labidi@ehu.es.

[2] Chemical Engineering Department, University of Córdoba, Campus de Rabanales, C/3, 14071, Córdoba, Spain.

ABSTRACT

Since the last 30 years lignin has been subjected to an intensive investigation due to its unique structure that makes it useful for many applications, including polymer synthesis, obtaining of value added chemicals or as an additive with interesting properties. In this work a series of 4 black liquors from different origin, including kraft liquor from pine (*pinus radiata*), soda liquors from flax (*linum usitatissimum*), this one using anthraquinone as catalyst, and grapevine (*Vitis vinifera*) vineshoot, and another one from wild tamarind (*leucaena leucocephala*) extracted by the organosolv Alcell method, have been subjected to chemical treatments in order to isolate different types of lignin. Subsequently, these lignins have been characterized using Fourier transform infrared spectroscopy (FT-IR) and ^{1}H-NMR to analyse the chemical structure, gel permeation chromatography (GPC) for determining molecular weight (MW) and molecular weight distribution (MWD) and thermogravimetric analysis (TGA) to analyse the thermal degradation. Results show that kraft pine lignin has higher molecular weight and hydroxyl groups' content than the other samples, what seems to be related to its higher content in guaiacyl-type units.

Keywords: lignin, organosolv, annual plants

INTRODUCTION

Lignin is the natural amorphous matrix that bonds cellulose fibres together in the cell wall of all plants. With the exception of cellulose no other renewable natural resource is more abundant in the Earth. Lignin is created by enzymatic polymerisation of coniferyl alcohol, synapyl alcohol and, in a minor extent, *p*-coumaryl alcohol (leading to guaiacyl (G), syringyl (S) and *p*-hydroxyphenyl propane (*p*-H)-type units, respectively). The result is a complex macromolecule with a great variety of functional groups as well as ring substitutions, and over 10 different types of linkages between the monomers [1-4]. Depending on its origin and pulping method used the physicochemical characteristics of lignins and thus their suitability to be used in different applications, can vary noticeably. Kraft and soda processes are, by far, the most pulping methods used in the industry for, respectively, wood and non-wood materials. Due to environmental concerns, new pulping processes based on organic solvents, easily recoverable by distillation, are being tested for different raw materials. Within these organosolv methods, Alcell pulping that uses ethanol-water mixture as delignification medium is the most developed one. Pine and flax are two well-known systems. The former is the classical softwood (*Gymnospermae*) that has been used for many decades for paper production, and the latter is one of the most studied dicotyl crop residues (*Angiospermae*). The other two raw materials also belong to this last group but they have been scarcely studied. Wild tamarind belongs to the *leguminosae* family (hardwood type) and is one of the fastest-growing leguminous trees. Grapevine vineshoot are obtained in big quantities as an agricultural residue in large areas of Spain, and recently some studies have claimed for its usefulness in pulp and paper industry [5]. Lignins extracted from pine, flax, leucaena and vineshoot have been called, respectively, L1, L2, L3 and L4.

EXPERIMENTAL

Lignins from kraft and soda liquors, commonly named alkali lignins, were extracted by acid precipitation using 1mol/L hydrochloric acid solution. After lowering the pH to 2 the precipitated lignins were filtered on a Buchner funnel and successively washed with water twice to remove unreacted compounds and degraded sugars and then dried in an oven at 60 ºC under vacuum. Isolation of Alcell lignin was performed under a liquor-to-water ratio of 1:2 and acidulation with 1mol/L HCl to pH 2. Such conditions are reported to be adequate for extraction [6, 7]. The lignin sample obtained after centrifugation at 3500 r/min for 10 min was washed twice and dried in an oven at 60℃ under vacuum until constant weight was obtained.

Lignin samples were subjected to acetylation in order to enhance their solubility in organic solvents,

used in both GPC and NMR techniques. This reaction implies the substitution of all the hydroxylic functions by new acetyl groups. With that purpose, the lignins were placed in an acetyl anhydride/acetyl acid mixture (1:1 by weight) containing sodium acetate as a catalyst (0.5 equivalents per mole of acetyl anhydride), being the final lignin concentration 20 wt % [8]. Reactions were carried out at room temperature for 48 h and then refluxed for 1 h. Acetylated lignins (AL) obtained by precipitation in ice-cold water with 1% HCl were filtered, washed with distilled water and dried in the same way as the isolated lignin samples.

FT-IR measurements were performed in a Perkin-Elmer 16PC instrument by direct transmittance using KBr pellet technique. Each spectrum was recorded over 20 scans, in the range from 4000 to 400 cm^{-1} with a resolution of $4cm^{-1}$. Background spectra were collected before every sampling. KBr was previously oven-dried to avoid interferences due to the presence of water. The chemical structure of samples was also studied through ^{1}H-NMR spectrometry using a Bruker 500 MHz spectrometer at a frequency of 250 MHz with an acquisition time of 0.011 s. DMSO was used as solvent.

Gel permeation chromatography provides a rapid way to obtain information on the molecular weight of polymers. Samples have been examined through THF-eluted GPC using a Perkin Elmer instrument equipped with an interface (PE Series 900). Three Waters Styragel columns (HR 1, HR 2 and HR 3) ranging from 100 to 5105 and a refractive index detector (Series 200) were employed, with a flow rate of 1 mL/min. The calibration was made using polystyrene standards. The thermal stability of lignins was measured using a TGA-92 thermobalance from Setaram under dynamic scans from 30 to 800℃ at 10 ℃/min with helium atmosphere.

FT-IR spectroscopy

All lignin samples, as seen by FT-IR (Figure 1), show the same phenylpropane skeleton (1610, 1517 and 820 cm^{-1}) containing different amounts of hydroxyl groups (3400, 1040 cm^{-1}). Bands in the range of 1705~1715 cm^{-1} can be attributed to non-conjugated carbonyl groups. Apart from that, some remarkable singularities due to their different origin and delignification method applied are observed between them.

The network in softwood lignins is primarily formed by G moieties, the rest containing S type units and only traces of p-H [9], while in hardwoods and dicotyl crops various amounts of G/S have been reported [10]. These characteristics are clearly visible in the spectra of the studied lignins. L1, the softwood L, present mainly G bands (1270 cm^{-1}, 1125 cm^{-1}, 1040 cm^{-1}, 857 cm^{-1} and 810 cm^{-1}), while L2, extracted from a non-woody plant, shows typical S bands (1330, 1115 and 830 cm^{-1}). L3 and L4 present a mixture of both types of groups, as remarked in Figure 1b. Delignification method under which lignin has been isolated also plays an important role in its final structure. Kraft method cleaves α-O-4 and β-O-4

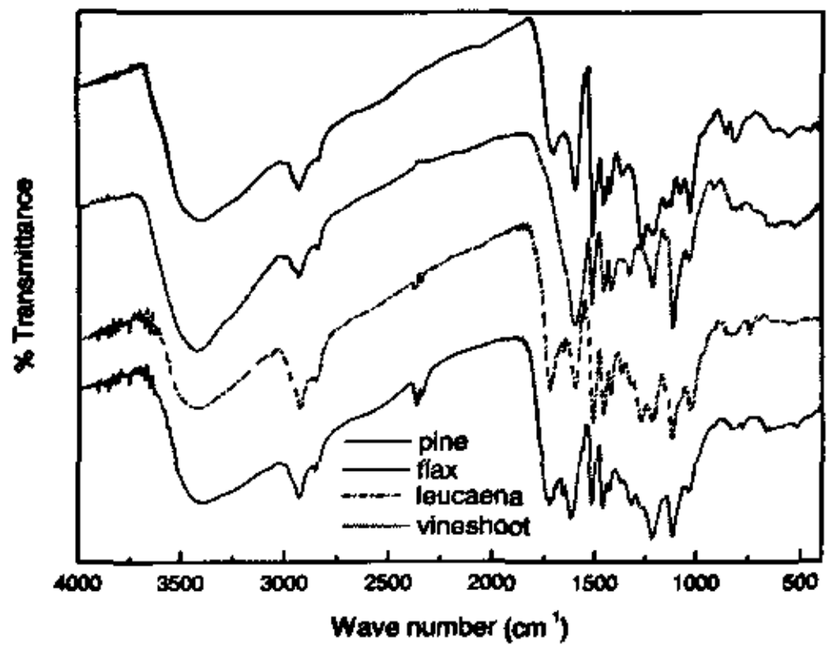


Figure 1 (a) FT-IR spectra of the lignins, and (b) detail of the 1480 to 900 cm^{-1} range

linkages through a two-step process leaving non-etherified phenolic OH in L, visible in L1 spectrum with a band at 1360 cm^{-1}. On the other hand, soda pulping of non-woody material produces the cleavage of those aryl-ether linkages through the formation of small quantities of phenolic hydroxyls [11] and the loss of primary aliphatic OH. This fact can be seen in L2 and L4 spectra where there is little or no vibration at 1360 cm^{-1} and the signal of 1030 cm^{-1}, attributed to primary OH (among others), is less

intense than in the other samples. The widening of the band at 1610 cm^{-1} in L2 spectrum is due to quinonic vibration. Alcell method promotes the acid hydrolysis of lignin generating both phenolic hydroxyl groups (visible at 1360 cm^{-1}) and new carbonyl groups (1715 cm^{-1}) in its structure.

G-type units have a free C5 position (*ortho* to the phenolic hydroxyl) in the ring that confers some reactivity to the macromolecule towards electrophilic substitutions, what is very interesting, for example, for being used as a copolymer in a modified phenolic resin synthesis. On the other hand, in S-type units both C3 and C5 positions are linked to a methoxy group, resulting in little or no reactivity of the aromatic ring. From this point of view, lignins with G groups as the principal structural unit must be *a priori* more suitable for formulations involving phenolic ring substitutions. Another factor that must be considered is the existence of big quantities of phenolic hydroxyls in the structure that results in higher no-covalent interactions between lignin fragments that makes it behave as a crowded and stiff macromolecule [12, 13]. In some applications this fact can cause an important loss in final properties.

^{1}H-NMR spectrometry

The chemical structure of acetylated samples has been studied through ^{1}H-NMR spectrometry. Acetylation produces derivatives that display broad proton signals in regions where small interference exists with other hydrogen signals. In addition, aromatic and aliphatic alkoxy groups (OAcetyl) are sifted differently and give rise to separate peaks (Figure 2). Thus, ^{1}H-NMR spectrometry reveals both total OAcetyl content (proportional to OH content) and the ratio between aromatic and aliphatic substituents [8], as well as OCH_3 content per phenylpropane (C_9) unit, what gives an idea of G to S proportion.

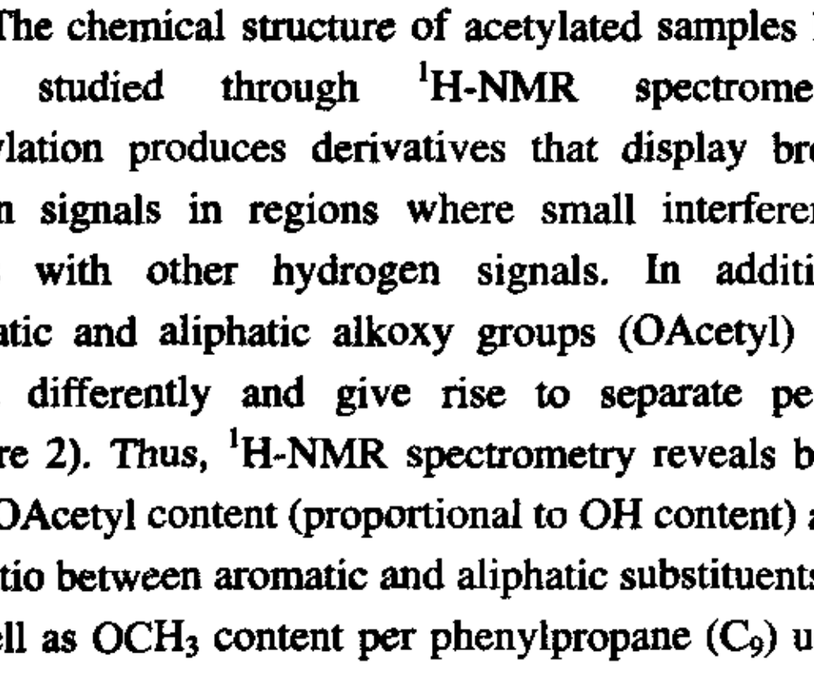


Figure 2 ^{1}H-NMR spectra of acetylated lignins.

As expected, AL1 exhibits higher content of aromatic protons than the other samples (data not shown), as it is composed mainly by G units. On the other hand, AL2, AL3 and AL4 with higher contribution of S units, show higher quantities of methoxy groups. Total OH content, related to both origin of L and extraction method used is much bigger for kraft than for soda and organosolv lignins, what is again in agreement with FT-IR results. On the other hand, the relative quantity of aromatic and aliphatic moieties is similar in all samples.

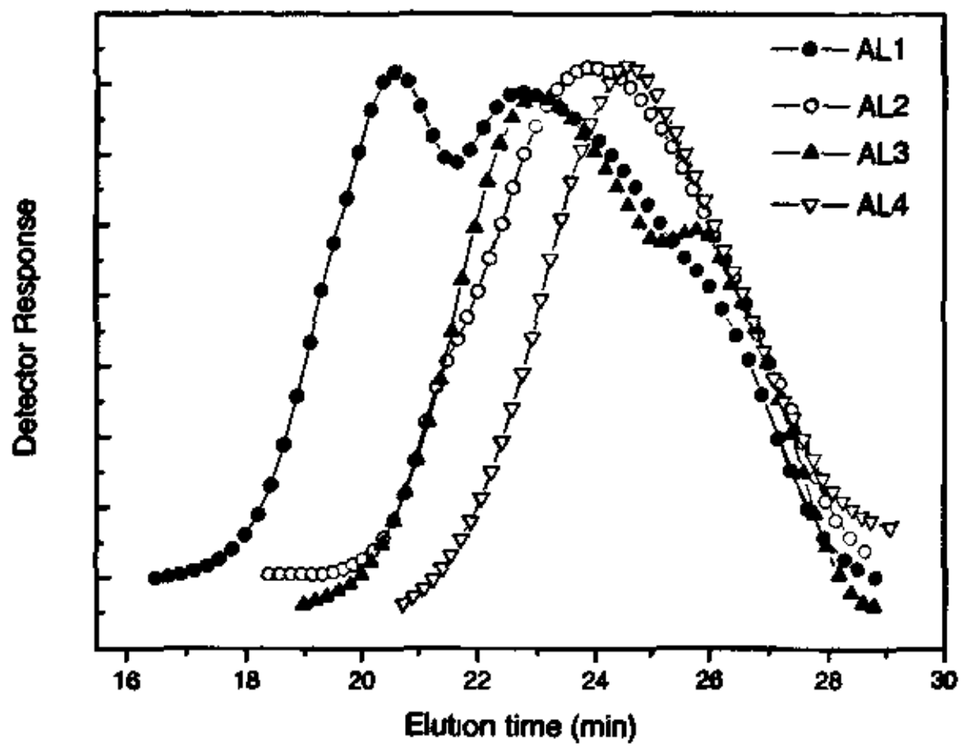


Figure 3 GPC chromatograms of acetylated lignin samples

Table 1 Average Molecular Weight ($\overline{M_w}$), *MW*

Sample	$M_w/10^3$	$M_n/10^3$	M_w/M_n
AL1	8.7	2.4	3.6
AL2	2.6	1.5	1.8
AL3	3.1	1.7	1.8
AL4	2.0	1.4	1.5

($\overline{M_n}$) and polydispersity ($\overline{M_w}$ / $\overline{M_n}$) of acetylated lignin samples analysed by GPC

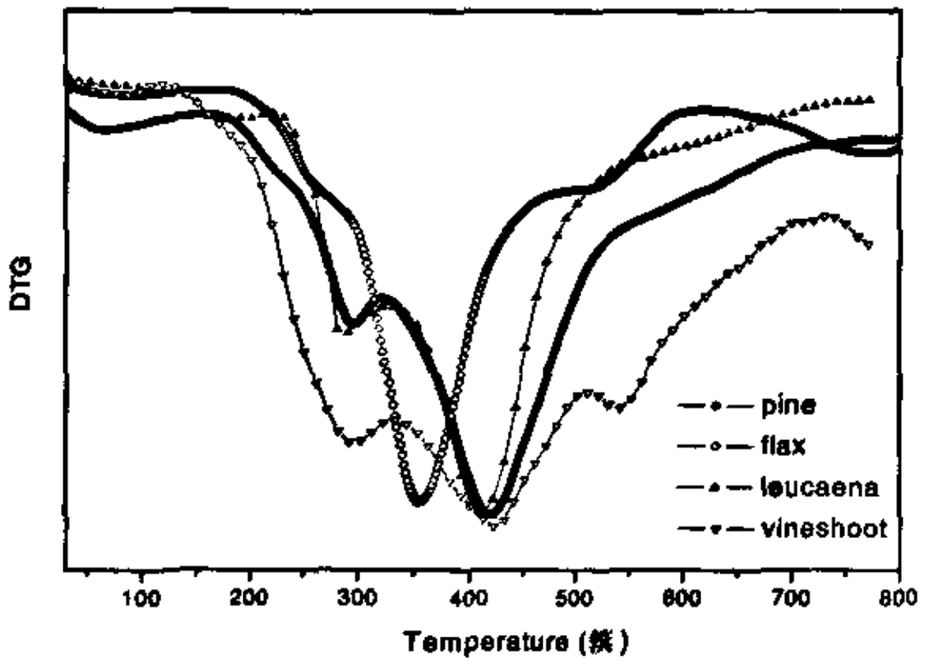
Gel permeation chromatography (GPC)

Figure 3 and Table 1 show the results obtained from the chromatographic analysis of the samples. AL2, AL3 and AL4 samples show similar weight average *MW*, ranging from 2×10^3 to 3.1×10^3, while AL1 presents a much higher value, close to 10^4. These results can be explained attending to the different lignin composition. Although β-O-4 is the most common linkage in all lignin types, there are also important quantities of C-C bonds between the structural units; among them, those involving C5 of

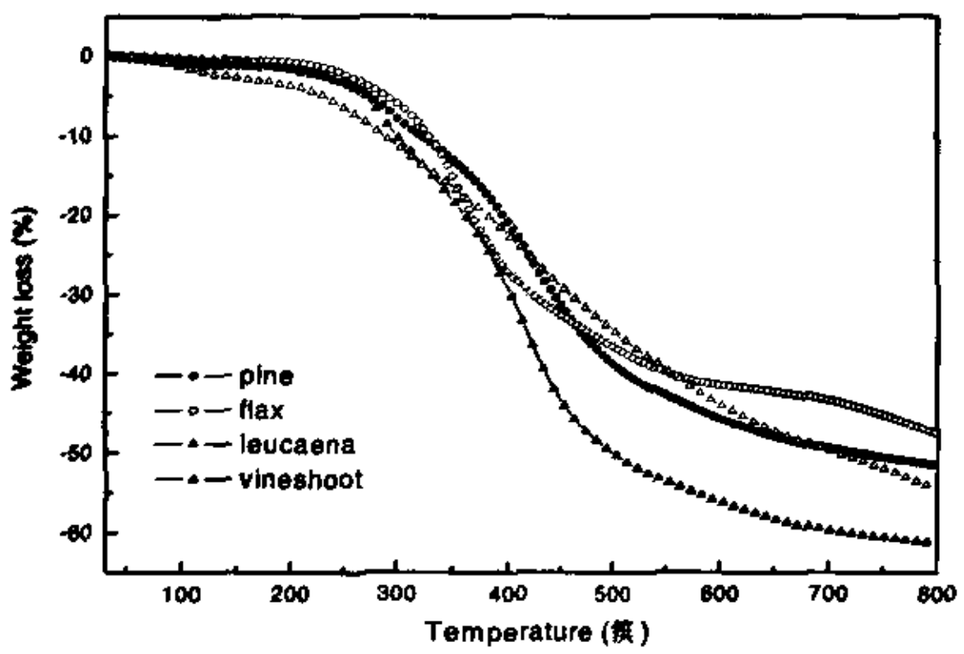
the aromatic ring are the most abundant [4]. G-type units are able to form this kind of bonds, but this is not possible in S-type units as they have C5 position substituted by a methoxy group. This is a very important feature when studying the *MW* of lignins because these C-C bonds are not cleaved during the pulping of wood due to their higher stability. As a consequence, lignins strictly composed by G units are expected to show higher *MW* than those presenting high contents of S units. This seems to be valid for the lignin samples studied in this work, as their *MW* is correlated with their G content.

Thermogravimetric analysis (TGA).

The thermal decomposition of organic polymers is commonly determined by thermogravimetric analysis under helium or nitrogen atmosphere. TG curves reveal the weight loss of substances in relation to the temperature of thermal degradation. The first derivative of the TG curve (DTG) shows the corresponding rate of weight loss. Both DTG and weight loss graphics are shown in Figure 4.



(a)



(b)

Figure 4 (a) DTG and (b) TG curves of lignins obtained from TGA analysis

The main peak of DTG curve may be expressed as a single thermal decomposition temperature (DTG_{max}) and can be used to compare thermal stability characteristics of different materials. The DTG_{max} is between 350℃ and 425℃ for all lignin samples. Pyrolytic degradation in this region involves fragmentation of inter-unit linkages, releasing monomeric phenols into the vapour phase, while above 500℃ the process is related to the decomposition of aromatic rings. The high thermal stability shown by all lignins may be an interesting characteristic to be used in many applications.

CONCLUSION

Physico-chemical characterisation of four lignin samples from different origins and extracted by different methods has been performed. FT-IR spectroscopy and ^{1}H-NMR spectrometry reveal that kraft pine lignin are mainly composed by G units with non-etherified hydroxyl groups, while alkaline flax lignin has mainly S units and less free hydroxyls. Organosolv lignin from *leucaena leucocephala* and alkali-extracted vineshoot lignin show an intermediate behaviour. Molecular weight of acetylated samples has been studied through THF-eluted GPC, showing that kraft pine lignin has the highest molecular weight probably due to its higher G content. Finally, all lignins show high thermal resistance (up to ~400ºC) what can be very useful for many applications.

ACKNOWLEDGEMENTS

The authors wish to thank Ministerio de Educaciόny Cienciaof Spain (CTQ2004-06564-C04-03/PPQ) for financial support.

REFERENCES

1 Abreu H.S; do Nascimento A M and Maria M A. Lignin structure and wood properties. Wood Fiber Sci, 1999, 31: 426-433

2 Tsujino J; Kawamoto H and Saka S. Reactivity of lignin in supercritical methanol studied with various lignin model compounds. Wood Sci. Technol., 2003, 37: 299-307

3 Ralph R; Hatfield R D; Piquemal J; et al. NMR characterization of altered lignins extracted from tobacco plants down-regulated for lignification enzymes cinnamyl-alcohol dehydrogenase and cinnamoyl-CoA-reductase. Proc Natl Acad Sci, 1998, USA 95: 12803–12808

4 Brunow G; Lundquist K; Gellerstedt G. Lignin. In: Sjöström, E. and Alén, R. (Eds.). Analytical Methods in Wood Chemistry, Pulping and Papermaking. Berlin Heidelberg New York, Springer-Verlag, 1999, 77-124

5 Jiménez L. Pastas Celulósicas de Materias Primas Alternativas a las Convencionales. Ecija, Spain: Ed. Gráficas Sol; 2005.

6 Botello J I; Gilarranz M A; Rodríguez F; et al. Recovery of solvent and by-products from organosolv black liquor. Separation Science and Technology, 1999, 34(12): 2431-2445

7 Vila C; Santos V and Parajó J C. Simulation of an organosolv pulping process: generalized material balances and design calculations. Ind. Eng. Chem. Res., 2003, 42: 349-356

8 Glasser W G; Jain R K. Lignin derivatives. I. Alkanoates. Holzforschung, 1993, 47: 225-233

9 Boeriu C G; Bravo D; Gosselink R J A and van Dam J E G. Characterization of structure dependent functional properties of lignin with IR spectroscopy. Ind. Crops Prod., 2004, 20: 205-218

10 Dence C W. General structure features of lignins. In:Lin, E.S., Dence, C.W. (Eds), Methods in Lignin Chemistry, Berlin Heidelberg: Springer-Verlag, 1992, 3-6

11 Gellerstedt G; Lindfors E L. Structural changes in lignin during kraft pulping. Holzforschung, 1984, 38: 151-158

12 Thring R W; Ni P and Aharoni S M. Molecular weight effects of the soft segment on the ultimate properties of lignin derived polyurethanes. Int. J. Polym. Mater., 2004, 53: 507-524

13 Feldman D; Banu D; Campanelly J and Zhu H. Blends of vinylic copolymer with plasticized lignin: thermal and mechanical properties. J. Appl. Polym. Sci., 2001, 81: 861-874