

Polyurethanes and Polyesters from Lignin

Carlo Bonini, Maurizio D'Auria, Lucia Emanuele, Rachele Ferri, Rachele Pucciariello, Anna Rita Sabia

Dipartimento di Chimica, Università della Basilicata, Via N. Sauro 85, 85100 Potenza, Italy

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ABSTRACT: Lignin, obtained through steam explosion from straw, was completely characterized via elemental analysis, gel permeation chromatography, ultraviolet and infrared spectroscopy, and ^{13}C and ^1H nuclear magnetic resonance spectrometry. Polyurethanes were obtained by treating steam-exploded lignin from straw with 4,4'-methylenebis(phenylisocyanate), 4,4'-methylenebis(phenylisocyanate)-ethandiol, and poly(1,4-butandiol)tolylene-2,4-diisocyanate terminated. The obtained materials were characterized by using gel permeation chromatography, infrared spectroscopy, and scanning electron microscopy. Differential scanning calorimetry analysis showed a T_g at -6°C , assigned to the glass transition of the poly(1,4-butandiol)

chains. The presence of ethylene glycol reduced the yields of the polyurethanes. The use of the prepolymer gave the best results in polyurethane formation. Steam-exploded lignin was used as the starting material in the synthesis of polyesters. Lignin was treated with dodecanoyl dichloride. The products were characterized by using gel permeation chromatography, infrared spectroscopy, ^{13}C and ^1H nuclear magnetic resonance spectrometry, and scanning electron microscopy. © 2005 Wiley Periodicals, Inc. *J Appl Polym Sci* 98: 1451–1456, 2005

Key words: biomaterials; polyesters; polyurethanes

INTRODUCTION

Lignin is a three-dimensional phenylpropanoid polymer mainly linked by ether bonds between monomeric phenylpropane units. The cell walls of various cell types of plants, for example, wood fibers, vessels, and tracheids, have lignin as an important constituent. It constitutes 20–30% of the weight of wood. Lignin encrusts as an amorphous mass of cellulose fibers, which gives high mechanical strength to the lignified cell wall and increases the resistance to microbial degradation.

Lignin is the second most abundant natural renewable polymer after cellulose. Its isolation in papermaking, hydrolysis, and other biomass refineries leads essentially to its use as a fuel. However, growing research and technological interest have been devoted to alternative ways of utilizing this massive resource.

Several uses of lignin in the synthesis of new materials have been reported. In particular, lignin has been used as raw material in the preparation of polyurethanes^{1–9} and in the synthesis of graft copolymers.^{10–22}

Pulping for paper production is presently mainly based on sulfate and sulfite processes, which favor chemical passivation of the resulting technical lignins by the increase in their degree of condensation

through reactive groups. This leads to poorer reactivity and to the presence of often-undesirable physical (ashes) and chemical impurities (sulfur-containing moieties).

Steam explosion is a technology useful for the treatment of every lignocellulosic material. In the steam explosion, saturated vapor at high pressure is used to rapidly warm the biomass in a digester. The biomass is maintained at the desired temperature (130–180°C) for a short time; during this period the hemicellulose is hydrolyzed and dissolved. At the end of this period, an explosive decompression gives rise to a loss of water from the cells (due to the immediate evaporation of water) and the cleavage of cellular structures.

Recently we reported that steam-exploded lignin from straw could be used as a starting material in the synthesis of graft copolymers with alkenes.^{23,24}

In this work we explored some other possible uses of lignin. Isocyanates are commonly used in the preparation of wood adhesives.²⁵ In this case, heat is able to form polyurethanes after adsorption on wood. We describe our results on the interaction between a lignin from steam explosion and diisocyanates to give polyurethanes. The aim of this study is to verify the possible use of lignin as an additive with ultraviolet (UV) protective properties in this type of adhesive. In fact, we showed that lignin has a UV protective action on polyethylene and polystyrene blends.^{26,27}

Furthermore, several examples of the synthesis of polyesters from lignin have been reported.^{28–32} Polyesters can be used in the formulation of polyurethane

Correspondence to: M. D'Auria (dauria@unibas.it).

TABLE I
Polyurethanes from Steam-Exploded Lignin

Entry	Lignin (g)	Diisocyanate ^a (g)		mEq	Ethandiol (g)	Yield (g)
		A	B			
1	1.000	0.138		2.04		0.826
2	1.000	0.200		3.06		0.806
3	1.000	0.270		4.08		0.830
4	1.000	0.138		2.04	0.070	0.752
5	1.000	0.138		2.04	0.100	0.710
6	1.000	0.200		3.06	0.070	0.650
7	1.000	0.200		3.06	0.100	0.810
8	1.000	0.270		4.08	0.070	0.830
9	1.000	0.270		4.08	0.100	0.802
10	1.000		0.891	1.02		1.784
11	1.000		1.510	1.53		2.451
12	1.0		2.103	2.04		3.063

^a A: 4,4'-methylenebis(phenylisocyanate); B: poly(1,4-butanediol)tolylene-2,4-diisocyanate terminated.

coatings. The applicability of this procedure with lignin from straw obtained by using steam explosion is reported in this study; the formation of polyesters can broaden the possible uses of steam-exploded lignins.

EXPERIMENTAL

Isolation of lignin

The material used as the source of lignin was mechanically reduced in pieces of about 1 cm of length and added with water to raise its initial content to the value of 50 wt %. Steam explosion runs were carried in a 10 L batch reactor, loading about 0.5 kg of material each cycle. Treatment conditions allowed having a severity parameter $\log R_0 = 3.94$. The raw material (100 g) was extracted two times with hot water (250–300 mL, $65 \pm 5^\circ\text{C}$) to eliminate sugars and hemicelluloses. The extraction of lignin from exploded materials has been carried out by 1.5% sodium hydroxide solution (250 mL) at 90°C in 15 min for two times. Lignin in still warm solution was precipitated at pH 2 with 20% H_2SO_4 , filtered, washed, and dried at 105°C .

Elemental analyses were obtained with a Carlo Erba Elemental Analyzer 1106. ^{13}C and ^1H NMR spectra were recorded with a Bruker 300 AM instrument. All the ^{13}C NMR spectra were recorded in dimethylsulfoxide ($\text{DMSO}-d_6$). All the ^1H NMR spectra were recorded on acetylated samples in CDCl_3 . Gel permeation chromatography analyses were performed on a Hewlett-Packard HPLC by using an H-P Plgel 5 μ column. The lignin samples were acetylated (acetic anhydride and pyridine) before gel permeation chromatography (GPC). Tetrahydrofuran (THF) was used as the mobile phase. Spectrophotometric grade THF was used and distilled (over LiAlH_4) before use. The chromatograms were obtained using a UV detector at 280 nm. A calibration obtained by using polystyrene samples was used to perform the conversion from

elution time to molecular weight. A Cary 2300 spectrophotometer was used for the UV spectra. Spectrophotometric grade 1 : 1 acetonitrile–ethanol mixture and DMF were used as solvent. The thermal behavior was examined by a differential scanning calorimeter (DSC 7, Perkin–Elmer) on 5 ± 0.25 mg samples of the benzene soluble extracts of polymers, in a nitrogen atmosphere, at a scanning rate of $20^\circ\text{C min}^{-1}$. Scans were performed in the temperature range -30 to 180°C . The data were analyzed through the software PYRIS running under Windows NT 4.0 on a Compaq Prolinea 5133 computer. The glass transition temperature, T_g , has been taken, as usual, at the temperature corresponding to the point where half the increase of the heat capacity has occurred.

Synthesis of polyurethanes

Lignin and 4,4'-methylenebis(phenylisocyanate) were suspended in THF for 5 h in the presence of a catalytic amount of stannous octoate. After solvent evaporation, the product was maintained in an oven at 72°C overnight (Table I).

The same procedure was performed using ethandiol as reagent (Table I). In this case lignin, 4,4'-methylenebis(phenylisocyanate), and ethandiol were suspended in THF for 5 h in the presence of a catalytic amount of stannous octoate. After evaporation of the solvent, the residue was treated in an oven at 72°C overnight.

The reaction was carried out using poly(1,4-butanediol)tolylene-2,4-diisocyanate terminated (Table I). In this case, lignin and the prepolymer were suspended in THF for 5 h in the presence of a catalytic amount of stannous octoate. After solvent evaporation, the residue was maintained at 72°C in an oven overnight (Table I).

TABLE II
Average Molecular Weights for Polyurethanes Obtained from Steam-Exploded Lignin from Straw and Poly(1,4-butandiol) Terminated with Toluene-2,4-disocyanate

Entry ^a	M_n	M_w	M_z	M_p
10	766	5517	35268	939
11	1301	7819	37927	3268
12	1371	6830	28857	4047

^a The entry refers to those of Table I.

Synthesis of polyesters

Lignin (1 g) and dodecandioyl dichloride (Table II) were dissolved in THF (25 mL) in the presence of a stoichiometric amount (referred to the acyl chloride) of triethylamine. After 94 h, the mixture was extracted with ethyl acetate and dried over Na_2SO_4 . The ^{13}C NMR spectrum showed signals at δ 179, 173.9, 169.6, 67.6, 67.4, 63.3, 44.4, 29.2, 29.1, 29.0, and 24.1 ppm. The ^1H NMR spectrum showed signals at δ 7.0, 4.1, 3.6, 2.4, 2.3, 1.8, 1.6, and 1.3 ppm.

RESULTS AND DISCUSSION

To perform our experiments we used a steam-exploded lignin from straw. The results of the elemental analysis were C: 62.13, H: 5.88; N: 1.26; S: 0.00; O: 30.73%. We analyzed the presence of carbon and hydrogen to characterize the lignin, but also the presence of both nitrogen, as a marker of the presence of proteins in the lignin, and sulfur, as a marker of the presence of sulfate lignin. The presence of sulfur in our sample was not detected. The elemental analysis allowed us to give the molecular weight of the lignin expressed in phenylpropanoid (C_9) units. In our case, the molecular formula was $\text{C}_9\text{H}_{10.22}\text{O}_{3.34}$ with a molecular weight of 172. Elemental analysis showed that this sample was highly oxidized, with a large amount of oxygen in the molecular formula.

The distribution of the molecular weights of acetylated lignin was obtained by using GPC; it gave $M_n = 3509$, $M_w = 15,096$, and $M_z = 40,966$. These data confirmed the evidence that the steam explosion process induced a strong destructureation in the lignin structure, giving samples with relatively low molecular weight.

The UV spectrum of the lignin from straw was recorded in DMF. It showed absorption at 231 nm ($D = 16.8 \text{ L g}^{-1} \text{ cm}^{-1}$). We recorded the differential spectrum, carrying out the spectrum in 1M NaOH versus the standard solution in DMF. These data allowed us to give the amount in mEq g^{-1} of some structural features in the lignin sample. We could give the amount of syringyl and guaiacyl phenols (Type I), the amount of phenols containing conjugated double bonds (i.e., $\text{HO-Ar-CH=CH-CH}_2\text{OH}$, Type II), and

the amount of stilbenic phenols (Type IV). We found in our sample Type I (0.43 mEq g^{-1}) and Type IV (0.12 mEq g^{-1}).

The infrared spectrum showed absorptions at 1702 (carbonyl stretching), 1655 (C=O stretching in aryl ketones), 1605 and 1513 (aromatic stretching), 1459 (C-H bending in methyl and methylenic groups), 1424 (aromatic vibration coupled with C-H bending in plane), 1330 (C-H bending in plane in syringyl and guaiacyl rings substituted on C-5), 1220 (C-C, C-O, and C=O stretching), 1123 (C-H bending in syringyl units and C-O stretching in secondary alcohols), 1030 (C-H bending in plane in guaiacyl units and C-O stretching in primary alcohols), and 840 cm^{-1} (aromatic C-H bending out of plane).

The ^{13}C NMR spectrum of lignin from straw gave signals at δ 173 (C=O), 153 (C-3/C-3' in 5-5' etherified units), 148 (C-4 in etherified guaiacyl units), 145 (C-4 in β -O-4 non etherified guaiacyl units), 138 (C-1 in β -O-4 etherified syringyl units), 135 (C-4 in β -O-4 etherified and non etherified syringyl units), 133 (C-1 in β -O-4 non etherified guaiacyl units), 130 (C-2/C-6 in benzoate), 120 (C-6 in etherified and non etherified guaiacyl units), 115 (C-5 in etherified and non etherified guaiacyl units), 112 (C-2 in guaiacyl units), 111 (C-2 in guaiacyl-guaiacyl stilbenes), 105 (C-2/C-6 in syringyl units), 87 (C- β in β -O-4 *threo* syringyl units), 72 (C- α in β -O-4 *erythro* guaiacyl and syringyl units), 60 (C- γ in β -O-4 *erithro* and *threo* syringyl and guaiacyl units), 56 (methoxy groups), and 34–20 ppm (CH_3 and CH_2 in saturated chains). The ^{13}C NMR spectrum was compatible with the presence of both guaiacyl and syringyl units. Furthermore, the ^1H NMR spectrum on acetylated lignin showed signals at δ 1.9–2.0 (aliphatic acetates), 2.18 and 2.30 (aromatic acetates), 2.6 (benzyl protons in 3-aryl-1-propanol units), 3.8 (methoxy groups), 6.6 (aromatic protons in syringyl units), 6.9 (aromatic protons in guaiacyl units), and 7.6 ppm (aromatic protons ortho to carbonyl groups). The ^1H NMR spectrum showed the presence of signals due to the presence of aromatic acetates, in agreement with the differential UV spectrum showing the presence of a large amount of phenolic hydroxy groups in the structure (0.55 mEq g^{-1}). Figure 1 represents the environmental scanning electron microscope (ESEM) image of the lignin from straw.

The synthesis of polyurethanes and polyesters involves the use of lignin as a source of hydroxyl groups. The total hydroxy groups in lignin was determined as described by Mansson.^{33,34} We obtained a value of 1.02 mEq g^{-1} . In the synthesis of polyurethanes we used two, three, and four equivalents of diisocyanate, respectively. The best result was obtained using two equivalents of diisocyanate.

The treatment of lignin with different amounts of 4,4'-methylenebis(phenylisocyanate) gave the results reported in Table I (entries 1–3). After treatment with

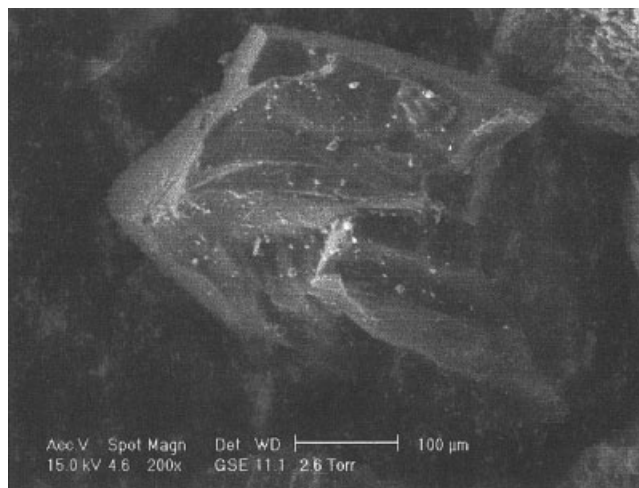


Figure 1 ESEM of lignin from straw.

the diisocyanate, the obtained material was maintained at 72°C in an oven to obtain crosslinking. The Fourier transform infrared (FTIR) spectrum of this material showed the presence of a peak at 1730 cm^{-1} (urethane) and peaks at 1643, 1551, and 1237 cm^{-1} that could be attributed to the stretching of the carbonyl group in urea and to the N-H bending. The ESEM of the same material (Fig. 2) showed that there was no relation between the morphology of native lignin and the obtained polymer.

Polyurethanes were obtained also by using ethylene glycol as coreagent (Table I, entries 4–9). The presence of ethylene glycol reduced the yields of the polyurethanes. The best result was obtained when 0.270 g of the diisocyanate and 0.070 g of the glycol were used (Table I, entry 8).

The FTIR spectrum showed the same type of absorption described before (1730, 1643, 1547, and 1236

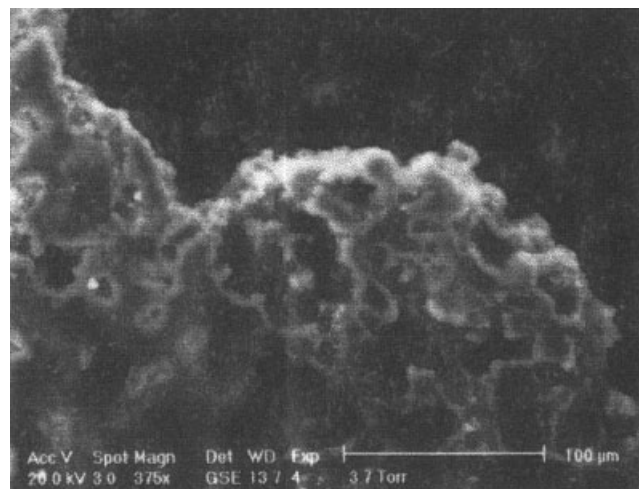


Figure 2 ESEM of the polyurethane obtained from lignin and 4,4'-methylenebis(phenylisocyanate).

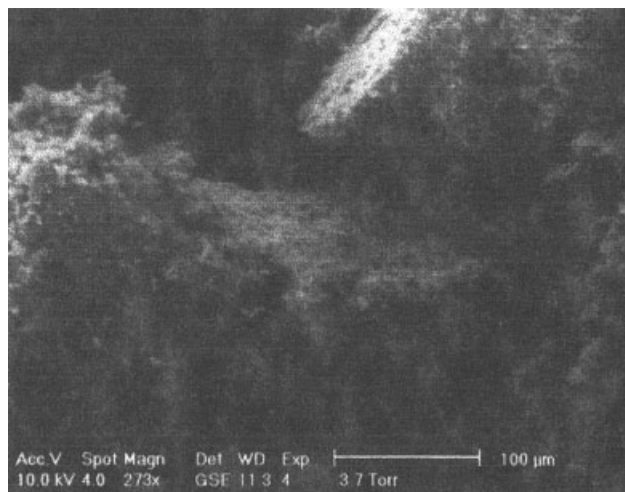


Figure 3 ESEM of the polyurethane from lignin and 4,4'-methylenebis(phenylisocyanate) in the presence of ethandiol.

cm^{-1}). ESEM (Fig. 3) showed that the morphological aspect of the new material was very different from that of lignin; while lignin showed the presence of grains of $\sim 50 \mu\text{m}$ diameter, the polyurethane appeared as grains with dimension higher than 200 μm .

We used also a poly(1,4-butandiol) terminated with tolylene-2,4-diisocyanate prepolymer (Aldrich, $M_n = 1600$). The results of our experiments are reported in Table I (entries 10–12). We used 1, 1.5, and 2 equivalents of the prepolymer in relation to the hydroxy content of lignin. The use of this prepolymer gave the best results in the formation of polyurethanes.

While using 4,4'-methylenebis(phenylisocyanate), the obtained materials were not soluble in common solvents used for GPC analysis; the material obtained by using the butanediol prepolymer allowed this type of analysis. In Figure 4 we report the molecular weight distribution observed. In Table II we have collected the average molecular weights for all the polyurethanes thus obtained. We observed a large increase of the molecular weight in comparison with the lignin used for the experiments.

The FTIR spectrum showed absorption at 1730, 1548, and 1223 cm^{-1} , in agreement with the formation of a polyurethane (Table III). The ^{13}C NMR spectra of these materials showed peaks at δ 155, 154 (C=O), 148, 147 (C-4 in etherified guaiacyl units), 138.5, 138 (C-1 in etherified β -O-4 syringyl units), 137 (C-1 in syringyl units), 131 (C-2/C-6 in *p*-hydroxyphenyl units), 130, 126 (aromatic carbons), 116 (C-5 in etherified and non etherified guaiacyl units), 112 (C-2 in guaiacyl units), 107 (aromatic carbons), 104.5 (C-2/C-6 in syringyl units), 70, 64.5, 62.5, 61 (etheral and alcoholic carbons), 56.5 (methoxy group), 33.5, 31.5, 30, 26, 24.5, 23, 18, 16, and 14.5 ppm. These data were in agreement with the presence of signals of both lignin and aliphatic ethereal prepolymer. The same conclu-

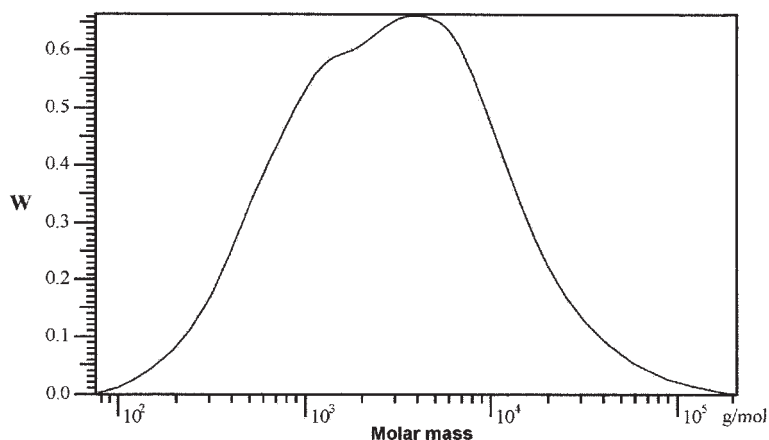


Figure 4 Molecular weight distribution in the polyurethane obtained from steam-exploded lignin and poly(1,4-butandiol) terminated with tolylene-2,4-diisocyanate.

sion could be obtained from the ^1H NMR spectrum (Table III). It showed signals due to the presence of lignin and prepolymer; in particular, the peaks at δ 1.3, 1.7, 2.0, 3.3, and 5.1 could be attributed to the presence of the polybutandiol moiety. The ESEM image of the obtained materials showed the presence of very large grains (Fig. 5). Differential scanning calorimetry (DSC) analysis showed a T_g at -6°C , assigned to the glass transition of the poly(1,4-butandiol) chains. In the temperature range used in DSC analysis, no thermal decomposition was observed.

On the basis of the results described above, we have shown that steam explosion lignin from straw can be used as a partner in wood adhesive; in fact, it reacts thermally with diisocyanates to give polyurethanes. This result is particularly significant considering that in our experimental conditions only a gentle thermal treatment (very different from the 90 – 170°C used in the farm) was used. The presence of lignin as an

additive in wood adhesive could be important to have a more stable material.^{26,27}

We tested also the possible use of this type of lignin in the preparation of polyesters. We used lignin from steam explosion as the substrate in reactions with dodecandioyl dichloride. We used different lignin/dodecandioyl dichloride ratios on the basis of hydroxy content of the lignin (Table IV). In Table IV we collected the average molecular weights of the obtained

TABLE III
FTIR and ^1H NMR Data for Polyurethane Obtained from Lignin and Poly(1,3-butandiol)tolylene-2,4-diisocyanate Terminated and for a Polyester

Polyurethane		Polyester
IR absorptions (cm^{-1})	^1H NMR peaks (δ , ppm)	IR absorption (cm^{-1})
3357	8.71	3449
2941	7.54	2921
2857	7.22	2854
1730	5.45	1811
1602	5.04	1736
1542	4.28	1473
1450	3.80	1412
1370	3.32	1335
1227	2.36	1269
1111	2.08	1176
	1.60	1075

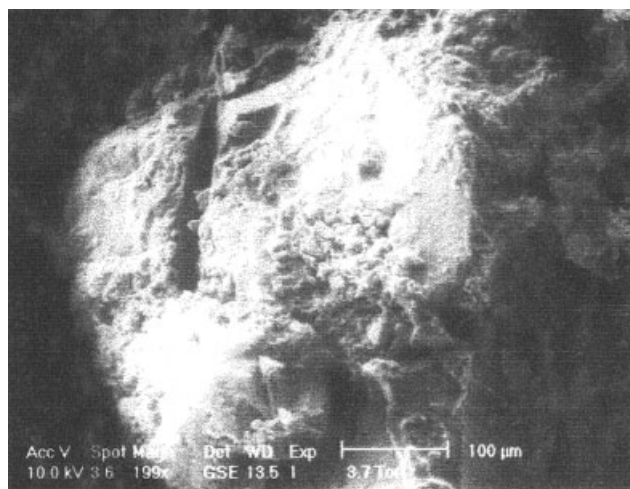


Figure 5 ESEM of the polyurethane obtained from steam-exploded lignin and poly(1,4-butandiol) terminated with tolylene-2,4-diisocyanate.

TABLE IV
Polyesters from Lignin

Entry	Lignin (g)	R(COCl) ₂ (g)	Yield mEq (g)	M _n	M _w	M _z
1	1.0	1.0	3.7 0.8	1915	18863	49371
2	1.0	0.7	2.6 0.6	2312	20153	355141
3	1.0	0.5	1.9 0.4	6382	29069	76416

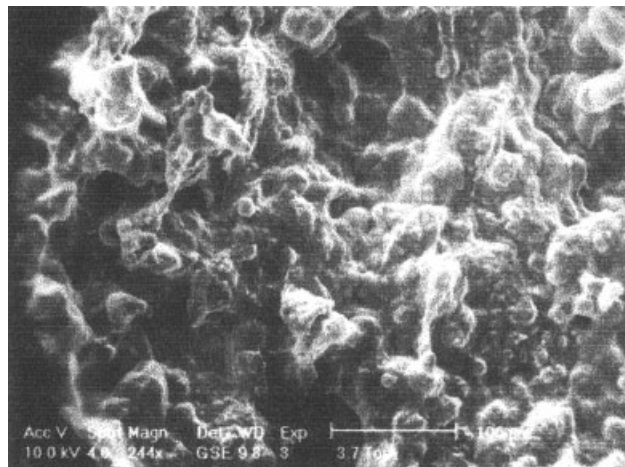


Figure 6 ESEM of the polymer between lignin and dodecandioyl dichloride.

polymers. The polyester with the highest values of M_w , M_n , and M_z , and, then, with a low amount of molecules with high molecular weight, was obtained by using the conditions reported in entry 2. FTIR spectra were in agreement with the formation of polyesters (Table III). The absorptions at 1736 (C=O stretching) and 1074 cm^{-1} (C-O stretching) were diagnostic for the presence of the ester function.

The ESEM image of the obtained polyester showed that the new material had a homogeneous structure (Fig. 6). ^{13}C and ^1H NMR spectra of the polyesters showed signals in agreement with the presence of the ester function (see Experimental section, above).

In conclusion, we showed that lignin from straw obtained through the steam explosion process can be used as the starting material for the preparation of polyurethanes potentially useful in the formulation of wood adhesive and in the synthesis of polyesters that can be used in the formulation of polyurethane coatings. Results on the possible use of lignin in the formulation of wood adhesive will be presented in the near future.

References

- Cheradame, H.; Detoisien, M.; Gandini, A.; Pla, F.; Roux, G. *Br Polym J* 1989, 21, 269.
- Kelley, S. S.; Glasser, W. G.; Ward, T. C. *Polymer* 1989, 30, 2265.
- Yoshida, H.; Morck, R.; Kringstad, K. P.; Hatakeyama, H. *J Appl Polym Sci* 1990, 40, 1819.
- Reimann, A.; Morck, R.; Yoshida, H.; Hatakeyama, H.; Kringstad, K. P. *J Appl Polym Sci* 1990, 41, 39.
- Kelley, S. S.; Ward, T. C.; Glasser, W. C. *J Appl Polym Sci* 1990, 41, 2813.
- Thring, R. W.; Vanderlaan, M. N.; Griffin, S. L. *Biomass Bioenergy* 1997, 13, 125.
- Vanderlaan, M. N.; Thring, R. W. *Biomass Bioenergy* 1998, 14, 525.
- Evtuguin, D. V.; Andreolety, J. P.; Gandini, A. *Eur Polym Mater* 1998, 34, 1163.
- Sarkar, S.; Adhikari, B. *Eur Polym Mater* 2001, 37, 1391.
- Kundu, S. K.; Ray, P. K.; Day, A.; Sen, S. K. *J Appl Polym Sci* 1951 1989, 38.
- Lathia, A.; Chang, F. F.; Meister, J. J. *Polym Prepr* 1990, 31, 648.
- Meister, J. J.; Li, C. T. *Polym Prepr* 1990, 31, 653.
- Lathia, A.; Meister, J. J. *Polym Prepr* 1990, 31, 660.
- Meister, J. J.; Lathia, A.; Chang, F. F. *J Polym Sci Part A: Polym Chem* 1991, 29, 1465.
- Meister, J. J.; Li, C. T. *Macromolecules* 1992, 25, 611.
- Gunnels, D. W.; Gardner, D. J.; Chen, M. J.; Meister, J. J. *Polym Mater Sci Eng* 1992, 67, 227.
- Meister, J. J.; Zhao, Z. *Polym Mater Sci Eng* 1992, 67, 228.
- Meister, J. J.; Chen, M. J. *J Appl Polym Sci* 1993, 49, 935.
- Chen, M. J.; Meister, J. J.; Gunnels, D. W.; Gardner, D. J. *Polym Mater Sci Eng* 1993, 68, 243.
- Meister, J. J.; Zhao, Z. *Polym Prepr* 1993, 34, 606.
- Meister, J. J.; Aranha, A.; Wang, A. *Polym Prepr* 1993, 34, 608.
- Marchetti, V.; Gerardin, P.; Tekely, P.; Loubinoux, B. *Holzforchung* 1998, 52, 654.
- Bonini, C.; D'Auria, M.; Mauriello, G.; Pucciariello, R.; Teghil, R.; Tofani, D.; Viggiani, L.; Viaggiano, D.; Zimbardi, F. *J Appl Polym Sci* 2001, 79, 72.
- Bonini, C.; D'Auria, M.; Ferri, R.; Pucciariello, R.; Sabia, A. R. *J Appl Polym Sci* 2003, 90, 1163.
- Phanopoulos, C. In *The Polyurethanes Book*; Randall, D.; Lee, S., Eds.; Wiley: London, 2002; p 395.
- Ferri, R. *EPA Newsletter* 2004, 77, 50.
- Pucciariello, R.; Villani, V.; Bonini, C.; D'Auria, M.; Vetere, T. *Polymer* 2004, 45, 4159.
- Gandini, A.; Naceur, B. M.; Guo, Z. X.; Montanari, S. In *Chem Modification, Properties and Usage of Lignin*; Hu, T. Q., Ed.; Kluwer Academic/Plenum Publisher: New York, 2002; p 57.
- Glasser, W. G.; Jain, R. K. In *Chemicals and Materials from Renewable Resources*; Bozell, J. J., Ed.; American Chem Society: Washington DC, 2001; p 191.
- Evtugin, D. V.; Gandini, A. *Acta Polym* 1996, 47, 344.
- Guo, Z. X.; Gandini, A.; Pla, F. *Polym Int* 1992, 27, 17.
- Guo, Z. X.; Gandini, A. *Eur Polym Mater* 1991, 27, 1177.
- Manssonm, P. *Holzforchung* 1983, 37, 143.
- Chen, C.-L. In *Methods in Lignin Chemistry*; Lin, S. Y.; Dence, C. W., Eds.; Springer-Verlag: Berlin, 1992; Chapter 7.1.