Graft Copolymers of Lignin with Electron Poor Alkenes

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ABSTRACT: The synthesis of copolymers between lignin and electron poor alkenes is described. Lignin from steam-exploded pine, from steam-exploded straw, and organosolv were used as starting materials. Beforehand, lignins were fully characterized by using elemental analysis, ultraviolet spectroscopy, gel permeation chromatography (GPC), Fourier transform infrared (FTIR), and both ^{1}H and ^{13}C nuclear magnetic resonance (NMR) spectroscopy. The synthesis of copolymers was performed using a previously described procedure utilizing calcium chloride and hydrogen peroxide as reagents. FTIR of copolymers showed absorptions due to the presence of both lignin and the electron withdrawing group on the alkene. GPC analysis showed the presence of fractions with high molecular weights: the M_z of lignin from pine was 3729 while the copolymer with methyl acrylate showed $M_z = 383790$. Differential calorimetry showed the presence of glass transitions in the range of -9 to 4.5°C due to the presence of grafted polyalkene chains. When acrylonitrile was used as starting material DSC analysis of the product showed a glass transition at 119°C, which can be attributed to grafted polyacrylonitrile chain. Lignin from steam explosion could be a good raw material in the preparation of graft copolymers. Furthermore, lignin from pine gave better results than that from straw. Finally, lignin from steam explosion gave better results than organosolv lignin. These results can be explained on the basis of the structural properties of used lignins. Both UV and ^{13}C NMR spectra showed that lignin from pine contained a consistent amount of double bonds. © 2003 Wiley Periodicals, Inc. J Appl Polym Sci 90: 1163–1171, 2003

Key words: lignin; gel permeation chromatography; FTIR; differential scanning calorimetry; graft copolymers

INTRODUCTION

Lignin is a three dimensional phenylpropanoid polymer mainly linked by ether bonds between monomeric phenylpropane units, most of which are not readily hydrolysable. Lignin is constituent of the cell wall of various cell types of plants, such as wood fibers, vessels, and tracheids. It constitutes 20–30% of the weight of wood. Lignin encrusts as an amorphic mass the cellulose fibers, which gives the lignified cell wall high mechanical strength and increases the resistance to microbial degradation. Lignin is a by-product of pulping and bleaching processes and represent an important environmental problem. Most lignin extracted from lignocellulosic materials for cellulose and paper production in modern pulp mills is burned to generate energy and recover chemicals. The lack of other value added applications is mainly caused by the heterogeneity, odor, and color problems of lignin-based products. The common technologies in pulp industries to extract lignin have been focused on the optimum cellulose yield and maximum deactivation and degradation of lignin. The concept of integrated plant conversion is one of the issues for development of a sustainable agriculture, and requires the valorization of residues from agro-industrial production, such as lignin from cereal straw pulping and from annual fiber crops.

Several uses of lignin as starting material in the synthesis of new material have been reported. In particular, lignin has been used as raw material in the preparation of polyurethanes,[1–8] and in the synthesis of graft copolymers.[9–21]

Pulping for paper production is presently mainly based on sulphate and sulphite processes which favor chemical passivation of the resulting technical lignins by the increase in their degree of condensation through reactive groups and consequently of their polydispersity. This leads to poorer reactivity and to the presence of often undesirable physical (ashes) and chemical impurities (sulphur-containing moieties).

Another problem connected with the use of lignin is related to its heterogeneity. The heterogeneity of lignin is caused by variations in the polymer composition, size, crosslinking and functional groups. Differences exists in molecular composition and linkage type between the phenylpropane monomers (*p*-hydroxyphenyl, guaiacyl, and syringyl units, derived from coumaryl, coniferyl, and sinapyl alcohol precursors, respectively). Lignin composition will be different not only between plants of different genetic origin, but also between different tissues of an individual plant. In softwood lignin, the structural elements are
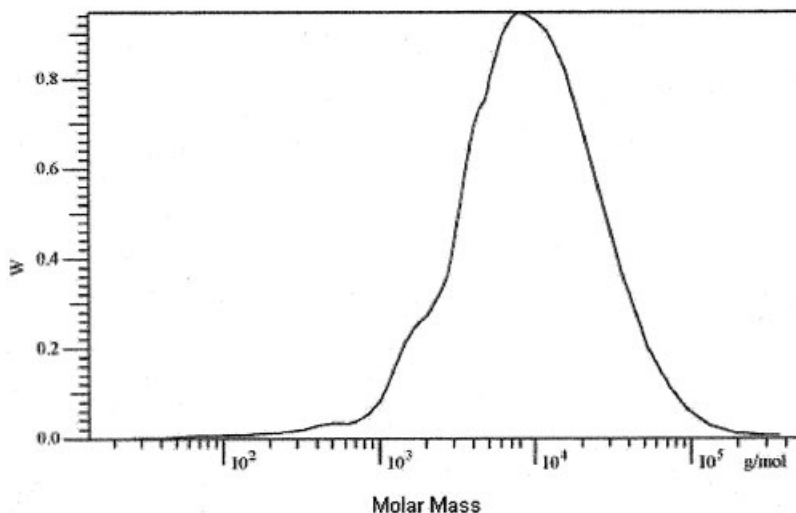
Figure 1   Molecular weight distribution in lignin from straw.

predominantly derived, for more than 95%, from coniferyl alcohol. In hardwoods (and dicotyl crops such as flax and hemp) various ratios of coniferyl/sinapyl have been observed, whereas in lignin derived from cereals straws and grasses the presence of coumaryl alcohol is typical.

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 for a short time: during this period the hemicellulose is hydrolyzed and dissolved. At the end of this period, the pressure rapidly decreases to atmospheric one in order to stop the chemical reaction. The explosive decompression gives rise to a loss of water from the cells

and the cleavage of cellular structures. The time during which the biomass is maintained in the reactor and the temperature defines the severity of the treatment. The severity parameter R_0 is defined as

$$R_0 = t \cdot \exp[(T - 100)/14.74]$$

where t is the time in minutes and T the temperature in °C.

Recently we reported that steam-exploded lignin from straw could be used as starting material in the synthesis of graft copolymers with 1-ethenylbenzene.[22] These reactions were performed by using the procedure described by Meister.[23–25]

In this article we report results obtained by using electron-poor alkenes instead of the electron-rich sty-
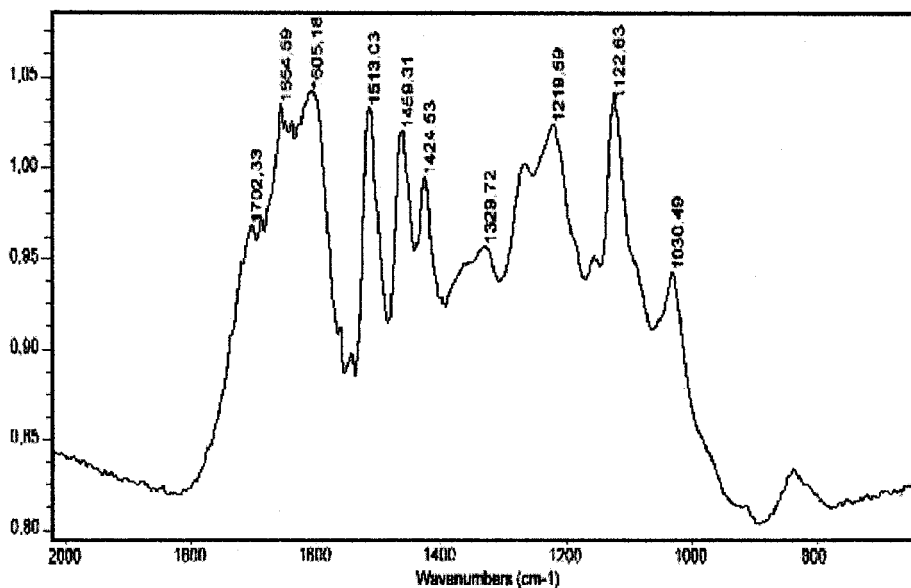

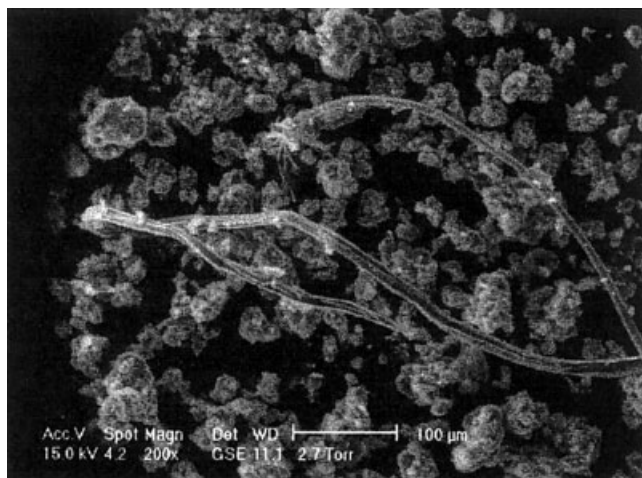**Figure 2**   FTIR spectrum of lignin from straw.

Figure 3 ESEM of lignin from straw.

rene. Furthermore, in this study we study the effects of the substituents on the efficiency of the copolymerization reactions. Finally, we compare copolymer properties of materials obtained from different lignin sources: in particular, we compare the results obtained starting from two different types of steam-exploded lignins (pine and straw) and these results with those obtained organosolv lignin.

EXPERIMENTAL

Steam-exploded lignin

The materials used as source of lignin were mechanically turned 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 out in a 10 L batch reactor, loading about 0.5 Kg of material each cycle. Treatment conditions allow to

have a severity parameter $\log R_0 = 3.94$. The raw material (100 g) was extracted two times with hot water (250–300 mL, $65 \pm 5°C$) in order 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.

Instruments

Elemental analyses were obtained with a Carlo Erba Elemental Analyzer 1106. ^{13}C and ^{1}H NMR spectra were recorded with a Bruker 300 AM instrument. All the ^{13}C NMR spectra were recorded in dimethyl sulfoxide (DMSO)-d_6. All the ^{1}H NMR spectra were recorded on acetylated samples in CDCl$_3$. Gel permeation chromatography (GPC) analyses were performed on a Hewlett-Packard HPLC by using H-P Plgel 5 μ column. The lignin samples were acetylated (acetic anhydride and pyridine) before the use. Tetrahydrofuran (THF) was used as mobile phase. Spectrophotometric grade THF was used and distilled (oven LiAlH$_4$) before the use. The chromatograms were obtained using an UV detector at 280 nm. The conversion from elution time to molecular weight was performed by using a calibration obtained by using polystyrene samples.[26] Cary 2300 spectrophotometer was used for the UV spectra. Spectrophotometric grade 1:1 acetonitrile–ethanol mixture and DMF were used as solvent.

The thermo behavior was examined by a differential scanning calorimeter (DSC 7, Perkin Elmer), on 5 $\pm$ 0.25 mg samples of the benzene soluble extracts of copolymers, in a nitrogen atmosphere, at a scanning rate of 20°C min^{-1}. Scans were performed in the temperature range of -30 to180°C. The data were ana-
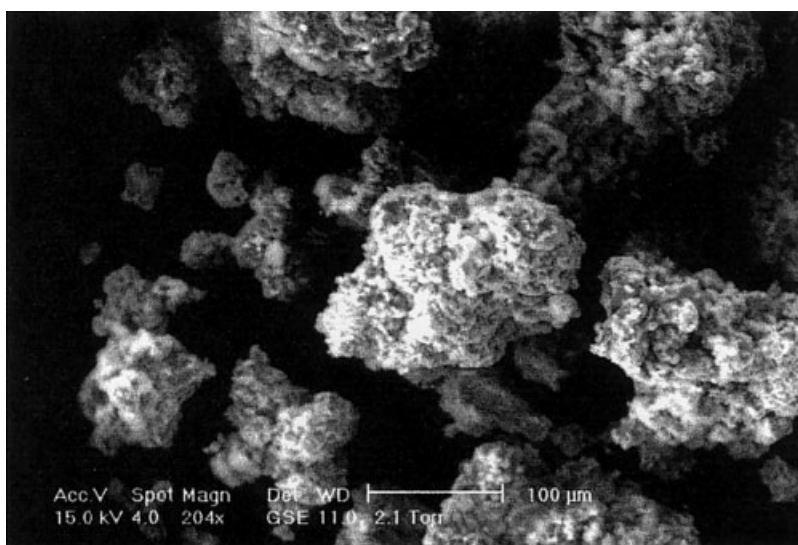

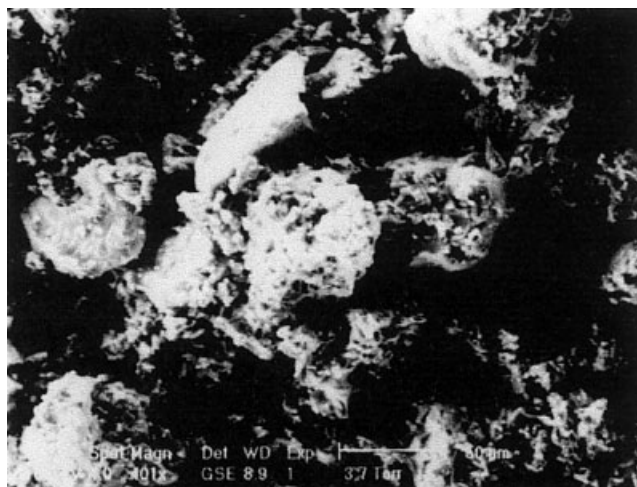**Figure 4** ESEM of lignin from pine.

Figure 5 ESEM of organosolv lignin.

lyzed 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.

Characterization of lignins from steam explosion

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 in order to characterize the lignin, but also the presence of both nitrogen, as a marker of the presence of proteins in the lignin, and of sulfur, as a marker of the presence of sulfate lignins. The presence of sulfur in our sample was not detected. The elemental analysis allows us to give the molecular weight of the lignin expressed in phenylpropanoid (C9) units. In our case the molecular formula was $C_9H_{10.22}O_{3.34}$ with a molecular weight of 172.

The distribution of acetylated lignin considering their molecular weights was obtained by using GPC. The results are depicted in the Figure 1. This way we can obtain $M_n = 3509$, $M_w = 15096$, and $M_z = 40966$.

The UV spectrum of the lignin from straw was recorded in dimethylformamide (DMF). It showed an

absorption at 321 nm (D = 16.8 L g^{-1} cm^{-1}). We recorded also the differential spectrum obtained carrying out the spectrum of the samples in 1M NaOH versus the standard solution in DMF. These data allow us to give the amount in mEq g^{-1} of some structural feature in the lignin samples. In this case we can give the amounts of syringyl and guaiacyl phenols (Type I), the amount of phenols containing conjugated double bonds (i.e., HO—Ar—CH=CH—CH$_2$OH, Type II), and the amount of stilbenic phenols (Type IV).[27] We found in our sample Type I (0.43 mEq g^{-1}) and Type IV structures (0.12 mEq g^{-1}).

The infrared spectrum of lignin is reported in Figure 2. We can observe absorption 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 vibrations 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).[28]

The ^{13}C NMR spectrum of lignin from straw showed 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 nonetherified guaiacyl units), 138 (C-1 in β-O-4 etherified syringyl units), 135 (C-4 in β-O-4 etherified and nonetherified syringyl units), 133 (C-1 in β-O-4 nonetherified guaiacyl units), 130 (C-2/ C-6 in benzoate), 120 (C-6 in etherified and nonetherified guaiacyl units), 115 (C-5 in etherified and nonetherified 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 syrigyl units), 60 (C-γ in β-O-4 erythro and threo syringyl and guaiacyl units), 56 (methoxy groups), and 34–20 ppm (CH$_3$ and CH$_2$ in saturated chains). Furthermore, the ^{1}H 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-

TABLE I
Reaction Conditions for Copolymer Synthesis

Entry	Lignin[a]	Alkene	Alkene (g)	CaCl$_2$ (mg)	H$_2$O$_2$ (mL)	DMSO (mL)	Yield (g)
1	SELP	Methyl acrylate	1.551	203	0.2	2	1.403
2	ORG	Methyl acrylate	1.551	203	0.2	2	0.622
3	SELS	Methyl methacrylate	1.803	203	0.2	2	0.012
4	SELS	Acrolein	1.011	203	0.2	2	0.616
5	ORG	Acrolein	1.011	203	0.2	2	0.183
6	SELS	Acrylonitrile	0.957	203	0.2	2	0.859

[a] SELP = steam-exploded lignin from pine; SELS = steam-exploded lignin from straw; ORG = organosolv.
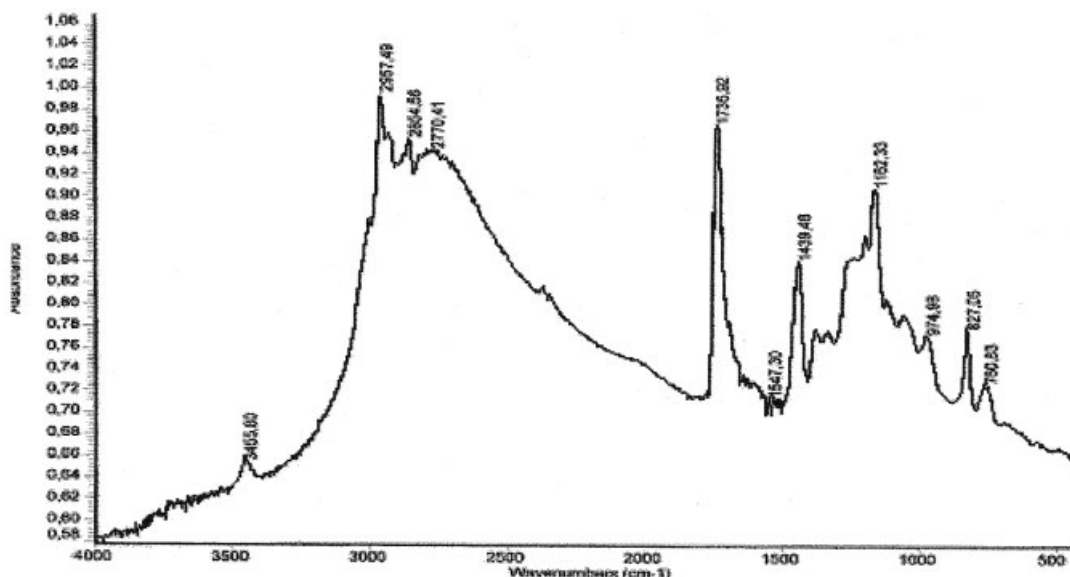
Figure 6 FTIR spectrum of the copolymer lignin from pine-methyl acrylate.

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 proton ortho to carbonyl groups).[29,30]

Figure 3 represents the environmental scanning electron microscopy (ESEM) image of the lignin from straw, where we can observe the presence of grains and fibers.

The elemental analysis of lignin from pine gave the following results: C: 68.46; H: 7.26; N: 0.00; S: 0.00; O: 24.28%. These results gave the molecular formula of $C_9H_{11.44}O_{2.40}$ with a molecular weight of 158. GPC analysis of this sample gave $M_n = 269$, $M_w = 1418$, and $M_z = 3729$. In the FTIR spectrum we can observe absorptions at 1705, 1658, 1598, 1513, 1462, 1425, 1330, 1220, 1123, 1031, and 841 cm^{-1}. The UV spectrum showed absorptions at λ 278 nm (D = 22.46 L g^{-1} cm^{-1}) and 340 nm (D = 13.00 L g^{-1} cm^{-1}). Differential spectrum showed the presence of Type II (2.03 mEq g^{-1}) and Type IV phenols (0.27 mEq g^{-1}). ^{13}C NMR spectrum showed signals at δ 180 (C=O), 148 (C-4 in etherified guaiacyl units), 135 (C-1 in etherified β-O-4 guaiacyl units), 130 (C-2/C-6 in benzoate), 129 and128 (C-α and C-β in Ar—CH=CHCH$_2$OH), 127 (C-β in ArCH=CHCHO), 124, 123, 121 (C-1 in benzoate), 120 and 119 (C-6 in etherified and nonetherified guaiacyl units), 115 (C-5 in etherified and nonetherified guaiacyl units), 113, 112 (C-2 in guaiacyl units), 111 (C-2 in guaiacyl-guaiacyl stilbenes), 110, 56 (methoxy groups), 51, 45, and 35–10 ppm (CH_3 and CH_2). The ^{1}H NMR on acetylated lignin gave signals at δ 2.0, 2.3. 3.8, 4.2, 4.4, 4.5, 5.1, 5.3, 5.8, 6, and 6.5–7.1 ppm. The ESEM image of steam exploded lignin from pine is reported in Figure 4.

Characterization of organosolv lignin

In our experiment we used also organosolv lignin (Aldrich, Milan, Italy). GPC analysis of this lignin gave $M_n = 192$, $M_w = 1570$, and $M_z = 3407$. FTIR spectrum showed absorptions at 1710, 1605, 1515, 1462, 1425, 1327, 1216, 1115, 1032, and 841 cm^{-1}. The UV spectrum (registered in 1:1 acetonitrile/ethanol mixture) had absorptions at λ 200 (D = 75.77 L g^{-1} cm^{-1}) and 268 nm (D = 16.92 L g^{-1} cm^{-1}). ^{13}C NMR spectrum showed signals at δ 148, 115, 112, 105, 60, 56, 31, and 29 ppm. The ESEM image of organosolv lignin is reported in Figure 5.

Synthesis of the copolymers

In an Erlenmayer flask lignin (200 mg) and $CaCl_2$ (Table I) were dissolved in dimethylsulfoxide (Table I). The mixture was stirred for 5 min under nitrogen. To this 30% hydrogen peroxide (Table I) was added and, after stirring for 20 min, the alkene (Table I), previously bubbled with nitrogen for 10 min, was
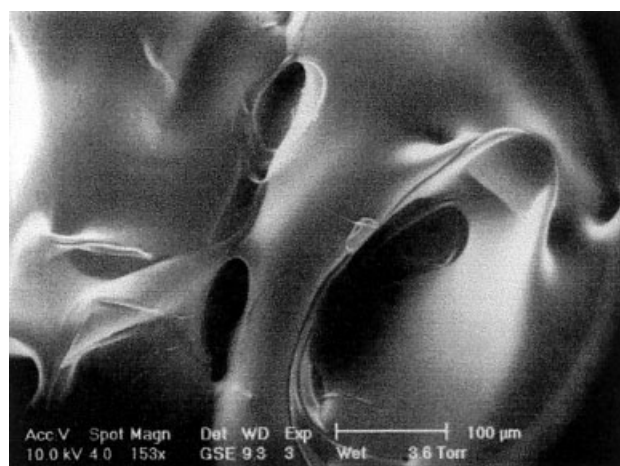

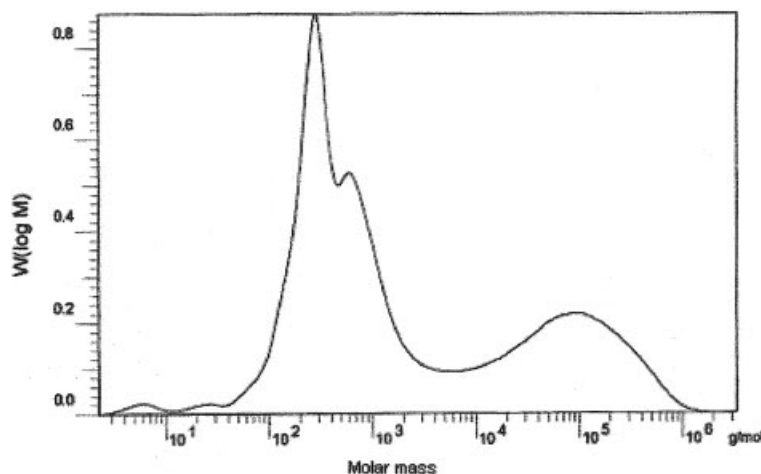**Figure 7** ESEM of the copolymer lignin from pine-methyl acrylate.

Figure 8 Molecular weight distribution in the copolymer lignin from pine-methyl acrylate.

added under nitrogen. The Erlenmayer flask was maintained at 30°C under mechanical stirring for 48 h. The mixture was treated with diluted hydrochloric acid solution (pH 2) (2 mL) and filtered on büchner. The filtered polymer was dried in an oven at 100°C overnight. The raw material was purified through extraction in benzene (200 mL) in a Soxhlet apparatus for 12 h. Lignin is not soluble in benzene: then, this procedure can allow to purify the copolymer from unreacted lignin.

All the experiments were replicated three times. We have to note that lignin is not soluble in benzene at the reflux temperature.

RESULTS AND DISCUSSION

We tested the formation of copolymer lignin-methyl acrylate. They were obtained by using the procedure described in Meister and Chen.[23] The amounts of reagents considered the best result obtained in the synthesis of the copolymer with ethenylbenzene.[22] In this experiment we use lignin from pine. The obtained results are summarized in Table I (Entry 1). The for-

mation of the copolymer was confirmed by the Fourier transform infrared (FTIR) spectrum (Fig. 6). The presence of absorptions at 1735 and 1162 cm^{-1} (C=O stretching and C—O stretching, respectively) are diagnostic for the presence of ester groups, while the same spectrum showed absorption typically present in the lignin (2922, 2855, and 3455 cm^{-1}). Also ESEM image showed that the original lignin has been deeply modified. The comparison between the images of Figures 4 and 7 clearly showed that the original granular surface has been modified into a homogeneous one.

Further information about the nature of the copolymer was obtained performing GPC analysis. In this case the analysis was carried out without acetylation of the sample: in fact, the sample was soluble in THF. The result is reported in Figure 8. We observed the formation of a large peak due to the presence of high molecular weight polymers. In this case we obtaining $M_n = 170$, $M_w = 47219$, and $M_z = 383790$, confirming the presence of a copolymer.

The thermogram of the sample showed, at 150°C, a gradual increase of the specific heat, which can be easily attributed to the glass transition of lignin (Fig.
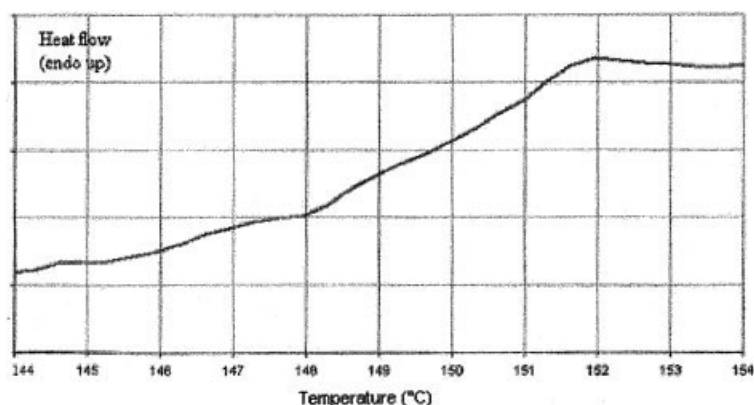

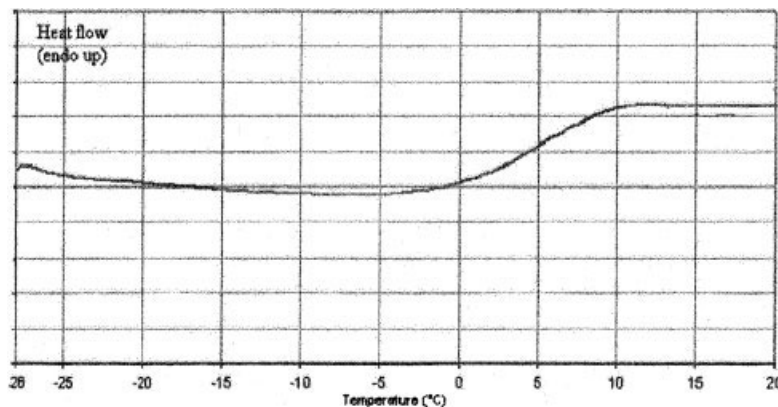**Figure 9** Thermogram of the copolymer lignin from pine-methyl acrylate.

Figure 10 Thermogram of the copolymer lignin from pine-methyl acrylate.

9). Furthermore, we observed a transition at 4.5°C, which is likely to correspond to the glass transition of grafted poly(methyl acrylate) (Fig. 10).

We tested this reaction by using a different source of lignin: in this case we used organosolv lignin. The results are reported in Table I, entry 2. The yields were lower but the properties of the obtained copolymer is similar to those described above. GPC analysis showed $M_n = 729$, $M_w = 13632$, and $M_z = 65298$. It is noteworthy that M_w and M_z were lower than those obtained by using steam-exploded lignin from pine. The FTIR spectrum showed both absorptions due to the presence of lignin (3430, 2950, 2850, 1460–1440, 1390 cm^{-1}) and absorptions due to presence of esters (1735 and 1165 cm^{-1}). ESEM image of this copolymer is similar to that reported in Figure 7.

We carried out the reaction between steam exploded lignin from straw and methyl methacrylate. The results are reported in Table I, entry 3. We can see that we did not obtain relevant amount of the product. Furthermore, this product did not show any properties diagnostic for the presence of a copolymer. In conclusion, in this case, we could not obtain the copolymer.

The reaction conditions for the reaction between steam exploded lignin from straw and acrolein are reported in Table I, entry 4. The reaction product can not be purified through extraction in benzene. The product is insoluble in all the solvent we tested; the acetylated product maintained the insolubility. Then, we could not perform GPC analysis of the product. However, the FTIR spectrum is in agreement with the formation of the copolymer (Fig. 11). We can see the band at 1721 cm^{-1}, due to the presence of aldehydic groups, and the bands at 1655, 1510, 1459, and 1124 cm^{-1}, due to the presence of lignin. The morphological analysis of the product showed that it has a granular structure with grains of greater dimension than those observed in the original lignin. The thermogram showed a gradual increase of the specific heat near -9°C, which can be attributed to the glass transition of grafted polyacrolein (Fig. 12). We do not observe the glass transition of lignin: this behavior can be explained assuming that an extensive reticulation pro-
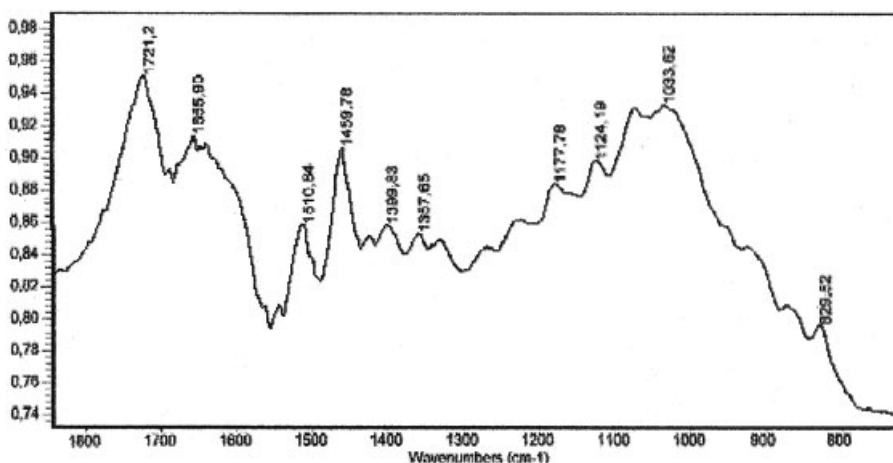

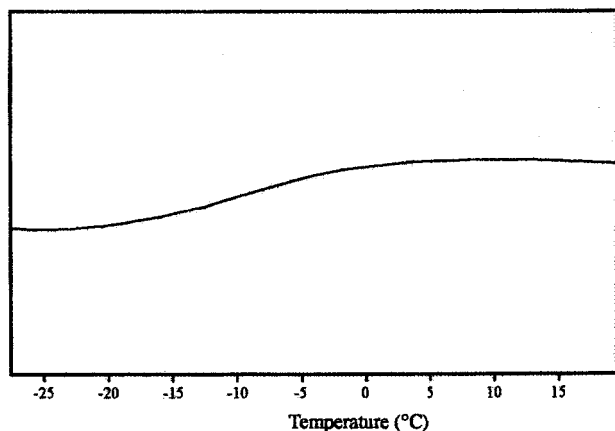**Figure 11** FTIR of the copolymer lignin from straw-acrolein.

Figure 12 Thermogram of the copolymer lignin from straw-acrolein.

cess occurred during the copolymer formation. The presence of a reticulated polymer is able to explain the low solubility of the material in the most common solvents.

Entry 5 in Table I collects the reaction conditions used in the preparation of the copolymer between organosolv lignin and acrolein. In this case, lower yield of the copolymer were obtained. This material can be analyzed by using gel permeation chromatography. This way we obtained $M_n = 685$, $M_w = 3100$, and $M_z = 5482$ in agreement with the formation of the copolymer. FTIR spectrum showed the absorption at 1720 cm^{-1}, and the thermogram the glass transition at $-8°C$.

Finally, we performed the copolymerization reaction between steam exploded lignin from straw and acrylonitrile. The reaction conditions and the yields are reported in Table I, entry 6.

GPC analysis of the product could not be performed considering the low solubility of the acetylated copol-
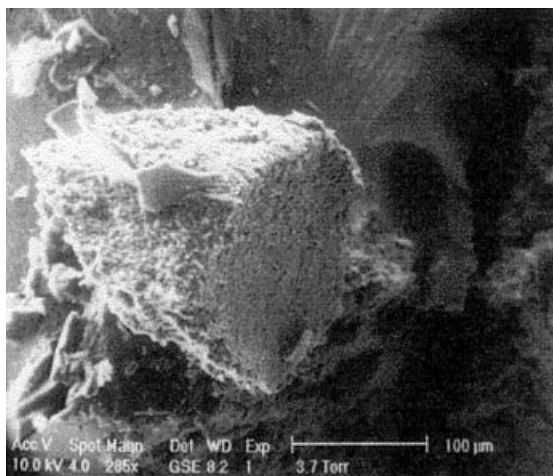

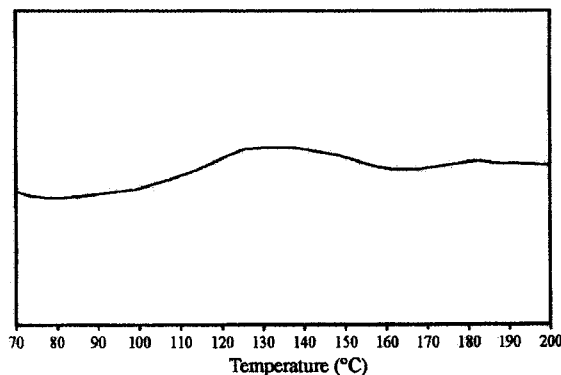**Figure 13** ESEM of the copolymer lignin from straw-acrylonitrile.

Figure 14 Thermogram of the copolymer lignin from straw-acrylonitrile.

ymer in THF. FTIR spectrum of the product showed a band at 2245 cm^{-1}, due to the C≡N stretching, together bands which can be attributed to lignin (1654, 1458, 1126, 1026 cm^{-1}). ESEM image (Fig. 13) showed the completely different morphological structure of the product in comparison with the lignin. DSC analysis of the product showed a glass transition at 119°C, which can be attributed to grafted polyacrylonitrile chains, and a gradual increase of the specific heat near 178°C, which can be attributed to the glass transition of lignin (Fig. 14). The high value of T_g can be explained assuming a more reticulated structure for lignin after the copolymerization process.

CONCLUSIONS

In conclusion, we have shown that lignin from steam explosion could be a good raw material in the preparation of graft copolymers. We were able to prepare copolymers from all the samples. Furthermore, in spite of the only experiments we could carry out, lignin from pine gave better results than that from straw. This behavior can be explained on the basis of the structural properties of the used lignins: both UV and ^{13}C NMR analyses showed in the lignin from pine a consistent amount of structures bearing a double bond, while this moiety was not identified in lignin from straw. Obviously, we need the presence of double bond to induce copolymerization.

Finally, lignin from steam explosion gave better results than organosolv lignin. Also in this case, structural properties of this lignin showed a low content of double bonds able to participate to the formation of the copolymers.

It is interesting to note that we was not able to synthesize graft copolymers between steam explosion lignin and methyl methacrylate, as described in a previous work.[19]

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