

Sulfur-Free Lignins as Composites of Polypropylene Films

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SYNOPSIS

To elucidate the effect of lignin addition, polypropylene films containing 2–10 wt % of spruce organosolv lignin and/or beech wood prehydrolysis lignin were compared with lignin-free polymers with respect to tensile strength and elongation before and after aging. The physicochemical properties of the lignin-containing films were investigated by conductivity measurements, surface behavior, and UV and IR spectroscopy. © 1993 John Wiley & Sons, Inc.

INTRODUCTION

Recently, lignin coproducts of pulping have attracted great attention for their utilization in engineering plastics because it has been well recognized that lignin in its natural or degraded state is a crosslinked polymer with tetrafunctional branch points.¹ At present, the typical technical lignins are kraft lignin and lignin sulfonate. The characteristics of kraft lignin as a polymer are utilized in preparation of three-dimensional polymers such as polyurethanes or phenol resins.^{2–5} Kraft lignin was also tested as a specific filler, improving tensile strength and modulus for rubber, which leads to an increase of hardness and improvement of abrasion.^{6,7}

The objective of the present article was to study sulfur-free lignins derived from the methanol-based organosolv pulping of spruce wood, as well as from beech wood prehydrolysis, as a composite of polypropylene (PP) films. In our experiments, lignin was not examined with the aim to replace a synthetic component but rather to investigate the effect of lignin addition on modification of mechanical and physicochemical properties of polyolefin films.

EXPERIMENTAL

Materials

Isotactic nonstabilized PP (melt index = 3–4) (TATREN HPE Slovnaft, Bratislava) was used as matrix polymer.

Organocell lignin (OL) (Organocell Gm 6H Corp., München) is a coproduct of organosolv pulping of spruce wood. In the first stage of this process, the chips are cooked in a 50/50 mixture of water and methanol (190°C, 50 min) and in the second stage sodium hydroxide, at a concentration of 18–28%, is added (165°C, 60 min).

Water-soluble lignin (WL) was obtained as a coproduct of a prehydrolysis stage of kraft beech wood pulping (Bukóza, Vranov). The prehydrolysis was carried out at 170°C under a pressure of 1 MPa for 1 h with the ratio of wood to water 1 : 2.5. The pH of the obtained prehydrolyzate was 4.5.

Lignin Characterization

¹³C nuclear magnetic resonance (NMR) spectrum was recorded in Me₂SO at 303 K on a Bruker AM 300 spectrometer operating at 300 MHz. The carbohydrate content was determined by the method involving acid hydrolysis, NaBH₄ reduction, acetylation, and gas chromatographic separation of the alditol acetates.⁸ Gel permeation chromatography (GPC) was performed on a column (53 × 8 cm) of Sephadex LH 60 using a mixture of dioxane and water containing 0.005M aqueous NaOH and 0.001M LiCl (7 : 3) as the eluant. The ultrastructure was determined by using a scanning electron microscopy JSM-U3.

Polymer Samples

Polymer blends were prepared by mixing PP powder and lignin in a two-roll mill for 1 h in the presence or absence of 0.15 wt % 2,6-di-tert-butyl-4-meth-

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Table I Characteristics of the Lignin Preparations

Sample	Elemental Composition	\overline{M}_w	\overline{M}_n	<i>D</i>	Carbohydrates	
					Content (%)	Molar Ratio (Gl : Xyl : Man : Gal)
Organocell lignin	C ₉ H _{8.10} O _{2.50} /OCH ₃ /0.95	3300	1100	3.0	2	1 : 3 : 2 : 2
Water-soluble prehydrolysis lignin	C ₉ H _{8.66} O _{2.36} /OCH ₃ /1.00	2000	1660	1.2	17	1 : 3

ylphenol (AO4K) and 0.15 wt % calcium stearate. The content of lignin was 2, 4, 6, 8, and 10 wt %. Then, the blends were homogenized in a single screw extruder at 200°C. The extrudates obtained were then cut into pieces for grinding in a granulator. Films about 40–60 μm thick were molded from the mixture at 200°C.

Polymer Characterization

Thermogravimetric analyses were carried out using a Paulik-Paulik-Erdel simultaneous TG-DTA apparatus at a heating rate of 6°C min⁻¹ in nitrogen. The flow properties of the composite blends were obtained with a plastomer VP-05 Chemopetrol Sa-

talice at 230°C. Electrical conductivities of PP films were determined using a Picoammeter NC 0120 by measuring resistance (V/I) at voltage V = -100. Tensile strength and elongation data were obtained with an Instron tester on specimens cut in accordance with CS standards procedure 640 604. IR and UV spectra were measured with a Perkin-Elmer 457 spectrometer and Specord Carl Zeis M 40, respectively.

RESULTS AND DISCUSSION

Lignin-containing PP films were prepared using two sulfur-free lignins differing in their genetic origin,

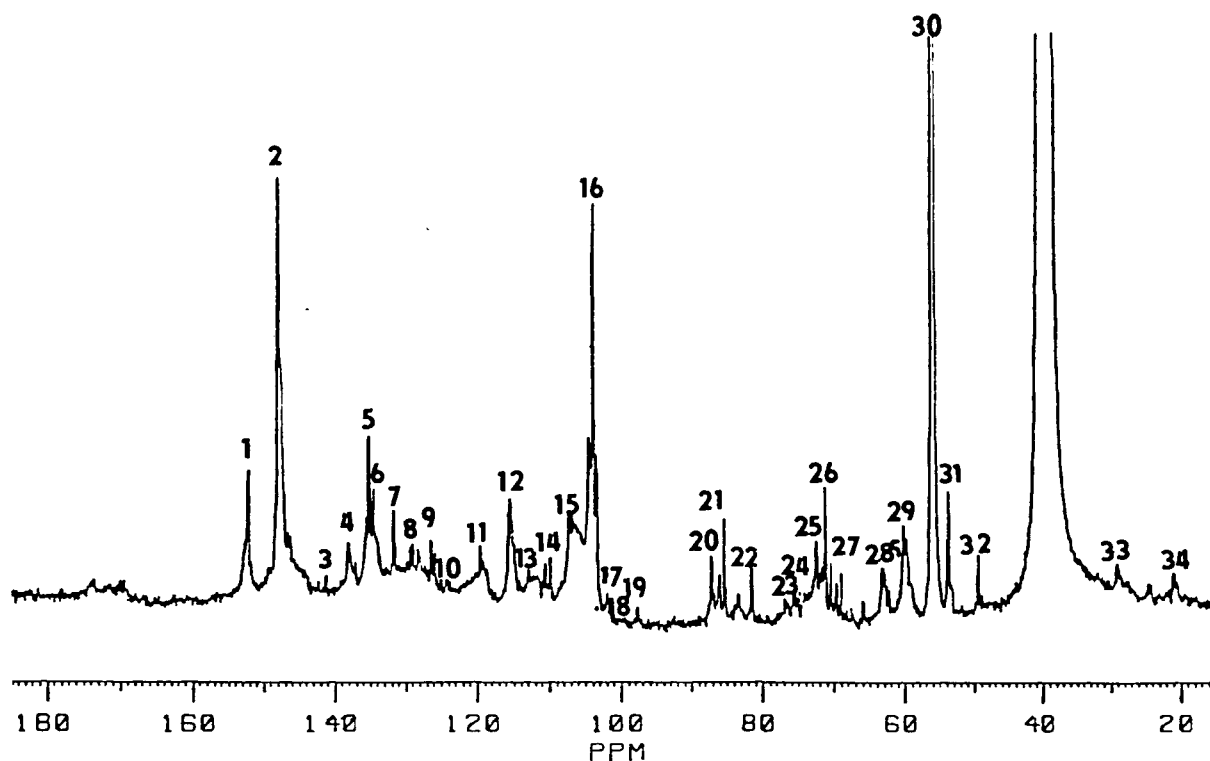


Figure 1 ¹³C NMR spectrum of lignin isolated from water prehydrolyzate of beech wood (WL).

Table II Assignments of ^{13}C NMR Signals in the Spectrum of Lignin Precipitate from Beech Wood Prehydrolyzate

Signal	δ ppm	Assignment of Signals
1	152.1	C-3/C-5 (S) β -O-4 e
2	147.4	C-3 (G), C-3/C-5 (S) n
3	141.8	C-4 (G) substituted on C-5
4	138.0	C-1/C-4 (S) e, C-6 in α -6
5	134.4	C-1 (G) e, C-4 in β - β
6	134.0	C-1 in α -6
7	131.4	C-2/C-6 <i>p</i> -hydroxybenzoates
8	129.3	C $_{\beta}$ vinyl in cinnamaldehyde
9	126.5	C-6 with $\alpha\text{C}=\text{O}$, C-1 in 5-5, α -6
10	124.0	C-6 C-5 C-1 in 5-5
11	119.5	C-6 in β -5
12	115.1	C-5 (G) e, n
13	111.7	C-2 (G) e, n
14	110.0	C-2 in β -5
15	106.8	C-2/C-6 (S) with $\alpha\text{C}=\text{O}$
16	104.4	C-2/C-6 (S) β -O-4, with C $_{\alpha}$ HOH
17	103.6	C-2/C-6 (S)
18	101.7	C-1 xyl internal unit
19	97.3	C-1 xyl red. end unit
20	87.0	C $_{\alpha}$ in β -5
21	85.9	C $_{\alpha}$ in pinoresinol
22	85-82	C $_{\alpha}$ in β -O-4
23	75.5	C-4, xyl internal unit
24	74.0	C-3, xyl internal unit
25	72.2	C $_{\alpha}$ in β -O-4
26	71.8	C $_{\alpha}$ in syringaresinol/pinoresinol
27	69.5	C-4 xyl non red. end unit
28	62.9	C $_{\alpha}$ in β -O-4 with $\alpha\text{C}=\text{O}$
29	60-59	C $_{\alpha}$ in β -O-4
30	55.9	OCH $_3$
31	53.4	C $_{\beta}$ in syringaresinol
32	49.0	
33	28.8	CH $_2$ in side chain
34	21.0	αCH_3

(G), guaiacyl; (S), syringyl; e, etherified; n, not etherified.

method of isolation, molecular weight, polydispersity, and carbohydrate content and composition. The characteristics of lignins used in this study are summarized in Table I. The OL of average molecular mass $\bar{M}_w = 3000$ was isolated by acidification of the combined water-methanol and sodium hydroxide-spent liquors from organosolv pulping of spruce wood. The chemical structure of OL was described by Linder and Wegener.⁹

In contrast, the lignin dissolved during prehydrolysis together with hemicelluloses, as a result of solvolytic reactions in beech wood, and precipitated

during evaporation of prehydrolyzate was not investigated in detail. Its ^{13}C NMR spectrum is illustrated in Figure 1. The chemical shifts and signal assignments of different structural entities are compiled according to literature data^{10,11} (Table II).

The precipitated lignin is a copolymer of guaiacyl and syringyl units containing, in comparison to other technical lignin preparations, a higher amount of polyether bonds and a certain amount of hemicelluloses, mainly xylan, evident from the ^{13}C NMR spectrum as well as from the results of its acid hydrolysis. This confirms that part of lignin is dissolved during prehydrolysis as the lignin-xylan complex isolated from the native beech wood in our previous article.¹² The weight average molecular mass of WL was, as determined by GPC analysis, 2000. Its molecular mass distribution was much narrower than that of the OL (Table I).

The ultrastructure of lignin preparations was established by scanning electron microscopy (SEM). As shown in Figure 2, lignin globular particles vary

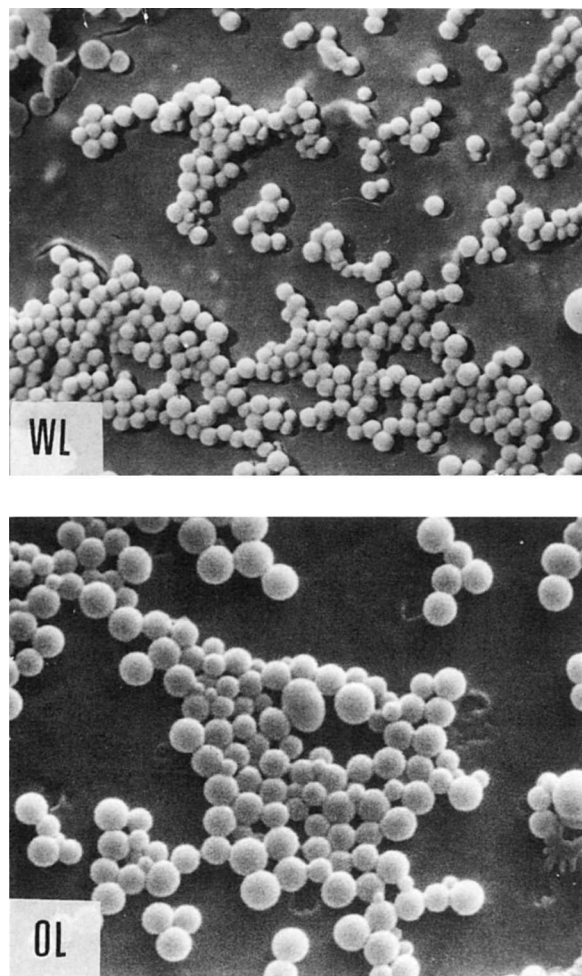


Figure 2 SEM of lignins. Magnification $\times 10,000$.

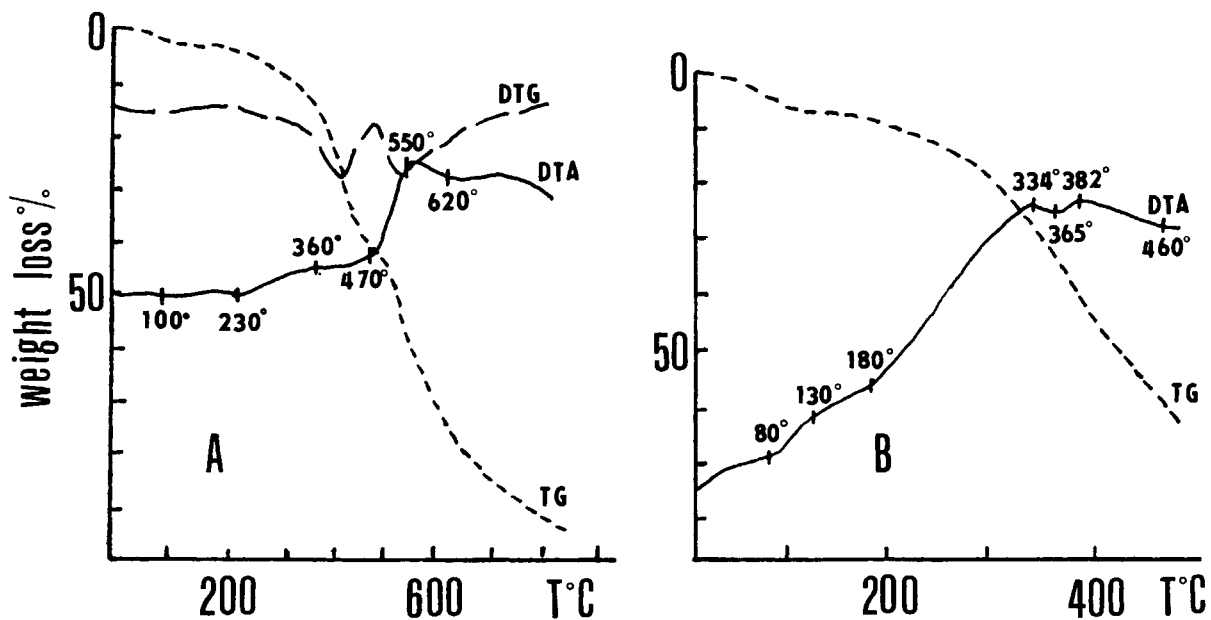


Figure 3 DTA, TG, and DTG curves of organocell lignin (A) and water prehydrolysis lignin (B).

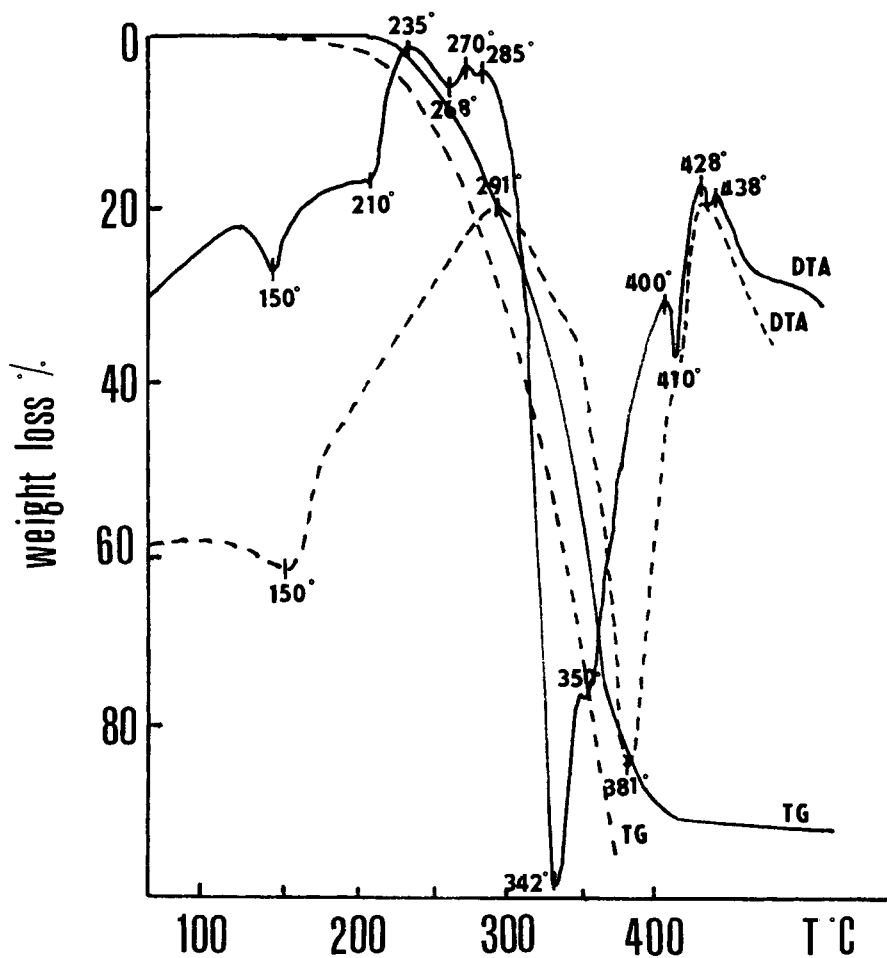


Figure 4 DTA and TG curves of lignin-free PP blend (---) and PP blend containing 2 wt % (—), lignin (WL).

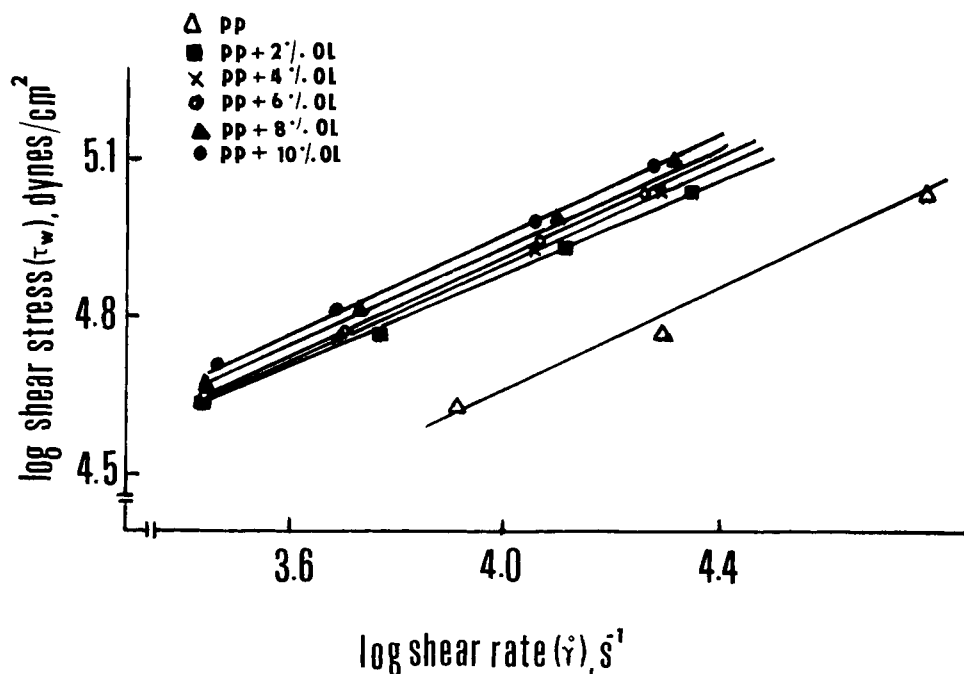


Figure 5 Flow curves of PP blends modified with organocell lignin (OL).

slightly in size similar to those of wood lignin preparations (BNL, methanollignin).¹³ The irregular aggregates, typical for technical lignins isolated from spent liquors, were not observed.¹⁴

Thermogravimetric analysis of both lignins (Fig. 3) showed that their thermal stability is sufficient up to 200°C. The determined weight loss was less

than 5%. The lignin-containing PP blends were therefore prepared at 200°C to avoid thermal decomposition and/or evaporation of volatile components from lignin. The mutual comparison of both lignin preparations indicates that OL is more thermostable compared to WL. This is in agreement with the observation of Sergeeva,¹⁵ that lignin from soft-

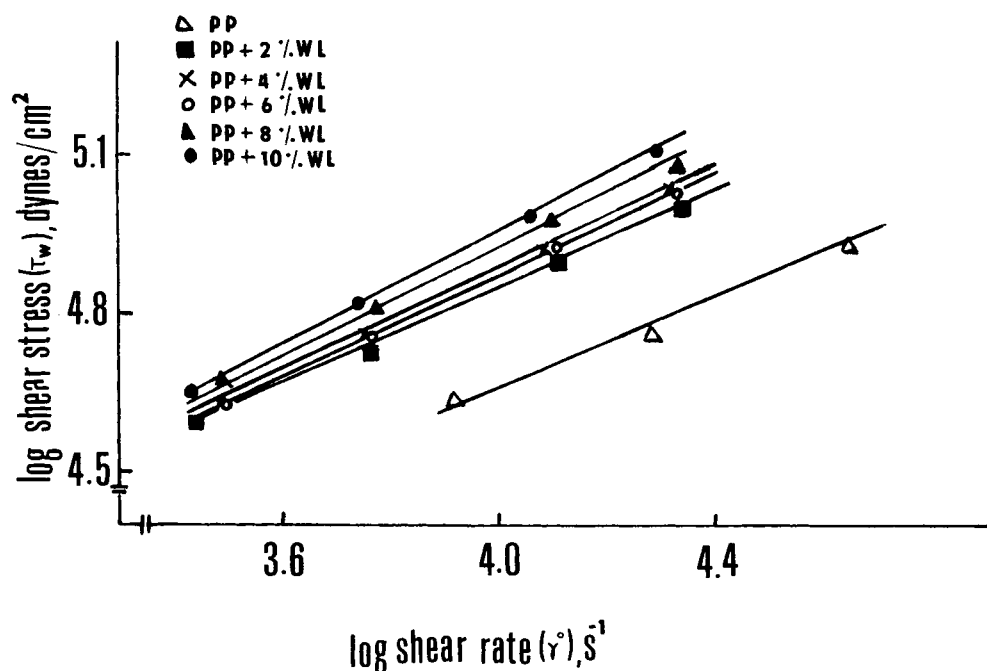


Figure 6 Flow curves of PP blends modified with water prehydrolysis lignin (WL).

Table III Mechanical Properties of PP Films

Sample No.	Composition	Tensile Strength δ_r (MPa)	Elongation ϵ_r (%)	Retention after Aging ^a	
				Tensile Strength δ_r (%)	Elongation ϵ_r (%)
1	Stabilized PP	70.9	700	51.6	48.5
2	Stabilized PP + 2 wt % WL	80.1	700	56.2	100
3	PP + 2 wt % WL	76.5	600	43.6	52.8
4	PP + 2 wt % OL	76.0	780	41.5	51.8
5	PP + 4 wt % OL	73.2	780	34.1	49.2
6	PP + 6 wt % OL	72.7	780	—	—

^a Aging at 100°C for 168 h.

woods, regardless of the isolation methods, has higher thermal stability than lignin from hardwoods.

With regard to the molecular, structural, and thermal characteristics, both sulfur-free lignin preparations seem attractive for incorporation into polymeric materials. In our experiments, a series of PP blends containing weight lignin fractions 2, 4, 6, 8, and 10 wt % was prepared in the presence or absence of stabilizer by mechanical mixing of both powdered components in a homogenizer at 200°C.

The thermal effects that accompanied the interaction between PP and lignin are evident from the comparison of differential thermal analysis (DTA) curves of pure PP and PP containing 2 wt % lignin (Fig. 4). The latter contains an exothermic peak starting at 200°C. The presence of this peak in thermograms of lignin-modified PP indicates a chemical reaction between PP and lignin during thermal processing of the composite blends.

The rheological characterization of the blends investigated was carried out at 230°C. The flow curves in Figures 5 and 6 are plotted in terms of logarithm shear stress (τ_w) vs. logarithm shear rate ($\dot{\gamma}_w$) over a range of lignin content from 2–10%. The curves are all straight lines with slopes of about 0.5 over shear rates ranging from 10^3 – 10^4 s⁻¹. Although the shape of the flow curves was similar in all cases, the absolute values of shear rates were lower in the case of lignin-containing PP blends compared to pure polymer. This observation indicates the increased viscosity of the blends. On this basis, the chemical interaction between PP and lignin, resulting in an increase of crosslinks, can be suggested.

The polymer granulation products were used for the preparation of films with thickness 40–60 μ m. The lignin-containing PP films obtained were optically transparent and appeared to be homogenous. To elucidate the effect of lignin addition, these films were compared with lignin-free polymers with re-

spect to mechanical and physicochemical properties. From Table III it is seen that tensile strength and elongation were not significantly influenced by addition of both types of lignins over the range from 2–10 wt %. The heat aging of PP films, carried out at 100°C for 168 h, results in a similar worsening of the stability of both lignin-free and lignin-modified PP films. Only in the case of the stabilized PP containing 2 wt % of WL the elongation value remained unchanged (Table III).

The physicochemical properties of the lignin-modified PP films were studied by conductivity measurements, surface behavior, and UV and IR spectroscopy. The data summarized in Table IV show the electrical properties of PP films with various weight percent of lignin. The conductivities of the films prepared are slightly higher than those prepared without lignin.

The relationship between water contact angle and the weight percents of both lignins in the composite films (Fig. 7) illustrates a mild drop of the contact

Table IV Effect of Lignin Content on the Conductivity of PP/Lignin Composites

Composite	Conductivity (s cm ⁻¹)
PP	1.74
PP + 2 wt % WL	1.89
PP + 4 wt % WL	1.91
PP + 6 wt % WL	1.92
PP + 8 wt % WL	1.93
PP + 10 wt % WL	1.93
PP + 2 wt % OL	1.88
PP + 4 wt % OL	1.90
PP + 6 wt % OL	1.92
PP + 8 wt % OL	1.96
PP + 10 wt % OL	1.97

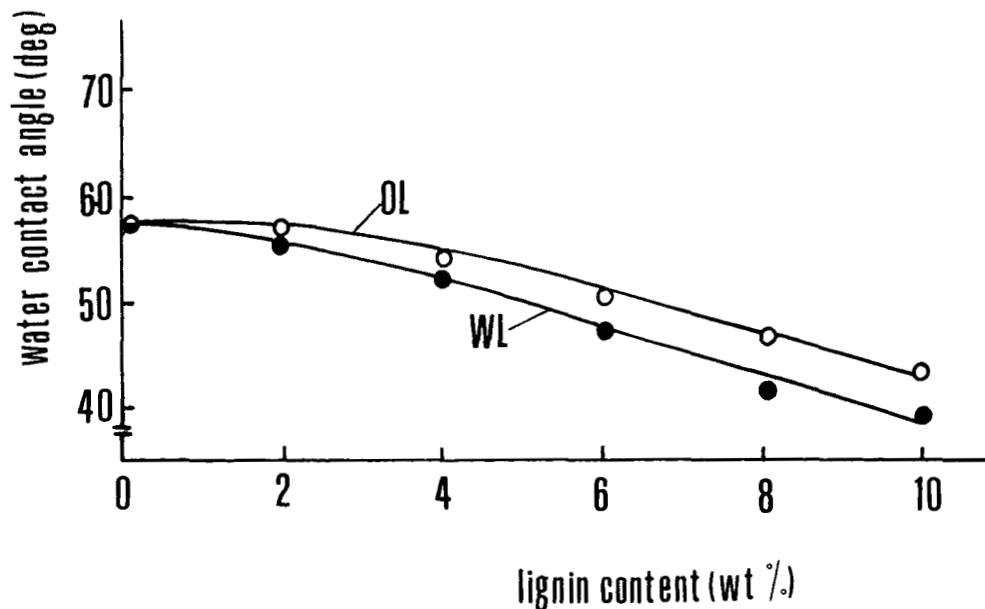


Figure 7 Relationship between water contact angle and lignin content in PP films.

angles with the increasing lignin content, particularly in the case of WL. Based upon the obtained results, it can be concluded that lignin addition modified the surface properties of PP, resulting in increase of its hydrophilicity.

The structural changes of lignin during film processing were investigated by IR spectroscopy. The comparison of the spectrum of original OL with the difference spectrum of PP film containing 4 wt % OL and pure polymer (Fig. 8) revealed some differ-

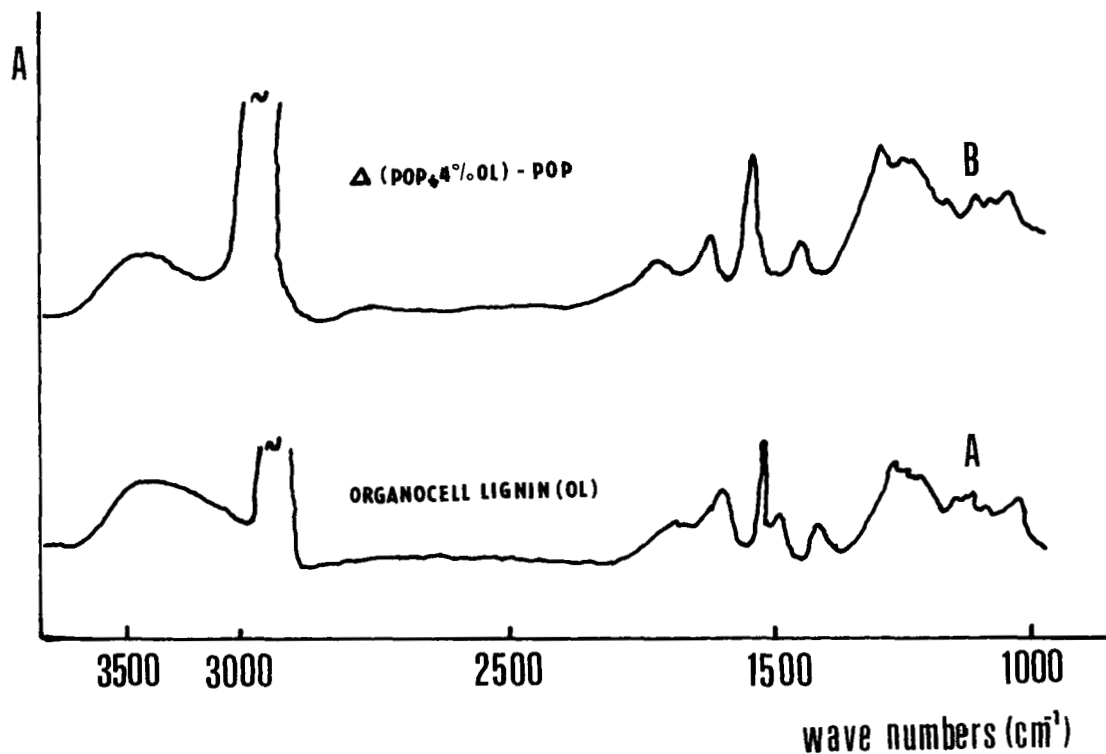


Figure 8 Infrared spectrum of organocell lignin in nujol (A) and difference spectrum of organocell lignin (B): PP subtracted from the spectra of PP film containing 4 wt % organocell lignin.

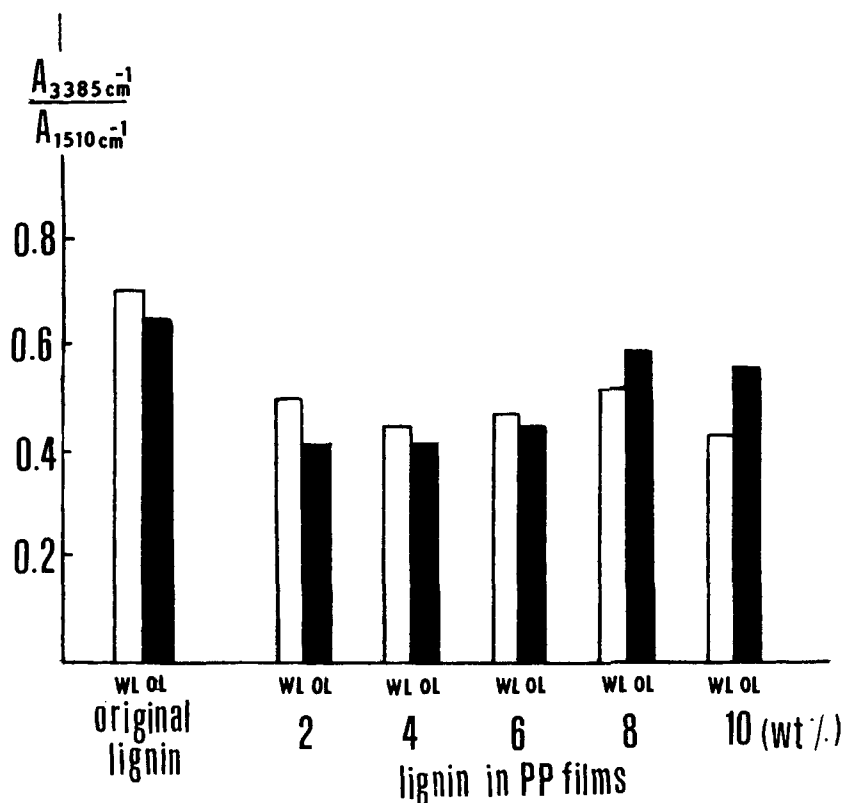


Figure 9 Relationship between OH stretching vibrations ($A_{3385\text{ cm}^{-1}}/A_{1510\text{ cm}^{-1}}$) and the weight percents of lignin in the PP films.

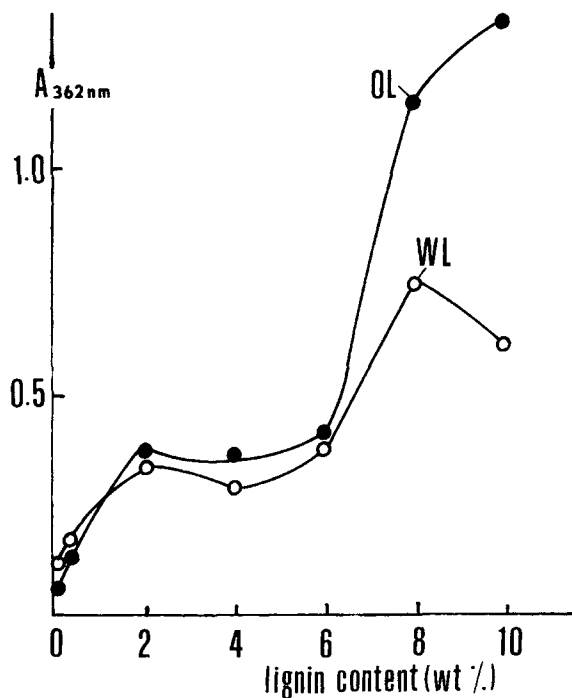


Figure 10 Hydroperoxide radical concentration ($A_{362\text{ nm}}$) as a function of lignin content in PP films.

ences in the absorbance of hydroxyl groups, considered the most effective functional groups regarding thermooxidation stability of PP films. The quantitative changes in the intensity of the O—H band at 3385 cm^{-1} in the spectra of the lignin component in PP films investigated are shown in Figure 9. The absorbance of this band related to 1510 cm^{-1} (aromatic vibrations) is lower in all composite samples than that in the original lignin sample. The decrease is most remarkable in the films containing OL and/or WL in 2–3 wt %, which is probably optimal regarding lignin function as stabilizer.

The hydroperoxide radical measurements in the PP film containing lignin, determined by UV spectroscopy ($A_{362\text{ nm}}$), supported the above-described conclusion (Fig. 10). The plot of the concentration of hydroperoxide radicals vs. lignin content in PP reveals minimum at concentration of lignin about 2–3 wt %. The obtained results confirm the suggestion¹⁶ that phenolic structures in lignin represent potential radical scavengers by terminating chain reaction of polymers induced by oxygen and its radical reduction products, whereby phenoxy radicals are formed. Higher lignin content probably

initiates the competition radical reactions, leading to oxidative degradation of PP by hydroperoxide radical mechanism. OL is more effective in this direction.

CONCLUSIONS

1. The incorporation of sulfur-free nonderivatized biopolymers as OL and/or wood prehydrolysis lignin into PP in amounts from 2–10 wt % represents a cheap and simple process for their utilization.
2. The rheological behavior of the composite polymer blends indicates good compatibility of lignin with PP.
3. Thermal effects of composites as well as structural characteristics of lignin components in the films investigated indicate chemical interaction of lignin with PP, resulting in crosslink formation.
4. The lignin-modified PP films with sufficient tensile strengths could be obtained in the absence of commercial stabilizers with lignin content 2–10 wt %.
5. Lignin-modified PP films absorbing UV light could be prospectively utilized in the food packing industry.

REFERENCES

1. K. V. Sarkanen and C. H. Ludwig, *Lignins—Occurrence, Formation, Structure and Reactions*, Wiley Interscience, New York, 1971, p. 758.
2. S. I. Falkehag, *Appl. Polym. Symp.*, **28**, 247 (1975).
3. V. P. Saraf, W. G. Glasser, G. L. Wilkes, and J. E. McGrath, *J. Appl. Polym. Sci.*, **30**, 2207 (1985).
4. H. Yoshida, R. Mörck, K. P. Kringstadt, and H. Hatakeyama, *J. Appl. Polym. Sci.*, **34**, 1187 (1987).
5. H. H. Nimz, in *Wood Adhesives*, A. Pizzi (Ed.), Marcel Dekker, New York, 1983.
6. E. G. Lubeskina, *Usp. Khim.*, **52**, 1196 (1983).
7. E. G. Lubeskina, L. T. Belova, and M. L. Fribman, *Mech. Polym.*, **3**, 535 (1977).
8. J. Shapira, *Nature*, **222**, 792 (1966).
9. A. Linder and G. Wegener, *Papier*, **42**(10A), V1 (1988).
10. H. Nimz, D. Robert, O. Faix, and M. Nome, *Holzfor-schung*, **35**, 16 (1981).
11. M. Bardet, M. F. Foray, and D. Robert, *Macromol. Chem.*, **186**, 1495 (1985).
12. B. Košíková, J. Polčín, and D. Joniak, *Cell. Chem. Tech.*, **7**, 605 (1973).
13. B. Košíková, L. Zákutná, and D. Joniak, *Holzfor-schung*, **32**, 15 (1978).
14. J. Mlynár, B., Košíková, L. Zákutná, M. Micko, and L. Paszner, *Cell. Chem. Tech.*, **24**, 475 (1990).
15. B. N. Sergeeva, *Chim. Drevesiny*, 245 (1968).
16. K. Kratzl, P. Claus, W. Lonsky, and J. S. Gratzl, *Wood Sci. Tech.*, **8**, 35 (1974).

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