Photooxidation of the Composite Lignin/Polypropylene Films

[a]B. KOŠÍKOVÁ, [a]M. KAČURÁKOVÁ, and [b]V. DEMIANOVÁ

[a]Institute of Chemistry, Slovak Academy of Sciences, CS-842 38 Bratislava

[b]Department of Fibres and Textile, Faculty of Chemical Technology, Slovak Technical University, CS-812 37 Bratislava

The course of photooxidation of the films prepared in the absence of commercial stabilizers from polypropylene blends containing beech prehydrolysis lignin or spruce organosolv lignin in content up to 10 mass % was examined. The results obtained demonstrate that lignin can act as stabilizer or initiator of degradation of polypropylene depending on the type and content of lignin preparation in polymer blends.

Lignin is one of the main wood components. A unique property of lignin is that it is very stable in nature and actually acts as a stabilizer towards various stresses to which the plant is subjected. It is a commercially available nontoxic amorphous phenylpropane biopolymer which is obtained as co-product in pulp production by sulfite or sulfate processes. Both technologies cause reactivity change of lignin that is the limiting factor for its utilization in polymer production.

According to literature data [1—3] lignin can be incorporated after the chemical modification into different polymer materials as polyurethane and/or phenolformaldehyde resins. Kraft lignin was also shown as effective additive for rubber leading to the improvement of abrasion [4, 5]. Moreover, its positive effect on cross-linking of polypropylene (PP) was described [6].

As to some disadvantages of kraft lignin application, the effect of new types of lignin products, derived from new chemical technology of wood treatment based on using of organic solvents or high-temperature wood steaming, on the photooxidation of PP was investigated in this paper. The rheological and thermal behaviour of the lignin/PP blends as well as the physicomechanical properties of the resulted composite films were described in our previous study [7]. The results obtained showed good compatibility of both lignin preparations with PP.

EXPERIMENTAL

Prehydrolysis lignin (PL) $(C_9H_{8.66}O_{2.36}(OCH_3)_{1.00})$ is commercially available product (Bukóza, Vranov) precipitable from water prehydrolyzate of beech wood (170 °C, 1 h) during its evaporation.

Organocell lignin (OL) $(C_9H_{8.10}O_{2.50}(OCH_3)_{0.95})$ (GmbH corporation, München) was obtained by

Table 1. Composition of Polymer Blends Based on Polypropylene and Lignin Preparations PL and OL

w(PP)/%	w(Stabilizer)/%	Lignin preparation	
		w(PL)/%	w(OL)/%
99.7	0.3	–	–
97.7	0.3	2	–
98.0	–	2	–
96.0	–	4	–
94.0	–	6	–
92.0	–	8	–
90.0	–	10	–
99.9	–	–	0.1
99.6	–	–	0.4
99.3	0.3	–	0.4
99.3	–	–	0.7
99.0	–	–	1.0
98.0	–	–	2.0
96.0	–	–	4.0
94.0	–	–	6.0
92.0	–	–	8.0
90.0	–	–	10.0

acidification of the combined spent liquors from two-step delignification of spruce wood (methanol—water $(\varphi_r = 1 : 1)$, 190 °C, 50 min; 18—28 % NaOH, 165 °C, 60 min).

The polymer blends (Table 1) were obtained by mixing of polypropylene powder (TATREN, Slovnaft, Bratislava) with powdered lignin samples in roll mill for 1 h and then granulated in homogenizer (FORTUNA) at the temperature of 200 °C. The composite lignin/PP films (40—60 μm) were prepared from the granulates by extrusion in the presence or absence of commercial stabilizer 2,6-di-*tert*-butyl-4-methylphenol (0.15 mass %) + calcium stearate (0.15 mass %).

Photooxidation was carried out in an equipment described elsewhere [8] using 125 W medium-pressure mercury arc RVC (Tesla, Holešovice) at 60 ± 5 °C (λ = 310 μm). IR spectra of prepared films were measured with a spectrophotometer G 983

(Perkin—Elmer). ^{13}C NMR spectrum was recorded in DMSO at 303 K on a spectrometer AM 300 (Bruker) operating at frequency 300 MHz.

The lignin preparations were analyzed by gel permeation chromatography on a column (53 cm × 0.8 cm) of Sephadex LH 60 using a mixture of dioxane and water containing 0.005 M-NaOH and 0.001 M-LiCl (φ_r = 7 : 3) as the eluant. The column was calibrated with a series of lignin fractions the molecular masses of which had been determined by ultracentrifugation [9]. The mass average molecular masses ($\bar{M}_m$) of the samples were calculated from molecular mass distributions according to *Faix et al.* [10].

RESULTS AND DISCUSSION

A series of PP films of 0.1 to 10 mass % lignin content was prepared in the absence of commercial stabilizers by using of lignin precipitate (PL) formed during evaporation of beech wood prehydrolyzate as well as of organosolv lignin (OL), precipitated by acidification of spent liquor from methanol-based organosolv pulping of spruce wood. The composition of the polymer blends is summarized in Table 1.

The elemental analysis as well as the comparison of the infrared spectra of both samples (Fig. 1) indicates the structural differences as a result of different genetic origin and method of isolation. PL is the typical hardwood lignin that is dissolved during prehydrolysis of beech wood together with xylan. Spruce organosolv lignin (OL) isolated from softwood

consists mostly of guaiacyl units. The quantitative analysis of its IR spectrum shows that the band at $\bar{\nu}$ = 1270 cm^{-1} corresponding to the aromatic methoxyl groups in the guaiacyl units is more intense than that at $\bar{\nu}$ = 1230 cm^{-1} assigned to C—O stretching vibration in syringyl derivatives related to the band at 1510 cm^{-1} (aromatic vibrations): A(1230 cm^{-1})/A(1510 cm^{-1}) = 0.91 and A(1270 cm^{-1})/A(1510 cm^{-1}) = 1.04, respectively. The reverse is true for PL, containing both guaiacyl and syringyl moieties: A(1230 cm^{-1})/A(1510 cm^{-1}) = 1.08 and A(1270 cm^{-1})/A(1510 cm^{-1}) = 0.81, respectively. OL contains higher amount of phenolic hydroxyl groups (5.0 %) compared to PL (4.4 %) as was determined from IR spectra of acetylated derivatives. Further structural characteristics of OL were described earlier [11].

The lignin nature of PL, undesired coproduct of beech wood prehydrolysis, was also confirmed by ^{13}C NMR analysis (Fig. 2, Table 2). The spectrum obtained is very similar to that of milled wood lignin (MWL) isolated from native birch wood [12]. The intensities of the signals *18, 19, 23, 24* corresponding to hemicelluloses, mainly xylan, were very low.

With regard to the mass average molecular mass ($\bar{M}_m$ = 2000 and 3300) for PL and OL, respectively, both commercially available lignin preparations seem to be attractive for incorporation into PP.

To elucidate the effect of lignin addition, the films (thickness 40—60 μm) prepared from the lignin/PP composite blends were compared with lignin-free polymer with respect to the photooxidation rate. All samples were photo-irradiated in air at 60 °C. Oxygenated products formation has been monitored by

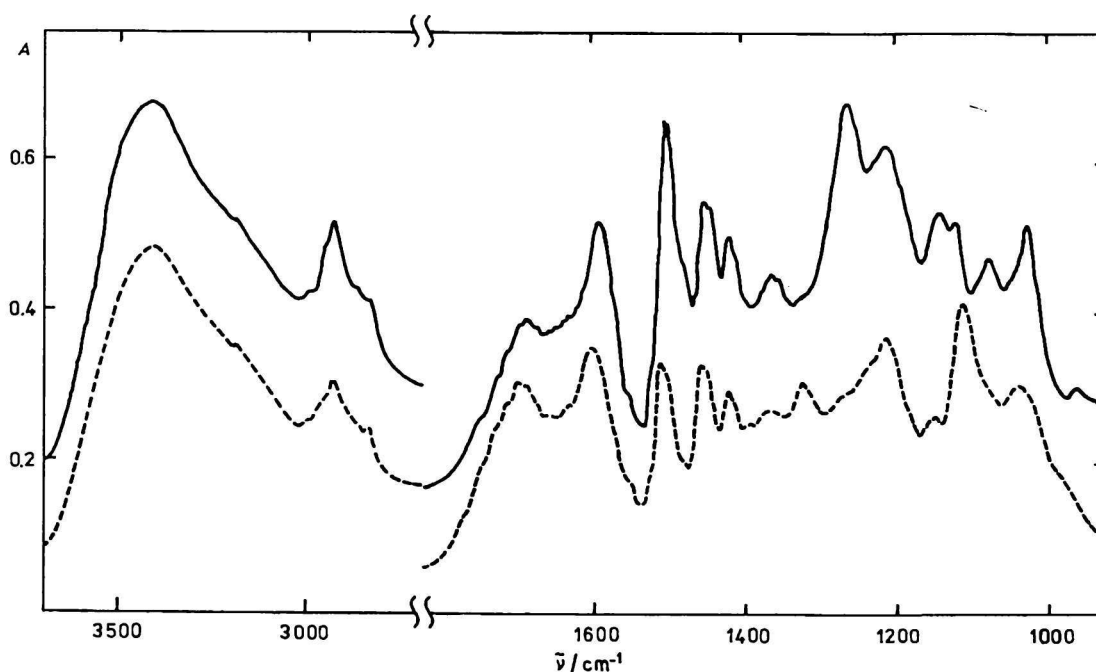Fig. 1. IR spectra of prehydrolysis lignin (– – –) and organosolv lignin (——).
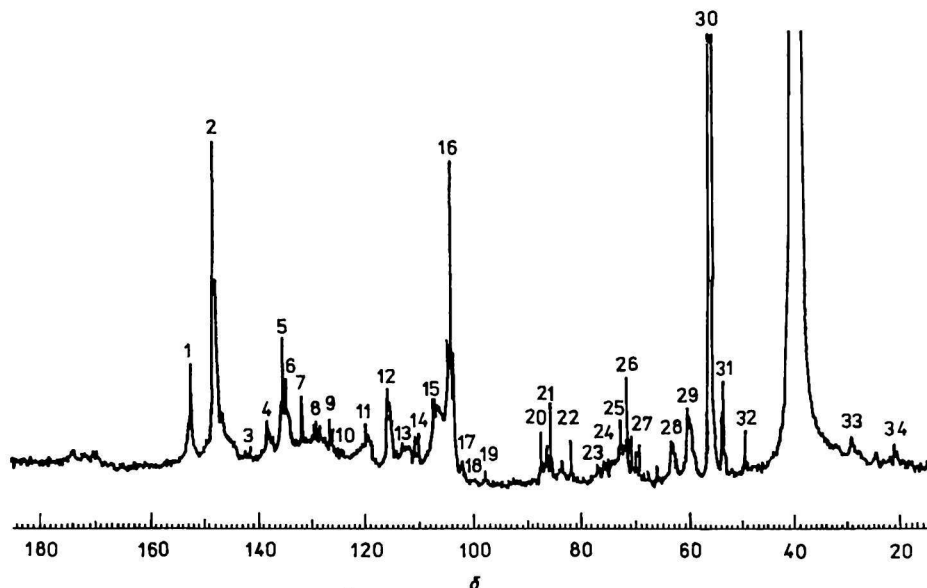
Fig. 2. ^{13}C NMR spectrum of prehydrolysis lignin.

Table 2. Assignment of Signals in the ^{13}C NMR Spectrum of Prehydrolysis Lignin (PL)

Signal	δ	Assignment of signals*	Signal	δ	Assignment of signals*
1	152.1	C-3/C-5 of S, β-O-4 e	18	101.7	C-1 of Xyl internal unit
2	147.4	C-3 of G, C-3/C-5 of S n	19	97.3	C-1 of Xyl red. end unit
3	141.8	C-4 of G substituted on C-5	20	87.0	C_α in β-5
4	138.0	C-1/C-4 of S e, C-6 in α-6	21	85.9	C_α in pinoresinol
5	134.4	C-1 of G e, C-4 in β-β	22	82—85	C_β in β-O-4
6	135.0	C-1 in α-6	23	75.5	C-4, Xyl internal unit
7	131.4	C-2/C-6 of p-hydroxybenzoates	24	74.0	C-3, Xyl internal unit
8	129.3	C_β of vinyl in cinnamaldehyde	25	72.2	C_α in β-O-4
9	126.5	C-6 with C_α=O, C-1 in 5-5, α-6	26	71.8	C_γ in syringaresinol or pinoresinol
10	124.0	C-6, C-5, C-1 in 5-5	27	69.5	C-4 of Xyl nonred. end unit
11	119.5	C-6 in β-5	28	62.9	C_γ in β-O-4 with C_α=O
12	115.1	C-5 of G e or n	29	59—60	C_γ in β-O-4
13	111.7	C-2 of G e or n	30	55.9	OCH_3
14	110.0	C-2 in β-5	31	53.4	C_γ in syringaresinol
15	106.8	C-2/C-6 of S with C_α=O	32	49.0	undetermined
16	104.4	C-2/C-6 of S, β-O-4 with C_αHOH	33	28.8	CH_2 in side chain
17	103.6	C-2/C-6 of S	34	21.0	$C_\gamma H_3$

*According to *Bardet et al.* [12]. G guaiacyl, S syringyl, e — etherified, n — nonetherified.

the increase of the peak at $\tilde{\nu}$ = 1720 cm^{-1} (ν(C=O)) in IR spectra. The spectra of the wavenumbers region of 1500—4000 cm^{-1} before and after medium-pressure mercury arc irradiation are given for sample containing 10 mass % of PL in Fig. 3. It is evident that the prominent lignin absorption bands at $\tilde{\nu}$ = 1510 and 1600 cm^{-1} are not visible in the IR spectra of the film. Based on these results it can be suggested that the changes in the intensity of the absorption band at 1720 cm^{-1} with irradiation time reflect only photodegradation of PP.

Kinetic curves for the increase of carbonyl absorption of PP films containing 2, 4, 6, 8, and 10 mass % PL during the course of irradiation of composite PP films shown in Fig. 4 demonstrate that the course of photooxidation changes significantly with the content of lignin component. All composite films show

higher photostability in comparison to the lignin-free sample. The PP film containing 2 mass % PL exhibits comparable photostability with that of lignin-free polymer stabilized with 2,6-di-*tert*-butyl-4-methylphenol (0.15 %).

The results obtained indicate that lignin component of composite films, which has a unique hindered phenol structure, acts as stabilizer causing terminating chain reaction of polymers induced by oxygen and its radical reduction products [13]. Higher lignin content initiates radical reactions leading to oxidative degradation of PP by hydroperoxide radical mechanism. The kinetic curves illustrated in Fig. 5 indicate that OL is more effective initiator of the oxidation reaction in relation with PL.

Because of this, the composite samples with lower OL content (1, 0.7, 0.4, and 0.1 mass %) were pre-
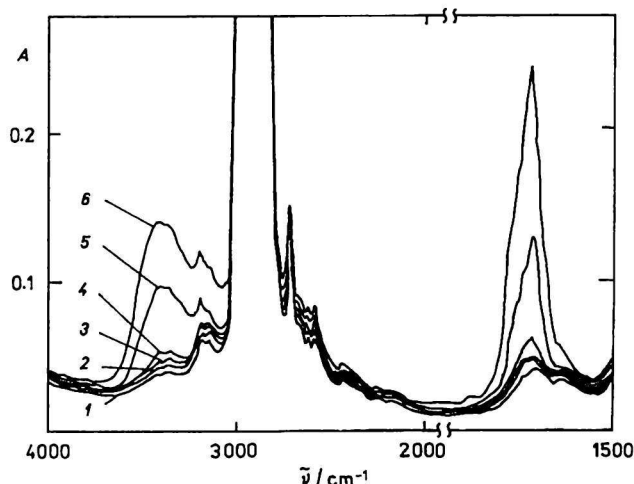
Fig. 3. IR spectra of photo-irradiated PP film containing 10 mass % of prehydrolysis lignin (PL). Time of irradiation/h: *1.* 0, *2.* 20, *3.* 44, *4.* 92, *5.* 164, *6.* 212.

pared. The latter sample has the course of photooxidation approximately comparable to PP containing the commercial stabilizer. Since photooxidation is the principal reaction in the outdoor weathering of polymer materials, the observed effect of lignin preparations in the composite films as initiators of PP degradation is interesting from the viewpoint of ecological problems with house waste plastics. It is likely that the presence of lignin in the composite polymer materials will significantly enhance their degradation.

CONCLUSION

The study of photooxidation of the films prepared from the composite lignin/PP blends showed that lignin component can act as a stabilizer or initiator of polymer degradation depending on the type and content of lignin preparations.

Photostabilizing efficiency of prehydrolysis lignin in PP films is comparable with used commercial stabilizer if the content of lignin is 2 mass %.

Mutual differences of both commercial preparations tested with regard to the course of photooxidation of the composite films may be explained by their various genetic origin and method of isolation.

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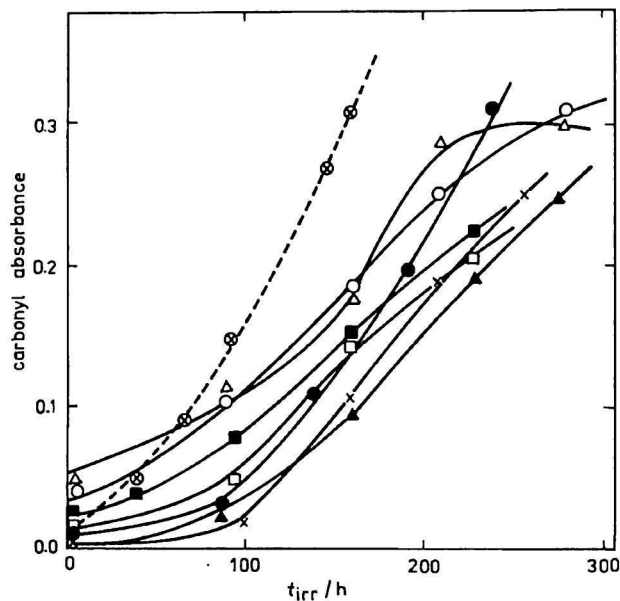6. Chodák, I., Brežný, R., and Rychlá, L., *Chem. Papers 40,* 461 (1986).

Fig. 4. Courses of photooxidation of PP films containing prehydrolysis lignin (PL). ⊗ PP nonstabilized, ● PP stabilized, ▲ PP stabilized + 2 % PL, × PP + 2 % PL, □ PP + 4 % PL, ■ PP + 6 % PL, ○ PP + 8 % PL, △ PP + 10 % PL.

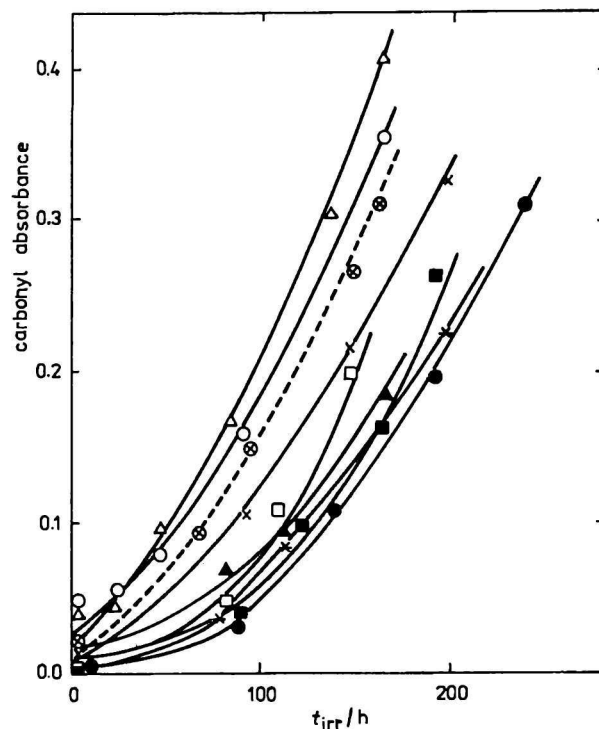**Fig. 5.** Courses of photooxidation of PP films containing organocell lignin (OL). ⊗ PP nonstabilized, ● PP stabilized, ■ PP stabilized + 0.4 % OL, * PP + 0.1 % OL, ▲ PP + 0.4 % OL, □ PP + 1 % OL, × PP + 2 % OL, ○ PP + 4 % OL, △ PP + 6 % OL.

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Translated by B. Košíková

OBITUARY

In Memoriam Ing. Viliam Klimo, CSc.

We regret to record that on April 19, 1993, Ing. *Viliam Klimo,* research worker of the Polymer Institute of the Slovak Academy of Sciences, died after serious illness. Ing. V. Klimo was born on May 25, 1947 in Banská Bystrica. He graduated from the Chemical High School in Svit and later, in 1971, from the Faculty of Chemical Technology of the Slovak Technical University. During his studies he specialized in physical chemistry. In the year of his graduation he started to work at the Polymer Institute of the Slovak Academy of Sciences.
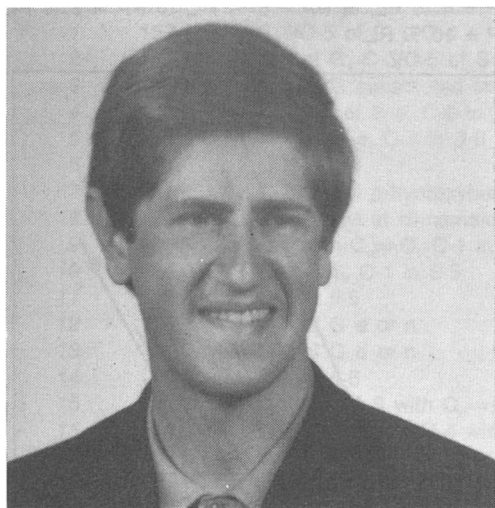
The seventies were the climax of efforts to elaborate the methodology of research connected to theoretical interpretation of spectra of electron spin resonance. The search was directed mainly to quantum-chemical calculations of spin densities. V. Klimo systematically worked on methodological basis for open-shell molecules to contribute efficiently and competently to the problem of spin densities. It was as soon as this that his talent to outline the essence of task and find original answers had shown. This field remained to be the focus of his PhD. thesis defended in 1977. In connection to this he elaborated an unrestricted Hartree—Fock method that was a top level achievement of contemporary quantum chemistry. This effort led to the extended Hartree—Fock method. The results were formulated in the joint book with Russian authors.

Experience with methodological basis for open-shell molecules led him to the problem of calculation of energy hypersurfaces. Considering the contemporary state of computer technology in our country he concentrated on formulation of the effective method with chemical basis that can supply correct qualitative description of hypersurfaces. Later he used it to solve problems connected with atomic and molecular collisions. In Slovakia it was a pioneer step. He has gained recognition for the development of collision theory. Unfortunately, Ing. Klimo could not complete this work. This part of his scientific activity was summarized in another book.

His scientific efforts can be characterized as calm, inquiring and altruistic. He did not like superficiality and hated pretense. Considering his work he always spoke to the point, using formulas and numbers. Even though he had been achieving very good results (almost all his works were published in renowned international journals) he did not like to travel. Yet, he was responded to by the world around. As a result he cooperated with research workers of Universities of Leicester, Donetsk, Novosibirsk, and Bochum. He published 3 books and 50 articles in special journals, and these were quoted in more than 140 publications of other scientists.

Slovak theoretical chemistry has lost an outstanding personality — a scientist of exact thinking, modern orientation, enthusiasm for work and sense of team research. His qualities and his friendliness created atmosphere free of conflicts. This way he became a highly moral authority. He will certainly be a model for many of his young colleagues from the Institute and outside of it.

He will be remembered with gratitude by all who knew him.

J. Tiňo