Blends of polypropylene with lignin
I. Influence of a lignin addition on crosslinking
and thermooxidation stability of polypropylene

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Dedicated to Professor Ing. A. Hrivík, CSc., in honour of his 60th birthday

The investigation was carried out on the influence of the addition of a small amount of lignin or its derivatives on the reaction of polypropylene crosslinking initiated by peroxides. Thermooxidation stability of the crosslinked samples was also studied. Unmodified oak lignin is the only additive affecting the crosslinking process significantly. The increase of thermooxidation stability was observed in samples containing lignin or most of its derivatives but the effect was small.

Исследовано влияние прибавки небольшого количества лигнина или его производных на реакцию сшивания полипропилена, инициируемую перекисями, и на термоокислительную устойчивость таким образом полученных образцов. Обнаружено, что значимый активационный эффект на реакцию сшивания проявляет только немодифицированный буковый лигнин. Термоокислительная устойчивость в результате прибавления лигнина или большинства его производных повышается, но эффект этот относительно мало значителен.

Fillers and additives are used frequently for effective modification of properties of polyolefins. The properties, processability as well as the price of original polymer can be altered by choosing a proper filler. The investigation on new fillers is necessary since it broadens the possibility of modification of desired properties. Special attention is paid to secondary raw materials which did not find adequate utilization up to now.

Technical kraft lignins are formed in great amount at cellulose production by sulfate process from wood. The industrial use of lignins is rare and in most cases the lignins are burnt covering partially the necessary energy for production.

Utilization of kraft lignin itself or in a modified form has been studied recently

[1], especially because new raw materials for chemical industry are searched for with enhanced interest in renewable sources. Several modes of lignin use in chemistry are described in literature. Active surface of lignin or its water-soluble salts found the application [2], *e.g.* for emulsion stabilization, dyes and pigment dispergation, or at concrete processing. Polymers based on lignin have been also synthesized [3], *e.g.* thermoreactive resins prepared by polycondensation with phenol, urea, *etc.*

Lignin can be used also as a specific filler to polymer composites. Its addition to rubber leads to an increase of hardness and to improvement of abrasion but it causes the decrease of certain mechanical properties, especially of tensile strength and modulus [4]. Admixtion of lignin into polypropylene leads to better cold resistance [5]. It was found that crosslinked product was formed during thermal processing of this mixture. Degree of crosslinking can be enhanced by the addition of a radical initiator [6]. Thermooxidation stability of polypropylene is also influenced by lignin [7].

The above-mentioned papers describe mostly the mixtures with higher lignin amount and lignin acting as a specific filler. However, it is assumed that the properties of mixture are influenced by addition of only several percent of the active component. In this paper we investigated more thoroughly the influence of lignin addition on polypropylene crosslinking initiated by thermal decomposition of peroxide. Thermooxidation stability of these samples was studied as well. To show the effect of various functional groups of lignin on the properties in question kraft lignin and several of its derivatives were investigated as additives.

Experimental

Unstabilized isotactic polypropylene powder Tatren HF 411 (Slovnaft, Czechoslovakia) was used, having viscometric molecular mass $M_v = 220\ 000$ kg mol^{-1}. *tert*-Butyl perbenzoate (Fluka AG) 95 % of purity was used as an initiator of radical processes. Pine wood kraft lignin L_A was precipitated from concentrated industrial pine kraft liquor (Sepap, Czechoslovakia) with diluted sulfuric acid. The colloidal lignin precipitate was coagulated with acetic acid anhydride [8], then filtered, washed, and vacuum dried at 50 °C. Oak wood kraft lignin L_B was prepared in the same way from concentrated oak kraft liquor (Bukóza, Czechoslovakia). The derivatives were prepared from original lignins L_A or L_B under reaction conditions according to Scheme 1.

Thermally processed lignins L_A-4 and L_B-2 were prepared from the original lignin by heating in an oven in air. The lignin L_A-6 was obtained by precipitation with lime suspension of sulfide liquor of cellulose production (Gemerská Hôrka, Czechoslovakia) [12].

The samples of polypropylene or polyethylene with lignin were prepared by mechanical mixing of both powdered components. The peroxide was added to the mixture in acetone

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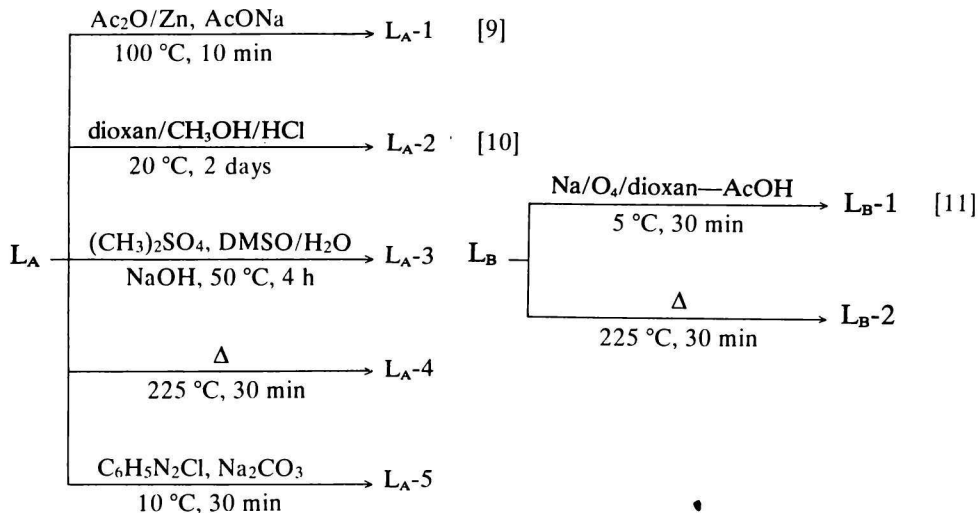
Scheme 1

solution. After removing the solvent the samples were pressed for 5 min at 175 °C. Under these conditions complete decomposition of *tert*-butyl perbenzoate took place and consequent sol-gel analysis as well as thermooxidation stability measurements were not affected by any radical reaction initiated by peroxide decay. The gel amount was determined according to weight of unsoluble portion after 14 h extraction in boiling xylene. Lignin was left in unsoluble portion almost completely bound into polymer network either by chemical or physical bonds. Thermooxidation stability of the samples was measured by chemiluminescence spectrometer PUSNK 7M with photomultiplier FEU-38 at 190 °C in oxygen. The photomultiplier worked at 1400 V. Kinetic parameters of oxidation were calculated from the time course of chemiluminescence intensity.

Results and discussion

Lignins

Modification of lignins was aimed to investigating the influence of lignin functional groups on the properties of polypropylene—lignin mixture. Kraft lignin is partially crosslinked polydisperse polymer of complex structure. Aralkyl units are the basic structural elements. Aromatic 4-hydroxy-3-methoxy phenyl (guaiacyl) rings are characteristic of lignins of coniferous woods. Deciduous wood lignins contain also 4-hydroxy-3,4-dimethoxy phenyl (syringyl) groups.

Chemical reactivity of lignin is given by main functional groups, *i.e.* by hydroxyls

Table 1

Analytical data of the used lignins

Derivative	Nature	w_i(found)/% ; Formula
L_A	Pine wood kraft lignin	64.6 % C, 5.8 % H, 1.7 % S, 13.3 % OCH_3; $C_9H_{6.7}OS_{0.1}(OH)_{1.4}(OCH_3)_{0.8}$
L_B	Oak wood kraft lignin	62.2 % C, 5.4 % H, 2.1 % S, 18.1 % OCH_3; $C_9H_{5.2}O_{0.7}S_{0.1}(OH)_{1.8}(OCH_3)_{1.1}$
L_A-1	Reductively acetylated L_A	63.5 % C, 6.0 % H, 1.0 % S, 13.3 % OCH_3;
L_A-2	Partially methylated L_A	62.8 % C, 6.1 % H, 1.8 % S, 17.2 % OCH_3; $C_9H_{8.4}O_{2.4}S_{0.1}(OCH_3)_{1.1}$
L_A-3	Methylated L_A	66.7 % C, 6.4 % H, 1.1 % S, 28.5 % OCH_3; $C_9H_{7.0}O_{1.3}S_{0.1}(OCH_3)_{1.8}$
L_A-4	Thermally treated L_A	67.3 % C, 5.7 % H, 1.3 % S, 16.4 % OCH_3; $C_9H_{7.2}O_{1.9}S_{0.1}(OCH_3)_{0.9}$
L_A-5	Phenylazo derivative of L_A	63.1 % C, 5.5 % H, 1.7 % S, 13.1 % OCH_3, 0.3 % N; $C_9H_{7.8}O_{2.6}S_{0.1}(OCH_3)_{0.8}(C_6H_5N_2)_{0.02}$
L_A-6	Ca-lignosulfonate	5.6 % S, 12.1 % OCH_3, 1.4 % ash, 0.45 $SO_3Ca_{0.5}$ groups per OCH_3
L_B-1	L_B oxidized with periodate	61.4 % C, 4.4 % H, 2.2 % S, 8.4 % OCH_3; $C_9H_{6.5}O_{3.2}(OCH_3)_{0.5}$
L_B-2	Thermally treated L_B	65.1 % C, 5.4 % H, 2.0 % S, 18.7 % OCH_3; $C_9H_{6.6}O_{2.1}S_{0.1}(OCH_3)_{1.1}$

mostly of phenolic nature, arylmethyl-etheric groups, olefinic double bonds conjugated with aromatic rings, and small portions of carbonyl, carboxyl, thiol, and sulfidic groups. Activated aromatic rings are essential for lignin reactivity in electrophilic substitution reactions.

The analytical data in Table 1 show that the lignins L_A and L_B are typical specimens of guaiacyl and guaiacyl-syringyl kraft lignins, having the hydroxyl groups molality 7.7 mol kg^{-1} and 9.4 mol kg^{-1}, respectively as determined from ^{1}H NMR spectra of acetylated derivatives [13].

It is known that HCl solution in methanol causes the methylation of carboxy and hydroxy groups of benzylalcoholic type. As it is shown in Table 1, this partial methylation of lignin L_A leads to the modification of 20 % of original OH groups (L_A-2). 71 % of total hydroxyl content reacted during methylation with dimethyl sulfate, as can be concluded from the data for L_A-3 derivative (Table 1). It means that all phenolic and part of aliphatic hydroxyls have reacted. Analytical data of thermally treated lignins (L_A-4 and L_B-2) show that extended elimination and condensation reactions proceed in guaiacyl lignins, aliphatic OH groups reacting

preferentially. Since arylmethyl-etheric bonds are stable at reaction temperature, a conclusion can be drawn that $C_{1.8}H_{1.4}O_{1.0}S_{0.05}$ and $H_{0.4}O_{0.7}$ are eliminated per methoxy group during thermal treating of lignins L_A and L_B, respectively. Only small fraction of phenylazo groups namely 0.017 per one C_9 lignin group could be incorporated onto lignin macromolecule by azocoupling. Calcium lignosulfonate (L_A-6) is considered to be sulfo derivative of guaiacyl lignin containing 0.45 $SO_3Ca_{0.5}$ groups mostly of aliphatic nature per one OCH_3 group. The increase of o-quinone groups in lignin L_B was reached by oxidation with periodic acid. Analytical data regarding the derivative L_B-2 show that the conversion of o-methoxy phenol groups to o-quinone moieties proceeded up to 0.62 per lignin C_9 group. On the other hand, the content of quinone and other chromophoric structures decreases in original lignin L_A by reductive acetylation. The resulting derivative L_A-1 was not analyzed in detail, but substantial discoloration of the product was observed.

Formation of gel

Table 2 shows the gel content formed in a mixture of polypropylene with oak wood lignin L_B. Lignin addition causes a significant increase of gel amount. The lignin acts as a coagent of crosslinking in this case. When lignin L_A or any of derivatives described is used instead of lignin L_B at the same concentration, crosslinking retardation is observed and the amount of the gel formed does not exceed 1 %. Therefore, the influence of lignin modification on the crosslinking of polypropylene was investigated at the presence of higher concentration of peroxide which initiates the gel formation even without the coagent. The results of gel amount with various lignin derivatives are shown in Table 3.

It is seen that some derivatives cause an enhanced gel formation but practically in

Table 2

Mass fraction of gel formed (w_g) in a mixture of polypropylene with lignin L_B and initiator *tert*-butyl perbenzoate (TBPB)

$\dfrac{w(\text{TBPB})}{\%}$			$w_g/\%$		
2	0	0	0	0	9
3	0	—	1	2	18
4	8	14	17	27	42
$w(L_B)/\%$	0.0	0.5	1.0	2.0	4.0

Table 3

Mass fraction of gel formed (w_g) in a mixture of polypropylene with various lignin derivatives
and 5 mass % of *tert*-butyl perbenzoate

$w(L_i)$	$w_g/\%$						
%	L_A-1	L_A-2	L_A-3	L_A-4	L_A-5	L_B-1	L_B-2
0.0	35	35	35	35	35	35	35
0.5	36	40	37	39	43	42	44
1.5	33	47	38	31	47	37	32
4.0	36	42	29	28	37	21	41

Table 4

Mass fraction of gel formed (w_g) in a mixture of polyethylene with various lignin derivatives
and 2 mass % of *tert*-butyl perbenzoate

$w(L_i)$	$w_g/\%$						
%	L_A-1	L_A-2	L_A-3	L_A-4	L_A-5	L_A-6	L_B-2
0.0	83	83	83	83	83	83	83
0.5	89	87	88	87	86	88	88
1.5	85	88	82	86	88	89	89
4.0	83	84	68	83	85	87	86

all cases the increase of additive content leads to a decrease of unsoluble portion.
To compare the effect of polymer matrix on the crosslinking reaction, crosslinking
of polyethylene was investigated under analogical conditions. The results are
shown in Table 4.

Similarly to polypropylene, the addition of small amount of modified lignin to
polyethylene leads to a slight increase of gel content. Further increase of lignin
concentration brings about a decrease of the unsoluble portion. If different
efficiency of the crosslinking in polyethylene and polypropylene is taken into
account, a conclusion can be drawn from Tables 3 and 4 that the influence of lignin
in both polymers is qualitatively the same. The effect of the additive consists only in
the influencing the initiation reaction and does not depend on polymer matrix.
However, when discussing the results from Tables 3 and 4 it is necessary to
consider only small differences in gel content when changing the additive concen-
tration in respective polymer. Since the gel amount can be determined with accuracy
± 3 %, the obtained values of the gel content are apparently within this limit in
most cases. However, analyzing the plot of gel amount on lignin concentration from
Tables 3 and 4, it can be said that the trend of the increase or decrease of gel
content with concentration of the additive is identical for both the polyethylene and

polypropylene and for any lignin derivative. Regarding this fact the qualitative conclusions can be drawn concerning the influence of lignin modification on its activity in crosslinking process.

Modified lignins can be divided approximately to three groups:

1. Derivatives with no significant effect on crosslinking (L_A-1);

2. derivatives influencing the gel formation positively when added in small quantities (L_A-2, L_B-2, L_A-5, L_A-6);

3. derivatives with tendency to decrease the amount of the unsoluble portion (L_A-3, L_A-4).

Lignin L_B-1 exhibits exceptionally high influence of concentration. It acts as an activator of crosslinking when present in small amount, but the crosslinking is significantly retarded at higher concentration. Similar phenomenon was observed for many coagents of polypropylene crosslinking [14]. It was explained by competitive reactions of primary radicals with polymer and with coagent. The ratio of the rates of both processes is changing in favour of reaction of primary oxy radicals with coagent at higher concentration of the latter.

The results show that radical transformation reactions of polyolefins are influenced mainly by hydroxyl groups of lignin as was expected. Original unmodified lignin has the highest positive effect on gel formation. Any modification leads to a decrease of gel content. Deactivation of additive is caused by acetylation which proceeds unselectively on both aliphatic and aromatic hydroxyls of lignin. Methylation of these groups (L_A-3) does not cause the decrease of activity but this lignin retards the gel formation when present in higher concentration. Dehydrolyzed lignin L_A-4 behaves similarly. Positive effect on gel formation is observed when aliphatic hydroxyls are methylated and aromatic ones remain intact (L_A-2). Similar increase in gel content has been found when other reactive sites in lignin than hydroxyls are modified (L_B-2, L_A-5, L_A-6). Activation effect in these cases is, however, much lower than with unmodified oak wood lignin L_B, apparently due to steric hindering of the hydroxyl groups, *e.g.* by bulk phenylazo groups, or because of decrease of miscibility of the filler with polymer matrix caused by highly polar —SO_3H groups. The increased probability of various side reactions cannot be excluded, too, namely those of functional groups of lignin and radical intermediates formed in the course of reaction.

Thermooxidation stability

Fig. 1 shows the plots of chemiluminescence intensity on time during thermally initiated oxidation of the samples of polypropylene with oak kraft lignin L_B and two derivatives L_A-2 and L_B-2 at two different concentrations. The different functional groups in lignin molecule lead apparently to some differences between derivatives when thermooxidation stability is considered, similarly to investigation of the gel

formation. At low lignin concentration (0.5 %) the effect is small and almost equal for all three additives. When increasing the concentration, derivative L_A-2 is almost inactive unlike lignin L_B and derivative L_B-2 which act as oxidation retarders.
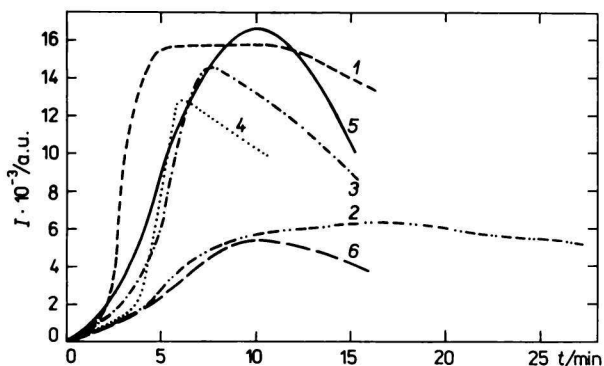

Fig. 1. Dependence of chemiluminescence intensity on time during the oxidation of the mixture of polypropylene with lignin. $w(L_B)$: *1*. 0.5 % ; *2*. 1.5 % ; $w(L_A$-2): *3*. 0.5 % ; *4*. 1.5 % ; $w(L_B$-2): *5*. 0.5 % ; *6*. 1.5 %. Concentration of the crosslinking initiator *tert*-butyl perbenzoate 3 mass %.
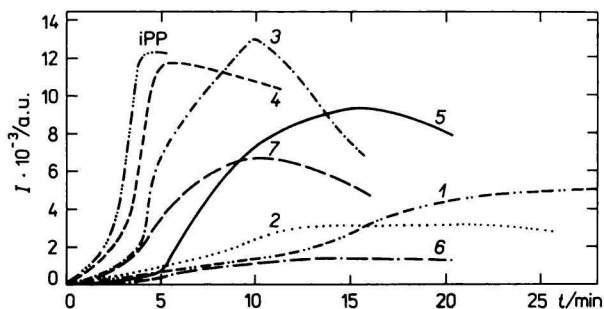

Fig. 2. Course of oxidation of mixtures of polypropylene with lignin derivatives, $w(L_i) = 4$ mass %. *1*. L_A; *2*. L_B; *3*. L_A-1; *4*. L_A-2; *5*. L_A-3; *6*. L_A-5; *7*. L_B-2. iPP — original isotactic polypropylene. Concentration of *tert*-butyl perbenzoate 3 mass %.

The effect of several modified lignins on thermooxidation stability of polypropylene is compared in Fig. 2. The dependence of chemiluminescence intensity on time of oxidation is shown for lignin concentration of 4 %. The most efficient thermooxidation stabilizer seems to be the coniferous wood lignin L_A exhibiting the highest induction period of oxidation. The induction period of the mixture of polypropylene with oak wood lignin L_B is somewhat lower and similar to that of methylated lignin L_A-3. The activity of the derivative L_A-3 is surprising since most

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of hydroxyl groups on both aliphatic chain and aromatic ring of lignin are blocked by methylation and the hydroxyls are considered to be the most effective functional groups regarding thermooxidation stabilization. On the other hand, apparently other effective centres are formed which can interfere with radical processes during thermal oxidation. This assumption is supported also by observed significant inhibition of gel formation by derivative L_A-3.

Thermally treated lignin L_B-2 and acetylated derivative L_A-1 is less efficient, though thermooxidation stability is enhanced at presence of both. Derivative L_A-2 proved to be poor thermal stabilizer, though it affects the gel formation positively. The last three derivatives prove that fair activity from point of view of crosslinking does not guarantee high stabilizing efficiency at thermal oxidation (L_B-2). On the other hand, the lack of functional groups supporting the crosslinking does not always mean that the derivative is ineffective as thermooxidation stabilizer (L_A-1).

Conclusion

Small addition of lignin leads to an activation of polypropylene crosslinking, though the effect is relatively small. Modification of lignin brings about a significant decrease even a loss of this effect in all cases. It is suggested that crosslinking is activated by a presence of hydroxyl groups on aromatic ring as well as of various groups having quinoid structure.

The lignin addition affects also thermooxidation stability of polypropylene. The effect is positive but relatively small with both unmodified lignin and the derivatives. Higher thermostability is usually observed with derivatives that are active also in the crosslinking process, though opposite cases have been also observed.

It is suggested that other than chemical effects of reactivity of introduced functional groups may be responsible for the observed phenomena. An important role is played by · the change of physical properties of additives caused by modification, especially the change in solubility or miscibility of the particular additive in polypropylene, the formation of aggregates, and the absorption or adsorption of an initiator.

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