

## USE OF LIGNIN AND PLA AS RENEWABLE ADDITIVES OF POLYPROPYLENE FILMS

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### ABSTRACT

The new type of films was prepared by blending of polypropylene with lignin and polylactic acid (PLA). Both used additives are particularly attractive as sustainable alternatives to petrochemical-derived products, since they can be obtained from renewable resources. Introduction of both additives into polypropylene blends allows to prepare the films with thickness 50-60  $\mu\text{m}$ . In order to increase biodegradability of polypropylene plastics, the films of blends of polypropylene, containing 2 wt % lignin and 3-10 wt % polylactic acid were prepared in the absence of the commercial stabilizers and investigated from the view point of their stability during thermo-oxidative aging and accelerated weathering. The obtained results showed that lignin acts as a stabilizer of polypropylene matrix against thermo-oxidation. In contrast to neat PP, the mechanical properties of the films containing lignin and PLA were decreased during biodegradation as well as during long-term artificially accelerated weathering.

**KEYWORDS:** Polypropylene films, lignin, PLA, thermo-oxidative aging, long-term weathering, biodegradation.

### INTRODUCTION

Polypropylene (PP) during manufacturing, processing, and service life is subjected to numerous factors (oxygen, metals, heat, light, and mechanical shear) that change its matrix and mechanical and chemical properties. Its stabilization has taken a long time for solving by various kinds of antioxidants (Gugumus 2000). The most of synthetic stabilizers decelerates the decomposition of plastic waste. Using a natural antioxidant, which is non-toxic and could affect degradation of polyolefin matrix, can solve this problem. Lignin phenolic polymers with predominantly hydroxyl, methoxyl, and carbonyl substitutions occur in higher plants, mainly in woody tissues (20-30 %). Lignins are predominantly obtained in larger amount as by-product of the pulp production during wood delignification. Most lignin by-products in the pulping industry are used as fuel, and only about 2 % wt is utilized in any other way (Lora and Glasser 2002).

Technical lignins can be used in engineering plastics, in phenolformaldehyde resins and

polyurethane films (Saraf and Glasser 1984). In our previous studies, lignin was used for the preparation of pulping additives (Košíková et al. 1990, Košíková et al. 1994), biodegradable surface active agents (Joniak et al. 1999, Košíková et al. 2000) and dispersants for disperse dyes (Demianová et al. 1995). The application of lignin as filler into natural rubber-based composites increased the resistance of vulkanisates to thermooxidative degradation in air (Košíková et al. 2007). Recently, lignin-stimulated protection of polypropylene films and DNA in cells of mice against oxidation damage was investigated in our research (Košíková and Lábaj 2009).

With the rapid developments of polymeric materials, there is growing interest in understanding the degradation behaviour of polyolefins. Thus, the objective of the present study was the preparation of the new type of films by blending of polypropylene with lignin and polylactic acid in order to increase biodegradability of polypropylene plastics. Both used additives are particularly attractive as sustainable alternatives to petrochemical-derived products, since they can be obtained from renewable resources. Drawing on our knowledges about the ability of some yeast species to biotransform the lignin macromolecule (Košíková and Sláviková 2004) biological treatments with yeast strains *Sporobolomyces roseus* and *Geotrichum klebahnii* were used for determination of biodegradability of the prepared films.

## MATERIAL AND METHODS

Kraft lignin (L1) of average molecular mass 4200 and with 18.6 % OCH<sub>3</sub> and 6.9 % phenolic OH was precipitated from the concentrated beech spent liquor (total solid 60.4 %, ash 28.8 %) with diluted sulphuric acid (25 ml sulphuric acid and 375 ml water). Kraft lignin (L2) of average molecular mass 6800 with 15.2 % OCH<sub>3</sub> and 6.5 % phenolic OH was precipitated from the concentrated spruce spent liquor (total solid 59.9 %, ash 27.2 %) with diluted sulphuric acid (25 ml sulphuric acid and 375 ml water). Polylactic acid (PLA) was purchased from Sigma-Aldrich. Gel permeation chromatography was performed on a column (53 x 8 cm) of Sephadex LH 60 using a mixture of dioxane and water containing 0.005 mol.l<sup>-1</sup> of aqueous NaOH and 0.001 mol.l<sup>-1</sup> of LiCl (7:3) as the eluant (Košíková and Mlynár 1992). Phenolic hydroxyl groups were determined by FTIR spectroscopy (Faix et al. 1992).

A commercial polypropylene (Moplen 500N, Slovnaft, Bratislava, Slovak Republic) was mixed and extruded with lignin (2 wt %) and PLA (3, 6 and 10 wt %) using a Brabender Plasticorder at 200°C. Polypropylene with 0.1 % Chimasorb 944 was treated in the same way as a control. The extrudates obtained were disintegrated for subsequent injection molding. Films about 50–60 µm were molded from the mixture at 200°C. Tensile strength and elongation data were obtained with an Instron tester according to standard STN EN ISO 527-1.3. Thermal aging was performed at 100°C in an air-circulating oven for 168 h. The artificially accelerated weathering experiments were performed in tester XENOTEST-450 according to standard STN EN ISO 105 B02 at 35°C with 55 % relative humidity and time of exposition 100, 200, 300, 400 h (length of sample 31–35 cm).

The Tesla BS 300 scanning electron microscope was used for the observation of polypropylene films containing lignin and PLA coated with gold. Thermogravimetric analyses were done using TA Instrument (SDT 2960 Simultaneous DTA-TGA) at linear heating rate 10°C.min<sup>-1</sup> in nitrogen atmosphere. Fourier Transform Infrared (FTIR) spectra were measured with Nicolet 6700 (Thermo Fisher Scientific, USA) spectrometer equipped with DTGS detector and Omnic 8.0 software. The spectra were collected in the middle region from 4.000 to 400.cm<sup>-1</sup> at a resolution of 4.cm<sup>-1</sup>, the number of scans was 128.

Changes in polymer chemical composition during artificially accelerated weathering were monitored using Fourier Transform Infrared Spectrophotometer (FTIR). Carbonyl index values, defined as the ratio of absorbance peak at  $1715\text{ cm}^{-1}$  with respect to  $974\text{ cm}^{-1}$  of PP films containing lignin and PLA were measured as a function of exposure time in Xenotest. Crystallinity of PP films containing lignin and PLA was calculated by FTIR spectroscopy from the respective ratios of optical intensities of crystalline absorption bands at  $998$  and  $974\text{ cm}^{-1}$ .

The yeast treatment of the polypropylene films containing lignin and PLA were performed with the yeast species *Geotrichum klebahnii* (CCY 74-6-2) and *Sporobolomyces roseus* (CCY 19-6-6) in the absence of glucose. These strains were obtained from the Culture Collection of Yeasts (Institute of Chemistry, Slovak Academy of Sciences, Bratislava) and maintained on malt agar at  $5^{\circ}\text{C}$ . They were cultured in a medium containing  $6.7$  g of yeast nitrogen phase (Difco) and lignin-polypropylene films. The pH was adjusted to  $6.5$ . Incubation took place on a rotary shaker at  $2.7$  Hz and  $28^{\circ}\text{C}$  for 16 days.

## RESULTS AND DISCUSSION

Because of its biodegradability and compatibility polylactid acid was used together with lignin as natural additives for polypropylene films in our research. PLA can be derived from the fermentation of agricultural by-products such as corn starch. Lignin samples are available in chemical processing of wood usually aims at separating soluble lignin fractions from solid cellulose-rich fiber component.

Scanning electron microscopy was used to observe the dispersion of lignin and PLA in polypropylene. The SEM micrographs illustrated in Fig. 1 and Fig. 2 confirm that both types of additives are uniformly dispersed in the PP matrix.

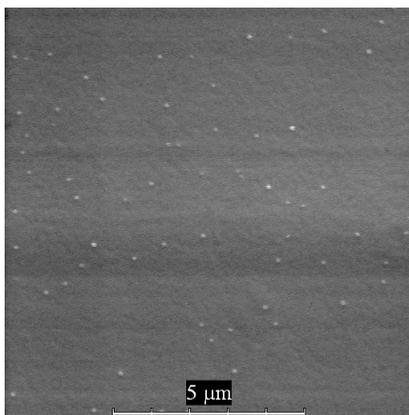


Fig. 1: SEM of PP film containing 2 wt % L1.

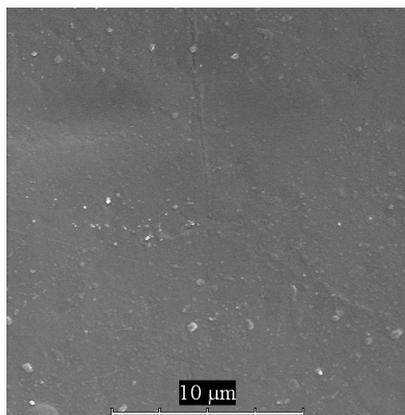


Fig. 2: SEM of PP film containing 2 wt % L1 and 6 wt % PLA.

Introduction of lignin and PLA additives into polypropylene blends allows to obtain the films with thickness  $50\text{--}60\ \mu\text{m}$  in the absence of commercial stabilizers. As can be seen, both types of additives are uniformly dispersed in the PP matrix. The most of the lignin particles are in nano-meter scale. The addition of nanoparticles of PLA improved the compatibility of lignin with PP and increased the transparency of the prepared films.

Heating to 100°C films exposed to NaOH (0.1M) lead to formation of uniformly dispersed nanoscopic pores (Fig. 3). The obtained results indicate potential use of prepared nanoporous plastics for different applications.

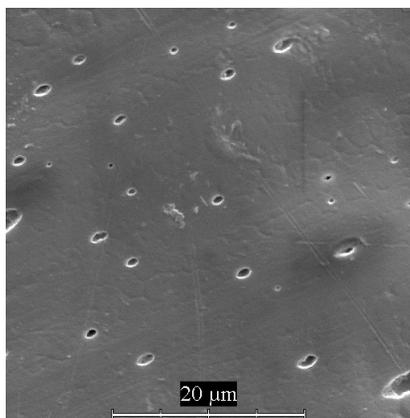


Fig. 3: SEM of PP film containing 2 wt % L1 and 6 wt % PLA after alkaline treatment.

Thermogravimetry was applied to examine the thermal stability of the prepared polypropylene films. As it is evident, the thermal decomposition for the neat PP film (Fig. 4) occurs at lower temperature than that for the PP film containing 2 % kraft lignin and 6 % PLA (Fig. 5).

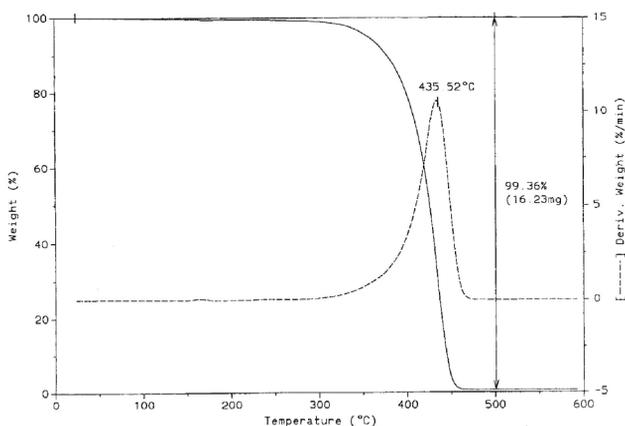


Fig. 4: TG and DTG traces of PP film.

The obtained results show a shift in the DTG peak ( $T_{max}$ ) towards a higher temperature from 435.52°C to 442.65°C, which reflects the improved thermal stability of polypropylene filled with lignin and PLA.

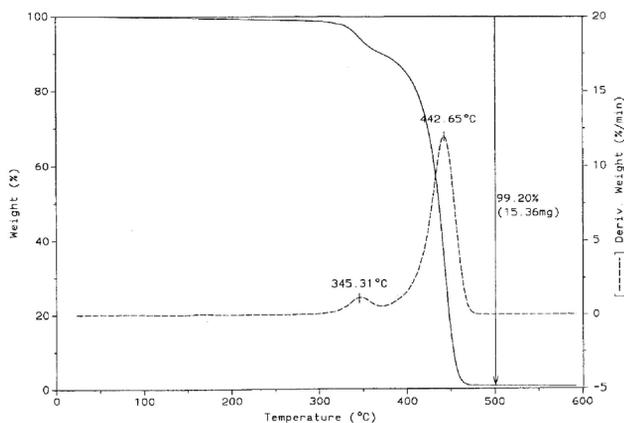


Fig. 5: TG and DTG traces of PP film containing 2 wt % L1 and 6 wt % PLA.

Further experiments were focused on behaviour of a series PP films containing 2 % lignin and 3-10 % PLA during thermo-oxidative aging and artificially accelerated weathering. The values of tensile strengths before and after aging (Fig. 6) show that PP films containing lignin and PLA are comparable with that of lignin-free film stabilized with commercial stabilizer. The increase of PLA content results in improvement of tensile strength. The selected tapes of PP films were subjected to hot air oxidative exposures using circulating air oven at 100°C. The concentration of PLA 6 % seems to be optimal in whole range of thermal exposition during aging. The results obtained prove that both used lignins act as an effective antioxidant during thermal treatment of PP films.

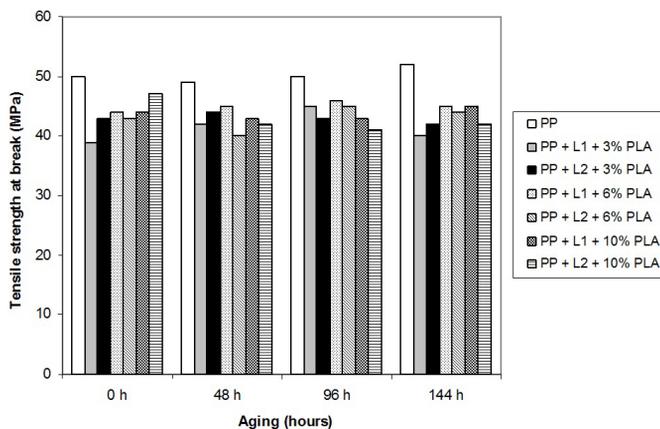


Fig. 6: The effect of thermo-oxidative aging on tensile strength of polypropylene films containing lignin (2 wt %) and polylactic acid (3, 6 and 10 wt %).

The values illustrated in Fig. 7 show that PP films containing lignin (2 %) and polylactic acid (3, 6 and 10 %) exhibit acceptable mechanical properties in artificially accelerated weathering for exposure time 100 and 200 h. The increasing of the exposure time to 400 h leads to significant decrease of mechanical properties of films. The exposure time of polypropylene tapes corresponding to 50 % retained tensile strength increased with the concentration of PLA.

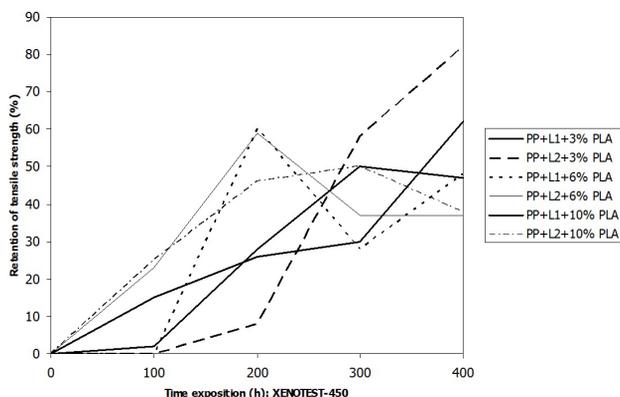


Fig. 7: The effect of the time exposition on decrease of tensile strength of PP films containing lignin and PLA during artificially accelerated weathering.

The results illustrated in Fig. 8 show that the crystallinity of neat PP film was increased with the time exposition in XENOTEST-450. In contrast, the crystallinity of PP films containing lignin and PLA decreases with the time of artificial weathering. This correlated with the changes of tensile strength.

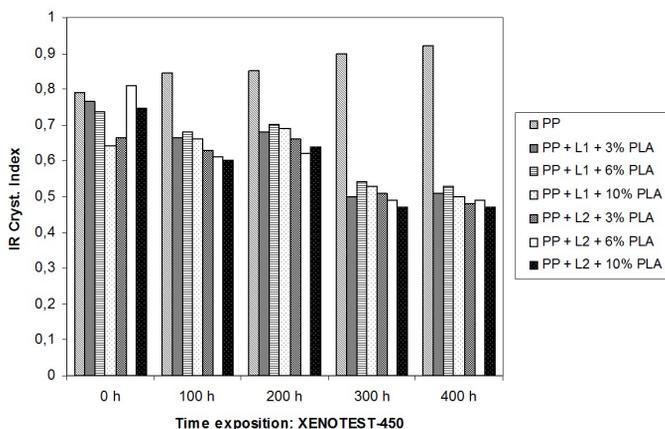


Fig. 8: Changes in crystallinity of PP films containing lignin and PLA as a function of exposure time in Xenotest.

Carbonyl index values, defined as the ratio of absorbance peak at  $1715.\text{cm}^{-1}$  with respect to  $974.\text{cm}^{-1}$ , illustrated in Fig. 9, are measures of carbonyl species produced during artificial aging in Xenotest. It is clearly seen that the relative absorbance of carbonyl index (CO) at  $1720.\text{cm}^{-1}$

with respect to  $974.\text{cm}^{-1}$  increased with the increasing time of exposition, as lignin can act as photoinitiator of oxidative break down of polymer matrix due to presence of carbonyl groups absorbing UV light.

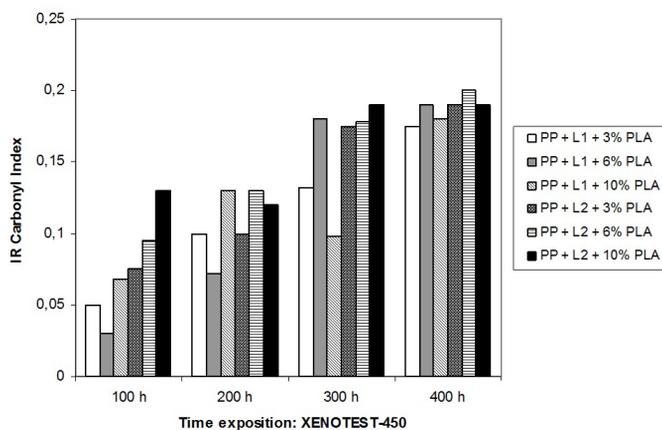


Fig. 9: Changes in carbonyl absorbance of PP films containing lignin and PLA as a function of exposure time in Xenotest.

The yeast microorganisms *Sp.roseus* and *G.klebahnii* were shown to be able to modify the structure of lignin in our previous paper (Košíková and Sláviková 2004). Therefore, the selected PP tapes were subjected to biodegradation with *Sp.roseus* as well as *G. klebahnii*. Figs. 10 and 11 show the scanning electron micrographs of the PP film containing 2 % L1 and 6 % PLA before and after 8 weeks of biodegradation. In contrast to the rigid structure of neat PP, it is very clear from the micrograph of PP film containing 2 % L1 and 6 % PLA that degradation process with *Sp.roseus* caused small cavities opened on the surface of this film. Similar morphological changes were observed for polypropylene films containing lignin (4 % wt) treated with *Ph. chrysosporium* in our previous paper (Košíková et al. 1994).

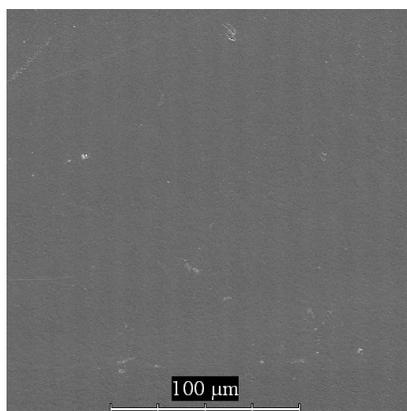


Fig. 10: SEM of PP film.

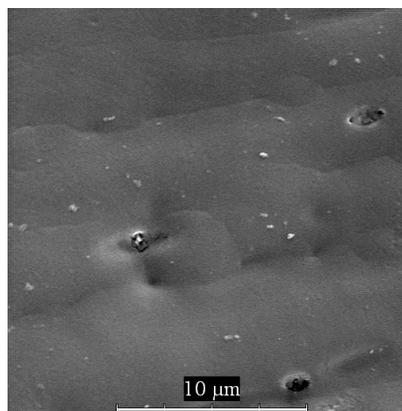
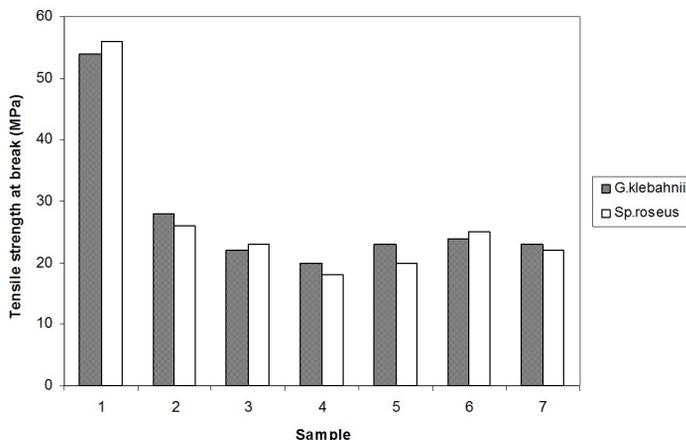


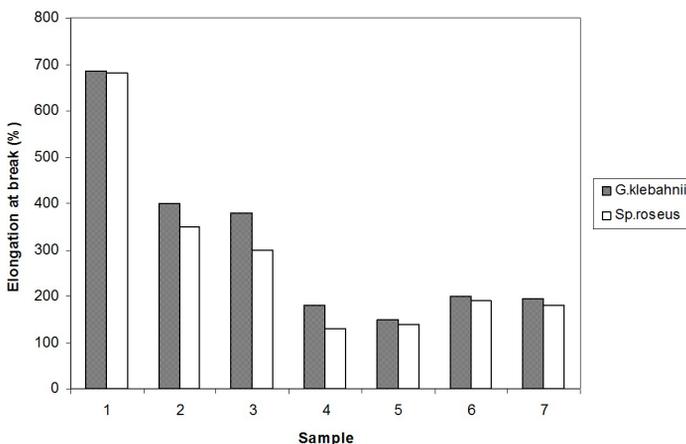
Fig. 11: SEM of PP film containing 2 wt % L1 and 6 wt % PLA after yeast treatment with *Sp.roseus*.

The yeast strains *Sp. roseus* and *G. klebahnii* were used for biological treatment of the series of films containing 2 % lignin and 3-10 % PLA with thickness 50-60  $\mu\text{m}$ . Because of measurement of mechanical properties offers a mean of direct estimation of polymer degradation, the changes tensile strength of break (Fig. 12) and elongation (Fig. 13) after 8 weeks of incubation were determined.



1 - PP, 2 - PP+2% L1+3% PLA, 3 - PP+2% L2+3% PLA, 4 - PP+2% L1+6% PLA,  
5 - PP+2% L2+6% PLA, 6 - PP+2% L1+10% PLA, 7 - PP+2% L2+10% PLA

Fig. 12: Tensile strength at break of PP films containing lignin and PLA after treatment with *G. klebahnii* and *Sp. roseus* at 28°C for 8 weeks.



1 - PP, 2 - PP+2% L1+3% PLA, 3 - PP+2% L2+3% PLA, 4 - PP+2% L1+6% PLA,  
5 - PP+2% L2+6% PLA, 6 - PP+2% L1+10% PLA, 7 - PP+2% L2+10% PLA

Fig. 13: Elongation at break of PP films containing lignin and PLA after treatment with *G. klebahnii* and *Sp. roseus* at 28°C for 8 weeks.

Based on the obtained results, it can be suggested that the incorporation of lignin and PLA biopolymers into polypropylene composites will bring a positive effect on environment. The modification of lignin preparations by *Sp. roseus* resulting in the formation of aliphatic carboxyl groups, which is typical for humic-like polymer, was confirmed on veratryl alcohol, representing lignin monomer containing  $\alpha$ -hydroxyl group by  $^{13}\text{C}$  NMR analysis (Košíková and Sláviková 2004). Recently, it was revealed that composting – the first phase of conversion of lignocellulosic material of grass - caused dissolving of lignin due to its biological modification resulting in the introduction of carboxyl groups (Bikovens et al. 2002).

## CONCLUSIONS

The concentration of PLA 6 % in the blends seems to be optimal for production of PP films with acceptable mechanical properties. For the preparation of -films lignin stabilizers were used. Decrease of strength properties of the PP films containing lignin to 50 % retained tensile strength observed during artificially weathering in Xenotest-450, mainly in the interval 300-400 h, correlates with increasing of their carbonyl groups content.

It can be concluded that introduction of lignin and PLA biopolymers into polypropylene should be a successful way to obtain thermally stable, partly biodegradable and light-decomposable polypropylene films. Moreover, both additives could be incorporated into plastics without health hazard. The results of biodegradation confirmed that application of lignin and PLA biopolymers as additives into polypropylene plastics will bring a positive effect on environment.

## ACKNOWLEDGMENTS

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## REFERENCES

1. Bikovens, O., Iiyama, K., Gravitis, J., 2002: Biologically modified lignin from grass compost. 7<sup>th</sup> European Workshop on Lignocellulosics and Pulp, Turku. Pp. 471-473.
2. Demianová, V., Košíková, B., Hodul, P., 1995: New lignin derivatives as dispersants for disperse dyes. *Fibers and Textiles* 2: 152-154.
3. Faix, O., Grunwald, C., Beinhoff, O., 1992: Determination of phenolic hydroxyl groups content of milled wood lignins (MWLs) from different botanical origins using selective aminolysis, FTIR,  $^1\text{H}$  NMR, and UV spectroscopy. *Holzforschung* 46(5): 425-432.
4. Gugumus, F.L., 2000: Polyolefin stabilization: from single stabilizers to complex systems. In: Hamid, S.H., *Handbook of Polymer Degradation*, 2<sup>nd</sup> ed. Marcel Dekker, Inc.: New York – Basel. Pp.1-38.
5. Joniak, D., Poláková, M., Košíková, B., Demianová, V., 1999: Synthesis and properties of novel lignin surfactants. *Wood Research* 44(3-4): 60-66.
6. Košíková, B., Demianová, V., Mikulášová, M., 1994: Effect of lignin on degradation of polyolefins with *Phanerochaete chrysosporium*. *Wood Research* 39(1): 15-23.

7. Košíková, B., Ďuriš, M., Demianová, V., 2000: Conversion of lignin biopolymer into surface-active derivatives. *Eur. Polym. J.* 36(6): 1209-1212.
8. Košíková, B., Gregorová, A., Osvald, A., Krajčovičová, J., 2007: Role of lignin filler in stabilization of natural rubber-based composites. *J. Appl. Polym. Sci.* 103(2): 1226-1231.
9. Košíková, B., Lábaj, J., 2009: Lignin-stimulated protection of polypropylene films and DNA in cells of mice against oxidation damage. *Bioresources* 4(2): 805-815.
10. Košíková, B., Mlynár, J., 1992: Effect of soda-additive pulping on molecular characteristics of residual pulp lignin. *J. Wood Chem. Technol.* 12(3): 243-259.
11. Košíková, B., Mlynár, J., Joniak, D., 1990: Effect of lignin derivatives on the macromolecular properties of lignin in NSSC cooking. *Holzforschung* 44(1): 47-51.
12. Košíková, B., Sláviková, E., 2004: Biotransformation of lignin polymers derived from beech wood pulping by *Sp.roseus* isolated from leafy material. *Biotechnology Letters* 26(6): 517-519.
13. Lora, J.H., Glasser, W.G., 2002: Recent industrial applications of lignin: A sustainable alternative to nonrenewable materials. *J. Polym. Environ.* 10(1-2): 39-48.
14. Saraf, V.P., Glasser, W.G., 1984: Engineering plastics from lignin. III. Structure property relationships in solution cast polyurethane films. *J. Appl. Polym. Sci.* 29(5): 1831-1841.

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