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USE OF LIGNIN PRODUCTS DERIVED FROM WOOD PULPING AS ENVIRONMENTALLY DESIRABLE ADDITIVES OF POLYPROPYLENE FILMS

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ABSTRACT

The blending of polypropylene with lignin preparations obtained from by-products of wood prehydrolysis and kraft pulping allows to prepare optically transparent films (thickness 50–60 µm) with acceptable mechanical properties in the absence of commercial stabilizers. They exhibit strength properties comparable with those of lignin-free PP films. The lignin preparations in the concentration 1–2 wt % possess the ability to act as processing stabilizers. The changes of mechanical properties during biodegradation and long-term artificial weathering indicate that the prepared lignin-polypropylene films are potentially nonpersisting.

KEY WORDS: antioxidant, lignin, polypropylene, thermo-oxidative aging, accelerated weathering

INTRODUCTION

Degradation of polymeric materials is a commonly encountered phenomenon that leads to changes on their chemical, physical and mechanical properties. There are many factors causing polymer degradation: solar light or other light energy radiations, heating, chemicals attack, stress loading, water absorption, biological sources and so forth (Allen and Edge 1992). Generally, free radical character of degradation is considered for very frequent mode. Therefore major interest is devoted just to free radical scavenging additives, especially phenolic and amine antioxidants (Hamid 2000). Nowadays, new criteria for chemicals are required such as environmental friendliness, nontoxicity, economical accessibility, and desirable waste disposal. Lignins are three-dimensional amorphous natural phenolic polymers with predominantly hydroxyl, methoxyl and carbonyl substitutions. They occur in higher plants, mainly in woody tissues (20–30 wt %). Lignins are predominantly obtained in larger amounts as by-products of pulp production during 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 in polyuretane films (Saraf and Glasser 1984). In our previous studies, lignin was used for the preparation of pulping additives (Košíková et al. 1993) and biodegradable tensides (Košíková et al. 2000).

It is known that lignin›s hindered phenolic hydroxyl groups enable to act as stabilizer of reactions induced by oxygen and its radical species. Lignin ability to scavenge the radicals responsible for the oxidation is influenced by limited diffusion into polymer matrix. It was revealed that the antioxidant activity of lignins varies with their genetic origin, isolation methods, and molecular characteristics (Pouteau et al. 2003) Even from the one type of lignin, e.g. kraft lignin, fractions with different antioxidant activity were prepared. In our previous work (Košíková et al. 2001) the influence of lignin (10, 20 and 30 wt %) on rheological and strength properties of polypropylene composites was examined. It was revealed that with increasing lignin content the mechanical properties of these composites deteriorated.

With the rapid developments of polymeric materials, there is growing interest in understanding the thermal stability and degradation behaviour of polyolefins. Thus, the objective of our research was the characterization of the antioxidative behaviour of lignin biopolymers as natural antioxidants in polypropylene films containing 0.5-5 wt % lignin and the comparison their effectiveness with that of synthetic phenolic stabilizer in processing, thermo-oxidation and accelerated weathering. Moreover, degradation of lignin-polypropylene films by yeast microorganisms was examined.

MATERIAL AND METHODS

Lignin 1 of average molecular mass 2000 with 19.1 % OCH_3 and 4.3 % phenolic OH was obtained by fractionation of by-product of beech wood prehydrolysis (170 °C, 1 h). Lignin 2 of average molecular mass 6800 with 15.2 % OCH_3 and 6.5 % phenolic OH was prepared by fractionation of kraft lignin precipitated from concentrated spruce kraft liquor. Both lignin samples were prepared in Lignin Laboratory, Institute of Chemistry, Slovak Academy of Sciences, Bratislava. The commercial isotactic polypropylene (PP) TATREN HPE was suplied by Slovnaft, Bratislava, Slovak Republic.

Polymer blends were prepared by compounding PP powder and lignin in a laboratory size Brabender at 200 °C in the presence or absence of 0.15 wt % 2,6-di-tert-butyl-4-methylphenol. The content of lignin was 0.5, 1, 2 and 5 wt %. Then the blends were homogenized in a single screw extruder at 200 °C. The extrudates obtained were disintegrated for subsequent injection moulding. 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 carried out by using tester XENOTEST 450 at 35 °C with 55 % relative humidity for 100, 200 and 400 h according to the STN EN ISO 105 B02 (length of sample 31-35 cm).

The yeast treatment of the lignin-polypropylene films were performed with yeast species *Geotrichum klebahnii* (CCY 74-6-2) and *Trichosporon pullulans* (CCY 30-1-10) in the absence of glucose. There strains were obtained from the Culture Collection of Yeasts (Institute of Chemistry, Slovak Academy of Sciences, Bratislava) and maintained on malt agar at 5 °C. It was 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 °C for 16 days.

RESULTS AND DISCUSSION

In our experiments, two series of PP films containing 0.5, 1, 2 and 5 wt % lignin 1 (L_1) and lignin 2 (L_2), respectively were prepared in the absence of stabilizer. These films were compared with lignin-free PP stabilized with commercial stabilizer with respect to mechanical properties. From Tab. 1 it is seen that tensile strength and elongation at break were not significantly influenced by addition of both types lignins over the range from 0.5 – 2 wt %. The films containing 5 wt % lignin exhibit lower mechanical properties.

Tab. 1: Mechanical properties of lignin-polypropylene films before and after oven aging

Sample composition	Tensile strength (MPa)		Elongation at break (%)	
	Before aging	After aging	Before aging	After aging
PP	13.5	15.7	589.4	335.3
PP + 0.5 % L_1	14.6	18.4	541.2	374.7
PP + 1 % L_1	13.3	20.1	541.5	569.1
PP + 2 % L_1	12.9	18.9	497.3	504.5
PP + 5 % L_1	6.0	6.2	109.6	37.5
PP + 0.5 % L_2	12.8	19.0	556.2	485.5
PP +1 % L_2	14.5	21.9	573.2	622.1
PP + 2 % L_2	13.6	20.6	494.0	597.7
PP + 5 % L_2	4.5	5.1	71.1	33.0

Values represent the mean of at least five independent experiments.

Further experiments were focused on behaviour of lignin-PP films during thermo-oxidative aging and artificially accelerated weathering experiments. The values of mechanical properties before and after aging summarized in Tab. 1 show that PP films containing lignin up to 2 wt % are rather stable towards thermo-oxidation in comparison with lignin-free films containing the commercial stabilizer. The results obtained prove that both lignins used act as an effective antioxidant during thermal treatment of PP films.

The values summarized in Tab. 2 show that PP films containing 0.5–2 wt % lignin exhibit acceptable mechanical properties in accelerated weathering for exposure time 100 and 200 h. The increasing of the exposure time to 400 h leads to significant decrease of tensile strength and elongation at break of the films containing higher amount of lignin than 1wt % resulting in their destruction (Tab. 3).

Tab. 2: The effect of accelerated weathering on mechanical properties of polypropylene films

Sample composition	Exposure time 100 h		Exposure time 200 h	
	Tensile strength (MPa)	Elongation at break (%)	Tensile strength (MPa)	Elongation at break (%)
PP	11.4	359.7	16.6	369.2
PP + 0.5 % L_1	14.4	586.0	14.6	588.0
PP + 1 % L_1	15.0	494.6	15.0	447.5
PP + 2 % L_1	14.6	465.5	11.3	163.3
PP + 5 % L_1	6.0	109.6	4.5	45.6
PP + 0.5 % L_2	16.2	579.5	15.7	583.7
PP +1 % L_2	15.2	501.0	13.4	393.0
PP + 2 % L_2	15.9	596.8	12.5	62.8
PP + 5 % L_2	4.5	71.1	3.5	44.5

Values represent the mean of at least five independent experiments

Tab. 3: The effect of accelerated weathering (exposure time 400 h) on mechanical properties of lignin-polypropylene films

Sample composition	Tensile strength	Elongation at break
	(MPa)	(%)
PP	11.4	576.6
PP + 0.5 % L_1	12.6	65.2
PP + 1 % L_1	8.2	3.7
PP + 2 % L_1	destruction	destruction
PP + 5 % L_1	destruction	destruction
PP + 0.5 % L_2	13.5	82.3
PP +1 % L_2	9.3	5.8
PP + 2 % L_2	destruction	destruction
PP + 5 % L_2	destruction	destruction

Values represent the mean of at least five independent experiments.

Our previous studies concerning the biotransformation of lignin with *Geotrichum klebahnii* and *Trichosporon pullulans* (Košíková and Sláviková 2004, Sláviková et al. 2002) confirm that these microorganisms produce ligninolytic enzymes in the cultural medium particularly when lignin was the only carbon source. Therefore, these yeast strains were used for biological treatment of the prepared lignin-polypropylene films. Because of measurement of mechanical properties offers a mean of direct estimation of polymer degradation, the changes of break of elongation and tensile strenght of PP films during treatment with a mixture *Geotrichum klebahnii* and *Trichosporon pullulans* were determined (Tab. 4).

Tab. 4: Mechanical properties of lignin-polypropylene films before and after treatment with a mixture of yeast microorganisms Geotrichum klebahnii and Trichosporon pullulans

Sample composition	Tensile strength (MPa)		Elongation at break (%)	
	Before biodegradation	After biodegradation	Before biodegradation	After biodegradation
PP	13.5	14.0	589.4	570.6
PP + 2 % L_1	14.3	10.1	465.5	14.7
PP + 5 % L_1	6.2	4.1	109.6	12.2
PP + 2 % L_2	13.9	9.0	494.0	303.2
PP + 5 % L_2	4.5	3.4	71.1	12.5

Values represent the mean of at least five independent experiments.

In contrast to the rigid structure of lignin-free PP films, mechanical properties of polypropylene films containing 2 and 5 wt % lignin were significantly decreased during biodegradation. The followed exposition of the biologically treated films to artificially accelerated weathering results in their total destruction.

CONCLUSIONS

The application of lignin preparations into polyalkylene polymers used in our work is attractive due to lignin abundance and renewable nature. The optically transparent homogeneous lignin containing PP films (thickness 50-60 μm) with sufficient tensile strengths and elongation at break could be obtained by blending of polypropylene with 0.5-5 wt % lignin in the absence of commercial stabilizers. It was revealed that lignin may act an effective stabilizer of polypropylene films in their processing, thermo-oxidative aging and in accelerated weathering for exposure time 100 and 200 h. The results obtained by accelerated weathering during 400 h as well as biodegradation with yeast microorganisms revealed that the prepared lignin-polypropylene films are potentially nonpersisting. The ability of lignin-based antioxidants to protect polymeric materials from oxidative damage highlights a new avenue for utilizing lignin waste products from the pulp and paper industry.

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