Radical Scavenging Capacity of Lignin and Its Effect on Processing Stabilization of Virgin and Recycled Polypropylene

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ABSTRACT: The radical scavenging capacity of lignin was determined using spectrophotometric method by means of scavenging of the free radical 2,2-diphenyl-1-picrylhydrazyl (DPPH$^\bullet$) and compared with that of synthetic antioxidant Irganox 1010. Lignin reacted progressively with the DPPH$^\bullet$ reaching a steady state in 6 h, showing high antiradical activity with a stochiometry of 5.5 reduced DPPH$^\bullet$ molecules. Irganox 1010 showed lower antiradical activity reaching a steady state with DPPH$^\bullet$ after 13 h. Moreover, stabilization efficiency of lignin has been investigated in virgin and recycled polypropylene. The stabilization effect of lignin was evaluated by melt volume rate (MVR). The efficiency of lignin as processing stabilizer in both series polypropylene samples was compared with that of synthetic antioxidant Irganox 1010. The presence and behavior of free radicals in the lignin/polypropylene composites formed during processing was determined by electron paramagnetic resonance (EPR). It was observed that used lignin sample could stabilise both virgin and recycled polypropylene. © 2007 Wiley Periodicals, Inc. J Appl Polym Sci 106: 1626–1631, 2007

Key words: biopolymers; polyolefins; radical scavenging; rheology; stabilization

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 (stabilizers).[1–7] From the view point of the various principles of degradation processes antioxidants are divided into a few series such as scavengers of free radicals, hydroperoxide decompositors, metal deactivators, antiozonants, photoantioxidants, photostabilizers and heat stabilizers.[8,9] 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.[8] Nowadays, new criteria for chemicals are required such as environmental friendliness, nontoxicity, economical accessibility, and desirable waste disposal. According to CMAI (Chemical Market Associates) analysis polyolefins represent the largest segment of the global thermoplastic business, which was 92 million metric tons for the year 2004.[10] This high global consumption requires being interested in plastic recycling area. It is known that even though manufacturing of plastic materials was stabilized at first, their reprocessing for use achieving required properties required stabilization.[8,11] On the other hand, the most of synthetic stabilizers decelerates the decomposition of the plastic waste. Using a polymeric natural antioxidant, which is nontoxic and compatible with the base polymer and could affect the degradation of the polyolefin matrix, can solve this problem. As results from our previous study[12] the biotransformation of lignin component with *Phanerochaete chrysosporium* causes partial degradation of polypropylene matrix. Based on this, it can be suggested that the incorporation of lignin biopolymer into polypropylene composites brings a positive effect of environment. The main aim of this work was to evaluate the performance of lignin as natural antioxidant and to compare its effectiveness with the synthetic phenolic antioxidant Irganox 1010.

Lignins are three-dimensional amorphous natural nontoxic polymers composed of phenyl propane units with carbonyl, hydroxyl, and methoxyl substitutions, occurring in higher plants, mainly in wood.

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They are the second most abundant organic polymers in nature, only to cellulose. Lignins are predominantly obtained as by-product in pulp production. The majority of lignin by-products are used as a fuel in paper industry and only about 2 wt % is utilized in another way.[13] However, lignin wastes from pulp and industry represent and ideal source of chemicals. 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. The incorporation of lower amounts of lignin derived from wood prehydrolysis and organosolv pulping allowed the preparation polypropylene films with acceptable mechanical properties[14] and to stabilize this material against photooxidation.[15] Pouteau et al. characterized 15 lignin samples from the viewpoint of their antioxidant properties in polypropylene.[16] It was revealed that the antioxidant activity of lignins varies with their genetic origin, isolation methods, and molecular characteristics. Even from the one type of lignin, e.g. kraft lignin, fractions with different antioxidant activity were prepared. In our previous work[17] we examined influence of this lignin in concentration from 10 to 30 wt % on rheological properties of lignin–polypropylene composites. It was revealed that with increasing lignin content for polypropylene composites the mechanical properties of these composites deteriorated. Recently, we have presented the stabilization effect of low molecular weight and narrow polydispersity lignin sample derived from beech wood prehydrolysis in polypropylene and natural rubber during accelerated thermo-oxidative aging.[18–20]

The purpose of this study was to determine the radical scavenging activity of lignin by a method using 2,2-diphenyl-1-picrylhydrazyl (DPPH•) free radical and the influence of lignin's concentration up to 10 wt% on processing stability of virgin and recycled polypropylene. In addition, the aim of this work was to evaluate the performance of lignin as natural antioxidant and to compare its effectiveness with the synthetic phenolic antioxidant Irganox 1010 as well as to examine of the prepared polypropylene blends by electron paramagnetic resonance spectroscopy.

EXPERIMENTAL

Materials

The lignin sample was prepared by fraction extraction of co-product of beech-wood prehydrolysis (weight average molecular weight M_w = 2000; polydispersity M_w/M_n = 1.2; $\rho_{23°C}$ = 1.312 g/cm^3) in Lignin Laboratory, Institute of Chemistry, Slovak Academy of Sciences Bratislava, Slovakia. Irganox 1010 (pentaerythrityl terakis [3-(3,5-di-*tert*-butyl-4-hydroxyphenyl) propionate]) (M_w = 1178 g/mol) was supplied by Ciba Specialty Chemicals (Lampertheim, Germany). 2,2-Diphenyl-1-picrylhydrazyl (DPPH• with M_w = 394.32 g/mol) and dioxane (spectrophotometric grade) was purchased from Sigma-Aldrich Chemie, Germany. The commercial isotactic polypropylene (PP), Tatren HF (melt flow index MFI$_{200°C, 2.16 kg}$ = 3.12 g/10 min; density $\rho_{23°C}$ = 0.886 g/cm^3, melting temperature T_m = 164.5 ± 1°C), was supplied by Slovnaft Bratislava, Slovakia. The recycled polypropylene, recPP (MFI$_{200°C, 2.16 kg}$ = 2.99 g/10 min; $\rho_{23°C}$ = 0.880 g/cm^3, T_m = 164.4 ±1°C), was taken from municipal plastic waste (containers for cleaning cosmetics) and further grounds.

DPPH radical scavenging assay

Radical scavenging activity of lignin and Irganox 1010 against stable DPPH• was determined spectrophotometrically at 515 nm on a UV–visible light spectrophotometer (Libra S12, Biochrom, England) according the slightly modified method of Brand-Williams et al.[21] Lignin (Irganox 1010) solution was prepared by dissolving in dioxane-water mixture (9:1). The solution of DPPH• in dioxane (6 × 10^{-5} M) was prepared before UV measurements. Different concentrations of lignin (Irganox 1010) were mixed with 3 mL of DPPH• solution in 1 cm path length disposable microcuvettes (expressed as the number of moles of lignin/moles DPPH•). Decrease in absorption was measured after estimated intervals until reaching a steady state. Radical scavenging activity was characterized in terms of antiradical power ARP, which was defined as an inverse value of EC$_{50}$ (amount of lignin in mol/L necessary to decrease the initial DPPH• concentration by 50%).

Fourier-transformed infrared spectroscopy

Fourier-transformed infrared spectroscopy (FT-IR) spectrum was measured in KBr pellets (2 mg sample/200 mg KBr) with Nicolet Magna 750 spectrometer equipped with a DTGS detector. The spectrum was acquired and manipulated with the use of Omnic (version 3.1) FT-IR software at 4 cm^{-1} resolution and 128 scans.

Determination of processing stability of PP and recPP

All samples with the composition described in Table I were prepared by compounding in a laboratory size Brabender single-screw extruder at 200°C and 80 rpm. Multiple extrusions were carried out with
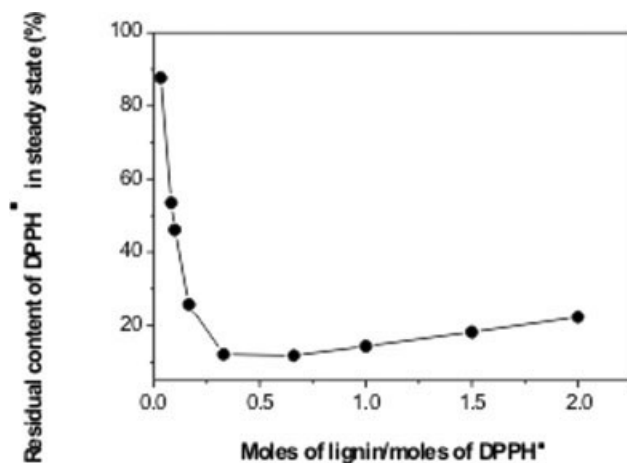
TABLE I
Designation and Composition of Samples

Designation of samples	Composition (wt %)			
	Polymer matrix		Stabilizer	
	PP	Recycled PP	Irganox 1010	Lignin
PP1	100.0	–	–	–
PP2	99.5	–	–	0.5
PP3	99.0	–	–	1.0
PP4	98.0	–	–	2.0
PP5	95.0	–	–	5.0
PP6	90.0	–	–	10.0
PP7	99.5	–	0.5	–
PP8	–	100.0	–	–
PP9	–	99.5	–	0.5
PP10	–	99.0	–	1.0
PP11	–	98.0	–	2.0
PP12	–	95.0	–	5.0
PP13	–	90.0	–	10.0
PP14	–	99.5	0.5	–

TABLE II
Antiradical Power and Reaction Stochiometry of Lignin and Irganox 1010

Compound	Reaction time[a] (min)	ARP[b]	Stochiometric value	Number of reduced DPPH$^\bullet$
Lignin	360	11.10	0.18	5.55
Irganox 1010	780	1.16	1.72	0.58

[a] At the steady state.
[b] Antiradical power.

prepared composites. Processing stability of PP or recycled PP was evaluated by measuring of the melt volume rate (MVR) of the extruded samples. MVR was determined at the temperature 200°C and 2.16 kg load, using Melt flow tester Ceast 6841 according to the standard ASTM D1238 Method B. The standard deviations were no higher than 10%.

Mechanical properties of PP and recPP composites

The mixtures of PP or recPP obtained were moulded into sheets in the electric press at 150°C and 10 MPa for 5 min and cooled at the room temperature. Moulded sheets were disintegrated for subsequent injection moulding at 200°C and 60 kPa using a manual infection-moulding machine. Mechanical properties were tested using flat dumb-bell shaped specimens (25 × 4.2 × 2.65 mm) using Instron 1112 mechanical testing machine (50 mm/min cross-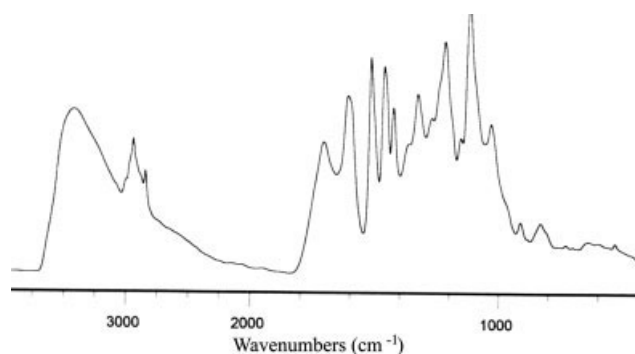head speed and 50 kN tension), according to standard ASTM D 638. Hardness was determined by using tester with ball indentation method according to standard EN ISO 2039-1. The values obtained came from the average of 5 specimens.

Determination of free radicals amount in lignin–polypropylene composites

The concentration of free radicals in lignin–polypropylene samples was monitored by means of electron paramagnetic resonance (EPR) spectroscopy. The measurements were performed using an X-band continuous-wave Bruker EMX spectrometer maintaining the temperature at 20°C using temperature control unit ER 4111 VT. EPR spectra were recorded and evaluated by means of standard equipment and programmes (WINEPR, SimFonia) installed in spectrometer. Operating parameters for the EPR spectrometer were as follows: microwave power 10 mW, centre field 3375 G, sweep width 100 G, conversion time 20.48 ms, time constant 81.92 ms, modulation frequency 100 kHz, modulation amplitude 5.0 G, receiver gain 1×10^5, 5 scans per one spectrum. All scans for one series of experiments were carried out using the same instrument settings with a similar sample shape and its position in the cavity of spectrometer. The g-value and spin concentrations were determined using DPPH standard.

Figure 1 Plot of percent residual DPPH$^\bullet$ at the steady state as a function of the molar ration of lignin to DPPH$^\bullet$.

Figure 2 FT-IR absorption spectrum of lignin.

TABLE III
Processing Stability of Isotactic Polypropylene Stabilized with Lignin

Melt volume rate (cm³/10 min) at 200°C/2.16 kg	Polypropylene with lignin (wt %)					
	0	0.5	1	2	5	10
1st extrusion	3.12 ± 0.29	2.92 ± 0.24	2.38 ± 0.19	2.26 ± 0.19	2.67 ± 0.20	3.03 ± 0.18
2nd extrusion	3.57 ± 0.35	3.29 ± 0.29	2.49 ± 0.22	2.29 ± 0.23	2.66 ± 0.26	2.98 ± 0.27
3rd extrusion	3.98 ± 0.39	3.92 ± 0.23	2.54 ± 0.16	2.25 ± 0.18	2.57 ± 0.25	2.61 ± 0.28
4th extrusion	4.80 ± 0.31	4.07 ± 0.27	2.66 ± 0.14	2.24 ± 0.20	2.58 ± 0.18	2.63 ± 0.22
5th extrusion	5.79 ± 0.36	5.42 ± 0.43	2.83 ± 0.14	2.25 ± 0.23	2.60 ± 0.19	2.59 ± 0.19
6th extrusion	7.37 ± 0.45	6.06 ± 0.53	3.04 ± 0.24	2.28 ± 0.22	2.57 ± 0.23	2.52 ± 0.16
7th extrusion	10.16 ± 1.06	7.42 ± 0.43	3.14 ± 0.20	2.44 ± 0.23	2.52 ± 0.14	2.36 ± 0.22
8th extrusion	16.21 ± 2.08	8.06 ± 0.83	3.40 ± 0.33	2.52 ± 0.30	2.55 ± 0.20	2.20 ± 0.19
9th extrusion	26.57 ± 4.03	9.92 ± 0.84	4.94 ± 0.29	2.78 ± 0.26	2.58 ± 0.11	2.02 ± 0.18
10th extrusion	30.46 ± 4.12	10.80 ± 0.96	5.02 ± 0.35	2.82 ± 0.29	2.71 ± 0.19	1.98 ± 0.16

RESULTS AND DISCUSSION

Radical scavenging properties

From the plot of the percentage residual DPPH• as a function of the molar ratio of lignin to DPPH, the EC_{50} was obtained (Fig. 1). From the Figure 1 it can be seen that percentage residual DPPH decreased with increasing amount of lignin, however from the 0.66 molar ratio of lignin to DPPH the percentage residual DPPH has increasing tendency. It can be explained by lignin self-color power, which causes the change in color of measured solution. For that reason spectrophotometric investigations of lignin samples for antioxidant effectiveness should be settled in low lignin concentrations. ARP and stochiometric data are listed in Table II. Stochiometric value, obtained by multiplying EC_{50} by 2,[21] gives the theoretical efficient concentration of lignin and Irganox 1010 needed to reduce 100% of the DPPH•. Consequently, the inverse value of stochiometric value (number of reduced DPPH•) gives the information how many moles of DPPH• were reduced by one mole of lignin or Irganox 1010. From the obtained results in Table I it can be seen that lignin exhibits higher radical scavenging efficiency with DPPH• in comparison with that of Irganox 1010. The revealed

high antiradical power of the tested lignin (ARP is 11.1) isolated from beechwood can be explained by its structure. It consists mostly from the syringyl units, as it is evident from the high intensity of absorption band at 1217 cm^{-1} corresponding to methoxyl vibrations (Fig. 2). It is known that ortho-substitution with electron-donating methoxy groups increases the antioxidant and antiradical efficiencies.[22–24] Moreover, the high antioxidant activity of this lignin is also due to its low-molecular weight and polydispersity. As was described earlier[16] these factors tend to improve the compatibility and consequently the antioxidant activity of lignin.

Melt properties

The thermo-oxidative degradation of isotactic polypropylene and recycled polypropylene stabilized with lignin was studied measuring the melt volume rate of the extruded samples after multiple extrusions at 200°C by method described in literature.[8,24] MVR values obtained after multiple extrusions of both polypropylene samples containing lignin in concentration from 0.5 to 10 wt % are shown in Table III and 4. From these results it is obvious that MVR of both nonstabilized polypropylene increased

TABLE IV
Processing Stability of Recycled Polypropylene Stabilized with Lignin

Melt volume rate (cm³/10 min) at 200°C/2.16 kg	Recycled polypropylene with lignin (wt %)					
	0	0.5	1	2	5	10
1st extrusion	3.00 ± 0.27	3.02 ± 0.21	2.62 ± 0.25	2.64 ± 0.28	3.19 ± 0.20	3.05 ± 0.35
2nd extrusion	3.32 ± 0.24	3.19 ± 0.18	2.59 ± 0.29	2.62 ± 0.27	3.04 ± 0.24	3.12 ± 0.32
3rd extrusion	3.52 ± 0.34	3.32 ± 0.30	2.64 ± 0.36	2.62 ± 0.25	2.95 ± 0.18	2.76 ± 0.28
4th extrusion	3.92 ± 0.33	3.63 ± 0.24	2.66 ± 0.24	2.63 ± 0.25	3.00 ± 0.30	2.57 ± 0.24
5th extrusion	4.67 ± 0.39	4.45 ± 0.35	2.76 ± 0.32	2.67 ± 0.25	2.65 ± 0.23	2.48 ± 0.24
6th extrusion	5.34 ± 0.48	4.63 ± 0.32	2.94 ± 0.34	2.69 ± 0.26	2.92 ± 0.21	2.42 ± 0.21
7th extrusion	6.16 ± 0.45	4.96 ± 0.25	3.25 ± 0.34	2.74 ± 0.26	3.02 ± 0.17	2.46 ± 0.24
8th extrusion	6.58 ± 0.61	5.23 ± 0.36	3.78 ± 0.32	2.80 ± 0.27	3.02 ± 0.15	2.47 ± 0.23
9th extrusion	10.12 ± 0.56	5.89 ± 0.38	3.82 ± 0.28	2.86 ± 0.26	3.02 ± 0.18	2.48 ± 0.23
10th extrusion	11.92 ± 0.85	6.25 ± 0.45	3.83 ± 0.32	2.89 ± 0.28	3.41 ± 0.32	2.41 ± 0.20

TABLE V
Processing Stability of Isotactic Polypropylene and Recycled Polypropylene Stabilized with Irganox 1010

Melt volume rate (cm^3/10 min) at 200°C/2.16 kg	Polypropylene with 0.5 wt % of Irganox 1010	Recycled polypropylene with 0.5 wt % of Irganox 1010
1st extrusion	2.86 ± 0.23	3.08 ± 0.25
2nd extrusion	3.00 ± 0.27	3.23 ± 0.30
3rd extrusion	3.34 ± 0.30	3.33 ± 0.31
4th extrusion	3.54 ± 0.31	3.41 ± 0.31
5th extrusion	3.75 ± 0.33	3.72 ± 0.25
6th extrusion	4.12 ± 0.28	3.81 ± 0.25
7th extrusion	4.38 ± 0.39	4.03 ± 0.37
8th extrusion	4.85 ± 0.44	4.25 ± 0.30
9th extrusion	5.07 ± 0.44	4.40 ± 0.12
10th extrusion	5.82 ± 0.33	4.77 ± 0.63

rapidly with the number of extrusions, which indicate the degradation of polypropylene matrices due to the chain scission similarly as described in literature.[25,26] The MVR values of the isotactic polypropylene extruded samples increased more intensively than those of the recycled polypropylene. The observed differences probably resulted from the presence of previous stabilizers in recycled polypropylene. Already 0.5 wt % of lignin addition as stabilizer into both polypropylene decelerated the increase of MVR during multiple extrusions. The effect of MVR stabilization increased with lignin concentration. However, at the 10 wt % lignin concentration in both polypropylene and recycled polypropylene there is reverse change of MVR that can be related with high hardness of samples and consequently lower flow possibility. For comparison of lignin processing stabilizing efficiency, both types of polypropylene were stabilized with synthetic phenolic processing stabilizer Irganox 1010 (Table V). It

TABLE VI
Mechanical Properties of Polypropylene and Recycled Polypropylene Composites

| Samples	Tensile strength at break (Mpa)	Elongation at break (%)	Young modulus (MPa)	Hardness (N/mm^2)
PP1	26.9 ± 2.0	456 ± 33	805 ± 30	35.8
PP2	22.7 ± 1.1	282 ± 30	796 ± 15	36.0
PP3	23.7 ± 1.5	214 ± 16	800 ± 10	37.0
PP4	19.2 ± 2.9	183 ± 25	821 ± 40	37.5
PP5	29.9 ± 4.0	26 ± 7	900 ± 80	39.2
PP6	32.4 ± 1.9	17 ± 2	940 ± 82	42.0
PP7	26.6 ± 1.7	436 ± 10	755 ± 35	35.6
PP8	21.4 ± 1.3	238 ± 18	644 ± 22	32.2
PP9	20.5 ± 2.0	240 ± 10	685 ± 52	33.0
PP10	18.7 ± 1.5	220 ± 16	720 ± 46	33.4
PP11	16.7 ± 1.9	208 ± 20	773 ± 10	33.8
PP12	17.6 ± 2.6	221 ± 16	790 ± 15	35.0
PP13	21.6 ± 4.3	82 ± 15	819 ± 9	38.0
PP14	18.6 ± 1.2	230 ± 5	677 ± 20	32.0

can be concluded that the stabilizing effect of Irganox in 0.5 wt % concentration is comparable with that of lignin in 1 wt % concentration.

Mechanical properties

The results of mechanical properties of PP and recPP composites filled with lignin up to 10 wt % are shown in Table VI. The incorporation of a low amount of lignin (up to 2 wt %) causes the decrease of tensile strength, elongation, and Young modulus. For higher lignin content from 2 wt %, the improvement of tensile strength and Young modulus was observed. Decrease of elongation is connected with breaking of PP matrix continuity. The hardness increased with lignin concentration. The change of mechanical properties of lignin–PP composites is analogous to that of lignin–recPP composites; however initial values of recycled polypropylene were lower. The influence of adding of 0.5 wt % Irganox 1010 on mechanical properties is negligible.

Electron paramagnetic resonance

The spin concentrations of PP and recPP samples stabilized with lignin or Irganox after each extrusion are summarized in Figures 3 and 4. EPR spectra were obtained in the field from 3320 to 3420 G with g-value at 2.0032. From these data, it is evident that lignin rapidly raises the radical concentration with its increasing content in both polypropylene. However the addition of lignin in 0.5–2 wt % keeps the radical concentration after multiple extrusions in steady level, comparable with Irganox 1010. Isotactic polypropylene and recycled polypropylene composites with lignin concentration above 5 wt % are presented with greater formation of free radicals after multiple extrusions. Lignin in concentration of about
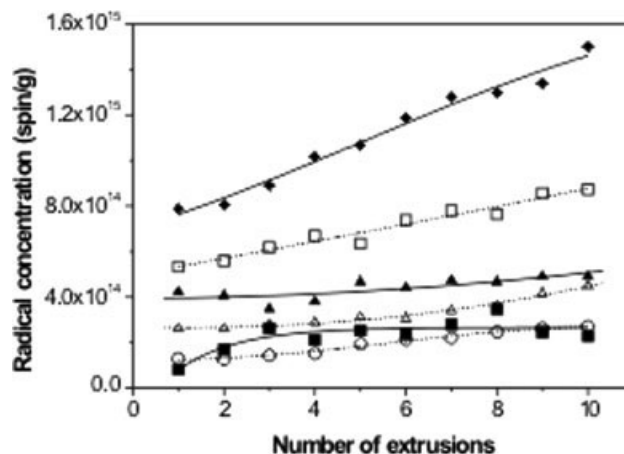
Figure 3 Dependence of radical concentration in polypropylene samples on number of extrusions; ◇: PP2, △: PP3, ▲: PP4, □: PP5, ◆: PP6, ■: PP7.
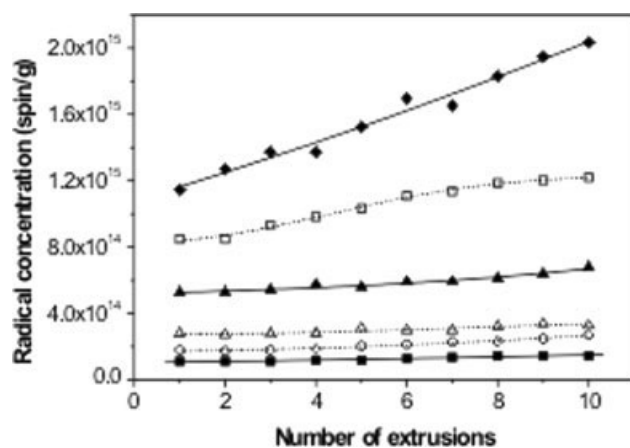
Figure 4 Dependence of radical concentration in recycled polypropylene samples on number of extrusions; ◇: PP9, △: PP10, ▲: PP11, □: PP12, ◆: PP13, ■: PP14.

1–2 wt % in both types of polypropylene caused minimum change of radical concentration after multiple extrusion, which indicates the applicable concentration of lignin to achieve the required stabilizing effect. Based on our previous results the observed minimum of free radicals at lignin concentration of about 2 wt % could be explained by the interaction at the boundary of two phases between paramagnetic sites of polypropylene and lignin.[27]

CONCLUSIONS

The determined MVR values of the prepared polypropylene composites after multiple extrusions showed that lignin acts as the processing stabilizer for both virgin and recycled polypropylene. Their processing stability was increased with lignin concentration. The obtained mechanical properties of lignin–polypropylene (recPP) composites revealed that the tested lignin sample has ability to increase some of these properties as Young modulus and hardness in all concentration range and also tensile strength at break in the case of higher concentration as 5 wt %.

The determination of radical concentration of each extruded sample established that the optimal concentration of lignin in both polypropylene samples for enhancing of processing stability is about 1–2 wt%. This revealed stabilizing effect of lignin is comparable with that of Irganox 1010 in concentration 0.5 wt %. Moreover, the radical scavenging capacity of both stabilizers was investigated using the free radical DPPH• method. The revealed differences

between the results obtained by determination of MVR values and ARP values can be explained with different behavior of lignin in solution and solid system.

The obtained results indicate that lignin could be considered as potent processing stabilizer for polypropylene composites, while its biopolymeric nature may be an advantage in certain applications.

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