IPPI

Polyolefins Journal Vol. 1 No. 1 (2014) 17-24

ORIGINAL PAPER

In situ stabilization of polypropylene by lignin using a Ziegler-Natta catalyst

Maria Fatima Vieira Marques*, Renato Jonas Benne Oliveira, Rafael Silva Araujo,
Bruno Pereira Amantes

Instituto de Macromoléculas (IMA) - Universidade Federal do Rio de Janeiro - UFRJ, CP 68525, CEP 21941-590, Rio de Janeiro-RJ, Brazil

Received: 26 December 2012, Accepted: 30 June 2013

ABSTRACT

A fourth-generation Ziegler-Natta catalyst was prepared to synthesize polypropylene (PP), which was stabilized by in situ polymerization employing lignin as antioxidant. The antioxidant properties of lignin were compared with those of the commercial antioxidant Irganox 1010. The presence of lignin in the reaction medium slightly decreased the catalytic activity of the reaction. The isotacticity index (I.I.) of PP synthesized with lignin (PP-lig) was not affected by the presence of the additive in the reaction medium. The thermal properties, characterized by differential scanning calorimetry, showed slightly decreased degree of crystallinity (X_c), but the melting temperature (T_m) and crystallization temperature (T_c) were not affected when compared with the neat polymer. Lignin showed good activity as a stabilizer by thermogravimetry. The initial temperature of degradation (T_{onset}) increased when compared to the pure PP and PP stabilized with the commercial antioxidant. The lower carbonyl index of the PP, evaluated by infrared spectroscopy (FTIR) after thermo-oxidative treatment, also revealed the stabilizing action of lignin. **Polyolefins J (2014) 1:17-24**

Keywords: antioxidant, polypropylene, Ziegler-Natta catalyst

INTRODUCTION

Lignin is a complex phenolic polymer (Figure 1) occurring in higher plant tissues and is the second most abundant terrestrial polymer after cellulose [1-3]. Typical molecular masses of isolated lignin are in the range of 1,000–20,000 g/mol, although the degree of polymerization in nature is difficult to measure, since lignin is invariably fragmented during extraction and consists of several types of substructures which repeat in an apparently haphazard manner [1-4]. Commercial lignin is currently produced as a co-product of the pulp and paper industry, separated from fibers by a chemical pulping process [2]. The antioxidant properties of lignin allow stabilizing PP composites against photo and thermo-oxidation, so the main objective of incorporating lignin in polyolefins is to stabilize the materials against oxidation under UV radiation or at elevated temperatures [4-9]. Canetti et al. [9] observed an increase in the thermal stability of PP with lignin

---

* Corresponding Author - E-mail:fmarques@ima.ufrj.br

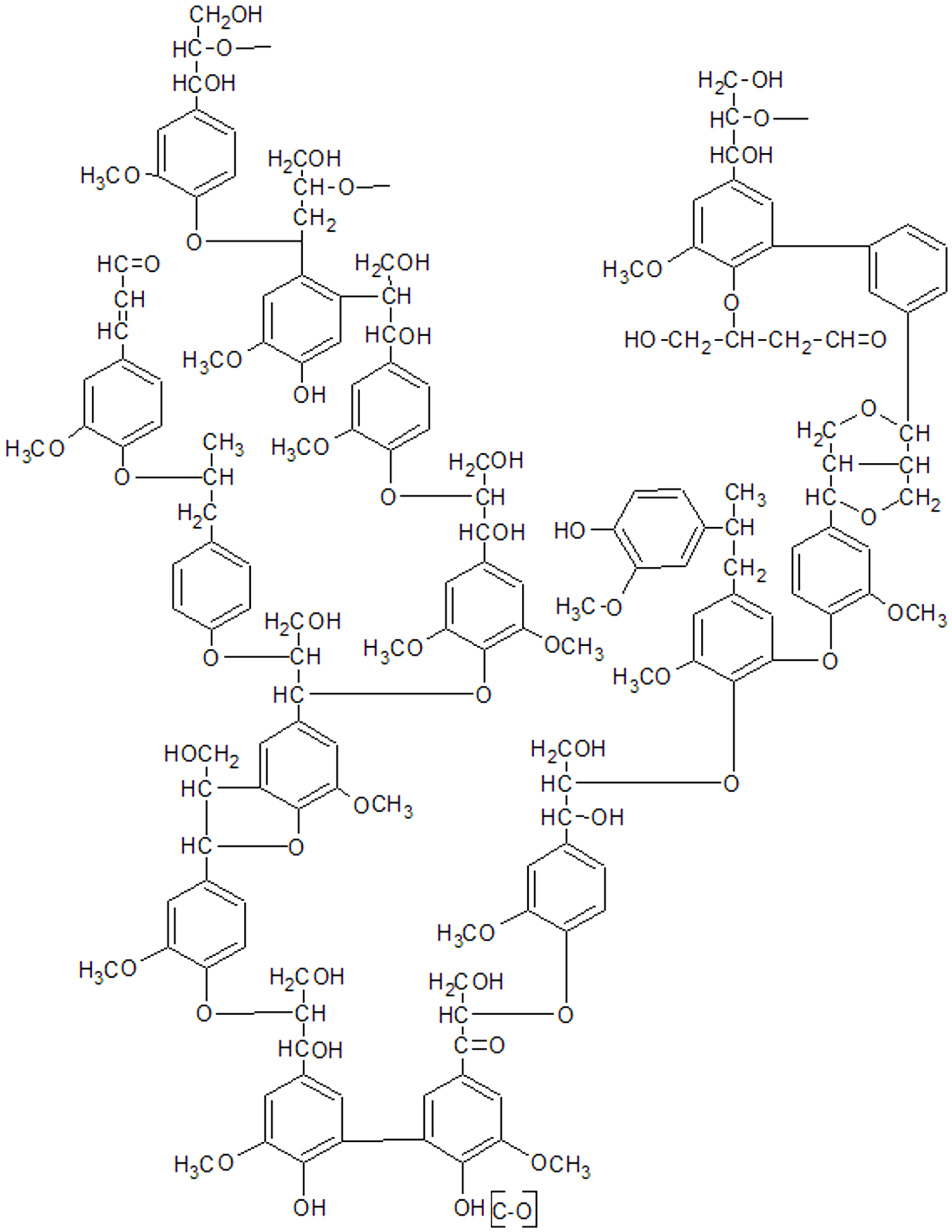


Figure 1. Partial structure of a lignin molecule [1]

compared with neat PP, where the onset degradation temperature was shifted to higher values.

Most adopted methods of mixing additives with polypropylene involve an extrusion process for production of pellets [10-12]. During the extrusion process, the material which is exposed to high temperatures and shear rates may undergo destructive reactions, resulting in a combination of mechanical and chemico-thermal degradations. On the other hand, the technique of in situ polymerization involves the incorporation of additives during polymer synthesis, eliminating the subsequent mixing step and thereby reducing the cost of production [13-15]. Since one-third of the energy for the production of polypropylene is consumed in the pelletization process, avoiding this step would be of practical interest to the polyolefin industry.

The latest generations of Ziegler-Natta systems can control the morphology of the catalyst particles so that the polymerization results in products with spherical particles by the replica phenomenon. Therefore, this process produces grains of polymers directly from the reactor that do not need pelletization, although it needs introduction of additives [16].

Hence, the addition of an antioxidant into the polymerization reactor would allow producing stabilized polypropylene in the form of grains. Especially in the case of using a natural polymer like lignin as antioxidant, avoiding one extrusion processing step would be of great interest. However, the antioxidant may affect the active species to some extent, since it contains polar groups, which can deactivate those polymerization sites, resulting in a decrease of catalyst activity and of isotacticity of the polypropylene.

In the present work, a Ziegler-Natta catalyst was prepared to synthesize polypropylene (PP), which was stabilized by in situ polymerization with lignin. Polymerizations were performed by adding the antioxidant into the reactor. In addition to the polymer synthesized in the presence of lignin, we also produced pure polypropylene (without antioxidant), and polypropylene with a commercial antioxidant for comparative purposes. The degradation process was monitored by determining the weight loss and oxidation was observed by infrared spectroscopy (FTIR), while surface morphology was characterized by scanning electron microscopy (SEM) and optical microscopy (OM).

EXPERIMENTAL

Materials

The lignin was provided by Fibria, Brazil, directly from the black liquor from paper making. It was not purified prior to use. For the catalyst preparation, we used purified propylene from Braskem, Brazil; titan tetrachloride from Aldrich, USA; triethylaluminum (TEA) from Akzo Nobel, USA; n-butyl phthalate (internal electron donor)from Elekeiroz S.A., Brazil, purified with a column of silica/anhydrous $MgSO_4$,dimethoxy-diphenylsilane(external electron donor) fromTokyo Kasei Kogyo Co., LTD, Japan, and anhydrous magnesium chloride (TMT-4)from Toho Catalyst Co., LTD, Japan.

Methods

Preparation of Ziegler-Natta catalyst

For this work, titanium-based Ziegler-Natta catalyst supported on $MgCl_2$was prepared. Three grams of anhydrous $MgCl_2$ was added into the reactor containing oil. The reactor containing the mixture was placed in an ice bath and 6 mL of anhydrous ethanol was added under stirring. After 15 min, the ice bath was replaced with an oil bath and the temperature was increased slowly to 120°C. After melting of $MgCl_2$, the material was transferred under stirring to a flask containing dry isoparaffin at -40°C. The precipitated adduct was then dealcoholized for 4 h at 60°C with $TiCl_4$. The product was washed with anhydrous hexane until the termination of gas release, and it was then impregnated with the internal donor under magnetic stirring for 2 h and 90°C. Then, $TiCl_4$was added under stirring and then the temperature was raised and maintained at 100°C for 2 h. After this period, the catalyst was washed with dry hexane until no gas was released and it was dried under nitrogen to constant weight.

Polymerizations were carried out with addition of antioxidants in the polymerization reactor. PP-crud was the polymer synthesized without antioxidant, PP-1010 was polypropylene synthesized in the presence of Irganox 1010, a commercial synthetic antioxidant, and PP-lign was the polypropylene synthesized in presence of the lignin. The polymerizations were conducted under 2 bar and 70°C. Triethylaluminum (TEA) was used as cocatalyst and an external donor (ED) was also added in the reaction medium to increase the PP's isotacticity. The antioxidants were maintained in the presence of TEA for 30 min before being introduced in the reaction medium in order to promote the reaction of TEA with the polar groups of the antioxidants employed. The amount of antioxidant used was 0.0192 g, corresponding to 0.2% w/w. An average of 5 PP polymerizations was carried out without antioxidant. In the case of lignin, its reaction with hexane solution of TEA dissolved the lignin and gas release occurred.

Scanning electron microscopy (SEM)

The morphology of the catalyst support was observed using a Shimadzu SS 550 Superscan scanning electron microscope. The samples were gold-sputtered prior to observation.

Optical microscopy (OM)

The morphology of the synthesized polypropylene was analyzed under a stereo microscope coupled to a camera.

Isotacticity index (I.I.)

The isotacticity index of the polypropylene was evaluated by determining the content of insoluble fraction, by submitting 0.5 g of polypropylene to extraction in heptane at reflux for 6 h (ASTM D 297). The insoluble fraction was determined by the ratio between the mass of the insoluble fraction and the initial polymer.

Differential scanning calorimetry (DSC)

For DSC analysis, about 10 mg of sample was used, and the polymer was heated from room temperature to 180°C at a rate of 10°C/min and then cooled to 25°C. The melting temperature (T_m) was obtained from the second heating curve and the degree of crystallinity (Xc) was calculated from the enthalpy of melting given by this technique, according to the following equation.

$$X_c = \frac{\Delta H_m^a}{\Delta H_m^{100}} \times 100$$

Xc= degree of crystallinity (%)
ΔH_m^a = heat of melting sample (J/g)
ΔH_m^{100}= heat of melting of polypropylene with 100% crystallinity (J/g)
The enthalpy of melting of theoretical 100% isotactic crystalline polypropylene = 195 J/g.

DSC was performed with a TA Instruments series Q model Q 1000. The samples were heated from room temperature to 180°C at 10°C/min. The material went through two heating steps, the first serving to erase the thermal history of the synthesized polymer. Then, the sample was cooled to room temperature at a rate of 10°C/min under nitrogen flow and then heated again at the same rate.

Thermogravimetric analysis (TGA)

The polymers were characterized by thermogravimetric analysis (TGA), which involved measuring the variation in mass of the sample as a function of temperature. The onset temperature (T_{onset}) was calculated, which represented the start of degradation. TG was performed with a TA Instruments series Q model Q 500. The samples were heated from room temperature to 700°C at a heating rate of 10°C/min under nitrogen atmosphere.

Infrared spectroscopy (FTIR)

The oxidation of the materials was measured by determining the carbonyl index, calculated as the ratio of intensity at 1710 cm^{-1} (carbonyl stretching vibration in FTIR spectrum) to the reference peak of isotactic polypropylene at 1165 cm^{-1} (A_{1710} / A_{1165}) after the samples were subjected to a temperature of 180°C for 1 h in an oven under ambient air. IR spectra were recorded with a Varian Excalibur 3100 FTIR using KBr pellets.

RESULTS AND DISCUSSION

The Ziegler-Natta catalysts of the latest generations are able to control the morphology of polymers. This is possible because of the replica phenomenon, where the polymer reproduces the shape of the catalyst. Therefore, during the catalyst preparation, control in all stages was exercised so that the catalyst particles with spherical shape were produced. The micrograph of the catalytic support precursor (adduct $MgCl_2.3EtOH$, before the dealcoholization process) is shown in Figure 2.

Figure 2 shows that there was a control over the morphology of the catalyst support particles, i.e., the particles have spherical morphology. Furthermore, the catalyst support particles also had relatively homogeneous size distribution.

As it is shown in Figure 3, the pure PP and PP stabilized by in situ polymerization with Irganox 1010 (PP-1010) both have globular shapes. However, the shape of the polymer particles stabilized by in situ polymerization by lignin (lignin-PP) showed irregular morphology. Although the shape of some particles of PP with lignin appeared spheroidal, it was not possible to confirm the shape of polymer particles, since most

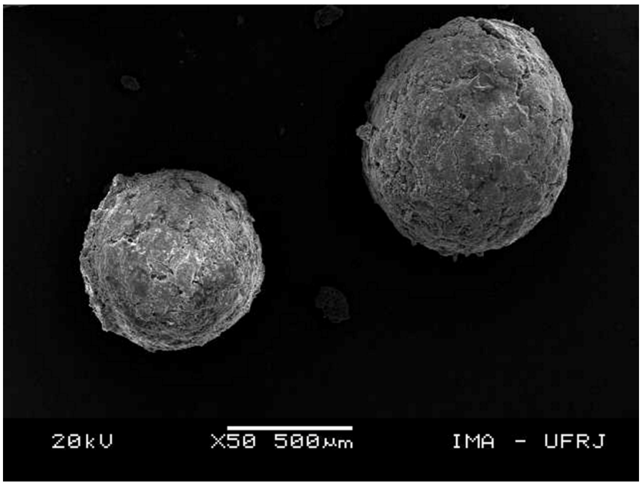
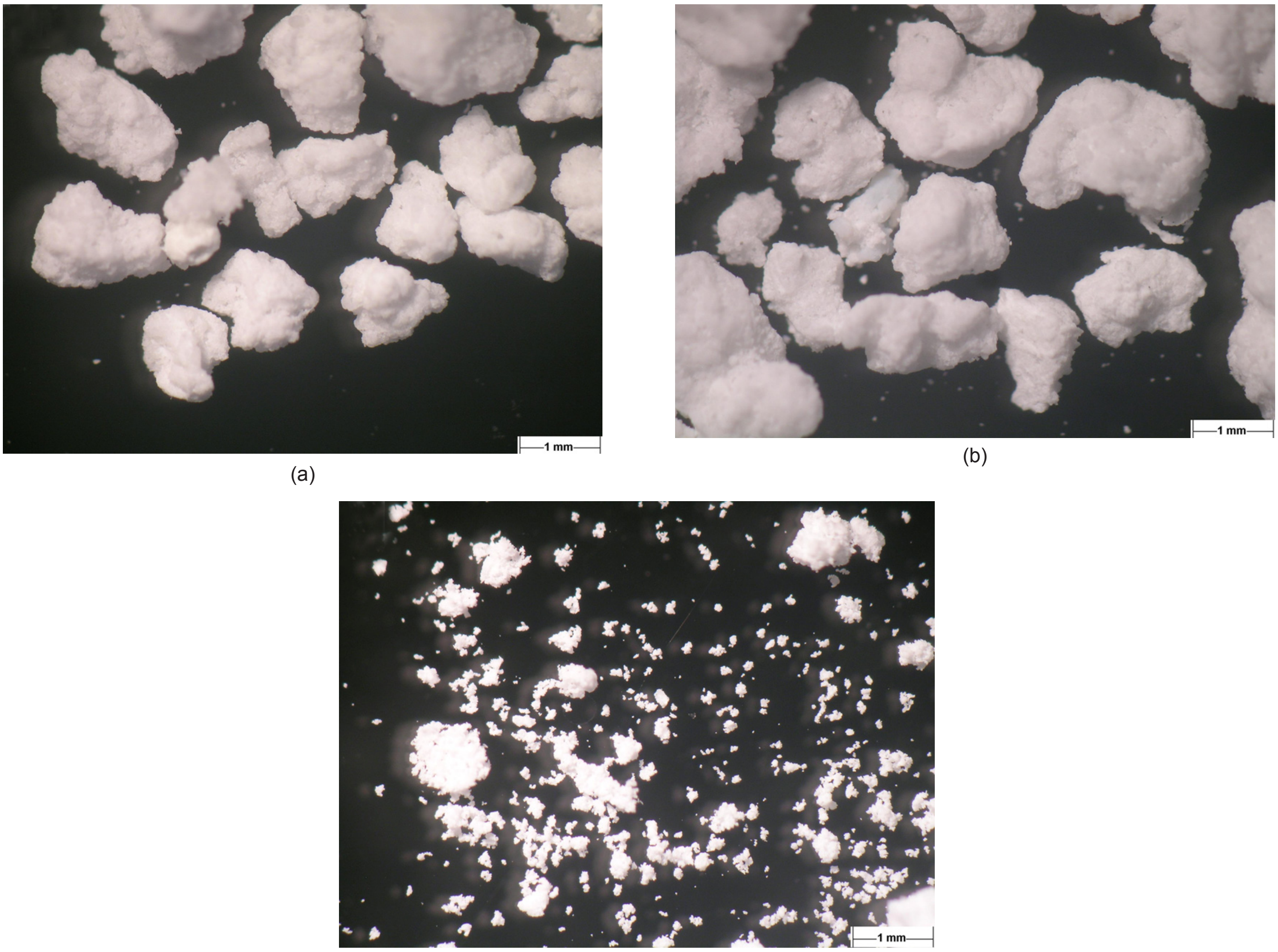


Figure 2. Micrograph revealed by SEM of the catalytic support precursor



(a)

(b)

(c)

Figure 3. Micrographs of the polymers revealed by optical microscopy:(a) pure PP (PP-neat); (b) PP stabilized with by Irganox(PP-1010); (c) PP stabilized by lignin (PP-lig)

of the materials were obtained as small particles rather than spherical granules. This is probably because we did not purify lignin from the black liquor. Also, the color of the polypropylene samples obtained with Irganox and also with lignin was not affected by the antioxidant addition, that is, the grains were white, just like pure PP.

Polymerizations conducted with or without antioxidants were performed and the results of yield and polymer characteristics are listed in Table 1. These polymerizations were conducted under pressure of 4 bar and a temperature of 70°C in a 4 L reactor. The standard deviation of the reaction was determined from Eqn 1, which is based on 5 polymerization yields without antioxidant. The result of the experimental error was 13%.

$$\sigma^2_{EXP} = \sum_{i=1} \frac{(y_i - \overline{y})^2}{N-1} \qquad (1)$$

Table 1. Catalytic activity, isotacticity index and thermal properties obtained by DSC of the produced polymers

Sample	Yield (gPP)	I.I. (%)	T_m (°C)	T_c (°C)	X_c (%)
PP-neat	9.60±1.24	99	158	116	46
PP-1010	7.01±0.91	96	159	118	41
PP-lig	6.23±0.81	99	159	118	28

Propylene polymerization conditions: 4 bar; 100 mL of heptanes; 70°C; 50 mg cat; [TEA] = 7.5 mmol; Internal and external donors were employed to control the stereoselectivity of polypropylene; 0.5% p/p antioxidant was used. PP-neat = PP without antioxidant; PP-1010 = PP with Irganox 1010; PP-lig = PP with lignin

N = number of experiments at the midpoint;

σ^2 = variance of the experimental measurements;

y_i= measurement i;

$\bar{y}$= mean of the measurements;

As it is presented in Table 1, the presence of stabilizers in the reaction medium did not affect the crystalline melting temperature or the crystallization temperature of the polymers stabilized by in situ polymerization. However, the degree of crystallinity of PP stabilized with lignin was significantly low indicating that lignin in the reaction adversely affected the relative content of crystals, while the commercial Irganox did not have a significant influence. This is due to the fact that we introduced unpurified lignin, which contained amorphous materials from the black liquor.

Further, according to Table 1 it can be observed that the presence of Irganox in the reaction medium slightly affected the isospecific sites of the catalyst, since the isotacticity of the PP-1010 was reduced to a small degree compared to that of PP-neat. On the other hand, the introduction of lignin in the reaction medium did not affect the isotacticity of the polymer obtained. In fact, the antioxidant sample was reacted with TEA for 30 min before its addition into the polymerization reactor. Therefore, we did not expect sharp changes in the isotacticity of the catalyst. This means that TEA protected the polar groups of those compounds so that they did not react with the catalyst sites.

Table 1 also shows that for the crystallization temperature (T_c), the presence of antioxidant in

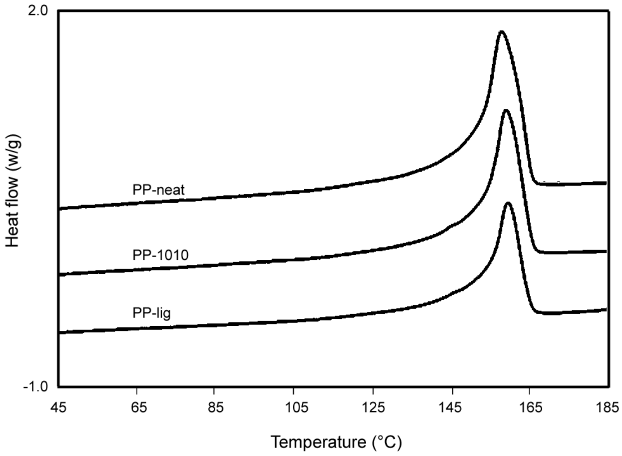


Figure 4. Profiles of DSC curves of the polymers obtained:PP-neat = PP without antioxidant; PP-1010 = PP with Irganox 1010; PP-lig = PP with lignin

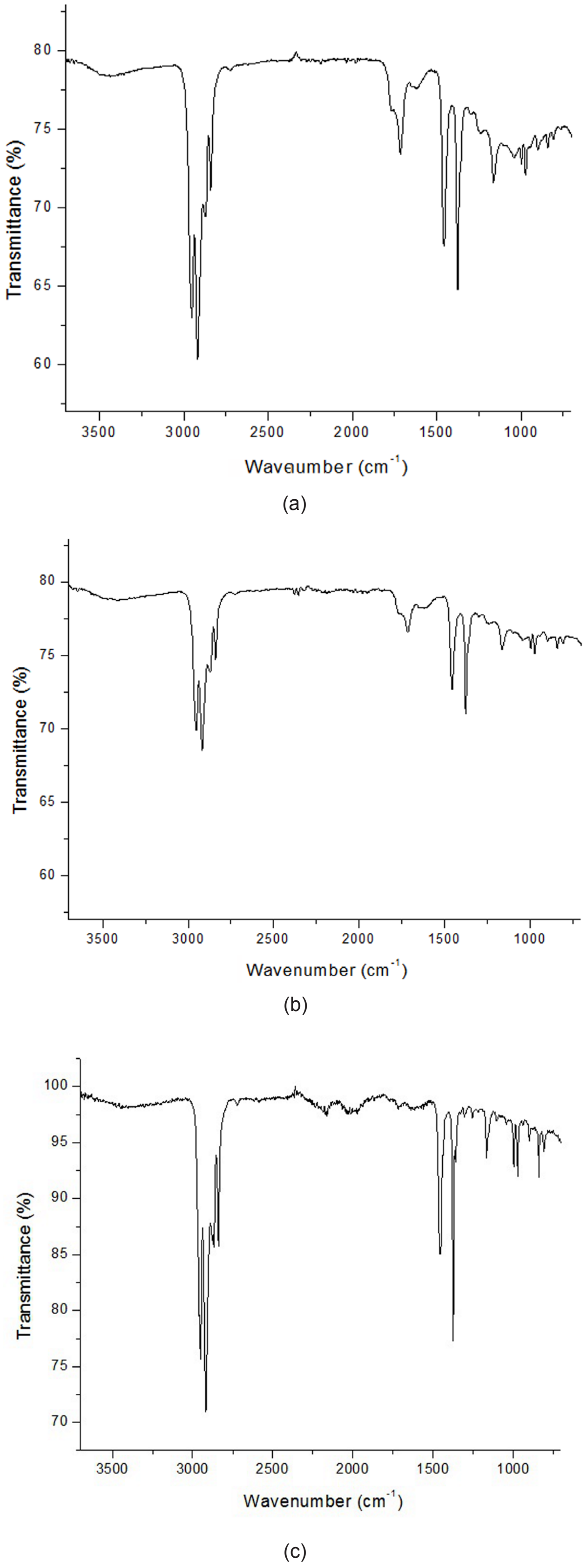


Figure 5. FTIR spectra for the polymers, where (a) PP-neat = PP without antioxidant; (b) PP-1010 = PP with Irganox-1010; (c) PP-lig = PP with lignin

Table 2. Stabilizing properties of the materials used as antioxidants

Sample	A_{1710}	A_{1165}	A_{1710}/A_{1165}	T_{onset} (°C)
PP-neat	0.006	0.006	1.000	317
PP-1010	0.009	0.019	0.474	348
PP-lig	0.007	0.019	0.368	422

PP-neat = PP without antioxidant; PP-1010 = PP with Irganox 1010; PP-lig = PP with lignin

the reaction slightly increased the temperature of crystallization of the polymer compared to that of pure PP. However, the degree of crystallinity (X_c) was affected with a slight reduction for the PP-1010, while the PP-lig was reduced most significantly, indicating that the antioxidant must have interfered with the formation of crystals. Since the isotacticity index (I.I.) of the PP-lig did not change, we believe the antioxidants affected the quantity of isospecific sites of the catalyst. The crystalline melting temperature (T_m) did not undergo a large variation, indicating that the antioxidant did not significantly influence the size of the isotactic PP crystals. This suggests that the stereoselectivity of the catalytic sites that produced isotactic PP was not influenced by the antioxidants. Figure 4 shows the profiles of DSC endotherms of the polymers.

A higher carbonyl index indicates greater degradation of the polypropylene. Therefore, the decrease of the carbonyl index in PP with the antioxidants Irganox 1010 and lignin indicates better protection exerted by the antioxidant. As noted in Table 2, the carbonyl index of PP-lig was significantly lower than that of pure PP (PP-neat), which shows the antioxidant activity of lignin. In addition, also PP-lig presented a lower rate than the PP-1010, which was stabilized by the commercial antioxidant widely used in the industry. Figure 5 shows the FTIR spectra of the synthesized polymers.

From the data in Table 2 it can be observed that the initial temperature of degradation (T_{onset}) of PP-lig increased significantly compared to pure PP. This shows that lignin has much stronger stabilizing action on polypropylene than Irganox since the PP-lig presented a much higher T onset value than that of PP-1010. Figure 6 shows the thermogravimetry profiles of the polymers.

A shift in T onset profile of the PP to higher values can be observed compared with other samples, for the better protective effect on the polymer, although mass loss is observed for PP-lignin at low temperatures. This is due to the content of impurities from the black liquor in the lignin sample.

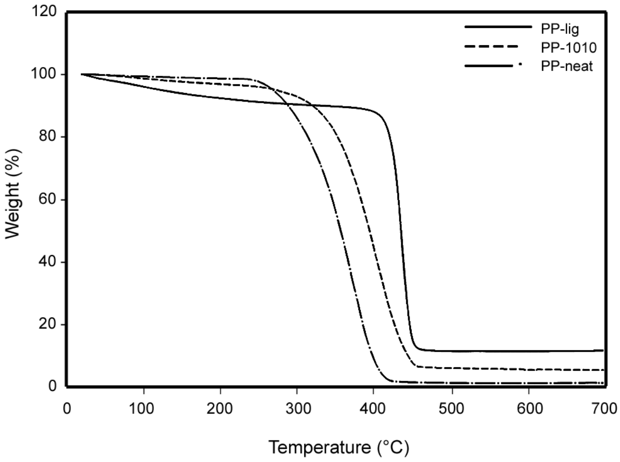


Figure 6. Thermogravimetric profiles of the polymers, where (a) PP-neat = PP without antioxidant; (b) PP-1010 = PP with Irganox-1010; (c) PP-lig = PP with lignin

CONCLUSION

The stabilization of polymers by antioxidants was achieved successfully with the direct addition of antioxidants into in situ polymerization batch, though the presence of lignin in the reaction medium resulted in slight decrease in catalytic activity.

The SEM images showed that the shape of the catalyst was satisfactorily controlled. However, the same morphologic control was not observed for the polymer, which appeared more globular with uneven surfaces, as disclosed by OM images.

The presence of lignin in the reaction medium did not affect the isotacticity of the polymer although it may have hindered the formation of crystals, since the DSC analysis showed a decrease in the degree of crystallinity of the polymer stabilized by in situ polymerization as compared with the pure polymer.

The stabilizing action of lignin was evaluated by FTIR. The lower carbonyl index of PP stabilized with lignin compared to pure PP showed the protective effect of this additive. The TGA analysis also highlighted the protective effect of lignin, since the initial temperature of degradation of PP-lig shifted to much higher values than that of pure PP.

In the light of the results obtained, we can conclude that lignin has good potential to act as a reducing agent or antioxidant, replacing the use of synthetic antioxidants, and in situ polymerization is an effective method for mixing the additives with the polymer. The in situpolymerization eliminates the step of extrusion to stabilize the PP, and even if the lignin is not used as a long-life antioxidant, new additives can be added to the PP during processing to produce the final article.

ACKNOWLEDGEMENTS

CNPq - National Council for Scientific and Technological, CAPES–Office to Improve University Personnel, Brazil.

REFERENCES

1. Gregorova´A, Cibulkova Z, Košíková B, Šimon P (2005) Stabilization effect of lignin in polypropylene and recycled polypropylene. Polym Degrad Stabil 89:553-558
2. Dohertya WOS, Mousavioun P, Fellows CM (2011) Value-adding to cellulosic ethanol:lignin polymers- a review. Ind Crop Prod 33:259-276
3. Vinardell MP, Ugartondo V, Mitjans M (2008) Potential applications of antioxidant lignins from different sources. Ind Crop Prod 27:220-223
4. Pouteaua C, Dole P, Cathala B, Averous L, Boquillon N (2003) Antioxidant properties of lignin in polypropylene. Polym Degrad Stabil 81:9-18
5. Pouteaua C, Dole P, Cathala B, Averous L, Boquillon N (2004) Lignin-polymer blends:evaluation of compatibility by image analysis. CR Biol 327:935–943
6. Oliveira RJB, Forrester AMS, Marques MFV (2011) In-reactor stabilization of poly(propylene) with natural antioxidants. Macromol Symp 299/300:215-219
7. Alexya B, Košíková B, Podstránska G (2000) The effect of blending lignin with polyethylene and polypropylene on physical properties. Polymer 41:4901–4908
8. Rosu L, Cascaval C N, Rosu D (2009) Effect of UV radiation on some polymeric networks based on vinyl ester resin and modified lignin. Polym Test 28:296-300
9. Canetti M, Bertini F, de Chirico A, Audisio G (2006) Thermal degradation behaviour of isotactic polypropylene blended with lignin. Polym Degrad Stabil 91:494-498
10. Chatterjee AM (1989 Aug 1) In-reactor stabilization of polyolefins via coated stabilizers. US Patent 4853426
11. Chatterjee AM (1991 Nov 12) In-reactor stabilization of polymer via coated stabilizers. US Patent 5064878
12. Chatterjee AM, Robert CJ (1989 Apr 12) Process for the in-reactor stabilization of polyolefins. US Patent 4818799
13. Rodrigues PC,Muraro M, Garcia CM, Souza GP, Abbat M, Schreiner WH, Gomes MAB(2001) Polyaniline/lignin blends: thermal analysis and XPS. Eur Polym J 37:2217-2223
14. Gregorová A, Kosíková B, Moravcík R (2006) Stabilization effect of lignin in natural rubber. Polym Degrad Stabil 91:229-233
15. Fernandes DM, Hechenleitner AAW, Job AE, Radovanocic E, Pineda EAG (2006) Thermal and photochemical stability of poly(vinyl alcohol)/modified lignin blends. Polym Degrad Stabil 91:1192-1201
16. Rotzinger B, Brunner M(2008) In-reactor stabilization of polypropene. Polym Degrad Stabil 93:316-320