In-Reactor Stabilization of Poly(propylene) with Natural Antioxidants

*Renato J.B. Oliveira, Amanda M.S. Forrester, Maria F.V. Marques**

Summary: Poly(propylene) is one the polymers with the widest range of commercial applications, though as all polymers, it is susceptible to degradation reactions. The addition of antioxidants to polymers is the main way to prevent or retard the degradation process. Extrusion is the most used industrial process to mix additives to the polymer, but this technique involves processing under high temperatures and shear, which causes polypropylene to degrade. Therefore, a Ziegler-Natta catalyst system based on $MgCl_2/TiCl_4$ was prepared with morphology control and the antioxidant was added directly in the polymerization medium, thereby producing spherical and stabilized PP.

Keywords: antioxidant; polymerization; poly(propylene); stabilization; Ziegler-Natta catalyst

Introduction

Poly(propylene) (PP) is susceptible to degradation when exposed to environmental conditions such as light and heat. To slow the degradation process, additives generically called stabilizers are mixed with PP. Among the most commonly used stabilizers are antioxidants.[1] Antioxidants are defined as compounds that slow or inhibit the oxidation process.[2]

The method traditionally used to introduce additives in polypropylene during production involves mixture by extrusion, to produce pellets.[3–5] During the extrusion process, the material is exposed to high temperatures and shear rates, which cause destructive reactions, causing a combination of mechanical and chemical thermal degradation.[6] Another disadvantage of the technique that uses a mixture of additives in the molten state is that many additives are sensitive to heat, that is, they volatilize or degrade under high processing temperatures.[4]

Universidade Federal do Rio de Janeiro – UFRJ, Instituto de Macromoléculas Professora Eloisa Mano – IMA, Rio de Janeiro, RJ, Brazil
E-mail: fmarques@ima.ufrj

Natural antioxidants cause less risk to human health, and therefore they are of great interest in polymer industry.[7] Their use is still very limited, since many of them have low thermal stability, making it difficult to mix them with the polymer by extrusion.[8] It would be advantageous to develop a technique to introduce additives into the polymer material without the need for extrusion. Such a method would be of great economic advantage and would allow the use of a greater variety of antioxidants for stabilization of poly(propylene).[9] Thus, the production of stabilized poly(propylene) pellets would eliminate the extrusion step in the second generation industry. If this could be performed with some grades of PP, the energy savings would be tremendous. The formulation of PP with other additives continues to be necessary, although it could be completed in the transformation industry for production of the final article.

The advantage of using a last-generation Ziegler-Natta catalyst system is the fact it is able to control the morphology of the polymer produced. However, the effectiveness of the morphological control will depend on how the system is prepared and also the polymerization conditions[10].

Copyright © 2011 WILEY-VCH Verlag GmbH & Co. KGaA, Weinheim

Rotzinger et al.[9] investigated the addition of synthetic antioxidants directly during propylene polymerization, showing that the catalyst activity did not decrease when using a high concentration of triethylaluminium. In that work, the properties of the polymers obtained were not evaluated, nor was the antioxidant performance. In another study [5], synthetic antioxidants were evaluated after combination with the cocatalyst of a highly active Ziegler-Natta system. The authors observed that the in-reactor introduction of antioxidants decreased the polypropylene isotacticity, although the polymer was stabilized for most of the antioxidants studied.

The objective of the present study was to evaluate the stabilization of polypropylene by the addition of antioxidants within the polymerization reactor. The synthesis of PP was conducted by a Ziegler-Natta system of the $TiCl_4/MgCl_2$ type, prepared as spherical particles.

The present work reports the first experiments where natural antioxidants are introduced in the reactor for propylene polymerization.

Experimental Part

Propylene and nitrogen were purified by sequential passage through columns containing 4 A molecular sieves and copper catalyst to remove oxygen, carbon dioxide and moisture. Hexane (purchased from Petroflex, Brazil), used as polymerization solvent and for catalyst preparation, was treated with a molecular sieve and bubbled with N_2 before use. Anhydrous ethanol (Vetec Química Fina Ltda, Brazil) were dried with a 4A molecular sieve. $TiCl_4$ was distilled under nitrogen atmosphere prior to use. Isoparaffin (Unipar Comercial, Brazil) was also treated with a molecular sieve. All the other materials were used as received: mineral oil (Ipiranga), triethylaluminium (TEA) (10 wt. % solution in hexane, obtained from Akzo Nobel, USA) and anhydrous $MgCl_2$ (Toho Catalyst Co. Ltd, Japan).

The natural antioxidants belonging to the classes of polyunsaturated fatty acids (Ant-2), essential oils (Ant-3), lactones (Ant-4) and terpenes (Ant-5) were used and compared with the synthetic Irganox 1010 (Ant-1).

Materials and Methods

Poly(propylene) was synthesized using a Ziegler-Natta catalyst ($TiCl_4/MgCl_2$) of 4[a] generation with control of particle morphology. This control is possible due to the phenomenon of replication, in which the polymer particles copy the shape of the catalyst.

Polymerizations were carried out with addition of antioxidants in the polymerization reactor. PP-1 is the polymer synthesized without antioxidant while Ant-1 is polypropylene synthesized in the presence of the commercial synthetic antioxidant usually employed for stabilization of PP, Irganox 1010. Ant-2 to Ant-5 are those obtained in the presence of different naturals antioxidants. 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 minutes before being introduced in the reaction medium in other to promote the reaction of TEA with the polar groups of the antioxidants employed.

Characterization

The morphology of the catalyst precursor obtained was observed with a scanning electronic microscope (SEM).

A sample of polypropylene was extracted under reflux in heptane for 6 h. The insoluble fraction was determined by the ratio between the mass of the insoluble fraction and that of the total sample and was identified as an isotactic index (I.I.) of polypropylene.

For the DSC analysis, about 10 mg of the sample was used. The polymer was heated

Copyright © 2011 WILEY-VCH Verlag GmbH & Co. KGaA, Weinheim

from room temperature to 180 °C at a rate of 10 °C / min and then cooled to 25 °C. The melt temperature (T_m) was obtained from the second heating curve and the degree of crystallinity (X_c) was calculated from the enthalpy of fusion given by this technique, according to the following Equation 1,

$$X_c = \frac{\Delta H_m^a}{\Delta H_m^{100}} \quad (1)$$

where X_c = degree of crystallinity (%); ΔH_m^a = melting enthalpy of the sample (J/g); ΔH_m^{100} = melting enthalpy of 100% crystalline polypropylene (J/g). The theoretical melting enthalpy of 100% crystalline isotactic polypropylene was considered = 195 J/g.

Infrared absorption spectroscopy analyses were carried out to determine the degree of oxidation of the PPs after they had been heated for 4 hours under an oxidizing atmosphere. The oxidation of the materials was measured through the carbonyl index, A_{1710}/A_{1165}, which is the ratio between the absorbance of the carbonyl band and the internal standard absorption band of PP.

The thermogravimetric analysis (TGA) was carried out by heating samples of PP from room temperature to 700 °C at a heating rate of 10 °C/min under oxidative atmosphere (air). The initial degradation temperature (T_{onset}) and the temperature of maximum degradation rate (T_{max}) were measured.

Results and Discussion

Figure 1 shows the image of a catalyst precursor obtained in this work revealed with a scanning electron microscope (SEM). Figure 1 shows the spherical shape of the catalyst precursor.

The results obtained in the polymerization of propylene with a Ziegler-Natta catalyst based on titanium supported on magnesium chloride ($MgCl_2/TiCl_4$) are shown in Table 1. The polymerizations were carried out at a pressure of 2 bar and temperature of 70 °C.

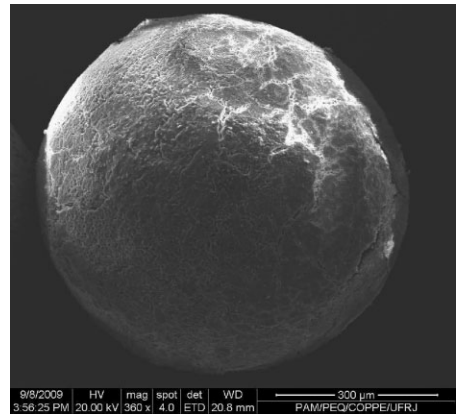

Figure 1.
Image of the catalyst precursor revealed by SEM.

Although it is known that the presence of polar groups can cause deactivation of the polymerization catalyst Ziegler-Natta catalyst sites, we observed that the activity increased in the majority of the polymerizations carried out in the presence of an antioxidant.

The isotactic index data in Table 1 show that the addition of the antioxidants Ant-1 and Ant-2 led to a decrease in the PP isotactic index (I.I.), while the addition of other antioxidants did not significantly change this parameter.

Table 1 also shows a slight variation in the T_c values from PP-1, a decrease with the

Table 1.
catalytic activity and properties of PP obtained with the addition of antioxidants.

Sample	I.I. (%)	T_c (°C)	X_c (%)	Polymer Yield (g PP)
PP-1	92.4	118 ± 2	31 ± 3	5.78 ± 1.24
Ant-1	75.1	117 ± 2	40 ± 3	8.19 ± 1.24
Ant-2	83.1	116 ± 2	46 ± 3	9.14 ± 1.24
Ant-3	91.4	121 ± 2	31 ± 3	4.22 ± 1.24
Ant-4	90.7	120 ± 2	36 ± 3	6.37 ± 1.24
Ant-5	91.3	121 ± 2	14 ± 3	3.95 ± 1.24

Propylene polymerization conditions: 2 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. PP-1 = polypropylene without antioxidant; PP with Irganox 1010 (Ant-1); polyunsaturated fatty acid (Ant-2), essential oil (Ant-3), lactone (Ant-4), terpene (Ant-5).

Copyright © 2011 WILEY-VCH Verlag GmbH & Co. KGaA, Weinheim

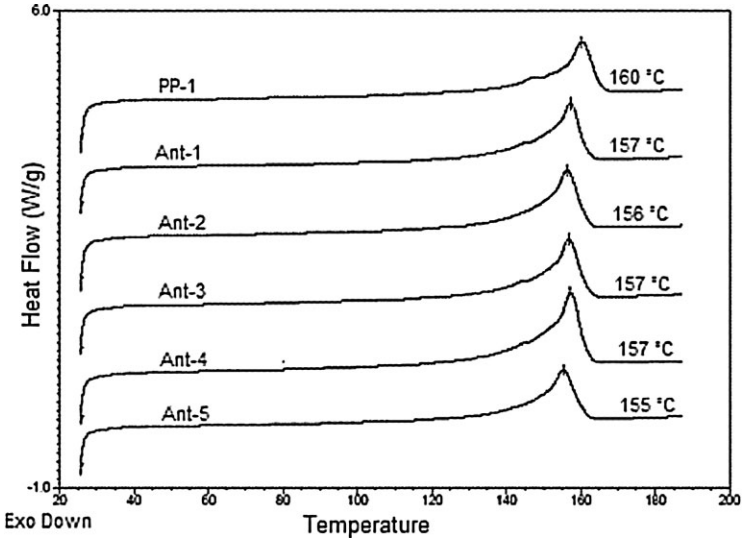

Figure 2.
DSC endotherms for PPs synthesized in the presence of antioxidants.

introduction of Ant-1 and Ant-2 and an increase for all other PPs.

Regarding the melting T_m (the melting profiles are shown in Figure 2), there was a decrease when Ant-1 and Ant-2 were added during the reaction, indicating that both antioxidants affected the catalytic sites, reducing their isospecificity. Moreover, the addition of Ant-3 and Ant-5 increased the T_m of the PPs obtained. The degree of crystallinity increased with the addition of most antioxidants, except for Ant-5, which resulted in a value much smaller than the others.

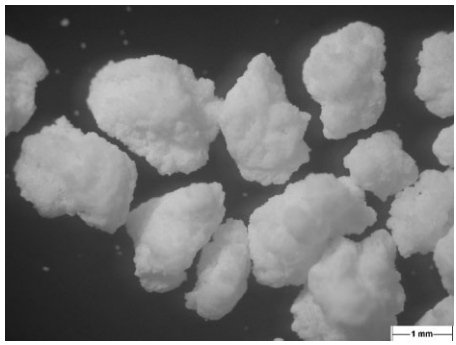

Figure 3.
Image of PP synthesized in the presence of antioxidant.

Originally, PP does not show the carbonyl band, but when oxidized at high temperatures for long periods there is a pronounced carbonyl band (1710 cm^{-1}) due to the incorporation of oxygen in the PP structure (Figure 3). The antioxidant effect is observed due to the reduced carbonyl band. Table 2 shows the absorbance values at 1710 cm^{-1} and 1165 cm^{-1} and the A_{1710}/A_{1165} ratio for polypropylenes with antioxidants added during polymerization and subjected to oxidation at high temperatures.

The lowest carbonyl index indicates that the antioxidant is slowing the oxidative degradation of poly(propylene). These results indicate that most of the antiox-

Table 2.
Values of absorbance of PPs after thermal oxidation.

Samples	A_{1710}	A_{1165}	A_{1710}/A_{1165}
PP-1	0.068	0.014	4.857
Ant-1	0.034	0.023	1.478
Ant-2	0.079	0.016	4.938
Ant-3	0.016	0.003	5.333
Ant-4	0.033	0.014	2.357
Ant-5	0.009	0.004	2.250

A_{1710}/A_{1165} = carbonyl index, ratio between the carbonyl absorbance at 1710 cm^{-1} and the internal band of PP at 1165 cm^{-1}

Copyright © 2011 WILEY-VCH Verlag GmbH & Co. KGaA, Weinheim

Table 3.
Results of TGA analysis of PPs synthesized with antioxidants.

Samples	Weight loss (%) a 700 °C	T_{onset} (°C)	T_{max} (°C)
PP-1	84	246	290
Ant-1	94	299	354
Ant-2	95	255	327
Ant-3	80	232	254
Ant-4	86	271	306
Ant-5	79	251	276

idants used in this work had good stabilizing effect, especially the natural antioxidants Ant-4 and Ant-5, whose antioxidant activity was close to that of Ant-1, a synthetic antioxidant widely used in the PP industry. The exception was the antioxidant Ant-2. This fact can be attributed to the increased fraction of atactic PP, which is more susceptible to degradation in relation to the crystalline fraction.[11]

The thermogravimetric analysis was performed at a heating rate of 10 °C/min under an oxidative atmosphere. The results are shown in Table 3. The initial degradation temperature (T_{onset}) increased with the addition of antioxidants directly in the reactor, except with Ant-3, which slightly obtained the onset temperature. T_{max} declined sharply with the addition of Ant-3 and more gradually with Ant-5, and increased with all other antioxidants. The mass loss values were highest with antioxidants and Ant-1 and Ant-2. We attribute this to increased activity in these cases, which resulted in a lower percentage of catalytic residue.

Generally, PP is extruded to produce pellets and mix it with additives. But control of particle morphology combined with stabilization within the reactor can produce spherical beads of stabilized PP. This eliminates a later extrusion stage, resulting in great energy and time savings in the production process. Figure 3 shows an optical micrograph of the globular PP particles. The production of spherical particles depends on the catalyst shape, which was previously shown to be spherical, and also on the polymerization rate. In the present work, Rp is not very high due to the mild polymerization conditions employed, and therefore we did not obtain a more homogeneous particle shape.

Conclusion

From the images revealed by SEM and OM it can be concluded that the catalyst produced showed good control of particle morphology, and there was no variation of properties (measured by DSC and I.I.) of the majority of PPs produced in the presence of antioxidant. It can be also concluded that there was good stabilizing effect for most polymers produced in the presence of antioxidant. In the near future, the application of synthetic antioxidants will decrease still further and that of natural antioxidants will substantially increase. In-reactor polymerization is thus a promising technique for industrial production.

Acknowledgements: We thank the Office to Improve University Research (CAPES) and the National Research Council (CNPq) for financial support.

[1] C. Krönke, P. Staniek, U.S. Patent 7105590; **2006**.
[2] A. A. Carelli, I. C. Franco, G. H. Crapiste, *Grasas y Aceites.* **2005**, *56*, 303.
[3] A. M. Chatterjee, U.S. Patent 4853426; **1989**.
[4] A. M. Chatterjee, U.S. Patent 5064878; **1991**.
[5] A. M. Chatterjee, R. C. Job, U.S. Patent 4818799; **1989**.
[6] W. Voigt, R. Todesco, *Plolym. Degrad and Stab* **2002**, *77*, 397.
[7] K. Nagai, H. Hosaka, S. Kubo, T. Nakabayashi, Y. Amagasaki, N. Nakamura, *J. of Hepatol.* **1999**, *31*, 142.
[8] S. Al-Malaika, C. Goodwin, S. Issenhuth, D. Burdick, *Polym. Degrad and Stab.* **1999**, *64*, 147.
[9] B. Rotzinger, M. Brunner, *Polym. Degrad and Stab.* **2008**, *93*, 316.
[10] H. L. Rönkkö, T. Korpela, H. Knuuttila, T. T. Pakkanen, P. Denifl, T. Leinonen, M. Kemell, M. Leskela, *J. of Mol. Catal A: Chemical* **2009**, *309*, 40.
[11] S. H. Hamid, *Handbook of polymer degradation.* **2000**, *2*, 291.

Copyright © 2011 WILEY-VCH Verlag GmbH & Co. KGaA, Weinheim