INFLUENCE OF PROCESSING ON PROPERTIES OF ADITIVED POLYPROPYLENE, STARCH PLASTICIZED WITH GLYCEROL FROM BIODIESEL AND THEIR BLENDS

Marcelo A. G. Bardi[1*], Luci D. B. Machado[1], Cristina G. F. Guedes[2], Derval S. Rosa[3]

[1] *Instituto de Pesquisas Energéticas e Nucleares (IPEN-CNEN/SP), Centro de Tecnologia das Radiações, São Paulo, SP – marcelo.bardi@usp.br*
[2] *Universidade São Francisco (USF), Itatiba, SP*
[3*] *Universidade Federal do ABC (UFABC), Santo André, SP*

Plastics have been used on short-life products and they have presented harmful consequences for the nature, due to the low degradation rate reached by the most common polyolefins, such as the polypropylene. By this way, the incorporation of pro-oxidants has been shown nice results to the bio-assimilation of the common polymers. The aim of this work is to obtain a modified polypropylene (PP) by the incorporation of pro-oxidant agents, and the influence of plasticized starch (TPS) to iPP. TPS was obtained by the incorporation of glycerin (sub-product of biodiesel), in a proportion of 80/20 (wt. starch/wt. glycerin) processed into an extruder LGEX 25/26 with L/D=25 and zone temperatures of 120ºC and 240ºC. iPP was additived using a masterbatch contained, individually, calcium stearate (CaSt) and magnesium stearate (MgSt) in a proportion of 80/20 (wt. iPP/ wt. stearate) using temperatures of 200/210°C. By the end, it was reached a final amount of stearate of 0.2% in the blend. The TPS was incorporated to the modified iPP using the same process described above, in the following compositions (modified iPP/TPS): 95/5, 90/10, 80/20 and 70/30. The mechanical properties were evaluated, using a 20 kgf-load cell and stretching speed of 50 mm/min (ASTM D-638/99). The melting flow index was performed in an extrusion plastometer using temperature of 190ºC and pressure of 2.16 kg (ASTM-D-1238/99). The addition of TPS progressively decreased the mechanical properties for all the blends. The formulations 80/20 and 70/30, presenting MgSt and CaSt respectively, presented the highest values of Young's Modulus, which were almost 20% higher than pure iPP. It was also observed that the incorporation of TPS to the iPP increased the melting flow index of the polyolefin and the formulations 80/20 and 70/30, in the presence of SMg, which have reached values 30% higher that the pure iPP.

Keywords: *Polypropylene; Stearates; Plasticized starch; Glycerol from biodiesel*

Introduction

Plastics have been applied in the large majority of short-life products, such as packaging developments, due to some of the characteristics of these materials e.g. low specific weight, mechanical resistance, a trouble-free processability and considerable durability [1]. Alariqui and collaborators still consider that resistance to external agents, the photo-oxidative degradation and to the microbiological attack have leaded the polymeric materials to a highlighted position in the transformation industries nowadays [1].

By another side, the great number of polyolefinic products has caused harmful consequences to the Nature due to the low degradation rates reached by the traditional polyolefins, e.g. low-density polyethylene (LDPE) and polypropylene (iPP).

By this way, researchers have studied the incorporation of biodegradable polymers, such as the starch, to the traditional polyolefins, which is justified by the presence of hydrolysable groups in the natural polymer molecules that are capable of inducing the biodegradation of the polyolefins [2-4].

Ramis et al. [5] evaluated the biodegradability of iPP/starch blends under simulated soil and observed the materials decomposition under nitrogen and oxygen atmosphere, by different mechanisms of degradation. The biodegradation affected the starch but not the iPP matrix.

When dealing with starch-derivative materials, this last can present a thermoplastic characteristic (commonly called thermoplastic starch or TPS) when incorporating glycerin to it, acting as a plasticizer [6]. Besides of it, the use of glycerin, as described by Carvalho [6], can increase the fragmentation rate of the material (morphological structure), obtaining though materials with many distinct characteristics just by varying the amount of glycerin on the starch.

In this context, it's assumed the possibility of using glycerin derived from biodiesel production process as a plasticizer for starch. As described by Bouças [7], during the processing of biodiesel, each 70 ℓ of biodiesel generates 30 ℓ of glycerin. Because of it, environmental problems have been observed around the discharge place of the residues in Brazil.

In general, it is said that in order to let the polyolefins more susceptible to degradation, some kind of modification is necessary, such as modifications on the crystallinity degree [8] chemical degradation and reduction on the molar mass of polymers to create short molecules that are capable of being absorbed by microorganisms [9].

It's also interesting the advances on understanding the effects of directly incorporating carbonyl groups present on the pro-oxidative agents [5,9] by using masterbatches [5] or ultraviolet irradiation (UV) [9]. The UV irradiation or the sun light action can reduce the size of the polymeric chains and then generative oxidative groups, such as carbonyl, carboxyl and hydroxyl. The intermediary products – hydroperoxides, peroxides, alcohols, ketones and some aldeydes – are also present in lower amounts because there are continuously suffering oxidation.

The usage of substances that catalyze the thermal or photo-oxidative degradation, known as pro-oxidant, is generally composed by transition metals (e.g. zinc, copper, cobalt, manganese etc). Bikiaris [9] studied the effect the use of cobalt stearate in LDPE/starch blends and Roy [10] evaluated the influence of the latter agent in the degradation of LDPE films.

By this way, this paper presents the mechanical and morphological properties of isotatic polypropylene (iPP) and thermoplastic starch (TPS) plasticized with glycerin from biodiesel blends, as well as the effects of the presence of calcium and magnesium stearates on the iPP and its behavior on the blends iPP/TPS by the properties described above.

Experimental

Materials

- Isotatic polypropilene (iPP) – type Prolen®, in the form of pellets, lot D00617, supplied by Suzano Petroquímica S.A. (São Paulo, SP, Brazil).

- Starch – type Amidex 3001TM, in powder form, molar mass of 34,000 g·mol-1 and gelatinization temperature of 90-95ºC, supplied by Corn Products Ingredientes Industriais (Jundiaí, São Paulo, Brazil).
- Glycerin – in liquid form, obtained from the process of production of biodiesel, density of 1.29 g·cm^{-3}, containing 80% of glycerol, 7% of humidity, 0.2% of methanol, supplied by Granol Ltda. (Anápolis, Goiás, Brazil).
- Calcium stearate (CaSt) – in the form of powder, supplied by Dacarto Benvic S.A. (Diadema, São Paulo, Brazil).
- Magnesium stearate (MgSt) – in the form of powder, lot 200604295, produced by The Spherd Chemical Company and supplied by AMC do Brasil Ltda. (São Paulo, SP, Brazil).

Isotatic polypropylene modification

Pure iPP and masterbatches containing 80% of iPP and 20% of pro-oxidant additive (stearates of calcium (CaSt) or magnesium (MgSt), individually), in mass, were developed by extrusion process in an extruder LGEX 25/26 with L/D=25. The temperatures used for zones 1 and 2 were 190ºC and 210ºC, respectively, and 50 rpm.

The modified PP was obtained by extruding the iPP and the latter masterbatches so that it was reached a final concentration of 0.2% of stearate, in mass, in the iPP, following the conditions described in the last paragraph. The compositions are then denominated as iPP, iPPCaSt and iPPMgSt for unmodified iPP, iPP containing 0.2% of CaSt and iPP containing 0.2% of MgSt, respectively.

Plastification of starch

Starch was plasticized with glycerin derived from the process of obtaining biodiesel using a mechanical powder mixer, in a proportion starch/glycerin 80/20 (wt./wt.) and let to mixture during 10 min. TPS was obtained by extrusion process in an extruder LGEX 25/26 with L/D=25. The temperatures used for zones 1 and 2 were 130ºC and 140ºC, respectively, and 50 rpm.

Preparation of blends

Blends of iPP/TPS, iPP_{MgSt} /TPS and iPP_{CaSt}/TPS were developed by extrusion process in an extruder LGEX 25/26 with L/D=25. The temperatures used for zones 1 and 2 were 190ºC and 210ºC, respectively, and 50 rpm. The following compositions iPP/TPS (wt./wt.), with/without pro-oxidant agents, were obtained: 95/5, 90/10, 80/20 and 70/30.

Obtaining the films

The films were obtained by a thermostatized compression moulder model MA-098 (Marconi Equipamentos e Calibração para Laboratórios Ltda., Piracicaba, SP, Brasil) under a temperature of 210 ± 5ºC and time exposition of 15 min and, then, let to cool until environment temperature. Films of pure TPS were obtained by the same methodology but a temperature of 140 ± 5ºC.

Mechanical properties

Plates (200 mm × 200 mm × 1.0 mm) and type IV specimens (ASTM D-638/99) were stamped with a cutting tool. The tests were done using a universal testing machine model DL 2000 NS 5921 (EMIC Equipamentos e Sistemas de Ensaio Ltda., São José dos Pinhais, PR, Brazil). The control program used was Tesc version 3.01 and the load cell had a capacity of 20 kgf. The specimens were 25 mm long and the speed of stretching was 50 $mm \cdot min^{-1}$.

Melt flow index (MFI)

The melt flow indices for iPP and its modifications were determined using a model MI-1 plastometer (DSM Instrumentação Cientifica Ltda., São Paulo, SP, Brazil), according to ASTM-D-1238 (190ºC/2.160 kg).

Scanning electron microscopy (SEM)

Photomicrographs of iPP and its modifications surfaces after freezing in liquid nitrogen were obtained using a JEOL model JSM-5900LV scanning electron microscope (JEOL Ltd, Akishima, Japan).

Results and Discussion

Mechanical properties

Figure 1-3 show the mechanical properties for pure iPP and TPS, and their blends, without/with modifications for the iPP.

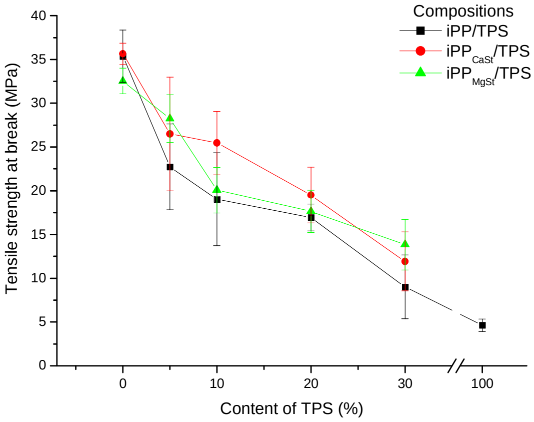


Figure 1 – Values of tensile strength at break for pure iPP and TPS, and their blends without/with the presence of pro-oxidant agents.

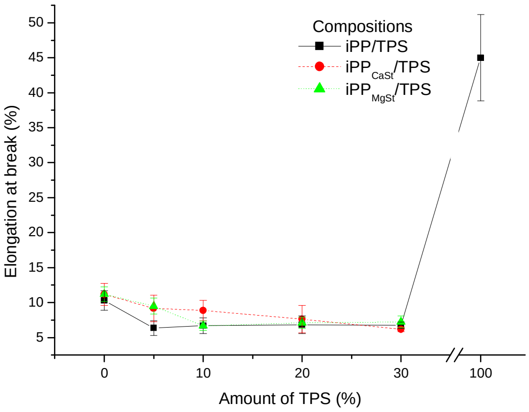


Figure 2 – Values of elongation at break for pure iPP and TPS, and their blends without/with the presence of pro-oxidant agents.

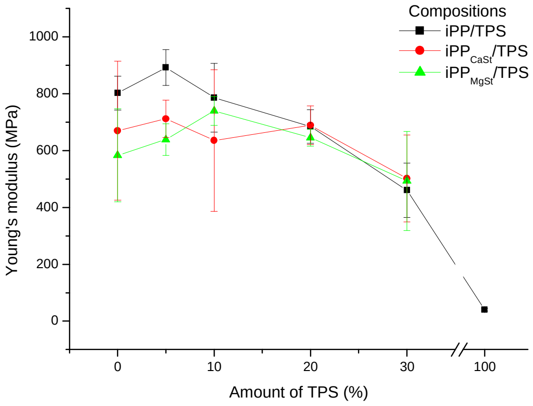


Figure 3 – Values of Young's modulus for pure iPP and TPS, and their blends without/with the presence of pro-oxidant agents.

By analyzing Figure 1, it can be observed that the incorporation of TPS reduces the values for tensile strength at break for iPP, that is, the higher concentrations of TPS in the blend, the lower values for the properties were reached. This can probably be justified by the low tensile strength presented by pure TPS, almost 90% lower than the one presented by iPP. By this way, it's suggested that the characteristics of TPS was predominant in the blend. The incorporation of the pro-oxidant agents did modify neither the mechanic behavior of the blend nor for the pure iPP.

The observation of Figure 2 reflects that the incorporation of TPS to PP reduced meaningfully the elongation at break of the blends, when compared to the unmodified iPP (40% of reduction) and to the TPS (85% of reduction). It's also important that the amount of TPS is not important for the values of the latter property, so there are no meaningful variations among the compositions iPP/TPS

95/5, 90/10, 80/20 and 70/30. The presence of pro-oxidant agents has not caused any alterations for the iPP and their blends with TPS.

Finally, Figure 3 shows that the incorporation of TPS to PP caused a reduction for Young's modulus to the blends, indicating that the blend presents now a lower toughness than the pure iPP. It can be analyzed, otherwise, that an increasing of 11% on the Young's modulus probably was caused by a better compatibilization and higher molecular organization for the iPP and TPS chains. As presented in the latter paragraphs, the pro-oxidant agents did not cause any meaningful alteration.

So, it can be seen that the mechanical properties were not modified by the incorporation of pro-oxidant agents what suggest no influence of the processing of the materials, differently of observed by Coaquira [11], in which the temperature of processing has already initiated the degradation of the materials, activating the function of catalyzing the referred process.

Melting flow index

Figure 4 presents the values of melting flow index for pure iPP and their blends with TPS, without/with modifications for the iPP.

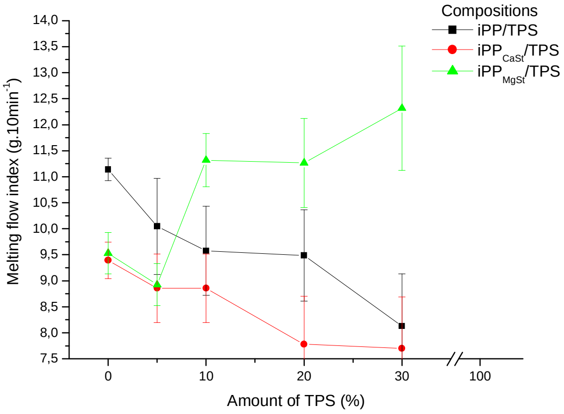


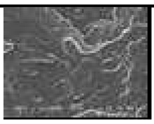
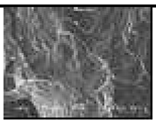
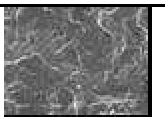
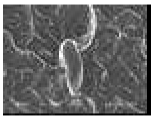
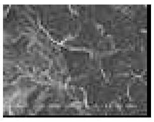
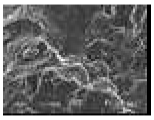
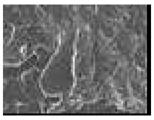
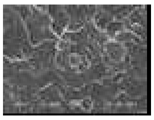
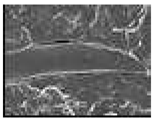
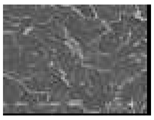
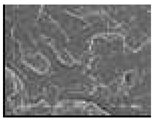
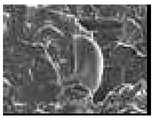
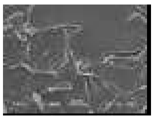
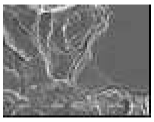
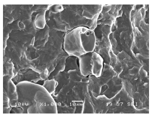
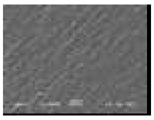
Figure 4 – Values of melting flow index for pure iPP and their blends with TPS, without/with the presence of pro-oxidant agents.

It can be seen that, as observed for the mechanical properties (Fig.1-3), the increasing on the amount of TPS has reduced the melting flow index of the blend for the lower 10% (Fig.4), what can be justified by the amorphous domain presented by TPS and its influences in the structure of the blend.[12]

Analyzing the presence of the pro-oxidant agents, it can be seen that the compositions iPP$_{CaSt}$/TPS presented a reduction on the melting flow index when compared to the blends iPP/TPS. For the compositions iPP$_{MgSt}$/TPS, it was observed a highlighted increasing for the referred property when compared to all the other compositions, what suggests that, under high temperatures, the magnesium stearate is activated and it starts a chain reaction of breaking the chemical chains and producing low molecular weight products, which have a higher potentiality for melting.

Morphological characteristics

Figure 5 presents the surface electron micrographs for pure iPP and TPS, and their blends, without/with modifications for the iPP.

iPP/TPS compositions (wt./wt.)	Without any pro-oxidant agent	With *CaSt*	With *MgSt*
100/0			
95/5			
90/10			
80/20			
70/30			
0/100			

By the analysis of Figure 5, it can be noted that the increasing of the amount of TPS in the blend increases the morphological disorder in the compositions, leading to an amorphous characteristic, possibly due to the same disposition presented by starch, which reflects all the discussions done for all the properties analyzed.

Morphologically, it can be seen that the composition iPP_{CaSt}/TPS 70/30 presents bigger crystalline domains than any other composition and the formulation iPP_{MgSt}/TPS 90/10 also presents a very well defined crystalline structure but with a superficial area lesser than the former composition.

Conclusions

The modification of iPP did not cause a meaningful reduction on the mechanical properties and melting flow index for the polyolefin, what suggests that there was not any degradation due to the processing of the material. For the compositions iPP/TPS, iPP_{CaSt}/TPS and iPP_{MgSt}/TPS, it was observed that the mechanical properties and the melting flow index were reduced by increasing of the amount of TPS. For the blends with the MgSt, the melting flow index was increased for the compositions with TPSt, what suggests a high-sensibility of the stearate when exposed to elevated temperatures, and that the stearate acts more properly in the blends containing high amounts of TPS, so changing the amorphous domains of the blends.

Aknowledgments

The authors thank *Suzano Petroquímica*, Rhodia Corn Products, Dacarto Benvic Ltda. and Granol Ltda. for supplying the materials for this research. This work was supported by CNPq and FAPESP (grant nº. 04/13359-8) and by the *Universidade São Francisco*. The authors also thank *Laboratório Nacional de Luz Síncrotron* by allowing obtaining of the SEM's

References

1. S. A. S Alariqui; A. P. Kumar; B. S. M. Rao; R. P. Singh *Polym. Degrad. Stab*. 2006, *91*, 1105.
2. D. Żuchowska; D. Hlavatá; R. Steller; W. Adamiak; W. Meissner *Polym. Degrad. Stab.* 1999, 64, 339.
3. P. Shah; S. Bandopadhyay; J. R. Bellare *Polym. Degrad. Stab.* 1995, *47*, 165.
4. D. Żuchowska; R. Steller; W. Meissner *Polym Degrad. Stab.* 1998, *60*, 471.
5. X. Ramis; A. Cadenato; J. M. Salla; J. M. Morancho; A. Vallés; L. Contat; A. Ribes *Polym. Degrad. Stab.* 2004, *86*, 483.
6. C. L. Carvalho, Master Thesis, Universidade São Francisco, 2005.
7. A. S. Ramadhas; S. Javarai; C. Muraleedharan. *Fuel* 2005, *84*, 335.
8. H. A. A. El-Rehim *Photobiol. A: Chem.* 2004, *163*, 547.
9. D. Bikiaris *Polym. Degrad. Stab*. 1997, *57*, 313.
10. P. K. Roy; P. Surekha; C. Rajagopal; R. Raman; V. Choundhary *J. App. Polym. Sci.* 2006, *99*, 236.
11. C. A. C. Coaquira, Master Thesis, Universidade Federal de São Carlos, 2004.
12. D. S. Rosa; D. R. Lopes; M. R. Calil. *Polym. Test.* 2005, *24*, 756.