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Starch plasticized with glycerol from biodiesel and polypropylene blends

Mechanical and thermal properties

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Abstract Plastics have been used in short-life products, which 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 study is to evaluate the mechanical and thermal properties of pure iPP, plasticized starch (TPS) with biodiesel glycerol (TPS_{Bio}) or commercial glycerol (TPS_{Com}), and their blends (iPP/TPS_{Plas}). TPS was plasticized in proportions of 80/20 (wt starch/wt glycerin). Blends of iPP/TPS_{Plas} were obtained by extrusion in the following composition rates: 95/5, 90/10, 80/20, and 70/30 of modified PP/TPS_{Plas}. Mechanical properties, calorimetric analysis, and thermogravimetric data were obtained, and biodegradation under simulated soil was performed. It can be verified that there were no meaningful variation induced by the incorporation of TPS_{Plas} on the melting temperature on the blends, when compared to pure iPP. The addition of TPS_{Plas} caused an increasing on the crystallinity of iPP, mainly for the compositions 90/10 and 80/20 of iPP/TPS_{Plas}, probably due a morphological alteration such as crosslinking, which may have modified the molecular arrangement of the iPP macromolecules by the presence of glycerol, which was also indicated by mechanical evaluations.

Keywords Thermoplastic starch · Biodiesel · Blends · Polypropylene · Biodegradation

Introduction

The increase of the consumption of polymers by the industry has become really noticeable since the twentieth century [1–7]. As described by Albertsson [1], the focus of the early 1930s was exactly to obtain very much better materials in sense of lifetime. Although this choice has caused harmful consequences for the environment, they continue being widely applied in low lifetime materials, such as packages, and incorrectly disposed in holes in the ground on the peripheries of cities [2].

Scott [2] comments that there is an increasing recognition that society should treat waste as a resource to be re-utilized in products to be useful for themselves rather than just burying them. Some of the suggested processes are the mechanical recycling, energy recycling and biocycling, where the last one is the most complete solution to the problem of plastics wastes [2, 3, 5–7].

The first environmental approach for the problem was taken in the early 1970s, when the oil crisis took place, initiating the development of materials filled with renewable content, such as the starch [1], which were designed to degrade upon disposal by the action of living organisms (biodegradation) [4, 5].

Some authors [2, 8–20] describe the development of starch-based materials, where starch is blends with traditional polyolefins (e.g., polyethylene, polypropylene). It is

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known that the polyolefins are not naturally biodegradable, but they can be more sensitive to heat or light in the presence of oxygen after use to give bioassimilable products. And that is the role that starch takes in the blends, which is responsible by starting the hydro-biodegradation of the samples, i.e., when the assimilation is preceded by hydrolysis [2].

In order to access a plastic character to starch, the incorporation of plasticizing agents, such as glycerol, formamide, acetamide and urea, is evaluated by some authors [8, 9, 14, 16, 18, 21–26]. Ma and Yu [22] observed the oxygen present in C–O–H and C–O–C groups in starch could form hydrogen bonds with the plasticizers and the properties of the thermoplastic starch (TPS) mainly relies on the hydrogen bond-forming abilities between plasticizer and the starch matrix.

The plasticizer glycerol is synthetically produced at an industrial scale from epichlorohydrin by saponification or transesterification [27, 28], where soap-making and biodiesel production are the respective examples. Glycerol is a 10% by-product of biodiesel production, since 10 lbs of biodiesel produces 1 lb of glycerol [29–32], but this co-product has not been considered by the cosmetic and other industries to be applied as a substitute to the synthetic one. So, crude glycerol is rapidly becoming a "waste product" with a disposal environmental cost attributed to it [29, 32–34].

The incorporation of TPS to the polyolefins can cause meaningful alterations to the properties of the former, specially when high concentrations of starch, in mass, is used (superior to 40% [12, 14]). The thermal and mechanical characterizations are two complete techniques to evaluate the conformation of the polymeric system and their behavior under stress and temperature as well [20].

Rosa et al. [9] evaluated mixtures of high-density polyethylene (HDPE) and polypropylene (PP) with thermoplastic starch (TPS). It was verified that the incorporation of TPS reduced the melting flow index (MFI) of PP and increased of HDPE and HDE/PP blends. A decreasing of the mechanical properties of all formulations developed was observed, what can be justified by a phase separation between the polyolefins and TPS.

Rodrigues et al. [11] evaluated the natural weathering of low-density polyethylene (LDPE)/starch blends and observed that the starch degradation was able to form voids and improve the blends fragmentability at relative low weathering times.

Shujun et al. [15] studied the thermal behavior of LDPE/starch blends when maleic anhydride (MA) was incorporated to the binary system, which has improved the thermal stability of the samples, suggesting an increasing on the compatibility of the blends.

Ramis and collaborators [17] evaluated the thermal stability of the PP matrix on blends PP/TPS before and after the burial tests. The kinetic parameters show the effect of degradation in soil on the blends studied. All the materials studied decompose by type R_n and A_n, respectively, in a nitrogen and oxygen atmosphere. The biodegradation was seen to affect the starch but not the PP matrix.

Santonja-Blasco and collaborators [19] evaluated the biodegradation of blends of HDPE and LDPE with a master batch containing starch. The soil burial test leads to changes in the crystalline content of the biodegradable material, which is influenced by the polyolefinic matrix used. Thermogravimetric results reveal that the thermo-oxidative treatment causes a decrease in the activation energy of the thermal decomposition process of both components in the blends, regardless of the type of polyethylene used. Synergetic degradation of these blends is a complex process that is dependent on the polyolefinic matrix used and mainly causes morphological changes.

The aim of this article is to evaluate the mechanical and thermal properties of pure iPP, plasticized starch (TPS) with biodiesel glycerol (TPS_{Bio}) or commercial glycerol (TPS_{Com}), and their blends (iPP/TPS_{Plas}).

Experimental

Materials

Isotactic polypropylene (*iPP*)—Prolen®, supplied as pellets by Polibrasil S.A. (Suzano, São Paulo, Brazil).

Corn starch—type Amidex 3001™, supplied as powder by Corn Product *Brasil Ingredientes Industriais* (Jundiaí, São Paulo, Brazil).

Commercial glycerol (*COM*)—type U.S.P., supplied by Labsynth *Produtos para Laboratório Ltda*. (Diadema, São Paulo, Brazil).

Biodiesel glycerol (*BIO*), supplied in crude form by Granol Ltda. (Anápolis, Goiás, Brazil), with density of 1.29 g cm^{-3} and the characteristics described in Table 1.

Plasticization of starch

Starch was mixed to either commercial glycerol or crude biodiesel glycerol in a mixer by 2 min in order to obtain

Table 1 Composition of crude biodiesel glycerol

Substance	Amount/%
Glycerol	62.8
Moisture	7.0
Methanol	0.20
Sodium chlorate	10.0
Ash	10.0

different thermoplastic starches: TPS_{Com} and TPS_{Bio}, depending of the plasticizer present, in the proportion starch/plasticizer (wt/wt) 80/20.

Preparation of blends

iPP, TPS_{Com}, TPS_{Bio}, and their blends were prepared by extrusion, and the temperatures used for zones 1 and 2 were 210 and 190 °C, respectively. The iPP/TPS_{Plas} mass ratios used were 95/5, 90/10, 80/20, and 70/30.

Plates (130 mm × 140 mm × 0.5 mm) were prepared by compression molding at a temperature of 210 ± 5 °C for the iPP/TPS_{Plas} blends and 140 ± 5 °C for TPS_{Com} and TPS_{Bio}.

Mechanical properties

Plates (200 mm × 200 mm × 1.0 mm) were prepared by compression molding, and type IV specimens (ASTM D-638/99) were stamped with a cutting tool. The tests were done using a model DL 2000 NS 5921 universal testing machine (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 196.3 N. The specimens were 25 mm long, and the speed of stretching was 50 mm min^{-1}.

Thermal analysis

Thermal analysis was done with a differential scanning calorimeter DSC 50 Shimadzu (Tokyo, Japan) in an atmosphere of nitrogen gas (flow rate: 50 mL min^{-1}). The materials (average mass: 5 mg) were heated to 200 °C at a heating rate of 10 °C min^{-1}. All of the DSC experiments were done in duplicate. The crystallinity of PP was determined using a heat of fusion value (ΔH_o) of 209 J kg^{-1} [35] for 100% crystalline PP.

Thermogravimetry was done with a TG 50 thermal balance (Shimadzu, Tokyo, Japan) in an atmosphere of air (flow rate: 50 mL min^{-1}) at a heating rate of 10 °C min^{-1}. The materials (average mass: 5 mg) were heated to 600 °C. All of the TG experiments were done in duplicate.

Results and discussion

Mechanical properties

Figures 1, 2 and 3 show the mechanical behavior for neat iPP, TPS_{Com} and TPS_{Bio}, and iPP/TPS_{Com} and iPP/TPS_{Bio} blends.

Figures 1 and 2 show that incorporating TPS into iPP reduced meaningfully the tensile strength at break and Young's Modulus of the blends, when compared to neat iPP. In general, the higher content of TPS_{Plas} presented on the samples, the less is the tensile strength at break. Some

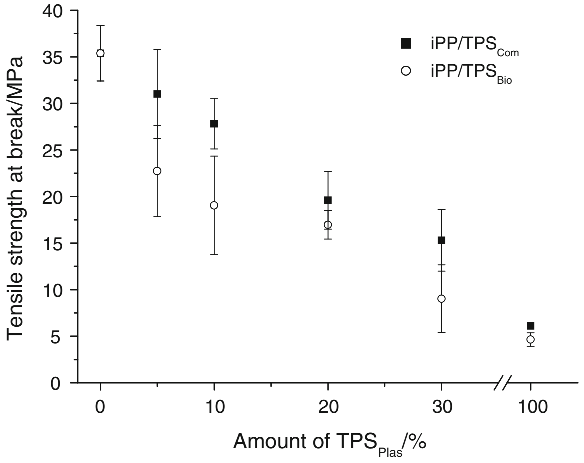

Fig. 1 Tensile strength at break for neat materials and their blends

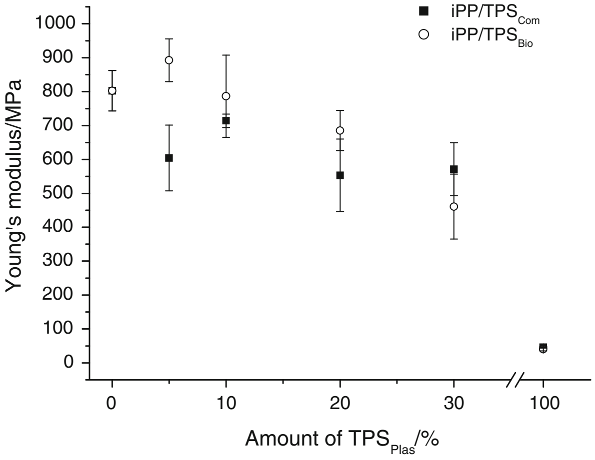

Fig. 2 Young's modulus for neat materials and their blends

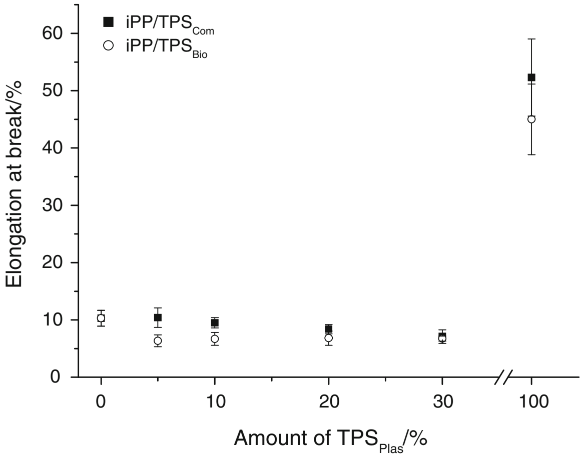

Fig. 3 Elongation at break for neat materials and their blends

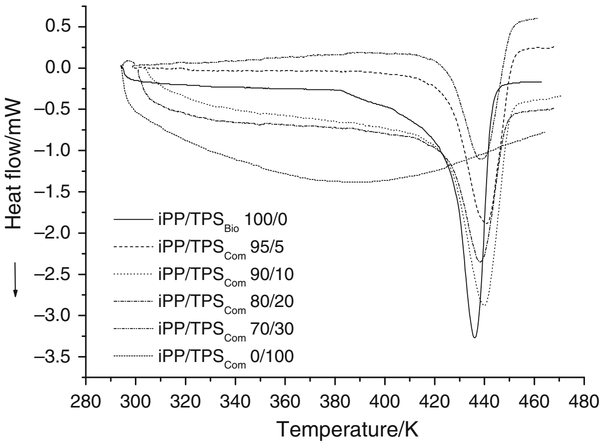

Fig. 4 DSC curves for iPP/TPS$_{\mathrm{Com}}$

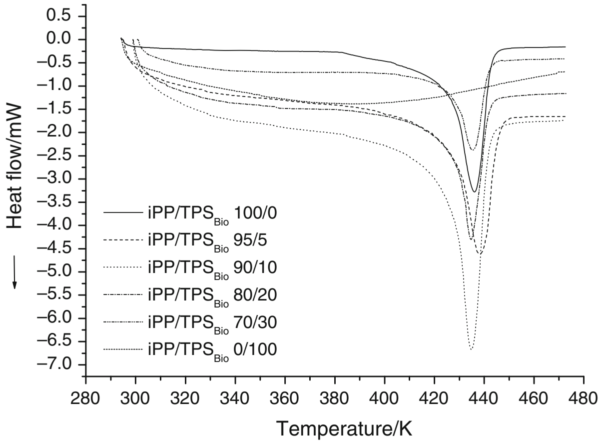

Fig. 5 DSC curves for iPP/TPS$_{\mathrm{Bio}}$

authors have proposed that low values for polyolefins/starch blends on the mechanical properties are coarse due to a small interaction between the components [9] and the greater sizes of starch particles not dispersed into the polyolefin matrix [8], causing a phase separation, as observed by SEM.

Figure 3 shows that no meaningful alterations were observed in the samples when compared to neat iPP, for elongation at break. Otherwise, it was seen that both TPS presented indexes of elongation superior to 400% of the value for iPP.

In general, blends plasticized with commercial glycerol have presented a slighter increase on the values for the mechanical properties than the ones containing crude biodiesel glycerol (Figs. 1, 2, 3), where to effects have taken place: a softening due to the plasticizing of the amorphous

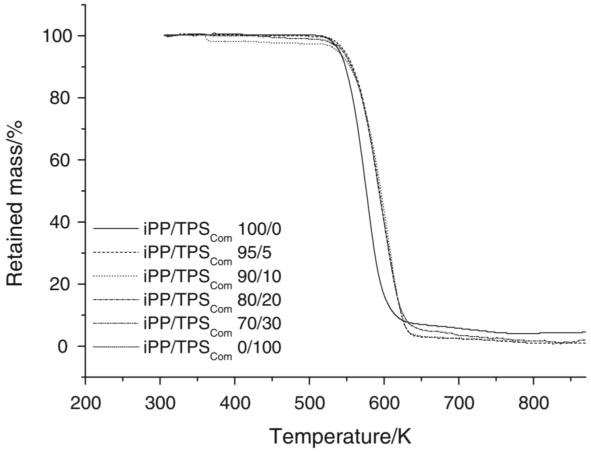

Fig. 6 TG curves for iPP/TPS$_{\mathrm{Com}}$

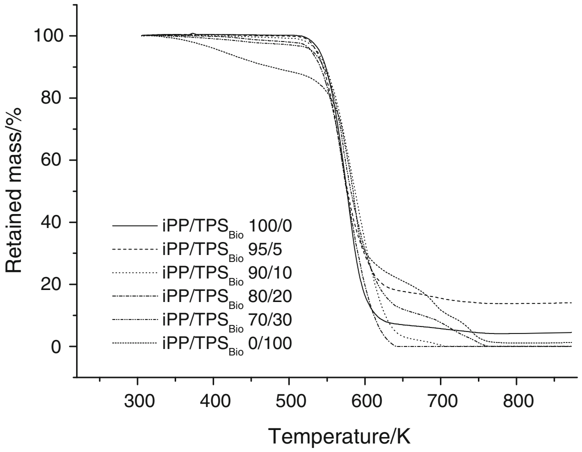

Fig. 7 TG curves for iPP/TPS$_{\mathrm{Bio}}$

Table 2 Melting temperature, fusion enthalpy, and crystallinity for iPP/TPS$_{\mathrm{Com}}$ and iPP/TPS$_{\mathrm{Bio}}$ blends

Composition iPP/TPS$_{\mathrm{Plas}}$ (wt/wt)	Melting temperature/°C		Fusion enthalpy/J g^{-1}		Crystallinity/%	
	TPS$_{\mathrm{Com}}$	TPS$_{\mathrm{Bio}}$	TPS$_{\mathrm{Com}}$	TPS$_{\mathrm{Bio}}$	TPS$_{\mathrm{Com}}$	TPS$_{\mathrm{Bio}}$
100/0	167.7		−103.8		54.6	
95/5	167.9	167.1	−70.7	−94.4	37.2	49.7
90/10	166.9	166.8	−73.1	−99.5	38.5	52.3
80/20	165.2	168.2	−70.8	−87.9	37.3	46.2
70/30	165.6	166.8	−67.8	−57.8	35.7	30.4

Table 3 Thermogravimetric behavior for iPP/TPS$_{\mathrm{Com}}$ and iPP/TPS$_{\mathrm{Bio}}$ blends

Composition iPP/TPS$_{\mathrm{Plas}}$ (wt/wt)	On set temperature/°C		Mid set temperature/°C		End set temperature/°C		Mass loss/%	
	TPS$_{\mathrm{Com}}$	TPS$_{\mathrm{Bio}}$	TPS$_{\mathrm{Com}}$	TPS$_{\mathrm{Bio}}$	TPS$_{\mathrm{Com}}$	TPS$_{\mathrm{Bio}}$	TPS$_{\mathrm{Com}}$	TPS$_{\mathrm{Bio}}$
100/0	272.4		302.3		328.21		95.70	
95/5	273.4	264.5	292.7	299.3	321.0	327.8	98.992	96.007
90/10	274.9	269.4	294.1	313.6	321.6	352.5	98.605	95.589
80/20	297.0	267.1	292.6	302.9	322.2	333.7	97.886	94.987
70/30	265.8	272.3	287.9	307.6	318.3	337.6	95.928	93.745
0/100	270.5	280.4	297.0	311.4	317.5	338.9	93.654	90.706

phase and stiffening due to a slight antiplasticization effect, as described by Da Róz and collaborators [36].

Thermal properties

Figures 4 and 5 show the DSC curves for iPP/TPS$_{\mathrm{Com}}$ and iPP/TPS$_{\mathrm{Bio}}$ blends, respectively, and Table 2 presents the melting temperature, fusion enthalpy, and crystallinity for iPP/TPS$_{\mathrm{Com}}$ and iPP/TPS$_{\mathrm{Bio}}$ blends.

Figures 4–5 and Table 2 show that the incorporation of TPS$_{\mathrm{Plas}}$ has not meaningfully modified the melting temperature (T_{m}) of iPP, as described by some authors when studying polyolefin/starch blends [37].

The fusion enthalpy and crystallinity for iPP, as observed in Table 2, were reduced by the incorporation of TPS$_{\mathrm{Plas}}$. The enthalpy was widely affected when TPS$_{\mathrm{Com}}$ was present, suggesting that crude biodiesel glycerol has helped to increase phase adhesion ant then increasing the crystalline phase on the samples, as described by Lima and Felisberti [38], and probably due to an influence of polyolefin matrix [39].

Figures 6–7 and Table 3 present the thermogravimetric behavior for iPP/TPS$_{\mathrm{Com}}$ and iPP/TPS$_{\mathrm{Bio}}$ blends.

It can be seen by Figs. 6 and 7 and Table 3 that iPP and TPS$_{\mathrm{Plas}}$ have presented similar degradation temperatures, although the TG curves for TPS$_{\mathrm{Plas}}$, especially TPS$_{\mathrm{Bio}}$, had shown some alterations during the beginning of the test, suggesting a reduction on the thermal stability for this composition [40].

The incorporation of TPS$_{\mathrm{Com}}$ to iPP has not modified the onset temperature for all the blends, but a slight reduction was observed for the samples iPP/TPS$_{\mathrm{Bio}}$, characterizing a more suitable temperature effect on them due to the presence of crude biodiesel glycerol.

It was also observed that the degradation kinetics for the containing iPP/TPS$_{\mathrm{Com}}$ was quite different from the iPP/TPS$_{\mathrm{Bio}}$, in which the latter had a slower pace of loss mass than the former, indicating that they were able to present higher endset temperatures, although the compositions containing biodiesel glycerol had been less thermal stable and also containing some undesired substances originated from the biodiesel fabrication process.

Conclusions

The incorporation of TPS$_{\mathrm{Plas}}$ to iPP has generally reduced the mechanical properties of iPP, and no meaningful variations were observed between the plasticizing agents. The DSC curves showed that highest concentrations of TPS$_{\mathrm{Bio}}$ increased the melting temperature for iPP, suggesting that TPS$_{\mathrm{Bio}}$ performs as a reinforcing source to the blend. By TG curves, a reduction on the fusion peak for the blends is observed by increasing the percentage of TPS$_{\mathrm{Bio}}$ to the blends, suggesting a reduction on thermal stability of the samples.

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