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Mechanical and Thermal Properties of Poly(3-Hydroxybutyrate) Blends with Starch and Starch Derivatives

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Summary: Poly(3-hydroxybutyrate) (PHB) is a highly crystalline, biodegradable and biocompatible thermoplastic. However, its limited utilization as a commodity plastic is associated to both high cost and very poor mechanical properties. Blending PHB with a natural polymer, such as starch, is one way to improve its properties and to get low price raw materials, though they are not miscible since there are no strong interactions between the hydrophilic starch and the hydrophobic PHB. In this study binary blends of PHB were prepared with natural starch, starch-adipate and grafted starch-urethane derivatives. The PHB blends were characterized in terms of their mechanical and thermal properties. For all blends a decrease of the Young modulus was observed as compared to the pure PHB. However, blends containing natural starches and starch adipate resulted in brittle materials. A significant decrease of both glass transition temperature (Tg) and melting point (Tm) was observed for all formulations. The best results, lower modulus and Tg were obtained with grafted starch-urethane blends using poly(propylene glycol).
Keywords: biopolymers; mechanical properties

Introduction

The development of biodegradable plastics is motivated by the increasing amount of plastics waste, that is around 25 million ton/year, accumulated in the environment [1]. In this respect, the environmentally degradable plastics or EDPs are very promising materials and they are being studied in several countries since they may be disposed in the environment without causing any deleterious effect. Further, their complete biodegradation give products that can be re-integrated in the natural life cycle.

Nowadays, a family of biodegradable polyesters that is receiving considerable attention is the polyhydroxyalkanoates or PHAs. The 3-PHAs derivatives are very attractive because, as the other PHAs, they have similar properties to conventional plastics and are completely

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biodegradable. The most common of them is poly(3-hydroxybutyrate) (3-PHB), which is synthesized and accumulated as carbon and energy source by numerous bacteria like *Alcaligenes eutrophus*, the most studied due its ability to produce large amount of this polymer [2, 3, 4].

However, EDPs are not competitive material due several aspects as the high cost of production compared to petrochemical plastics, high crystallinity, narrow processability window and poor mechanical properties. Therefore, to get low cost materials with good physical properties, it is reasonable to study the blending of PHB with natural or synthetic polymers, such as PEO, PVAc, PVOH, starch and cellulose, as well as PHB copolymers, like poly(3-hydroxybutyrate-co-3-hydroxyvalerate) (PHBV) [5, 6].

The development of blends with PHB and other natural polymers like starch is very attractive because they are completely biodegradable in the environment, and also starch is an abundant low cost material.

Starch is a natural occurring polymer obtained from renewable sources, it is degradable in biologically active environments like soil and sewage where some kinds of microorganisms are active. This polysaccharide is composed of a linear polymer (amylose) and a branched polymer (amylopectin). The degree of starch crystallinity is directly associated with the amilose content which depends the starch source. Heating and shearing forces are responsible for the rapid loss of the crystalline structure of starch, in a process known as gelatinization, resulting in a flexible thermoplastic material more suitable for blend preparation. [7, 8]

When PHB or polyethylene (PE) and natural starch, in its spherulitic crystalline grain form, were mixed together, the resulting materials presented poor mechanical properties due the high cristallinity of both polymers. Even when a more flexible PHB copolymer, like PHBV (12% of HV units) or PE were mixed with a thermoplastic derivative starch, they did not result in materials with improved mechanical properties [9, 10, 11]. This behavior is not difficult to explain since the hydrophobic character of PHB, PHBV and PE makes their mixing with starch, a highly hydrophilic material, difficult. As a consequence, the mixture of hydrophobic and hydrophilic polymers will give incompatible products with very poor mechanical properties. Yet, very brittle materials result due the high degree of crystallinity of both natural polymers, giving inadequate products for commercial applications. Better properties can be achieved when these materials are modified by suitable plasticizers and/or compatibilizers or chemical modifications are made in one of those polymers to change their crystallinity and/or their hydrophobic/hydrophilic character.

The use of plasticizers to decrease the crystallinity of highly crystalline polymers and increase their flexibility is a commom solution that is being studied in this work with PHB and starch. In the case of starch, it is well known that water and glycerol are good external plasticizers, but since they are not strongly bound to starch, they will exude out in time and/or at high temperatures, leaving the starch stiffer again due its retrogradation [10].

Chemical modification of starch includes grafting with different chemical groups like ethers, esters, isocyanates, and anhydrides in order to substitute some of the hydroxyl groups [10].

The properties of PHB/Starch blends depends on their degree of miscibility as well as compatibility. In this way, the role of the interfacial adhesion between starch and PHB is very important to improve the mechanical properties of their blends [12]. In addition, processing conditions such as temperature, humidity, and screw design are parameters that must be well controlled to get a good mixture without degrading the polymers.

In this work the thermal and mechanical properties of different PHB/Starch blends were explored, by using natural and chemically modified starches in order to investigate the influence of the chemical grafting in those properties.

Experimental

Materials

Poly (3-hydroxybutyrate) (PHB) was supplied by Coopersucar S.A.; natural starch (NS), Amidex 3010 and starch adipate (AS) by Corn do Brasil; poly(ethylene glycol) (PEG) Mw = 600 and poly(propylene glycol) (PPG) Mw = 1000 by Aldrich; adipic acid polyester derivative (Rucoflex), Mw = 3200, by Ruco; triacetin (TAG) by Rhodia do Brasil; methylene-bis(4-ciclohexylisocyanate), or Desmodur W, by Bayer.; dimethyl sulfoxide (DMSO) by SYNTH.

Methods

Gelatinization of unmodified natural starch and starch adipate was performed in DMSO (50% wt) with the aid of a mechanical mixer (DRAIS).

Chemical modification of starch: natural starch with 12% wt of initial water content according to Karl Fisher analysis, was previously dried at 80ºC for 72 h. After that, 0.250 moles of grafting agent (PEG, PPG or Rucoflex polyester) were kept under stirring in nitrogen atmosphere at 110ºC for 1 h. The temperature was reduced to 60ºC and 0.250 moles of diisocyanate were added and kept under stirring for 30 min. Then, 0.400 moles of starch, relative to glucose monomers, were added and the system was kept under stirring for 30 min. The grafted starches, that is polyester Rucoflex (US1), PEG-US2 and PPG-US3) were thus obtained.

Blends preparation: the blends studied in this work consisted of PHB/US1, PHB/US2 and PHB/US3. All blends were prepared in a mechanical mixer (DRAIS) in which PHB and TAG (30%) were mixed with different kinds of starches at different proportions (10, 20 and 30% wt). All blends obtained were ground prior injection molding. TAG at 30% was used because it proved to be a good plasticizer for PHB.

Processing conditions: the dog-bone samples for tensile strain tests (165mm length/13mm width/3.2mm thickness) were obtained in an Arburg Allrounder 221k / 250-75 injection molding machine operating in the following conditions: constant moulding temperature: 60°C (circulating cooling water); 140/145/155/155/150ºC heating zones; 12.6 cm^3 injection volume; 20s cooling time; 1200bar (1st step) and 1000bar (2nd step) injection pressure; 3.5 cm/s (1st step) and 2.5 cm/s (2nd step) injection rate 3.5 cm/s (1st step); 2.5 cm/s (2nd step); 650 bar (1st step) and 700 bar (2nd step) holding pressure.

Materials Characterization

Fourier Transform Infrared (FTIR) analysis: the different starches and PHB blends were characterized using a Spectrum 2000 Perkin Elmer FTIR spectrometer in conjunction with an ATR accessory (Zirconium selenide crystal at 45° angle). The finely powdered dilute dispersions of solid materials in potassium bromide were analyzed in the form of pressed discs; paste materials were analyzed by ATR technique in a form of thin films.

Mechanical tests tensile strain tests were performed at 20° ± 5° C in a EMIC DL 2000 machine at a rate of 50mm/min, according to ASTM D638 – Tensile – Type 1, and at 50 ± 5% relative humidity.

Differential Scanning Calorimetry (DSC): the glass transition temperature (Tg), melting point (Tm), crystallization temperatures (Tc) and melting enthalpy (ΔHf) of the different blends were determined by DSC with a TA Instruments (Model 2020) calorimeter. The degree of crystallinity (Xc) was calculated from the experimental ΔHf by using ΔHf of 100% crystalline PHB (ΔHf_{100}) ($Xc = \Delta Hf/\Delta Hf_{100} \times 100$) [13, 14]. Samples, packed in aluminum pans were first heated from –100 to 200°C at 20°C/min heating rate, then cooled down to –100°C at the same rate, and finally heated to 200°C at the same scan rate.

Results and Discussion

Infrared Analysis

The FTIR spectra were analyzed following the appearance and disappearance of characteristic bands of the main chemical groups. When the FTIR spectra of natural starch (NS) (Fig. 1, spectrum 1) and of starch-adipate (AS) (spectrum not shown) were compared, no significant modification was noted. However, differences could be observed in the intensity of the OH stretching band at ~3200 cm^{-1} probably due the partial substitution of OH groups by adipate. The same figure shows also the spectra of the polyester and of the diisocyanate used to get the starch-polyester-urethane derivative.

The FTIR-ATR spectrum of starch-polyester-urethane derivative (Fig. 1) shows the characteristic N-H deformation band due to urethane groups at 1520 cm^{-1}. The presence of the band at 2265 cm^{-1}, related to the isocyanate stretching group (-N=C=O), suggest that the chemical reaction was not complete. When starch-PEG-urethane derivatives (US2) were analyzed (Figure 2), new bands appeared at 2356 and 1526 cm^{-1}, due to N-H stretching and N-H deformation of the urethane group, respectively. The bands at 2261 and 1730 cm^{-1} were attributed to unreacted NCO groups and to the carbonyl stretching band of urethane groups, respectively.

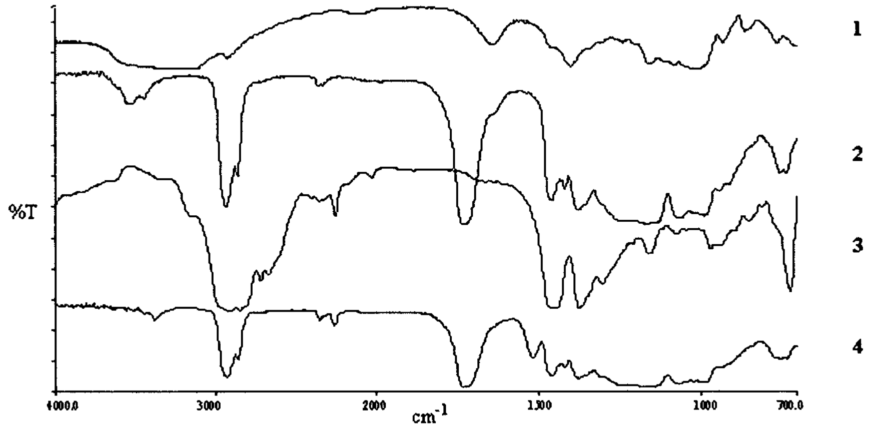

Figure 1: FTIR-ATR spectra of 1) natural starch (NS), 2) polyester, 3) methylene-bis(4-ciclohexylisocyanate), and 4) urethane starch 1 (US1).

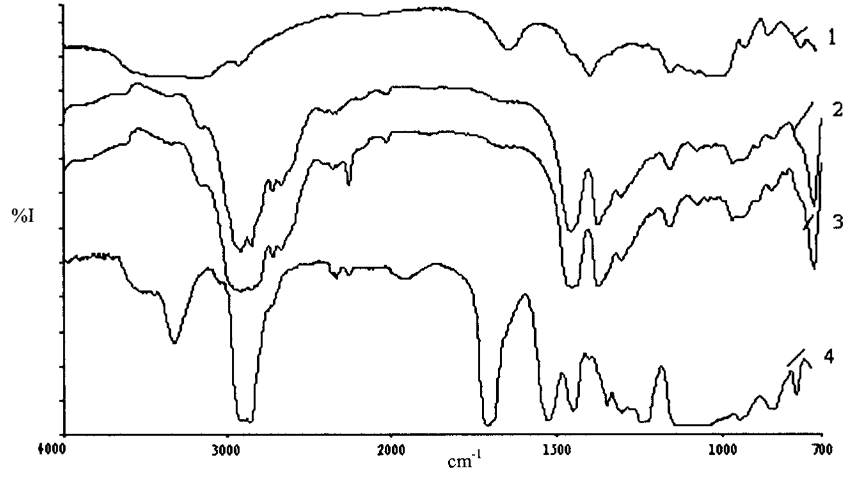

Figure 2: FTIR-ATR spectra of 1) natural starch (NS), 2) PEG, 3) methylene-bis(4-ciclohexylisocyanate), and 4) urethane starch 2 (US2).

Infrared analysis of all PHB blends with modified starch (US1, US2, and US3) showed some modifications after the mechanical mixing (DRAIS) process (Figures 3-5). In all cases, the disappearance of NCO characteristic bands and an increase of the intensity of the N-H urethane stretching band at 2338 cm^{-1} was observed, suggesting that isocyanate groups were consumed during the processing.

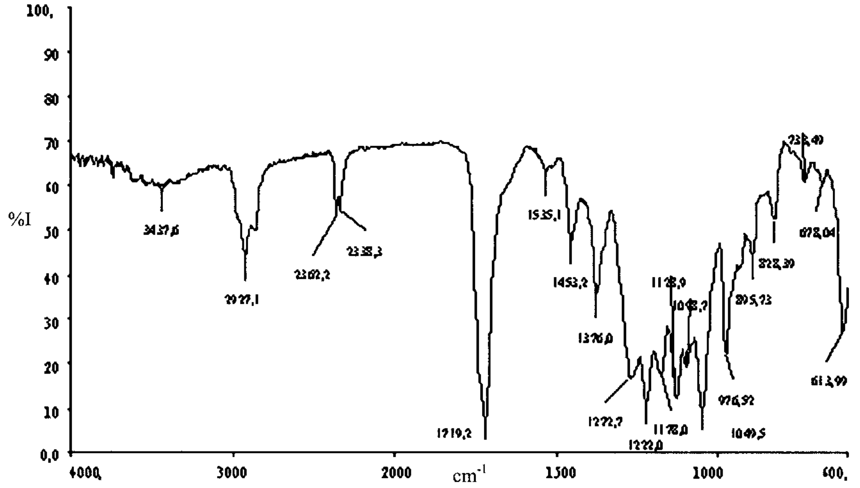

Figure 3: FTIR-ATR spectrum of the PHB blend with starch-polyester-urethane (US1).

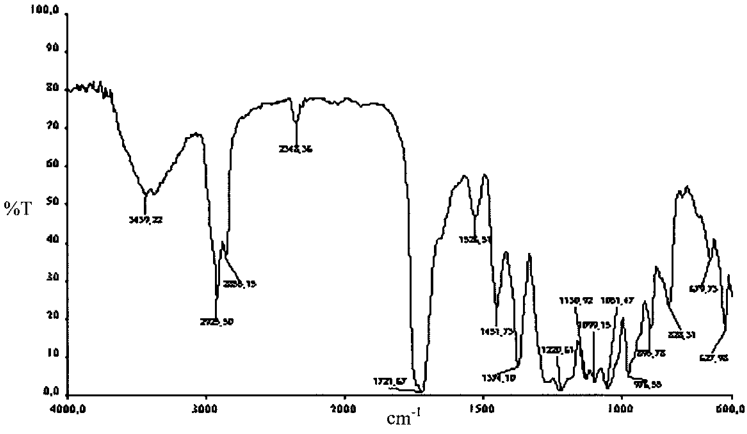

Figure 4: FTIR-ATR spectrum of the PHB blend with starch-PEG-urethane (US2).

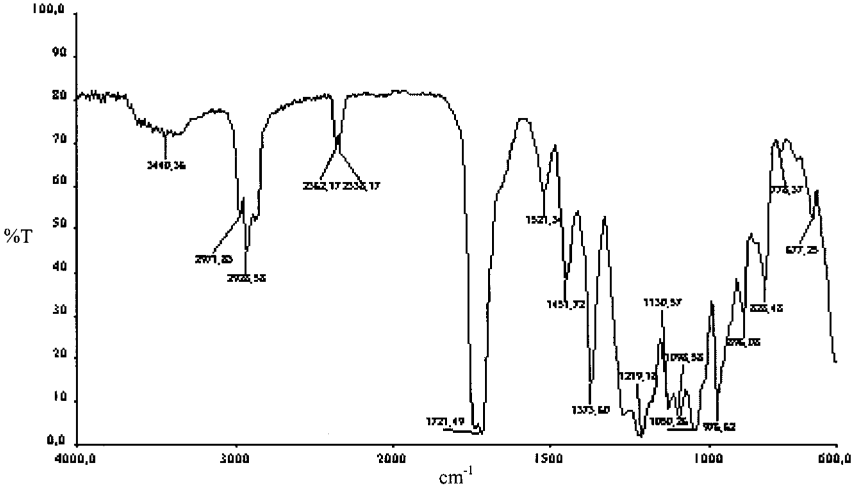

Figure 5: FTIR-ATR spectrum of the PHB blend with starch-PPG-urethane (US3).

Thermal and Mechanical Analysis

Thermal analysis of PHB blends showed that all analyzed parameters, such as Tg, Tc, ΔHc, Tm, ΔHm and Xc decreased significantly with respect to pure PHB (Table 1).

Table 1: Thermal Analysis (DSC) of PHB blends with different types of starch.

Blend	Tg (°C)	Tc (°C)	ΔHc (J/g)	Tm (° C)	ΔHm (J/g)	Xc (%)
PHB	0.7	47.7	39.7	170.8	55.8	38.3
TAG 30%	-25.7	28.7	25.2	158.4	41.1	28.1
NS10%	-38.9	25.4	20.4	142.5	29.4	20.1
NS 20%	-37.3	25.4	14.7	141.5	21.1	14.5
AS 10%	-36.1	17.1	17.6	146.9	26.2	17.9
AS 20%	-36.3	25.5	20.6	145.0	28.8	19.8
US1 10%	nd[c]	18.2	22.5	148.6	35.2	24.1
US1 20%	-58.8[a] /-30.1[b]	18.3	17.5	151.4	32.7	22.4
US1 30%	-54.8[a] /-19.2[b]	32.2	21.9	159.1	29.2	20.0
US2 10%	*	18.1	17.8	150.5	28.0	18.9
US2 20%	-45.4[a] / -28.3[b]	19.5	11.2	152.3	18.5	12.7
US2 30%	-42.2[a] / -25.2[b]	24.6	16.9	156.0	28.8	19.7
US3 10%	*	24.6	20.8	146.4	29.7	20.4
US3 20%	-50.6[a] / -24.9[b]	41.9	26.0	156.2	40.1	27.5

[a] Relevant to modified starch. [b] Relevant to PHB component. [c] not observed.

The differences on the amounts of these parameters showed in Table 1, for the several groups of blends (PHB-USs, PHB-NS, PHB-AS), could be attributed to the non homogeneity of the starch dispersion in the PHB matrix.

It was possible to prepare thermoplastic starches by external plasticization of natural starch (NS) and starch adipate (AS) with dimethylsulfoxide (DMSO). It was noted that when blended with PHB, these starches retrograde due a probable migration of DMSO to PHB because their affinity. The resulting materials showed poor mechanical properties (Table 2), such as low elongation, probably because the amount of DMSO was not enough to plasticize both polymers. In addition, the incompatibility between hydrophobic PHB and hydrophilic natural starch and adipate starch (having a low degree of substitution as confirmed by FTIR-ATR analysis) also contributed to decrease the mechanical properties.

The migration of the plasticizer did not occur in the case of the chemically modified starches by grafting process or internal plasticization (US1, US2 and US3). This behavior can be attributed to the steric hindrance of the side chains that inhibits starch crystallization (retrogradation). Accordingly, the lowest Tg and Tm (Table 1) were observed for the blends containing these grafted starches as a consequence of the internal plasticization.

Table 2: Mechanical Properties of PHB blends with different types of starch.

Blend	**Tensile Stress at Break (MPa)**	**Young Modulus (MPa)**	**Elongation at break (%)**
PHB	31.0 ± 0.3	911.9 ± 20.3	7.0 ± 0.1
TAG 30%	11.3 ± 0.7	185.6 ± 13.3	15.5 ± 1.3
NS 10%	6.5 ± 0.8	142.0 ± 21.6	4.8 ± 0.6
NS 20%	3.0 ± 0.3	171.6 ± 22.6	2.3 ± 0.2
AS 10%	5.7 ± 0.5	176.4 ± 24.3	3.9 ± 0.3
AS 20%	3.3 ± 0.2	119.2 ± 13.5	2.7 ± 0.1
US1 10%	7.4 ± 0.4	161.8 ± 9.2	6.9 ± 0.4
US1 20%	4.2 ± 0.5	131.2 ± 79.8	3.1 ± 0.2
US1 30%	3.6 ± 0.3	139.7 ± 27.4	3.8 ± 0.3
US2 10%	8.6 ± 0.2	197.2 ± 9.0	6.7 ± 0.3
US2 20%	7.0 ± 1.0	209.7 ± 11.0	5.9 ± 0.8
US2 30%	6.5 ± 0.2	166.5 ± 57.5	6.5 ± 0.2
US3 10%	7.5 ± 0.2	206.0 ±5.8	5.0 ± 0.1
US3 20%	7.5 ± 0.1	200.7 ± 5.7	6.4 ± 0.2
US3 30%	*	*	*

* It was not possible to inject the PHB/ US3 30% blend.

It is interesting to note that at concentrations over 20% (US1, US2 and US3) there are two Tg attributed to the modified starches (lower Tg) and PHB, respectively. On the other hand, only one melting transition was observed at about 155°C, a temperature significantly lower than that of pure PHB (~ 170° C), thus improving their processability.

The mechanical properties of PHB blends with grafted starches (US1, US2, and US3) were better than those of blends with NS and AS, because of the chemical affinity between grafted starch and PHB. No significant difference was not observed between the elongation at break of pure PHB and that of blends with US2 and US3 grafted starches, whereas the elongation of PHB/US1 blend was 20-30% lower.

In all cases, the Young modulus of PHB blends (130-200 MPa) was much lower than that of PHB (912 MPa).

Conclusions

Binary blends of PHB with natural starch, starch-adipate, and grafted starch-urethane derivatives were prepared and analyzed by FTIR-ATR.

The PHB blends were characterized in terms of mechanical (elongation and tensile stress at break, Young modulus), thermal properties (Tg and Tm) and degree of crystallization. In all cases, glass transition temperature (Tg), melting point (Tm), crystallization temperature (Tc) and crystallinity were much lower than those of PHB. Blends containing natural starch or starch adipate resulted in brittle materials. As compared to PHB, all blends showed smaller Young modulus and the tensile stress at break, but no significant changes in the elongation at break.

The significant reduction in Tm improved the blend processability. The lowest Tg and Tm were observed for the blends using grafted starches due to internal plasticization. These materials showed two glass transitions, attributed to the modified starch and PHB, respectively.

Therefore, the best results as lower modulus and Tg were observed for the PHB blends obtained by using starch grafted with poly(propylene glycol)-urethane derivatives.

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