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Study of the Influence of Plasticizers on the Thermal and Mechanical Properties of Poly(3-hydroxybutyrate) Compounds

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Summary: The influence of four types of plasticizers, dioctyl phthalate (DOP), dioctyl adipate (DOA), triacetyl glycerol (TAG) and polyadipate (PA), in the thermal and mechanical properties of Poly(3-hydroxybutyrate) (PHB), a highly crystalline biodegradable polyester, was evaluated in this work. The plasticizers were introduced alone or mixtures of them, using concentrations that varied from 5 to 30% wt. Their influence in some important polymer parameters as Tg, Tm and degree of crystallinity, and on its mechanical behavior, elongation and tensile strain were investigated. The best results were obtained for the sample with 30% TAG and that one using a binary mixture of plasticizers PA 20% and TAG 10%.

Keywords: PHB, plasticizers, thermal properties, mechanical properties.

Introduction

The utilization of environmentally biodegradable polymers (EDPs) is an alternative to reduce the great amount of plastics in municipal solid waste and the pollution caused by them. In addition, the use of EDPs is based on renewable resources and contributes to material cycling analogous to biogeochemical cycles in nature. Poly(3-hydroxyalkanoates) (PHAs), an interesting family of polyesters, have attracted much attention in recent years as they are biocompatible and biodegradable thermoplastics with potential applications in different fields like agriculture, marine and medicine [1].

The PHAs synthesis normally occurs when there is an excess of carbon and energy and limitation of at least one nutrient (N, P, Mg, Fe, etc) needed for microorganisms growth. These polyester and a number of bacteria producing them, have been intensively studied nowadays by several groups of scientists in the world.[2,3].

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PHAs are synthesized and accumulated by several numerous prokaryotes as intracellular granules and have the general structure, shown in Figure 1 [4].

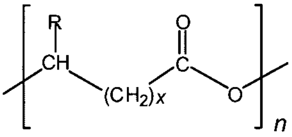

Figure 1 – General structure of poly(hydroxyalkanoate)s –(PHAs)

It is interesting to note that these polymers are thermoplastics and present properties that range from elastomeric behaviour up to brittle and fragile, according to the side groups (R) in their main chains.

Poly(3-hydroxybuyrate) or PHB (R = CH_3), one of the most common member of the PHAs family is a linear head-to-tail polyester discovered by Lemoigne in 1927 [5].

In 1982, the Imperial Chemical Industries (ICI) developed a process for an industrial production of PHB, using *Alcaligenes eutrophus* bacteria grown on glucose. At present, PHB is commercially available under the trademark BIOPOL® (ICI) [8].

As a thermoplastic, PHB can be extruded, moulded and spun on conventional processing equipment. These features make this polymer an ideal candidate for the production of biodegradable packaging materials and other disposables [8]. However, this material is highly crystalline (more than 60%) with a melting temperature (Tm) of 175 - 180 °C and a glass transition temperature (Tg) between 4 – 7 °C, similar to polypropylene (PP). But, differently from the latter, the former is stiffer and more brittle due to its high crystallinity, resulting in very poor mechanical properties with low extension break that limits its range of application [5,6,7].

Among the routes to prepare useful materials from PHB, the addition of plasticizers contributes to improve the polymer thermal and mechanical properties. As a consequence, the glass transition temperature (Tg) and the melting point (Tm) of the polymer decrease allowing the processing at lower temperature thus avoiding thermal degradation. In addition, plasticizers improve the toughness and softness of the polymer by decreasing its cristalinity.

Another way to obtain more flexible PHB is to produce bacterial random copolymers of 3-HB and other hydroxyalkanoate monomers, such as 3-HV (3-hydroxyvalerate). Furthermore, the production of polymer blends using PHB and other polymers, is a good alternative to improve the thermal and mechanical properties of the final product [9,10,11,12,13].

In this way, we focused our attention on the influence of some known plasticizers on the thermal and mechanical properties of PHB compounds, with the aim of getting a more flexible and useful final material.

Experimental

Materials

PHB from Copersucar (Cooperativa de Produtores de Cana, Açúcar e Álcool do Estado de São Paulo Ltda), triacetyl glycerol (TAG) from Rhodia do Brasil, dioctyl phthalate (DOP) and dioctyl adipate (DOA) were obtained from Scandiflex do Brasil S.A. and polyadipate (PA/ Mn 3,800) from Cognis Brasil Ltda.

Compound preparation

Poly(3-hydroxybutirate) (PHB) was loaded with different amounts of plasticizers up to a maximum concentration of 30% (wt) relative to PHB, as shown in Table 1.

Table 1 – PHB formulations with different kinds of plasticizers

Plasticizer Formulations	**DOP (%)**	**DOA (%)**	**TAG (%)**	**PA (%)**	**Plasticizer Formulations**	**DOP (%)**	**DOA (%)**	**TAG (%)**	**PA (%)**
1	5				12			30	
2	10				13				5
3	20				14				10
4	30				15				20
5		5			16				30
6		10			17	10		20	
7		20			18	10			20
8		30			19			10	20
9			5		20			20	10
10			10		21	10		10	10
11			20						

All formulations were prepared in a single screw extruder Wortex WEX 30 at a screw speed of 90 rpm, with the barrel thermal profile of 140, 155, 165, 175 and 175°C, and 32 L/D ratio. The extrudate was obtained in the form of narrow long rods and pelletized.

Samples moulding

The samples for tensile strain tests were obtained in an Arburg Allrounder 221k / 250-75 injection moulding machine, with the barrel thermal profile of 145, 150, 165, 165 and 160°C, operating in the following conditions:
Injection volume: 12.6 cm^3
Injection Pressure: 1200 bar (1st step); 1000 bar (2nd step).
Injection Velocity: 3.5 cm/s (1st step); 2.5 cm/s (2nd step).
Holding Pressure: 650 bar (1st step); 700 bar (2nd step).
Cooling time: 20s
The samples were moulded to form type 1 dogbone-shape - 165mm / 13mm / 3.2mm (length / width / thickness). The mould temperature was maintained constant at 60°C by a circulating water bath.

Differential Scanning Calorimetry (DSC)

Differential scanning calorimetry (DSC) of pure and plasticized PHB samples was performed to study the thermal parameters of the systems as glass transition temperature (Tg), melting point (Tm), crystallization temperatures (Tc) and melting enthalpy (ΔHf). The degree of crystallinity (Xc) was calculated using ΔHf of PHB 100% crystalline (ΔHf_{100}) and ΔHf obtained [$Xc = \Delta Hf/\Delta Hf_{100} * 100$] [14,15].
Samples packed in aluminium pans were first heated from –50° C to 200°C, at a heating rate of 20°C/min; cooled at the same rate down to –50°C and then re-heated to 200°C at the same scanning rate. This procedure was done to eliminate the effects of sample processing.

Mechanical tests

Tensile tests were performed, using five probes for each measure, at a temperature of 20° ± 5° C , with an EMIC DL 2000 machine at a rate of 50mm/min, according to ASTM D638 – Tensile – Type 1, and relative humidity of 50 %± 5% .

Results and Discussion

Thermal properties

The results from thermal analysis of each formulation are summarised in Tables 2 - 6 and Figures 2 - 4.

Table 2 – DSC analysis of PHB formulations plasticized with DOP

FIRST HEATING							SECOND HEATING					
DOP (%)	**Tg (°C)**	**Tc (°C)**	**ΔHc (J/g)**	**Tm (°C)**	**ΔHm (J/g)**	**Xc (%)**	**Tg (°C)**	**Tc (°C)**	**ΔHc (J/g)**	**Tm (°C)**	**ΔHm (J/g)**	**Xc (%)**
0	*	*	*	170.9	66.5	45.5	0.7	47.7	39.7	170.8	55.8	38.3
5	*	*	*	167.5	57.5	39.4	-4.8	43.6	37.0	167.8	57.2	39.2
10	*	*	*	165.9	56.1	38.4	-8.8	41.6	35.4	166.2	56.0	38.3
20	*	*	*	164.5	60.4	41.4	-9.4	47.7	34.0	162.5	51.4	26.7
30	*	*	*	161.6	43.6	29.9	-10.8	41.8	28.1	161.9	44.6	30.6

* not detectable

Table 3 – DSC analysis of PHB formulations plasticized with PA

FIRST HEATING							SECOND HEATING					
PA (%)	**Tg (°C)**	**Tc (°C)**	**ΔHc (J/g)**	**Tm (°C)**	**ΔHm (J/g)**	**Xc (%)**	**Tg (°C)**	**Tc (°C)**	**ΔHc (J/g)**	**Tm (°C)**	**ΔHm (J/g)**	**Xc (%)**
0	*	*	*	170.9	66.5	45.5	0.7	47.7	39.7	170.8	55.8	38.3
5	*	*	*	169.5	55.1	37.7	-4.1	44.9	38.6	169.0	57.5	39.4
10	*	*	*	166.4	56.9	39.0	-8.3	41.4	34.2	167.2	52.9	36.3
20	*	*	*	165.5	49.6	34.0	-16.0	37.6	30.8	165.9	47.1	32.3
30	*	*	*	163.5	44.1	30.2	-21.8	35.2	27.3	163.7	44.0	30.1

* not detectable

Table 4 – DSC analysis of PHB formulations plasticized with DOA

FIRST HEATING							SECOND HEATING					
DOA (%)	**Tg (°C)**	**Tc (°C)**	**ΔHc (J/g)**	**Tm (°C)**	**ΔHm (J/g)**	**Xc (%)**	**Tg (°C)**	**Tc (°C)**	**ΔHc (J/g)**	**Tm (°C)**	**ΔHm (J/g)**	**Xc %)**
0	*	*	*	170.9	66.5	45.5	0.7	47.7	39.7	170.8	55.8	38.3
5	*	*	*	179.4	56.5	38.7	-5.8	41.3	36.4	168.0	55.0	37.6
10	*	*	*	168.1	55.0	37.7	-7.0	41.9	34.1	168.0	52.6	36.0
20	*	*	*	165.0	57.5	39.4	-6.9	43.5	31.7	165.3	48.8	33.4
30	*	*	*	165.4	48.0	32.9	-6.8	43.3	30.7	165.2	49.5	33.9

* not detectable

Table 5 – DSC analysis of PHB formulations plasticized with TAG

FIRST HEATING							SECOND HEATING					
TAG (%)	**Tg (°C)**	**Tc (°C)**	**ΔHc (J/g)**	**Tm (°C)**	**ΔHm (J/g)**	**Xc (%)**	**Tg (°C)**	**Tc (°C)**	**ΔHc (J/g)**	**Tm (°C)**	**ΔHm (J/g)**	**Xc (%)**
0	*	*	*	170.9	66.5	45.5	0.7	47.7	39.7	170.8	55.8	38.3
5	*	*	*	170.2	62.8	43.0	0.5	46.3	39.4	170.2	58.5	40.1
10	*	*	*	165.1	51.8	35.4	-9.7	37.7	33.6	165.7	52.0	35.6
20	*	*	*	159.6	50.8	34.8	-16.7	31.8	33.3	161.0	48.3	33.1

* not detectable

The values of Tg, Tc and ΔHc were obtained only for the second heating to eliminate the influence of the material processing.

The influence of each plasticizer on the thermal properties of PHB can be seen in Tables 2-5.

DOP, one of the most used plasticizer in the world, showed a good influence on the thermal properties of PHB, decreasing both Tg and Tm, and also the degree of crystallinity (or ΔHc), as seen in the second heating.

The same behaviour was observed using PA as plasticizer, but in this case Tg decreased markedly (-22.43°C) relative to PHB alone, as indicated in Table 3.

When DOA was used, the reduction on Tg was small and this plasticizer did not cause significant effect in the PHB thermal properties for concentrations higher than 5%. Yet, it presented a strong exudation from the systems, indicating the incompatibility of the components. Based on this evidence, it was decided to eliminate DOA from the investigations.

TAG, known as a good plasticizer for PHB, showed excellent results like PA, decreasing significantly the Tg of PHB at 10% concentration, but no significant effect was found at 5% content. It should be said that no measurements were made from 5 to 10% TAG.

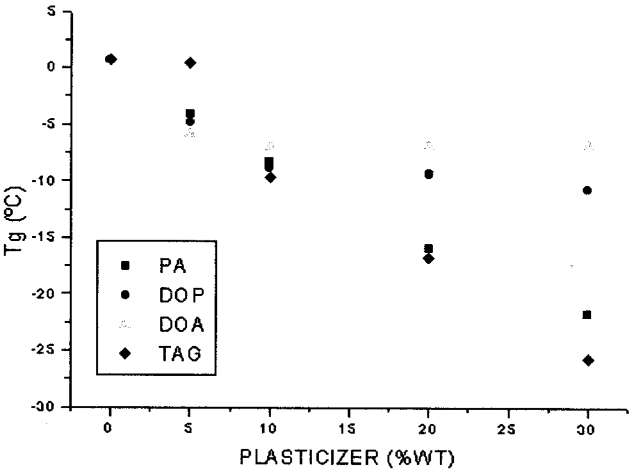

Figure 2 – Dependence of PHB Tg on the concentration of different plasticizers

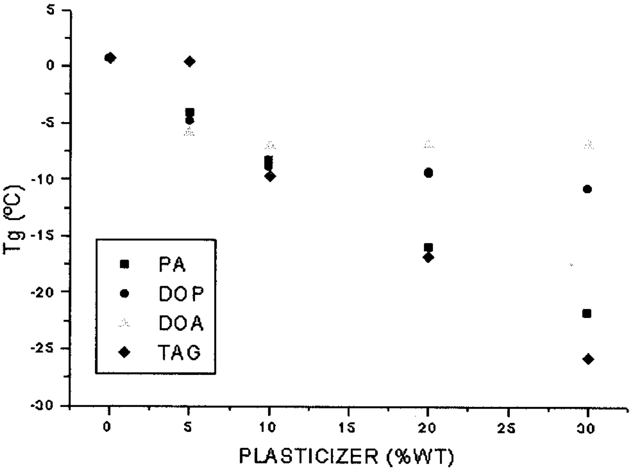

Figure 3 – Dependence of PHB crystallinigy on the concentration of different plasticizers

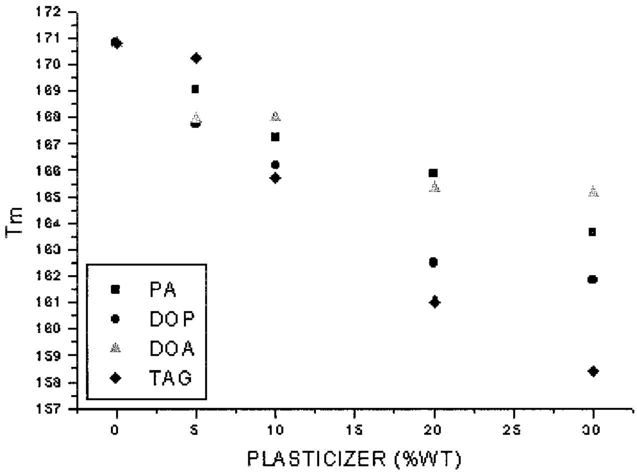

Figure 4 – Dependence of PHB Tm on the concentration of different plasticizers

Binary and ternary mixtures of plasticizers were prepared to investigate any synergistic effect on the thermal properties of PHB plasticized compounds. The total concentration of the mixtures of plasticizers in the studied systems was limited to 30% (by wt) and the DOP concentration was no more than 10% (by wt). As DOP is not a “green” component, it was decided to use a minimum amount of it.

The results presented in Table 6, indicate that none of the different plasticizers formulation presented an antagonistic effect.

Table 6 – DSC analysis of PHB formulations containing different plasticizer mixtures

PLASTICIZERS			**FIRST HEATING**			**SECOND HEATING**					
PA (%)	**DOP (%)**	**TAG (%)**	**Tm (°C)**	**ΔHm (J/g)**	**Xc (%)**	**Tg (°C)**	**Tc (°C)**	**ΔHc (J/g)**	**Tm (°C)**	**ΔHm (J/g)**	**Xc (%)**
—	—	—	170.9	66.5	45.5	0.7	47.7	39.7	170.8	55.8	38.3
20	**10**	—	162.7	44.4	30.4	-20.3	37.3	27.0	162.8	44.8	30.7
20	—	**10**	151.3	41.2	28.2	-30.0	21.4	25.9	151.8	37.8	25.9
10	—	**20**	155.6	39.2	26.9	-29.7	22.6	21.3	153.3	36.6	25.0
—	**10**	**20**	153.1	37.9	25.9	-29.9	20.2	23.4	152.9	43.7	29.9
10	**10**	**10**	158.2	39.1	26.8	-24.9	28.1	25.0	158.3	41.1	28.1

The effect of mixtures of TAG w.M. DOP and PA on the glass transition and melting point of PHB formulations, was higher when compared to the samples containing only one of these plasticizers. When mixed together, they caused a Tg decrease to lower values than those of samples containing only one plasticizer. Ternary plasticizer mixtures were less effective. The formulation that exhibited the lowest Tg contained 20% PA and 10% TAG. This formulation also caused a 7°C reduction with respect of the lowest Tm observed for the sample containing 30% wt of TAG.

Tensile properties

The tensile properties are summarized in table 7 and figure 5. When DOP was added to PHB, it caused a decrease of the tensile strength, resulting in lower Young's Modulus and more flexible material. The tensile strength at break was reduced down to 60% and the elongation at break increased up to 54% , relative to PHB alone. This well known behavior is due to the effect of the addition of a compatible plasticizer which contains more free volume than the pure polymer [16]. It could be also attributed to the decrease of the degree of crystallinity of the plasticized systems as shown in Table 2. At 30% DOP concentration, a higher fragility of the material was observed, probably due to the segregation of the excess plasticizer. To avoid this effect, a 10% DOP concentration was chosen as the appropriate value for those systems.

Regarding the PA plasticizer it was observed that the elongation at break increased as the concentration of PA increased over 20% wt. A 30% PA concentration represented the best formulation in terms of mechanical properties. In this case, there was a reduction of 53.4% in the tensile at break and an increase of 51% in the elongation at break.

DOA reduced the tensile at break of PHB by 57.8% whereas the elongation at break didn't increase. The material obtained was fragile and useless, indicating that this plasticizer was not effective for PHB as confirmed by the results of thermal analysis.

In this investigation the best results for elongation at break were obtained by 30% wt TAG. In this case, there was a reduction of 63.6% in the tensile strength at break and an increase in the elongation at break of 122.7%.

Satisfactory mechanical properties were obtained when mixtures of plasticizers were used, as compared to formulations with only one plasticizer, with the only exception of the formulation containing 10% DOP and 20% TAG. Nevertheless, this last formulation was better than PHB alone.

It is possible to say that the mixtures of plasticizers attack the mechanical and thermal properties of the formulations studied here. When added together, they increase significantly the elongation at break of the polymer matrix, and decrease significantly, tensile strength at break and Tg and Tm, suggesting their synergistic effect.

From the results of thermal and mechanical analysis obtained in this work, it may be confirmed that the two best formulations to satisfy the expectation for flexible PHB were those containing 30% of TAG alone or a binary mixture of 20% PA and 10% TAG.

Table 7 – Results of mechanical tests for all PHB formulations

	Tensile Stress at Break (MPa)	**Young Modulus (MPa)**	**Elongation at break (%)**
PHB	31.0 ± 0.3	911.9 ± 20.2	7.0 ± 0.1
PA 5%	27.6 ± 0.2	744.9 ± 20.2	8.6 ± 0.3
PA 10%	22.9 ± 1.2	683.5 ± 51.2	6.8 ± 1.5
PA 20%	17.6 ± 0.5	523.3 ± 39.0	8.8 ± 1.0
PA 30%	14.4 ± 0.2	424.5 ± 23.3	10.5 ± 0.5
DOP 5%	26.6 ± 0.6	680.5 ± 18.5	8.8 ± 0.5
DOP 10%	22.9 ± 0.2	553.9 ± 22.5	10.5 ± 0.8
DOP 20%	18.0 ± 2.3	447.8 ± 44.5	10.1 ± 0.4
DOP 30%	12.6 ± 0.4	339.7 ± 20.2	8.6 ± 0.6
DOA 5%	21.4 ± 0.9	649.8 ± 60.1	6.1 ± 0.6
DOA 10%	20.7 ± 0.4	745.4 ± 10.1	5.7 ± 0.1
DOA 20%	16.1 ± 0.3	576.1 ± 29.6	6.2 ± 0.2
DOA 30%	13.1 ± 0.7	557.4 ± 44.7	4.3 ± 0.1
TAG 5%	22.2 ± 0.4	683.4 ± 36.6	5.7 ± 0.3
TAG 10%	20.0 ± 0.4	520.1 ± 37.1	7.4 ± 0.5
TAG 20%	14.1 ± 0.3	238.4 ± 6.5	10.3 ± 0.3
TAG 30%	11.3 ± 0.7	185.6 ± 13.3	15.5 ± 1.3
PA 20% + DOP 10%	13.2 ± 0.2	313.1 ± 7.2	13.7 ± 0.9
PA 20% +TAG 10%	10.5 ± 0.2	163.9 ± 3.5	13.0 ± 0.4
PA 10% + TAG 20%	10.6 ± 0.3	181.3 ± 11.4	11.2 ± 0.6
TAG 20% + DOP 10%	10.7 ± 0.4	219.7 ± 15.1	8.3 ± 0.2
PA 10% + TAG 10% + DOP 10%	10.7 ± 0.3	184.4 ± 9.7	12.1 ± 0.6

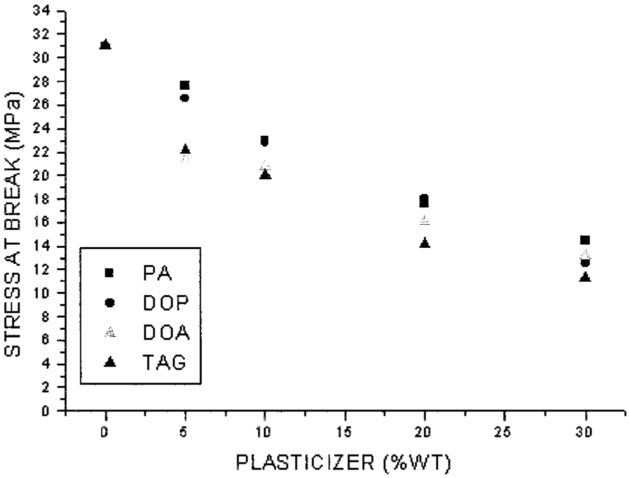

Figure 5 – Dependence of the stress at break of PHB formulations on the content of different plasticizers

Conclusions

Among the plasticizers used in this work, only DOA was not effective to improve the mechanical and thermal properties of PHB formulations. In fact, these properties did not change significantly.

DOP plasticizer made PHB more flexible, causing a 54% increase of tensile strength at break while decreasing Tg, Tm and the degree of crystallinity; however, at 30% DOP concentrations, the polymer matrix became fragile probably due the exudation of this plasticizer.

The best results were obtained using TAG and PA as plasticizers. At 30% wt concentration of TAG, Tg and Tm decreased by 26.3 and 12.4 °C respectively, whereas the elongation of break incresed by 123%. When 30% wt of PA was added to PHB, the Tg was reduced by 22.4 ºC and the Tm by 7.1ºC, and the elongation at break was increased by 51%. These results indicate that polyadipate is a promising plasticizer for PHB.

Promising results were also obtained when mixtures of plasticizers were used. In this case, the 10% TAG –20% PA mixture afforded the best results in terms of PHB thermal properties, resulting in a reduction of 30.7°C and 18.9 °C in its Tg and Tm, respectively, as well as in the lowest degree of crystallinity.

The mechanical properties presented satisfactory results. Indeed, the elongation at break increased by 97% for formulations containing 20% PA and 10% DOP, and by 86% for formulations containing 20% PA and 10% TAG.

Acknowledgments

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