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Mechanical and Thermal Performance of PLA and PHBV-based Biopolymers as Potential Alternatives to PET

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The evaluation of the mechanical and thermal properties of poly (3-hydroxybutyrate-co-3-hydroxyvalerate) (PHBV), polylactide (PLA) and their biocomposites (containing 30%wt of sisal in their composition) has been studied and compared to poly(ethylene terephthalate) (PET). The addition of sisal to the biopolymeric matrix increased the elastic stiffness of the bio-composites achieving a performance which is comparable to PET. All biocomposites presented lower traction resistance and elongation values respect to PET.The addition of natural fibers improved the thermal stability of PHBV-based samples. The trigger of decomposition happened at lower temperatures respect to PET, but always far above their melting point ensuring a good performance of the composites at high processing temperatures. The apparent activation energies for the biocomposites in inert conditions respect to those for PET indicates a more suitable scenario from the energetic valorisation point of view.

1. Introduction

Plastics are used for many varied applications in packaging ranging from sterile storage of medical and pharmaceutical goods, to extending the shelf life of foodand protecting sensitive products from damage. Among the different adequate polymers for this purpose, poly(ethylene terephthalate) (PET) has a widely extended use due to its excellent mechanical, chemical and thermal properties. However, its major disadvantage is its non-renewable nature and its lower possibility of recyclability while maintaining its initial properties.

Biopolymeric materials have been proposed as a potential and suitable replacement for PET as they present good processing properties and a much lower environmental impact. However, great attention should be paid to their competitiveness with the existing optimised plastic industry in terms of processing systems, performance and prices. Moreover, and taking into account that the accumulation of polymeric bio-waste would potentially increase, their management once their end of lifetime use is achieved should be evaluated.

Among all the biopolymers produced from renewable resources, polyhydroxyalkanoates (PHAs) have a very wide range of properties and applications (Weng et al, 2010, Bledzki and Jaszkiewicz, 2010). They are synthesized intracellularly by bacteria from agricultural raw materials as a source of carbon and energy. Poly (3-hydroxybutyrate-co-3-hydroxyvalerate) (PHBV) is among the most popular PHAs. This thermoplastic polyester mainly consists of hydroxybutyrate (HB), along with hydroxyvalerate (HV) units randomly repeated throughout the polymer chain. The physical properties of PHBV vary with the increase of HV content, which can be controlled by the carbon source supplied during biosynthesis (Gatenholm and Mathiasson, 1994). Similarly, polylactide (PLA) is an aliphatic polyester that can be obtained from agricultural resources as corn starch or sugarcane. Its synthesis is a multistep process which starts from the production of lactic acid, with an intermediate step with the formation of lactide and ending with the polymerisation reaction (Hartmann, 1998).

The compliance of the standards established by traditional fossil-derived plastics is crucial to ensure the applicability of biopolymers in an industrial level. Their mechanical performance has to be comparable with the already well-established materials. Moreover, the application of thermo-chemical operations must be carefully evaluated during the design of facilities for energy recovery purposes and, in this sense, the study of the thermal decomposition of materials stands out as the main basis for the correct tuning of the process.

Within this framework, the main aim of this work is to study the properties of pure polylactid acid (PLA) and poly(3-hydroxybutyrate-co-3-hydroxyvalerate) (PHBV) and their sisal-reinforced biocomposites and compare them with a reference commodity (PET) in order to evaluate their suitability as potential replacement materials from both mechanical and thermal points of view.

2. Experimental procedure

2.1 Materials and sample preparation

Poly (3-hydroxybutyrate-co-3-hydroxyvalerate) (PHBV) ENMAT Y1000P was obtained from Tianan Biologic (China). Polylactide (PLA) 3251D was purchased from Natureworks (Minnetonka, USA). Sisal fibre was supplied by Thai Royal project (Thailand). Maleic anhydride (MA) 98% of purity (Fluka) and dicumyl peroxide (DCP) 98% of purity (Sigma Aldrich) were used as coupling agent and free radical initiator, respectively. Processing of biocomposites was detailed in a previous work (Badia et al, 2014, Gil-Castell et al, 2014). Shortly, the samples were processed to obtain biocomposites with 30% in weight of sisal fibers, a 2.5 %wt MA and 0.3 %wt of DCP. All materials were mixed in an internal mixer (Brabender, Germany) during 5 min at 180 ºC and 50 rpm of speed and subsequently ground and pressed by compression moulding (Fontijne Presses, Holland) into 0,5 mm thick plates, used as specimens. Figure 1 shows the materials under study and their nomenclature.

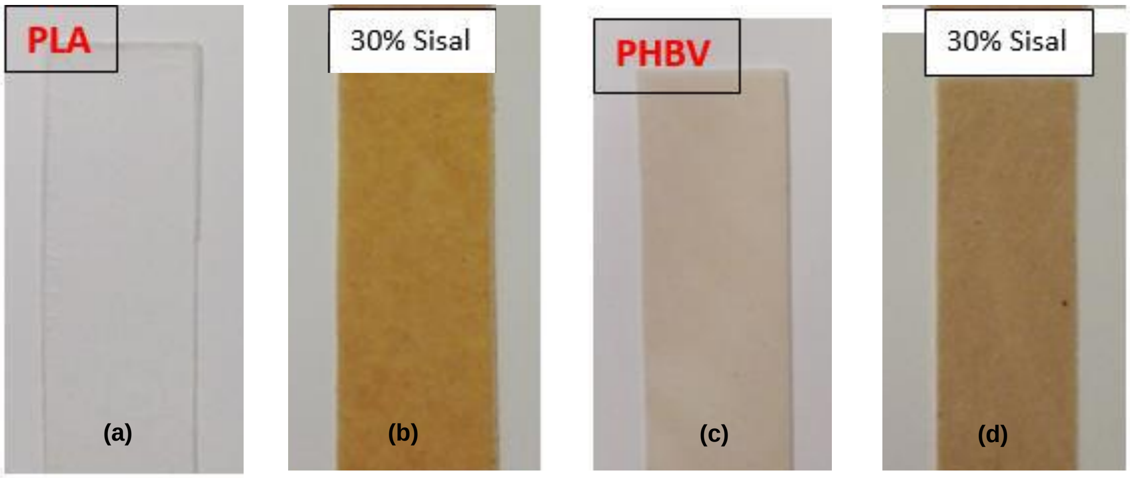


Figure 1. Virgin PLA (a); biocomposite PLA30 (b): virgin PHBV (c); biocomposite PHBV30 (d)

2.2 Mechanical analysis

Tensile tests were carried out according to the normative ASTM D638. The tests were carried out on a Zwick/RoellZ0.5. The testing parameters were as follows: 1 mm/min for estimating the tensile E-modulus and 10 mm/min for estimating tensile strength and elongations. The dimensions of the samples were 20x100x0.5 mm. The results were evaluated with the aid of the software testXpert.

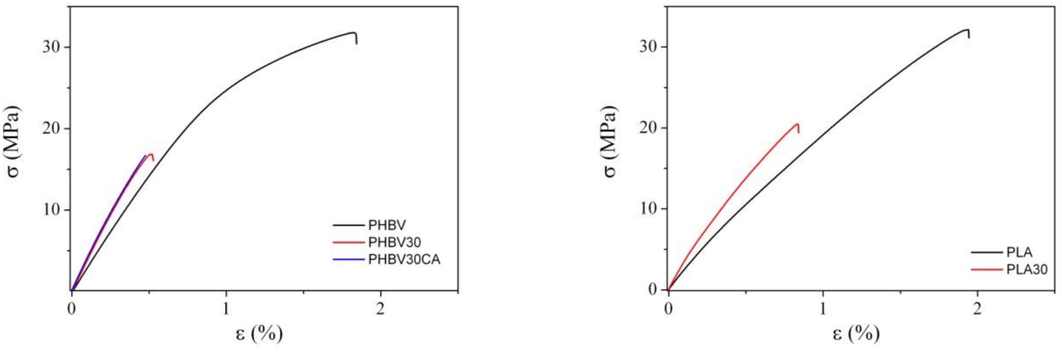
2.3 Thermogravimetric analysis

Multi-rate non-isothermal linear thermogravimetric experiments (TGA) were carried out in a Mettler Toledo TGA/SDTA 851 (Columbus, OH). Samples weighing around 5 mg were heated in an alumina holder with capacity for 70μL. Experiments were performed from 25ºC to 750ºC at different heating rates (β=2, 5, 10, 15ºC/min) under constant flow of 50 mL/min of gas of analysis. All samples were analysed under inert (Ar) atmosphere to characterise their thermal stability. Experiments were repeated at least three times and the averages were considered as representative values.

3. Results and discussion

3.1 Mechanical evaluation

Figure 2 shows the stress-strain deformation graphs of the tested biocomposites with an initial linear region followed by a curvature indicating the viscoelastic nature of the fibre. The results show that the elastic modulus of the reinforced composites (E_t) is higher compared to the unreinforced matrix. On the contrary, the tensile strength (σ_M) decreased considerably for the samples containing natural fibres with almost no elongation encountered by the samples (ε_M) after the maximum stress value. The addition of coupling agent (CA) in samples based on PHBV did not show a further increase in E_t and presented no elongation at break showing a behaviour similar to ceramic materials. The addition of CA in PLA-based polymers resulted in extremely fragile samples and tensile tests could not be carried out.



(a) (b)

Figure 2.Tensile tests for PHBV (a) and PLA (b) and their biocomposites.

Quantitatively, the main mechanical properties of the samples are gathered in Table 1.

Table 1: Mechanical properties of PHBV, PLA and their biocomposites and associated error values(%)

	E_t (GPa)	σ_M (MPa)	ε_M (%)
PHBV	3.09 (±0.01)	35.70 (±0.11)	2.30 (±0.21)
PHBV30	3.84 (±0.02)	20.29 (±0.17)	0.73 (±0.29)
PHBV30CA	4.02 (± 0.02)	13.97 (±0.19)	0.38 (±0.26)
PLA	2.55 (±0.09)	33.85 (±0.09)	2.04 (±0.11)
PLA30	3.57 (±0.04)	23.38 (±0.12)	1.09 (±0.24)
PLA30CA	-	-	-

As described before, the addition of fibres resulted in an increase of E_t for the two biopolymers, with a slight further increase with the addition of CA for the case of PHBV, indicating an improvement of their elastic stiffness. These results are in accordance with previous works using other natural fibres as reinforcing agents such as abaca or jute (Bledzki and Jaszkiewicz, 2010) or banana fibres (Albinante et al, 2014). On the contrary, the mechanical resistance (σ_M) and maximum elongation (ε_M) decreased with the addition of sisal and CA (the latter only for PHBV). This fact indicates a lower traction resistance of the samples containing sisal respect to the pure polymers probably caused by the addition of extra defects associated to the added short fibres (length 0.5 mm) or a lack of an appropriate adhesion of the fibres on the polymeric matrix (Sahari and Sapuan, 2011). The presence of CA caused a considerable lowering in the mechanical performance of the samples.

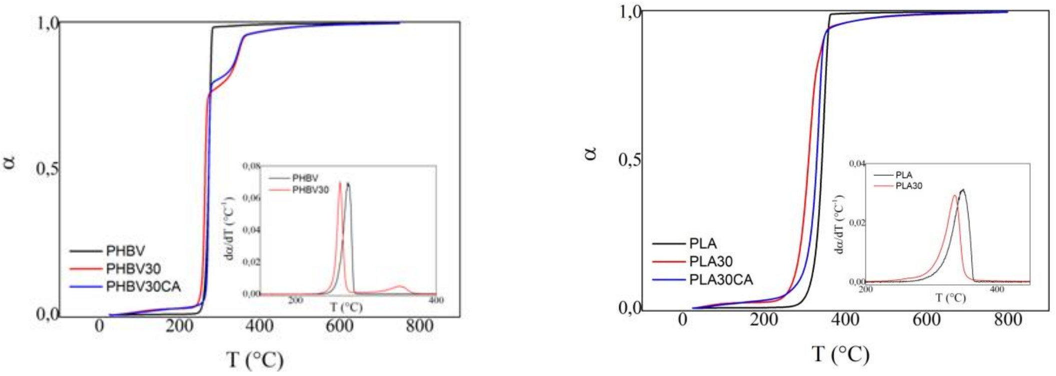
3.2 Thermal evaluation

In order to increase the use of biopolymers, they must have properties that ensure at least the same performance as traditional polymers. Studies on their thermal stability are required to characterise the decomposition profile of the samples and their degradation temperatures. With this aim, multi-rate linear non-isothermal thermogravimetric (TGA) experiments were performed under inert atmosphere to simulate their behaviour when facing pyrolysis reactions. These analyses provide information regarding two fundamental aspects: firstly, the definition of the thermal stability of all compounds and the evaluation of their performancein processes where high temperatures are applied (ie. 3D printing, extrusion and moulding …). In addition, the kinetic parameters associated to pyrolysis reactions can calculated for a potential energy recovery process when materials achieve their end of life service.

Figure 3 presents the evolution of the conversion degree of the reaction with temperature for PHBV (a) and PLA (b) together with their corresponding biocomposites at a heating rate β=2°C/min, with the conversion defined as:

$$\alpha = (m_0 - m_i)/(m_0 - m_\infty) \qquad (1)$$

with m the mass with the subscripts 0, i and ∞ standing for initial, instant and final respectively. Inset figures represent the Derivative Thermogravimetric (DTG) curves for each biocomposite.



(a) (b)

Figure 3.Evolution of the conversion degree with temperature for PHBV (a) and PLA (b) and their biocomposites. Inset: DTG curves of each biocomposite

Several observations can be made from Figure 3: pure PHBV decomposes in one single step decay whereas a two-step decay is observed for the samples containing natural fibers. This fact is also shown in the DTG curve where only one curve is obtained for PHBV (black line) while two differentiated peaks are present for PHBV30 (red line). In this curve, the first peak is assigned to the degradation of the polymeric matrix (around 270°C) and the second peak to that of sisal (around 350°C) in accordance with previous works (Joseph et al. 2003). Pure PLA and its biocomposites decompose in one single step indicating that both components (polymeric matrix and sisal) degrade at the same time and accordingly, only one peak was observed in the DTG curve.

In order to evaluate the thermal stability of all samples, the onset temperature (T_0) was calculated. T_0 is defined as the temperature at which the samples start their decomposition and it is calculated by the tangential method obtaining the temperature corresponding to a conversion degree of 0.05. Table 2 gathers the obtained values for all samples at the heating rate β=2°C/min.

Table 2: T_0 for PHBV, PLA and their biocomposites

	T_0 (°C)		T_0 (°C)
PHBV	231(±1.9)	PLA	239(±0.9)
PHBV30	239(±2.4)	PLA30	228(±1.2)
PHBV30CA	240(±0.8)	PLA30CA	215(±1.3)

The addition of sisal resulted in different trends depending on the studied polymeric matrix: an improved thermal stability was observed for the case of PHBV where the start of the degradation occurred at a higher temperature when fibers were present in the sample. Also, the addition of CA resulted in a slight increase of thermal stability. In contrast, the samples based on PLA decomposed at a lower temperature respect to that of the pure polymer, indicating a poorer thermal stability. This decrease was more accused in the samples containing CA in their composition. From these results it might be concluded that the addition of 30%wt of natural fibers to the polymeric matrix to improve the thermal stability of the samples only occurs for PHBV.

Finally, the activation energy associated to potential energy recovery process when materials achieve their end of life was obtained for all samples. The parameters were calculated using iso-conversional methods as explained in detail elsewhere (Moliner et al, 2016a, 2016b).The obtained averaged values for the main degradation process are gathered in Table 3. As it happened previously, the addition of sisal resulted in different behaviours for the two polymeric matrixes: Ea slightly increased for PHBV30 and did not vary for PHBV30CA respect to PHBV whereas a considerable decrease was observed for the biocomposites based on PLA. This fact is in accordance with the results obtained from the previous assessment of T_0 and confirms a worse thermal performance of PLA reinforced with sisal (30%wt).

Table 3: E_a for PHBV, PLA and their biocomposites

	E_a (kJ/mol)		E_a (kJ/mol)
PHBV	107(±2.9)	PLA	148(±6.1)
PHBV30	109(±5.6)	PLA30	130(±7.4)
PHBV30CA	107(±4.6)	PLA30CA	119(±6.9)

3.3 Comparison with PET

Table 4 gathers the most representative values for the mechanical and thermal properties of the biopolymers under study together with PET.

Table 4: Comparison of mechanical and thermal properties between biopolymers and PET

	E_t (GPa)	σ_M (MPa)	ε_M (%)	T_0 (°C)	T_M (°C)	E_a (kJ/mol)
PHBV	3.09	35.70	2.30	239	150**	107
PLA	2.55	33.85	2.04	228	170***	148
PET*	3.30	91.00	4.00	375	260	192

* Badia et al, 2013
**www.ensinger-online.com
*** Prajer and Ansell, 2009

Several considerations can be drawn from the table. E_t for pure biopolymers is always lower than that for PET but, as described in Section 3.1, the reinforcement of the polymeric matrix with 30%wt sisal permitted to achieve stiffness values higher than those for PET. The values of traction resistance for PET were found to be considerably higher than any tested biocomposite which showed their maximum values for the unreinforced samples.

The lower melting temperatures of the biopolymers make them an advantageous material for applications where moderate to high temperature arerequired (such as 3D-printing or where extrusion and molding are needed to obtain the final products) due to the lower energy requirements of the process. Moreover, the start of their degradation occurs at considerably lower temperatures ensuring that the material retains all its properties during the thermal process. This fact also enables the option of recycling materials for their re-use without losing their main properties and that will be addressed in further studies. Finally, the calculated values of Ea for both biopolymers were lower respect to PET indicating that lower energy requirements would be necessary in order to start pyrolysis reactions.

4. Conclusion

The evaluation of the mechanical and thermal properties of PHBV, PLA and their biocomposites has been studied and compared to PET. The addition of 30% (wt) of sisal to the biopolymeric matrix increased the elastic stiffness of the biocomposites achieving a performance comparable to PET. All biocomposites presented lower traction resistance and elongation values respect to PET.The addition of natural fibers to the polymeric matrixes improved the thermal stability of PHBV-based biocomposites. The trigger of decomposition happened at lower temperatures respect to PET, but always far above their melting point ensuring a good performance of the composites at high processing temperatures. The lower apparent activation energies for the biocomposites in inert conditions respect to those for PET indicates a more suitable scenario from the energetic valorisation point of view.

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