

DEVELOPMENT AND CHARACTERIZATION OF RENEWABLE SOURCE COMPOSITES TO REPLACE PETROL-BASED POLYMERS INTO INTERIOR DOOR TRIMS

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Abstract

The Mechanical properties of PHA/PLA blends can be optimized through the variation of the PHA contents on the blend.

It's possible to predict the flexural and tensile properties recurring to Rule of Mixtures, Kerner–Uemura–Takayanagi, Nicolai-Narkis and Béla-Pukánsky models. All of them will validate the experimental obtain values and they anticipate a good adhesion between both phases.

Nevertheless, for low levels of incorporation of PHA (up to 30%), where PLA is expectantly the matrix, the experimental data seems to deviate from the perfect adhesion models, suggesting a decrease on the adhesion between both polymeric phases.

The impact energy varies over 157% over the entire blend composition. It's possible to identify that for blends with PHA weight fraction lower than 50% the impact strength of the blend is higher than the pure base polymers. The highest synergetic effect is found for the blend PHA/PLA of 30/70. The second maximum is found for the inverse composition.

PLA has a Heat Deflection Temperature substantially lower than PHA. For the blends, the HDT increases with the increment upon the % of incorporation of PHA. Up to 50% PHA (PLA as matrix), the HDT is practically constant and equal to PLA value. Over this point (PHA matrix), the HDT of the polymer blends increases linearly with % of addition of PHA.

1 Introduction

The utilization of biodegradable polymers to replace the petro-source polymers is increasing. The actual growing of petroleum cost and the overuse of landfills combined with environmental factors and policies are making a swift on the general sense of the use of biopolymers.^[1] Several polymers and polymer blends are being used into a large spectrum of utilities. This new type of polymers allied to the life-cycle-analysis is making a turnover in the polymer industry. Since the relation price/quality is important, it's mandatory to find polymers blends with properties that fulfill the products technical specifications, at a low price. From the universe of biodegradable polymers from natural sources, the Polyhydroxycanoate (PHA) presents mechanical properties that can replace a large spectrum of petro-source polymers. However, due to its actual price, the solution isn't economically

viable for mass consumption. To make a competitive solution is necessary to reduce the price of the final polymer. One way is to blend it with less expensive biopolymers, such as Polylactic acid (PLA).

1.1 Biopolymers and their blends

PLA is a polymer produced by the fermentation of simple sugars such as glucose and maltose from corn or potato, sucrose from cane or beet sugar and lactose from cheese.^[2]

It's a linear aliphatic polyester thermoplastic, used as package materials and in production of cloths, carpet tiles, surgical and biomedical applications among others. The PLA mechanical properties have been reported in the literature. Several studies have been made on PLA blends with poly(ϵ -caprolactone)(PCL)^[3], poly(butyl acrylate)(PBA), Acrylonitrile Butadiene Styrene (ABS)^[4] among several others.

PHA is a generic designation of polyester polymers produced by the bacterial fermentation of sugars and lipids. These polyesters are a carbon storage and energy reserves in bacteria such as *Ralstonia Eutropha*, *Bacillus Megaterium*, *Azotobacter chroococum*, etc, and have a wide range of mechanical properties (e.g., strength and Young's Modulus). The PHAs are semi-crystalline polymers with melting temperatures ranging from 120° to 180°C depending on the chemical composition.

2 Mechanical properties Prediction Models

The mechanical properties of the blends can be predicted by usual models assuming different interfacial behaviors:

- Well disperse phases with perfect adhesion (rules of mixtures)
- spherical inclusions of one polymer in a continuous polymer matrix with perfect adhesion or no adhesion (Kerner–Uemura–Takayanagi – KUT - model)
- spherical inclusions with variable interphase interactions, ranging from poor to good adhesion (Nicolais-Narkis – NN- model);
- Effective load-bearing capacity (Béla-Pukánsky – BP – model);

3 Experimental Work

3.1 Materials

For this work we use a PHA, under the trade name PHI002, manufactured by Natureplast and a PLA, under the trade name Ingeo Biopolymer 3251D, manufactured by NatureWorks .

3.2 Preparation of Blends

The polymers were dried into an oven at 60°C for 24 hours before processing and kept into separate Ziploc bags. Just before the injection, the polymers are weighed and then mix into a rotational chamber. When the mixture period ends the blend is injected into a Ferromatik Milacron K85 injection machine, being produced tensile test specimens

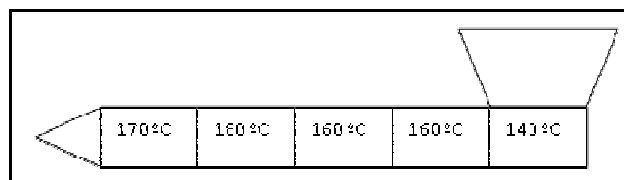


Figure 1. Injection temperature profile

The mold temperature was 20 °C and the injection temperature profile is described in figure 1. The temperature profile was established by combining the melting temperature of the polymers, the degradation temperature and the optimal injection conditions described into the

suppliers datasheet of the two polymers. The injection parameters were the following: Injection pression: 50 bar, Injection velocity: 20 mm/s; Injection time: 5 s, fuse travel: 20mm. Eleven different samples were prepared. Pure samples of pure PHA and PLA, and then increasing by a 10% (mass fraction) steps the amount of PLA on the blend.

4 Mechanical Characterization

4.1 Flexural

A Universal Tiratest 2705 Machine was used to measure the flexural properties according to ASTM D790 standard. It has been used a 3-point flexural test, with a crosshead speed of 2,56 mm/min and a span of 96 mm. Tests were performed at room temperatures (23 °C).

4.2 Tensile

To measure the tensile properties according to ASTM D638 a Universal Shamidzu AG-X 100kN, equipped with a 50 mm Shamidzu extensometer, tensile test machine was used. The crosshead speed used was of 5 mm/min and the testes were performed at room temperature.

4.3 Instrumented Impact

Instrumented impact tests are made according ISO 6603-2 standard in a CEAST Fractovis plus impact machine. All performed tests were carried out in a standard laboratory atmosphere of 23±2°C and 50±5% relative humidity.

4.4 Heat Deflection Temperature (HDT)

To measure the Heat Deflection Temperature, HDT, according to ISO 75-2, RAY-RAN HDT apparatus was used. This test used the method HDT A with a stress state of 1,8 MPa and an increasing temperature speed of 120°C/h. The tests were carried out in a standard laboratory atmosphere of 23±2 °C and 50±5 % relative humidity.

5 Results and Discussion

The results of the tensile tests of the PHA/PLA blends are given in Table 1.

PHA/PLA Blend [Mass Fraction]	Tensile Modulus [GPa]	Maximum Stress [MPa]	Strain at maximum Stress [%]
[0:100]	3,62 ± 0,03	59,17 ± 0,7	2,5 ± 0,03
[10:90]	3,15 ± 0,21	51,35 ± 1,0	2,4 ± 0,07
[20:80]	3,32 ± 0,06	43,61 ± 0,6	2,0 ± 0,13
[30:70]	3,36 ± 0,07	46,02 ± 1,5	2,0 ± 0,06
[40:60]	3,63 ± 0,05	43,19 ± 0,6	1,9 ± 0,10
[50:50]	3,55 ± 0,05	40,36 ± 4,1	1,7 ± 0,39
[60:40]	3,62 ± 0,06	43,02 ± 0,4	1,9 ± 0,02
[70:30]	3,69 ± 0,08	39,21 ± 0,4	1,8 ± 0,06
[80:20]	3,73 ± 0,25	35,99 ± 5,6	1,6 ± 0,26
[90:10]	3,74 ± 0,11	28,04 ± 3,7	1,3 ± 0,14
[100:0]	3,81 ± 0,12	29,19 ± 0,2	1,6 ± 0,19

Table 1. Tensile properties of PLA/PHA blends

Based on the models for prediction of the mechanical properties above presented, Table 2 shows the estimated tensile properties and fig. 2 shows the evolution of the initial modulus with the PHA weight fraction. The increase of PHA on the blend results in a general increase of the initial tensile modulus. This is expected since the initial modulus of PHA is slightly higher than PLA. In Figure 2 are also presented the predictions of E based on the abovementioned models: ROM and KUT models with perfect and no adhesion between phases. Two main issues can be withdrawn: i) the KUT model with no adhesion does not give

good predictions of E; ii) the ROM and KUT model with perfect adhesion both give good predictions of the variation of E with the weight fraction of PLA in the blend.

PHA/PLA Blend [Mass Fraction]	Tensile Modulus [GPa]		
	ROM	KUT perfect adhesion	KUT no adhesion
[0:100]	3,62	3,62	3,62
[10:90]	3,64	3,64	3,06
[20:80]	3,66	3,66	2,56
[30:70]	3,68	3,68	2,11
[40:60]	3,70	3,70	1,72
[50:50]	3,72	3,72	1,43
[60:40]	3,73	3,73	1,80
[70:30]	3,75	3,75	2,22
[80:20]	3,77	3,77	2,69
[90:10]	3,79	3,79	3,21
[100:0]	3,81	3,81	3,81

Table 2. Predicted Tensile Modulus

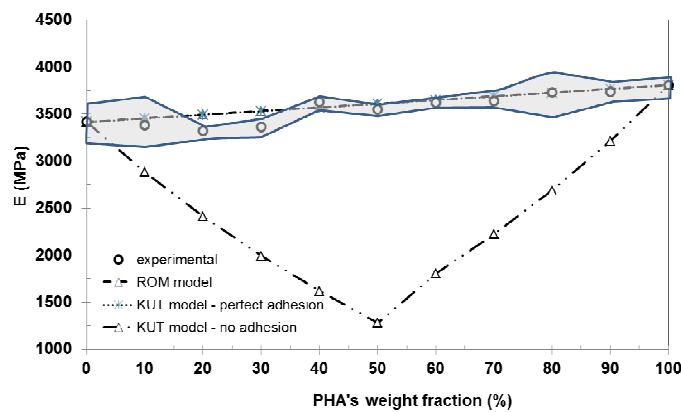


Figure 2. Tensile Initial modulus results and predicted values from models.

PHA/PLA Blend [Mass Fraction]	K (NN model)	B (BP model)
[10:90]	0,55	2,0
[20:80]	0,74	1,7
[30:70]	0,47	2,3
[40:60]	0,48	2,3
[50:50]	0,49	2,3
[60:40]	0,37	4,0
[70:30]	0,42	4,0
[80:20]	0,44	4,2
[90:10]	0,56	2,9
AVERAGE	0,50	2,1 (PLA Matrix) 3,8 (PHA Matrix)

Table 3. Calculated values for K and B for PLA/PHA blends

The maximum deviation between the KUT perfect adhesion prediction and the experimental value is about 5 %. These results anticipate a good adhesion between both phases in the PHA/PLA blends. Nevertheless, for low levels of incorporation of PHA (up to 30%), where PLA is expectantly the matrix, the experimental data seems to deviate from the perfect

adhesion models, suggesting a decrease on the adhesion between both polymeric phases when PHA is the disperse phase. The maximum stress of the blends can be estimated from the above presented prediction models. From the NN and BP models, the parameters K and B can be calculated giving estimations of the interphase interaction and of the load-bearing capacity of the disperse phase, respectively. The calculated values are expressed in Table 3 for each blend. K values are always lower than 1.21, meaning that a good adhesion between both phases is achieved. The values of B parameter are also relatively high, indicating a good adhesion between phases. Furthermore, in the PLA fraction 50-60% the values of K show a drop and that of B a sudden increment, which can be attributed to phase inversion in the blends. Fig. 3 shows the variations of the tensile maximum stress with % of PHA and respective models predictions. The increase of PHA on the blends drives to a general decreasing of the Maximum Stress. The ROM fits well with the experimental data for the larger amounts of incorporation of PHA, suggesting a very good adhesion between PHA matrix and the PLA disperse phase. For low % of PHA the phase adhesion is small, the experimental data deviates from ROM. In this regime, the values of K and B were adjusted in order to fit better the models predictions. Values of $K = 0,5$ and $B=2,3$ were found up to %PHA of 50% (above this value, a best fit is obtained for $k=-1,2$ and $B=4,0$). These values regarding both NN and BP models corroborate that the interphase adhesion is promoted when PLA is the disperse phase.

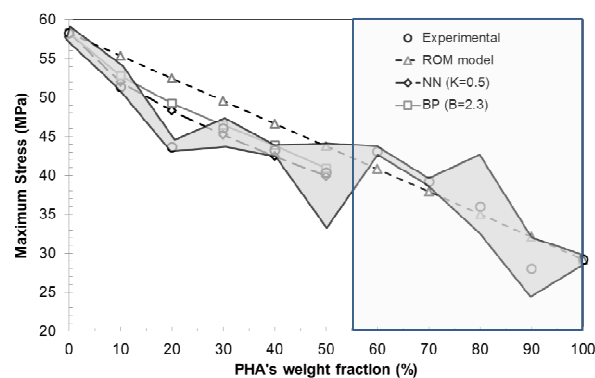


Figure 3. Tensile Maximum Stress Results and Predicted Values.

The flexural test results of the blends are given in Table 4. The maximum experimental error is of 6.4% (with an average of 2.3%). The experimental variation of the flexural modulus as function of the PHA fraction is small, of 3,52%. Fig. 4 shows the variations of E_f with % of PHA and respective models predictions. Conversely, to the tensile modulus, here for the flexural modulus the ROM does not apply over the full range of compositions. Only for high % of incorporation of PHA (as matrix), the ROM is valid. In the case of PHA as disperse phase, the variations of E_f with PHA fraction are not conclusive. The E_f of the blends seems to be more sensitive to the morphology of the low fraction component (e.g., dispersion, size, aspect ratio). Also, ROM and KUT-adhesion models give the same predictions of E_f as function of PHA fraction, with maximum error of 7.9% (an average of 2.1%). Fig. 4 also shows the variations of maximum flexural stress with % of PHA and respective models predictions. Again, the increase of PHA on the blends drives to a general decreasing of the Maximum Stress. As for the flexural modulus, the variations of σ_{max} with % of PHA are subjected to high fluctuations. In general, the ROM does not give satisfactory predictions, even for larger amounts of incorporation of PHA. For low % of PHA the experimental values are always smaller than the ones predicted by ROM, this evidencing a low level of adhesion between both phases. In this regime, the values of K and B were also adjusted in order to fit better the models predictions. Values of $K = 0,48$ and $B=2,2$ were

found up to %PHA of 50% for both NN and BP models, respectively. These values are very close to the obtained on the tensile tests ($K = 0,45$ and $B=2,3$). Adjustments for the case of PLA as disperse phase, gives $K= 0,22$ and $B=2,6$. The K value is reduced substantially when compared with PHA as disperse phase, this meaning a better adhesion between phases; B slightly increases as a reflex of this better adhesion, but the load-bearing capacity of the disperse phase seems to remain unchanged. When comparing with the tensile test results of $k=-1.2$ and $B=4.0$, it seems that under flexural loading the adhesion and load-bearing capacity of the PLA disperse phase are much smaller than for the case of tensile loading.

PHA/PLA Blend [Mass Fraction]	Flexural Modulus [GPa]	Maximum Stress [MPa]	Strain at maximum Stress [%]
[0:100]	3,59 ± 0,06	80,52 ± 2,6	2,3 ± 0,1
[10:90]	3,41 ± 0,08	57,36 ± 3,1	2,2 ± 0,1
[20:80]	3,46 ± 0,06	70,87 ± 4,7	2,6 ± 0,2
[30:70]	3,53 ± 0,02	62,30 ± 7,1	2,1 ± 0,4
[40:60]	3,79 ± 0,01	55,31 ± 2,6	1,6 ± 0,1
[50:50]	3,61 ± 0,08	79,93 ± 2,4	3,1 ± 0,1
[60:40]	3,56 ± 0,11	46,49 ± 3,0	1,3 ± 0,1
[70:30]	3,42 ± 0,03	66,10 ± 0,6	2,4 ± 0,1
[80:20]	3,42 ± 0,10	47,32 ± 2,9	1,5 ± 0,1
[90:10]	3,44 ± 0,22	53,94 ± 3,5	2,2 ± 0,4
[100:0]	3,40 ± 0,10	53,97 ± 0,6	2,2 ± 0,1

Table 4. Flexural properties of PHA/PLA blends

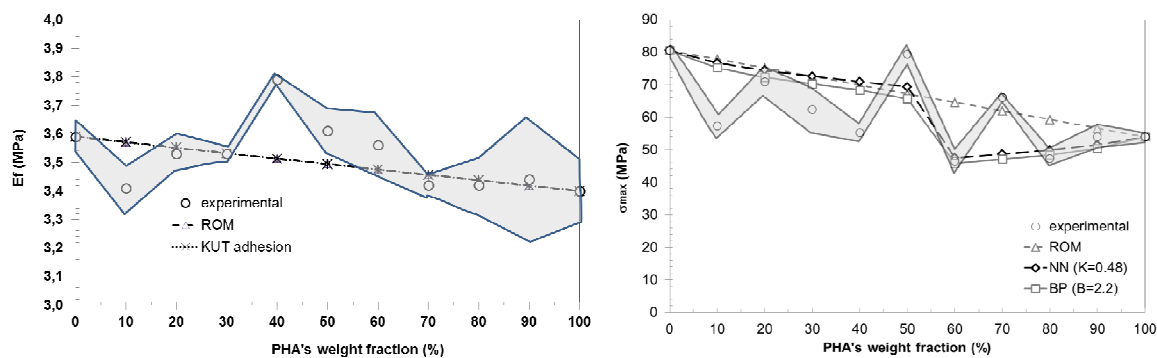


Figure 4. Left: Flexural results and predicted values. On left: Young's Modulus. On right: Maximum Stress

The impact results of the tested blends are given in Table 5. The impact energy establishes the amount of energy that the material can absorbed until it breaks. In the same table are shown the elongation at break. The impact energy varies over 157.7% over the entire bend composition. This is quite surprisingly has both neat polymers show quite similar impact energies (PLA has a higher value of c.a. 12%). Fig. 5 shows the variations of the impact energy with blend composition. Two local maximum can be found corresponding to different types of matrices. Phase inversion appears to occur for 50-60% of PHA, as already mentioned, but under impact conditions this is more evident. It is also interesting to observe that for blends with PHA weight fraction lower that 50% (i.e., PLA matrix and PHA as disperse phase) the impact strength of the blends is substantially higher than the pure base polymers. The highest synergetic effect is found when the PLA is the matrix and PHA the disperse phase for the blend PHA/PLA of 30/70. The second maximum is found for the inverse composition of 70/30. The toughening of polymer blends has been related to the ligament thickness, i.e., the distance between the disperse phase particles. This ligament thickness is dependent upon the amount of disperse phase and the diameter of the filled

particles. The variations of the elongation at break with blend composition shows a similar evolution as the impact energy, as depicted in Fig. 5. The elongation at break varies over 315.8% over the entire blend composition. Again, this is quite surprisingly, as PLA shows an elongation at break only 28,6% higher than PHA. Noda et al.[6] have reported a similar effect of the addition of PHA to PLA and observed that when 10% PHA was added to PLA, the percent elongation of the blends improved significantly. This was attributed to the increase of the amorphous phase of the blend. The maximum elongation was observed for the [PHA:PLA] 70:30 weight fraction, where the elongation was 119 and 182% higher than that of neat PLA and PHA, respectively.

PHA/PLA Blend [Mass Fraction]	Impact Energy [J/m]	Elongation at break [%]
[0:100]	3,8 ± 0,1	3,6 ± 0,1
[10:90]	4,7 ± 0,2	6,5 ± 1,4
[20:80]	6,1 ± 0,1	6,8 ± 0,7
[30:70]	6,7 ± 0,3	7,9 ± 1,4
[40:60]	6,1 ± 0,2	7,3 ± 1,3
[50:50]	4,9 ± 0,0	6,7 ± 1,6
[60:40]	2,6 ± 0,3	2,7 ± 1,0
[70:30]	3,0 ± 0,1	4,3 ± 1,0
[80:20]	4,2 ± 0,5	3,8 ± 0,9
[90:10]	3,2 ± 0,3	1,9 ± 0,0
[100:0]	3,4 ± 0,1	2,8 ± 0,4

Table 5. Impact properties of PHA/PLA blends

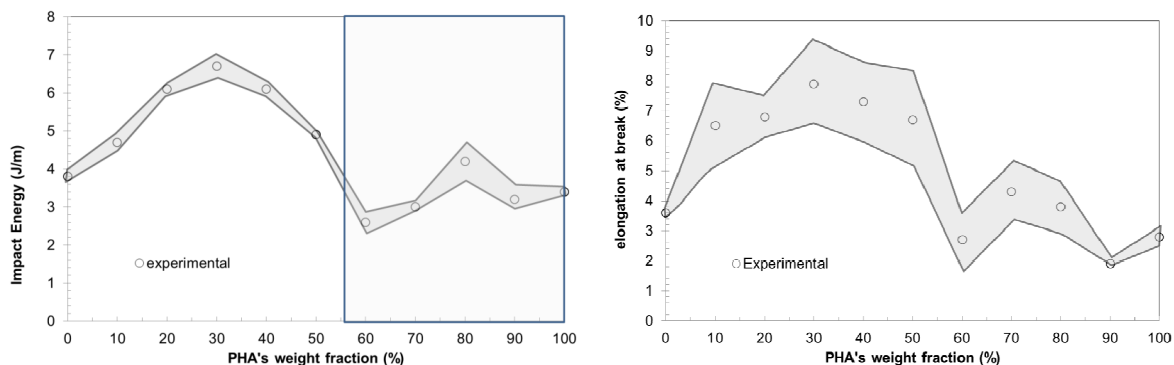


Figure 5. Left: Impact Strength (Experimental). Right: Impact elongation at break (experimental)

PHA/PLA Blend [Mass Fraction]	HDT [°C]
[0:100]	61,4 ± 0,7
[10:90]	60,8 ± 0,5
[20:80]	60,1 ± 0,6
[30:70]	62,1 ± 0,3
[40:60]	61,3 ± 1,0
[50:50]	64,0 ± 0,6
[60:40]	71,2 ± 1,7
[70:30]	74,0 ± 0,5
[80:20]	80,1 ± 1,1
[90:10]	89,6 ± 0,4
[100:0]	92,0 ± 1,8

Table 6. Heat Deflection Temperature of PHA/PLA blends

The Heat Deflection Temperature (HDT) results are given in Table 6 for all blend compositions. PLA (61,4 °C) has a HDT substantially lower than PHA (92,0 °C). For the PHA/PLA blends, the HDT increases with the increment upon the % of incorporation of PHA. Up to 50% PHA (PLA as matrix), the HDT is practically constant and equal to PLA value. Over this point (PHA matrix), the HDT of the polymer blends increases linearly with % of addition of PHA. This behavior is dependent upon the amount of disperse phase. It's possible to verify, as seen in the other tests, that around 50%PHA a phase inversion occurs and the thermal behavior changes. For weigh fractions of PHA lower than 50% the PLA assumes the matrix and states the HDT. When the PHA assumes the matrix of the blend (above 50% wf) it pushes the HDT near to the neat PHA. That explains the linear progression of the HDT from 50% PHA wf until neat PHA.

6 Conclusions

The properties of biodegradable polymers such as PHA and PLA can be tailored to achieve a given performance. PHA/PLA blends over the full ratio of compositions were injection molded. The increment of PHA fraction decreases both the tensile and flexural moduli of the blends. For the tensile modulus, a linear relationship is found, following the rules of mixtures (or a KUT model with perfect adhesion between phases). The maximum stress of the blends can be estimated from the presented prediction models. The incorporation of PHA leads to a decrease of the flexural maximum stress but, at the same time, increases the tensile maximum stress. Prediction models and material property characterization allowed unambiguous detection of the interfacial behavior of the polymer blends. PHA/PLA blends can have good impact properties. The best impact properties are achieved with a [PHA:PLA] 70:30 weight fraction ratio blend. The fitting parameters of the models allow to state that PLA/PHA blends present a good adhesion between phases.

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