1 Introduction

Because of the many environmental problems facing society, the ability to manufacture products from sustainable resources that are fully compostable at the end of their useful life is attractive. Poly(lactic acid) is linear aliphatic thermoplastic polyester derived from 100% renewable sources. Because of its good biocompatibility, biodegradability, mechanical properties and light weight, it has been used in many applications, and its processing, thermal stability and mechanical properties have been widely studied [1–9].

One method used to improve the mechanical and thermal properties of poly(lactic acid) (PLA) is to add fibres or filler materials. Various fibres, including glass fibres [10-11], bamboo [12], hemp [14-15], flax [16–18], ramie [19-20], jute [19, 21], kenaf [13, 22-23], abaca [24], [25] wood pulp [26] silk [27], [28] and chicken feathers [29], have been used to reinforce PLA. These works investigated that natural fibres can serve as reinforcements for PLA.

In recent years, the waste products have begun to be used to reinforce biocomposites. Beside of the aim to improve the properties of polymer, the use of waste product reinforce polymers reduce the price of the material and it contribute to protect the environment also. The global rice paddy production is 482 million tons, world rice inventories are forecast to rise to their highest level in ten years (FAO). Husk is one of the abundant waste products from agriculture throughout the world. Traditionally, husks are used for feeding animals, to keep animals warm or for burning. Recently, some researchers have explored the utilization of these by-products as fillers for the production of polymer matrix composites. Rice and wheat husks have been added to polypropylene [20],[22], polycaprolactone [30] or phenol formaldehyde [31]. Rice husk and Einkorn wheat husk have complex spikelet structures, but they are primarily composed of cellulose, hemicelluloses, and lignin [32], [33].

Previous research studies have shown that cellulose fibers can be used to reinforce Poly(Lactic Acid) PLA. Therefore, in this study, the mechanical properties, the thermal properties and the morphology of composites were analyzed to explore the potential of using rice husk/wheat husk as a possible reinforcement for PLA.

2 Materials and methods

2.1 Materials

Poly(lactic acid) PLA 7000D was supplied by Nature-Works LLC and had the following characteristics: Specific gravity: 1.25-1.28, glass transition temperature \( T_g = 55 \) - 60°C and crystalline melting temperature \( T_m = 145-155°C \).

In this research, both long-grain rice husk (denoted LR) and medium-grain rice husk (denoted MR) were studied. The rice husks were supplied by SOUFFLET group, France. Two husks of Einkorn wheat (Triticum monococcum – botanical name; denoted W1 and W2) were used. This is one of the earliest cultivated forms of wheat, and its husks tightly enclose the grains. The wheat husks were supplied by TOFAGNE Sarl (France).

2.2 Methods

PLA pellets and husks were dried under vacuum at 50°C for 24h before processing. Compounding was
achieved by twin screw extruder (Clextral BC21 900mm). The temperature profile screw is the following: 60°C (feeder) / 120°C / 170°C / 180°C / 180°C / 180°C / 180°C / 180°C / 180°C / 180°C / 180°C / 180°C / 180°C / 180°C / 180°C (die). The speed rate was kept at 250rpm and the feed rate was 4kg/h. A dry blend of the PLA and husks was introduced through two feeders. After compounding, granules were dried under vacuum at 50°C for 24h. Injection molding was then carried out on a Krauss Maffei KM50-T180CX. Temperature was set at 200°C and the mold temperature was maintained at 40°C.

- Mechanical properties were measured after conditioning the samples at room temperature under standard atmospheric conditions (22–24°C) for 24 h before testing. At least 5 specimens were used for each test to ensure reproducibility.

Three-point-bending tests were conducting standard ISO 178:2001. The sample size was 80 x 10 x 4 mm³, the load cell was 2.5 kN and the crosshead speed was 2 mm/min. The tensile and bending tests used a Zwick Z010.

Charpy impact strength was determined using a Zwick apparatus according to the ISO 1179-1:2000 standard (2J). The sample size was 80 x 10 x 4 mm³.

- Size-exclusion chromatography coupled with multi-angle light scattering detector (SEC-MALS) was used to determine the average molecular weights and polydispersity index of polymer.

The weights of samples were calculated by equation 1:

$$M_{sample}(mg) = \frac{90}{(100 - R)} \times 100 \ (\pm 5g) \quad (Eq. \ 1)$$

Where, R is the content of the rice husk in biocomposite (%).

Tetrahydrofuran (THF) was stabilized by 2,6-di-tert-butyl-4-methylphenol (BHT) (250 mg/L of THF). The samples were weighed and put in flask, add 30ml of tetrahydrofuran (THF) stabilized, then close tightly by screw cap. The flasks were kept in bath water 30°C for 3 days. Then the solutions were filtered with disposable filters (PTFE membrane, 0.45µm) and injected in SEC-MALS.

The SEC equipment (SUPAGRO, University Montpellier2, France) consisted of an online degasser (Elite™, Alltech), a Waters 515 pump, a refractive index detector (Waters 2410) and a multi-angle light (Dawn DSP, Wyatt Technology). The columns were three PLgel (Polymer Laboratories) Mixed-A mixed bed columns (20µm, 300mm×7.8mm I.D.) with a guard column. The columns were maintained at 45°C. The mobile phase was THF at a flow rate of 0.65ml/min for 45 min; the injected volume was 100µL. The data obtained with MALS detector were analyzed with ASTRA software (Wyatt Technology).

- Scanning electron microscopy (SEM) and SEM–EDX (SEM coupled with energy dispersive X-ray analysis) were performed using an environmental scanning electron microscope (ESEM) FEI Quanta FEG 200, equipped with an OXFORD Inca 350 energy dispersive X-ray microanalysis (EDX) system. The ESEM operated at an accelerating voltage of 15 kV.

- The melting and crystallization behavior of the matrix polymer and the biocomposites were studied using a Perkin Elmer apparatus (Pyris Diamond) equipped with a cooling attachment, under a nitrogen atmosphere. The data were collected by heating the specimen from 25°C to 200°C at a constant rate of 10°C/min. A sample weight of approximately 20 mg was used, and the samples were analyzed in standard aluminum DSC pans. The heat flow and energy changes in and out of the samples in the sealed aluminum pans were recorded with reference to an empty aluminum pan. At least 3 specimens were used for each test to ensure reproducibility. Melting temperature was obtained from the peak in the heating curve. The peak area was used to calculate the enthalpy of melting using Pyris 8.0 software.

- The thermogravimetric analyses were carried out in Perkin Elmer equipment (Pyris1 TGA). The samples were scanned from 25 to 600°C at a heating rate of 10°C/min in the presence of nitrogen.

3 Results and Discussion
3.1 Dimensional stability
During the injection molding, material is fed into a heated barrel, mixed, and forced into a mold cavity where it cools and hardens to the configuration of the cavity. In this study, the mold temperature is 40°C, so that the samples continue to cool down to the temperature environment after ejecting from the mold. Because of the thermal shrinkage, the dimensions of the samples are smaller than the mold. The difference between the mold and the sample is calculated by equation 2:

\[
\text{Shrinkage (S)}(\%) = \frac{D_m - D_n}{D_m} \times 100 \quad \text{(Eq.2)}
\]

After injection molding, shrinkage of 0.4% is obtained for PLA compared to 0.35, 0.14 and 0.09% for the biocomposites reinforced by 10, 20, 25wt% husk. The shrinkages of biocomposites reduce linear with the increase of weight content of husk (Figure 1). The presence of husk improves the dimension stability of mold specimens.

It is clearly show that the number average molecular weight (Mn) and the weight average molecular weight (Mw) of unreinforced PLA are always higher than those of PLA extracted from biocomposites. As the addition of rice husk increases viscosity of PLA, it will also result in an increase of shear during injection and induce molecular chain breakage. The average molecular weight decreases \[34][35][21]. Moreover, a linear decrease in Mn and Mw is observed with the rice husk increase with the same slope. It is the reason why the polydispersity index does not change as a function of rice husk content. Indeed, the polydispersity index of PLA is 1.24±0.004 and that of biocomposite is about 1.28±0.075.

3.3 Mechanical properties of biocomposites

The tensile and bending modulus increased with an increase in the filler loading for all composites, as would be expected (Figures 3 and 4). The bending modulus of neat PLA is 3449±25 MPa, and the tensile module is approximately 3573±41 MPa. With 10% weight content of rice husk (MR.10), an increase of 11.34% in the tensile modulus compared with PLA was observed. Similar results were obtained for other biocomposites. W2.25 had the highest bending modulus (4566±50 MPa), which is a 32.39% increase compared with neat PLA, and the highest tensile modulus (5026±94 MPa), which is an increase of 40.66%. The increasing bending modulus and tensile modulus are directly proportional with the ratio of the husk content in the biocomposites.
In contrast, the tensile and bending stresses decreased with increasing husk content. The decrease in the tensile stress is higher than those of the bending stress. With 10, 20 and 25 wt% filler content, the decreases in the bending stress were approximately 5%, 14%, and 17%, respectively; the decreases in the tensile stress were 17%, 22% and 25%, respectively. The mechanical properties of PLA biocomposite with different reinforcement fibres can be compared. PLA biocomposite with jute, ramie, abaca and flax have mechanical properties higher than rice husk and wheat husk. However, the phenomenon of decreasing tensile and bending stresses has not just happened to rice husk and wheat husk.

At the same weight content 10%, tensile strength of rice husk and wheat husk reduce 13 and 19% while that of chicken feather [29] decrease 23% and the reduction of destarched cassava flour and pineapple skin flour [36] are 17 and 24%.

Hemp is a kind of fibre used to use reinforced biocomposite. The flexural strength of PLA biocomposite with 20% weight content of hemp reduce 17% [14], it is higher than 9 and 14% of rice husk (MR) and wheat husk (W2). The flexural strength of PLA biocomposite with 20% destarched cassava flour and pineapple skin flour decrease 26 and 34%, this reduction is nearly 3 times higher than rice husk and with husk. A.A Yussuf et al. [23] extruded PLA with 20% rice husk also, and the results of that research show the flexural strength reduce 23%.

The authors suggested different mechanisms according to the fibre strength. For strong fibres, such as flax or ramie, a stronger composite is obtained with an increased stress. In contrast, if the fibre is weak, it will affect the strength of the composite.

Figure 5 shows the fracture surfaces of biocomposites that were investigated by SEM. It can be observed that the small husk pieces are separated from each other during the extrusion process and well disperse in the PLA matrix. The husks were randomly orientated. Few voids are found on the fracture surface because the husks are trapped by the PLA matrix. It can also be seen that there are many
husks that were broken off with in PLA matrix, instead of being drawn out. The broken husk reveals that rice husk and wheat husk do not have sufficient strength; this result may be explained by the decreased tensile and bending strength of the biocomposites. Mechanical results are related to the morphology of composites and show that there is a bad interface between the matrix and the fillers.

Figure 6 shows the difference in the elongation at break of neat PLA and biocomposites. It can be observed that the elongation at break of neat PLA is 6.56±0.94%, and that value is in agreement with technical data from Nature Works, Co. Irrespective of the filler type, incorporation of the filler resulted in a drop in elongation at break to approximately 2.5% to 3.5%. A similar observation has been reported, with a drop of elongation at break of PP from 600% to 2% for PP reinforced by 45 wt% rice husk powder [37]. This phenomenon may be explained by an increase in the brittleness of PLA due to its degradation during extrusion progress as previously discussed and a poor adhesion between PLA and husks.

Figure 7 presents the impact properties of different biocomposites compared to PLA. There is a regular decrease in impact strength with an increase in filler content for both rice husk and wheat husk biocomposites to compare with neat PLA. A lower decrease is obtained for MR reinforced biocomposites probable because of the final morphology after extrusion of MR. The size of MR after extrusion is the smallest in all type of husks. It is clear that, rice husk, Einkorn wheat husk cannot compete with flax, ramie and jute fibres to reinforce PLA to improve mechanical properties, however, it is a good competitor with hemp, bamboo fibre or other biomass likes destrached cassava flour and pineapple skin flour.

3.4 Thermal properties of biocomposites

3.4.1. DSC Analysis

The influence of husks on the glass transition temperature (Tg), cold-crystallization temperature (Tc) and melting temperature (Tm) is shown in Figure 8. Neat PLA has a Tg of 61.56 ±0.35°C; the addition of husks did not have any notable effect, as the Tg of the biocomposites varied by only 1–2°C. Two main factors control the crystallization of polymeric composite systems: (i) the additives hinder the migration and diffusion of polymer molecular chains to the surface of the growing polymer crystal in the composites, thus providing a negative effect on polymer crystallization which results in a decrease in the Tc; (ii) the additives have
a nucleating effect which gives a positive effect on polymer crystallization and leads to an increase in Tc [28].

Fig. 8 Glass transition temperature (Tg); Crystallization temperature (Tc); Melting temperature (Tm) of biocomposites.

Neat PLA has a Tc of 129.64±0.92°C. In the presence of husk, the Tc decreased to 118.07±0.43°C with 25% rice husk and to 114.39±2.14°C with 25% wheat husk. The decrease in Tc could be explained by two reasons: (i) the viscosity of the biocomposite mixture increased with the addition of husk, which hindered the migration and diffusion of PLA molecular chains in the biocomposite, and (ii) the decrease of the average molecular weight of matrix PLA after extrusion with husks. The cold-crystallization peaks of biocomposite are larger than PLA neat and may be explained that the presences of the husks obstruct the process organization of PLA in the thermal process (extrusion, injection). When the sample cool down, many initial crystallization molecules have not arrange yet, so that they rearrange when the temperature increase in DSC test.

The melting temperature of neat PLA is 155.38±1.99°C. With the addition of husk, the Tm shifted to a higher temperature. The presence of the husk could form a barrier to block the transfer heat flow in matrix PLA, such that the biocomposite requires a higher temperature for melting.

3.4.2 Thermogravimetric analysis (TGA)

The thermal stability of rice husk, wheat husk, neat PLA and the biocomposites was investigated through TGA experiments (Figures 9 and 10).

Fig. 9 Thermogravimetric curves of the two rice husks and wheat husks

Fig. 10 Thermogravimetric curves of neat PLA and wheat husk composites

Generally, husk degrades through three main stages: (i) first, the moisture absorbed during storage is released from the husk; the weight of water in the husk is approximately 8%; (ii) then, a second transition occurs from 290 to 420°C, and the husk undergoes degradation; and (iii) finally, from 420°C onwards, the husk starts to decompose. The char yield at 500°C of two types of rice husk was approximately 40%, which is slightly higher than wheat husk (30%).

As concerns PLA and the biocomposite, the weight drop starts at 280°C due to PLA degradation. A second transition begins at approximately 400°C when the materials start to decompose. The weight of char at 500°C for biocomposites increases with
the husk content. This enhancement of char formation can be argued to be the higher heat resistance introduced by the husk reinforcements. The curves show that the weight-loss temperature of the biocomposites are lower than that of neat PLA and that the addition of rice husk and wheat husk affect the stage of degradation of the PLA. This phenomenon can be explained by the lower degradation temperature of the husks compared to PLA.

4 Conclusions

The objective of this study was to investigate the possibility that rice husk and wheat husk can be used as fillers in biocomposite systems. The results show that PLA works very well as a matrix material for both rice husk and wheat husk.

The tensile and bending moduli of biocomposites from husks were improved when the filler loading was increased. Although the tensile and bending strength of biocomposites reduced, however, this phenomenon happens with some others natural fibres. An advantage of the husks addition is the dimensions of the biocomposites after injection molding are more stable than PLA. The thermal stability is not significantly different between neat PLA and the rice husk and wheat husk biocomposite. Tg did not change, Tc decreased and Tm increased with increasing husk content.

Some others authors critic biomasses have low mechanical properties, thus they cannot be a good candidate for reinforcing PLA. It is evident that biomass (rice husk and wheat husk) cannot compete with some nature like flax, jute or even hemp fibres, but their modulus are at least as interesting as those of sisal fibres which are commonly used for thermoplastic reinforcement, and the mechanical properties of biocomposites from rice husk, Einkorn wheat husk are higher than some others biomasses like destarched cassava flour rye husk. On the other hand, their advantages are biodegradable eco-friendly filler, rather to minimize environmental pollution and lower cost of the final products. Future studies should focus on the improvement of the interfacial bonding. With such improvements, it may be possible to achieve optimal dispersion of the filler and to optimize the filler-matrix adhesion.

References

[35] P. E. LE MAREC, « Modélisation du mélangeage à l’état fondu de biocomposites PLA/fibres...
