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Incorporation of natural fibres in a biodegradable thermoplastic polymer via a twin-screw extruder

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Abstract

Incorporation of a widely available agricultural by-product, wheat bran, into polylactic acid (PLA) have been investigated and compared to miscanthus and highly cellulosic fibres. They were compounded at different ratio from 10 to 40% wt. Influence on energy consumption during the process showed that the more filler added, the more energy needed but wheat-bran based composites consume less energy to be processed than the other fibres (131 W.h/kg for SME instead of 144 W.h/kg for miscanthus fibres in the case of the 40% wt fibre-filled PLA compounds). Viscosity behaviour was evaluated, highlighting a thinning effect of the wheat bran when compounded to PLA. Comparison of mechanical properties raised some negative effects on composite strength (-59% for tensile strength for the PLA-40% wheat bran compound) and stiffening was not as important as comparative fibres (4290 MPa for tensile modulus instead of 8790 MPa for miscanthus fibres in the case of the 40% wt fibre-filled PLA compounds). Complex chemical composition of the bran with lower fibre content can explain this. However, wheat bran is a promising filler to produce cheap sustainable composites.

Introduction

Environmental concerns have led over the past decade to new resources researches for plastic development. Green composites, which are a combination of bioplastics and natural fibres are of increasing interest because of their potential to substitute certain petroleum-derived composites. They offer a wide variety of advantages, such as low density, renewability, biodegradability, and better cost versus a certain required performance.

Poly lactide (PLA) is one of the most readily available thermoplastic polyesters that is derived from renewable resources such as corn, beet, and sugar. PLA is 100% biodegradable, has a high tensile strength of 59 MPa and tensile modulus of 3.5 GPa [1]. Commercial application of pure PLA is limited because of its inherent weakness, such as low impact strength, low thermal stability, and high brittleness. More research effort is being directed toward finding methods of addressing the weakness of PLA without compromising its biodegradability. Incorporation of natural fibres is a way to improve mechanical properties of PLA. The effect in PLA of various types of fibres, such as sugar beet pulp [2], kenaf [3,4], hemp [5], wood [6-8], flax [9], soy stalks, wheat straw, corn stover [10], oat and cocoa shells [11], has been extensively studied and is well understood. In several cases, the results have shown that the natural fibre composites own good stiffness but the composites do not reach the same level of strength as glass fibre composites for instance.

Wheat bran is an important and very cheap agricultural by-product. Wheat bran contains about 750 and 650 mg/g of cell wall polysaccharides, mainly heteroxylans, and cellulose but also lignins. Thanks to this fibre fraction, wheat bran can offer advantages as reinforcing materials. It was found to increase mechanical properties of starch-based edible films for food protection [12]. Its cellulose was also esterified to produce films [13]. But, no report of PLA composites reinforced with wheat bran has been found. This study includes miscanthus fibres and cellulose that were already studied in PLA [14-16], used as known natural fibre models.

The aim of this paper is to investigate the incorporation of wheat bran, miscanthus fibres and cellulosic fibres, derivate from pine, in PLA. In this study, the green composites have been prepared by twin-screw extrusion followed by injection-molding. It was shown that extrusion-injection cycle is more efficient than a mixer-compression cycle in the case of hemp fibre-filled acetate cellulose [17]. Processing of softwood flour with various biodegradable matrices has also been tested showing that needed energy rises with flour contents [18]. The final properties of bran-based biocomposites will be analysed and compared with standard fibres. The incorporation of this inexpensive agricultural residue, cheaper than agricultural fibres, into bioplastics is a key strategy that may help to create cheap sustainable injection molded composites. Biocomposites will be characterized by differential scanning calorimetry (DSC), dynamic mechanical analysis (DMA), and

mechanical testing (i.e., tensile, and flexural analysis). A lab-scale twin-screw compounder will be also used for rheological measurements.

Materials and methods

Materials

- The thermoplastic biobased polylactic acid in the form of pellets with a melt flow index (MFI) of 30-40 g / 10 min (190°C, 2.16 kg), was supplied by NatureWorks LLC.
- Wheat bran (*WB*) is a powder mixed with flake containing particles from 315 µm to 1.5 mm. No treatment has been made to remove residual starch. Composition of wheat bran can be found in Table 1.
- Miscanthus fibres (*MIS*) with length from 500 µm to 6 mm, diameter inferior to 500 µm and final aspect ratio l/d between 4 and 30, Miscanthus fibres are at 93% weight of dry matter, composed with cell wall polysaccharides and lignins.
- Refined cellulosic fibres (*CF*) were made from maritime pine, treated by oxygen and its derivative without chlorine. This cellulosic material have been grinded to size inferior to 250 µm. Fibres are composed at 90% dry matter of cellulose, the remaining being mainly hemicelluloses.

Table 1 – Chemical composition of wheat bran

	% dry matter	Methods
Cellulose	10.9 ± 0.8	ADF-NDF
Hemicelluloses	38.8 ± 12.5	ADF-NDF
Lignins	3.1 ± 0.4	ADF-NDF
Proteins	14.8 ± 0.1	Kjeldhal
Total starch	18.3 ± 1.0	Amyloglucosidase/ α -Amylase method
Lipids	4.8 ± 0.0	Cyclohexane extraction (Soxhlet)
Ash	6.5 ± 0.0	6 h in oven at 550°C

Methods

Compounding

Prior to extrusion, fibres have been dried overnight at 80°C.

Compounding was carried out in a Cleextral Evolum 25 (France) co-rotating twin-screw extruder, with increasing fibre concentration from 10 to 40% wt. PLA was fed in zone 1 of the extruder, out of 10 zones, and the fibre introduction was made through a side feeder in zone 4 after PLA

melting. Processing parameters as screw speed or torque have been recorded every five seconds thanks to Cleextral pilot software. Matter pressure and temperature in the die have been measured thanks to specific captors and recorded as processing parameters. Compounds were cooled with water, then pelletized on the production line and dried at 80°C for at least 3 hours.

Injection-molding

An Arburg injection press with 150 tons mould clamping force was used to make dumb-bell shaped samples for mechanical property measurements. PLA based biocomposites were injection-moulded with a temperature profile of 30-155-160-165-165-170°C and a mould temperature of 20°C. Screw speed during feeding was set at 150 rpm, and injection speed was 30.7 mm³/s.

Rheology

Relative viscosity measurements have been carried out on extruded pellets in a Thermo Haake (Germany) MiniLab presenting a twin co-rotating screw configuration. The MiniLab is equipped with a back flow channel designed as a slit capillary. Pressure is measured at the capillary entrance and exit. Shear stress is deduced from the pressure drop in the back flow channel, during melt polymer recirculation. Different relative shear rates were studied by changing screw speed. Measurements have been made at 170°C with screw speeds from 50 to 250 rpm, corresponding to relative shear rates between 177 and 889 s⁻¹.

MiniLab measurements have been completed by relative rheological analysis made on a Thermo Haake (Germany) Rheomex where matter is melted in a single-screw extruder with three temperature-controlled zones set at 170°C. Pressure is measured in the capillary die (diameter: 2 mm, ratio length/diameter: 20) and weight flow is measured thanks to scales at die exit. Six shear-level have been made with screw speeds from 50 to 200 rpm, corresponding to relative shear rates between 760 and 3500 s⁻¹, depending on compound density. Densities have been determined by measuring the dimensions and the weight of straight pieces of plastic rod at the Rheomex exit.

Mechanical testing

Tensile and flexural properties were measured using a Tilnius Olsen Instrument according to NF EN ISO standards 527 and 178, respectively. The crosshead speed for tensile testing was 5 mm/min and tensile modulus was determined thanks to extensometers at the speed of 1 mm/min. The crosshead speed for the 3-point bending flexural test was 2 mm/min. Samples were stored 2

weeks at room temperature before the measurements.

Dynamic mechanical analysis (DMA)

Visco-elastic behaviour of the injected compounds has been studied in a single cantilever bending mode, in a Triton Dynamic Mechanical Analysis device. Samples have been heated from 0 to 160°C at a heating rate of 2°C/min, in a multi-frequency testing mode (1 and 10 Hz at the same time) and amplitude of 0.05 mm. Results at 1 Hz are presented in this paper.

Differential Scanning Calorimetry (DSC)

The glass transition (T_g), crystallization (T_c), and melting (T_m) temperatures were determined using a Mettler Toledo DSC 821e under nitrogen flow. Samples for DSC analysis were obtained from composites that had been extruded, followed by injection-moulding. Approximately 10 mg samples were heated in a sealed aluminium pan at a ramp rate of 10°C/min to erase sample thermal history, cooled at a rate of 15°C/min, and subsequently heated at 10°C/min. The T_g was taken as the deflection of the DSC curve from baseline in this third heating cycle. Enthalpies of melting (ΔH_m) were evaluated using TA Universal software by integrating the area of the melting peaks. Enthalpies values were brought back to the real PLA mass in the sample.

Results and discussion

Compounding

SME is the specific mechanical energy transferred to the matter to ensure its transformation (W.h/kg). It is directly linked to electrical power provided by the extruder motor. It is related to the chosen screw speed S_s (rpm) and feeding rates (kg/h), as well as the resulting torque C (% C_{max}) by the following equation:

$$SME = \frac{U \times I \times \sqrt{3} \times \cos \varphi \times \frac{C}{C_{max}} \times \frac{S_s}{S_{max}}}{\sum \text{Feeding rates}}$$

where U is the motor's operating voltage (400 V), I the current feeding the motor (57 A), $\cos \varphi$ the theoretical yield of the extruder motor (0.90), C_{max} the maximum torque, and S_{max} the maximum speed (1200 rpm).

With this data, we can compare the electrical consumption during compounding. As seen in Figure 1, SME is increasing with fibre loading at a screw speed of 75 rpm and a total feeding rate of 10 kg/h. At the same loading, miscanthus fibres induced higher SME than wheat bran. This can be explained by differences in chemical compositions (miscanthus is composed at

91% dry matter of lignocellulosic fibres while wheat bran contains only 53% dry matter of fibres and various co-constituents such as starch, proteins and oil), and in fibre sizes between the two fillers.

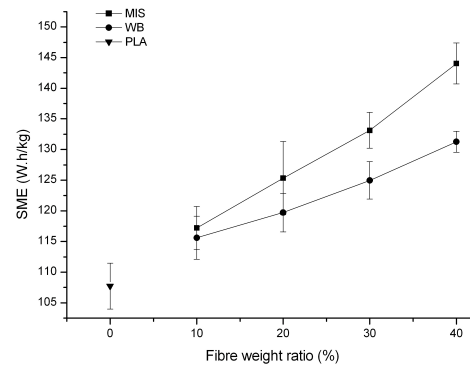


Figure 1 – Evolution of SME during extrusion of PLA, PLA-MIS and PLA-WB compounds (75 rpm for screw speed, and 10 kg/h for total feeding rate)

Figure 2 presents the increase of die pressure with fibre loading. This can be related to viscosity increase. As for SME, this increase appeared to be less important for wheat bran than for miscanthus fibres. However, at lower loading (less than 30% for fibre weigh ratio), die pressure is more important for wheat bran than for miscanthus. It is our opinion that this result is due to filler shape. Indeed, miscanthus fibrous aspect allowed it to get oriented in the flow so its diameter above 500 μm is much lower than the 2 mm die diameter. On the contrary, 1.5 mm flake shapes of the bran can have more difficulties to pass through the die, causing a slight increase of die pressure. This phenomenon is overcome by viscosity increase at higher loadings. Also bran composition containing fibre and thermoplastic compounds (starch, protein) can limit this viscosity increase [19,20].

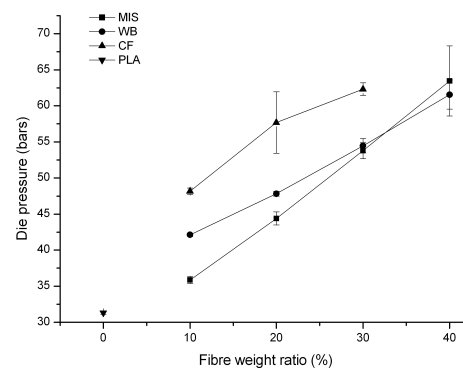


Figure 2 – Evolution of die pressure for PLA, PLA-MIS, PLA-WB ($T_{matter} = 157^\circ\text{C}$) and PLA-CF compounds ($T_{matter} = 161^\circ\text{C}$)

In the case of cellulosic fibres, matter temperature was around 161°C instead of 157°C for

the two other fibres. This increase of temperature was necessary to incorporate them. It can be noted on Figure 2 that die pressure is much higher for the cellulosic fibres than for the two other fillers. Considering that higher temperature tends to reduce viscosity, die pressure should be lower so it can be guessed that these fibres promote higher viscosity increase.

Rheology

Relative rheology has been determined at 170°C in a Thermo Haake MiniLab. As seen on Figure 3, relative viscosity raised with increasing amounts of cellulosic fibres. This tendency is more visible in the low shear regions. However, as shear during injection-moulding is high, viscosities must be close to each other. Figure 4 shows that in the case of wheat bran, relative viscosity tends to increase with upper loadings in the low-shear regions and, on the contrary, is reduced at higher shear. Some observations are interrogating like the plot slope, which is very high. According to Oswald-De Waele law, this will be attributed to a very high-entangled polymer chain system. It was guessed that secondary phenomenon, as degradation or mixing, can occur during measurement due to matter recirculation and measurement time. Furthermore, starch and wheat proteins, which remains in the bran after extraction, have thermoplastic behavior and influence the overall compound viscosity [19,20]. Miscanthus fibres cause also a viscosity increase at lower impact compared to cellulosic fibres, as their very small size causes more polymer chains entanglement.

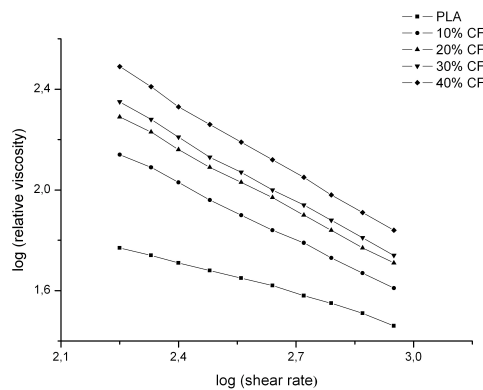


Figure 3 – Evolution of relative viscosity with shear rate (log scale) for PLA-CF compounds at 170°C (MiniLab)

That is why complementary measurements have been made on a Thermo Haake PolyLab where pellets are melted and extruded. Thus, measurements are made on matter that did not recirculate. As shear is higher (at least 1000 s^{-1} for shear rate), it was observed on Figure 5 the same

tendency than previously, i.e. viscosity is lower when filled with wheat bran. It can be noted that the slope is reduced significantly and this confirmed that previous remarks were due to a recirculation effect.

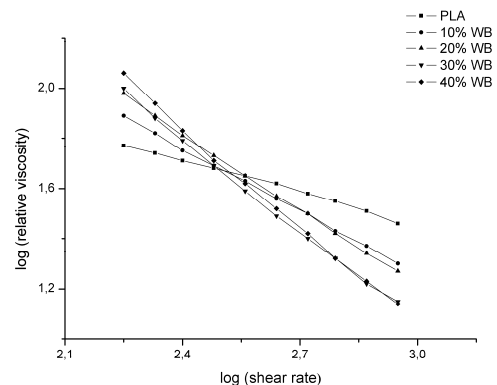


Figure 4 – Evolution of relative viscosity with shear rate (log scale) for PLA-WB compounds at 170°C (MiniLab)

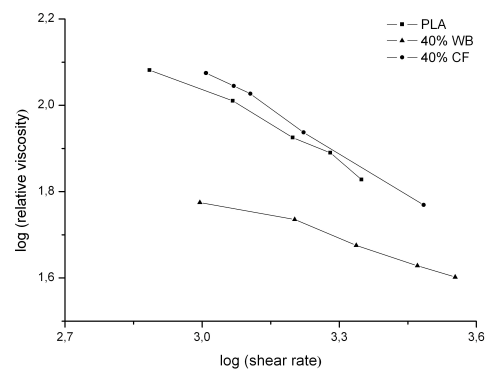


Figure 5 – Comparison of relative viscosity vs. shear rate plots for CF and WB filled PLA at 40% wt and 170°C (Rheomex)

Wheat bran appeared as a processing aid as it helps to reduce compound viscosity. This is coherent with observations made during twin-screw extrusion process, considering lower SME than cellulosic fibre and miscanthus-filled compounds. We believe that this faculty is linked to the wheat bran lipid content (4.8% dry matter) that can act as lubricant during process, but also probably to starch (18.3% dry matter) and proteins (14.8% dry matter) that enable the increase of the thermoplastic matrix content inside the compound.

Mechanical properties

Figure 6 presents the tensile properties for wheat-bran filled composites. Tensile modulus is increased thanks to the incorporation of wheat bran (+19% in the case of PLA-40% WB compound). At the same time, elongation at break as well as tensile strength are reduced (-59% for tensile strength in

the case of PLA-40% WB compound). Strength reduction has been attributed to a lack of affinity between the matrix and the bran, causing a few interactions and a poor interface.

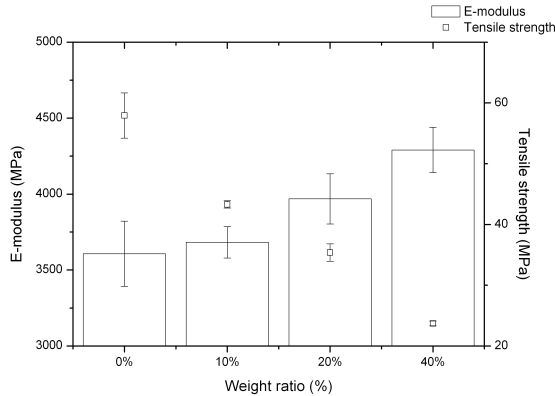


Figure 6 – Evolution of tensile modulus and tensile strength for PLA-WB compounds

Considering Nicolais and Narkis model [21], we can predict evolution of tensile strength σ into composite depending on filler volume fraction ϕ and matrix strength σ_0 through the following equation:

$$\sigma_c = \sigma_0 \times \left[1 - \left(K \times \phi^{2/3} \right) \right],$$

coefficient $K=1.21$ being the extreme case where there is no adhesion between the filler and the matrix.

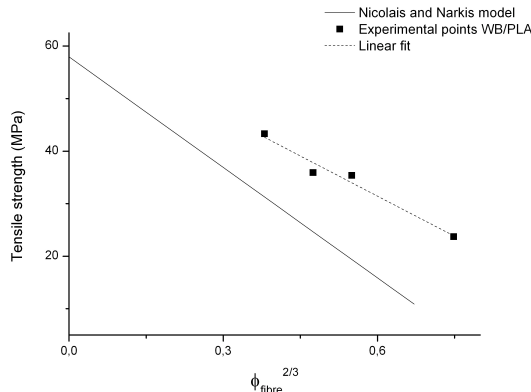


Figure 7 – Evolution of PLA-WB composite tensile strength with volume fraction (Nicolais and Narkis model)

The lower K coefficient is, the better the adhesion. In Figure 7, the case of wheat bran filled PLA have been treated. Observing the slope, we can see that wheat bran fit the model with a K value (0.82) lower than 1.21, showing some PLA-WB interactions

By comparing wheat bran with more common fibres, it can be observed that rigidifying power of the bran is quite lower than miscanthus or cellulosic fibres (Figure 8). Strength is also more reduced with the bran than with the two other fibres. Lack of modulus increase can be attributed to the lower ligno-cellulosic fraction, which brings the stiffening. Considering the Nicolais and Narkis model, it could have been concluded that there is more adhesion in PLA-MIS and PLA-CF composites. However, K coefficient is a decreasing function with l/d fibre aspect ratio [21]. Considering that miscanthus and cellulosic fibres have quite high aspect ratios, their low K values cannot be only attributed to a good adhesion.

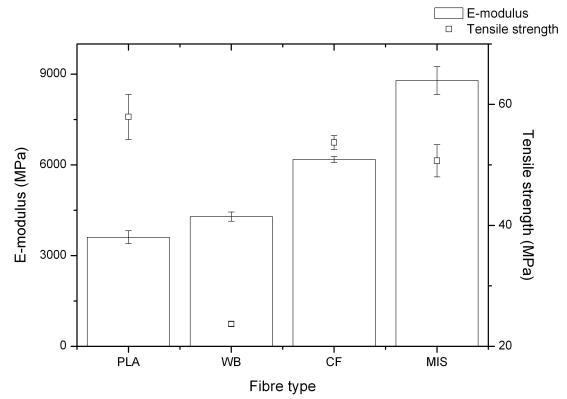


Figure 8 – Comparison of tensile properties for 40% wt fibre-filled PLA

Wheat bran is a complex hydrophilic material with various components such as proteins, cellulose, and starch, what added more source of incompatibility with the more hydrophobic PLA. What can cause the strength fall.

The same observations have been made on flexural properties (Table 2). It must be noted that miscanthus and cellulosic fibres strengthen the final material on three point bending results.

Table 2 – Tensile and flexural properties for the 40% wt fibre-filled PLA compounds

	Tensile modulus (MPa)	Tensile strength (MPa)	Elongation at break (%)	Flexural modulus (MPa)	Flexural strength (MPa)	Elongation at break (%)
PLA	3607 ± 215	57.9 ± 3.9	4.9 ± 0.5	2347 ± 98	69.3 ± 3.0	4.7 ± 0.2
40% MIS	8790 ± 459 (+144%)	50.7 ± 2.7 (-12%)	2.5 ± 0.1 (-48%)	5813 ± 190 (+148%)	74.6 ± 1.9 (+8%)	1.5 ± 0.1 (-66%)
40% CF	6179 ± 103 (+71%)	53.7 ± 1.1 (-7%)	3.2 ± 0.2 (-35%)	4169 ± 95 (+78%)	78.9 ± 3.0 (+13%)	2.3 ± 0.1 (-52%)
40% WB	4290 ± 149 (+19%)	23.7 ± 0.4 (-59%)	2.0 ± 0.1 (-58%)	2919 ± 82 (+24%)	41.6 ± 0.5 (-40%)	2.0 ± 0.1 (-56%)

Dynamic mechanical analysis (DMA)

Damping factor ($\tan \delta$) of biocomposites has been studied through DMA analyses and compared to the one of PLA. Peak height, as seen on Figure 9, is reduced with increasing amounts of wheat bran. This may suggest that the addition of the bran hinders PLA chain mobility. The same observations have been made for miscanthus and cellulosic fibres at the same ratio (Figure 10). Temperature of the transition is shifted to lower temperature, what can be analysed as a T_g reduction of PLA by the wheat bran (from 74.8°C for PLA to 69.9°C for PLA-40% WB compound taken at the peak height). This reduction for wheat-bran filled is comparable for at the two other fibres tested (71.5°C and 71.0°C for the T_g of PLA for PLA-MIS and PLA-CF compounds, respectively). No significant changes have been noted on the value of storage modulus for the three fillers. Reinforcement of visco-elastic properties is not as important as stiffening in mechanical properties, even for miscanthus and cellulosic fibres.

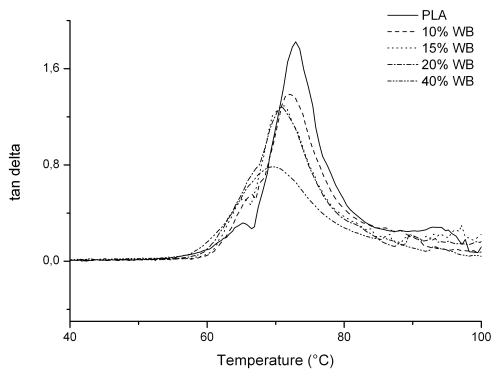


Figure 9 – Evolution of damping factor ($\tan \delta$) for the different PLA-WB compounds

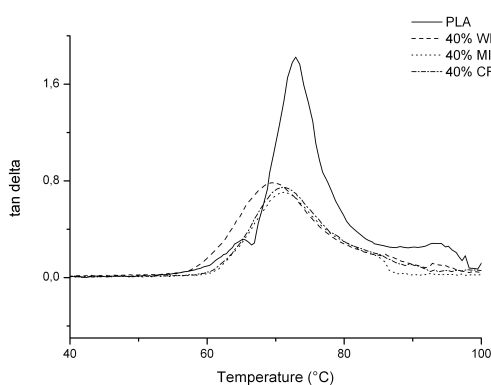


Figure 10 – Comparison of damping factor ($\tan \delta$) for the 40% wt fibre-filled PLA compounds

Differential Scanning Calorimetry (DSC)

Biocomposites glass transition temperature T_g becomes lower with wheat bran concentration as already observed with DMA analyses, and shifts under our detectable value (Figure 11). A slight decrease in melting temperature is also observed with this filler until 15% (from 166.9°C for PLA to 161.0°C for PLA-15% WB compound), then melting temperature increases again (respectively 162.7 and 166.3 for PLA-20% WB and PLA-40% WB compounds). Two possible explanations can be advanced. The first one is the reduction of PLA chains during the process in the presence of wheat bran. The second one is the influence of the bran chemical composition, which can provide a complex compound with various thermoplastic components.

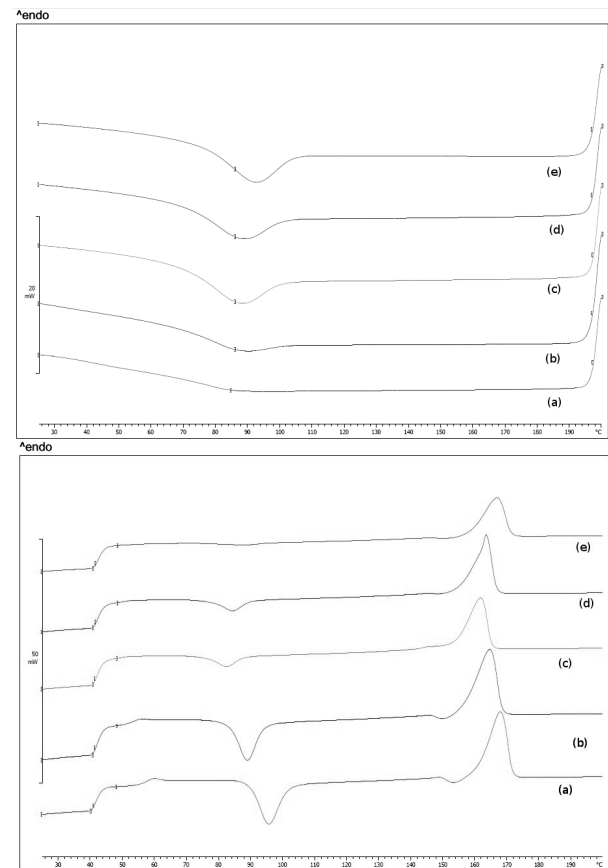


Figure 11 – DSC thermograms during cooling step (top) and second heating ramp (bottom) for (a) PLA, (b) PLA-10% WB, (c) PLA-15% WB, (d) PLA-20% WB, and (e) PLA-40% WB

It is interesting to see on thermograms that exothermic peak, i.e. cold crystallization peak observed for PLA at around 95°C is progressively reduced with increasing wheat bran amounts, in favour of a crystallization peak emergence during the cooling step. Thus, there is ample evidence that wheat bran eases crystallization of PLA. This

observed crystallization can also come from the residual starch contained in the bran. However, the same change has been made with highly cellulosic fibres. On the contrary, no changes have been noted with miscanthus fibres.

Enthalpies of melting per gram of PLA were found to increase by the addition of fibres (Table 3). This is linked to an increase of PLA crystallinity due to the fibre presence. Thus, it was seen that nucleation is promoted at the fibre surface, even if fibres hindering chain mobility, and crystallite growth was limited [16]. Cellulosic fibres promote more crystallinity considering the higher increase of PLA melting enthalpy.

Table 3 – Enthalpies of melting per gram of PLA

Compounds	Enthalpy of melting (J/g PLA)
PLA	42.5
10% WB	44.4
15% WB	45.5
20% WB	48.3
40% WB	48.1
40% MIS	52.1
40% CF	55.8

Conclusion

Wheat bran was successfully introduced onto PLA thanks to twin-screw extrusion. It was found that it helps reducing PLA viscosity while other fibres like miscanthus or cellulosic fibres caused high increase. This resulted in reduction of processing parameters and energy consumption during compounding. Dynamic behaviour was similar between the three fillers tested.

Even if mechanical properties improvement was not as important as for the two other fibres, wheat bran offers new opportunities for biocomposite production, as it is widely available and cheap. Work can be oriented in different ways, on one hand to increase cell wall polysaccharides contents by destarching and/or by extracting proteins, or on the other hand to plasticize and compatibilize these two potential thermoplastic matrices with PLA.

Tests are underway to study composite morphology, and to understand better wheat bran effects on PLA crystallinity or composite strength. GPC will be also carried out to investigate if no PLA chain degradation has occurred during the different process steps, what could explain notably T_g decrease.

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