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## Low-density polyethylene/poly (lactic acid) blends reinforced by waste wood flour

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### Abstract

The main purpose of this work was the valorization of waste wood flour as reinforcement in order to develop new wood based polymer composites (WBPC). For that purpose, LDPE/PLA blends were prepared in presence of poly (ethylene- co- glycidyl methacrylate) (PE-g-GMA) as compatibilizer and reinforced with 0 to 40 wt % of wood flour. The tensile properties, Charpy impact strength, morphology and thermal properties (differential scanning calorimetry (DSC) and thermogravimetric analysis (TGA, DTG)) of the LDPE/ PLA/ PE-g-GMA (20 /80/ 5) composites were characterized.

The results showed that Young's modulus increased with increasing the wood flour content and the composites are brittle. Globally, stress at break, elongation at break and Charpy impact decreased with increasing the content of wood flour. Morphological investigation revealed a good interfacial adhesion between LDPE/ PLA/ PE-g-GMA blend and wood flour. The stability of composites was affected by the incorporation of 10 wt % of wood flour and varied slightly with the increase in load. The values of speed of maximal weight loss of the composites were lower than that obtained for the blend without wood flour. The dispersion of wood flour decreased the onset degradation temperature of PLA, while the rate of thermal degradation of composites was improved. On the other hand, the degree of crystallinity of composites increased by the addition of wood flour indicating the possibility that wood flour can act as nucleating agent. Finally, the water absorption of the composites depends on the immersion time, the nature and the content of the load.

**Keywords:** Wood flour; low density polyethylene; polylactic acid; blends; composites; properties.

## **Introduction**

In recent years considerable research efforts were undertaken to develop new plastic materials with low environmental impact. This is why, researchers oriented towards natural resources. Wood flour and natural fibers like jute, ramie, sisal, flax and hemp have all proved to be good reinforcement in polymers like PE, PP, PLA and PBAT [1-8]. Wood flour and natural fibers have several advantages: renewable materials, low densities, low costs, non toxic, not abrasive to equipment, recyclable and biodegradable [9-11]. The use of wood flour in a polymer matrix reduces solid waste and produces a new environment friendly material with good properties. For this reason, thermoplastic/wood flour composites (WCP) are therefore widely used in various applications like furniture building, automotive and construction industries [12-16]. In order to give WPCs more potential, researchers have invested to better understand the WPCs. The researches often focus on the comparison between different processing ways, viscoelastic behaviour and improvement of the interfacial adhesion [17-20]. Today, biodegradable polymers are increasingly valued in the manufacture of biocomposites with natural reinforcements as they can be completely biodegradable in nature without emission of toxic substances [21-22]. Among the biodegradable polymers, polylactic acid (PLA) is increasingly used because it is a biodegradable and biocompatible polymer which can be produced from renewable resources. It has low cost, high specific strength and can substitute polymers derived from petroleum (PP, PE, etc) [21-24]. XXX

The properties of WPCs depend on the nature of the matrix, on the filler as well as on their compatibility. The mechanical properties and color of thermoplastic/wood flour composites depend on the wood flour type used [16, 22]. It was demonstrated that hardwood flour provides higher flexural strength and better tensile properties than softwood flour in composites [25].

Huda et al. [13] investigated the mechanical properties and the morphology of PLA/wood fibers and PP/wood fibers composites. The results showed that the addition of 20 wt% of wood fibers in PLA and PP composites improved their flexural strength by 20% and 31% respectively. The morphology, as indicated by scanning electron microscopy (SEM), showed good dispersion of wood fibers in the PLA. Petinakis et al. [2] studied the influence of matrix/particle interfacial adhesion on the mechanical properties and degradation of polylactic acid micro-composites. The results showed that the tensile strength and the Young's modulus of the micro-composites increase by 10 and 135%, respectively, indicating better interfacial matrix-particle adhesion by the incorporation of methylene diphenyl diisocyanate (MDI)

coupling agent. Cui et al. [15] investigated recycled HDPE/wood fiber composites (WRPCs). They found that the incorporation of wood fibers results in higher melting temperature than recycled HDPE, slower crystallization rate and decrease of the Charpy impact strength of WRPCs. Dairi et al. [26] manufactured and studied plasticized PVC/wood flour composites. The results indicated that the tensile strength and elongation at break decreased with incorporation of wood flour while the thermal stability of composites was satisfying. Altun et al. [27] studied the effect of an alkaline treatment of wood flour on mechanical and water absorption properties of PLA/wood flour biocomposites. The results showed that the treatment increased mechanical properties and impact strength, in agreement with good interactions between PLA and WF, while the alkaline treatment had no effect on the water absorption. Yao et al. [28] investigated the thermal properties of PLA/bamboo fibers (PLA/BF) and PLA/redwood flour (PLA/RWF) biocomposites. The results showed that the evolution of the thermal properties, the crystallization behavior ( $T_g$ ,  $T_c$  and  $T_m$ ) of PLA/BF and PLA/RWF biocomposites were different and changed regularly by increasing the amount of RWF and BF. Zimmermann et al. [29] studied the influence of wood flour particle size on the properties of poly (ethylene- co-vinyl acetate) EVA/wood cellular composites. The results indicated that decreasing the particle size of WF increases the viscosity of the composites. Furthermore, the composites reinforced with fine wood particles have a high density and larger thickness in the cell borders walls, thus influencing the mechanical responses of these composites. Optimal homogeneity was observed with WF (100–150 mesh), but the highest mechanical properties of strength were observed with WF (150–270 mesh). Donmez Caldar et al. [30] investigated the effect of boric acid (BA), borax (BX) and their combination (BA-BX) on the properties of the HDPE/wood flour composites. The results showed that the tensile strength decreased when increasing fiber loading while the Young's modulus rised. The composite samples with borax provided better tensile modulus compared to those of the samples with boric acid. Jeske et al. [31] used thermogravimetric method (TGA-DTG) to quantify the mass percentage of wood flour and polypropylene copolymer in wood plastic composites (WPC). The developed method showed good agreement between analyzed and actual fraction of wood flour and polymer.

Blends of PLA with several synthetic polymers have been prepared in order to enhance the mechanical properties and also to obtain new materials. Zhao et al. [32] found that the crystallization and rheological properties of PLA were improved significantly by the introduction of HDPE and PLA spherulites could generate from PLA/HDPE interfaces. Zhou

et al. [33] employed LDPE to improve the thermal and rheological properties as well as the supercritical CO<sub>2</sub> foaming behavior of PLA. They found that the introduction of LDPE had a slight effect for promoting the crystallization of PLA.

Wang et al. [34] proposed a facile methodology for improving the crystallization ability, rheological properties and microcellular foaming behaviors of PLA/LDPE blends through compatibilization by poly (ethylene octene) grafted with glycidyl methacrylate (GPOE) as reactive compatibilizer.

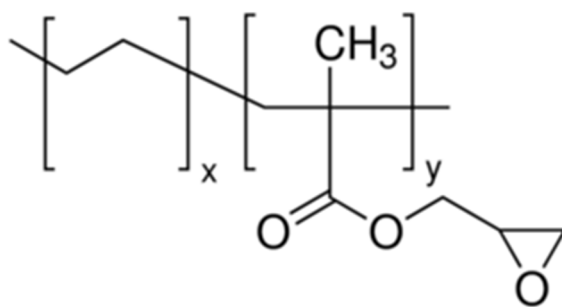
In a previous work, Boubekour et al. [35] found that LDPE and PLA have a low compatibility and used five functionalized polyolefins as compatibilizers for the LDPE/PLA (20/80) blend. The best results were obtained with poly (ethylene-co-glycidyl methacrylate) or PE-g-GMA (with 8% glycidyl methacrylate) which seems to strengthen the interactions between LDPE and PLA. The major reason for the use of such copolymer is that the epoxy group can easily react at normal melt processing conditions. Especially, polymers with hydroxyl and carboxylic acid groups like PLA can be effectively compatibilized using GMA functionalized copolymers. Since PLA used in this study has –OH and –COOH groups at the chain ends, it can form interchain linkages with the GMA unit in PE-g-GMA [35].

Based on these results, PE-g-GMA was selected as a potential compatibilizer candidate for PLA/LDPE blends and the objective of the present work is to investigate the effect of waste wood flour content on mechanical and thermal properties and morphology of LDPE/PLA blends compatibilized with PE-g-GMA.

## **Experimental**

### **Materials and methods**

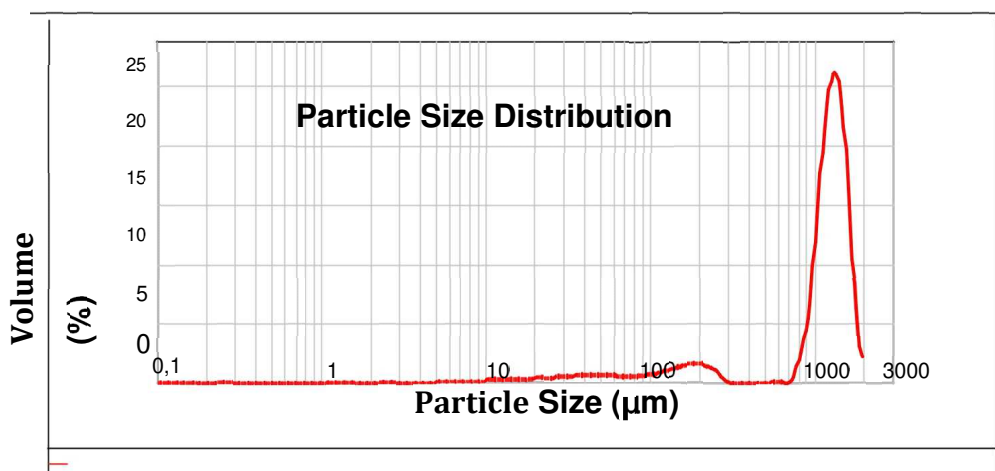
Polylactic acid (Nature Works 2002D) with a melt flow index (MFI) of 6.18 g/10 min, a density of 1.23, a glass transition temperature (T<sub>g</sub>) of 63°C and a melting temperature (T<sub>m</sub>) of 154°C was used. LDPE (Lyondell Chemical Company Petrothene NA980) is characterized by a melt flow index of 0.22 g/10 min, a density of 0.90 and a melting temperature of 115°C. The compatibilizer poly (ethylene-co-glycidyl methacrylate) containing 8 % glycidyl methacrylate (Lotader AX8840, Arkema France) has a melt flow index of 5 g/10 min, a density of 0.94 and a melting temperature of 106°C. The chemical structure is given in scheme 1.



Scheme 1. Chemical structure of poly (ethylene-co-glycidyl methacrylate)

The waste wood flour used was a mixture of wood pine Aleppo, eucalyptus wood and cedar product of the algerian company Transbois from Bejaia. The particle size was analyzed by Laser granulometer. A mastersizer 2000 apparatus was used and the results are shown in Figure 1. Particles size is concentrated between 1000 and 3000  $\mu\text{m}$ .

**Figure 1.** Particle size analysis of wood flour



### Biocomposites preparation

Before use, PLA was dried at 90°C for 2 hours while wood flour was dried at 105° for 24 hours. LDPE/PLA/PE-g-GMA blend (20/80/5) was reinforced with wood flour (10, 20, 30 and 40 wt %). All the samples were prepared using a twin-screw mini extruder (DSM Xplore Netherland micro of capacity 15 cm<sup>3</sup> twin screw compounder). The blends were injected into

a mold of dumbbell-type H2 specimen. The speed was 100 rpm and the processing time 4 minutes. Working conditions are summarized in table 1.

**Table 1.** Composition and processing setting for extrusion

Temperature	LDPE/PLA/PE-g-GMA/wood flour
200	20/80/5/0
190	20/80/5/10
185	20/80/5/20
180	20/80/5/30
175	20/80/5/40

### Characterization of biocomposites

#### Density

The density was measured using a METTLER Toledo balance. For each composition, at least three measurements were tested. Density is calculated using the equation (I).

$$d = \frac{A}{P} d_0 \quad (I)$$

A: sample weight in air;

P: mass of the sample in distilled water;

$d_0$ : density of water at experimental temperature.

#### Tensile properties

Tensile properties were measured at room temperature. The test was performed at a crosshead speed of 10 mm/min according to the standard NF T51-034 using an Instron Calibration Lab, Instron 33R4469 testing machine. The dimensions of the samples were (length x width x thickness: 75 x 4 x 2) mm<sup>3</sup>. The results obtained represent the average of five measurements for each sample at least.

### **Impact test**

Charpy impact tests were conducted on composites samples according to the standard ISO-179 using a testing machine type Instron CEAST 9050. Pendulum of 15J energy was used. Ten samples were tested for each formulation and the average value was reported.

### **Morphology**

Morphology of the samples was analyzed by scanning electron microscopy. The surface morphology of composites fractured in liquid nitrogen and coated with Au/Pd (gold, palladium) was observed by using a scanning electron microscope (SEM) (HITACHI 800) with an accelerating voltage of 12 kV.

### **Thermogravimetric analysis**

The thermogravimetric analysis measurements were performed using a TGA Q500 Instrument analyser in a nitrogen atmosphere at a heating rate of 10°C/min from room temperature to 590°C. The data collected were the onset temperature degradation ( $T_{\text{onset}}$  (°C)), the temperature of maximum weight loss ( $T_{\text{max}}$  (°C)) and speed of maximal weight loss ( $S_{\text{max}}$  (%/°C)) from TG and DTG curves respectively.

### **Differential scanning calorimetry analysis**

Differential scanning calorimetry (DSC) analysis was carried out with a TA Instrument Q20 V24.4 build 116 apparatus under the following operating conditions: equilibrium at 20°C for one minute followed by heating up to 250°C with a ramp of 20°C/min, isotherm of five minutes followed by cooling followed by an isotherm at 20°C, and finished with a one-minute isotherm. The glass transition temperature ( $T_g$ ), melting temperature ( $T_m$ ), cold crystallization temperature ( $T_{cc}$ ) and  $\Delta H_m$ , were determined from the thermograms.

The percentages of crystallinity ( $X_c$ ) of PLA in the biocomposites were estimated using equation (II) [24].

$$X_c (\%) = (\Delta H_m / \Delta H^{\circ} m) \times (100/W) \quad \text{(II)}$$

$\Delta H_m$ : experimental Enthalpy of fusion of PLA (J/g),



$\Delta H^{\circ}_m$ : Enthalpy of fusion of a sample (PLA 100% crystalline equal to (93J/g) [36].

W: Percent by weight of PLA in the mixture (%).

#### Water absorption Test

Water absorption of the LDPE/PLA/PE-g-GMA matrix and composites was determined.

Samples were cut into small squares of (length x width x thickness: 10 x 10 x 2) mm<sup>3</sup>. Prior to absorption experimental, the samples were dried in an oven at 105°C until constant weight. The specimens were immersed in a bath of distilled water at a constant temperature of 30°C for 33 days.

The rate of water absorption is expressed by the weight gain as a function of time. It is calculated according to equation (III) [37]:

$$WA (\%) = \frac{W_t - W_0}{W_0} \times 100 \quad (III)$$

Where  $W_t$  and  $W_0$  are the weights of the sample before and after immersion in distilled water, respectively. All the reported results are average of three test specimen.

## Results and discussion

### Characterization of LDPE/PLA/PE-g-GMA/wood flour

The evolution of the composites density as a function of the concentration of the wood flour is given in Table 2. The results show that the density increases slightly when increasing the weight percent of wood flour.

**Table 2.** Variation of density of LDPE/PLA/PE-GMA/wood flour biocomposites as a function of wood flour concentration

Wood flour	0	10	20	30	40
Density	1.151± 0,006	1.155± 0.007	1.165±0.0063	1.190± 0.003	1.227± 0.007

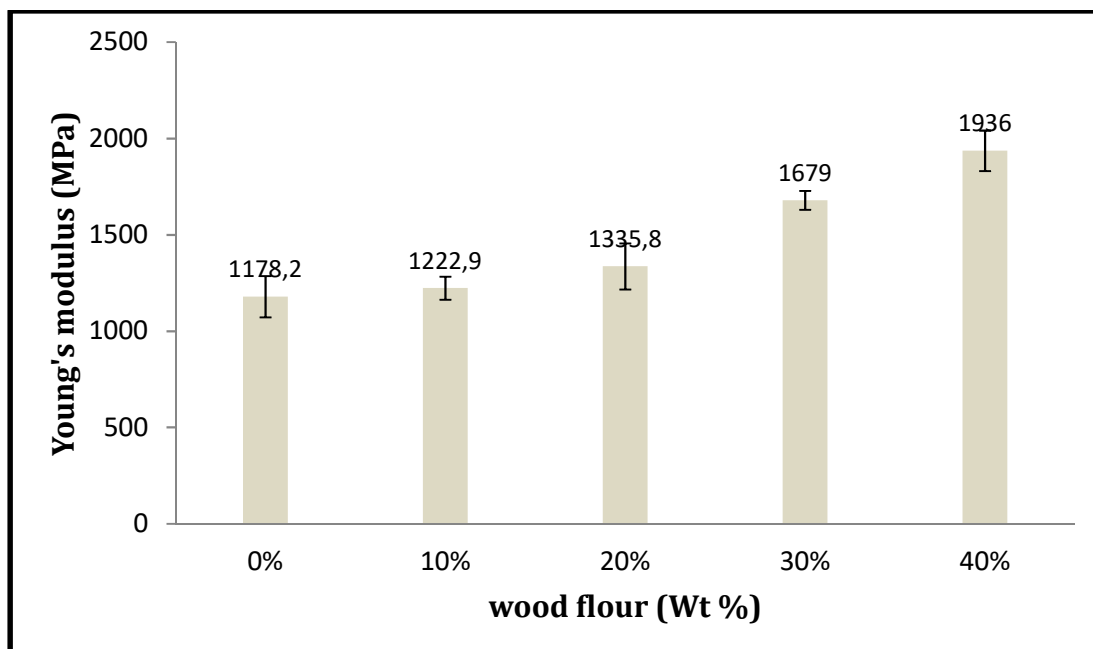
Young's modulus of the composites reinforced with wood flour (Figure 2) increased with increasing the rate of wood flour to reach a maximum value of 1936 MPa (about 40% wood flour) compared to that of the reference at 1180 MPa. This result is in good agreement with

the findings of several authors [13, 26- 27, 36]. Composite materials with high loading rates are systematically more rigid because natural fibers and wood flour are said to be much stiffer than polymer matrix thus adding stiffness to composites [26, 38, 39]. The tensile modulus values of all composites containing WF are higher than that of pure PLA [27]. The same result was observed in the majority of composites such as PLA/WF [27], PLA/ LDPE/ PE-g-GMA/jute [35] and PP/wood flour composites [40].

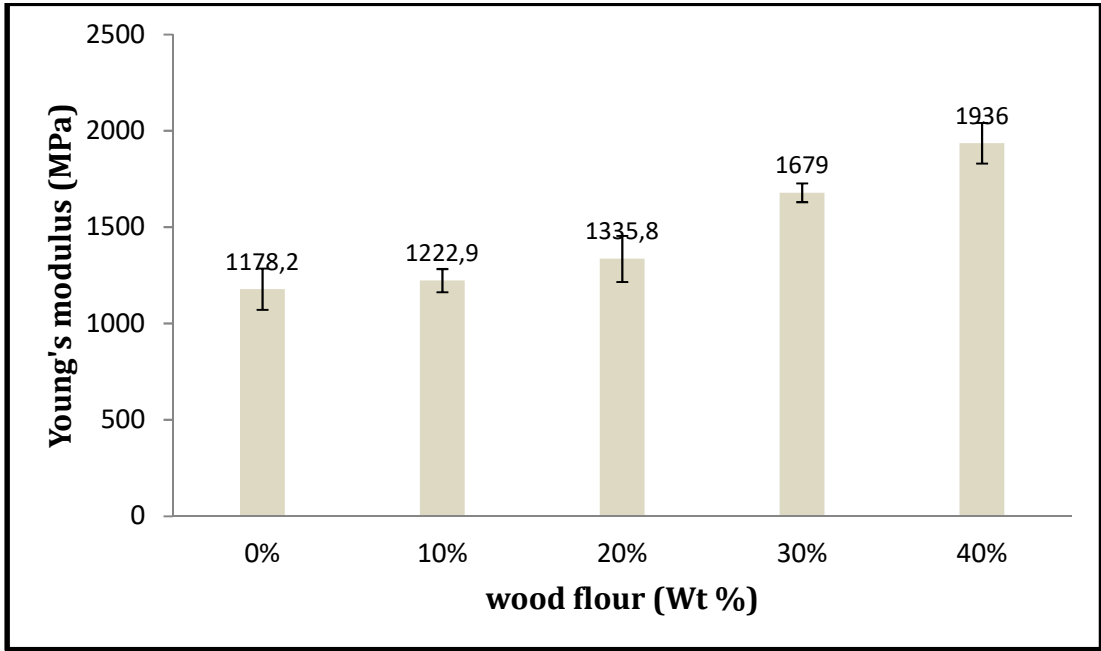
Nevertheless, it is noted that globally stress at break decreased with the incorporation of wood flour (Figure 3) which is attributed to the poor interfacial adhesion between the matrix and wood flour for high rates [26]. It is probably due to either aggregation of the wood flour or insufficient hydrogen bonding between the matrix and wood flour [13]. The same result was observed with PLA/wood [27] and PLA/pineapple flour composites [24].

The low elongation at break value (2.5%) obtained for the composite reinforced with 40 wt % wood flour (Figure 4) shows that this composite has a brittle character. This can be explained by the rigid character of PLA and wood flour [2, 7].

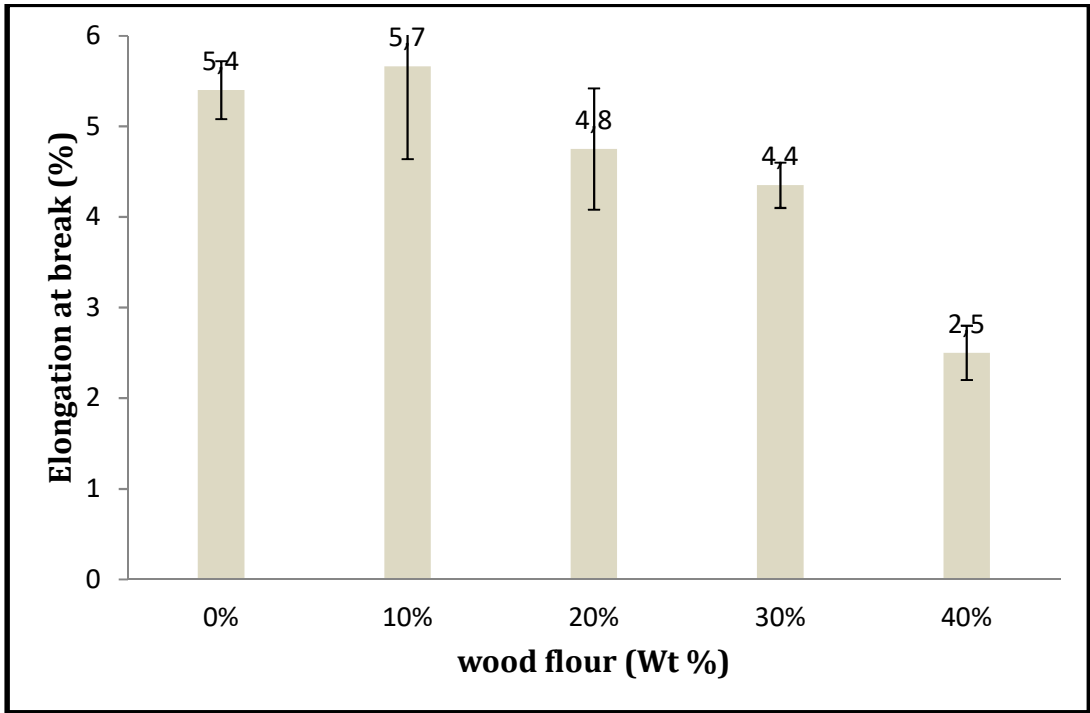
**Figure 2.** Young's modulus evolution with content of wood flour



**Figure 3.** Tensile strength evolution with content of wood flour



**Figure 4.** Elongation at break evolution with content of wood flour

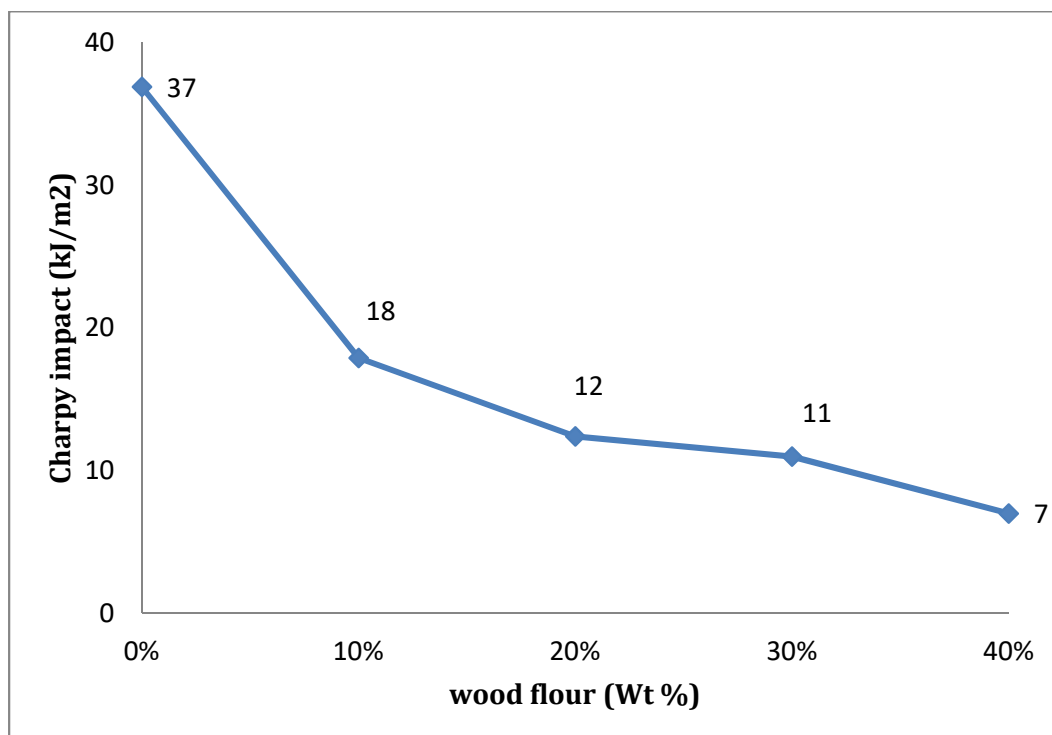


Charpy impact (Figure 5) decreased considerably with the incorporation of 10 wt % wood flour. The loss being about 50% compared to that of the PLA/ LDPE/ PE-g-GMA control. Beyond this weight percentage, Charpy impact decreased gradually to reach the value of 7 kJ/

m<sup>2</sup> for the composite containing 40 wt % wood flour. These results are similar to the literature [2, 9, 15].

The same result (5.2 kJ/ m<sup>2</sup>) was observed in the case of PLA/ wood flour (70/30) compared to pure PLA with 10 kJ/ m<sup>2</sup> [27] and PP/wood flour composite (70/30) which exhibited a very low value (0.2 kJ/ m<sup>2</sup>) compared to the PP reference (1.2 kJ/ m<sup>2</sup>) [25]. Singh et al. [41] showed that the impact strength of PHBV/ wood flour composites increased with the increase of the wood fiber content in PHBV. For composites (PHBV/ wood flour (70/ 30, 60/ 40), they found respectively, 30 and 24.4 J/m compared to 34 J/m for neat PHBV. A decrease in impact resistance was observed for all biomaterials. This important fall was explained by a ductile-fragile transition in the behavior of biomaterials [34, 38, 42]. It can be concluded that the impact resistance is a complex physical parameter characteristic of the nature of fiber, of wood (crystallinity, % cellulose, elongation, geometry and length) and of the polymer matrix. Globally, most mechanical properties results of LDPE/PLA/PE-g-GMA/wood flour composite were poor than those of samples without wood flour. These results were expected and can be explained by the fact that the obtained composites are more brittle due to the combined rigid character of PLA and wood flour.

**Figure 5.** Effect of wood flour content on Charpy impact of LDPE/PLA/PE-g-GMA bio-composites.



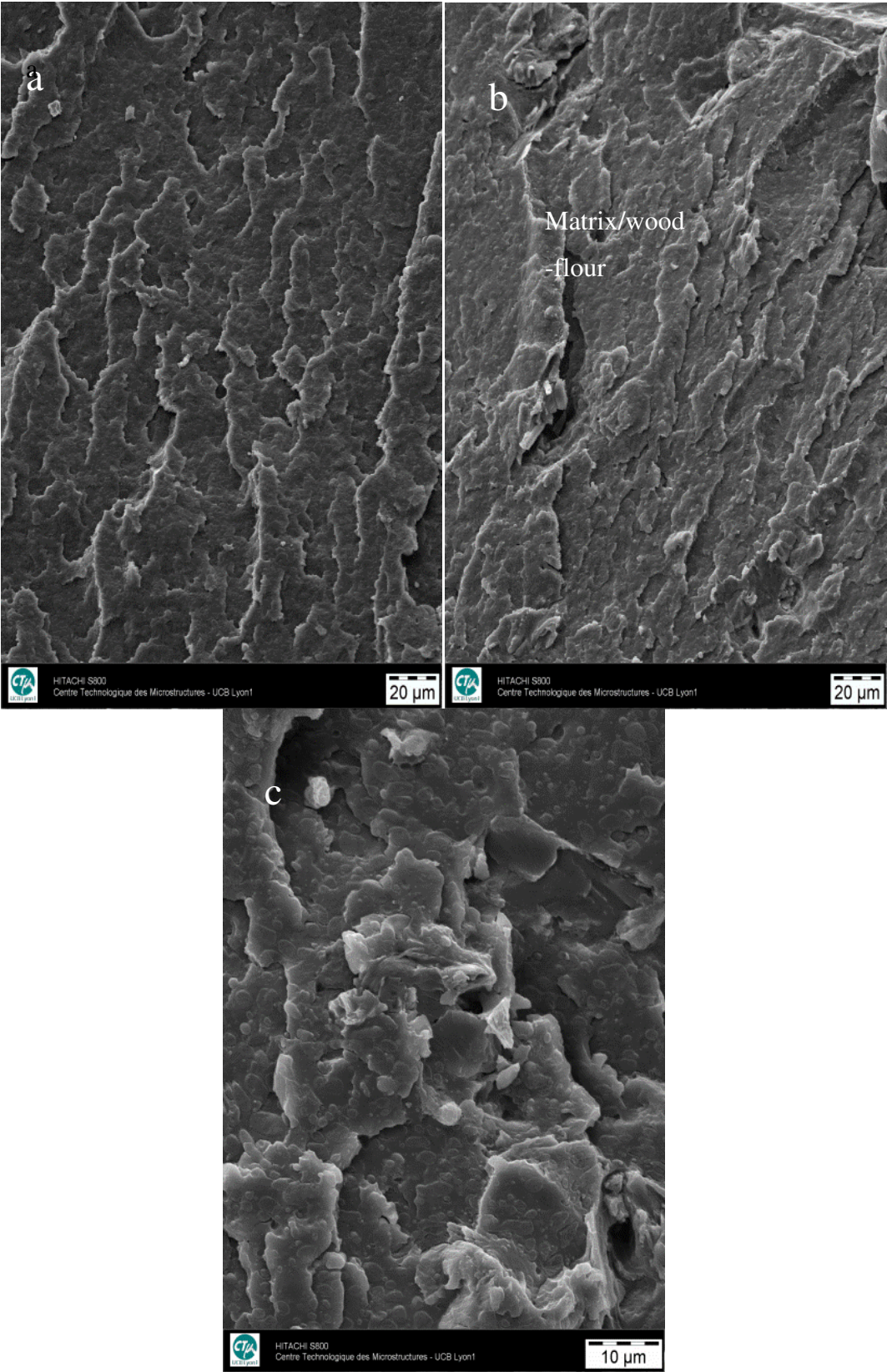
## **Morphology**

Figure 6 shows the state of dispersion and distribution of wood flour in the LDPE/ PLA/ PE-g-GMA matrix. The SEM image of the surface of LDPE/ PLA/ PE-g-GMA/ wood flour (20/80/5/20) composite shows that wood and flour seem to be embedded in the blend matrix. Despite some voids observed on the surface (Figure 6c), the adhesion is satisfactory because the majority of the wood flour is integrated into the polymer matrix.

A good dispersion of the wood flour in the matrix and an absence of agglomerates can be explained by an acceptable level of compatibility between the wood flour and the LDPE/ PLA/ PE-g-GMA matrix. The same results were observed with LDPE/ PLA/ PE-g-GMA/jute fibers [35].

Altun et al. [27] and Petinakis et al. [2] found that a composite of PLA-30 WF presents a gap around WF, a high degree of inhomogeneity at the fracture surface, with voids and wood flour particles being visible and the rough edges of the voids being the result of particle pull out, thus characterizing the poor adhesion between PLA and WF. Tsou et al. [36] found that many cavities are observed due to the poor adhesion between PLA and WF. This morphology is typical of incompatible blends and it was improved after MAH was grafted onto PLA. Anderson et al. [43] studied PHB /wood flour composites. The micrographic results showed that fibers were not embedded in the polymer matrix confirming the poor adhesion. This property was greatly improved in presence of polymethylene diphenyl diisocyanate (PMDI). The micrographs (Figure 6) of the composites present a satisfactory interfacial adhesion compared with those of the literature cited above. The PE-g-GMA compatibiliser both improved compatibility of LDPE/PLA blend [35] and formed strong interactions between the wood flour and the matrix.

**Figure 6.** SEM micrographs of fractured surface of LDPE/ PLA/ PE-g-GMA/ wood-flour (a): (80/20/5) and (b, c): (80/20/5/20)



### **Thermogravimetric analysis**

The TGA curve of wood flour displayed in Figure 7 is characterized by three steps. The first step whose temperature is below 200°C corresponds to water evaporation. The second step is characterized by many shoulders close together in the range (200-270°C). It is associated with the decomposition of hemicelluloses and slower decomposition of lignin. The broad peak between 270°C and 400°C corresponds to the degradation of  $\alpha$ -cellulose and lignin. Beyond this temperature, the weight loss varies slightly [43-46]. The final decomposition temperature noted at 568°C represents the carbon burn [35, 45]. On the other hand, the residual weight percentage is about 21%.

Figures 7 and 8 show the thermal decomposition of LDPE/PLA/PE-g-GMA/wood flour composites. The TG curve (Figure 7) shows that the onset temperature at LDPE/PLA/PE-g-GMA (20/80/5) blend is 301°C. The DTG shows two-step degradation at 368°C for PLA and 474°C for LDPE. The degradation temperature of LDPE/PLA/PE-g-GMA/wood flour composites decreases when increasing load of wood flour. Incorporation of 10, 20, 30, 40% wood flour decreases the onset temperature of PLA degradation from 301°C to 272°C, 238°C, 232°C, 229°C respectively. The stabilities of the composites are affected by the addition of wood flour. The decomposition temperature of wood flour is lower than that of the LDPE/PLA/PE-g-GMA sample. This result is in agreement with Petinakis et al. [43] who studied PLA/wood flour and PLA/starch composites and found that the decomposition temperature of wood flour and starch is lower than that of PLA. The decomposition temperature of PLA/wood composites gradually decreases with increasing wood flour content. The same phenomenon was observed with the PVC/wood flour [26] and PLA/coir fibers [47] composites. The weight loss values found for the residues for samples with 10, 20, 30 and 40% WF at the temperature 567°C are 1, 5, 8 and 10% respectively.

Table.3 summarizes the results of weight loss, temperature of maximum weight loss and speed of maximal weight loss determined from DTG thermograms as a function of time. It is observed in stage 2 that W, Tmax, Smax and Wtotal are lowered when increasing the level of wood flour. The rate of thermal degradation of biocomposites is better than that of the LDPE/PLA/PE-g-GMA control. The mass loss value of the control is double (22%/min) compared to the composite reinforced with 40% of wood flour (10%/min). This result is satisfactory because the incorporation of the wood flour delays degradation speed of composites. It can be said that the incorporation of cellulose filler significantly retards the

decomposition of LDPE/PLA/PE-g-GMA and plays a role of an inhibitor of thermal degradation [26].

**Table. 3** Results of thermogravimetric analysis of LDPE/PLA/PE-g-GMA/wood floor bio-composites

LDPE/PLA/ PE-g-GMA/ wood floor	Step 1			Step 2			Step 3			Wtotal		
	W1	Tmax	Smax	W2	Tmax	Smax	W3	Tmax	Smax			
80/20/5/0				76	368	22		24	476	6	100	
80/20/5/10				73	362	16		26	476	6	99	
80/20/5/20				70	346	12		25	474	6	95	
80/20/5/30		2	247	1	67	328	10		23	478	5	92
80/20/5/40		3	248	1	67	322	10		22	475	5	90
<b>wood floor</b>		<b>5</b>	<b>257</b>	<b>2</b>	<b>9</b>	<b>289</b>	<b>4</b>		<b>65</b>	<b>364</b>	<b>6</b>	<b>79</b>

*W*: Weight loss (%);

*T<sub>max</sub>*: Temperature of maximum weight loss(°C).

*S<sub>max</sub>*: Speed of maximal weight loss(%/min);

*W<sub>total</sub>*: Total weight loss (%).

*W*: Weight loss (%);

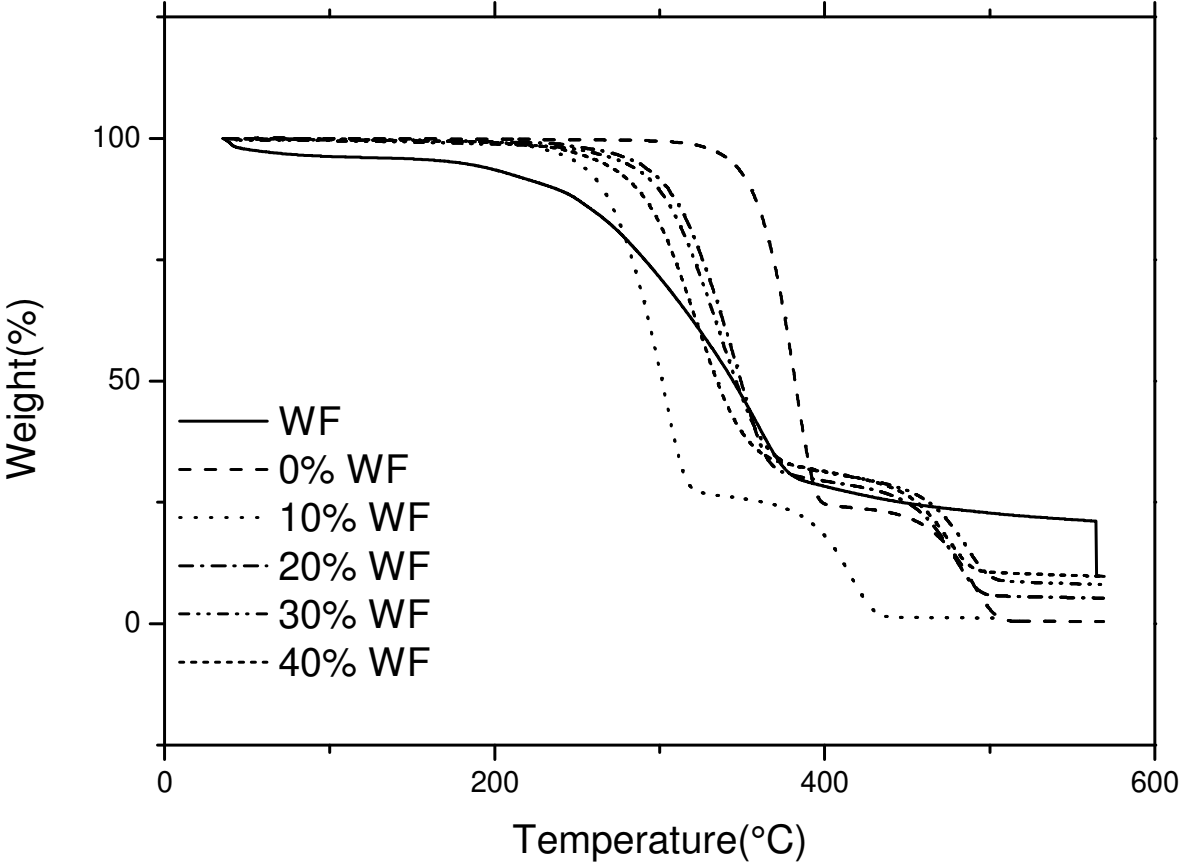
*T<sub>max</sub>*: Temperature of maximum weight loss (°C).

*S<sub>max</sub>*: Speed of maximal weight loss (%/min);

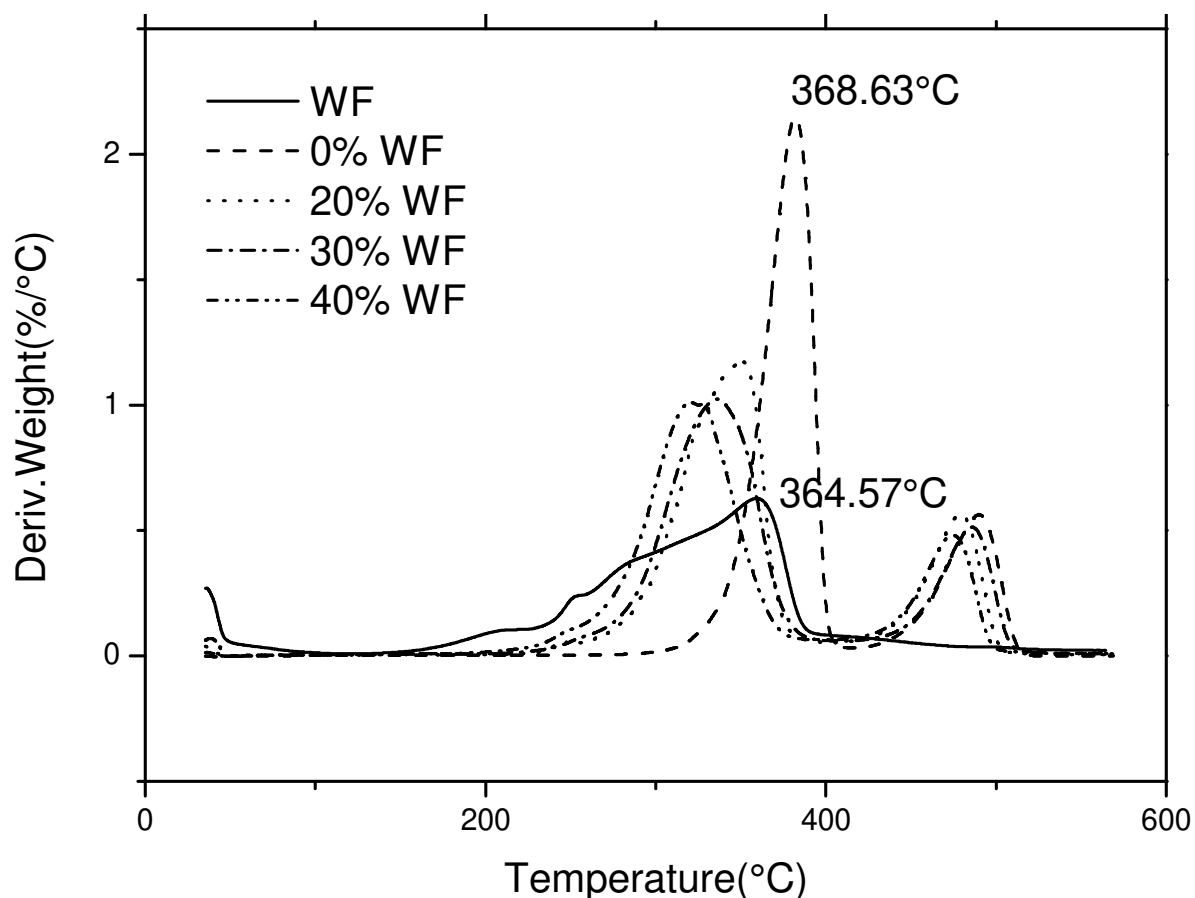
*W<sub>total</sub>*: Total weight loss (%).



**Figure 7.** Thermogravimetric analysis of LDPE/PLA/PE-g-GMA, wood flour and their bio-composites (0 – 40% wood flour)



**Figure 8.** Derivative weight loss of LDPE/ PLA/PE-g-GMA, wood flour and their bio-composites (0- 40% wood-flour)

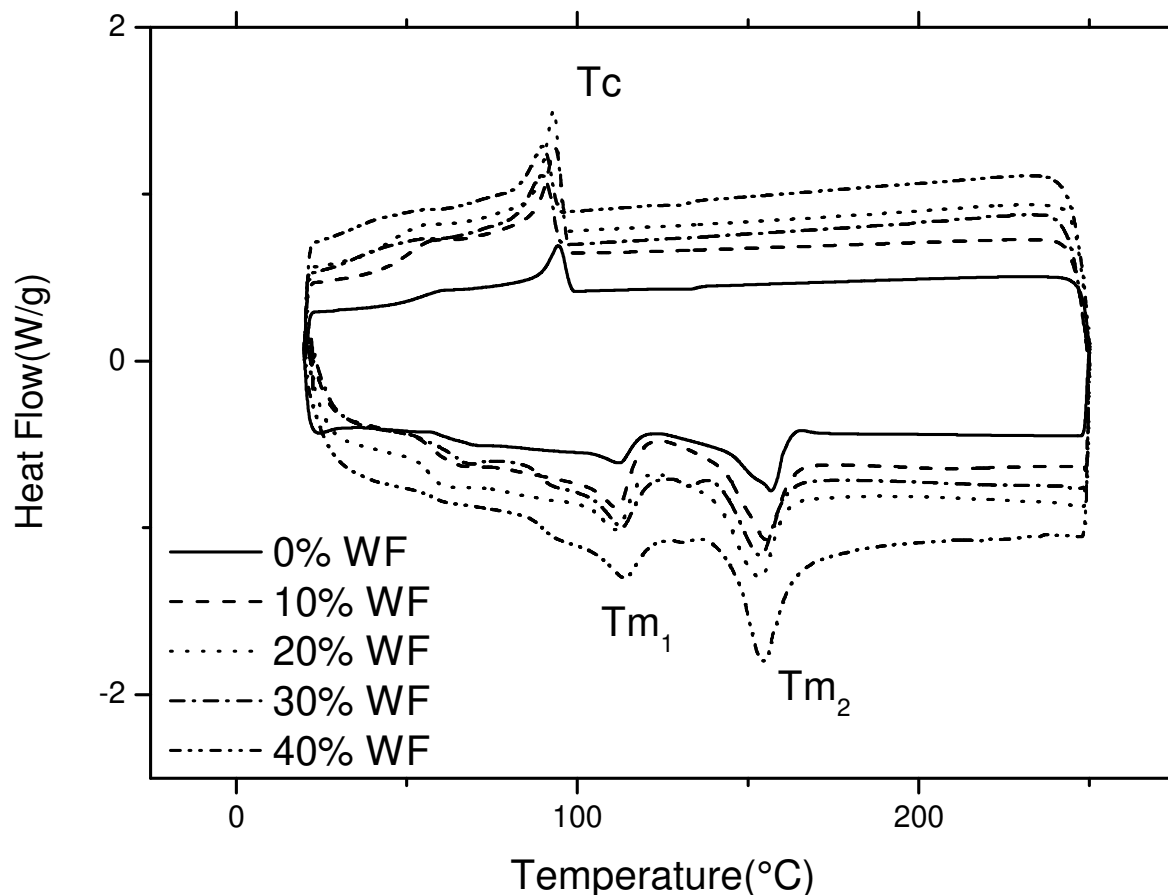


### DSC analysis

Figure 9 shows the DSC curves of the LDPE/PLA/PE-g-GMA blend and composites. After adding 30-40 wt% wood flour to the composite, the  $T_m$  of the blend composites showed two peaks. This means that the divided  $T_m$  of these composites had shifted. The same result was observed in PLA/wood [21] and PLA/cassava flour, PLA/pineapple biocomposites [24]. The reduction in  $T_m$  was due to reduced crystalline perfection of crystals nucleated on the wood surface [43]. The increase in  $X_c$  (Table 4) with wood flour load can be attributed to the possibility of wood flour acting sites during the composites preparation nucleated PLA [48-49]. The higher value percentage crystallinity (54%) was noted in the case of biocomposites loaded with 40% of wood flour. It could be possible that the addition of fibers is able to nucleate the matrix LDPE/PLA/PE-g-GMA and increase the degree of crystallinity [28, 48]. In other hand the  $T_c$  of the composites decreases with the increase of higher load. This is reported to wood flour which behaves as an inhibitor of recrystallization process at high wood

loads [48]. Cui et al. [15] attributed the decrease in  $T_c$  composites to the presence of wood fibers which slows down of flow polymer and limits its rearrangement causing a delay in the process of crystallization. These results confirm that the addition of natural fillers in PLA matrix increases significantly PLA crystallinity in the PLA/natural filler composite.

**Figure 9.** DSC thermograms of LDPE/PLA/PE-g-GMA (8/20/80/5) and bio-composites materials during heating and cooling



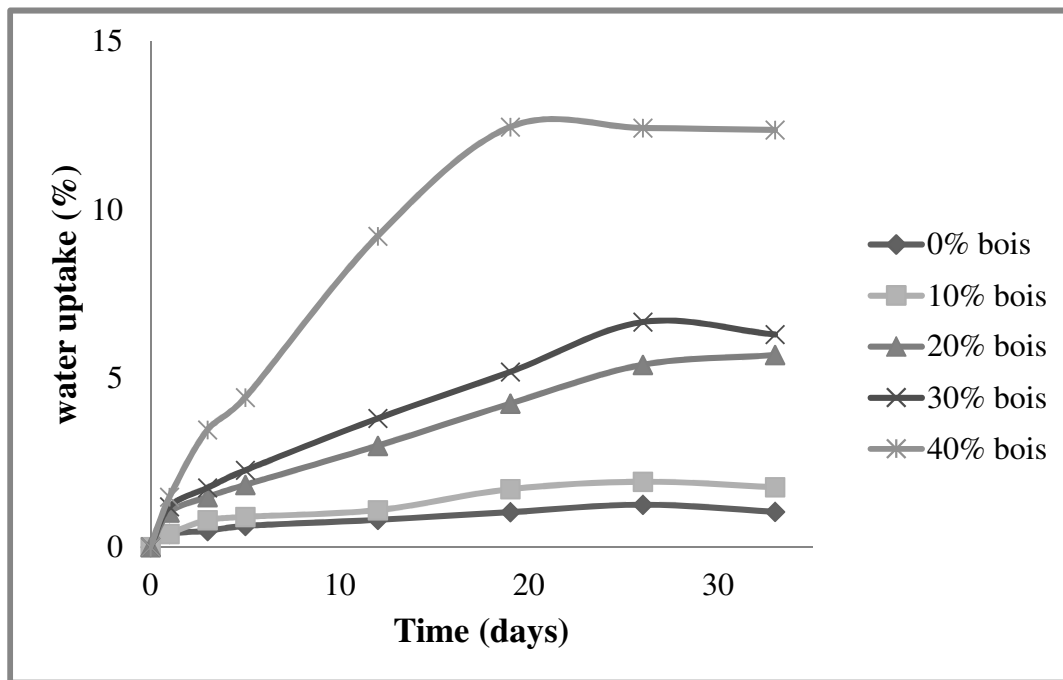
**Table. 4** DSC data of LDPE/PLA/PE-g-GMA and bio-composites

### Water absorption analysis

The results of water uptake are shown in Fig.10. It can be observed that the water absorption (WA) increases with the increase in filler loading. The water absorption phenomenon in wood polymers composites (WPC) is partly related to hydroxyl groups (-OH) present on cellulose molecules of wood. On the other hand, it may be due to the bad adhesion especially for high loads which increases the microvoids [26-27, 50, 51]. The water absorption rate of composites

(0, 10, 20, 30, and 40%) reached their water saturation with about 1.05%, 1.78%, 5.74%, 6.31%, and 12.38% respectively after 33 days of immersion. Badia et al. [51] and Altun et al. [27] showed that the composites PBHV/ sisal (30%) and PLA / WF (30%) absorbed a rate of 4% in 5 days and 8% in 33 days respectively. The results obtained in this study are better compared to those mentioned above.

**Figure 10.** Water absorption behavior of the composites



## Conclusion

From the above results, the following conclusions can be derived:

The incorporation of waste wood flour in LDPE/PLA/PE-g-GMA matrix improved the young's modulus, whereas the strength tensile and elongation at break decreases.

All the values of Charpy impact strength of composites were lower than that of blend without wood flour due to the nature of wood (rigidity and low elongation). According to the SEM micrographs, the wood flour is well incorporated into the mixing matrix indicating an appreciable adhesion between the matrix and the wood flour.

Thermal stability is not affect by the incorporation of high loads of wood flour which is an interesting feature. The degree of crystallinity of composites increased by the addition of wood flour indicating the possibility that wood flour can act as nucleating agent.

The rate of water absorption depends on the immersion time, the nature and the content of the load. Finally, the composites developed with LDPE/PLA/PE-g-GMA matrix and waste wood flour can be considered as an interesting way of valorization and recycling of this latter and can be considered as an environmentally friendly material.

## References

- [1] Yu T, Li Y, Ren J. Preparation and properties of short natural fiber reinforced poly(lactic acid) composites. *Trans Nonferrous Met Soc China*. 2009;19: s651-s655.
- [2] Petinakis E, Yu L, Edward G et al. Effect of Matrix-Particle Interfacial Adhesion on the Mechanical Properties of Poly(lactic acid)/Wood-Flour Micro-composites. *J Polym Environ*. 2009;17:83-94.
- [3] Mohanty S, Verma SK. Dynamic mechanical and thermal properties of MAPE treated Jute/HDPE composites. *J Compos Sci Tech*. 2006;66:538-547.
- [4] Hui ZP, Sudhakara P, Wang YQ, Kim BS, Song JI. Manufacturing and Mechanical Properties of Sisal Fiber Reinforced Hybrid Composites. *J. Compos. Resear*. 2013;26:273-278.
- [5] Oksman K, Skrifvars M, Selin JF. Natural fibres as reinforcement in polylactic acid (PLA) composites. *J Compos Sci Techn*. 2003;63:1317-1324.
- [6] Ayrilmis N, Jarusombuti S, Fueangvivat V, Bauchongkol, P. Effect of thermal-treatment of wood fibres on properties of flat-pressed wood plastic composites. *J Polym Degrad Stab*. 2011;96:818-822.
- [7] Sis AL, Ibrahim NA. Effect of (3-aminoprpyl) trimethoxysilane on mechanical properties of PLA/PBAT blend reinforced Kenaf fiber. *Iran Polym J*. 2013;22:101-108.
- [8] Mignault S, Koubaa A, Erchiqui F. Effects of processing method and fiber size on the structure and properties of wood-plastic composites. *J Compos Part A*. 2009;40:80-85.
- [9] Singh S, Mohanty AK, Sugie T. Renewable resource based biocomposites from natural fiber and polyhydroxybutyrate-co-valerate (PHBV) bioplastic. *J Compos Part A*. 2008;39:875-886.
- [10] Quazi TH, Alam AKMM, Gafur MA et al. Characterization of Plant and Animal based Natural Fibers Reinforced Polypropylene Composites and Their Comparative Study. *J Fibers and Polym*. 2010;5:725-731.
- [11] Khan MK, Khan RA, Haydaruzzaman et al. Study on the physic-Mechanical Properties of Strach-Treated Jute Yarn-Reinforced Polypropylene Composites: Effect of Gamma Radiation. *J Polym Plastics Tech and Eng*. 2009;48:542-548.
- [12] Keledi G, Sudar A, Burgstaller CH et al. Tensile and impact properties of three-component PP/wood/elastomer composites. *Express Polymer Letters*. 2012;3: 224-236.
- [13] Huda MS, Drzal LT, Mohanty AK, Misra M. Wood Fiber Reinforced Poly(lactic Acid) Composites. *Composite Conference*. 2005; sept 12-14. Troy, Michigan.

- [14] Stark NM, Matuana LM. Characterization of weathered wood-plastic composite surfaces using FTIR spectroscopy, contact angle, and XPS\*. *J Polym Degrad Stab.* 2007;92:1883-1890.
- [15] Cui YH, Tao J. DSC Analysis and Mechanical Properties of Wood-Plastic Composites. *J Reinf Plastics and Compos.* 2010;2:278-289.
- [16] Chen J, Wang Y, Gu CH et al. (2013) Enhancement of the Mechanical Properties of Basalt Fiber-Wood-Plastic Composites via Maleic Anhydride Grafted High-Density Polypropylene (MAPE) Addition. *J Materials.* 2013;6:2483-2496.
- [17] La Mantia FP, Scaffaro R, Morreale M, Lo Re G. Effect of the processing on the properties of biopolymer based composites filled with wood flour. *Int J Mater Form.* 2008;1:759–762.
- [18] Kozłowski M, Szczurek S, Szczurek T, Frackowiak S. Influence of matrix polymer on melt strength and viscosity of wood flour reinforced composites. *Int J Mater Form.* 2008;1:751-754.
- [19] Soccalingame L, Bourmaud A, Perrin D. Reprocessing of wood flour reinforced polypropylene composites: Impact of particle size and coupling agent on composite and particle properties. *J Polym Degrad Stab.* 2015;113:72-85.
- [20] Kaseema M, Hamad K, Deri F, Young Gun K. Material Properties of Polyethylene/Wood Composites: A Review of Recent Works. *Polym Sci SerieA.* 2015;57: 689–703.
- [21] Battezzato D, Alongi J, Frache A Poly(lactic acid)-Based Composites Containing Natural Fillers: Thermal, Mechanical and Barrier Properties. *J Polym Environ.* 2014;22:88–98.
- [22] Kim HS, Lee BH, Lee S et al. Enhanced interfacial adhesion, mechanical, and thermal properties of natural flour-filled biodegradable polymer bio-composites. *J Therm Anal Calorim.* 2011;104:331-338.
- [23] Kowalczyk M, Piorkowska E et al. Mechanical and thermal properties of PLA composites with cellulose nanofibers and standard size fibers. *J Compos Part A.* 2011;42:1509-1514.
- [24] Kim KW, Lee BH, Kim H.J et al. Thermal and mechanical properties of cassava and pineapple flour-filled PLA bio-composites. *J Therm Anal Calorim.* 2012;108:1131-1139.
- [25] Askanian H, Verney V, Commereuc S, Guyonnet R, and Massardier V. Wood polypropylene composites prepared by thermally modified fibers at two extrusion speeds: mechanical and viscoelastic properties. *Holzforschung.* 2015; 69:313-319.
- [26] Dairi B, Djidjelli H, Boukerrou A. Study and Characterization of composites Materials Based on Poly(vinylChloride) loaded with Wood flour. *J Mater Sci and Eng.* 2013;2:110-116.
- [27] Altun Y, Dogan M, Bayramlı E. Effect of Alkaline Treatment and Pre-impregnation on Mechanical and Water Absorption Properties of Pine Wood Flour Containing Poly (Lactic Acid) Based Green-Composites. *J Polym Environ.* 2013;21:850-856.
- [28] Yao L, Wang Y, Li Y et al. Thermal properties and crystallization behaviors of polylactide/redwood flour or bamboo fiber composites. *Iran Polym J.* 2017;26:161-168.

- [29] Zimmermann MVG, Turella TC, Ruth MC, Santana RMC, Zattera AJ. The influence of wood flour particle size and content on the rheological, physical, mechanical and morphological properties of EVA/wood cellular composites. *J Mater&Design*. 2014;57: 660-665.
- [30] Donmez Cavdar A, Mengeloglu F, Karakus K. Effect of boric acid and borax on mechanical, fire and thermal properties of wood flour filled high density polyethylene composites. *J Measurement*. 2015; 60:6-12.
- [31] Jeske H, Schip A, Cornelius F. Development of a thermogravimetric analysis (TGA) 22tiliz for quantitative analysis of wood flour and propylene in wood plastic composites (WPC). *J Thermochemica Acta*. 2012;543:165-171.
- [32] Zhao M, Ding X, Mi J, Zhou H, Wang X. Role of high-density polyethylene in the crystallization behaviors, rheological property, and supercritical CO<sub>2</sub> foaming of poly (lactic acid) . *J Polym Degrad Stab*. 2017; 146: 277-286.
- [33] Zhou H, Zhao M, Qu Z, Mi J, Wang X, Deng Y. Thermal and Rheological Properties of Poly(lactic acid)/Low-Density Polyethylene Blends and Their Supercritical CO<sub>2</sub> Foaming Behavior. *J Polym Environ*. 2018; 26 (9): 3564–3573.
- [34] Wang X, Li Y, Jiao Y, Zhou H. Microcellular Foaming Behaviors of Poly (Lactic Acid)/Low-Density Polyethylene Blends Induced by Compatibilization Effect. *J Polym Environ*. 2019; 27 (8): 1721–1734.
- [35] Boubekour B, Belhaneche- Bensemra N, Massardier V. Valorization of waste jute fibers in developing Low-density polyethylene/Poly(lactic acid) bio-based composites. *J Reinf Plastics*. 2015; 34:649-661.
- [36] Tsou CY, Wu CL, Tsou CH et al. Biodegradable Composition of Poly (lactic acid) from Renewable Wood Flour. *J Polym Sci Serie B*. 2014; 5: 473-480.
- [37] Hu R-H, Sun M-Y, Lim J-K. Moisture absorption, tensile strength and microstructure evolution of short jute fiber/Poly(lactic acid) composite in hydrothermal environment. *J Mat Design*. 2010;31:3167-3173.
- [38] Ashori A, Nourbakhsh A. Bio-based composites from waste agricultural residues. *J Waste Management*. 2010;30:680-684.
- [39] Al Maadeed M.A, Kahraman R et al. Date palm wood flour/glass fibre reinforced hybrid composites of recycled polypropylene, Mechanical and thermal properties. *J Mater & Design*. 2012;42:289-294.
- [40] Pérez E, Famá L, Pardo SG et al. Tensile and fracture 22tilizin of PP/wood flour composites. *J Compos Part B*. 2012;43 :2795-2800.
- [41] Singh S, Mohanty AK. Wood fiber reinforced bacterial bioplastic composites : Fabrication and performance evaluation. *J Compos Sci Techn*. 2007;67:1753-1763.
- [42] Latreche L, Haddaoui N. Etude des Proprietes Mecaniques d'un Materiau Bio-Composite Polyepoxymeyhylene/Farine de Bois. *J Verres Céramiques & Composites*.2015;4:15-19.

- [43] Anderson S, Zhang J, Wolcott MP. Effect of Interfacial Modifiers on Mechanical and Physical Properties of the PHB Composite with High Wood Flour Content. *J Polym Environ.* 2013;21:631–639.
- [44] Petinakis E, Liu X, Yu L, Way C, Sangwan P, Dean K, Bateman S. Biodegradation and thermal decomposition of poly(lactic acid)-based materials reinforced by hydrophilic fillers. *J Polym. Degrad Stab.* 2010;95:1704-1707.
- [45] Ndlovu SS, Van Reenen AJ, Luyt AS. LDPE- Wood composites utilizing degraded LDPE as compatibilizer. *J Compos Part A.* 2013;51: 80-88.
- [46] Anwer MAS, Naguib HE et al. Comparison of the thermal, dynamic mechanical and morphological properties of PLA-Lignin & PLA-Tannin particulate green composites. *J Compos Part B.* 2015;82: 92-99.
- [47] Dong Y, Ghataura A, Takagi H et al. Polylactic acid (PLA) biocomposites reinforced with coir fibres : Evaluation of mechanical performance and multifunctional properties. *J Compos Part A.* 2014;63:76-84.
- [48] Akos NI, Mat UW, Abdirahman AY. Effect of Fiber Reinforcement on Mechanical and Thermal Properties of Poly( $\epsilon$ -caprolactone)/Poly(Lactic Acid) Blend Composites. *J Fibers and Polym.* 2014; 3:574-582.
- [49] Moshiul Alam AKM, Mina MF, Beg MDH et al. Thermo-Mechanical and Morphological Properties of Short Natural Fiber Reinforced Poly (Lactic Acid) Biocomposite: Effect of Fiber Treatment. *Fibers and Polym.* 2014; 15:1303-1309.
- [50] Lee S-H, Wang S. Biodegradable polymers/Bamboo fiber biocomposite with bio-based coupling agent. *J compos Part A.* 2006; 37:80-91.
- [51] Badia J-D, Kittikorn T, Strömberg E, Santonja-Blasco L, Martínez-Felipe A, Ribes-Greus A, Ek M, Karlsson S. Water absorption and hydrothermal performance of PHBV/sisal. *J Polym Degrad Stab.* 2014; 108: 166-174.