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#### **Publisher's version / Version de l'éditeur:**

*Proceedings Annual Technical Conference(ANTEC 2011), 2011-05-01*

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# NEW WOOD FIBER BIOCOMPOSITES BASED ON POLYLACTIDE AND POLYLACTIDE / THERMOPLASTIC STARCH BLENDS

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## Abstract

This paper aims at developing natural fiber biocomposites based on biopolymers reinforced with wood fibers obtained from a thermo-mechanical refining process. Polylactide (PLA) and polylactide/thermoplastic starch blends (PLA/TPS) were used as matrices. Two grades of PLA, an amorphous and a semi-crystalline one, were considered with the purpose to investigate the effect of wood fibers on the crystallinity, and therefore, on mechanical properties of composites. Two grades of thermoplastic starch (TPS), different in plasticizer content and nature, were used. TPS content in the PLA/TPS blends was 50%. Moreover, two wood fiber types were selected, a hardwood (HW) and a softwood (SW), to state the effect of the fiber type on the biocomposite properties. Finally, the impact of different additives on biocomposite properties was studied with the purpose to enhance the biopolymer/wood fiber affinity with the best impact on the final mechanical performance. The biocomposites containing 30% by weight of wood fibers were obtained by co-rotating twin-screw extrusion. The properties are described in terms of morphology, thermal, rheological, and mechanical properties. With respect to wood type, there was almost no differentiation between reinforce ability of SW and HW for the studied formulations. Similar observations were done regarding the two grades of PLA on the mechanical properties (i.e. tensile strength and elastic modulus) of biocomposites. Concerning the thermal properties, semi-crystalline PLA biocomposites shown an increase in crystallization kinetics and a decrease of the fully crystallinity due to the wood fibers presence. A twofold increase in elastic modulus and an increment in tensile strength of 11% were observed for uncompatibilized PLA/wood fiber composites. Despite good tensile results and an inherent affinity between PLA and wood fibers, further improvement was reached by increasing the adhesion in adding coupling agents and by preserving the PLA molecular weight using a branching agent. The best mechanical results were achieved for composites containing the branching agent, most probably due to the branching of the PLA chains. PLA/wood fiber biocomposites present higher mechanical properties than polypropylene counterpart

and are very promising candidates for many applications, especially in construction interior applications.

## Introduction

Public awareness about the environment, increasing crude oil prices, and new regulations on the use of non-renewable resources to generate energy and materials are main drivers to move from petroleum-based plastics to bioplastics. The global capacity of bio-based thermoplastics was about 435 ktons / year at the end of 2009. The biodegradability is the most important property of bioplastics. However, polylactic acid (PLA), polyhydroxyalkanoate (PHA) and starch-based plastics each carry concerns about shelf life and hydrolytic stability.

The current research on the biopolymers and biocomposites development resulted in promising outcomes which led the market interest move from single-use to durable products. Different additives, impact modifiers and reinforcing agents have been used in bio-based polymers to improve their mechanical performance and hydrolytic stability. In many works, wood flour [1-3] and plant fibers, such as flax, kenaf and hemp [4-6] have been used as reinforcing phase in bio polymers. The introduction of wood, rice husk, and kenaf fibers into PLA improves the tensile and flexural properties of the composites. It has been shown that the addition of butantetracarboxylic acid modified wood fibers into the PLA reduces the water retention, swelling and moisture sorption of the PLA-based composites [7]. Also, triacetin, maleic anhydride grafted PLA and cellulose acetate can act as coupling agents [8, 9]. Mechanical performance of natural fiber-biopolymer composites was compared with flax fibre-PP counterpart. The tensile strength and modulus of PLA and PLA flax fibre composites were superior to those of PP flax fiber composites.

In this work, new biocomposites based on PLA and on PLA/TPS blends using wood fibers as reinforcement have been processed in a twin screw extruder and then injection molded. The effects of coupling agent, branching agent and wood fibers on the morphology,

mechanical, rheological, and thermal properties were studied.

## Experimental Part

### Materials

Two different grades of PLA supplied by NatureWorks were used in this study. PLA8302D is amorphous (aPLA) and PLA2002D is semicrystalline (cPLA), with approximately 10% and 4% respectively of *D*-lactic acid monomer. The two different thermoplastic starch materials, prepared through reactive extrusion processing, contain 36% glycerol (TPS36-1) and 24% glycerol + 12% sorbitol (TPS36-2) as plasticizers [10]. PLA/TPS were blended by extrusion using only the aPLA and TPS36-2 at a 50/50% weight ratio in order to screen the composite blend behaviour. The wood fibers, yellow birch (HW) and black spruce (SW), were supplied by FPIInnovations, Wood Products division in Quebec, Canada. They were obtained from wood chips via a thermo-mechanical refining process usually used to produce MDF wood fibres.

The grafting of maleic anhydride onto PLA was performed in a separate extrusion step using 2% maleic anhydride (MA) and 0.25% peroxide initiator, 2,5-dimethyl-2,5-di-(tert-butylperoxy)hexane (Luperox 101), both obtained from Sigma-Aldrich Chemical Company. The process configuration for the reactive extrusion was based on reference [10]. The triacetin (TA) was provided by MAT Laboratories and the cellulose acetate (CA) in the form of powder was provided by Scientific Polymer Products Inc. TA [8] and CA [9] are reported in the literature as coupling agents for cellulose fibers and are used in this study to verify their potential. The chain-extender (CE), CesaExtend OMAN698493 from Clariant, is an epoxy/styrene/acrylic copolymer, provided in masterbatch form in a PLA carrier. The epoxy groups are believed to react preferentially with the carboxyl end-groups of the PLA chains to form a branched chain structure. It has been reported that the addition of 2% CE in PLA upon extrusion increases PLA viscosity about one order of magnitude due to its branching effect [11].

### Extrusion Process

In order to facilitate the feeding of natural fibers into the extrusion process, a granulation step is essential because MDF wood fibers are fluffy and difficult to feed in this shape without compromising the fiber flow rate stability. A special pelletizing step of fibers was added prior to composite extrusion.

The equipment used to obtain the composites was a Buhler 20 mm co-rotating twin-screw extruder with a L/D ratio of 40. The polymer and pelletized wood fibers were fed simultaneously in the first zone. The extrusion temperature of 170-180°C, normally used for PLA and TPS, was ideal to keep the fibers away from their thermal degradation, which usually starts at 200-210°C.

The extruder, equipped with a 2 mm diameter capillary die was operated at a constant screw rotation speed of 150 rpm, and the flow rate was set at 2 kg/h. Care was taken to dry the polymers and fibers pellets for a 12 hours at 80°C before extrusion. The different biocomposite formulations are summarized in Table 1. In all composites, the wood fiber concentration was 30% in weight.

**Table 1.** Summary of processed formulations along with additive concentrations used in biocomposites.

Matrix	Fiber type	Compatibilizer					
		None	PLAg 20%	BA 2%	PLAg +BA	CA 10%	TA 5%
aPLA	none	√	√	√	√		
	SW	√	√	√	√	√	√
	HW	√	√	√	√	√	√
cPLA	none	√	√	√	√		
	SW	√	√	√	√	√	√
	HW	√	√	√	√	√	√
aPLA/TPS-2 50/50%	none	√	√		√		
	SW	√	√		√		
	HW	√	√		√		

### Rheology

The rheological properties were measured at 185°C using a rotational rheometer with a plate-plate geometry in dynamic mode. The plate diameter was 25 mm and the gap was around 1.7 mm. Frequency sweeps were carried out to determine complex viscosity over a frequency ranging from 0.1 to 100 rad/s. The tests were conducted for a deformation of 15%. Care was taken to dry the materials at 80°C for 48 hours before testing. The samples were kept under a nitrogen blanket during the testing to minimize oxidation and to maintain a dried environment.

### Morphology

Scanning electron microscopy (SEM) was carried out on samples coated with a gold/palladium alloy prior to the observation. JEOL JSM-6100 SEM at a voltage of 10 kV was used to analyze a) the dispersion of wood fibers into the matrix using polished surfaces and b) the interface between wood PLA and PLA/TPS matrices using the fractured specimens.

### Differential Scanning Calorimetry

The values of melting temperature, percent crystallinity and crystallization temperature of the materials were performed by DSC. Non-isothermal tests were done using a TA Instruments Q2000 calibrated with an indium standard. The samples were heated from 30 to 220°C at 20°C/min, kept at 220°C for 5 minutes to erase the thermal history and cooled down to 30°C at 20°C/min. For isothermal tests on biocomposites, the cycle consisted, after heating and equilibration, in a rapid cooling down to 110°C at 60°C/min, isothermal for 5 hours at 110°C and a heating from 110 to 220°C at

20°C/min. A value of 93 J/g was taken for PLA's theoretical heat of fusion [12].

## Mechanical Properties

After extrusion, the biocomposite pellet were dried at 55°C for 24 hours and then injection molded using a 30 tons Boy injection press with a screw temperature at about 190°C and mold temperature around 30°C. The tensile testing was carried out at a rate of 5 mm/min according to ASTM D638 on standard type I specimens with a thickness of 3.1 mm. The samples were conditioned at 50°C under vacuum for 40h before mechanical testing. At least 5 specimens were tested for each formulation.

## Results and Discussion

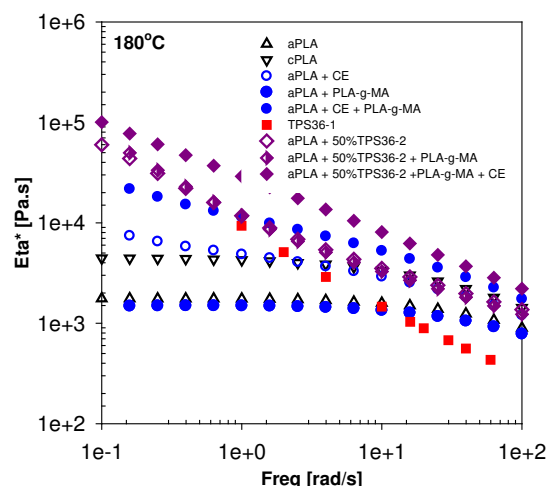
Wood fibers used in this work were received in a wet state with moisture content of 50%. This high water content was needed to facilitate the fiber pelletizing process. During this process, the wet wood fibers were pressed through a die plate by rotating roll-mills. There was no thermal degradation observed after the pelletizing step and the fiber integrity was preserved. The temperature monitored during the process was kept at 70°C. The length average fiber length, measured using a HiRes FQA, was 1.63 mm for SW and 1.36 mm for HW before pelletizing. Fibers gently separated from the wood pellets had a length average fiber length of 0.70-0.73 mm. The physical aspect of wood fibers before and after pelletizing is presented in Figure 1.



**Figure 1.** Physical aspect of wood fibers and pellets.

Rheological properties of PLA, TPS and blends at 50% TPS were analyzed. Figure 2 presents the complex viscosity of the non-reinforced polymer matrices as a function of frequency. At low shear rates, semicrystalline PLA had a higher shear viscosity than amorphous PLA. Both PLA grades exhibited clear Newtonian plateaus with a zero-shear viscosity around 1.8 kPa for aPLA and 4.4 kPa for cPLA. As the temperature increased, the shear viscosity decreased for both types of PLA. As expected, adding 2% CE to PLA increased viscosity and there was no Newtonian plateau observed in the investigated frequency range. On the other hand, PLA-g-MA had almost no effect on PLA melt viscosity. In the

presence of both PLA-g-MA and CE the viscosity is 50% higher than the CE containing matrix. TPS does not exhibit any Newtonian viscosity plateau and is highly shear thinning. This behaviour is typical of branched or highly entangled polymer melts. As well, the PLA blend with 50% TPS did not show a viscosity plateau and are highly shear thinning. They are more viscous than both TPS and aPLA. The introduction of PLA-g-MA in the blend as an interface modifier has a limited impact on the rheological properties. Adding CE to the blend significantly increases viscosity. This was expected as PLA chain mobility is reduced due to branching.



**Figure 2.** Complex viscosity as a function of frequency for polymer matrices.

**Table 2.** Non-isothermal data obtained during the 1<sup>st</sup> DSC heating cycle for cPLA and cPLA- biocomposites

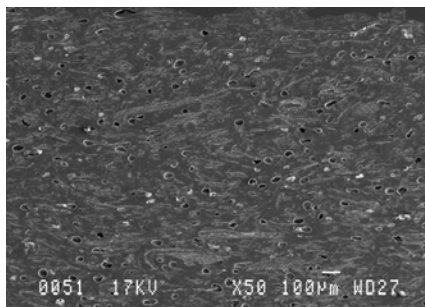
Based on cPLA	T <sub>g</sub> (°C)	T <sub>m</sub> (°C)	Xc Initial (%)
extruded	62.9	n/a	0.0
CE	64.3	146.0	0.8
PLA-g-MA	62.6	n/a	0.0
PLA-g-MA+CE	63.3	n/a	0.0
HW	62.8	146.6	1.1
SW	62.2	144.5	0.1
HW+CE	63.1	151.4	1.8
SW+CE	62.6	152.8	1.9
HW+ PLA-g-MA	61.7	146.5	0.6
SW+PLA-g-MA	60.8	145.9	0.8
HW+CE+PLA-g-MA	61.9	150.0	0.0
SW+CE+PLA-g-MA	61.7	150.7	8.7
HW+CA	60.7	145.4	0.8
SW+CA	60.2	145.9	0.5
HW+TA	50.3	149.5	12.1
SW+TA	49.1	147.7	15.4

Table 2 discloses the non-isothermal data for cPLA and its composites extracted from DSC curves resulted

from the first heat cycle. The extruded cPLA has a  $T_g$  of 63°C. As expected almost no crystallinity was observed because it has a very low crystallization rate for all formulations tested. The presence of CE slightly increased the  $T_g$  and PLA-g-MA had no observable effect. For formulation with wood fibers, the glass transition temperature was maintained around 62°C except for the biocomposites processed in the presence of TA as coupling agent. Indeed, TA demonstrated a high plasticizer effect and reduced  $T_g$  at around 50°C. The melting temperature was around 145°C for the composites with no additive, with CA and for the maleic anhydride-modified composites, while the  $T_m$  was increased by 5°C on the composites containing CE. This could be explained by the increment of cPLA molecular weight due to CE branching effect. Modest initial crystallinity content was developed in composites excepting in the presence of TA that enhanced the crystallization.

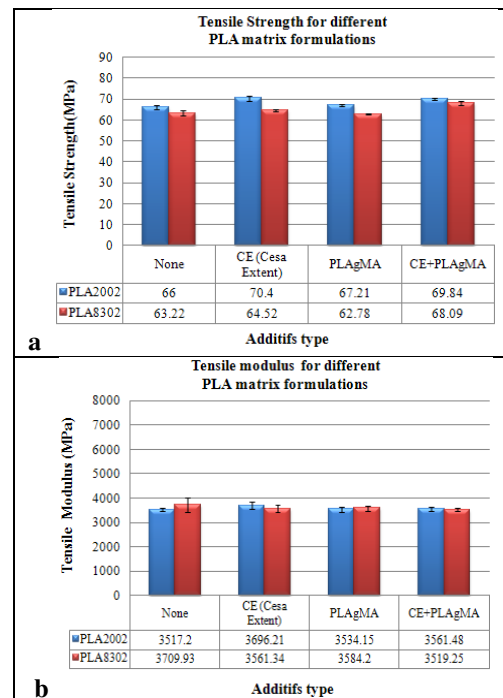
**Table 3.** Half-time of crystallization, crystallinity and melting temperature of biocomposites based on cPLA

Based on cPLA	$t_{1/2}$ (min)	Xc iso (%)	$T_m$ peak (°C)
extruded	89.7	33.4	148.5
CE	53.0	27.3	147.2
PLA-g-MA	85.7	32.7	148.0
CE+PLA-g-MA	27.3	26.6	149.4
HW	33.7	33.0	147.9
SW	25.1	26.5	145.2
HW+CE	12.3	25.2	152.6
SW+CE	11.0	23.8	151.2
HW+PLA-g-MA	26.8	28.5	148.1
SW+PLA-g-MA	20.7	28.2	147.6
HW+CE+PLA-gMA	17.8	27.6	149.6
SW+CE+PLA-g-MA	10.2	25.8	150.6
HW+CA	63.4	25.0	148.3
SW+CA	62.6	28.0	148.7
HW+TA	15.2	27.2	152.6
SW+TA	12.6	27.0	151.8



**Figure 3.** SEM micrograph for cPLA/30%SW.

Table 3 shows the isothermal crystallization data for the cPLA and related biocomposites. It can be observed that all materials undergone high isothermal crystallizations. The extruded cPLA had a crystallization half-time,  $t_{1/2}$ , of 90 minutes approximately. cPLA with CE presented a lower  $t_{1/2}$  of around 53 minutes and the crystallinity was decreased at 27.3%. The CE increased the crystallization rate but decreased the fully crystallinity due to its branching effect. PLA-g-MA had roughly no effect but in conjunction with CE displayed a  $t_{1/2}$  of 27 minutes. The introduction of wood fibers slightly lowers the full crystallinity. However,  $t_{1/2}$  was roughly divided by three, which points out that the wood fibers increased the crystallization rate but did not significantly modify the crystallinity. When the composite formulations incorporated CE,  $t_{1/2}$  was decreased down to 10 to 20 minutes. It is expected that the crystallinity developed in cPLA based biocomposites has an effect on its mechanical performance in comparison with the aPLA biocomposites that cannot crystallized.

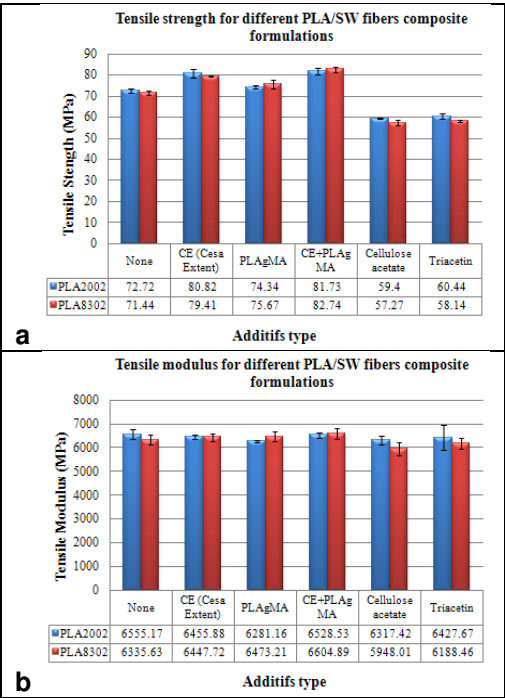


**Figure 4.** Tensile properties of different PLA based formulations: a) tensile strength at break and b) elastic modulus.

The screw configuration used in the extrusion experiments was designed to obtain a very good dispersion of the wood fibers into the polymer melt. Figure 3 unveils the morphology of polished longitudinal surface for cPLA/30% SW showing good fiber dispersion. The SEM observations showed that similar dispersions were obtained for all the formulated composites. This can be explained by the inherent

adhesion coming from the hydrophilic characteristics of both the polymer matrix (i.e. PLA or PLA/TPS) and the wood fibers.

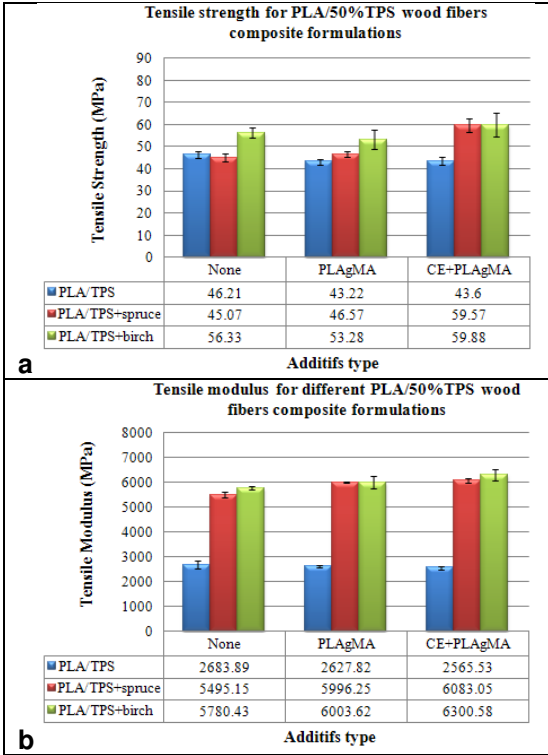
The effect of compatibilizers was investigated only on PLA matrices. Figure 4 summarizes the tensile test results. As can be seen, CE has a minor effect in the augmentation of tensile strength and no effect on tensile modulus. This is most probably due to its branching effect. On the other hand, PLA-g-MA alone has no effect on the measured tensile properties as expected. Concerning the two PLA grades, there could be seen a slightly higher tensile strength for cPLA this difference and an identical tensile modulus.



**Figure 5.** Tensile properties of biocomposites based on PLA and SW fibers: a) tensile strength at break and b) elastic modulus.

The tensile properties of cPLA and aPLA based biocomposites reinforced with SW are disclosed in Figure 5. The tensile properties of HW biocomposites are not presented here as the results obtained were very similar. The materials that contained CE in their formulation performed very well: the tensile strength values are increased by 11% compared to the uncompatibilized biocomposites and more than 20% compared to the virgin PLA materials (Figure 4). This improvement primarily is the result of the branching effect of the chain extender on the matrix. The tensile modulus proved an increment of nearly 100% in all cases compared to the pure PLA matrix. When CA and TA were used as compatibilizers, a high decrease in tensile strength was observed, contrarily to the results presented

in the literature [8, 9]. Further work has to be done to understand this behavior.

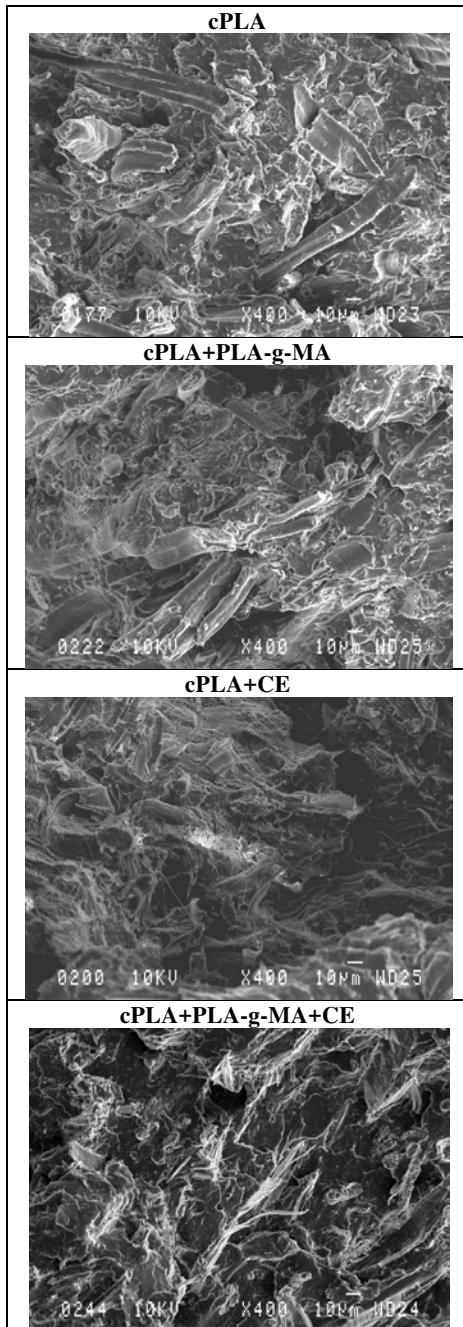


**Figure 6.** Tensile properties of composites based on aPLA/TPS: a) tensile strength at break and b) elastic modulus.

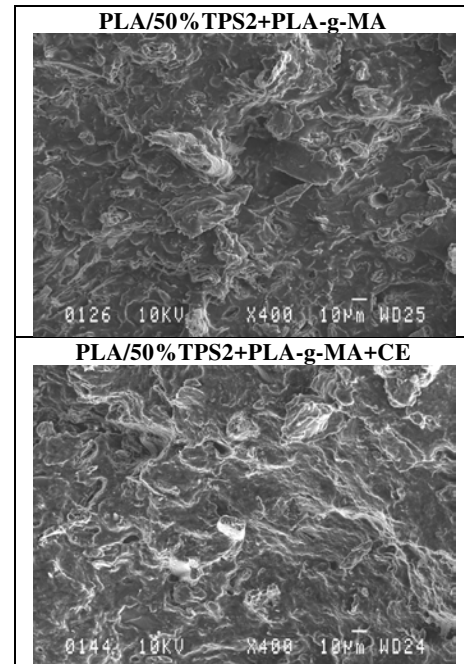
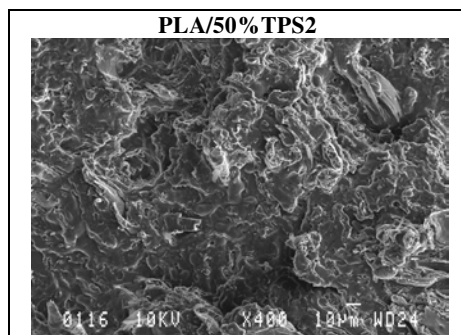
From the data presented in Figure 6, it is obvious that the wood fiber type did give the same composite behavior this reinforcement had a comparable effect on the PLA/TPS matrices as in PLA matrix alone. Indeed, the elastic modulus increased more than two times compared with the matrix (i.e. 6300 vs. 2600 MPa), which is similar to the PLA-based biocomposites. Tensile strength is also increased by 31% in comparison with the corresponding matrix. The more pronounced effect was observed when CE and PLA-g-MA were used simultaneously in the biocomposite formulation. The effect of CE and PLA-g-MA synergism on tensile strength can be observed only in the presence of wood fibers, while it cannot be seen on aPLA/50%TPS36-2 matrix alone.

Fractured surfaces were also analyzed and are presented in Figure 7. The addition of CE or CE/PLA-g-MA in biocomposites led to a high attenuation of fiber pull out phenomenon and the related composites displayed almost no sign of fiber pull out while a limited amount of pull out was visible in the case of PLA-g-MA formulations. The same microstructural observation, i.e. the disappearing of the pull out when CE was used, was done in the case of aPLA/50%TPS36-2 based biocomposites (Figure 8). This beneficial effect of the CE branching agent sustains the tensile results.





**Figure 7.** SEM microstructural details of surface fracture for cPLA-HW composites



**Figure 8.** SEM microstructural details of surface fracture for aPLA/50%TPS2-HW composites

## Conclusions

This work aimed at developing and characterizing novel biocomposites based on PLA or PLA/TPS blend reinforced with wood fibres by varying the matrix properties and wood fiber nature as well as using additives for their coupling ability. The ability of the studied wood fibers to reinforce PLA or PLA/TPS matrices has been assessed. A twofold increase in elastic modulus and an increase in tensile strength of 14% were obtained for uncompatibilized PLA biocomposites. In the presence of reactive additives, the best results were achieved for composites that contained the branching agent, and a combination of coupling and branching agent. PLA/wood fiber biocomposites present higher mechanical properties than PP counterpart and are very promising candidates for many applications, especially for the interior in the building and construction industry.

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Key Words: polylactide, thermoplastic starch, wood fibers, composites extrusion