COMPATIBILIZATION OF POLYLACTIDE-BASED FLAX FIBER BIOCOMPOSITES

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1 Introduction

Biocomposites production by the combination of thermoplastic polymers and natural fibers has experienced significant growth in recent years. This fact is mainly due to the continuous research focusing on developing sustainable materials that offer interesting mechanical properties and lower cost. The use of renewable resources can also contribute to energy savings. The plastic industry is interested in providing this bio-based materials to sectors such as automotive, aerospace and construction.

Cellulose fibers are attracting increased attention because of their potential as biodegradable reinforcements and the wide range of their properties and industrial applications. The main advantage of cellulose fibers over synthetic fibers is their low mass density. There is a wide variety of natural fibers to consider, the choice being based on the unique properties that each plant can offer. One of the best known and most widely used natural fibers are flax fibers, due to their high stiffness and strenght, availability and versatility [1]. The structure of the flax fibre is composite-like in itself, with long bundles consisting of elementary fibres with relatively thick walls mainly composed of cellulose and lignin [2].

Aliphatic polyesters, such as polylactide (PLA), have shown great potential as biodegradable plastics as they can degrade in just a few years, opposed to conventional plastics requiring hundreds of years to degrade [3]. PLA is produced from renewable resources through lactic acid fermentation, then converted into lactide, which is then subjected to ring-opening polymerization [4].

The mechanical performance of composites is deeply influenced by the properties of the fiber-matrix interface, the aspect ratio and the dispersion and orientation of the fibers [5-7]. The intrinsic characteristics of fibers and the matrix also have an impact on the behavior of the material. The transfer of stress from the matrix to the fibers can be maximized by increasing fiber-matrix interactions, as well as reducing the fiber degradation during compounding. The tensile modulus and tensile strength of composites generally increases with the L/D ratio of the reinforcing fibers [8]. Therefore, the mechanical properties may be sensitive to the production process of the composite, since fiber breakage is prone to ocur during the process of mixing, extrusion and molding [9].

The main drawback regarding the biocomposite performance is the low adhesion between the fibers (often polar and hydrophilic) and the matrix (often non-polar and hydrophobic). The polar hydroxyl groups on the surface of the fibers form a weak interface with the matrix. This low compatibility can lead to a significant loss of mechanical and thermal properties in the composites. Therefore, improving the fiber-matrix interface is extremely important in the composites industry [10]. Strong adhesion between the fibers and the matrix may also contribute to the reduction of moisture absorption by the composite [11].

In the last decades, numerous studies have examined the improvement of the fiber-matrix interface through three main approaches: (1) physicochemical modification of the fiber surface, (2) use of coupling agents such as maleic anhydride (MA), and (3) fiber irradiation [12-14]. The use of MA grafted polymers as a coupling agent between the fibers and the matrix might be considered a good example of compatibilization. MA grafted PLA (PLA-g-MA) is not commercially available, but it can be synthesized using solution polymerization or through reactive extrusion [15,16]. Several investigations have reported improvements in the range of ~10% on tensile and flexural strengths as biocomposites are compatibilized with PLA-g-MA. No significant

enhancements in glass or heat deflection temperatures were observed [10,15,17]. Most of the authors claim better fiber-matrix interactions when the modified MA matrix is added to the system; however, it is difficult to evidence this fact from the microscopy observations.

The present study aims at examining the compatibilization potential of PLA-g-MA on the fully bio-based and biodegradable PLA based flax fiber system. Tensile testing, size fibers analysis before and after compounding and scanning electron microscopy analysis have been used to investigate the biocomposite mechanical behavior and microstructure, respectively, with and without PLA-g-MA.

2 Experimental details

2.1 Materials

The polylactide (PLA) was obtained from NatureWorks LCC. It is a semi-crystalline grade (PLA 4032D) comprising around 2% D-lactide. Flax fibers, cut to a nominal length of 1 mm, were kindly supplied by *Laboratoire d'Ingénierie des MATériaux de Bretagne* (LIMATB, France). PLA-g-MA was prepared in a twin-screw extruder using 2 wt% maleic anhydride and 0.25 wt% of a peroxide initiator, following a procedure reported earlier [6].

2.2 Samples preparation

PLA-flax fiber composites were prepared by melt mixing in an internal mixer Plasticorder (C.W. Brabender) under a nitrogen atmosphere. PLA pellets and flax fibers were previously dried at 80 °C for 24 h under vacuum. The nominal flax fiber content was set at 5, 10 and 20 wt% and the PLA-g-MA was used at 2.5, 5 and 10 wt%. Two different batches of each blend were prepared to verify reproducibility; the total mass per batch was kept at 30 g in all cases. For comparison purposes, neat PLA and PLA-g-MA underwent the same thermo-mechanical cycle. Table 1 summarizes the formulations prepared with their nomenclature.

2.3 Characterization techniques

MA Content

The degree of grafting was evaluated by a titration method according to the procedure described by Nabar et al. and Hwang et al. [18,19]. Purified PLA-g-MA samples of ~1 g were dissolved in 100 mL of chloroform, and 10 drops of 1% phenolphthalein in ethanol were added. The titration was performed

with 0.03 N of potassium hydroxide (KOH) in methanol, and the pH at endpoint was measured. At least three samples of two different batches were analyzed. The determined average content of MA was 0,63 wt% ± 0.02.

Rheological characterization

The rheological properties of PLA-g-MA and PLA with different contents of PLA-g-MA were measured at 180 °C using a MCR 301 rheometer with a parallel plate flow geometry in dynamic mode. The thermal stability of the samples was verified by monitoring the complex viscosity at 1 rad/s over time. Frequency sweep tests were performed over a frequency range of 0.1 to 100 rad/s, from low to high frequency. At least two measurements of the same test were carried out.

Mechanical properties

Measurements were performed according to ASTM D638 for tensile properties of plastics. Tensile testing was carried out in an Instron universal testing machine using a load cell of 5 kN. For each formulation, six to twelve standard type V dog-bone shaped samples were tested using a crosshead speed of 1 mm/min at room temperature. An extensometer was directly mounted on each test specimen with elastic bands in order to evaluate the strain accurately. Statistical analysis was performed using two-tailed Student's t-test with a significance level of 0.05 and 0.10.

Optical Microscopy

As-received flax fibers and 80 μm thick PLA-based biocomposite films were observed using a Zeiss Axioskop 40 optical microscope in transmission mode. The size and state of dispersion of flax fiber before and after blending were evaluated. Diameter and length averages were calculated based on ~400 fibers for dry fibers, and ~400 fibers in the case of PLA composite films.

Scanning Electron Microscopy

The fracture surfaces of selected tensile specimens were analyzed by scanning electron microscopy (SEM). The samples were sputter-coated with a thin layer of gold in an Edwards Sputter Coater, and observed with a Jeol JSM 6460LV scanning electron microscope.

Table 1. Formulations prepared by melt compounding.

| Sample	PLA (wt%)	Flax Fiber (wt%)	PLA-g-MA (wt%)	α[1]
Neat PLA	100	--	--	--
PLA-g-MA	100	--	--	--
PLA/5 PLA-g-MA	95	--	5	--
PLA/10 PLA-g-MA	90	--	10	--
PLA/5	95.0	5.0	--	--
PLA/5/2.5	92.5	5.0	2.5	2
PLA/5/5	90.0	5.0	5.0	1
PLA/10	90.0	10.0	--	--
PLA/10/5	85.0	10.0	5.0	2
PLA/10/10	80.0	10.0	10.0	1
PLA/20	80.0	20.0	--	--
PLA/20/5	75.0	20.0	5.0	4
PLA/20/10	70.0	20.0	10.0	2

3 Results and Discussion

3.1 Rheology

Rheological measurements were carried out in order to study the thermal stability and behavior of PLA-g-MA and its blends with the PLA matrix. The complex viscosity of PLA-g-MA (Fig. 1a) was highly inferior in comparison with that of PLA matrix undergoing the same melt compounding (not shown). The latter presented an initial complex viscosity of ~3000 Pa.s [20]. The coupling agent showed an initial value of about 80 Pa.s, and this property decreased with time at an average ratio of 2.5%/min. This rapid drop was not evidenced in the blends of the PLA matrix containing 5 and 10 wt% of PLA-g-MA, for which the loss in complex viscosity after 10 min reached ~2% and ~5%, respectively. These blends exhibited initial values of ~2400 and ~2000 Pa.s (Fig. 1a). The low viscosity of PLA-g-MA is due to the grafting reaction taking place during the reactive extrusion process used to produce this coupling agent.

Figure 1b shows the frequency sweeps of the systems described above. Frequency sweep tests lasted for about 10 min; in this time range thermal degradation was not a major concern for the

formulations containing 5 and 10 wt% of PLA-g-MA. Their curves showed a Newtonian plateau at low frequency followed by a shear thinning behavior at angular frequency higher than 10 rad/s. In the case of PLA-g-MA, reproducibility at low frequencies was an important issue most probably for its low viscosity and considerable degradation over time. This sample presented a Newtonian behavior all over time range; no evidence of shear thinning was found, In terms of reproducibility, repeated tests presented error values less than 5% for PLA/PLA-g-MA systems. Reliability between time sweeps and frequency sweeps were also verified in all cases.

a)
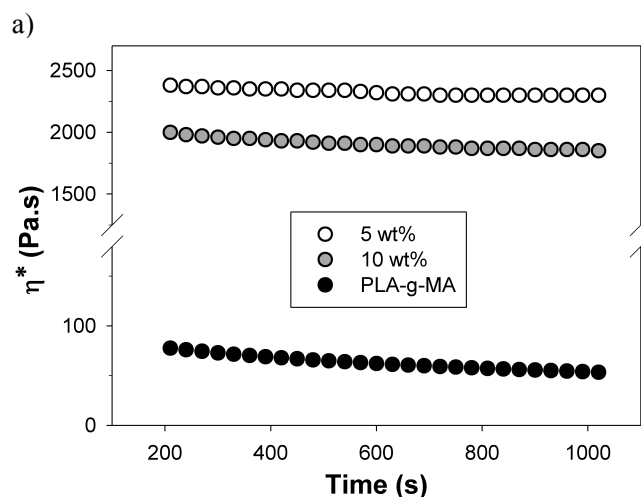
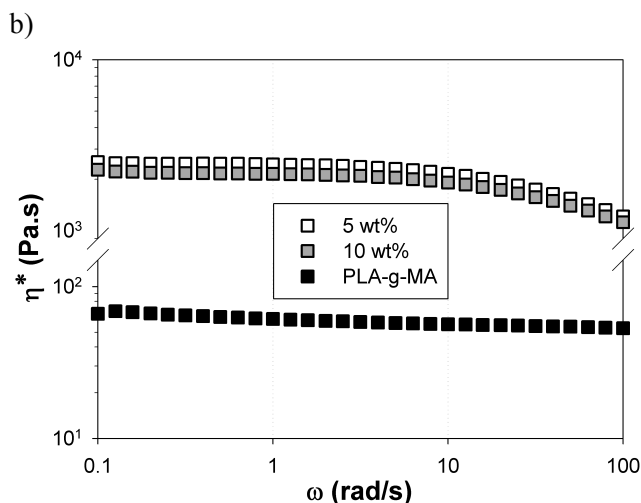1 α is the ratio between the weight content of flax fiber and PLA-g-MA.

b)

Fig. 1 Rheological properties of PLA-g-MA and blends of PLA containing 5 and 10 wt% of PLA-g-MA, a) Time sweeps and b) Frequency sweeps.

3.2 Mechanical properties

The tensile properties of various formulations are reported in Table 2. The Young Modulus of neat PLA increased by about 45% following the addition of 10 wt% of flax fibers, and was doubled at 20 wt% of flax fibers. The Young's modulus of the PLA-10 wt% flax fiber system increased slightly as the PLA-g-MA concentration was raised. Gains of ~4 and ~15% were found for 5 and 10 wt% of compatibilizer, respectively. However, at 20 wt% of flax fibers, the addition of PLA-g-MA did not augment the elastic modulus of the uncompatibilized biocomposite. In fact, at 5 wt% of PLA-g-MA, the modulus was reduced by ~6% and at 10 wt% this property remained constant. A statistical analysis indicated that there was not a significant improvement of the Young modulus for the PLA-g-MA compatibilized composites. This can be explained by the large standard deviations obtained for all composites.

Tensile strength exhibited improvements of 4 and 11% for the biocomposites containing 10 and 20 wt% of flax fibers, respectively. In the case of 10 wt% PLA-g-MA compatibilized biocomposites, this property showed a small increase of ~2.5%. Surprisingly, at 5 wt% of PLA-g-MA the tensile strength showed a slight decrease of ~8% for the 10 wt% flax fiber biocomposite and 2.5% in the case of 20 wt% of flax fiber. However, from a statistical point of view, none of these changes are significant.

Regarding the elongation at break, neat PLA presented a value of 3.1%, confirming its brittle character. This property was decreased by 25% to 45% for all biocomposites. As we could expect, elongation at break decreased further as flax fiber content rose. Addition of PLA-g-MA did not bring significant modifications of this property. All biocomposites containing 10 wt% of flax fibers showed an elongation at break of ~2.3%, whereas for 20 wt% of reinforcement, the measured elongation at break was ~1.9%.

Table 2. Tensile properties of various biocomposites. The two numbers following 'PLA' refer to wt% of flax fiber and PLA-g-MA, respectively.

Formulations	Number of samples tested	Young Modulus (MPa)	Tensile Strength (MPa)	Elongation at break (%)
Neat PLA	12	3170 ± 378	62.0 ± 2.3	3.12 ± 0.8
PLA/10	12	4550 ± 315	64.2 ± 1.5	2.28 ± 0.2
PLA/10/5	6	4738 ± 535	58.6 ± 2.6	2.28 ± 0.3
PLA/10/10	6	5212 ± 551	65.6 ± 0.7	2.33 ± 0.2
PLA/20	12	6324 ± 500	68.6 ± 1.5	1.94 ± 0.2
PLA/20/5	12	5940 ± 560	67.0 ± 3.9	1.70 ± 0.3
PLA/20/10	12	6380 ± 580	70.5 ± 3.3	1.97 ± 0.2

3.3 Aspect ratio distribution

Flax fiber breakage during compounding may result in two main consequences: (1) increased individual fiber content by breaking up fiber bundles, and (2) significantly reduced fiber length and therefore aspect ratio. On the other hand, coupling agents localized preferentially at the fiber-matrix interface may increase stress transfer at the interface.

Therefore using a coupling agent may affect fiber breakup during compounding step.

Figures 2a and b show the comparison between the aspect ratio distributions of as-received flax fibers and fibers after compounding. For the latter, distributions of uncompatibilized biocomposites at 5 and 10 wt% flax fibers are shown as well as compatibilized biocomposites at two different values of ratio "α": 2 and 1. This ratio is defined as the fraction between weight content of flax fiber and PLA-g-MA.

The aspect ratio of the as-received flax fibers before compounding varied from 5 to 75, and exhibited a mean around 30 [20]. After compounding, the aspect ratio distributions were considerably narrower for all biocomposites, varying in average from 5 to 30. At 5 wt% of reinforcement (Fig. 1a), ~50% of the fibers present in the uncompatibilized biocomposites showed an aspect ratio less than 10, and the other ~50% between 10 to 20. The mean was ~8 for this formulation. The same behavior was observed for the compatibilized biocomposites at α = 2 (i.e. 2.5 wt% PLA-g-MA). The formulation with α = 1 (i.e. 5 wt% PLA-g-MA) exhibited the highest decrease of aspect ratio; about 60% of fibers exhibited values below 10; the mean was around 6.5.

For the uncompatibilized biocomposite containing 10 wt% of flax fiber, the mean aspect ratio decreased from ~30 to ~15. In presence of PLA-g-MA, the highest decrease was exhibited at α = 2 (i.e. 5 wt% PLA-g-MA) with ~60% of flax fibers presenting aspect ratio values less than 10 and a mean value of ~6. The formulation with α=1 exhibited a mean aspect ratio of ~11.5.

These results first suggest that in the same compounding conditions, fiber attrition is less important as the reinforcement content rises. Secondly, the ratio "α" is not the parameter controlling fiber breakage for compatibilized biocomposites. Finally, the highest decrease in the aspect ratio was observed at 5 wt% of PLA-g-MA in all cases, which agrees with the tensile testing results. At the same PLA-g-MA concentration, different formulations showed a decrease either in tensile strength or Young modulus. Surprisingly, the formulations presenting the minimum degradation in length and diameter were the uncompatibilized biocomposites. The addition of PLA-g-MA is affecting the size degradation of flax fiber, possibly through stronger Matrix – Fiber interactions in the molten state.
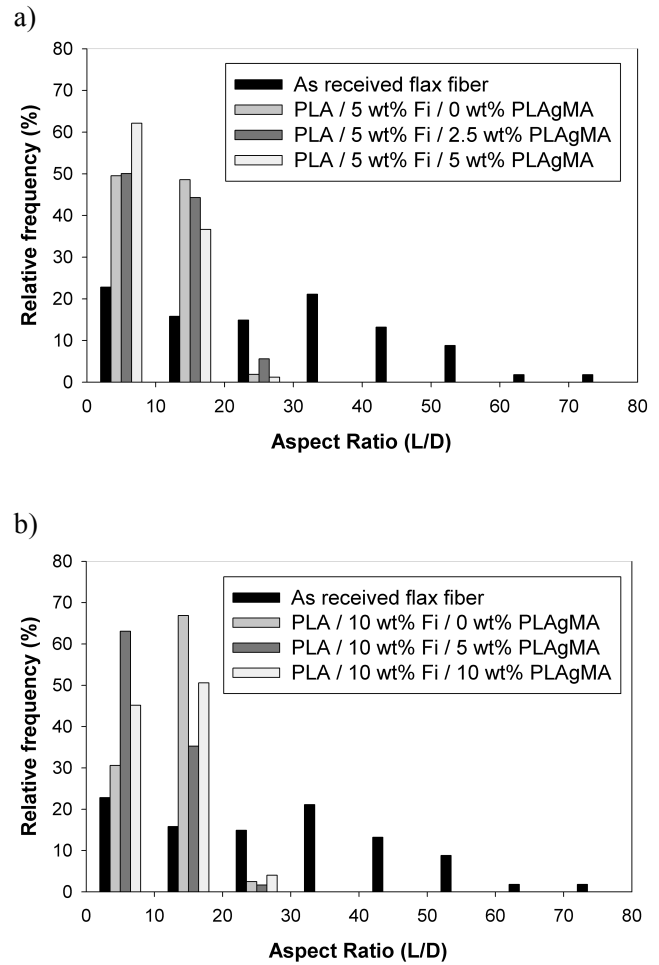
a)

b)

Fig. 2 Distribution of flax fiber aspect ratio before and after compounding: a) 5 wt% and b) 10 wt% of flax fibers.

3.4 Microscopy

The fracture surfaces of selected specimens after tensile testing were analyzed by SEM. Figure 3 presents micrographs of various PLA based flax fiber biocomposites at different magnifications. The left column shows the uncompatibilized sample and the left column the compatibilized pair. In general, the presence of the PLA-g-MA did not bring remarkable differences in the fracture mechanisms, both surfaces, without and with compatibilizer, presented similar phenomena.

Figures 3a-d exhibit an overview of the fracture surfaces of the biocomposites with 10 and 20 wt% of flax fiber. We can observe the heterogeneity of the surfaces, flax fibers showing a random orientation. A mixture of bundles and individual fibers is present. Traces of fiber pull out can be noticed in the four cases.

5

The next four micrographs show evidence of good interaction between flax fiber surfaces and PLA polymer chains. In Figures 3e-f, we can clearly observe the transversal breakup of several flax fibers, which is usually considered a sign of strong fiber-matrix interfaces. Figures 3g-h show examples of tearing of fiber bundles as a consequence of the mechanical solicitation. Both phenomena, fiber breakup and tearing, suggest high interaction at the fiber-matrix interface and good adhesion between the PLA polymer chains and the flax fibers. It is worth noting that these phenomena were identified both in compatibilized or uncompabilized samples.

Le Duigou et al. have studied the interfacial interactions of PLA/flax fiber using a microdebonding technique. Their results showed interfacial shear strengths (IFSS) between ~15 and ~22 MPa; these values are in the same range of those measured on Glass/Polyester [21]. Regarding the effect of the compatibilizer, the current investigation indicates that the addition of PLA-g-MA does not bring significant improvements in the fracture morphology; this fact agrees with the tensile testing results discussed in Section 3.1. Hence it seems that PLA-flax fiber interactions are naturally quite good, and it explains why the addition of PLA-g-MA does not bring noticeable improvement.

Finally, Figures 3i-l contains high magnification micrographs showing in detail the fiber surface after testing. Surfaces of pulled out fibers are partially covered by heterogeneous polymer layers, indicating once again strong adhesion. Individual fibers seem to have greater interaction with polymer chains than bundles, most probably because the total surface area play an important role for developing fiber-matrix interactions during melt compounding.
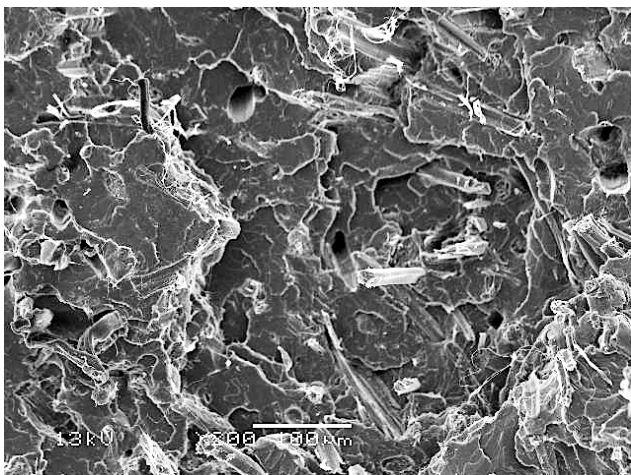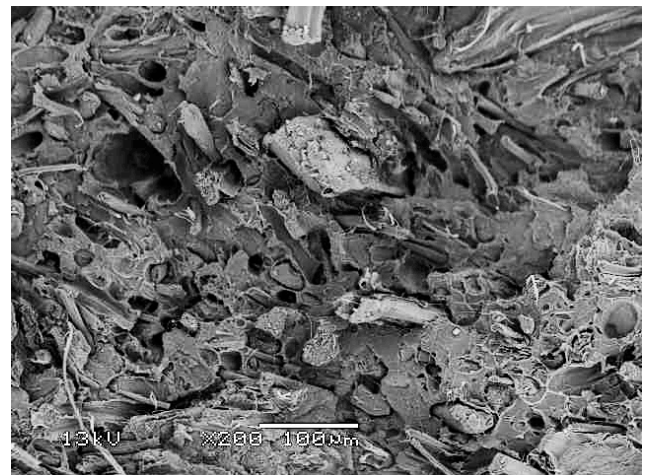

a) PLA/10
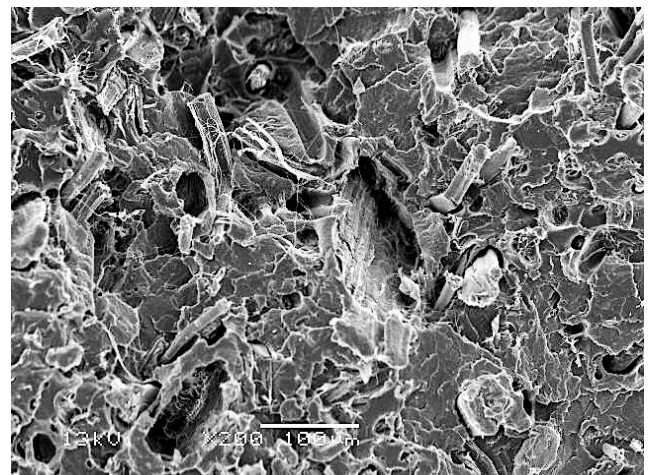
b) PLA/10/10
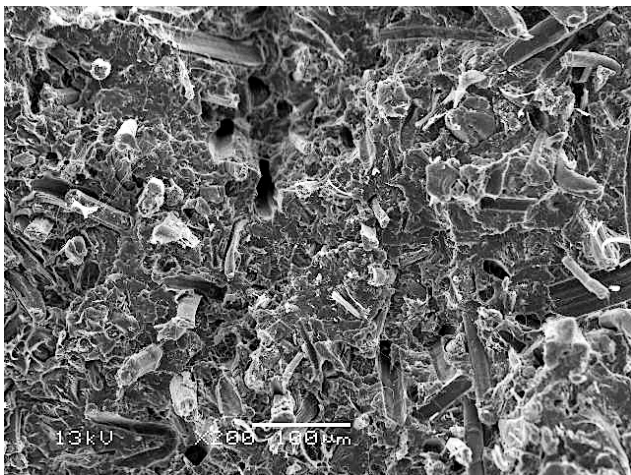
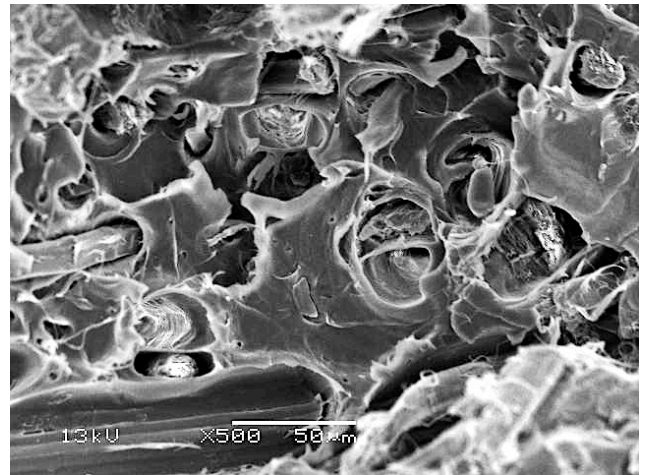c) PLA/20

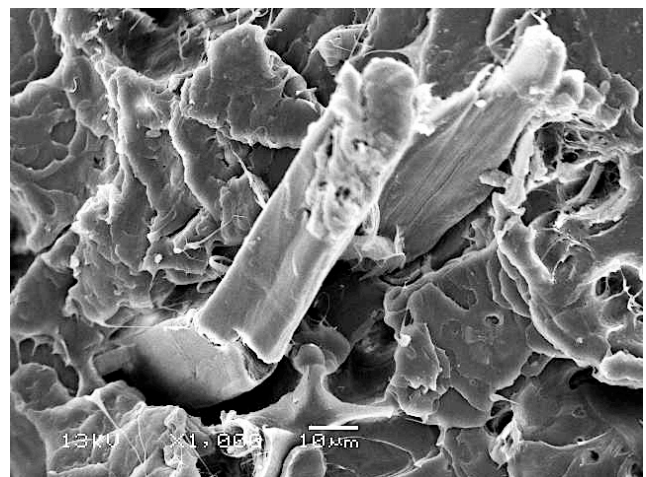d) PLA/20/10

e) PLA/10

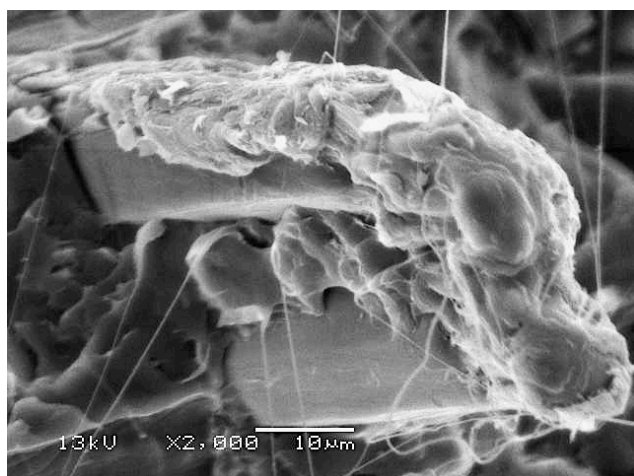f) PLA/10/10

g) PLA/20

h) PLA/20/10

i) PLA/10

j) PLA/10/10

k) PLA/20

l) PLA/20/10

Fig. 3 Scanning electron micrographs of uncompatibilized (left column) and compatibilized (right column) biocomposites at different magnifications of a-d) 200, e-h) 500 and i-l) 1000-2000.

4 Conclusion

In this study, PLA-g-MA was proposed as a potential compatibilizer for the PLA flax fiber biocomposites. In order to investigate the effect of PLA-g-MA on the biocomposites, rheological measurements, tensile testing, size fiber distributions and SEM observations were performed in different systems. Complex viscosity of PLA/PLA-g-MA systems was stable over time; decrease of this property was in the same range of neat PLA. The addition of a maleic anhydride compatibilizing agent into the PLA based flax fiber systems was shown to slightly modify the Young modulus and tensile strength of the biocomposites. Improvements in the range of ~10% were found at a compatibilization level of 10 wt%, nevertheless these properties exhibited small decreases at lower concentrations of PLA-g-MA. In accordance with tensile behavior, aspect ratio distributions of all systems containing 5 wt% PLA-g-MA showed the biggest degradation on fiber size. SEM observations allowed pointing out strong interactions between flax fibers and PLA polymer chains, evidences of strong fiber-matrix interface were found in the high magnification micrographs. The presence of PLA-g-MA did not bring remarkable difference in the fracture surface of compatibilized and uncompatibilized biocomposites. These results suggest that the use of PLA-g-MA as a coupling agent does not strongly contribute to the enhanced performance of PLA-flax fiber biocomposites.

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