Biocomposites based on poly(lactic acid) matrix and reinforced with lignocellulosic fibers: the effect of fiber type and matrix modification

Running head: Composites based on PLA and lignocellulosic fibers

Abstract

In composite materials, two or more different components are combined to produce a new material with different characteristics from the individual components. In the recent years, due to environmental concerns, the development of biocomposites based on natural fibers is attracting great interest of researchers. The mechanical properties of biocomposites are dependent, among other parameters, on matrix properties, fiber properties as well as fiber/matrix adhesion. There are different approaches to improve fiber/matrix adhesion, such as, the use of fiber surface treatments and the use of matrix modifiers i.e.: coupling agents. In this work, poly(lactic acid) matrix composites reinforced with two different lignocellulosic fibers (sisal and flax) were prepared and the mechanical properties of both type of composites were compared. On the other hand, poly(lactic acid) polymer was modified with maleic anhydride in the presence of dicumyl peroxide. The mechanical properties of PLA/lignocellulosic fibers composites modified with maleic anhydride modified poly(lactic acid) were also studied.

Keywords: poly(lactic acid); flax; sisal; composite; mechanical properties; coupling agent

1. Introduction

In composite material, two or more different components are combined to produce a new material with different characteristics from the individual components. Usually, the composite matrix is derived from petroleum resources and the reinforcing phase is a synthetic fiber. The degradation of petroleum-based plastics in nature takes a long time, which leads to severe ecological and environmental problems. Therefore, there is a growing trend to use natural polymers, biopolymers, in different applications replacing synthetic ones (De Silva et al. 2014; Ertas, Altuntas, and Donmez Cavdar 2019; Krishnaiah, Ratnam, and Manickam 2017; Sangeetha et al. 2018). Among biopolymers, poly(lactic acid), PLA, is considered the most promising candidate in many applications due to its interesting properties. On the other hand, lignocellulosic fibers obtained from plants are environmentally friendly materials. Besides, they show interesting specific mechanical properties (Arbelaiz et al. 2005a; Orue et al. 2015) due to their low density. From the environmental point of view, the development of biocomposites based on poly(lactic acid) matrix and reinforced with natural fibers is very interesting since in the end of its useful life, they can degrade completely by composting process (Majhi et al. 2010).

The mechanical properties of composites are dependent on matrix properties, fiber properties as well as fiber/matrix adhesion, among other variables. Fiber-matrix adhesion is crucial to ensure composites with superior mechanical properties (Narkis and Chen 1988; Netravali et al. 1989;). There are different approaches to improve fiber/matrix adhesion, such as, the use of fiber surface treatments (Arbelaiz 2005a; Furtos et al. 2013, Orue et al. 2015) and the use of matrix modifiers i.e.: coupling agents (Arbelaiz et al. 2005b; Beg and Pickering, 2008; Buetuen et al. 2019). In the literature, reactive functional groups are incorporated into synthetic polymer to enhance the miscibility between the

polymers and fiber. For example, maleated polypropylene copolymer is an effective compatibilizer to prepare polypropylene/lignocellulosic fibers composites with superior mechanical properties (Arbelaiz et al. 2005b; Beg and Pickering, 2008; Buetuen et al. 2019). Other authors used maleic anhydride as coupling agent to improve the poor surface adhesion between high polar character phase, fibers and starch, with PLA polymer (Iovino et al. 2008). It has been proven that a maleinated additive influences the interfacial region and after the addition of maleinated additive to composite, the impact energy of composite can increase extraordinarily (Jaszkiewicz, Bledzki, and Franciszczak, 2013).

In this work, composites based on two different type of lignocellulosic fibers were prepared and the mechanical properties of both composites were compared. On the other hand, PLA polymer was modified with maleic anhydride in the presence of dicumyl peroxide. Modified polymer (MA-PLA) was added to biocomposites and the effect of MA-PLA addition on the mechanical properties of composites was also studied.

2. Experimental part

2.1. Materials

Poly(lactic acid) commercial grade Ingeo[TM] biopolymer 3051D was provided by NatureWorks LLC (USA). According to the supplier, the D-lactide isomer content of PLA was approximately 4-5 % and this grade is characterized by a melt flow index of 10-25 g/10 min (2.16 kg load, 210 ºC) and a specific gravity of 1.25.

Celulosa de Levante S.A. (Spain) kindly supplied the sisal fiber used in the current study whereas Arctic Fiber Company (Finland) provided the flax fibers. The lignocellulosic fibers were isolated from leaf and bast of sisal and flax plants, respectively. Maleic anhydride (MA) chemical agent was kindly supplied by Cepsa Company (Spain) and

dicumyl peroxide (DCP) with a purity of 98 % was supplied by Sigma Aldrich Company (USA).

2.2. Preparation of the MA-PLA

PLA was modified with MA using the Haake Rheomix 600 internal mixer (Thermo Scientific, Karlsruhe, Germany) with two Banbury rotors at 185 ºC. After PLA was melted, 0.35 wt.% of peroxide was added and mixed at 50 rpm for 5 min. Finally, 10 wt.% of maleic anhydride was added and mixed for 5 min at 50 rpm.

2.3. Compounding and processing of composites

Before compounding, all materials used in the current study were dried at 90 ºC for 12 h to remove moisture. Compounding of composites was carried out in a HAAKE Rheomix 600 melt mixer with two Banbury rotors, and a mixing temperature of 185 ºC was selected. First PLA pellets were fed and after melting, sisal or flax fibers were added in the molten blend and mixed during 5 min at 40 rpm after the last fiber was introduced in the melt mixer. On the other hand, for composites modified with MA-PLA, first PLA was melted and after this, different MA-PLA contents were added. Finally, lignocellulosic fibers were added and mixed at 40 rpm for 5 min after the last fiber was introduced in the melt mixer. The fiber content of prepared composites varied from 20 to 50 wt.%.

All compounded systems were pelletized using the cutting mill SM200 (RETSCH, Hann, Germany). Pelletized systems were dried in an oven at 90 ºC for 12 h prior to obtain tensile test specimens (ASTM-D-638-10 type V) in a HAAKE Minijet II injection machine (Thermo Scientific, Karlsruhe, Germany). The selected injection and mold temperature values were 185 ºC and 75 ºC, respectively, while 820 bar molding pressure was applied for 8 s.

2.4. Characterization techniques

2.4.1. Fourier transform infrared spectroscopy

Attenuated total reflectance-Fourier transform infrared (ATR-FTIR) spectroscopy was used to analyze the characteristic functional groups of samples. Spectrum were recorded using a Nexus 670 spectrometer (Nicolet, Madison, Wisconsin, USA) equipped with a MKII Golden Gate accessory (Specac, Orpington, UK) with diamond crystal at a nominal incident angle of 45º and ZnSe lens. Data were obtained after 32 scans in a range from 4000 to 650 cm^{-1} with a resolution of 4 cm^{-1}.

2.4.2. Thermogravimetric analysis

Thermogravimetric measurements were carried out by using a TGA/SDTA 851 analyzer (Mettler-Toledo, Columbus, Ohio, USA). Samples between 5 and 10 mg were placed in ceramic crucibles and dynamic tests were run from 25 to 700 ºC at a heating rate of 10 ºC/min under nitrogen atmosphere in order to prevent a thermo-oxidative degradation.

2.4.3. Fiber tensile test

Tensile test of flax and sisal fibers were performed by using a Minimat 2000 tester (Rheometric Scientific, Piscataway, USA) at a testing speed of 1 mm/min. The clamping length used was 5 mm and at least 15 specimens were tested. Fiber diameter was measured by Eclipse E600 optical microscopy and the minimum diameter value measured at three different locations along the fiber length was taken for calculating the cross-section area of fibers. The strength values were fitted to a two parameters Weibull distribution function (Eq. (1)):

$$F(\sigma) = exp\left[-\left(\frac{\sigma}{\sigma_0}\right)^{\alpha}\right] \qquad (1)$$

where the cumulative probability of failure is related to the applied stress (σ) and the parameters α and σ_0 are the shape and scale parameter, respectively.

2.4.4. Tensile testing

Tensile properties of unreinforced polymer matrix and its composites were obtained as indicated in ASTM D638 standard using Instron Model 4206 Universal Testing Instrument equipped with a video extensometer and a load cell of 5 kN. All tensile tests were carried out at 5 mm/min deformation rate. Young´s modulus value of samples was determined using a video extensometer while the tensile strength and deformation at break values were determined from the stress vs strain curves obtained without video extensometer. At least five specimens for each system were tested and the average values were reported.

2.4.5. Scanning electron microscopy

Fracture surface of samples was observed by scanning electron microscopy (SEM). SEM micrographs were performed by JSM-6400 microscopy (JEOL, Tokyo, Japan) equipped with a wolfram filament operating at an accelerated voltage of 20 kV. Samples were previously coated with a thin gold layer using Q150TES metallizer (Quorum Technologies Ltd, Laughton, England).

2.4.6. Gel permeation chromatography

Analytical gel permeation chromatography (GPC) was performed with a Perkin–Elmer LC-295 chromatograph equipped with refractive index detector LC-30 RI to determine the changes in molecular weight and molecular weight distribution after modifying PLA with maleic anhydride. A kit of three Waters styragel columns, HR 1, HR 2 and HR 4, whose molecular weight range detection is 100-5000, 500-20,000 and 50,000-500,000, respectively, was used. The mobile phase was tetrahydrofuran at a flow rate of 1 mL/min at room temperature.

3. Results and discussion

3.1 Comparison of physico-mechanical properties of sisal fiber and flax fiber

Figure 1 shows the FTIR spectra of flax and sisal fibers. Both spectra show bands related with chemical groups of cellulose, hemicelluloses and lignin components. The bands at 1730 and 1240 cm^{-1} are related to groups in hemicelluloses and lignins (De Rosa et al. 2011).

On the other hand, the band at 1504 cm^{-1} is associated with C-C vibration of aromatic ring present in lignin (Garside and Wyeth, 2003,;Wang et al. 2009). In flax fiber spectrum, the band at 1504 cm^{-1} is hardly observed indicating that the amount of lignin in flax fiber is significantly lower than in sisal fiber one. Based on spectrum band intensities, sisal fiber showed higher amount of non-cellulosic components since the intensity of the bands at 1730, 1504 and 1240 cm^{-1} are higher than in flax fiber spectrum.

[Figure 1 near here]

Figure 2 shows TGA and DTGA thermograms of flax and sisal fibers. The water evaporation mass loss at 100 ºC observed in both fibers is similar, around 5-6 %. In DTGA curve, sisal fiber shows a prominent shoulder at 290 ºC related with pectins and hemicelluloses degradation, whereas in flax fiber DTGA curve a small shoulder at around 280 ºC is observed. This fact indicates that flax fiber has lower amount of hemicelluloses and pectins than sisal fiber. This result is in agreement with the FTIR results reported previously. Therefore, FTIR and TGA data indicates that the cellulose content in flax fiber is higher than in sisal fiber one.

[Figure 2 near here]

It was observed in a previous work (Mondragon, 2014.) by X-ray diffractograms, that both fibers showed cellulose I typical peaks. In flax fiber, peaks are more prominent than in sisal fiber one. It was reported crystallinity index values of 47 and 65 for sisal fiber and flax fiber, respectively. Probably, flax fiber showed higher crystallinity index value due to the presence of lower amount of non-cellulosic components than in sisal fiber one.

In Figure 3, tensile strength data of lignocellulosic fibers are shown. Weibull probability distribution provides a good fit to experimental data. In table 1, tensile properties of flax fiber and sisal fiber are summarized. Flax fiber showed considerably higher strength and modulus values than sisal fiber one. As observed by FTIR and TGA results, flax fibers are composed by more cellulose content than sisal counterpart, besides flax fiber showed higher crystallinity index than sisal fiber ones. These facts could be the main reasons because flax fiber shows higher tensile properties than sisal fiber one.

[Figure 3 near here]

[Table 1 near here]

Table 2 compares polar component, dispersive component and total surface energy of PLA matrix and lignocellulosic fibers. For a good fiber/matrix adhesion is necessary, but not the only condition, a close contact between both components. PLA and sisal fibers showed similar surface energies suggesting that probably sisal fibers would be better wetted with PLA polymer than flax fibers counterpart.

[Table 2 near here]

3.2 Mechanical properties of PLA/lignocellulosic fiber composites

In Figure 4, the effect of fiber loading on tensile properties of composites is shown. Even though the tensile strength of flax fiber is higher than sisal fiber one, composites reinforced with sisal fiber showed higher tensile strength values. After adding flax fiber to PLA matrix, the strength value decreased and irrespective to fiber loading, the strength value was around 50 MPa. However, when sisal fibers were added to PLA matrix, the strength value maintained similar to neat PLA, around 57 MPa. These facts suggested that fiber/matrix adhesion seems to be poor in both composites. Nevertheless, sisal fiber seemed to show better adhesion with the matrix than flax fiber one. Probably, the different

chemical composition as well as different superficial characteristic are the reasons for better fiber/PLA matrix adhesion in composites with sisal fiber than flax counterparts.

[Figure 4 near here]

All composites showed higher tensile modulus than neat PLA matrix. Composites reinforced with both type of fibers showed the same trend; as fiber loading was increased, the modulus value was increased. Composites reinforced with flax fiber showed higher modulus values than composites reinforced with sisal fibers. These results are in agreement with the fiber modulus values reported in table 1. Respect to elongation at break values, the addition of fibers results in a significant reduction of deformation, being the reduction more pronounced for composites reinforced with flax fiber.

3.3. PLA matrix modification with maleic anhydride

One of the most frequent method to improve mechanical properties of composite with lignocellulosic fibers is adding coupling agents. For example, maleic anhydride (MA) is a polar monomer that has been used to modify polymers to improve the compatibility between non-polar matrices and polar fibers. In polyolefin matrix composites, maleated polymers are frequently used as coupling agent (Caulfield et al. 1999; Keener, Stuart, and Brown, 2004; Mohanty et al. 2004). The addition of maleated polymers lead to improvements in mechanical properties due to enhanced fiber/matrix adhesion. Using a similar strategy, it is believed that grafting MA onto PLA would improve the compatibility between PLA matrix and lignocellulosic fibers.

Carlson et al. (1999) carried the first study about the functionalization of PLA chains with MA. They concluded that this functionalization can be performed by reactive extrusion, resulting in little degradation of the PLA. In the current study, the functionalization of high molecular weight PLA with maleic anhydride has been investigated via free radical

reaction using dicumyl peroxide (DCP) as a radical initiator. The possible reaction scheme of MA with PLA to produce MA-PLA is shown in Figure 5.

[Figure 5 near here]

The process of PLA maleation creates anhydride functional groups along the polymer backbone. These groups are potentially capable of reacting with the lignocellulosic hydroxyl groups during melt blending, thus providing interfacial bonding between fiber and matrix.

Figure 6 shows FTIR spectra and GPC chromatograms for the original PLA and MA-PLA samples. In the literature it was observed that MA-PLA sample showed two extra shoulders at 1785 and 1858 cm^{-1} (Wu, 2009). However, these bands are not observed in the current study for MA-PLA system. Dzul-Cervantes et al. (2017) confirmed the grafting of maleic anhydride onto PLA by means of the deconvolution of FTIR absorbance bands. Even though in FTIR spectra hardly differences between original PLA and MA-PLA are observed, in GPC chromatograms differences are very evident.

[Figure 6 near here]

The original PLA presents one peak at a retention time of 24.9 min whereas MA-PLA sample shows two peaks, a small peak at a retention time of 24.8 and a big peak at 28.4 min. The first peak appeared at the similar time to original PLA, suggesting that a low fraction of MA-PLA shows similar molecular weight to neat PLA. However, the peak that appeared at higher retention time suggests that after modifying PLA polymer with anhydride maleic chains scission was occurred. The presence of MA and peroxide in the melted PLA results in a considerable decrease in molecular weight. Therefore, anhydride maleic in addition to modify the chain structure of PLA in the melt, also side reactions take place reducing the chain length of PLA. Similar results were reported by Csikós et

al. (2015) after modifying PLA with maleic anhydride. They observed that reactive modification with maleic anhydride produced the chain scission of PLA.

To improve the fiber/matrix adhesion, in the next section the effect of MA-PLA addition on tensile properties of biocomposites was studied.

3.4 The effect of the addition of MA-PLA on tensile properties of composites

Figure 7 shows the effect of MA-PLA addition on tensile properties of composites with 30 wt.% of lignocellulosic fiber. In both type of composites, the same trend was observed. After the addition of only 1 wt.% of, the strength of composite increased, however, no further strength increment was observed as MA-PLA loading was increased.

[Figure 7 near here]

For composite reinforced of flax fiber, after the addition of 1 wt.% of MA-PLA, the strength increased from 52 MPa for unmodified system to 67 MPa for modified system. For composite with sisal fiber, the strength improvement was more moderate than for flax reinforced composite. After the addition of 1 wt.% of MA-PLA, the strength increased from 56 MPa for unmodified system to 62 MPa for modified system. The strength value increments suggested that the incorporation of MA-PLA improved fiber/PLA matrix adhesion.

Majhi et al (2010.) prepared poly(lactic acid)/banana fiber biocomposites using melt compounding technique. They observed that the tensile strength of biocomposite increased after the addition of 1 wt.% of MA as compared to unmodified counterpart. They suggested that the incorporation of MA may decreased interfacial tension leading to improved interface compatibility. However, the tensile strength decreased to 43.4 MPa and 40.9 MPa, with increase in concentration of MA to 3 wt.% and 5 wt.% respectively.

Fowlks and Narayan (2010) prepared Poly(lactic acid) (PLA)-talc composites and they used maleic anhydride-functionalized PLA as an interfacial additive. They observed that the addition of MA-PLA to the composites provided experimental evidence of increased adhesion at the interface between the PLA matrix and the talc filler. They suggested that the lower molecular weight of MA-PLA would enable good wetting during processing, allowing MA-PLA to coalesce at the interface of the PLA and talc, creating an interphase. This thin region was believed to be responsible for stronger interaction between the phases, as evidenced by the improvements in tensile strength (Fowlks and Narayan, 2010). Furthermore, they suggested that there was a critical value; and beyond that, no more improvements occur.

Contrary to this work, Bourmaud and Pimbert (2008) found that the presence of an experimental MA-PLA product did not increase the adhesion between PLLA/vegetable fiber composites. They suggested that it is critical the amount of compatibilizer added to the composite as well as the grafting rate of PLA. They mentioned that compatibilizer rate could be the reason of the decrease of the tensile properties of composites. Rigolin et al. (2019) prepared coir reinforced poly(lactic acid) composites and they used PLA-g-MA as compatibilizer. By SEM images they observed that the addition of the compatibilizer improved interfacial adhesion but this fact was not reflected in the mechanical properties of composites. They suggested that the high acidity content of the compatibilizer, along with the residual moisture of the fibers, significantly decreased molar mass of the polymer, impairing the composite matrix properties.

On the other hand, the incorporation of MA-PLA did not change significantly moduli values of composites. Even though, after the addition of MA-PLA the deformation at break values for composites with flax fiber are slightly higher than unmodified composite

ones, in composites reinforced with sisal fibers the deformation at break maintained similar or decreases slightly respect to unmodified system. Taking into account the tensile properties it was decided to study the effect of fiber loading when 1 wt.% of MA-PLA was added to biocomposites.

3.5 The effect of fiber loading on biocomposites modified with MA-PLA

Figure 8 shows the effect of fiber loading in tensile properties of composites modified with 1 wt.% of MA-PLA.

[Figure 8 near here]

The strength value of composites with flax fibers were higher than neat PLA. Contrary to unmodified systems, in all fiber loadings, composites reinforced with flax fibers showed higher strength values than composites with sisal fiber ones. Results indicates that after the addition of MA-PLA, composites reinforced with flax fibers showed higher strength value improvements than composites reinforced with sisal fibers. However, after MA-PLA addition no significant difference was observed in modulus values of composites. On the other hand, in composites with flax fiber, after the addition of MA-PLA the elongation at break increased slightly, whereas in composites with sisal fiber it was maintained similar to unmodified counterpart.

3.6 Scanning Electron Micrographies of fractured surfaces

Figure 9 shows SEM micrographies of fractured surfaces of unmodified and MA-PLA modified composites at the magnification of x200. In all micrographies pulled-out single fibers (orange arrows) and fiber bundles (white circles) are observed. On the other hand, the void created after pulling-out fibers are observed in all micrographs (green arrows) as well as broken fibers (red arrows). Some fibers were broken across their entire diameter at the level of the fracture surface (light blue arrows). In general, fibers were not coated

with the matrix suggesting that fiber/matrix adhesion was not strong However, in flax fiber composite modified with 1 wt.% of MA-PLA, pulled-out fiber length seems to decrease slightly respect to unmodified composite, suggesting that flax fiber/matrix adhesion was improved (Figure 9b). Even though fiber/matrix adhesion was improved respect to unmodified system, as observed in tensile strength values, fiber/matrix adhesion seemed not to be very strong since fibers hardly were coated with the matrix (purple arrows).

Ertas et al (2019) prepared natural fiber filled PLA-halloysite nanotube composites using melt blending followed by compression molding. They used PLA-g-MA to improve the interfacial bonding between hydrophobic and hydrophilic phases in the composites. They observed by SEM micrographs that the natural fiber were completely embedded into PLA matrix when MA-g-PLA was added, and the presence of coupling agent reduced interfacial gaps.

Dzul-Cervantes et al. (2017) studied the effect of the addition of microfibrillated henequen cellulose fiber and PLA-g-MA coupling agent contents on mechanical properties and the heat deflection temperature of biodegradable PLA composites. They observed in SEM micrographs many unbounded and pulled-out fibers in the specimen without coupling agent, suggesting a weak interfacial adhesion and poor compatibility between fiber and matrix. After adding PLA-g-MA coupling agent they suggested that some fibers seemed to be still coated with the matrix polymer and little fiber pull-out was observed, indicating improved fiber-matrix adhesion.

Rahem et al. (2019) prepared fully biodegradable composites based on luffa fiber (LF) and poly(lactic acid) matrix. To improve the adhesion between LF and PLA matrix, they incorporated maleic anhydride-grafted poly(lactic acid) compatibilizer to the composites. They observed by SEM that after adding PLA-g-MA coupling agent, the fiber seemed

well embedded into the matrix due to a better impregnation by the polymer. They suggested that the incorporation of coupling agent generated a strong interface between the two components.

Zhang et al. (2017) prepared PLA/wood fiber/MA-g-PLA composites with different proportions of compatibilizer by melt blending and injection molding. They observed by scanning electron micrographs that when the MA-g-PLA was used, wood fiber is well dispersed in the PLA matrix phase, and that the interfacial compatibility between the matrix and wood fiber improved.

On the other hand, when SEM micrographs of composites with sisal fiber are compared, Figure 9c-d, similar morphologies are observed and the incorporation of MA-PLA did not modified significantly the SEM micrograph of fracture. It must be mentioned that Faludi et al. (2014) indicated that the direct determination of interfacial adhesion by SEM of fractured surfaces, especially in short fiber reinforced composites, is difficult and cannot supply quantitative values for adhesion anyway. In addition, they mentioned that conclusions drawn from the analysis of SEM micrographs are very uncertain because several processes can take place simultaneously during the deformation and failure (debonding, fiber pull-out, fiber fracture) that made the interpretation of micrographs complex and difficult.

[Figure 9 near here]

4. Conclusions

Composites based on renewable materials were prepared and characterized. Even though flax fiber showed better tensile properties than sisal fiber, the unmodified sisal fiber composites showed higher tensile strength values than flax fiber composite ones. In the

current study, the effectiveness of PLA-g-MA as a compatibilizing agent for PLA/lignocellulosic fiber composites was demonstrated. The tensile strength of composites modified with 1 wt.% of MA-PLA were significantly higher than that of the unmodified ones. Furthermore, tensile properties of flax fibers composites modified with MA-PLA were superior to sisal fiber composites. However, even though after the incorporation of MA-PLA the tensile strength of composites increased respect to unmodified composites, SEM micrographs of the fractured surfaces indicated that fiber/matrix adhesion was yet poor.

5. Acknowledgements

6. References

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Figure captions

Figure 1. FTIR spectra of flax and sisal fibers.

Figure 2. (a) TGA and (b) DTGA thermograms of flax and sisal fibers.

Figure 3. Tensile strength data of lignocellulosic fibers fitted to a two paramenters Weibull probability distribution: experimental values (symbols) and theoretical values (lines).

Figure 4. Tensile properties of composites as a function of fiber loading: (a) strength, (b) modulus and (c) deformation at break.

Figure 5. Reaction scheme for grafting of MA onto PLA by free radical reaction.

Figure 6. (a) FTIR spectra and (b) GPC chromatograms for the neat PLA and MA-PLA.

Figure 7. The effect of MA-PLA addition on tensile properties of composites with 30 wt.% of lignocellulosic fiber: (a) strength, (b) modulus, (c) deformation at break.

Figure 8. The effect of fiber loading in tensile properties of composites modified with 1 wt.% of MA-PLA: (a) strength, (b) modulus and (c) deformation at break.

Figure 9. SEM micrographies of fractured surfaces of composites with 30 wt.% of fiber at the magnification of x200: (a) unmodified flax fiber composite; (b) flax fiber composite modified with 1 wt.% of MA-PLA; (c) unmodified sisal fiber composite and (d) sisal fiber composite modified with 1 wt.% of MA-PLA.
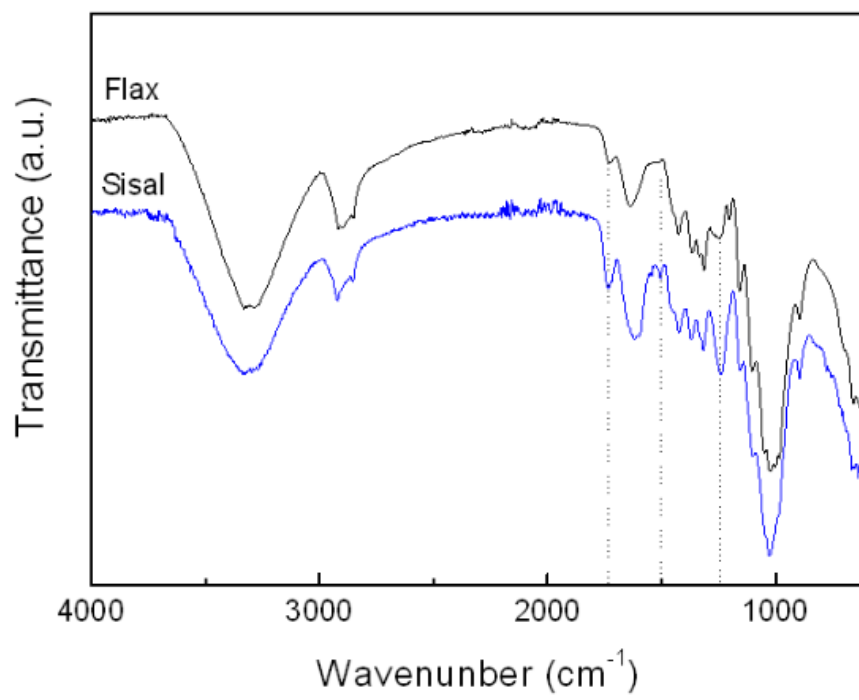
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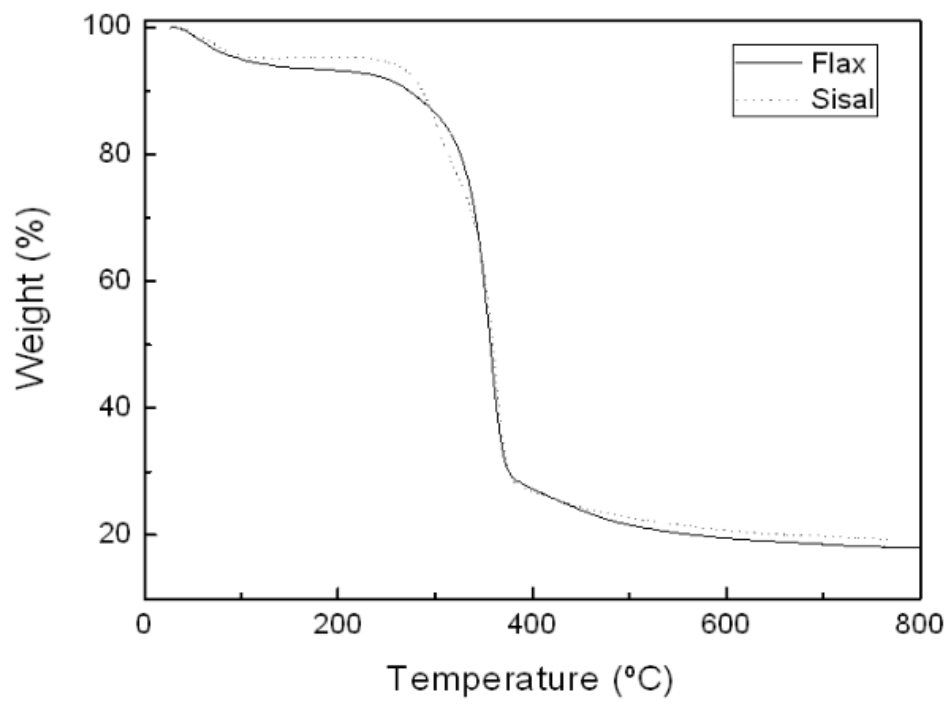
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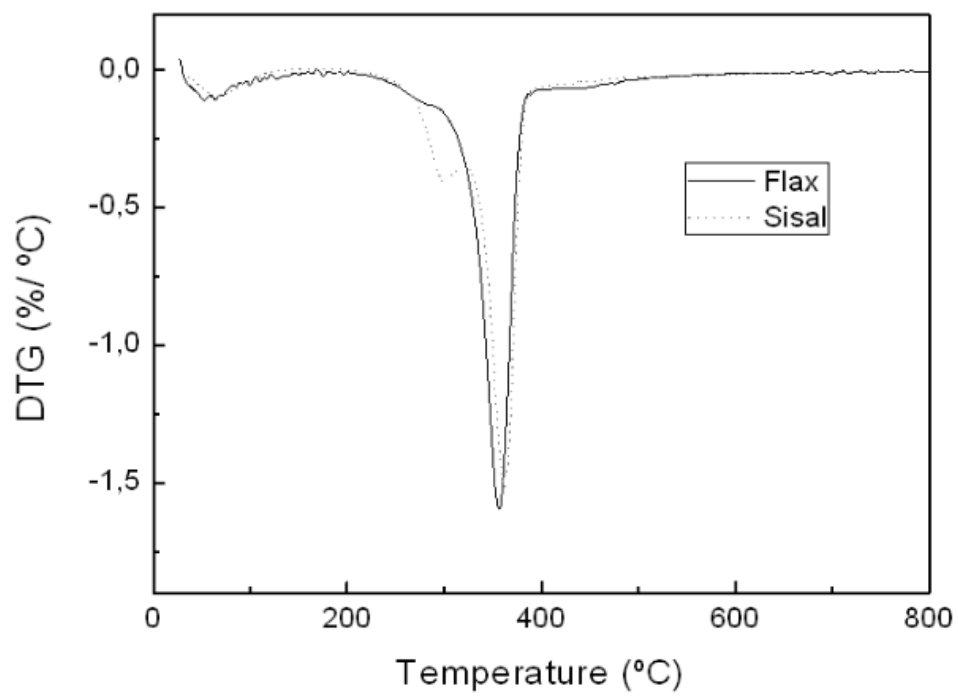
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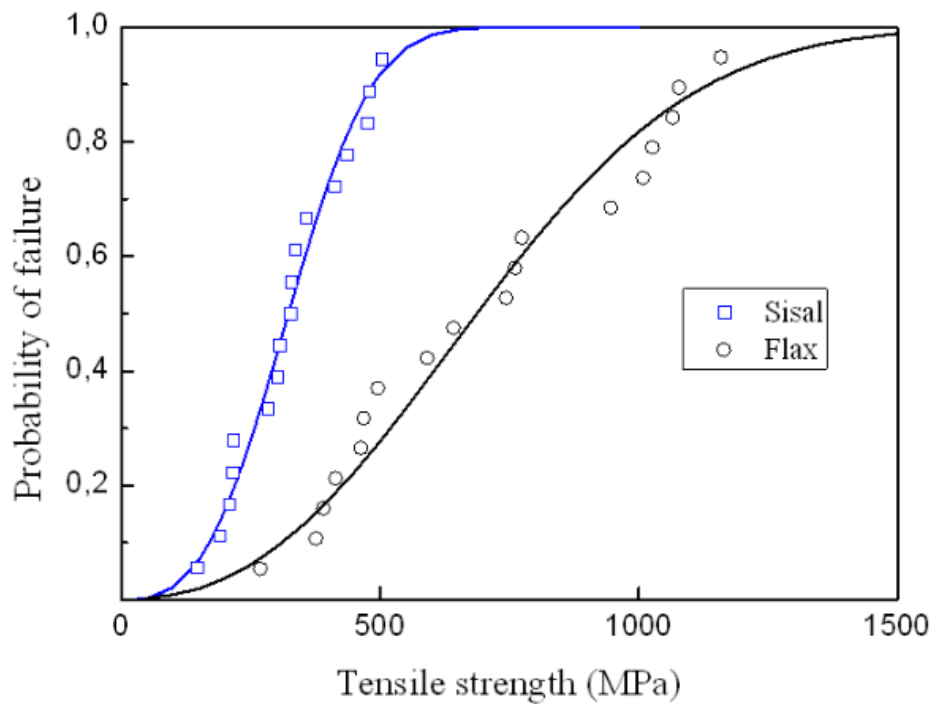
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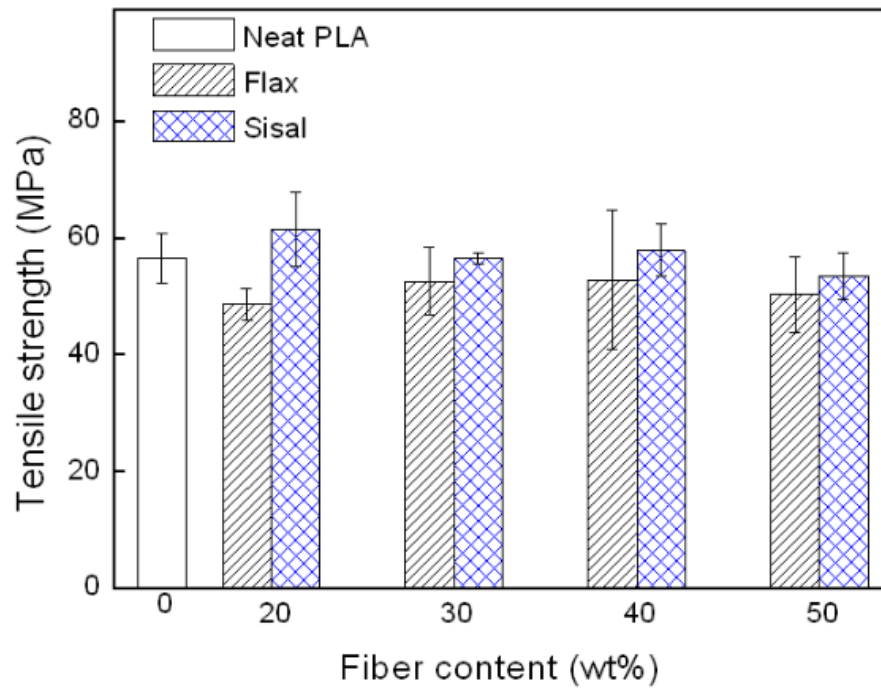
Figure 4a

Figure 4b

Figure 4c

PLA   PLA free radical   MA-PLA
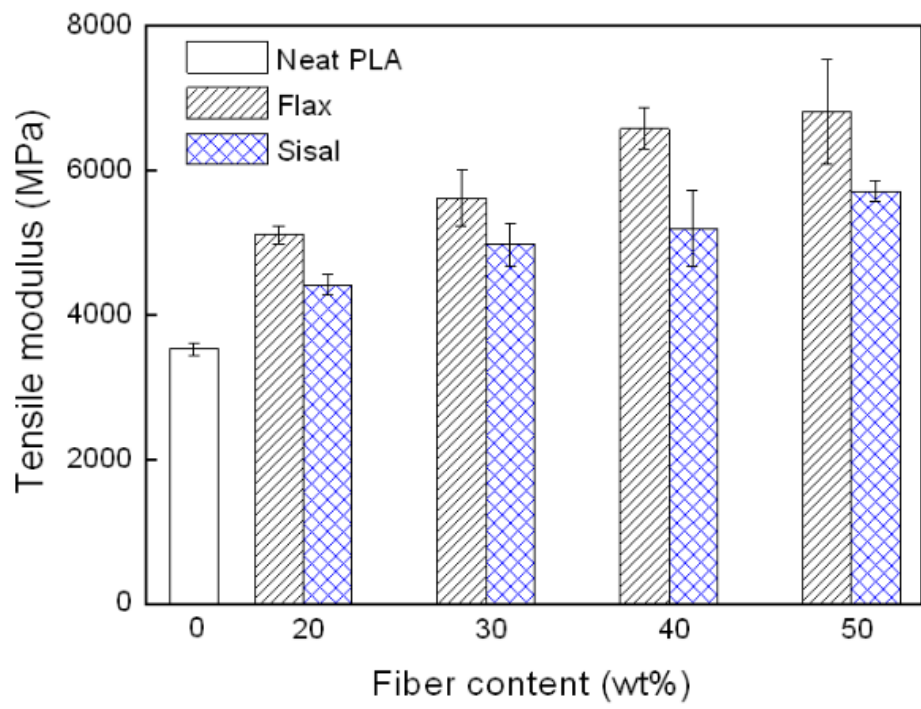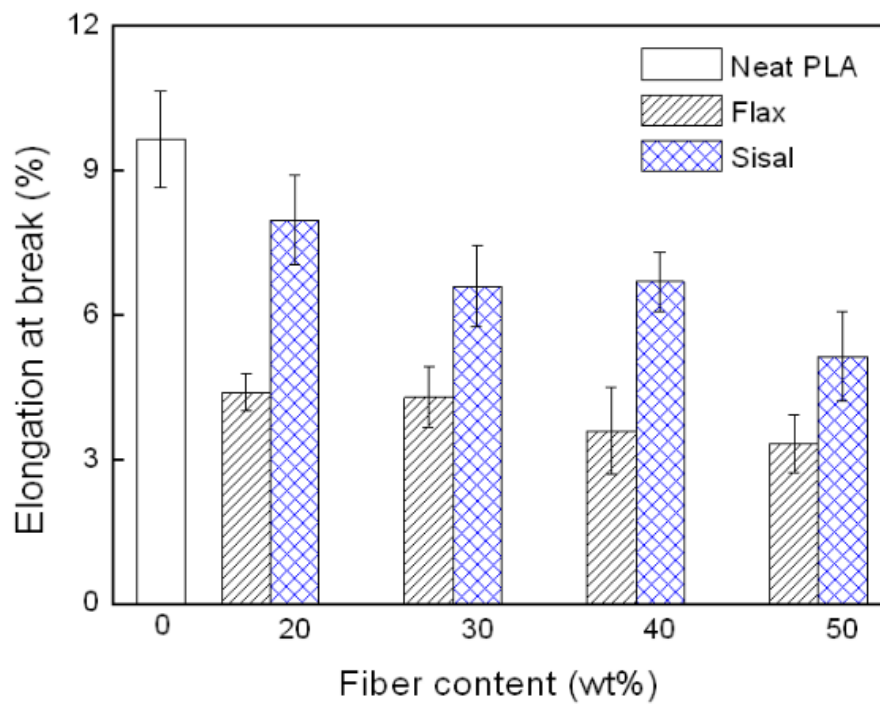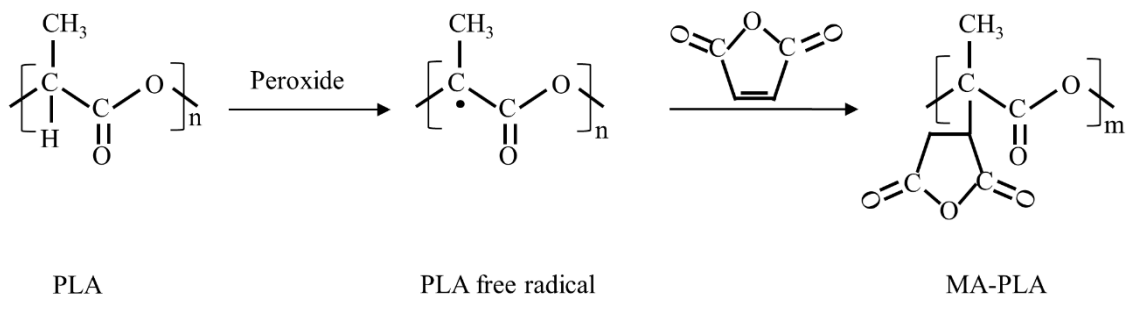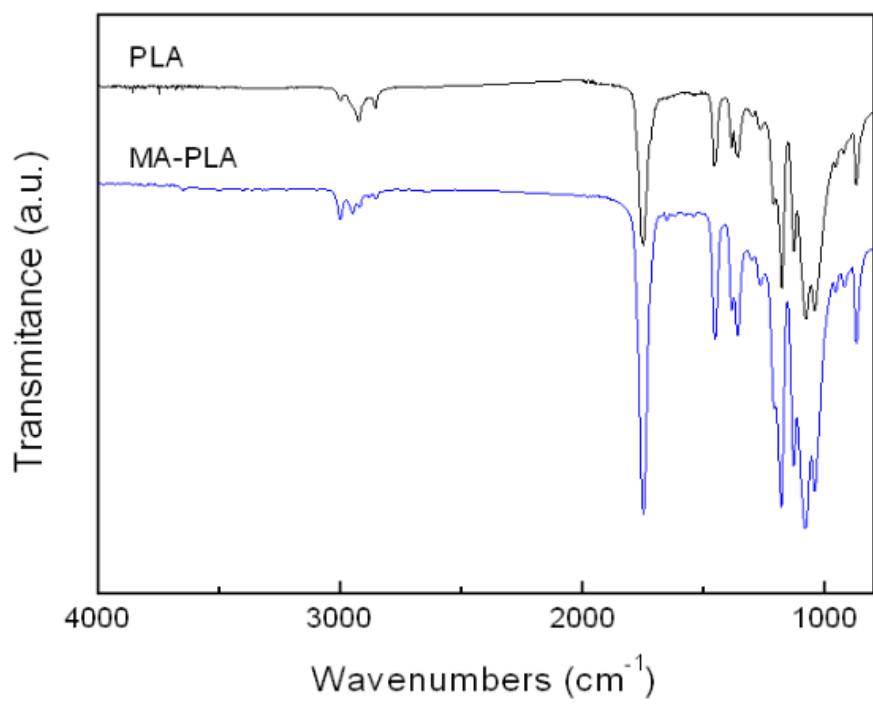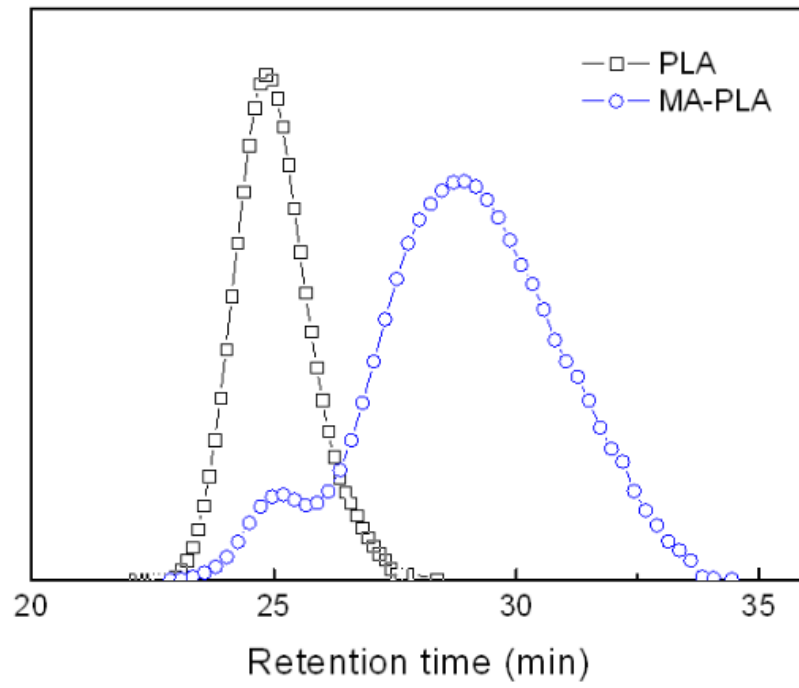
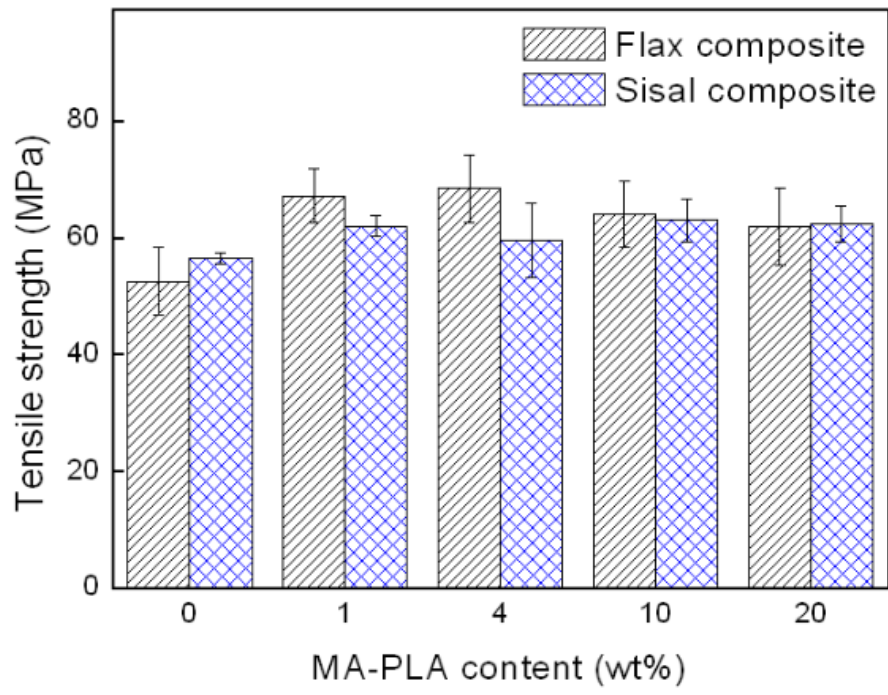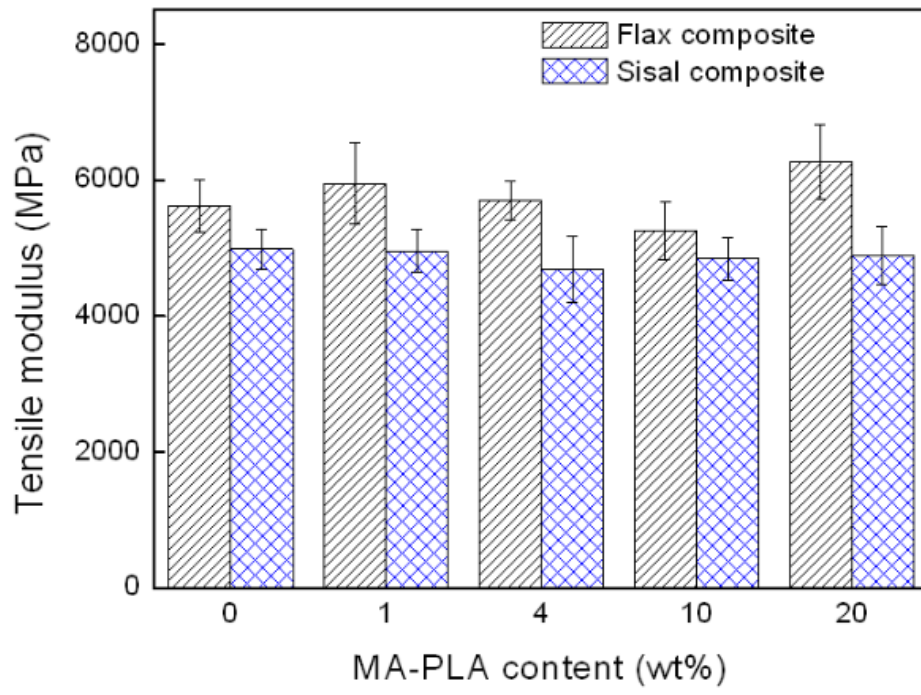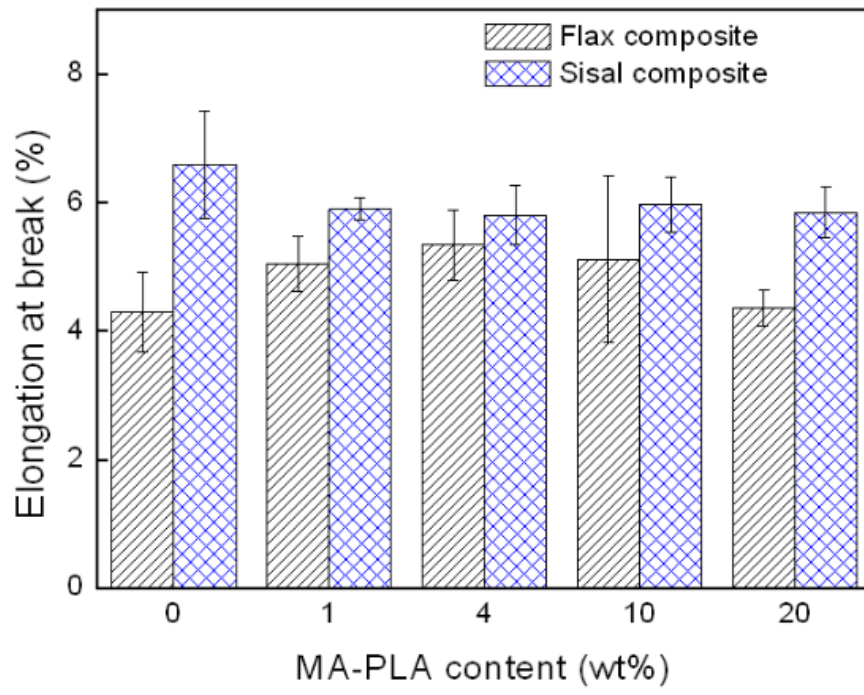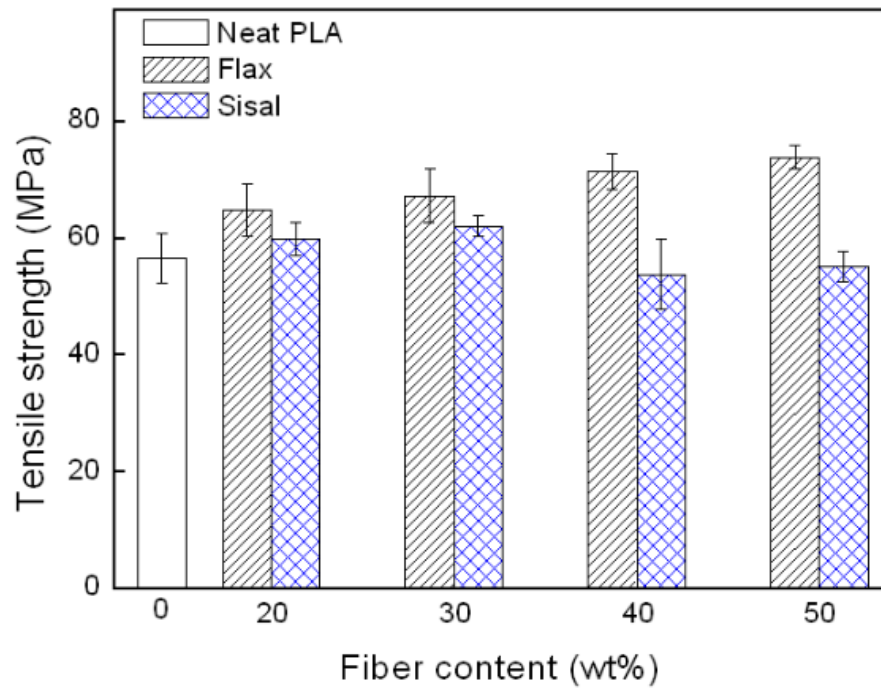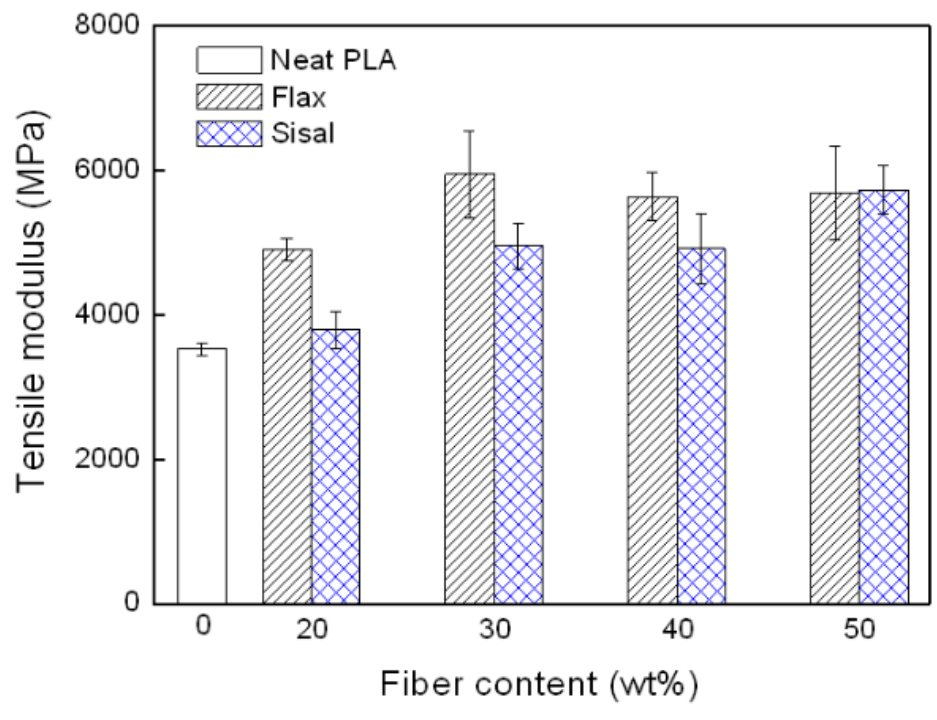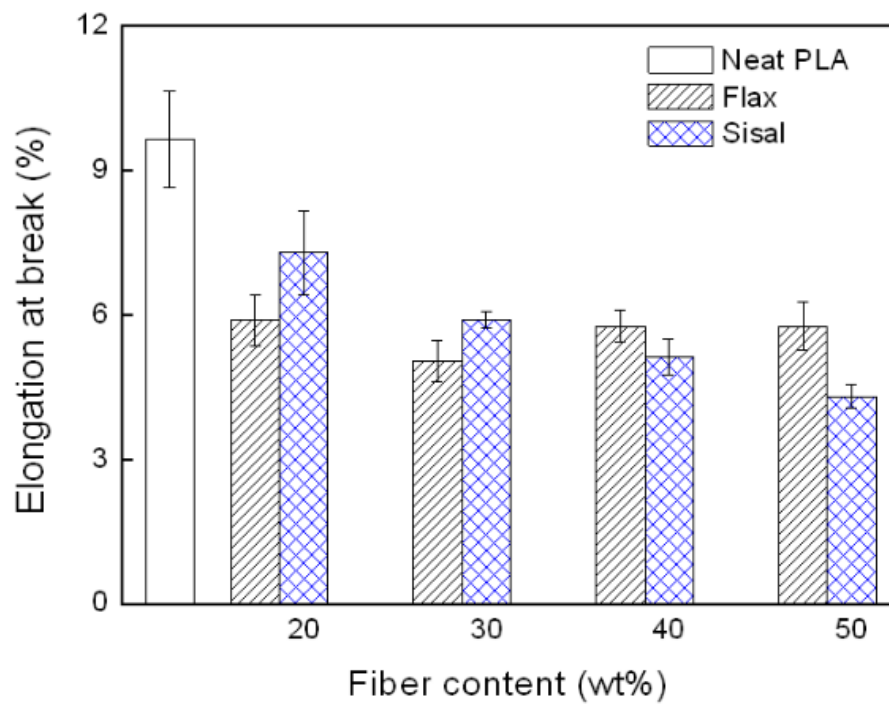Figure 5

Figure 6a

Figure 6b

7a

7b

7c

Figure 8a

Figure 8b

Figure 8c
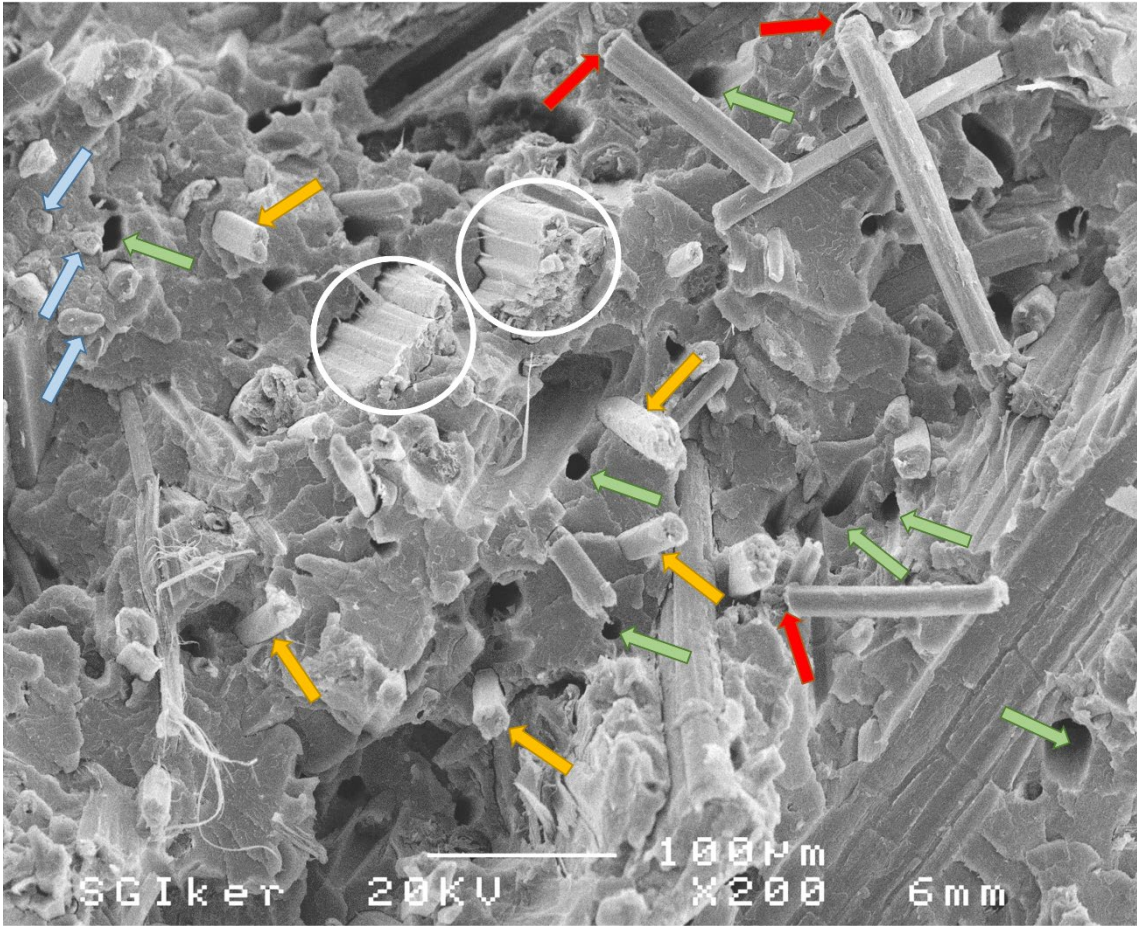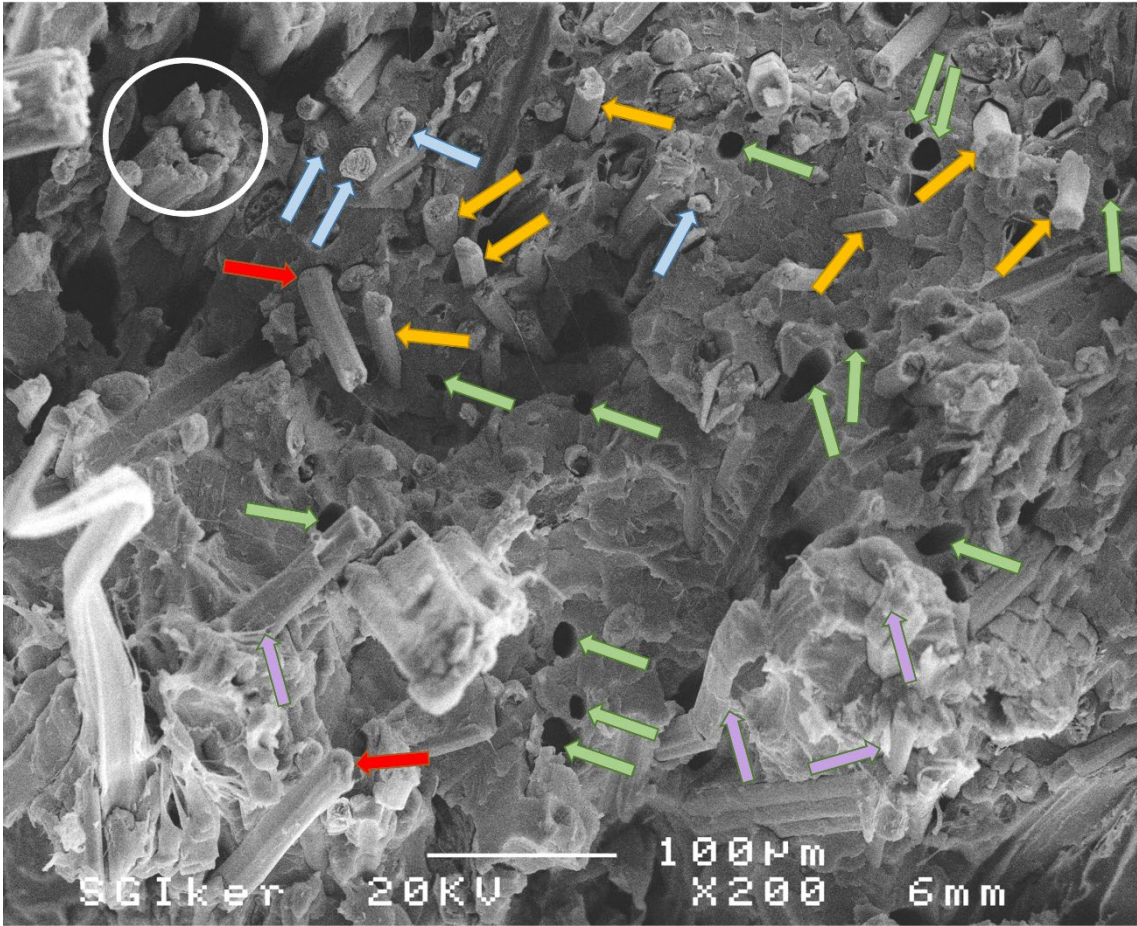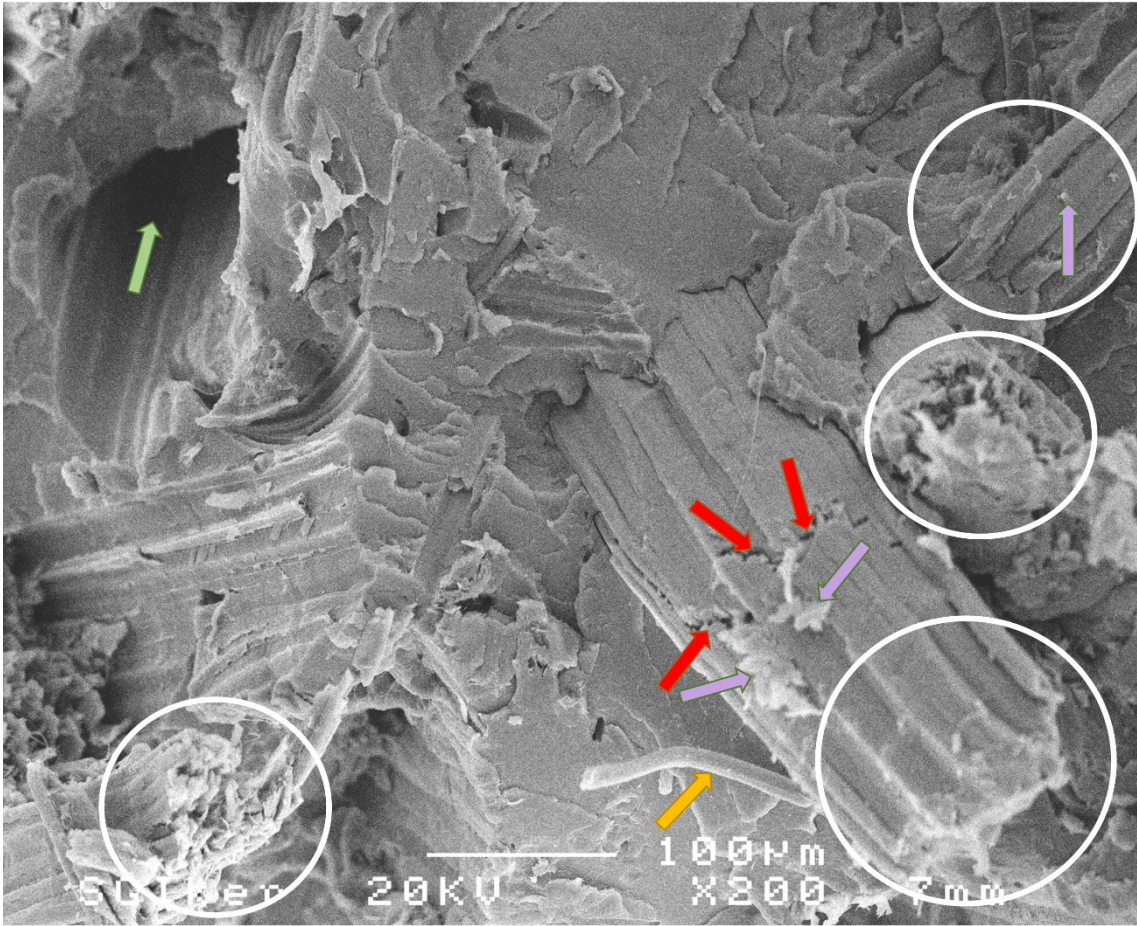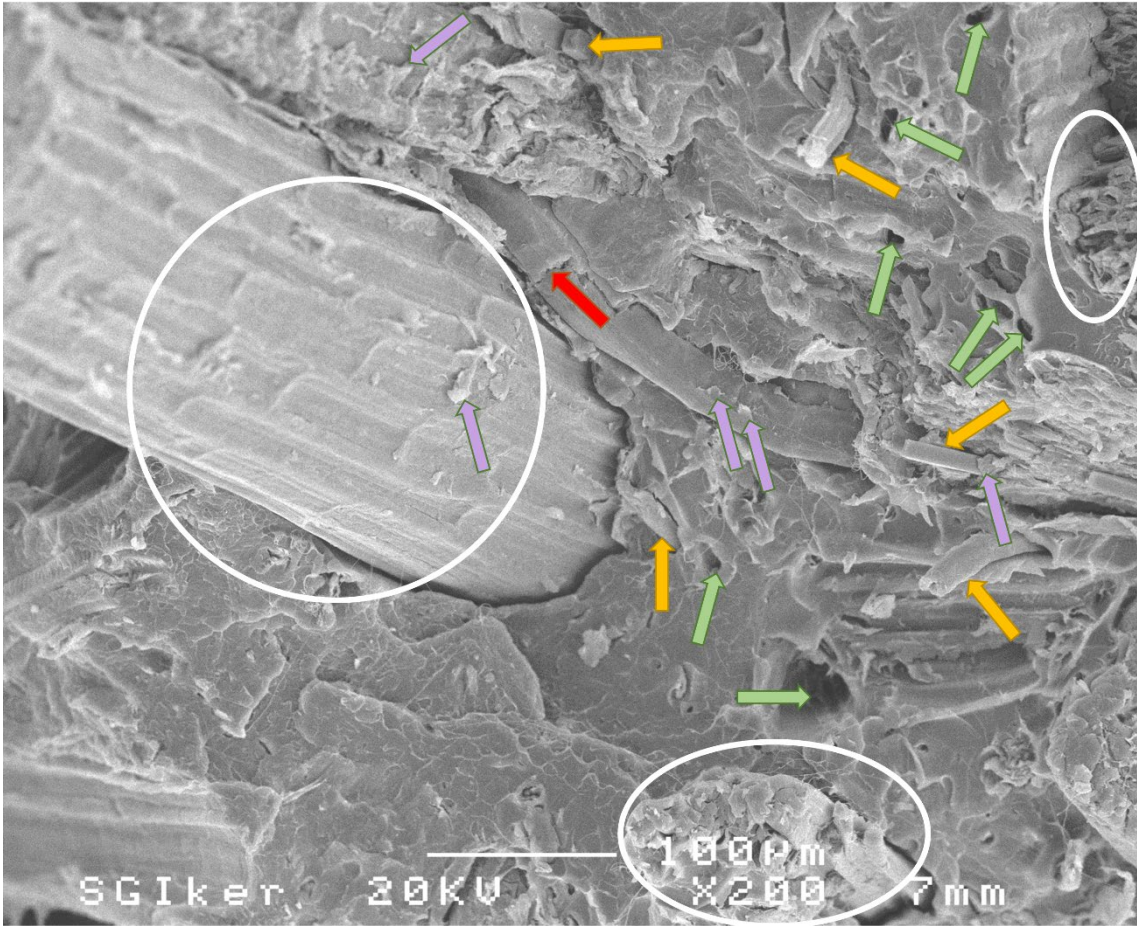
Figure 9a

Figure 9b

Figure 9c

Figure 9d

Table captions

Table 1. Tensile properties of flax fiber and sisal fiber.

Table 2. Polar component, dispersive component and total surface energy of PLA

matrix and lignocellulosic fibers.

Fiber	σ_o (MPa)	α	E (GPa)	Ref.
Flax	802	2.4	$41,0 \pm 17,7$	[5]
Sisal	366	2.9	$9,5 \pm 3,4$	[6]

Table 1. Tensile properties of flax fiber and sisal fiber

System	γ_S (mJ/m²)	γ_S^d (mJ/m²)	γ_S^p (mJ/m²)	γ_S^p/γ_S	Ref.
PLA	34.6	26.9	7.7	0.23	[6]
Flax	43.7	23.9	19.9	0.45	[5]
Sisal	34.7	25.3	9.4	0.27	[6]

Table 2. Polar component, dispersive component, and total surface energy

of neat PLA, flax fiber and sisal fiber