

**LAMINATED COMPOSITES REINFORCED WITH CHEMICALLY MODIFIED SHEETS-STALK OF *Musa cavendish*****MATERIALES COMPUESTOS LAMINADOS REFORZADOS CON LÁMINAS DE TALLOS DE *Musa cavendish* MODIFICADOS QUÍMICAMENTE**K.X. Rodríguez-Soto<sup>1</sup>, N.Y. Piñeros-Castro<sup>1</sup>, R. Ortega-Toro<sup>2\*</sup><sup>1</sup>Chemical Engineering Department, Universidad de Bogotá Jorge Tadeo Lozano, Cra. 4 # 22-61, Bogotá D.C., Colombia, 110221.<sup>2</sup>Food Engineering Department, Food Packaging and Shelf Life Research Group (FP&SL), Faculty of Engineering, Universidad de Cartagena, Avenida del Consulado, Calle 30 No. 48 152, Cartagena de Indias D.T. y C., Colombia, 130015

Received: February 9, 2019; Accepted: March 14, 2019

**Abstract**

A laminated material was developed using sheets of polylactic acid (PLA semicrystalline -PLAsc- and PLA amorphous -PLAa-), and thermoplastic starch (TPS) reinforced with natural fibre (NF) extracted from sheet-stalk of the plantain plant (*Musa cavendish*). A surface chemical modification of fibres (SMNF) was done in order to improve its compatibility with the polymers. The structural, mechanical, thermal, optical and biodegradation properties were studied. The characterisations show that chemical treatment of fibres increases the tensile strength in the laminates with PLAa, PLAsc and TPS in a 51.4%, 21.4% and 78.1% respectively. Likewise, the elastic modulus was increased by 104%, 57.4% and 124%, respectively. On the other hand, the structural analysis shows that fibres with chemical modification have higher interfacial adhesion to polymers, improving the stability of the materials. Finally, biodegradation tests confirm that the chemical treatment delays the degradation process slightly, but materials comply with international standards for bioplastics respect to degradation time and percentage. The properties of the laminates could be suitable for the development of trays or other semi-rigid packages for foods.

**Keywords:** polymer composites, biodegradable polymers, reinforcements, adhesion.

**Resumen**

Se desarrolló un material laminado utilizando láminas de ácido poliláctico (PLA semicristalino -PLAsc- y PLA amorfo -PLAa-), y almidón termoplástico (TPS) reforzado con fibra natural (NF) extraída de la hoja de tallo de la planta de plátano (*Musa cavendish*). Se realizó una modificación química de la superficie de las fibras (SMNF) para mejorar su compatibilidad con los polímeros. Se estudiaron las propiedades estructurales, mecánicas, térmicas, ópticas y de biodegradación. Las caracterizaciones muestran que el tratamiento químico de las fibras aumenta la resistencia a la tracción en los laminados con PLAa, PLAsc y TPS en un 51,4%, 21,4% y 78,1% respectivamente. Asimismo, el módulo elástico se incrementó en un 104%, 57,4% y 124%, respectivamente. Por otro lado, el análisis estructural muestra que las fibras con modificación química tienen una mayor adhesión interfacial a los polímeros, lo que mejora la estabilidad de los materiales. Finalmente, las pruebas de biodegradación confirman que el tratamiento químico retrasa ligeramente el proceso de degradación, pero los materiales cumplen con los estándares internacionales para bioplásticos respecto al tiempo y porcentaje de biodegradación. Las propiedades de los laminados podrían ser adecuadas para el desarrollo de bandejas u otros envases semirrígidos para alimentos.

**Palabras clave:** polímeros compuestos, polímeros biodegradables, refuerzo, adhesión.

**1 Introduction**

The global problem of polymer waste has grown significantly in the last decade due to the unsustainable massive production, considering the new market trends and mainly the environmental legislative

restrictions, the industry has been forced to adapt to the use of sustainable and more environmentally friendly materials for the production of their products (Porras and Maranon, 2012).

Conventional polymers are manufactured from petroleum derivatives, and they do not degrade, generating adverse effects on the environment and human beings (Layedra *et al.*, 2015). Several studies

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<https://doi.org/10.24275/uam/izt/dcbi/revmexingquim/2019v18n2/RodriguezS>

ISSN 1665-2738, issn-e: 2395-8472

have been conducted to use polymers from renewable sources such as chitosan and pepper tree essential oil biocomposites to inhibit the fungi growth (Chavez-Magdaleno *et al.*, 2018) or increase the shelf life of fruit and vegetables (Bautista-Baños *et al.*, 2018). Other interesting biodegradable and renewable polymers are polylactic acid (PLA) and thermoplastic starch (TPS). These have similar properties to those of conventional polymers such as polystyrene and polyethylene terephthalate that is used for the manufacture of packaging in the food industry (Dong *et al.*, 2014). The main handicap is that several physical properties of biodegradable polymers are poorly than those of conventional polymers (Oksman *et al.*, 2003).

Therefore, it is a research challenge the development of new materials with a biodegradable polymer matrix of renewable sources. The reinforcement with natural fibres can improve the tensile properties of biodegradable polymers. However, the improvement of interface affinity polymer-fibres is imperative. The improvement of the interfacial adhesion could be made by chemical modification of the fibre surface. An example would be the acetylation which generates a reaction of the hydroxyl groups (-OH) of the fibre (the minor components such as lignin, hemicellulose and the amorphous cellulose), with the acetyl groups (-CH<sub>3</sub>CO) (Hill *et al.*, 1998). In this way, the fibre surface becomes more hydrophobic. This treatment also increases the dimensional stability of the composite materials that are manufactured with them and give them greater thermal stability by improving the interactions of fibre-polymer.

In Colombia, there is a wide variety of natural fibres used mainly in handicraft applications which could be used in the industry. Plantain sheet stalk from agro-industrial waste, have been studied due to their promising mechanical properties (Rodríguez *et al.*, 2014). Showed the feasibility of their use as a reinforcement of thermoset synthetic resins such as polyester resin obtaining similar results to the glass fiber although the use of plantain sheet stalk as reinforcement in biodegradable polymers has not been explored.

This work aims to develop a laminated composite using plantain sheet-stalks as reinforcement layer and other layers of PLA or TPS as polymers. In this way, the layer of fibres improves mechanical properties and give structure to final material, and the other polymers improve structural continuity and barrier properties to oxygen (TPS) and water vapour (PLA)

to final material. Sheets of TPS and PLA was made by melt blending and compression moulding, and the plantain sheet-stalk was modified using acetic anhydride to improve chemical affinity with polymer sheets. The structural, optical, thermal, mechanical and biodegradation properties were studied.

## 2 Materials and methods

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### 2.1 Materials

Fibre sheets (NF) were obtained from plantain stalks (Sasaima, Cundinamarca, Colombia), the semicrystalline PLA (PLAsc) and amorphous PLA (PLAa) from NatureWorks LLC (Químicos y Plásticos Industriales S.A., Bogotá, Colombia) acetic anhydride (AA), acetone and glycerol were obtained from Vidcol S.A.S. (Bogotá, Colombia), native cassava starch from Cimpa S.A.S. (Bogotá, Colombia), ripe compost TENZEL was provided by Insumos Biológicos de Colombia (Bogotá, Colombia) and vermiculite from Control Biológico Integrado LTDA (Bogotá, Colombia).

### 2.2 Chemical pretreatment

The NF was cleaned, dried at 60 °C for 24 hours and stored at 20 °C until their use. The AA was dissolved in acetone (ratio of AA in acetone, 1:10) the fibres were immersed in the AA/acetone solution for 24 hours (solution: fibre ratio of 1:20) at room temperature. After several washes with acetone, to ensure the removal of all residues of the reagents. Finally, the treated fibres were dried in an oven at 60 °C for 24 hours (Rodríguez *et al.*, 2014).

### 2.3 Preparation of thermoplastic starch (TPS)

Native cassava starch was mixed with 30% w/w glycerol, and 5% w/w PLA in a Marshal Twin Roll Mill double roller mixer (Darteno Industries, Gujarat, India). The obtained TPS was conditioned at 50% RH and 25 °C for 7 days, TPS sheets were obtained by compression moulding.

## 2.4 Preparation of laminated composite material

NF sheets were obtained by cutting from stalks. PLAsc, PLAA and TPS sheets were obtained by compression moulding in a Marshal Hydraulic Press (Darteno Industries, Gujarat, India). For the TPS, preheating was used at 130 °C, 6 min at 3 kg/cm<sup>2</sup>, and 1 min at 232 kg/cm<sup>2</sup>. Finally, the mould was cooled at ambient conditions. The sheets of PLAsc were obtained at 175 °C, 3 Kg/cm<sup>2</sup> for 6 min and 1 min at 232 Kg/cm<sup>2</sup>. Those of PLAA were obtained at 175°C, 4 min at 4 Kg/cm<sup>2</sup> and 1min at 232 Kg/cm<sup>2</sup>. The laminated composites were obtained by compression of a sheet of NF (with surface modification -SMNF- and without chemical treatment -NF-) with a sheet of PLAsc or PLAA or TPS. In this sense, each laminated had two layers.

In case of PLAsc and PLAA, the composite was introduced into the machine at a constant temperature of 165 °C and pressures of 3 Kg/cm<sup>2</sup> for 3 min and 1 min at 130 Kg /cm<sup>2</sup> since at this temperature the PLA polymer it melts, and it could move through the fibres. For the composite with TPS a constant temperature of 130°C is maintained for 5 min at 130 Kg/cm<sup>2</sup>, upon completion of the time and pressure intervals, the obtained material was removed from the machine. Table 1 shows the studied formulations.

## 2.5 Characterization of the composite materials

### 2.5.1 Scanning Electron Microscopy (SEM)

The surface and cross-section of the composites was observed using an SEM JEOL Microscope (JSM-6490 LV) with an acceleration voltage of 10 kv and magnifications between and 2000. Before the analysis, the samples were cryo-fractured using liquid nitrogen and covered with a thin layer of gold (Huda, Drzal, Mohanty, & Misra, 2008).

### 2.5.2 Mechanical tests

The composite material was analysed using a universal test machine TA. XT plus (Stable Micro Systems, Godalming, Inglaterra) considering the ASTM D882 (ASTM, 2002). The mechanical properties (tensile strength TS (MPa), elastic modulus EM (MPa) and elongation E (%)) were obtained from strength-deformation curves of henky. The samples dimensions were 2.5 cm wide and 10 cm long. The test speed was

50 mm/min; the load cell was 200 N, 10 replicas of each sample were used.

### 2.5.3 Thermogravimetric analysis (TGA)

The thermogravimetric analysis (TGA) was carried out using a TGA Stare System Analyzer (Mettler-Toledo, Inc., Switzerland) under a nitrogen atmosphere, with a gas flow of 10 mL/min, the samples weighted about 3.5 mg. Measurements were taken in a heating range between 25 to 600°C with a rate of 20°C/min. Curves were analysed by STARe Evaluation Software (Mettler-Toledo, Inc., Switzerland). The initial degradation temperature and the maximum temperature (Peak) were recorded from the first derivative of the resultant weight loss curves (Ortega-Toro *et al.*, 2015).

### 2.5.4 Optical properties

For the colour test, a CR-410 colourimetry was used, which is a portable instrument for evaluating the colour of different objects with an observation angle of 10°. Several random points were taken on the surface of the samples by recording the coordinates L\*, a\*, b\* given by the instrument. For the gloss test, a Horiba IG-320 gloss meter with an incidence angle of 60° was used, the units were expressed as gloss units.

### 2.5.5 Biodegradation tests

The biodegradation of PLAsc, PLAA and TPS was done according to the ASTM D5338 (ASTM, 2003). The aerobic biodegradation of plastics was carried out under controlled conditions of composting (temperature, humidity, light and oxygen). Vermiculite was used to facilitate oxygenation. The compost has 49% of dry solids (DS), 28.4% of volatile solids (VS) and pH around 8.1 (Peinado *et al.*, 2014). The study was performed in an incubator BINDER BD 115 (BINDER, New York, Estados Unidos) at 58°C for 45 days. Samples of 2x2 cm<sup>2</sup> were put into 300 mL of compost, among which were test samples, control (compost only) and reference substance (cellulose).

The percentage of carbon dioxide generated in each device was determined using a Dansensor device (PBI Dansensor, Check Point O<sub>2</sub>/CO<sub>2</sub>, Minneapolis, United States). The carbon present in the sample is transformed into carbon dioxide (CO<sub>2</sub>). The theoretical amount of CO<sub>2</sub> is calculated (CO<sub>2</sub>T) through Eq. (1). According the CO<sub>2</sub>T and the data of CO<sub>2</sub> obtained during the test, the percentage of

biodegradation (% B) was calculated using Eq. (2) (ASTM, 2003).

$$CO_2T = Mm \times Cm \times \frac{PM_{CO_2}}{PMc} \quad (1)$$

Where  $Mm$ , is the weight in grams (g) of the dry film introduced in the composting device;  $Cm$ , is the proportion of carbon present in the sample (g C/ g dry sample);  $PM_{CO_2}$ , is the molecular weight of carbon dioxide (44 g/ mol) and  $PMc$ , is the molecular weight of carbon (12g/ mol).

$$\%B = \frac{CO_{2M} - CO_{2B}}{CO_{2T}} \times 100 \quad (2)$$

Where  $CO_{2M}$ , is the cumulative amount of  $CO_2$  in the test sample and  $CO_{2B}$ , is the cumulative amount of  $CO_2$  in the reference sample.

### 3 Results and discussion

The SEM analysis was carried out in PLAA, PLAsc, and TPS before and after the chemical treatment (chemical modification of NF by acetylation). In this way, the shape of the fibres and the adhesiveness of these with the polymeric matrix was observed. Fig. 1 shows the surface of each polymer film (left) and the surface of composite laminates exhibiting the layers of the polymer sheets using fibres without chemical treatment (middle) and fibres with chemical treatment (right). It can be observed the surface differences among the different materials, especially when the chemical treatment is applied. The chemical treatment could increase the affinity between two sheets, and in this sense, the form of some fibres (from the sheet of plantain-stalk) can be observed through of the continuous sheet of polymer. The effect is remarkable in the PLAA and PLAsc. In the case of TPS, the surface is more smoothly with the chemical treatment of the fibres.

Fig. 2 shows the SEM micrograph of cross-sections of different materials at different magnifications. It can be observed sheets of pure polymers (left), composite laminates without chemical treatment of fibre sheets (middle) and with chemical treatment of fibre sheets (right). The polymer sheets are continuous and homogeneous with some deformities caused by the cryo-fracture. On the other hand, the fibre sheets with chemical treatment exhibit great structural differences compared with those natural fibres.

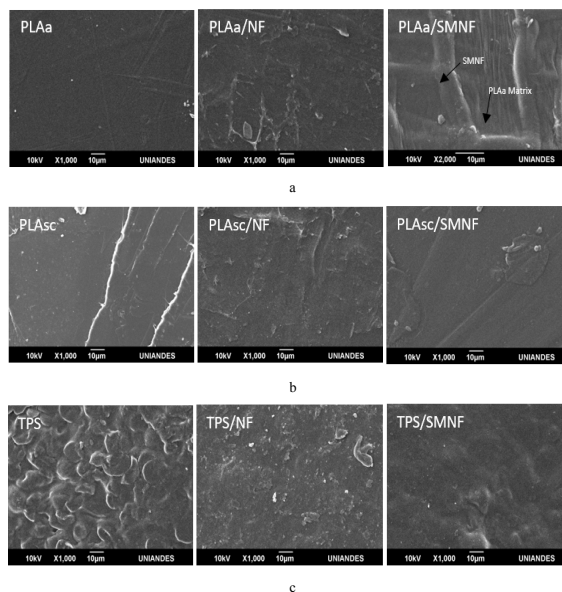


Fig. 1. SEM micrographs of the surface morphology of polymers, PLAA, PLAsc, TPS and laminates with and without chemical treatment.

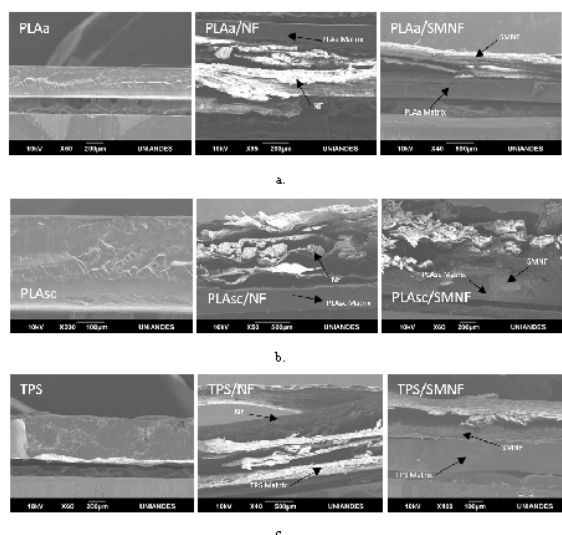


Fig. 2. SEM micrographs of cross-section of different studied materials.

The acetylation of fibres improves their compaction, and therefore the global structure of the composite laminates is improved. Besides, it can be observed that the interface affinity between polymer and fibre is enhanced. The surface modification of the fibres causes this effect, the acetyl groups introduced by chemical treatment to the fibres promote the affinity with the ester groups of the PLA and possibly

with the hydroxyl groups of the TPS (Frone *et al.*, 2011). Furthermore, the TPS has 5% of PLA in their formulation, and this is enough to increase the affinity using the ester groups.

Fig. 2a shows a general view of the PLAA. It exhibits a sheet with completely smooth defined morphology, the compound without chemical treatment has a disordered laminar morphology. In the dark areas, the low adhesiveness of the fibre with the polymer matrix is evidenced. For the materials with chemical treatment, fibres are structurally laminar and a little more orderly. The cryo-fracture of the material was performed in the same direction of the fibre orientation that allows seeing the longitudinal area of fibres arrangement.

The PLAsc in Fig. 2b presents an ordered structure with some irregularities. The laminate without chemical treatment shows clearly the fracture of the fibre. A very disordered structure is remarkable. This observation demonstrates a deficient interaction between the fibres and the polymer and an evident lack of compactness in the inner of the fibre sheet. The materials with chemical treatment display different arrangement, it is a disordered structure, but it has compact organisation. There are few signs of separation of the laminates (polymer and fibre sheets) which suggests that the interfacial adhesion between the acetylated surface and the polymeric matrix has become highly favourable and robust. Since the fracture occurred perpendicular to the orientation of the fibre, it can be seen the formation of a tubular and amorphous agglomeration, in certain areas, that are not in contact with the polymer layer.

In Fig. 2c the cross-section of the TPS matrix is observed. The structure is irregular and with some particles of PLA dispersed in the continuous matrix of thermoplastic starch. In materials without chemical treatment, the fibres are detached from the polymer and show lack of inner compactness. In addition to the chemical modification, the acetylation promotes the elimination of some impurities of the stalk sheets (Blackburn, 2005), it enhances the interactions between the sheets of TPS/PLA and fibres.

### 3.1 Mechanical properties

The tensile strength (TS) and the elongation (% E) are respectively the maximum tension and elongation that a sheet can withstand before breaking, the modulus of elasticity (EM) is related to the rigidity of the material, considering the first section of elastic deformation of the stress-strain curve (Pastor *et al.*, 2013). Table 1 shows tensile strength (TS), elastic modulus (EM) and elongation at the break point of studied materials.

It was found that for the composites with chemical treatment the elastic modulus and the tensile strength increased considerably, but the elongation decreased. This phenomenon has been reported in studies such as the one carried out by Jamshidian *et al.* (Jamshidian *et al.*, 2012), and it is due to the mechanical properties inherent to the fibres, those are rigid and have not deformation capacity. The acetylation carried out in the NF was able to eliminate impurities, amorphous hemicellulose content in addition to making the surface of the fibre more hydrophobic, thin and rough, which increases the rigidity of the material and caused a more significant interaction with the polymer matrix.

Table 1. Mean values and standard deviation of mechanical properties of PLAA, PLAsc, TPS and laminated composites conditioned at 53% RH and 25 °C for 7 days.

Formulation	Mechanical properties		
	TS (MPa)	EM (MPa)	E (%)
PLAA	35 ± 4 <sup>b</sup>	1350 ± 76 <sup>b</sup>	4.1 ± 0.2 <sup>b</sup>
PLAA/NF	48.0 ± 1.0 <sup>c</sup>	2695 ± 120 <sup>c</sup>	0.31 ± 0.03 <sup>a</sup>
PLAA/SMNF	51.5 ± 1.2 <sup>c</sup>	2710 ± 110 <sup>c</sup>	0.23 ± 0.03 <sup>a</sup>
PLAsc	42 ± 6 <sup>b</sup>	1810 ± 45 <sup>b</sup>	2.3 ± 0.4 <sup>b</sup>
PLAsc/NF	48.5 ± 2.5 <sup>c</sup>	2690 ± 106 <sup>c</sup>	0.24 ± 0.04 <sup>a</sup>
PLAsc/SMNF	50.1 ± 1.2 <sup>c</sup>	2720 ± 120 <sup>c</sup>	0.35 ± 0.03 <sup>a</sup>
TPS	12 ± 0.8 <sup>a</sup>	250 ± 34 <sup>a</sup>	28 ± 7 <sup>c</sup>
TPS/NF	50.0 ± 1.5 <sup>c</sup>	2690 ± 132 <sup>c</sup>	0.33 ± 0.08 <sup>a</sup>
TPS/SMNF	52.0 ± 1.0 <sup>c</sup>	2740 ± 121 <sup>c</sup>	0.25 ± 0.07 <sup>a</sup>

Different superscript letters in the same column indicate significant differences between the materials ( $p < 0.05$ ).

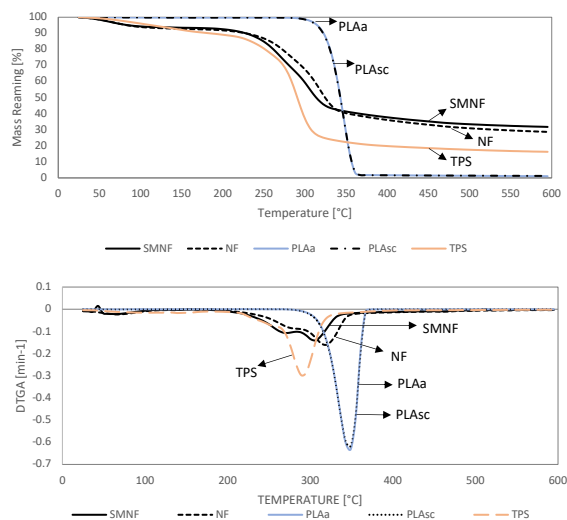


Fig. 3. TGA and DTGA curves for NF with and without chemical treatment and for PLAA, PLAsc and TPS.

The bi-laminates with chemical treatment have better mechanical behaviour in all cases. The enhancement of TS and EM respect to sheets of pure polymers is remarkable, although these have not significant differences with bi-laminates without chemical modification. Those with PLAsc matrix shows an increase in TS and EM of 19% and 50% respectively, in comparison to the PLAsc pure. These values of enhancement were lower than those exhibited by PLAA and TPS composites. The crystalline structure of PLAsc could reduce the capacity to create interactions between fibre and polymer sheets, as was observed in SEM micrographs. In the case of PLAA, the enhancement of TS and EM was 47% and 101%, respectively. For TPS, the increment in TS and EM was of 333% and 996% respectively. The TPS could be considered as the material that showed a more significant improvement due to their original properties are lower compared with those of PLA. Besides, the mechanical properties of bi-laminates were clearly influenced by the fibre sheets properties. On the other hand, as was expected, the elongation is reduced in all cases because of the low deformation capacity of the fibres.

### 3.2 Thermogravimetric analysis (TGA)

The thermogravimetric analysis studied the thermal stability of PLAA, PLAsc, TPS and NF with and without chemical treatment. Fig. 3 shows both the percentage of weight change (TGA) and the derivative

of weight concerning time (DTGA) in function of the temperature for each material.

In NF curves, three stages of degradation are evidenced. In the first region at 40°C-100°C, it is attributed to the evaporation of water of approximately 7.6%. The second stage is observed in the region between 135°C - 195°C and is due to the decomposition of chlorophyll, sugars, fats and other extractive components (Rodríguez *et al.*, 2014). The third stage at 217°C - 350°C, in which the hemicellulose (45% approximately) is degraded. The temperature of maximum degradation of the NF was 332°C. Similar results was reported by Collazo *et al.* (2018a, b) in composites of starch and cellulose from coffee and rice husks.

The behaviour of SMNF shows that the loss of mass, due to the evaporation of the water, was lower than that registered in the untreated fibres, with approximately 3.8% up to 225°C. Between 230 °C and 345°C, the loss of mass in the acetylated fibres was 60%, continuously and accelerated, with a maximum intensity at 319°C. This behaviour was different compared to untreated fibres that presented loss of mass due to the degradation of different compounds. The differences are related to the acetylation treatment in which were removed water and other fibre compounds such as amorphous hemicellulose. Studies such as the one carried out by Spinacé *et al.* (2009), describe that thermodegradation of polysaccharides, such as cellulose, can occur due to the breakdown of glycosidic bonds (CH, CO and CC), dehydration, decarboxylation reactions and decarbonylation, with formation of CC, C = C and CO bonds.

The degradation temperatures for PLAsc and PLAA occurred at a similar temperature (350 °C). In the case of TPS, the Peak of degradation temperature was at 290°C approximately. TPS presented two stages of degradation, the first one is observed between 50°C - 128°C may be due to the evaporation of water. This information is essential for because indicate that during the thermomechanical process for developing laminates, the materials did not suffer significant thermal damage.

### 3.3 Optical properties

Table 2 shows the respective colour parameters of the materials. The sheets showed values of L\* between 79.9 and 72.1 for all the samples. The change in this parameter is more remarkable in laminates with PLAA and TPS than in PLAsc. This parameter could be related to the surface roughness.

Table 2. Mean values and standard deviation in CIE L\*a\*b\* colour space for pure polymers and laminate composites.

	Colour parameters		
	L*	a*	b*
PLAsc	74.9 ± 1.2	6.9 ± 0.4	4.2 ± 0.5
PLAsc/SMNF	76.8 ± 1.1	10.7 ± 0.9	8.9 ± 0.4
PLAsc/NF	76.9 ± 1.2	10.1 ± 1.0	8.3 ± 0.9
PLAa	74.9 ± 1.4	6.9 ± 0.4	4.2 ± 0.3
PLAa/SMNF	77.0 ± 1.2	9.3 ± 0.3	7.5 ± 0.3
PLAa/NF	79.9 ± 1.0	9.2 ± 0.2	.5 ± 0.2
TPS	72.1 ± 0.5	6.9 ± 0.3	4.6 ± 0.2
TPS/SMNF	72.8 ± 2.1	9.0 ± 0.2	7.2 ± 0.4
TPS/NF	75.3 ± 2.3	9.9 ± 0.5	12.5 ± 0.2

L\* (Luminosity), a\* (Coordinates red / green), b\* (Coordinates yellow / blue).

Table 3. Mean values and standard deviation of gloss at 60° (gloss units) for pure polymers and laminate composites.

Formulation	Gloss (60°)	
	Polymer layer	Fiber layer
PLAsc	56.4 ± 1.2	
PLAsc/SMNF	24.6 ± 0.8	2.9 ± 0.2
PLAsc/NF	28.2 ± 0.9	3.8 ± 0.3
PLAa	51.2 ± 1.5	
PLAa/SMNF	11.5 ± 0.3	4.2 ± 0.2
PLAa/NF	14 ± 0.5	3.3 ± 0.2
TPS	13.2 ± 0.8	
TPS/SMNF	9.8 ± 0.7	3.7 ± 0.4
TPS/NF	14.9 ± 0.7	3.3 ± 0.5

The luminosity of the materials is higher as the roughness is lower. In general, the values of L\* as lower in fibres with chemical modification because the sheets of pure polymer and fibre interact more efficiently and, in consequence, the layer of polymer take the heterogeneous superficial relief of the fibre layer. The values of a\* vary between 10.7 and 6.9, suggesting that no remarkable changes occurred among formulations being the trend to subtle red. Finally, regarding b\*, the values were positive oscillating between 12.5 and 4.2 which are still small values, but with a tendency to subtle yellow.

Table 3 shows the gloss of pure polymer layer and laminate composites. It can be observed that the fibre layer has lesser gloss values than polymer due to the surface roughness of fibres. In the same way, laminate composites with chemical treatment have slightly lesser gloss than those without chemical treatment.

These phenomena have the same explanation than the luminosity effect exposed above. The higher the interactions between polymer-fibre sheets, higher the surface irregularities, due to fibre surface topography. In this sense, PLAa could interact more efficiently with fibre sheet than PLAsc. On the other hand, the lesser values of this parameter in TPS could be due to the retrogradation phenomena during storage time, the molecular rearrangement of amylose and amylopectin promotes the surface irregularities (Ma *et al.*, 2005).

### 3.4 Tests of biodegradation

Fig. 4 shows the results for biodegradation tests using a controlled composting system with a CO<sub>2</sub> sensor. The biodegradation of cellulose was taken as a reference, and after 45 days of composting at a constant temperature of 58 °C, 73.5% biodegradability was obtained. For PLAsc, PLAa and TPS was 78.3%, 75.5% and 73.2% respectively. It can be observed that the TPS has a behavior in terms of its degradation similar to the reference, this is due to its high content of glycerin which increases the capacity to absorb water from the medium. The moisture facilitates the proliferation of fungi and bacteria that degrade the starch, and catalysis is generated by the action of enzymes that break the bonds between the glucose units (Merchán *et al.*, 2009). Also, it can be observed that the TPS degrades faster than both PLAa and PLAsc and reaches equilibrium in less time. However, the PLA has higher final degradation (Fukushima *et al.*, 2013). On the other hand, PLAa shows a faster degradation compared to PLAsc since when it is in contact with water, it diffuses more easily in the amorphous regions because its structure is less

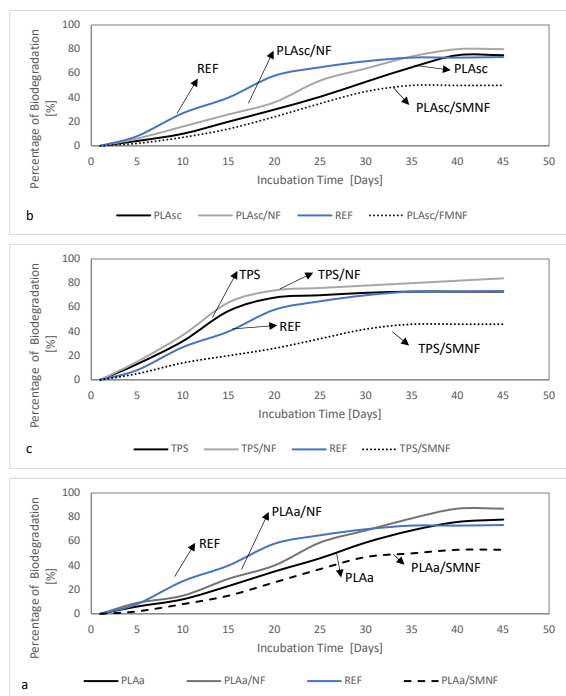


Fig. 4. Percentage of biodegradation of the polymers tested: a. PLAa materials; b. PLAsc materials; and c. TPS materials.

compact.

Respect to chemical treatment effect, the composites that contained NF without chemical treatment have a higher percentage of biodegradation. This fact is due to that the fibres can absorb water from the medium and it causes an increment the free volume which favours the microbial attack and leads to the hydrolysis of it (Wu *et al.*, 2017). The biodegradation percentages for PLAa/NF, PLAsc/NF and TPS/NF without chemical modification were 87.2%, 85.3% and 83.6% respectively. When a chemical treatment is carried out on the fibre sheets, a decrease in the degradation of the material is evidenced because the fibre becomes more hydrophobic which does not allow the absorption of water. Also, the hydrolysis is delayed because the polymer matrix increases its inner molecular attraction which makes water diffusion difficult (Yu, 2009).

## Conclusions

Sheets of semicrystalline PLA, amorphous PLA and TPS were assembled with sheets-stalk of *Musa*

*cavendish* by compression moulding. This process was done to improve the mechanical resistance of net polymers as was evidenced in mechanical properties, especially in tensile strength and elastic modulus. Besides, acetylation was done on fibre sheets to improve its interfacial adhesion with the polymer sheets, as was seen in SEM micrographs and affect mechanical and optical properties. Thermogravimetric analysis showed slightly higher thermal stability of fibres without chemical treatment. In the same way, the stability to degradation was higher in materials with chemical modification. Considering its physicochemical properties, the laminate composites with chemical treatment could be promissory for food packaging of dry and fat foods.

## Acknowledgements

The authors thank Jorge Tadeo Lozano University and the University of Cartagena for their support in carrying out this work.

## Nomenclature

AA	Acetic anhydride
CO <sub>2T</sub>	Theoretical amount of CO <sub>2</sub>
Cm	Proportion of carbon present in the sample
E	Elongation
EM	Elastic modulus
Mm	Weight in grams
NF	Natural Fibre
PLAsc	Polylactic Acid semicrystalline
PLAa	Polylactic Acid amorphous
PMCO <sub>2</sub>	Molecular weight of carbon dioxide
PMc	Molecular weight of carbon
SMNF	Surface chemical modification of fibres
SEM	Scanning Electron Microscopy
TGA	Thermogravimetric analysis
TPS	Thermoplastic starch
TS	Tensile strength
% B	Percentage of biodegradation

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