



## WEATHERING AND BIODEGRADATION OF POLYLACTIC ACID COMPOSITE REINFORCED WITH CELLULOSE WHISKERS

## EL INTEMPERISMO Y LA BIODEGRADACIÓN DE MATERIAL COMPUESTO DE ÁCIDO POLILÁCTICO REFORZADO CON WHISKERS DE CELULOSA

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Received 9 of October 2012; Accepted 28 of November 2012

### Abstract

This work focuses on analysis and comparison of accelerated weathering of samples of polylactic acid reinforced with cellulose whiskers (PLA-CW), conducted in QUV chamber-Panel, and their subsequent exposure to biotic soil environment. The cellulose whiskers (microfibrils) were obtained from banana rachis and pseudostem *Musa cavendish*. Changes in thermal, structural and mechanical properties, due to degradation processes of PLA-CW, were studied using DSC, IR Spectroscopy, XRD, NMR, GPC and Mechanical test. The results show that the percentage of biodegradability in soil, based on CO<sub>2</sub> release, is higher for samples of PLA-CW that have been previously exposed to UV-photodegradation, which induces hydrolysis that stimulates the biodegradability of PLA-CW. The results indicate that PLA-CW has short half-life after biodegradation in soil and it is suitable for land disposal.

**Keywords:** weathering, biodegradation, cellulose whiskers, poly (L-lactic) acid biocomposite.

### Resumen

En este estudio se investigó la biodegradación en suelo del material compuesto de ácido poliláctico reforzado con whiskers (microfibrillas) de celulosa (PLA-CW), obtenidas de raquis y pseudotallo de *Musa cavendish* previamente expuesto y no a los efectos de radiación UV (intemperismo acelerado en cámaras QUV-Panel). Los cambios en las propiedades térmicas y estructurales, debido a los procesos de degradación de muestras de PLA-CW, fueron determinados usando Calorimetría Diferencial de Barrido, Espectroscopia de Infrarrojo, Difracción de Rayos-X, Resonancia Magnética Nuclear y Cromatografía de Permeación en Gel. Los resultados obtenidos muestran que existe un efecto sinérgico para el proceso de biodegradación, cuando las muestras PLA-CW son expuestas a intemperismo y posteriormente a biodegradación en suelo. La fotodegradación del material induce reacciones de hidrólisis, mejorando y acelerando el proceso de biodegradabilidad de PLA-CW, ya que el polímero compuesto se vuelve más susceptible a las reacciones bióticas. Los resultados reportados aquí indican que los materiales tienen un corto tiempo de vida media en ambientes bióticos y por lo tanto después de su uso son adecuados para su eliminación en suelo.

**Palabras clave:** intemperismo, biodegradación, whiskers de celulosa, biocompuestos de ácido poliláctico.

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## 1 Introduction

The commercial importance of polymeric materials has been derived from its wide range of applications covering various fields such as aerospace, automotive, marine, infrastructure, military, packaging, etc. However, the vast majorities of them are not biodegradable and usually have degradation times over 50 years. Attempts have been made to replace some components of those non-biodegradable polymeric materials, such as fillers and/or reinforcements, introducing some that are biodegradable and producing eco-friendly compounds (Pandey *et al.*, 2005). The last ten years have been tested biodegradable resins, as much more attractive strategy for the replacement of conventional plastics. The use of biodegradable polymers in agriculture, as well as in the packaging area or other disposable items, has increased in a major way in the last five years and it is expected a rapid increase in their use in the coming years, driven by cheap biodegradable resins and greater awareness of the population regarding the need to halt environmental degradation. The thermoplastic polyesters based on lactic acid, such as polylactic acid (PLA), are known to be biodegradable and compostable polymers that rapidly and completely decompose in a compost environment to carbon dioxide, water and biomass. PLA is not toxic and it is derived from natural renewable resources during microbial fermentation of biomass. The biocomposites are usually formed by biodegradable polymers as matrix and natural fibers as reinforcements (Kumar *et al.*, 2010). Microfibrils (whiskers) of cellulose (CW) have been introduced as reinforcements in many types of polymeric matrices in order to replace glass-reinforced plastics. The cellulose may undergo a complete degradation and the cellulose fiber-reinforced biodegradable polymeric matrices, such as PLA, are regarded as a more environmentally friendly, leaving no harmful residues during its microbial attack (Pandey *et al.*, 2010). When biodegradable polyesters are exposed to the environment, photodegradation, biodegradation and hydrolytic degradation occur (Tsuji and Nishimura, 2006). It has been reported that UV-radiation reduces the molecular mass, stress and strain at break of PLA films after a long exposure time (Ho and Pometto, 1999; Ho *et al.*, 1999) and the influence of temperature and humidity on the PLA degradation films has been described separately. The simultaneous action of UV-radiation, temperature and humidity on the PLA degradation has been investigated (Copinet *et*

*al.*, 2004; Tsuji and Nishimura, 2006) and it was observed an increase in molecular mass distribution (Mw/Mn) for PLA films exposed to UV light, for time scales greater than 200 hours. It was suggested that the photodegradation of pure PLA proceeds via Norrish II mechanism, which explains the chain scission (low molecular weight) and the formation of C = C double bonds (Ikada and Ashida 1991; Ikada 1993; 1997; 1999). The effects of the photosensitizer N,N,N',N'-tetramethyl-p-phenylenediamine (TMPD) on the UV photodegradation of PLA films have been also reported (Sakai *et al.*, 2002; Tsuji *et al.*, 2005; Janokar *et al.*, 2007). The results revealed that the molecular mass, for example, decreased significantly with exposure time of 12 h and the PLA film after exposure was remarkably fragile. PLA degradation in various environments, such as liquid medium (Torres *et al.*, 1996a), composted (Iovino *et al.*, 2007) in soils (Rudnik and Briassoulis 2010; Torres *et al.*, 1996b) has been reported. The PLA biodegradation in soil is not yet understood at all although the degradation of PLA has been studied extensively (Tokiwa and Calabria 2006). The results reported on photodegradation and biodegradation of PLA and composite materials based on this polymer matrix are difficult to compare, because they generally have been obtained under different conditions with respect to process parameters, thickness of samples and their previous chemical treatments.

This study focuses on analysis and comparison of accelerated weathering of samples of polylactic acid reinforced with cellulose whiskers (PLA-CW), conducted in QUV chamber-Panel and their subsequent exposure to biodegradation in soil. The whiskers were obtained from agro-industrial wastes of bananas (*Musa cavendish* pseudostem and raquis), cultivated in the Mexican state of Tabasco (Gulf of Mexico), and using acid hydrolysis (Bolio *et al.*, 2011). Weathering conditions in QUV chamber have been designed in such ways that simulate the humid tropical climate of the Gulf of Mexico. The soil type Fluvisol was collected from the banana plantations in Tabasco and prepared according to the ASTM D6002 (ASTM D6002) "Standard Guide for Assessing the compostability of environmentally degradable plastics", Practice D5988-96 "Standard Test Method for determining aerobic biodegradation in soil of plastic materials or residual plastic materials after composting".

## 2 Experimental

### 2.1 Materials

PLA composite (PLA-CW), including 2% by mass of cellulose whiskers (CW), microfibers obtained from banana (*Musa cavendish* pseudostem and raquis), was elaborated by acid hydrolysis (4N HCl and subsequent 64% H<sub>2</sub>SO<sub>4</sub>), according to the procedure previously reported (Bolio *et al.*, 2011), the suspension of CW was mixed with a chloroform solution of the biodegradable PLA matrix and assisted with the sonication process, to prevent an agglomeration of the CW in the PLA matrix. The mixture was dried in the oven in Petri dishes, at a temperature of 60°C under vacuum, and then the PLA-CW were ground in a “Brabender” mill (mesh size of 1 mm). Flat samples were produced, using an automatic laboratory press “Carver” at 7000 lb of pressure and temperature of 160°C. The plates obtained were cut in a tire cutter, obtaining samples for test (12cm × 12 cm × 1 mm).

### 2.2 UV-Weathering test

Triplicate composite samples PLA-CW were exposed in a QUV accelerated aging chamber QUV/SE (Q-Panel Co.), with UVA-340 fluorescent lamps, with a typical irradiance of 0.89 W/m<sup>2</sup>/nm and approximate wavelength of 340 nm (ASTM D5208-01, practice G154-06). Two cycles were performed during 8 days, simulating the humid tropical climate of Gulf of Mexico: 8 hours of UV-irradiation at 50°C and 30% of air relative humidity (RH), followed by 4 hours condensation at 40°C and 100% RH. The test was run in the QUV-Panel according to the methodology of Practice G154-06 (ASTM D5208-01).

### 2.3 Biodegradability in soil

The aerobic biodegradability in soil of PLA-CW composite samples was determined according to the methodology of ASTM D6002 “Standard Guide for Assessing the compostability of environmentally degradable plastics”, Practice D5988-96 “Standard Test Method for determining aerobic biodegradation in soil of plastic materials or residual plastic materials after composting”. The soil of our interest was a Fluvisol type, from the Chontalpa area, State of Tabasco (Mexico), which is classified texturally as sandy clay-loam with 30% clay, 46% silt and 24% sand, taken from the surface up to 8 cm deep and then sieved to 2 mm particle. The organic matter content

was 2.4%, C:N ratio 10:1, organic carbon (C.O.) 1.4% and pH= 6.0. The composite and soil were mixed, as recommended by ASTM D5988-96. The frequency of titration was done every 48 hours during the first 2 weeks and once a week after the third week, according to the rate of degradation (CO<sub>2</sub> release) of the composite. Assay containers were stored in dark room at 22 ± 3°C. A control substance, known as biodegradable (cassava starch), was subjected to the same test in order to check the activity level of soil CO<sub>2</sub> balance, important for the biodegradability of the material.

### 2.4 Instrumental analysis

#### 2.4.1 Gel Permeation Chromatography (GPC)

Samples (20 g) of PLA-CW 0D (not weathered) and PLA-CW 8D (UV-weathered for 8 days) were dissolved in 10 ml of tetrahydrofuran (THF). The mobile phase was of the THF system, at a flow rate of 1 ml min<sup>-1</sup> and temperature of 40°C, was analyzed for molecular mass distribution. The results were expressed as percentage loss of molecular mass (%M<sub>0</sub>):

$$M_0(\%) = \frac{M_0 - M_t}{M_0} \times 100 \quad (1)$$

where:  $M_0$  is the initial molecular mass of PLA and  $M_t$  is the molecular mass of the composite that corresponds to each period of time during its degradation.

#### 2.4.2 X-ray Diffraction (XRD)

The patterns of X-ray diffraction of the composite samples, not weathered (PLA-CW 0D) and UV-weathered during 8 days (PLA-CW 0D 8D), were analyzed with a “Siemens D 5000” diffractometer using CuK $\alpha$  radiation ( $\alpha = 1.5418 \text{ \AA}$ ) at a 34 kV and a current of 25 mA, in a 2 $\theta$  angular range between 10 and 30 degrees, making measurements every 0.04° for 6 s. The percentage of crystallinity ( $X_c\%$ ) of the composite PLA-CW was calculated according to Segal equation (Segal *et al.*, 1959):

$$X_c(\%) = \left(1 - \frac{I_1}{I_2}\right) \times 100 \quad (2)$$

where:  $I_1$  is the minimum peak intensity in the XRD graph and  $I_2$  the crystalline peak intensity, respectively. The crystal size ( $t$ ) was calculated using the equation proposed by Scherrer (Cullity, 1978)

$$t = \frac{K\lambda}{\cos\theta} \quad (3)$$

where:  $\lambda$  is the wavelength of the radiation ( $\lambda$ Cu), B is the width at half height of the diffraction peak of the sample,  $\theta$  is the diffraction peak position and K is the dimensionless form factor which has a typical value of about 0.9, but varies with the actual shape of the crystallites.

#### 2.4.3 Differential Scanning Calorimeter (DSC)

Thermal parameters of UV-weathered or not samples of PLA-CW composite (7 mg of sample), such as glass transition temperature, melting and crystallinity, were determined using “Perkin Elmer DSC-7” in the temperature range of 30°C to 250°C, at a heating rate of 10°C min<sup>-1</sup>.

#### 2.4.4 Infrared Spectroscopy (FTIR)

PLA-CW samples, UV-weathered or not, subjected to biodegradation in soil (for 0, 60 and 120 days), were dissolved in deuterated chloroform at 25°C and their spectra <sup>1</sup>H NMR was processed using a Bruker spectrometer, operated at a frequency of 400.17 MHz, with an acquisition time of data equal to 3 seconds, to determine the molecular distribution of mass (Mn).

#### 2.4.6 Carbon mineralized as CO<sub>2</sub>

Aerobic degradation (mineralization) of PLA-CW samples, after their exposure in soil, was determined measuring the released CO<sub>2</sub> and then calculated as a percentage of mineralization:

$$\% \text{Mineralization} = \frac{nCO_{2(\text{material})} - nCO_{2(\text{blank})}}{nThCO_2} \quad (4)$$

where: nThCO<sub>2</sub> is the potentially available theoretical initial amount of CO<sub>2</sub> (mmol) in the PLA-CW composite and nCO<sub>2(material)</sub> and nCO<sub>2(blank)</sub> are the amounts of CO<sub>2</sub> produced during sample degradation test in the soil and soil control, respectively. The CO<sub>2</sub> release monitoring was ended when the biodegradation process reached the steady state (Calmon *et al.*, 1999).

### 3 Results and discussion

#### 3.1 Aerobic degradation of the composite PLA-CW in soil

Biodegradation kinetics of composite polymer material in soil, expressed as percentage of released CO<sub>2</sub>, is shown in Fig. 1.

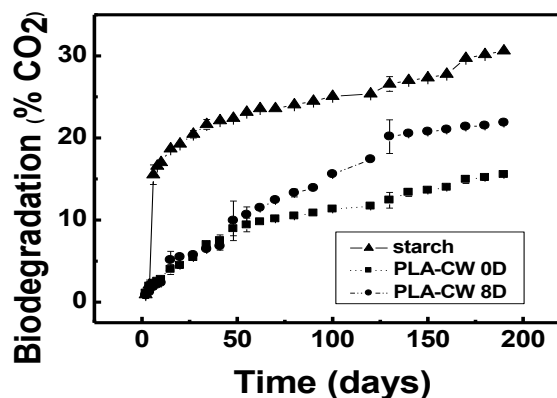


Fig. 1. Biodegradation (%CO<sub>2</sub>) of the composite PLA-CW: samples without prior cycles of UV-weathering (PLA-0D CW); UV-weathered for 8 days (PLA-CW 8D); cassava starch samples (reference substance).

The behavior of PLA-CW is compared to that of starch, used as reference biodegradable substance. The high amount of CO<sub>2</sub> released from the starch since the first days confirms that this soil is quite active in microorganisms. Comparing the biodegradation tendencies of the samples, it should be noted that starch powder samples have higher surface area, compared to that of the polymer composite ones, and besides, the starch is more hydrophilic than PLA. The polymer composite samples, previously UV-weathered in cycles for 8 days (PLA-CW 8D), biodegraded faster than those that were not subjected to weathering (PLA-CW 0D). The temperature and relative humidity, as weathering parameters of UV-cycles, are important factors that facilitate the hydrolytic degradation of PLA-CW composite, inducing fundamental changes in the microstructure and rearrangements, which take place before the action of microorganism in the soil. Scott (Scott, 1997) suggests that the first step for aliphatic polyester bioassimilation is probably preceded by abiotic hydrolysis, which transforms the long polymer chains in monomers and oligomers, easily assimilated by microorganism. In fact, during the biodegradation it is expected that the amorphous regions of polymeric materials degrade faster than the crystalline regions (Tudorachi *et al.*, 2000). Similar changes have been observed during the mineralization of starch in liquid, inert solid and compost (Gattin *et al.*, 2002).

### 3.2 Evolution of the molecular mass (*Mn*) of PLA-CW

Figure 2 presents the evolution of molecular mass (*Mn*) with time of biodegradation of PLA-CW composite in soil. As can be seen, PLA-CW polymer decreases its molecular mass during the biodegradation process and this fact is more pronounced for samples subjected previously to UV-weathering cycles. The molecular mass of unirradiated composite (PLA-CW 0D) decreased gradually in 69% at 120 days (*Mn* < 22000), while the molecular mass of UV-weathered (PLA-CW 8D) with 78.9% at 60 days without significant changes to the end of the experiment (*Mn* < 9942). However, it should be noted that the UV-weathered composite samples previously have lost 30% of its initial molecular mass (Table 1), due to their photodegradation process and besides, the samples after the UV-weathering appeared fragile.

The decrease in molecular mass of the samples buried in soil is explained by the combined effect of their hydrolysis and biodegradation, which are produced by chemical cleavage of the main polymer chain by the reaction with water (Fig. 3), initiated by protonation, followed by the addition of water and cleavage of the ester linkage (Schnabel, 1981).

It could be considered that the main fragmentation in the polymer PLA chain occurs in the -C-O ester bonds, as the main chain functional groups, that are susceptible to hydrolysis. Initially the random non-enzymatic cleavage of the ester group chain leads to a reduction in molecular mass (Schnabel, 1981). This step is accelerated by acids and likewise affected by humidity and temperature (Auras *et al.*, 2004). The biofragmentación is induced mainly by enzymes that belong to oxido-reductases and hydrolases. Enzymes are catalytic proteins that lower the activation energy of the molecules promoting chemical reactions. A polymer is considered fragmented when molecules of low molecular mass are found in the media.

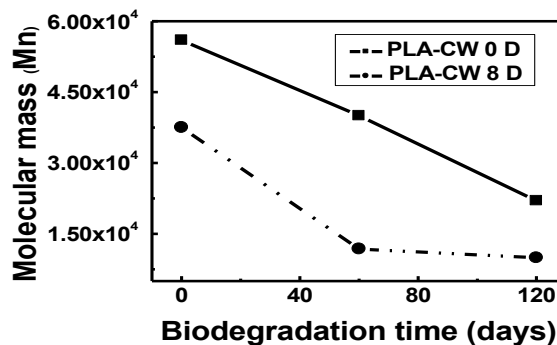


Fig. 2. Evolution of molecular mass (*Mn*) with time of biodegradation of PLA-CW composite in soil: samples without prior cycles of UV-weathering (PLA-0D CW); UV-weathered for 8 days (PLA-CW 8D).

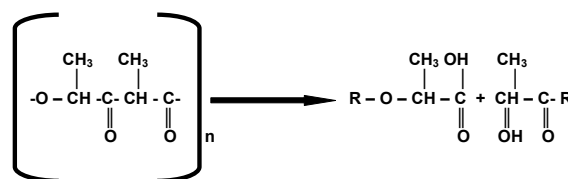


Fig. 3. Hydrolysis reaction of ester bonds (Schnabel, 1981).

In our study, it was observed that PLA-CW samples subjected to UV-weathering prior to the test in soil experienced more fragmentation than those non-weathered. Fragmentation is a lytic phenomenon necessary for the assimilation of the polymer by microorganisms (Lucas *et al.*, 2008). The release of CO<sub>2</sub> (Fig. 1) could be associated with the low molecular mass reached by the weathered PLA-CW sample at 60 days (Fig. 2), due to the oligomers and monomers formed as products of degradation and being available for the microorganisms in soil, which could assimilate these small molecular mass products and the hydrolysis takes place, converting them into carbon dioxide, water and humus.

Table 1. Molecular mass (*Mn*, *Mw*) and polydispersity (PD) of PLA-CW composite at different time of UV-weathering cycles

UV-Weathering (Days)	<i>Mn</i> (g·mol <sup>-1</sup> )	<i>Mw</i> (g·mol <sup>-1</sup> )	PD <i>Mw</i> / <i>Mn</i>
PLA-CW 0D	56,645	81,678( <i>Mw</i> 0)	1.4
PLA-CW 4D	41,855	54,945	1.3
PLA-CW 8D	37,539	46,365	1.2

Table 2. Crystallinity Index and crystal size of PLA-CW composite exposed to biodegradation in soil for 60 days (a) and 120 days (b): samples without UV-irradiation (PLA-CW 0D) and prior irradiation for 8 days (PLA-CW 8D)

PLA-CW 60 days (a)	Crystallinity Index Xc (%)	Crystals size (nm)
PLA-CW 0D	Amorphous	-
PLA-CW 8D	69.7	20.6
PLA-CW 120 days (b)	Crystallinity Index Xc (%)	Crystals size (nm)
PLA-CW 0D	71.8	15.7
PLA-CW 8D	82.7	19.4

### 3.3 Crystallinity of PLA-CW (XRD)

The degree of crystallinity of PLA as a matrix of the polymer composite and of samples of PLA-CW, UV-weathered or not, and then subjected to biodegradation in soil, was determined by X-ray diffraction (Fig. 4 and Fig. 5). XRD spectra of the PLA-CW samples showed sharp peaks at 16.8° and 19.2° 2θ angular position, which are characteristics for PLA.

The main peak at 2θ =16.8° in XRD-spectra indicates a reflection of the α-form of the monocrystal structure, similar to that observed by (Gonzalez *et al.*, 1999), after PLA degradation to lower molecular mass. It can be seen that the intensity of the XRD-peaks of the irradiated composite (Fig. 5) is greater than that of not UV-weathered samples (Figure 4), which are initially amorphous and later, after 60 days exposure in soil presented crystallinity.

During the exposure in biodegradation in the soil, XRD patterns of PLA-CW composite showed the same angular position, but with greater intensity, indicating a higher crystallinity index (Table 2). The crystal size of PLA-CW samples, either UV-weathered or not, and subsequently exposed to biodegradation in soil, was determined and it is shown in Table 2. As can be seen, the results indicate that there is not a significant change in the average crystal size.

It is suggested that the hydrolysis of PLA occurs faster in the amorphous regions, where the degradation of the polymer chains occurs preferentially (Gaurav *et al.*, 2006; Gopferich, 1997) and the crystal structure is formed during the degradation process (Gonzalez *et al.*, 1999).

The increase in the crystallinity index ( $X_c$ ) and the crystal size of the composite PLA-CW after 120 days of exposure in soil (Table 2) was attributed to selective degradation of amorphous part of the film coupled with migration and assimilation of low molecular weight products. During incubation in soil

the the fraction of the crystalline phase increases. The amorphous interfacial edge between the crystallites in spherulites is attacked first and the small crystallites are released. As the degradation of small crystals is considerably faster than large ones, the average size of the remaining crystals becoming larger, resulting in the increase in average crystal size (Kawai *et al.*, 2011). Moreover Mathew *et al.*, (2006) comment that the reinforcement particles of the composite, in this case the whiskers (microfibrils) of cellulose, can act as nucleation sites for crystallization, affecting the size of crystals.

### 3.4 Evolution of thermal transitions

Table 3 shows the values of glass transition temperature ( $T_g$ ), melting temperature and crystallization. One ( $T_c$ ), obtained by DSC technique and measured in the first heating of PLA- CW composite samples, before and after being subjected to biodegradation in soil. As can be seen, the  $T_g$  shows a slight tendency to decrease at 120 days of biodegradation in soil, while the  $T_m$  maintained a constant value (152-151 °C). It should be noted that the composite PLA-CW 0D showed a melting peak at 152°C, despite its X-ray spectrum revealed an amorphous halo (Fig. 4). The crystallinity percentage determined by DSC yielded a value of 3%. The glass transition temperature tended to lower value as a consequence of the average molecular mass diminution (Longieras *et al.*, 2007). This is a fact consistent with the results reported by Zhang *et al.* (2008). The crystallization temperature  $T_c$  of previously UV-irradiated samples PLA-CW 8D is almost constant or slightly decreased, after their biodegradation in soil (Table 3). This can be explained with the adsorption of water by the matrix of PLA, resulting in the hydrolysis of ester bonds and breaking

Table 3. Thermal transitions of PLA-CW composite samples at 60 (a) and 120 days (b) of biodegradation in soil: samples without UV-irradiation (PLA-CW 0D) and prior irradiation for 8 days (PLA-CW 8D).

PLA-CW 60 days (a)	T <sub>g</sub> (°C)	T <sub>c</sub> (°C)	T <sub>m</sub> (°C)
PLA-CW 0 D	57.0	90.0	152.0
PLA-CW 8 D	54.0	88.5	152.0

PLA-CW 120 days (b)	T <sub>g</sub> (°C)	T <sub>c</sub> (°C)	T <sub>m</sub> (°C)
PLA-CW 0 D	55.0	92.0	152.0
PLA-CW 8 D	53.0	87.0	151.0

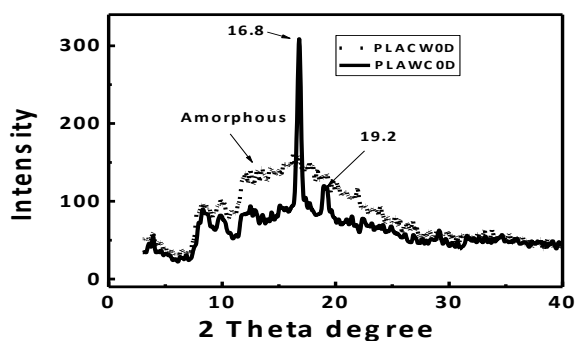


Fig. 4. X-ray diffraction spectra of PLA-CW composite samples without UV-weathering (PLA-CW 0D), after their exposure for 60 and 120 days in soil biodegradation.

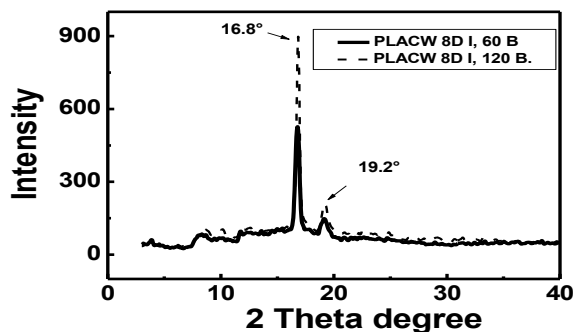


Fig. 5. X-ray diffraction spectra of PLA-CW composite samples UV-weathered for 8 days (PLA-CW 8D), after their exposure for 60 and 120 days in soil biodegradation.

the long macromolecular chains. These results are consistent with those reported by Gonzalez *et al.* (1999) and Gattin *et al.* (2002).

### 3.5 Structural changes in PLA-CW composite (FTIR)

The structural changes that occurred in PLA-CW composite, due to its previous photodegraded by UV-irradiation (weathering in cycles) and the subsequent biodegradation in soil up to 120 days, were detected by FTIR (Fig. 6). As can be seen, various bands of the IR spectrum increase in intensity with time of biodegradation of the composite. This tendency is valid, for example, for bands at 1454 and 1380  $\text{cm}^{-1}$ , caused by bending vibrations of  $-\text{CH}-$  symmetric and asymmetric  $\text{C}-\text{H}_3$ , respectively, present in polylactic acid segments, which have been previously reported by Chlopek *et al.* (2009) and Ristic *et al.* (2011). The band in 1180  $\text{cm}^{-1}$  attributed to asymmetric vibration and  $\text{C}-\text{O}-\text{C}$  bond of 1110  $\text{cm}^{-1}$ , corresponding to symmetric vibrations of the same link of the aliphatic chain. The lactide monomer appears at 1265  $\text{cm}^{-1}$  and 1095  $\text{cm}^{-1}$ , as similar bands reported by Ristic *et al.* (2011). With fewer changes in intensity are the bands in the ranges 960 to 850  $\text{cm}^{-1}$ , attributed to bending vibrations outside the plane of the OH bonds of carboxylic acids (Coates, 2000).

Figure 7 shows another region of the IR spectrum, from 1600 to 1900  $\text{cm}^{-1}$ , which reveals that the intensity of the band corresponding to  $\text{C}=\text{O}$  at 1715  $\text{cm}^{-1}$  is also increased with time of biodegradation of PLA-CW composite in soil. Similar results have been reported by Kumar *et al.* (2010) in the biodegradation study. That band is associated with the number of terminals in the polymer carboxylic chain and  $\text{C}=\text{O}$  vibrations of aliphatic ester (Ristic *et al.*, 2011; Coates, 2000).

FTIR study clearly shows the degradation of PLA-CW composite, evidenced by the increase of band intensity corresponding to the CH deformation

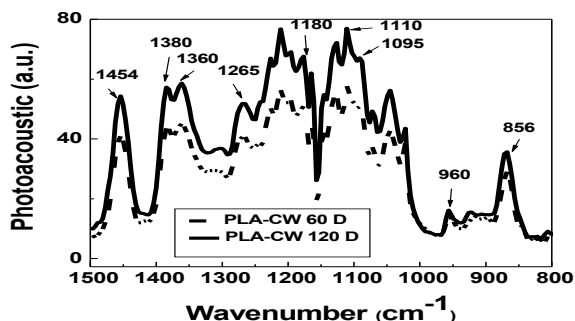


Fig. 6. IR spectrum of the composite PLA-CW (800 to 1500  $\text{cm}^{-1}$ ), previously UV-irradiated in weathering cycles (8 days) and then subjected to biodegradation in soil for 60 and 120 days.

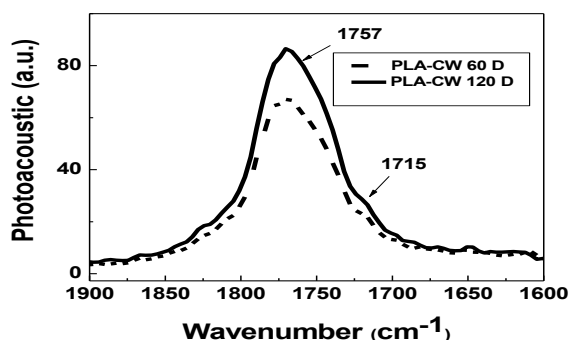


Fig. 7. IR spectrum of the composite PLA-CW (1600 to 1900  $\text{cm}^{-1}$ ), previously UV-irradiated in weathering cycles (8 days) and then subjected to biodegradation in soil up to 120 days.

vibrations of  $\text{CH}_3$  groups, present in segments of polylactide (1.360 and 1.380  $\text{cm}^{-1}$ ), and also the increase of  $\text{C}=\text{O}$  intensity band after the biodegradation process in soil. The changes in the band of  $\text{C}=\text{O}$  are associated with an increase in the number of carboxyl end groups in the polymer chain which occurs during hydrolytic degradation, as well as the cycle of microbial attack. Similar behaviors were reported by Sambha'a *et al.* (2010) and Chlopek *et al.* (2009), studying the hydrothermal effect in the polylactic acid degradation and degradation under in vivo conditions of poly (lactide-co-glycolide) and hydroxyapatite.

## Conclusions

This work focuses on analysis and comparison of accelerated weathering of samples of polylactic

acid reinforced with cellulose whiskers (PLA-CW), conducted in QUV chamber-Panel, and their subsequent exposure to biotic soil environment. The cellulose whiskers (microfibrils) were obtained from banana rachis and pseudostem *Musa cavendish*. The results showed that:

1. Relative humidity, as weathering parameters of UV-cycles, is important factor that facilitate the hydrolytic degradation of PLA-CW composite.
2. PLA-CW polymer decreases its molecular mass during the biodegradation process in soil and this fact is more pronounced for samples subjected previously to UV-weathering cycles. XRD patterns of PLA-CW composite revealed a higher crystallinity index, but not a significant change in the average crystal size. The glass transition temperature  $T_g$  tended to lower value that could be related with the average molecular mass diminution. The changes in the band of  $\text{C}=\text{O}$  were associated with an increase in the number of carboxyl end groups in the polymer chain, which occurs during hydrolytic UV-degradation, as well as during the microbial attack in soil.
3. Initial UV-degradation weathering was very important to stimulate biodegradation of the composite films (PLA-CW) in soil. The final percentage of biodegradation, calculated based on the released  $\text{CO}_2$ , was higher for PLA-CW samples that have been previously subjected to weathering. The results indicate that PLA-CW has shorter half-life after biodegradation in soil and it is suitable for land disposal.

## Acknowledgements

The authors wish to thank MS. Daniel Aguilar Treviño (CINVESTAV-Merida, Applied Physics Department) for the technical support in the study of the XRD diffractograms. M.S. Veronica Moreno Chulim (CICY-Polymeric Materials Unit) for his advice on the use and management of DSC and FTIR. Ing. Wilma Aracely González Kantún (CICY-Biochemistry and Molecular Biology Unit) for their support to the growth chamber for the study of biodegradation and Ing. Rodolfo Martín Mex GeMBio Laboratory, (CICY-Biotechnology Unit) by testing for growth of microorganisms in PLA-CW.



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