

# Evaluation of natural biodegradation of low-density polyethylene/modified corn flour composites

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## Abstract

*Composites based of low density polyethylene (LDPE) reinforced with acetylated corn flour (ACF) at proportion of 10, 30 and 50 (%.Wt) were prepared. The biodegradation of resulting composites was studied in the environment using the soil burial test. The biodegradation were evaluated by different analysis techniques and were compared with the results recorded on these composites before the biodegradation test. Differential scanning calorimetry (DSC) analysis showed an increase of the melting enthalpy and crystallinity of LDPE with evidence of degradation. The biodegradability of the composites was enhanced with increasing ACF content in the matrix. This result was supported by decrease in mechanical properties, by weight loss and degraded surface of composites observed through morphological studies.*

**Keywords:** *Low density polyethylene, Corn flour, Properties, Biodegradation.*

## I. Introduction

Synthetic polymers are increasingly present in daily life. However, they are rarely used alone, but combined with other materials, thus allowing the properties of each to be associated.

Also, the properties of a single polymer are insufficient to confer on the object that one wishes to manufacture all the desired properties in terms of rigidity, mechanical resistance, lightness or other physico-chemical, electrical, optical property, which has led to the first research on the development of plastic materials including renewable raw materials of natural origin. Passed to the background as an additional motivation the preservation of the environment and public health.

In fact, with a concern for the preservation of fossil resources, and in an effort to reduce pollution, biodegradable composite materials have been developed alongside traditional composites. These new materials are of additional interest. They are easily degradable and therefore harmless to the environment.

In a mixture or not with others synthetic polymers, raw material of vegetable origin most widely used are starch. It was incorporated in conventional plastics with the aim to give a certain level of biodegradability in the resulting composites and it is an inexpensive, renewable and natural polymer [1]. However, applications of starch materials are limited by poor mechanical strength properties and high moisture [2].

To improve the mechanical properties of materials blending starch with other polymers such as low-density polyethylene (LDPE), chemically modified starches was used, this modification often makes the starch more hydrophobic, which improves the interfacial contact between starch granule and polymer, thereby enhancing stability of resulting materials in water [3]. (Kim, 2003) [4]. Cao et al. [5] found 13% improvement in tensile strength, 14% in flexural strength and 30% in impact respectively for polyester reinforced with bagasse fiber after alkali treatment.

In this study the possibility to prepare LDPE/acetylated corn flour blends instead LDPE/acetylated corn starch was investigated because corn flour is cheaper than corn starch (is obtained with less processing steps and thus less water and energy consumption) [6]. In addition, corn flour is completely biodegradable by microorganisms. It composed of 75–87% starch and 6–8% protein [7].

Several formulations with LDPE and acetylated corn flour (ACF) were prepared and characterized. The study of their biodegradability in a natural environment by burial in soil was developed and compared to those before degradation.

## II. Material and methods

### II.1 Materials

Low density polyethylene (LDPE), BASEL 2420F, was obtained from Flay packaging, Bejaia, Algeria. Corn flour was provided by the AGRO CEREALES/Moulin Royal-Akbou Algeria and it has less than 7 % moisture content and the particle size was 90  $\mu\text{m}$ . Acetic anhydride and sodium hydroxide were obtained from Fluka.

## II.2 Methods

### Acetylation of corn flour

Acetylation was done with the method proposed by Gunaratne and Corke [8]: Corn flour was dissolved in distilled water. The pH was adjusted with 1 M NaOH to 8.0-8.5. Acetic anhydride was added to the blend and then mechanically stirred for 30 min. The blend was washed with distilled water three times and dried at 35 °C.

### Samples preparation

LDPE (F0) and LDPE/ACF composites at ratio of 90:10 (F10), 70:30 (F30) and 50:50 (F50) (wt.%) were prepared using twin-screw extruder (model Micro compounder DSM Explore). The extrusion conditions were as follows: the temperature mixing zone of the barrel was maintained at 150 °C, with a screw speed of 50 rpm and a mixing time of 5 min. After extrusion, the products are injected into a mold at 5 atm and at room temperature. The material was then compacted, and maintained under pressure and the cooled part is ejected. The injection mold used in this machine is only one fingerprint in dumb-bell shape, with the following dimensions: useful length 63 mm, useful width 10 mm and thickness 3 mm.

### Biodegradability test

The biodegradability test was produced by burying samples in the soil. It was carried out as described by Santayanon and Wootthikanokkhan [9] with some modifications. The soil burial was recovered from a landfill. Ten specimens of each formulation were buried at a depth of 10 cm and after 180 days of burial, they were collected. The specimens were weighed before and after burial. In the latter case the specimens were first rinsed with distilled water after removal from the burial site and then dried at 60 °C for 48 h prior to their weighing and analyzed. The specimens of each composition were weighed at precision 0.0001 g.

### Spectroscopy analysis (FTIR)

FTIR spectra were recorded using an infrared spectrophotometer Fourier Transform Model SHIMADZU FTIR. Potassium bromide (KBr) disks were prepared from powdered samples mixed with dry KBr in the ratio of 1:100. The spectra were recorded in a transmittance mode from 4000 to 400  $\text{cm}^{-1}$  at a resolution of 4  $\text{cm}^{-1}$ .

### Morphological studies

SEM analyses were performed using Scanning Electron Microscope (Jeol JSM 6100 Model). The specimens had been coated with thin film of gold/vanadium before observation.

### Differential scanning calorimetry (DSC)

The melting temperatures ( $T_m$ ), the melting enthalpy ( $\Delta H_m$ ) and the degree of crystallinity ( $X_c$ ) of LDPE were determined using a differential scanning calorimeter (DSC) (model Q200, TA Instrument). Two heating cycles were used for each sample. The samples were first heated from -20 to 200 °C at a constant rate of 20 °C/min to eliminate their thermal history, and then cooled to -20 °C and immediately reheated to 200 °C. The second scan was done at the same heating rate. Nitrogen gas was supplied to purge the system at a flow rate of 150 ml/min.  $T_m$  was determined from the second scan, it was taken as the maximum of the endothermic melting peak from the heating scans.  $\Delta H_m$  was obtained from the areas of melting peaks.  $X_c$  was obtained from the ratio between the melting enthalpy of the samples ( $\Delta H_m$ ) and the melting enthalpy of 100% crystalline LDPE (277,1 J/g) (Pedroso, Rosa, 2005).

### Mechanical properties

Measurements of the tensile properties were performed using a Shimadzu tensile testing machine (Model Autograph AGS-X 10kN). Measurements were performed at a 10 mm  $\text{min}^{-1}$  crosshead speed at ambient temperature. The device provides access to the force  $F$  as a function of elongation ( $L-L_0$ ) where  $L_0$  is the initial length of the film. For each formulation, five specimens were tested. The Young's modulus, strain and stress were determined.

### Morphological studies

SEM analyses were performed using Scanning Electron Microscope (Jeol JSM 6100 Model). The specimens had been coated with thin film of gold/vanadium before observation.

## III. Results and discussion

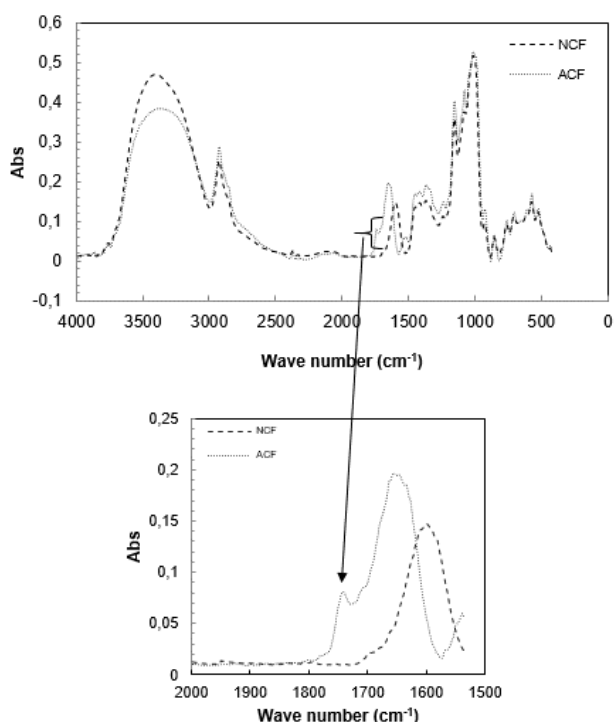
### FTIR analysis

The FTIR spectra of corn flour before and after treatment are shown in Fig. 1. The spectra of corn flour have characteristic profiles to native starch. According to the literature [10, 11], the chemical functions for each absorption band which appears on the FTIR spectra of starch are given as follow:

There are three characteristic bands of starch between 990  $\text{cm}^{-1}$  and 1160  $\text{cm}^{-1}$ , attributed to C-O bond stretching. The bands at around 1150  $\text{cm}^{-1}$ , 1080  $\text{cm}^{-1}$  were characteristic of C-O-H in starch, and the band between 990  $\text{cm}^{-1}$  and 1030  $\text{cm}^{-1}$  was characteristic of the anhydroglucose ring O-C stretch. The band at 1655  $\text{cm}^{-1}$  is attributed to the water adsorbed in the amorphous region of starches. The band at 2920  $\text{cm}^{-1}$  is characteristic of C-H stretch. An extremely broad band due to

hydrogen-bonded hydroxyl groups appeared at  $3400\text{ cm}^{-1}$  which ascribed to the complex vibrational stretches coupled with free, inter and intramolecular bound hydroxyl groups, which made up the gross structure of starch.

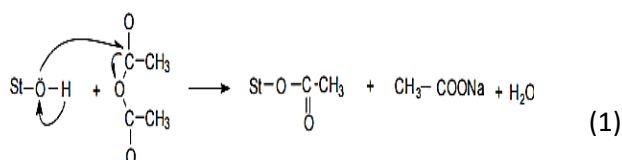
The FTIR spectra of native corn flour (NCF) and treated corn flour (TCF) show similar profiles (Fig. 1) except for the band located between  $3700$  and  $3000\text{ cm}^{-1}$ , which is reduced on ACF.



**Figure 1.** FTIR spectra of treated (ACF) and untreated corn flour (NCF)

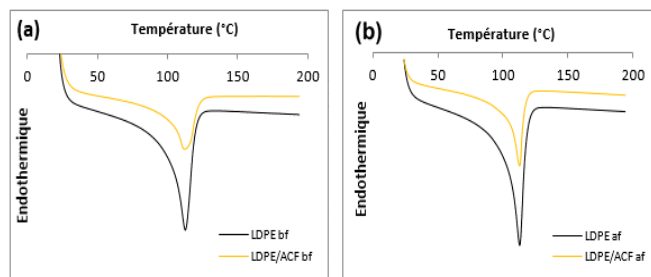
The reduction in this band is mainly attributed to the decrease in the hydrophilic nature of corn flour after treatment, as following in the reaction (1).

Other relevant peak is that obtained for ACF at  $1745\text{ cm}^{-1}$ , arising from the acetyl group ( $\text{C}=\text{O}$  stretching) in the products [12].



#### Differential scanning calorimetry (DSC) analysis

Fig. 2 shows the DSC curves obtained during second heating of the different formulations before (bf) and after (af) 180 days of burial in soil.



**Figure 2.** DSC curves of LDPE and LDPE/ACF composites: (a) before and (b) after 180 days of burial in soil.

We see that the thermograms recorded one endothermic peak corresponding to the melting temperature of the matrix. The  $T_m$  was taken by the maximum of the endothermic melting peak.

Table 1 shows the average values of the melting temperature ( $T_m$ ), melting enthalpies ( $\Delta H_m$ ) and crystallinity ( $X_c$ ) of all composites before and after 180 days of burial in soil.

**Table 1.** DSC test results of LDPE and LDPE/ACF composites obtained from the second heating curves, before (Bf) and after (Af) 180 days of burial in soil.

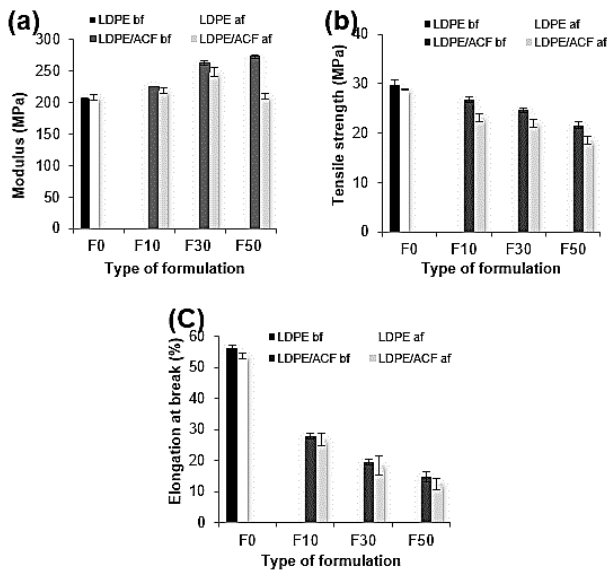
Type of formulation		$T_m$ (°C)		$\Delta H_m$ (J/g)		$X_c$ (%)	
		Bf	Af	Bf	Af	Bf	Af
LDPE	F0	112,7	112,8	79,12	97,72	28,55	35,27
LDPE/ACF	F10	112,4	112,1	45,8	76,03	16,53	30,57
	F30	112,5	114,0	38,07	65,85	13,74	23,76
	F50	112,5	112,8	34,13	54,15	12,32	18,82

We can see that the  $T_m$  remained constant for different samples. This temperature corresponds to that of pure LDPE which is  $110\text{ °C}$  (Pedroso, Rosa, 2005 and Walker et al., 2007).

However, the enthalpy of fusion increased, indicating an increasing in the crystallinity of LDPE, which may reflect biodegradation of the amorphous portion of the matrix by the microorganisms present in the soil. Therefore, microbial degradation leads to an increase in the overall degree of crystallinity of the polyethylene sample. These results are confirmed experimentally by several researchers [13, 14].

#### Tensile properties

Figs. 3 illustrate a comparison in mechanical properties (a) Young's modulus, (b) tensile strength and (c) elongation at break of pure LDPE and those reinforced with ACF for different formulations before and after degradation.

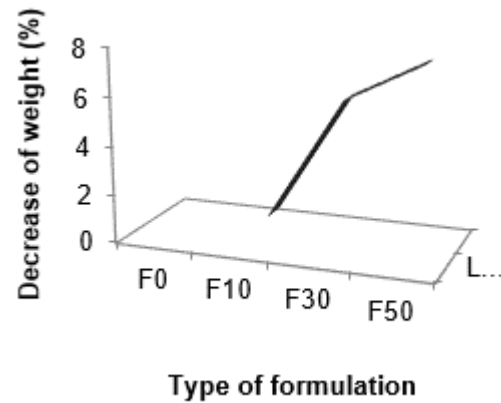


**Figure 3.** Tensile properties of pure LDPE and LDPE/ACF composites before and after 180 days of burial in soil (a) Young's modulus, (b) tensile strength and (c) elongation at break.

After 6 month of burial in th soil, the trend remains the same in all samples and the same behavior was observed for Modulus, tensile strength and elongation at break (i. e. these parameters had a trend to decrease with increasing filler content in the matrix). Comparing these results with those before degradation, the decrease in these properties can be seen clearly in particular for formulations F50 indicating that the samples became weaker after biodegradation. This result indicated that the addition of ACF enhanced the biodegradability of LDPE. It was also observed that the biodegradability of the composites enhanced with increasing ACF content. Shah et al. [15], indicated that the variations in the tensile property are often taken as a direct indication of the biodegradation.

#### Weight loss

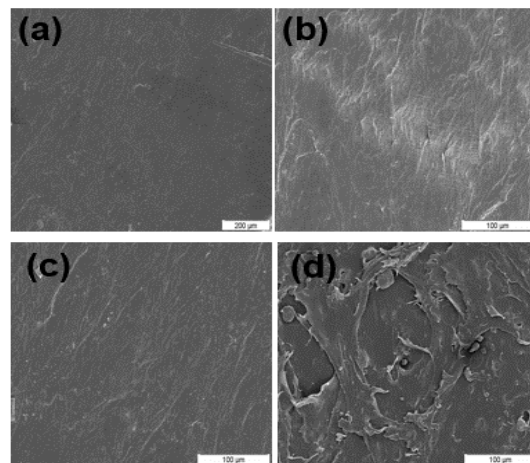
Figure 4, shows the weight loss results recorded for pure LDPE and its composites with ACF after 180 days burial in soil. The percentage loss in weight of pure LDPE maintained at 0.12%, but this loss becomes more important with incorporation and the increase of ACF content in the matrix, this due to the presence of corn flour which easily susceptible to the attack of microorganisms [6]. After burial in sol, we recorded 5.65% in decrease of weight for LDPE reinforced with 30 (wt.%) of ACF and it was 7.32% for those blended with 50 (wt.%). Danjaji et al. [16] recorded 2% in decrease of a weight for PE/sago starch 40 (wt.%) composite after 12 months inside a sandy soil containing left-over food. Therefore, we can say that this method is an accelerated method of degradation compared to others.



**Figure 4.** Weight loss of pure LDPE and LDPE/ACF after 180 days of burial in soil.

#### Morphological test

SEM micrographs of the pure LDPE and composites with the highest ACF content (F50) before and after 180 days of burial in soil are presented in Fig. 5. The latter shows a smooth surface of pure LDPE. However, LDPE/ACF blends were sensitive to biodegradation. This result was evident by the presence of various holes on the surface. These be a sign of the rate of biodegradation and confirmed the ACF elimination by microorganisms. Corn flour consumption by bacteria caused holes in the polymer matrix and eventually the degradation of LDPE.



**Figure 5.** SEM micrographs of: pure (a) LDPE before; (b) LDPE after; (c) LDPE/ACF at 50 (wt.%) before; and (d) LDPE/ACF at 50 (wt.%) after 180 days of burial in soil.

#### IV. Conclusions

Study consists on the incorporation of acetylated corn flour in LDPE matrix. Soil burial test was carried to evaluate the biodegradation of resulting composites. As well a comparative study before and after soil burial was made. Degradation study shows that landfills soil burial resulting in weight loss,



presence of the holes in surface and decrease of mechanical properties. LDPE/ACF composites show rapid degradation after 180 days in soil. Therefore, the use of ACS as filler in LDPE is advantageous from both economic and environmental points of view and has potential applications in the development of biodegradable composite materials.

#### **Conflict of interest**

The authors declare that they have no conflict for financial interests or personal relationships that how can influence the work reported in this paper.

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