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CHEMICAL MODIFICATION OF CORN FLOUR FOR USE IN LOW DENSITY POLYETHYLENE MATRIX: EFFECT IN THE THERMAL, MECHANICAL AND MORPHOLOGICAL PROPERTIES OF THE RESULTING COMPOSITES

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ABSTRACT

In order to obtain a cost-effective partially biodegradable plastic, corn flour (CF) has been used as a reinforcing phase in commodity thermoplastic matrix (low density polyethylene-LDPE). But CF and LDPE blend are incompatible due to the strong polarity of filler and the low polarity of the matrix. This problem may be reduced by the pretreatment of corn flour, which can enhance compatibility. In this study, CF was treated with NaOH and anhydride acetic (AAc). The effect of pretreatment on the hydroxyl groups of the corn flour was examined by Fourier Transform Infrared. LDPE-treated corn flour composites at ratio of 70:30 (wt.%) were prepared and the microstructure, the thermal, tensile and the water absorption properties of resulting composites were evaluated and compared. The highest properties (tensile strength and water absorption) were obtained for the LDPE/alkali treated corn flour composites.

KEYWORDS

Corn flour; surface modification; SEM; mechanical properties.

1. INTRODUCTION

The disposal of plastics, especially those used in packaging, poses a serious challenge to waste management. Conventional methods of plastic waste management such as land-filling, recycling, incineration, etc, have proved inadequate. Plastic waste is now regarded as a worldwide environmental problem. Polyethylene, the largest volume plastic used in packaging, is the worst offender. Polyethylene is highly resistant to

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biodegradation. Although starch continues to play its traditional role in food formulations, its use as a biodegradable additive in plastics is fast gaining prominence. One way by which the biodegradation of polyethylene can be accelerated, is by the incorporation of biodegradable filler such as starch into the polymer matrix. 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. It can be added to synthetic polymers to lower the cost of the final product and blend films containing starch are potential materials in the agriculture, medicine, textile and packaging industries (Lu et al., 2005). However, applications of starch materials are limited by poor mechanical strength properties and high moisture (Avérous, 2004). 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. Starch can be modified by esterification, etherification, and oxidation (Kim, 2003). Alkali treatment has been considered as a good technique to modify the surface of starch to obtain better adhesion between the filler and the matrix. (Ray et al., 2002) characterized the physical and mechanical properties of the composites reinforced with alkali treated jute fibers. (Rout et al., 2001) reported 26% improvement in tensile strength, 15% in flexural strength and 20% in Charpy impact strength after the coir fibers were treated with 2% NaOH solution for 1 h. (Cao et al., 2006) 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/treated corn flour blends instead LDPE/treated corn starch was investigated because for both economic and environmental reasons : corn flour is cheaper than corn starch and is obtained with less processing steps (and thus less water and energy consumption) (Jbilou et al., 2010). In addition, corn flour is completely biodegradable by microorganisms (Jbilou et al., 2013). Corn flour is composed of 75–87% starch and 6–8% protein, such as zein, presenting film-forming properties, as presented in Fig. 1.

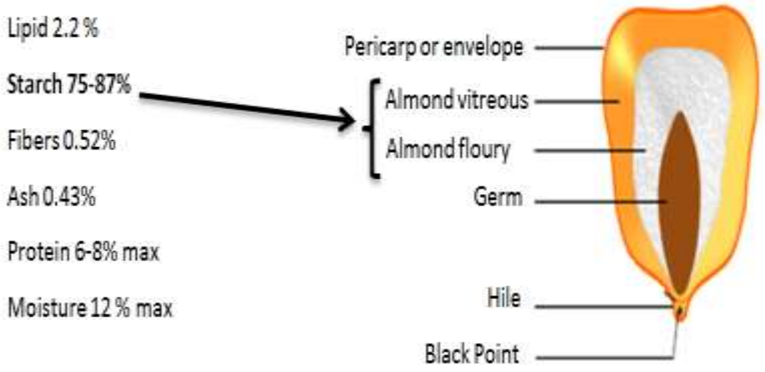


Figure 1: Composition of corn flour grain

2. EXPERIMENTAL

2.1. 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 µm. Acetic anhydride and sodium hydroxide were obtained from Fluka.

2.2. Alkali treatment of corn flour

The alkali treatment was done with the method proposed by (Cao et al., 2006). The corn flour was soaked in 1% NaOH solution at 25 °C for 2 h, maintaining a liquor ratio of 20:1. The corn flour were washed repeatedly with water to eliminate traces of NaOH sticking to the granules surface, then neutralized with dilute acetic acid and then washed again with water. Finally, it was dried at 70 °C for 72 h.

2.3. Acetylation of corn flour

Acetylation was done with the method proposed by (Gunaratne, Corke, 2007): 100 g of corn flour was dissolved in distilled water (185 ml). The pH of the blend was adjusted with 1 M NaOH to 8.0-8.5 and then mechanically stirred for 30 min. Acetic anhydride (8 g) was added to the blend and the pH was maintaining at 8.0-8.5. The stirred was continued for 60 min. finely the blend was washed with distilled water three times and dried at 35 °C.

2.4. Samples preparation

LDPE/treated corn flour composites at ratio of 70:30 (wt/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.

2.5. 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 cm^{-1} at a resolution of 4 cm^{-1}.

2.6. 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.

2.8. Differential scanning calorimetry (DSC)

The melting temperatures(T_m), the melting enthalpy (ΔH_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 °Cat 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. ΔH_m was obtained from the areas of melting peaks. X_c was obtained from the ratio between the melting enthalpy of the samples (ΔH_m) and the melting enthalpy of 100% crystalline LDPE (277.1 J/g) (Pedroso, Rosa, 2005).

2.9. 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 min^{-1} crosshead speed at ambient temperature. The device provides access to the force F as a function of elongation ($L-L_0$) whereL_0isthe initial length of the film. For each formulation, five specimens were tested. The Young's modulus, strain and stress were determined.

2.10. Water absorption

Water absorption measurements were performed by soaking the samples in distilled water at 23 °C. At regular time intervals, each sample was removed from the water tank, dried by wiping with blotting paper and then weighed to determine water uptake. The samples were placed back in water after each measurement. For each formulation, three specimens were tested. The water absorption was calculated as the weight difference and is reported as per cent increase of the initial weight as follows:

$$\%W_f = \frac{W_W - W_C}{W_C} \qquad (1)$$

Where W_f is the final increased weight percentage, W_w the wet weight and W_c the conditioned weight of the testing samples.

3. RESULTS AND DISCUSSION

3.1. FTIR analysis

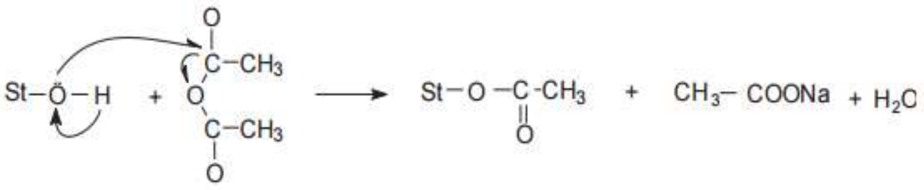
The FTIR spectra of corn flour before and after treatment are shown in Fig. 2. The spectra of corn flour have characteristic profiles to native starch. According to the literature (Xin et al., 2012 and Solano, Gante, 2014), the chemical functions for each absorption band which appears on the FTIR spectra of starch are given as follow:

There are three characteristic bands of starch between 990 cm^{-1} and 1160 cm^{-1}, attributed to C-O bond stretching. The bands at around 1150 cm^{-1}, 1080 cm^{-1} were characteristic of C-O-H in starch, and the band between 990 cm^{-1} and 1030 cm^{-1} was characteristic of the anhydroglucose ring O-C stretch. The band at 1655 cm^{-1} is attributed to the water adsorbed in the amorphous region of starches. The band at 2920 cm^{-1} is characteristic of C-H stretch. An extremely broad band due to hydrogen-bonded hydroxyl groups appeared at 3400 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 (CF) and treated corn flour (TCF) show similar profiles (Fig. 1) except for the band located between3700 and 3000 cm^{-1}, which is reduced on ATCF and ACF. The reduction in this band is mainly attributed to the decrease in the hydrophilic nature of corn flour after treatment, as following in the reactions (1) and (2) respectively.

Other relevant peak is that obtained for ACF at 1745 cm^{-1}, arising from the acetyl group (C=O stretching) in the products (Muljana et al., 2010). This confirms the acetylation of corn flour.

$$\mathrm{Starch - OH + NaOH} \leftrightarrow \mathrm{Starch - O^- + Na^+ + H_2O} \tag{1}$$



$$\mathrm{St{-}\ddot{O}{-}H} + \begin{array}{c}\mathrm{O}\\ | \\ \mathrm{C{-}CH_3}\\ \mathrm{O}\\ \mathrm{C{-}CH_3}\\ | \\ \mathrm{O}\end{array} \longrightarrow \mathrm{St{-}O{-}\underset{\underset{O}{\|}}{C}{-}CH_3} + \mathrm{CH_3{-}COONa} + \mathrm{H_2C} \tag{2}$$

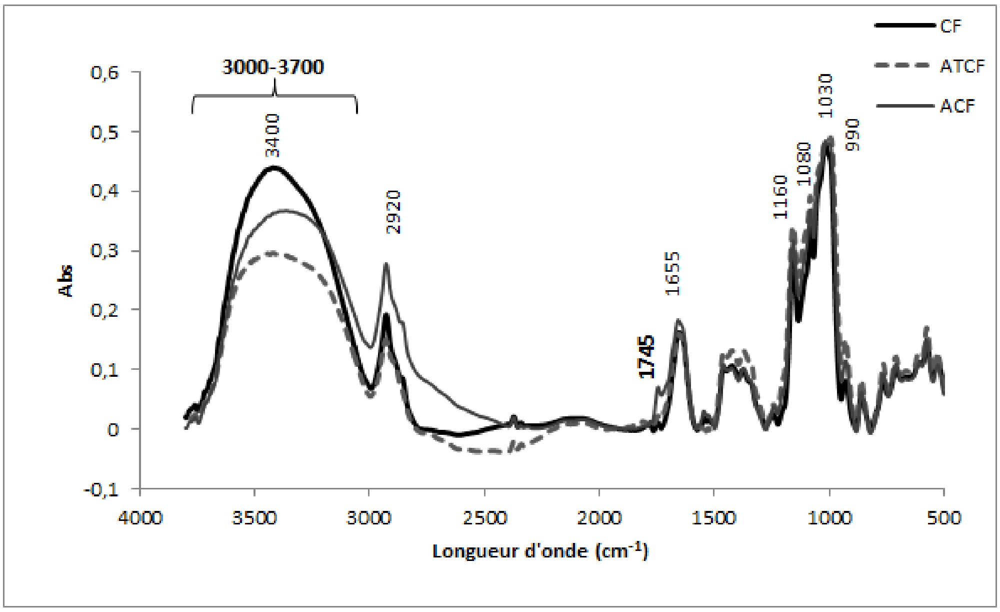


Figure 2: FTIR spectra of the treated and untreated corn flour

3.2 Morphological studies

Fig. 3 shows the SEM micrographs taken on the fracture surfaces of materials made of virgin LDPE and composites formulated with TCF. For non-reinforced materials i.e LDPE, the fracture area is smooth and clear. Comparing this micrograph with composites materials, corn flour granules can be clearly identified in the surface. We also noticed there was a good adhesion between the polymer matrix and the TCF granules, which results in the absence of any empty in the surface. This is explained by the reduction in hydroxyl groups of the treated corn flour, therefore a good attraction between the filler (TCF) and the matrix (LDPE). (Nawang et al., 2001) reported that the low polarity of the matrix (LDPE) and high polarity of starch was responsible of weak compatibility and the absence of contact between the matrix and native corn starch.

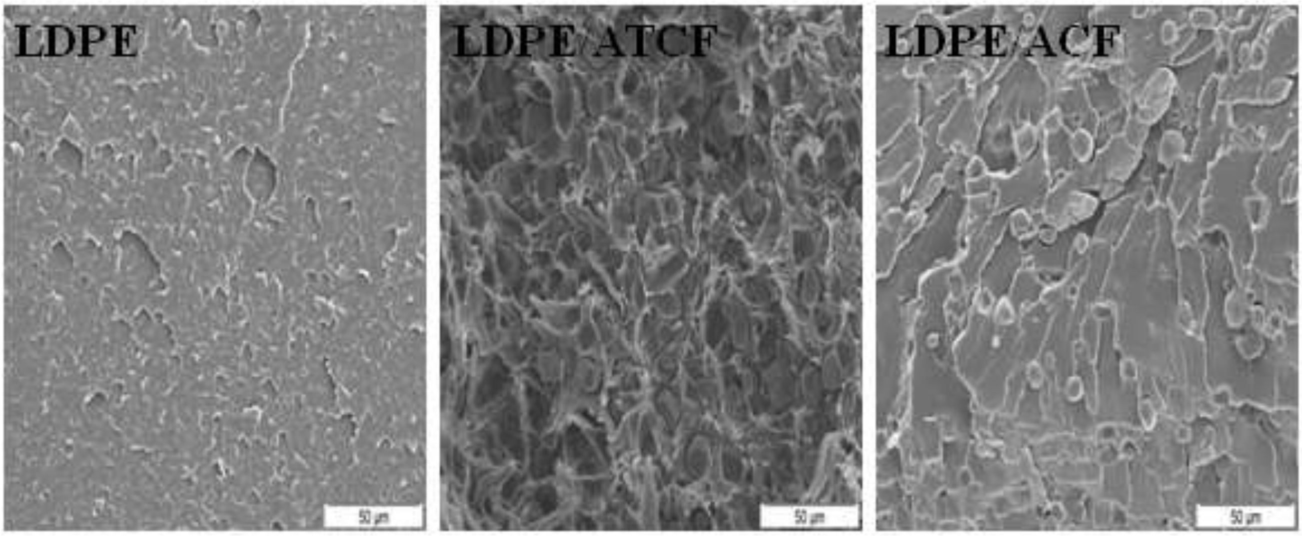


Figure 3: SEM micrographs of pure LDPE and LDPE/TCF composites

3.3. Differential scanning calorimetry (DSC) analysis

Fig. 4 shows the DSC curves obtained during second heating of the different formulations. 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 (ΔH_m) and crystallinity (X_c) of all composites. We can see that the T_m remained constant for different samples. This temperature corresponds to that of pure LDPE which is 110 °C (Pedroso, Rosa, 2005 and Walker et al., 2007).

As the melting enthalpy is directly proportional to the amount of crystalline LDPE in the sample, it decreased with the incorporation of TCF in the matrix. This is due to the growing less in the weight fraction of crystalline LDPE in the composites due to the presence of the TCF groups. The decrease in the crystallinity can be explained as the content of TCF increases, as do the amorphousness of the blends also increases. Theoretically the cristallinity of the LDPE in the blends was reduced by 30% compared with that of pure LDPE (Table 1). For example, the cristallinity of LDPE containing 30 (%.wt) of ACF was 18.62%, this represents 65.24% (~70%) of the cristallinity of pure LDPE (28.55%).

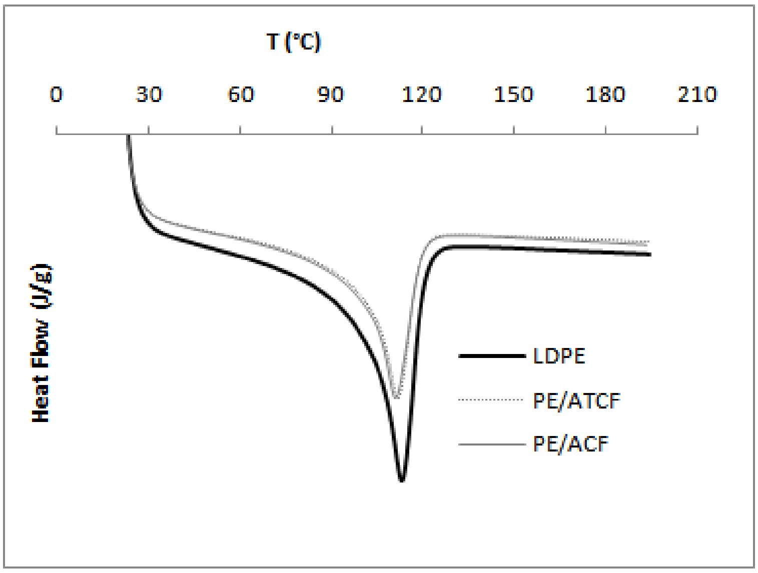


Figure 4: DSC curves of LDPE and LDPE/TCF composites corresponding to the second heating run

Table 1: DSC test results of LDPE and LDPE/TCF composites obtained from the second heating curves.

	T_f (°C)	ΔH_f (J/g)	T_c (°C)	X_c (%)
LDPE	112.7	79.12	98.2	28.55
PE/ATCF	112.6	55.28	97.9	17.31
PE/ACF	112.5	51.59	97.6	18.62

3.4. Mechanical properties

Figure 5 (a-c) shows the Young's modulus, tensile strength and elongation at break respectively for different composites. The results show increases in Young's modulus with incorporation of TCF in the matrix. This behavior can be explained by the fact that the corn flour is more rigid than LDPE, which induced to a higher stiffness of LDPE/TCF composites. Indeed, the hydrogen bonding in starch gives it much higher than the module semi-crystalline polymers such as LDPE, which has no hydrogen bonding. Therefore, there is a direct relationship between the amount of starch in mixtures and the increase in the modulus value.

The tensile strength of all composites decreased with increasing filler content, indicating that composites materials are weakened by the presence of TCF and the later behave as non-reinforcing filler. (Kim et al., 2006) attributed the decrease of tensile strength of the materials resulting from rice husk flour to the formation of microcracks at the interfaces or restrict the transfer of mechanical stress at the interface. It was interesting to note that tensile strength did not affected in a great extension, maybe due to the good interfacial attractions between LDPE and filler as confirmed with SEM micrographs.

As in the case of the tensile strength, elongation at break decreased as the TCF content increased, it passed from 56.06% for LDPE to 18.82 and 19.47% for those prepared with ATCF and ACF respectively. The addition of TCF granules to LDPE produced the general trend for filler effects on polymer properties; i.e. the modulus increased through stiffening of the granules and elongation decreased as the TCF content increased. In synthetic polymer blends, the addition of a second immiscible phase to a ductile matrix material usually significantly decreases the elongation at break and it is considered to be highly sensitive to the interfacial interaction between the phases of the blends (Pedroso, Rosa, 2005).

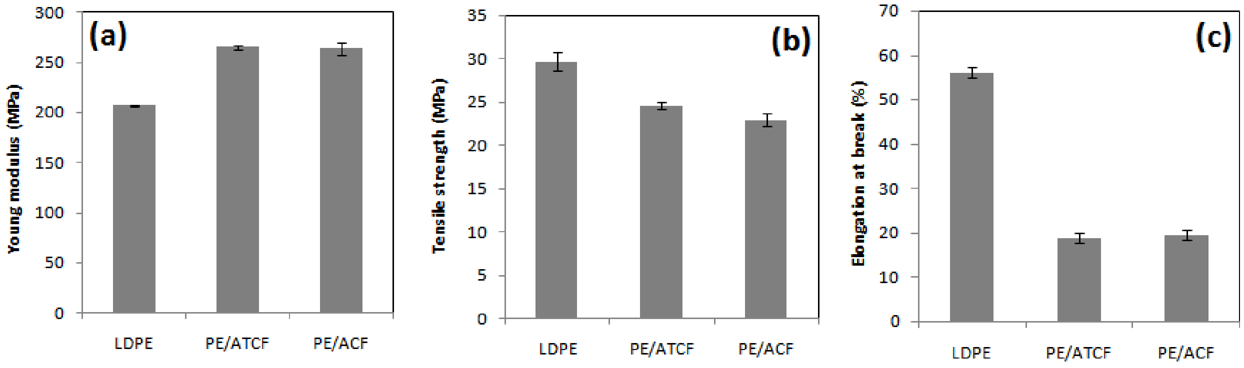


Figure 5: Mechanical properties of LDPE and LDPE/TCF composites: (a) Young modulus, (b) tensile strength and (c) elongation at break.

3.5. Water absorption

The water uptake of the pure LDPE and their blends with ATCF and ACF are shown in Fig. 6. Moisture uptake increased with immersion time and rapid moisture uptake was observed for all samples within the first few days of immersion, but this decreased slowly with time. The decrease in the rate of moisture uptake with time of immersion could be due to the higher absorption of water molecules by starch. When all of the available hydroxyl groups are used up in this way, the water absorbed became less (Mortazavi et al., 2013). It was found that the water absorption of LDPE/ATCF composites is less than for those prepared with ACF. This is due to the fact that ACF is more hydrophilic that ATCF (confirmed by FTIR analysis) (Fig. 2). For the pure LDPE, there was a very low water absorption which is of the order of 0.038 %, which is due to the hydrophobic nature of this polymer.

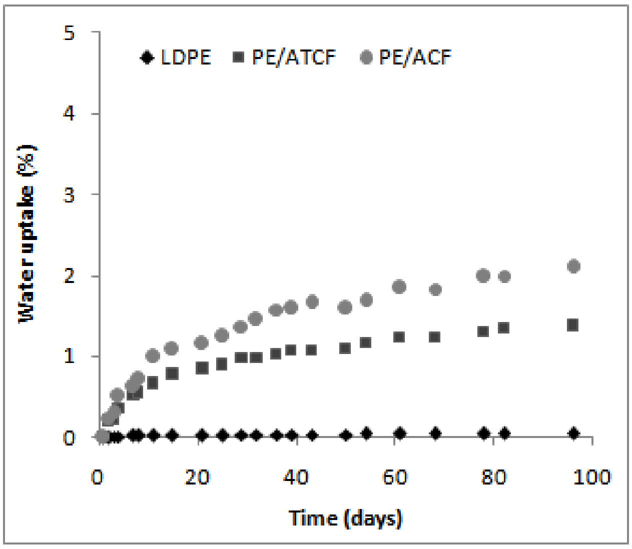


Figure 6: Percentage water uptake of LDPE and LDPE/TCF composites during water absorption

4. CONCLUSIONS

Compounding and filler content were the main factors that influenced the composite properties. The FTIR spectra of native corn flour (CF) and treated corn flour (TCF) confirmed the reduction of hydrophilic character and the acetylation of CF after treatment. SEM micrographs of the films showed that there was a good adhesion between the two polymers. The DSC spectra of the composites were not conclusive of any strong interaction between corn flour and LDPE. The introduction of treated corn flour in the LDPE increases Young's modulus. The tensile strength and elongation at break of blends are lower compared to pure LDPE and elongation at break was more affected by the presence of TCF. The highest properties (tensile strength and water absorption) were obtained for the LDPE/alkali treated corn flour composites.

According to these results, we can conclude that the LDPE/TCF composites have the added benefit of containing large quantities of a renewable resource and hence represent a more sustainable alternative to pure synthetic polymers and the combination of LDPE and TCF is advantageous from environmental points of view and has potential applications in the development of partially biodegradable materials.

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