



## IMPACT OF HYGROTHERMAL AGEING OF LOW-DENSITY POLYETHYLENE/SHORT FLAX FIBRE COMPOSITES ON THE MULTI-SCALE PROPERTIES.

Hajer Rabii<sup>1\*</sup>, Laetitia Van Schoors<sup>1</sup>, Marielle Gueguen<sup>1</sup>, Peter Davies<sup>2</sup>

<sup>1</sup>Ifsttar, Département Matériaux et Structure, Laboratoire CPDM, Marne La Vallée, France.

<sup>2</sup>Laboratoire Comportement de Structures en Mer, Ifremer, Centre de Bretagne, France

\* Corresponding author; e-mail: [hajer.rabii@ifsttar.fr](mailto:hajer.rabii@ifsttar.fr)

### Abstract

Flax reinforced polyethylene composites were subjected to a long sorption /desorption/resorption cycle, at 30°C and 100% relative humidity. Then, a multi scale characterization was conducted. The sorption kinetics revealed the influence of the fibre content and the interface quality on the diffusion mechanisms. Chemical analysis has revealed the oxidation of the polyethylene matrix and the loss of hydrosoluble fibres components during ageing. A microbiological survey revealed that under these weathering conditions, the composites were sensitive to microbial development. These modifications have affected the global performances in terms of mechanical properties.

### Keywords:

Flax fibre composite, hygrothermal ageing, sorption kinetic, multi-scale properties, fungi development.

## 1 INTRODUCTION

The addition of natural fibres to thermoplastic matrix in composites has been growing in the last decade for the numerous advantages of natural fibres such as their low cost, bioavailability and low impact on the environment [Arbelaiz 2005; Baley 2005; Joseph 2002]. Besides, many authors have reported that plant fibers are in general suitable to reinforce plastics due to their relative high strength and stiffness and low density [Bledzki 1999; Almaded 2014]. This explains the development of these composites mainly for building construction applications.

According to a study published by ADEME in 2011, the needs of the plant fiber materials industry to the horizon 25 years will be of 63.6 Kilotonnes for the composites building sector compared to about 2 Kilotonnes in 2005. Amongst the natural fibers, flax fibres generate relatively high interest for this kind of application and have been shown to be competitive, owing to their good mechanical properties [Gourier 2010], as well as wide availability in France [Baley 2002].

However plant fibres have certain drawbacks, such as low thermal stability [Yang 2007], hydrophilic nature and low resistance to moisture [Arbelaiz 2005], natural fibres are also sensitive to microbial growth [Feng 2014] and to seasonal quality variations [Di bella, 2010]. These parameters could reduce the potential of plant fibers to be used as reinforcement for polymers.

The quality of the interface is significant for the final global performances of the composites, so several methods can be used to optimize the adhesion and compatibility between hydrophilic natural fibre and hydrophobic polymer [Bledzki 1999]. Among these techniques, the modification of the matrix by grafting copolymerization seems to be an effective chemical method that has proven its benefits. [Arbelaiz 2005] investigated the effect of the matrix modification with several amounts of maleic anhydride polypropylene copolymer (MAPP) on the short flax fibre composite properties. They found that mechanical properties were improved and water sorption characteristics were clearly reduced.

The main concern for the use of natural fibre reinforced composites is their susceptibility to moisture absorption and the effect on chemical, structural, mechanical and thermal properties [Joseph 2002]. If hydrogen bonds between fibres and in fibre-matrix interfaces are reduced by the absorbed moisture, stiffness and strength are further diminished and in the presence of moisture, cellulose is also more susceptible to microbial attacks [Dhakal 2007; Almgren, 2010].

The purpose of this study is to evaluate the multi-scale properties of composites subjected to hygrothermal ageing in order to investigate the possible reversibility of their behavior, to improve understanding of composite stability and durability. These composites are intended for exterior applications such as outdoor residential decking, where the exposure to the natural environment results in a concern about their long term durability.

## 2 EXPERIMENTAL

### 2.1 Materials

Model materials were supplied by Depestele Group. All analyses were performed on plates (60 x 60 x 2mm) and specimen's type 1BA, made of low density polyethylene LD600 and composites reinforced with 40% mass fractions of short flax fibre with and without a 1% mass fraction of a coupling agent, Licocene MAPE 4351. LDPE samples were injected at 180°C and 50 bar. Composites with 40% of fibre content were injected at 190°C and 55 bar. Analysis was performed on non-dried samples.

### 2.2 Hygrothermal ageing

Temperature and humidity aging conditions were chosen to be 30°C and 100% R.H. These correspond to be close to outdoor application conditions. Besides, another reason to explain this choice is to investigate a possible microbial development under these conditions.

Prior to the ageing campaign, all samples were dried at 30°C to remove moisture, so they were weighed regularly until reaching a constant mass. Long Hygrothermal ageing cycles were composed of a first cycle of absorption (120 days), followed by a desorption cycle (100 days) and finally a resorption cycle (160 days): the main aim of cycling is to determine the reversibility of the observed sorption properties once the diffusion kinetic parameters have been determined.

The samples were placed in a desiccator half filled with distilled water; they were kept in a climatic chamber regulated at 30°C and 100% R.H. At regular intervals, samples were taken out, wiped dry to remove the surface moisture, weighted and replaced in the desiccator.

The moisture content  $M(t)$  adsorbed by each specimen is calculated from its weight before,  $w_0$  and after,  $w_t$ , absorption as follows:

$$Mt(\%) = \frac{(w_t - w_0)}{w_0} \times 100 \quad (1)$$

Diffusion coefficient  $D$  ( $\text{mm}^2/\text{s}$ ) was calculated from the slope of moisture content versus the square root of time:

$$\frac{Mt}{Ms} = \frac{4}{h} \times \frac{\sqrt{D}}{\sqrt{\pi}} \quad (2)$$

Where  $M_s$  is the equilibrium moisture content (%) and  $h$  is the thickness of specimen.

Both equations were used to determine sorption and desorption cycle kinetic parameters

### 2.3 Sample characterization

#### Chemical analysis:

FTIR spectroscopy analysis was performed in order to follow chemical evolution during ageing. Due to the opacity of the samples, the attenuated total reflectance ATR method was used with a diamond Durascope fixture. FTIR spectra were recorded on a Nicolet™ impact 380 spectrometer with 32 scans per measurement, in a wave number range from 400 to 4000  $\text{cm}^{-1}$ , with a resolution of 4  $\text{cm}^{-1}$  and signals were analyzed with Omnic™ 3.1 software. Absorbance intensities were normalized according to 2915  $\text{cm}^{-1}$ , which is supposed not to evolve during ageing.

#### Microstructural analysis

Aged and non-aged samples were analyzed using a modulated DSC-TA Instrument Q100. All

measurements were conducted under nitrogen atmosphere, at a heat rate of 1°C.min<sup>-1</sup> and an amplitude of 0.159. The sample mass is between 3 and 4 mg equivalent of polyethylene. Crystallinity ratio was determined according to the equation:

$$X_c(\%) = \frac{\Delta H_f PE}{\Delta H_f^\infty} \times 100 \quad (3)$$

Where  $\Delta H_f PE$  is the melting enthalpy of polyethylene in (J/g) and  $\Delta H_f^\infty$  is the melting enthalpy of a 100% crystalline polyethylene [Almanza 2005].

#### Density measurements

Density measurements were performed based on the buoyancy method. The solvent used was dodécane. Average density ( $n=3$ ) was calculated using the following formula:

$$\text{Density} = \frac{(M1 \times \rho_{\text{solvent}} - M2 \times \rho_{\text{air}})}{(M1 - M2)} \quad (4)$$

Where  $M1$ : the mass (g) of a sample in air,  $M2$ : the mass of the same sample in dodecane,  $\rho_{\text{solvent}} = 0.7487 \text{ g/cm}^3$   $\rho_{\text{air}} = 0.0006 \text{ g/cm}^3$

#### Mechanical analysis

Tests were carried out on standard (1BA) dogbone specimens using an Instron™ Tensile test machine equipped with an extensometer, with a 100 N load cell and 2 mm/min crosshead speed. Elasticity modulus (MPa) and elongation at break (%) values correspond to the average of three to four samples. Values were directly obtained from the stress-strain curves. The modulus was determined from the initial slope between 0.1 and 0.3% of elongation.

## 3 RESULTS

### 3.1 Water uptake

Fig.1 presents the moisture uptake evolution for each material during the three hygrothermal cycles as a function of ageing time. First, polyethylene showed no water uptake. Being hydrophobic, the polyethylene matrix has no contribution to the water uptake process.

The water uptake of the composite was entirely due to the presence of natural fibres.

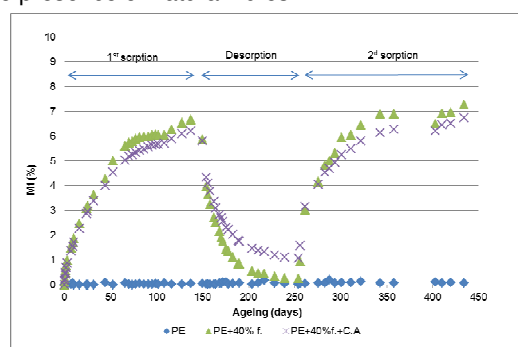


Fig. 1: Water uptake of composites as function of ageing time.

During the first sorption cycle, the diffusion process appears to be faster considering the moisture adsorption at the initial stages of ageing; then the water uptake reached a saturated moisture level indicating that composites became equilibrated with R.H. Samples exhibit a Fickian behavior model allowing determination of a diffusion coefficient based on equation 2, values are summarized on Tab. 1.

For the second ageing cycle, during which samples were dried at 30°C, desorption process has occurred

slightly more rapid than during the first cycle (see Tab.1), this may be due to the creation of favored paths due to fibre degradation.

Nevertheless, according to fig. 1, the desorption cycle should have lasted longer to make sure that the water content disappeared completely. However, for the composite with a coupling agent, it could be also possible that the maleic anhydride have reacted with water molecules, and thereby the initial moisture uptake could not be reached.

During the second sorption cycle, both composites have undergone a slight irreversible degradation phenomenon resulting in an increase of D and Ms compared to the first sorption cycle.

### 3.2 Evolution of mechanical properties

In order to evaluate the effect of each Hygrothermal cycle, tensile tests were performed at room temperature on specimen samples at specific ageing periods. The main evolutions of elastic modulus and elongation at break are highlighted below.

As shown on fig. 2, ageing seems not to have influenced the polyethylene's elastic modulus as it remains constant around 167±81MPa. Besides, there's a slight decrease of the polymer's elongation at break at initial stages of sorption (see fig. 3 (a)). But when removing water molecules, the elongation at break returns to its original value.

For the composites, elastic modulus decreased after the moisture uptake due to the effect of the water molecules, so that increasing water content results in more flexible composites. Then, it appears that all composites' modulus had undergone a significant increase at the end of the drying cycle. One can even note that the use of a coupling agent led to highest initial values of modulus, but the evolution tendency during the ageing cycles is almost the same as without a coupling agent.

Considering the strength at break, there was no effect of these ageing conditions on composites' strength (results not shown).

With regard to the evolution of elongation at break, and on the basis of the results on fig. 3 (b), it is apparent that the changes in the strain at maximum load with hydrothermal ageing are more complex. So even if they do not evolve a lot because of the very low initial values as a result of fibre incorporation, we have noticed that elongation at break increases after water absorption. During desorption, the elongation at break shows a decreasing trend to reach initial values, indicating a possible reversible evolution.

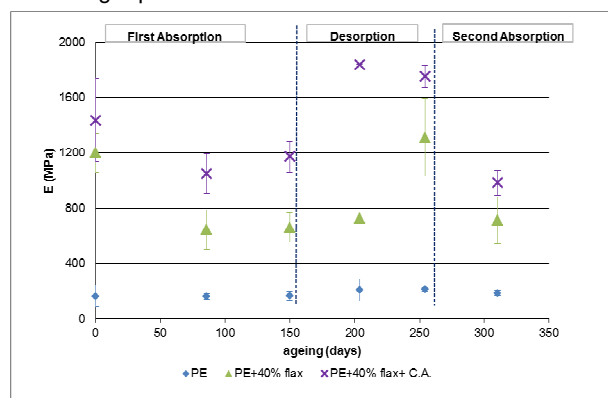
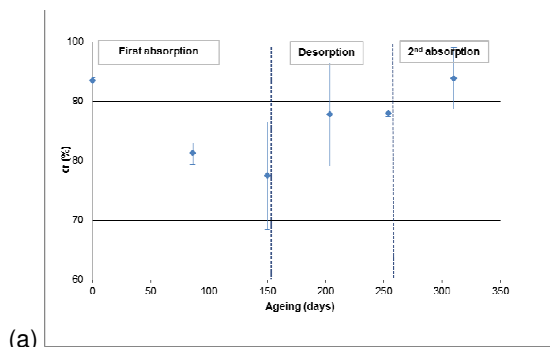
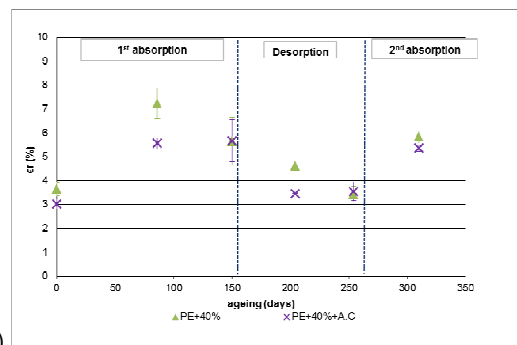


Fig. 2: Effect of ageing on elastic modulus of composites.



(a)



(b)

Fig. 3: Effect of ageing on elongation at break of (a): PE matrix only; (b): composites.

## 4 DISCUSSION

### 4.1 Initial properties of composite

Intrinsic characteristics of fibres could influence the mechanical performance of the composite. Thus, the highest modulus values obtained for composites are usually related to the elevated modulus of cellulose microfibrils compared to the matrix. This statement was confirmed by a molecular scale analysis, where the chemical composition of composite revealed, in addition to polyethylene components, the presence of specific peaks associated with the main lignocellulosic constituents of flax fibre. The different components of cellulose are localized between 1800 and 600 cm<sup>-1</sup> as shown in figure 4.

Moreover, adding short flax fibre resulted in a reduction of elongation at break. This effect can be explained by the fragile nature of natural fibres, but filler particles also introduce defects and stress concentrations that significantly reduce the ductility of the matrix [Almaadeed 2014].

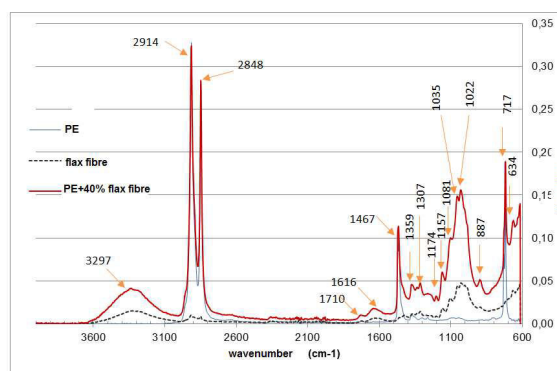


Fig.4: IR-TF analysis of PE, flax fibre, and PE+40% fibre composite.

## 4.2 Impact of flax fibre on the aged composite properties

### Effect on water uptake

Since PE matrix is hydrophobic, water uptake of composites is entirely due to the presence of flax fibre and the interface regions between fibres and matrix. Equilibrium water uptake values of composites increased with fibre content as shown in table 1. Similar water uptake behavior to that obtained by other authors [Arbelaiz 2005; George 1998; Joseph 2002].

The presence of cellulose and hemicellulose containing many hydroxyl groups enhances water molecule sorption by increasing possible hydrogen linkages as proved by FTIR analysis (fig. 4 and 9). Spectral analysis demonstrated the increase of hydroxyl group region absorbance (The bond at  $1632\text{ cm}^{-1}$ ) assigned to OH groups of water molecules, has undergone a slight evolution with fibre addition.

### Effect on mechanical properties

The decrease of composite modulus after water sorption (fig. 2) can be explained by a plasticizing effect of water molecules that change the structure and properties of the fibres. Water molecules can reduce internal hydrogen bonding between polymer chains in cellulose and/or at the interface while increasing molecular space and then increasing flexibility [Arbelaiz 2005; Mali 2004].

Hygrothermal ageing may also lead to the irreversible degradation of natural fibres by a hydrolysis mechanism; this was investigated by FTIR chemical analysis of the ageing solution hydrolysate. The results revealed some release of hydrosoluble components from the fibres into the ageing solution. After desorption, the composites showed an increase of modulus at the end of the drying cycle, this indicates the reversibility of the modulus evolution.

In this context, several authors [Clark 1978; Kato 1999; Le Moigne 2010] have mentioned the effect of the so-called fibre hornification which can be described as the changes that occur on water loss in cellulose. It is believed that the irreversible pores closure that occurs upon drying can be explained by hydrogen bonding preventing pores from re-opening when the fibres are dried and rewetted [Le Moigne 2010]. A mechanism proposed to explain hornification is the reorganization of the fibre cell wall structure.

Based on DSC results, the crystallinity ratio of the polyethylene matrix decreased during ageing as shown in fig.5. The composite with 40% of fibre content presented an opposite trend of crystallinity evolution, where we have noticed an increase of the crystallinity ratio during the aging time. This may be due to the formation of new crystals originating from fibres. According to [Clark 1978], adjacent surfaces of cellulose and hemicelluloses previously separated come into contact upon drying. This would result in the creation of additional crystalline zones that prevent the separation of the two adjacent surfaces of cellulose and hemicelluloses as suggested by [Clark 1978], and thereby it induces the stiffening of the fibres.

In the near future scanning electron microscopy observations will be performed in order to confirm the possible pores closure, as density measurements didn't show any evolution during ageing (Fig. 6).

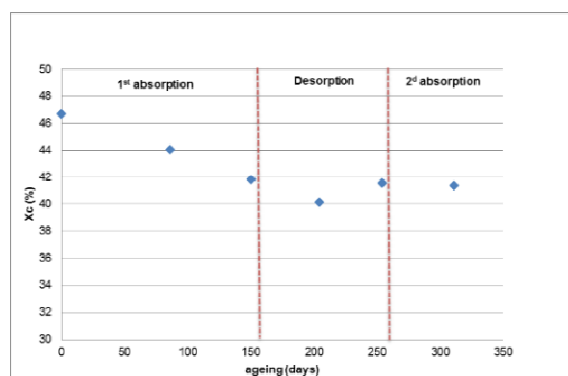


Fig. 5: Crystallinity ratio of polyethylene at different times of ageing.

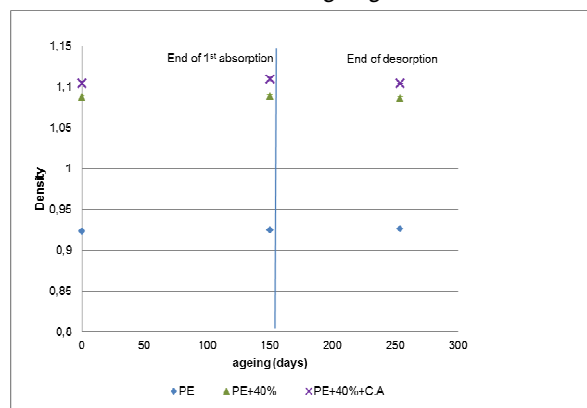


Fig. 6: Density measurements at different times of ageing.

Concerning the elongation at break, it has been shown that it decreased for PE matrix during water absorption then it re-increased at longer exposure times, this behavior can be understood as a consequence of the polyethylene oxidation confirmed by the FTIR results shown in fig. 7.

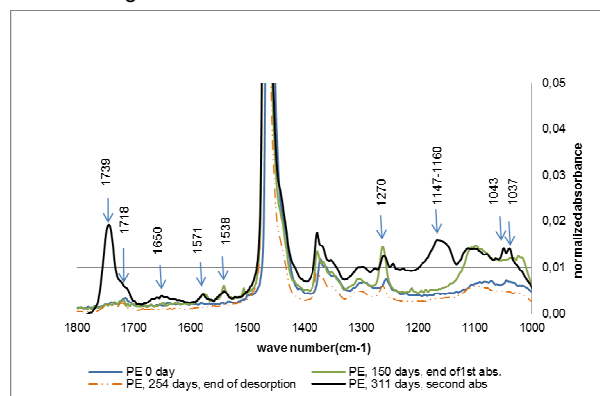


Fig. 7: Infra-red analysis of Polyethylene's chemical composition at different times of ageing

The Tab. 3 details the main absorption bands having experienced some changes such as the carbonyl ( $1680\text{--}1800\text{ cm}^{-1}$ ), vinyl ( $1630\text{--}1650\text{ cm}^{-1}$ ) and hydroxyl zones.

At the microstructural scale, it has been demonstrated that the crystallinity ratio of polyethylene decreased slightly during ageing from 46% to almost 42% (Fig. 5). This could be related to the vinyl's formation upon the oxidation of the polyethylene. On one hand, the chain scission makes it easier for the small molecules formed to align to regular structure, and hence generates a "chimicrystallization" phenomenon. On the other hand, the chain rupture leads to vinyl formation,

by means of crosslinking reactions which prevents crystallization. The results support predominant crosslinking reactions as the crystallinity ratio diminishes, this mechanism would reduce the elongation at break of the polymer.

With adding fibre, it appears that the elongation at break increases for wet composites. Water molecules act as a plasticizer that enhances chains segments' molecular mobility in the amorphous phase [Joseph 2002]. After desorption, the elongation values are compared to the initial ones, the plasticizing effect of absorbed water is then reversible.

Even though composites have experienced an oxidation mechanism that increased with ageing time as evidenced by carbonyl groups signals between 1800 and 1680  $\text{cm}^{-1}$  (Fig. 8) [Fabiya 2008], oxidation extent seems to be lower for the composite than for the polyethylene alone thanks to the antioxidant activity of phenolic compounds within the flax fibre such as lignin.

This property of the lignin was mentioned by several authors [Gadioli 2014; Giannetti 2012] and it was confirmed by oxidation induction time measurements.

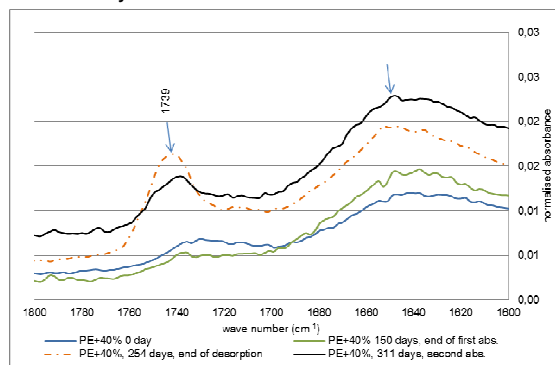


Fig. 8: IR-TF analysis of PE+40% fibre composite at different ageing times - zoom on hydroxyl and carbonyl group region

#### 4.3 Effect of maleic anhydride on Water uptake and mechanical properties of aged composites

The use of a maleic anhydride coupling agent results initially in improved stiffness of the composite, in terms of elastic modulus. In fact, hydrophilic groups are relatively blocked by the coupling agent which reacts with hydrophilic fibre -OH groups leading to the formation of ester linkages and hence to a better interfacial adhesion.

The effect of maleic anhydride on water uptake properties can be seen on Tab. 1, considering the equilibrium water uptake values of composites with and without coupling agent in the first sorption cycle. Similar observations were highlighted by various authors [George 1998; Joseph 2002; Arbelaz 2005]. This reduction is attributed to an improved adhesion between matrix and fibres that hinders an easy penetration of water molecules into the modified composite. Reducing water penetration would limit its accumulation in the interfacial voids. Nevertheless, this statement deserves to be confirmed with SEM analysis, as density measurements showed an almost constant value during the whole ageing duration.

For longer exposure times, and based on resorption characteristics determination, the evolution of moisture uptake indicate that a possible degradation of the interfacial could have occurred. This contributes to the loss of compatibilization between fibres and matrix,

which results in debonding and weakening of the interface adhesion.

#### 4.4 Perspective: Microbial survey

During ageing, visual observation showed distinct proof of microorganism development on the surface of flax fibre composites. Fig. 9 shows the mold growth and composite surface colonization.

This was quite expected since fungi need several conditions for their growth: food (carbon source coming from the fibre components since polyethylene is a non-biodegradable material), air (oxygen), optimal temperature (10-35°C) and moisture. As highlighted by [Feng 2014], all wood polymer composites exhibit an interfacial gap between the wood and the polymer matrix, mycelium concentration would appear to be concentrated initially in the interfacial gaps between the fibre and the matrix, especially for rough materials, then it will penetrate into the material.

We isolated three different species of fungi that have been developed and used them for a microbial ageing campaign on composites. Prior to the incubation at 30°C and 100% R.H., some composites were immersed in a mixed fungi suspension with a mineral medium to promote fibre consumption by microorganisms, while others were sterilized prior to ageing and are considered as control specimens. Aged samples will be characterized based on their chemical, morphological and mechanical properties in order to uncouple and identify the effect of fungi on the global performance degradation.

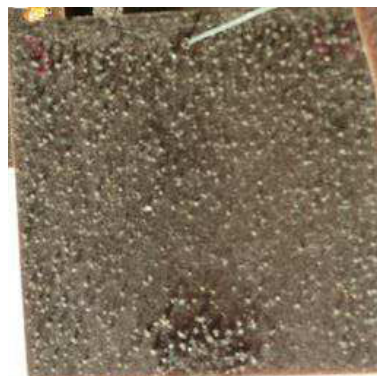


Fig. 9: Fungi development on PE+40% flax fibre plate composite after 440 days of ageing.

## 5 CONCLUSION:

The focus of this work was to study the evolution of the multi-scale properties of polyethylene reinforced with short flax fibre under specific weathering conditions. Some features of composites behavior were highlighted. Above all, water sorption was proved to follow the kinetics of a Fickian diffusion process, where kinetics parameters were slightly influenced by the content of fibre and the quality of the interface. Furthermore, it is believed that maleic anhydride modified polyethylene can improve the compatibility between fibres and matrix, which permits a better adhesion between the PE matrix and the hydroxyl groups on the fibres. The sorption/drying cycle influences fibre properties by creating damage within the fibre, and long term exposure of the matrix has influenced its chemical composition. Mechanical properties are affected by the water absorption as water-saturated samples presented lower values of Young's modulus. This is mainly due to a plasticizing effect of water molecules that change the structure and

properties of the fibres. Moreover, under these ageing conditions, composites materials were subjected to microbial development. The fungi growth would influence chemical composition of the flax fibres, and could result in, in addition to water action, a reduction in some mechanical properties.

In this study, it was shown that the effects of plasticization, chain scission and crystallinity changes as well as interfacial degradation and microbial growth were the major mechanisms to consider for the ageing of flax fibre/polyethylene composite. Likewise, other results conducted after increasing temperature weathering to 80°C have demonstrated a faster water uptake and a greater thermo-oxidative extent of matrix. It also seems that the development of internal mechanical strains with the increase of temperature has created irreversible damage and cracks affecting the physical and chemical properties of both the fibres and the matrix.

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Tab. 1: Equilibrium moisture content (%) and diffusion coefficient  $D$  ( $\text{mm}^2/\text{s}$ ) of composites during different ageing cycles at  $30^\circ\text{C}/100\% \text{ R.H.}$

	PE		PE+40%		PE+40%+C.A	
	Ms	D	Ms	D	Ms	D
1 <sup>st</sup> sorption	0	0	6,05	8,55E-08	5,62	7,54E-08
Desorption	0,07	0	0,84	2,22E-07	1,77	1,36E-07
Resorption	0,06	0	6,9	1,59E-07	6,14	1,47E-07

Tab. 2: IR adsorption frequencies of non-aged PEId.

Wave number ( $\text{cm}^{-1}$ )	assignment	Vibration's type and phase	references
2915	-CH <sub>2</sub> -	Asymmetric stretch	[Gulmine 2002]
2849	-CH <sub>2</sub> -	symmetric stretch	[Gulmine 2002]
1470	-CH <sub>2</sub> -	Bending deformation. Crystalline phase	[Stark 2004]
1463	-CH <sub>2</sub> -	Bending deformation. Amorphous phase	[Stark 2004]
1376	-CH <sub>3</sub>	symmetric stretch	[Gulmine 2002]
728	-CH <sub>2</sub> -	Rock deformation. Crystalline phase	[Stark 2004]
718	-CH <sub>2</sub> -	Rock deformation. Amorphous phase	[Stark 2004]

Tab. 3: IR adsorption frequencies of aged PEId.

Wave number ( $\text{cm}^{-1}$ )	assignment	groups	references
1739	O=C-O	Esters	[Castillo Montes 2012]
1718	-C=O	Carboxylic acids	[Fabiya 2008]
1650-1550	C=C	Vinyls	[Castillo Montes 2012]
1270, 1043, 1039	C-O-C		[Castillo Montes 2012]
881, 802	C=CH <sub>2</sub> -		[Castillo Montes 2012]