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EFFECT OF WATER ON THE CHARACTERISTICS OF POLYETHYLENE / FLAX FIBERS COMPOSITES

L. Van Schoors[1*], M. Gueguen-Minerbe[1], S. Moscardelli[1], H. Rabii[1], P. Davies[2]
[1] Université Paris Est, IFSTTAR, MAST, CPDM, F-77447, Champs-sur-Marne, France
[2] Laboratoire Comportement de Structures en Mer (LCSM), Ifremer, Centre de Bretagne, France
*Corresponding author; laetitia.van-schoors@ifsttar.fr

Abstract
Flax reinforced polyethylene composites were subjected to sorption /desorption cycles, at 96% relative humidity and 30°C. Then, a multi scale characterization was realized. The mechanical properties of composites decrease during the sorption cycle, in particular the modulus which may be related to plasticizing phenomena, but recover their initial values after drying. No physico-chemical changes were observed during this ageing. Moreover, a microbiological survey revealed that the composites were sensitive to microbial development, especially when the percentage of fibers was high. This can affect the mechanical performance of the composites.

Keywords: Flax fibre composite, hygrothermal ageing, biological ageing, physico-chemical properties, Mechanical properties,

1 INTRODUCTION

The use of composites with vegetable fibres and thermoplastic matrix has been growing in the last decade because of their low cost, availability and low impact on the environment [Arbelaiz 2005; Baley 2005; Joseph 2002]. Flax fibers are, for some applications, suitable to reinforce plastics due to their strength and stiffness associated with low density [Bledzki 1999; Al Madeed 2014], resulting in interesting specific properties. This explains the development of these composites.

For building applications, their growth is just beginning, and could be multiplied by 30 in 25 years according to an ADEME study published in 2011 [ADEME 2011]. For this kind of applications, flax fibres generate relatively high interest and these are widely available in France [Baley 2002].

However the vegetable fibers can show high variability in their characteristics according to the plant variety, the climate, the cultivation conditions..... [Di Bella, 2010]. Among their specificities are a low thermal stability [Yang 2007], a strong hydrophilicity which makes them sensitive to water and moisture [Arbelaiz 2005], and a chemical composition sensitive to degradations of biological origin [Dhakal 2007; Almgren 2010].

One of the other weaknesses of these composites results from the poor quality that the interface can have, especially in the case where the highly hydrophilic fibres are associated with a hydrophobic matrix.

However, several methods exist to counteract this last problem and to optimize the adhesion and compatibility between hydrophilic natural fibres and hydrophobic polymers [Bledzki 1999]. One of the methods is to use a coupling agent and thus create chemical bonds between the matrix and the fibres.

Another concern related to the use of composites reinforced by vegetable fibres is their long term behaviour. Studies have been carried out on the effects of immersion on the fibres and the composites characteristics, but the impact of humidity still needs to be explored in detail [Le Duigou 2012, Joseph 2002, Arbelaiz 2005, Thuault 2014].

In this study the impact of the ageing on the mechanical and physico-chemical properties of composites subjected to hygrothermal ageing at 30°C and 96% H.R will be evaluated. Under these conditions, micro-organisms can develop and a study on micro-organisms impact has been conducted. This ageing condition has been chosen because these composites could be used as outdoor residential decking, where the exposure to the natural environment results in a concern about their durability.

2 EXPERIMENTAL

2.1 Materials

This study has been realized on short flax fibers / low density polyethylene model composites. The materials presented in this study have 0%, 18%, 38%, and 42%wt. of short flax fibres. The composite with 42%wt of fibres also has 1% wt. of a coupling agent, Licocene

MAPE 4351. LDPE and composites were manufactured by Depestele group. LDPE and composite with 18%wt. of fibres were injected at 180°C and 50 bars and the others with 38% and 42%wt. of fibre content were injected at 190°C and 55 bars, due to a higher viscosity.

2.2 Hygrothermal and biological ageings

The model materials were studied in controlled ageing in the laboratory. Temperature and humidity ageing conditions were selected to be 30°C and 96% R.H. These conditions have a double interest. On one hand, this is close to outdoor application conditions and on the other hand it is conducive to the development of micro-organisms.

Before ageing, all samples were dried at 30°C and were regularly weighed until reaching a constant mass. Hygrothermal ageing cycles consisted of a first sorption cycle (137 days), followed by a desorption cycle (117 days).

The samples were weighed at regular intervals.

The moisture content M_t(%) for each specimen was calculated with the following equation (1):

$$M_t(\%)=\frac{(w_t-w_0)}{w_0}\times 100 \qquad (1)$$

With w_t the mass (g) of the composite at time t and w_0 the initial mass (g) of the sample.

Simultaneously, biological ageing was conducted at 30°C and 96% R.H.. Specific processing procedures had been previously carried out on native (non-aged) samples:

- In sterile conditions: samples were cleaned with ethanol then exposed to U.V. during 30 minutes,
- In inoculated conditions: samples were inoculated with a suspension of 1.4×10^4 CFUs.ml^{-1} (colony-forming units).

Strains were isolated from solutions where composites samples were immerged at 30°C, then grew in specific culture medium.

2.3 Physico-chemical and mechanical characterization

Chemical analysis:

FTIR spectroscopy analysis was used in order to identify chemical changes during ageing. The samples were analyzed by attenuated total reflectance ATR method 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 cm^{-1}, with a resolution of 4 cm^{-1} and signals were analyzed with Omnic™ 3.1 software. Absorbance intensities were normalized according to 2915 cm^{-1}, which is supposed not to evolve during ageing.

Density measurements

Density analyses were performed based on Archimede's method. The solvent used was dodecane. Average density (n=3) was calculated using the equation 2:

$$\text{Density}=\frac{(\text{M1}\times\rho\ \text{solvent}-\text{M2}*\rho\ \text{air})}{(\text{M1}-\text{M2})} \qquad (2)$$

Where M1: the mass (g) of a sample in air, M2: the mass of the same sample in dodecane, ρ solvent = 0.7487 g/cm^3 ρ air = 0.0006 g/cm^3

Water quantity

Thermogravimetric analysis with mass spectrometer was realized to quantify the water in the samples, before and after ageing. The samples were analyzed with a ATG-SM Netzsch sta 449F1 and QMS403C diamond. The temperature of the furnace was programmed to rise at constant heating rate of 10°C/min. The tests were performed under Nitrogen.

Morphological analysis

A Philips XL30 Scanning Electron Microscope was used in the secondary electrons mode, between 10 and 15 kv voltage and a working distance of 10 mm. The tensile fracture surfaces were inspected.

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. Tensile modulus (MPa) and strength (MPa) values correspond to the average of three or 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% elongation.

3 RESULTS AND DISCUSSION

3.1 Hydrothermal ageing - Water uptake

Figure 1 presents the moisture uptake evolution for each material during the hygrothermal cycles as a function of ageing time. Polyethylene materials do not take up water because they are hydrophobic materials. So, for the composite, mass gain is due to the presence of flax fibres.

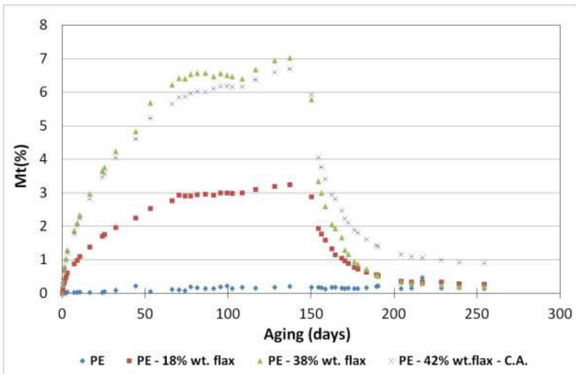


Fig. 1: Water uptake of materials as function of ageing time.

During the sorption cycle, for the composites with 18 and 38%wt. of flax fibres, it appears that the higher the fiber content, the greater the water intake is. This increase in the percentage of fibres is attributed to the hydrophilic behaviour of the fibers and in particular to the formation of hydrogen bonds between the water molecules and the hydroxyl and carboxyl groups of the fibres [Joseph 2002; Dhakal 2007, Beg 2008, Chevali 2010]. Moreover, the ratio of fibres between composites with 38%wt. and 18%wt. is 2.1 and the ratio of mass to saturation is 2.3. Thus, it appears that the saturation masses are for these materials proportional to the quantity of fibers.

Regarding the composite containing 42% wt. of flax and a coupling agent, its maximum mass gain is slightly lower than for the composite with 38% wt. flax and without coupling agent. This suggests the coupling agent slightly reduces the absorbed quantity of water.

For the desorption cycle, masses after desorption are almost similar to the initial ones for composites without coupling agent. However at the end of the desorption cycle, for the composite with coupling agent, residual mass is 1%. To determine the origin of this residual mass, thermogravimetric analyses with a mass spectrometer were realized. They showed the sample after desorption only contains 0.3% water more than the composite at t=0. So the 1% mass after desorption could be attributed to the chemical reactions between water and one of its composites, such as a partial hydrolysis of ester functions formed by maleic anhydride and OH functions of fibres.

3.2 Hygrothermal ageing: Evolution of mechanical and physico-chemical properties

In order to determine the effect of this ageing on the materials properties, tensile tests were performed on specimen samples at the end of the sorption and desorption cycles and compared to the initial values.

As shown in Figure 2, ageing seems not to impact the tensile strength whatever the material and the ageing time.

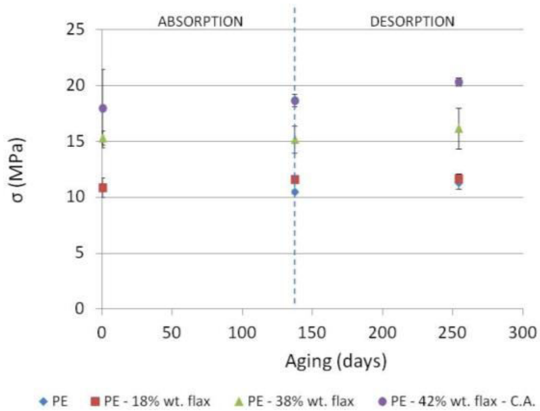


Fig. 2: Evolution of tensile strength of PE and composites with ageing time at 30°C and 96% R. H.

For the composites in Figure 3, elastic modulus is lower at the end of the sorption cycle than initially. For polyethylene only, no significant evolution is observed. The drops in modulus observed for composites can be attributed to plasticization phenomena, which are already widely described in the literature [Thuault 2014, Le Duigou 2009, Beg 2008]. As mentioned before, in particular by Thuault, water molecules could generate plasticization phenomena, especially with cellulose microfibrils.

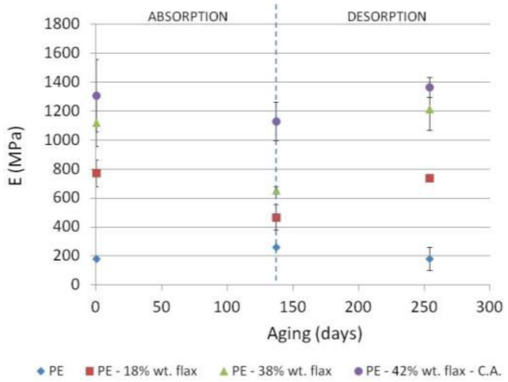


Fig. 3: Evolution of tensile Modulus of PE and composites with ageing time at 30°C and 96% R. H.

In addition, when comparing initial modulus to final modulus at the end of the desorption cycle, no significant evolution is observed whatever the material. So this type of ageing does not generate any irreversible degradation that leads to decreases in the mechanical characteristics.

Also, the residual mass, measured after drying of composites with coupling agent, did not induce drops in mechanical properties; the quantity of water was undoubtedy too low to impact mechanical properties.

Other physico-chemical analyses have not revealed any evolution of the composite characteristics during this ageing. As shown in figure 4, normalized IRTF spectra of 18% wt. flax composites, unaged and after desorption, are not significantly different. So no chemical evolution was observed. Similar trends were observed on other composites aged under the same conditions.

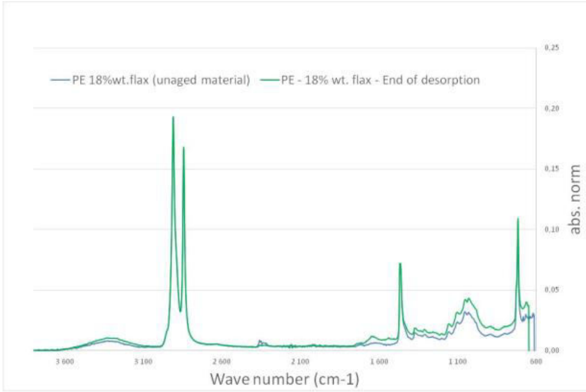


Fig. 4: Normalized FTIR Spectrums of native and aged (end of desorption cycle) composite with 18%wt. of flax fibres

Density measurements were conducted on these composites, with no significant evolution observed whatever the materials studied (cf. Figure 5).

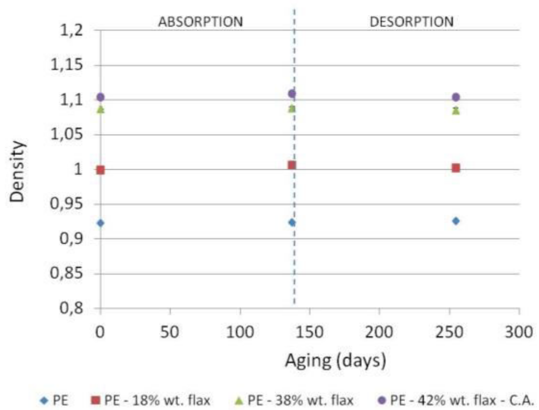
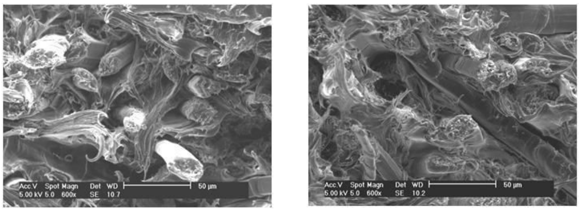


Fig. 5: Evolution of density of PE and composites with ageing time at 30°C and 96% R.H.

Some SEM pictures of representative tensile breaks of unaged and aged (end of the sorption cycle) composites are shown in Figure 6. No significant difference has been observed either at the fibres level or at the interface after ageing.

In this study, it appears that these ageing conditions do not ultimately have any significant impact on physico-chemical, morphological and mechanical characteristics.



(a) (b)

Fig. 6: SEM picture of the tensile fracture of (a)unaged and (b) aged (end of the desorption cycle) composite PE with 38%wt. of flax fibres *(magnification ×600)*

3.3 Biological ageing - Evolution of properties

During ageing, micro-organism growth has however been observed on the composite surface. In order to understand the consequences that could have these micro-organisms on the composites properties, we have compared the mechanical properties of a PE composite with 38% wt. short flax fibres, sterilized and incubated, after 90 days of ageing at 30°C and 96% R.H.

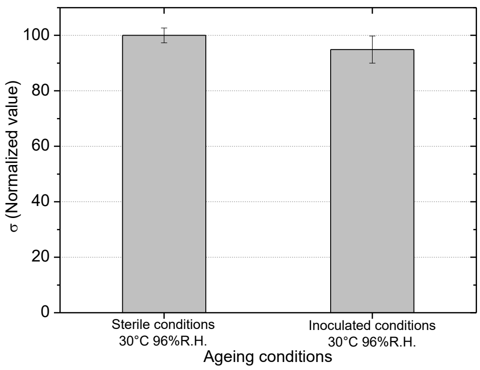


Fig. 7: Normalized Tensile strength of PE with 38%wt. after 90 days of ageing at 30°C and 96% R. in sterile and inoculated conditions

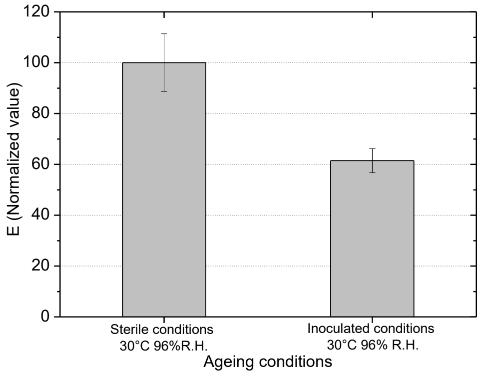


Fig. 8: Normalized Tensile Modulus of PE with 38%wt. after 90 days of ageing at 30°C and 96% R. in sterile and inoculated conditions

As shown in figures 7 and 8, the presence of micro-organisms has few consequences on the tensile strength, but leads to a drop in modulus even after only 90 days of ageing.

To understand the origins of these evolutions, IRTF analyses were performed. No significant difference was observed through this method. On the same flax fibres but not coated by a polyethylene matrix, ageing up to 14 months was studied in the same conditions as the composites; it results in the intake of two fibres components: lignin and cellulose[Guéguen-Minerbe, 2014]. The drops in modulus should be related to the intake of these two components by the micro-organisms. It is relevant to notice that a study on PE only has not revealed any evolution.

The development of micro-organisms in composites with vegetable fibres was already observed, in particular by Feng [Feng 20014] at the fibre-matrix interface, but its consequences on mechanical characteristics were not studied.

4 CONCLUSION

In this study, flax reinforced polyethylene composites were subjected to sorption /desorption cycle, at 96% relative humidity and 30°C. During the sorption cycle, no water is absorbed by the PE, but for the composites without coupling agent it appears that the higher the fiber content, the greater is the water intake and it seems that the saturation masses are, for these materials, directly proportional to the quantity of fibers. Moreover, for the composite with 42%wt. of fibres, the coupling agent slightly reduces the absorbed quantity of water.

At the end of the desorption cycle, unlike composites without coupling agents, a 1% residual mass of composites with coupling agent was measured. This desorption could be attributed to the hydrolysis of ester functions produced by maleic anhydride and OH functions of fibres.

So, for these ageing conditions, no significant degradation has been highlighted for all materials. The only evolutions of mechanical properties can be attributed to the phenomenon of plasticization in a humid environment, a physical phenomenon that seems to be reversible.

Finally, by comparing mechanical properties of the composite with 38% of flax fibres under sterile and inoculated conditions of ageing, it appears that the presence of micro-organisms leads to a slight decrease in strength and a sharp drop in modulus. By analyses on fibers, these changes can be attributed in particular to the consumption of cellulose by the micro-organisms during biological ageing.

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