# ESTUDIO DEL RETARDO DE LLAMA DE BIOCOMPOSITES HECHOS A PARTIR DE FIBRAS DE LINO Y PLA

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FACULTAD DE INGENIERÍAS FISICOQUÍMICAS
ESCUELA DE INGENIERÍA QUÍMICA
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# RESUMEN

**TITULO**: ESTUDIO DEL RETARDO DE LLAMA DE BIOCOMPOSITES HECHOS A PARTIR DE FIBRAS DE LINO Y PLA[1]

**AUTOR**: OSCAR ANDRES GALVIS PEREZ[2]

**PALABRAS CLAVE:** COMPOSITES, LINO, PLA, IGNIFUGACIÓN, RETARDANTES DE LLAMA, GRAFTING, APTES, DEPTES, SULFAMATO DE AMONIO

El desarrollo y mejoramiento de composites ambientalmente amigables, resistentes térmica y mecánicamente es objeto de estudio en la actualidad. El lino (Flax) en conjunto con el ácido poli láctico (PLA) presenta una alternativa que puede cumplir los anteriores requerimientos.

En el presente trabajo se pretrataron fibras de lino y PLA con hidróxido de sodio (NaOH), luego se impregnaron con retardantes de llama (FR): Amino propil trietoxisilano (APTES), Dietil fosfatoetil trietoxisilano (DEPTES) y Sulfamato de Amonio (AS), para observar la respuesta en retardo de llama en su forma fibrosa y en forma de composite, por medio de pruebas de caracterización (SEM, DSC, RMN, FTIR) degradación y combustión (TGA, PCFC, MLC, etc.). Se observó principalmente una reducción entre el 23 y 25% en la velocidad de liberación de calor (HRR) de las muestras pretratadas, juntamente con una alteración en el mecanismo de degradación y un aumento de la masa residual de las muestras en porcentajes mayores al 15%.

Finalmente, se concluyó que el pretratamiento con NaOH de las fibras mejora y aumenta la superficie reactiva de las fibras, no la degrada considerablemente y contribuye al retardo en llama de los composites. Asimismo, se llevó a cabo el injerto químico de los retardantes de llama sobre las fibras exitosamente.

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[1] Trabajo de grado

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# ABSTRACT

**TITLE:** STUDY OF CHEMICAL GRAFTING OF FLAME RETARDANTS ON FLAX FIBER/PLA BIOCOMPOSITES[1]

**AUTOR:** OSCAR ANDRES GALVIS PEREZ[2]

**KEY WORDS:** COMPOSITES, FLAX, PLA, IGNIFUGATION, FLAME RETARDANTS, GRAFTING, APTES, DEPTES, AMMONIUM SULFAMATE

The development and improvement of environmentally friendly, thermally, and mechanically resistant composites is currently under study. Flax in conjunction with polylactic acid (PLA) present an alternative that can accomplish the above requirements.

In the present work, flax fibers and PLA were pretreated with Sodium hydroxide (NaOH) and then impregnated with flame retardants (FR): Amino propyl triethoxysilane (APTES), Diethyl phosphate ethyl triethoxysilane (DEPTES) and Ammonium Sulphamate (AS), to observe the flame retardant response in its fibrous form and in composite form, by means of characterization (SEM, DSC, NMR, FTIR), degradation and combustion tests (TGA, PCFC, MLC, etc.). A greater reduction between 23 and 25% in the heat release rate (HRR) of the pretreated samples was observed, along with an alteration in the mechanism of degradation and an increase in the residual mass of the samples in percentages higher than 15%.

Finally, it was concluded that the pretreatment with NaOH of the fibers increase the reactive surface of the fibers, does not considerably degrade it, and contributes to the flame retardation of the composites. Likewise, the chemical grafting of the flame retardants on the fibers was successfully carried out.

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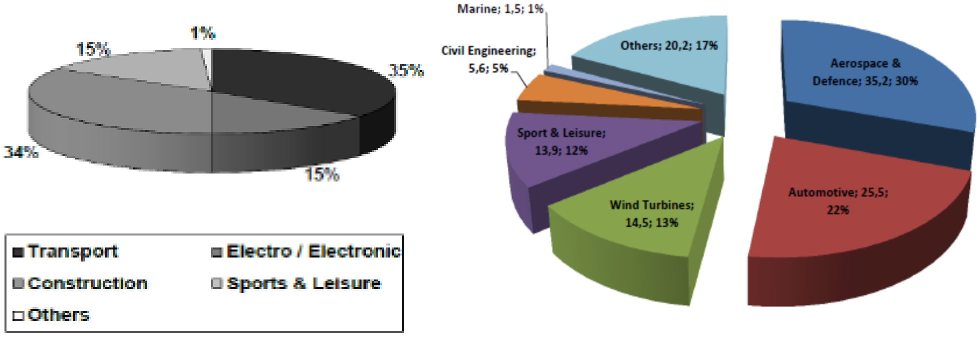
# INTRODUCTION

Composites are materials made from two or more constituent materials with different physical or chemical characteristics, which, once put together give as a result a new material with different properties from those of its original components. One of these components fulfill the role of reinforcing agent (discontinuous phase) and another of matrix (continuous phase) [1]; Different matrix's types and reinforcing agent can be used. In one hand, the reinforcement can be made from natural (flax, jute, sisal, etc.) or synthetic fibers (carbon, glass, aramid fibers). On the other hand, the matrix can be organic (polymers) or inorganic (ceramics, metal, concrete).

Nowadays, the composite industry is divided into two major markets, the production of composites from glass fibers and carbon fibers. 95% of the composites manufactured in the world are made from glass fibers [2]. The sectors most interested in the development of composites are the transport and construction sectors that cover more than 50% of the demand for composites in the world (Figure 1). Among the main uses of composites are the development of parts in automobiles, engines, wings, and fuselage in airplanes, and in areas of construction and development of materials for athletes.

**FIGURE 1. Percentage of applications of composites by sector in the world in 2015. (Left) From glass fibers. (Right) From carbon fibers.**



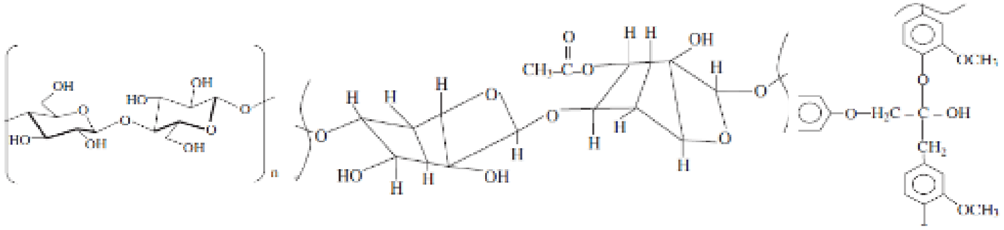
Source: WITTEN, E., KRAUS, T., KÜHNEL, M. Composites Market Report 2016, Carbon Compos., no. November, p. 46, 2016.

According to the same report by Witten and Kraus, during the year 2014, 8.8 million tons of composites were produced worldwide, of which 83,000 tons were made from carbon fibers. And while growth in glass fiber production was 2.5% in 2015, growth in demand and production of carbon fibers was 9.6% and is expected to increase to 23.2% by 2020 [2].

Regarding their impact, composites from carbon and glass fibers are not biodegradable and contribute to increased environmental pollution. During its production process, carbonization of the material is necessary, which generates toxic gases and liquids that are highly polluting and harmful to human health and the environment. Glass fibers, are considered by the World Health Organization as a possibly carcinogenic compound and investigations are being carried out [3].

For this reason, it is imperative to develop new materials that, little by little, can replace the use of traditional synthetic fibers and achieve the same standards of quality and strength. Currently, the composites market is moving towards the use of natural fibers as reinforcement, due to its great advantages: low cost, low density, high resistance, flexibility during processing, abundance and, more importantly, its bio origin and contribution to the reduction of climate change. That makes these fibers a chance for future applicability [4], [5]. Different authors have evaluated several fiber varieties and have found that flax, hemp, jute, and sisal fibers exhibit similar properties than fiberglass. In case of flax, it can compete for its specific strength and Young modulus. In general, natural fibers have a higher elongation at break and a lower thermal conductivity, making the fiber a natural thermal barrier [6].

**FIGURE 2. Cellulose (*left*), hemicellulose (*center*), lignin (*right*).**



Source: KOZŁOWSKI, Ryszard; WŁADYKA-PRZYBYLAK, Maria. Flammability and fire resistance of composites reinforced by natural fibers. *Polymers for Advanced Technologies*, 2008, vol. 19, no 6, p. 446-453.

To obtain a 100% bio resourced composite, it has been proposed to use PLA as a polymeric matrix and flax fiber as reinforcement, due to its high production rate in European countries. Natural fibers cause an acceleration in the biodegradation process of the composites from a few years to reach the complete degradation of PLA, to a few months under the presence of fibers [7]. Presently, the EU leads the production of natural fibers. In 2012, 92,000 tons of composites from natural fibers were produced, with Germany at the lead [2]. Their main application has been in the automotive industry due to its capacity of energy absorption [8].

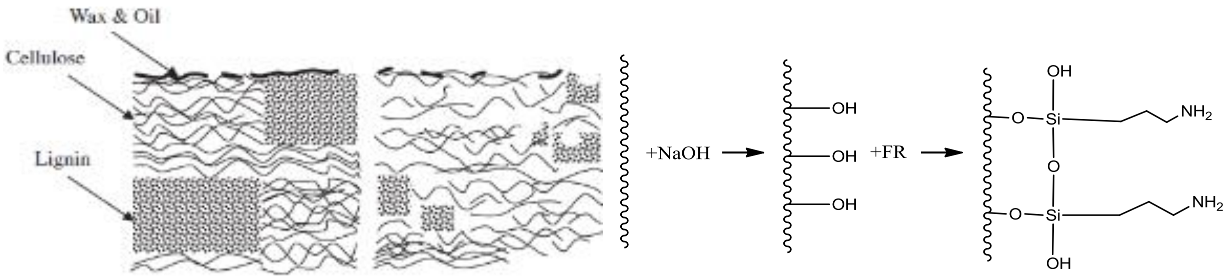
However, natural fibers present several problems that can significantly affect their performance compared to traditional synthetic fibers. The first major difficulty they present is the hygroscopic nature caused by the high amount of hydroxyl groups present in their structures; the flax has on average 70% cellulose, 20% hemicellulose and 3% lignin (figure 2) [9]. This gives the structure a hydrophilic property, which considerably affects the reinforcement/matrix interface in the composites; when the natural fibers absorb moisture from the medium, a tension in the matrix (which is generally hydrophobic) is generated by the swelling of the fibers. After drying, the fibers decrease their size by propagating the formation of cracks in the matrix [10] that deteriorates the mechanical properties of the composites. Secondly, as natural and organic materials, they have high flammability and it is necessary to find solutions that provides protection to the materials.

Flame retardants (FR) that improve the fire performance of materials, have been developed based on halogen, phosphorus, sulfur compounds, etc. Halogenated flame retardants have been the most effective ones but at the same time the most harmful and pollutants, so new alternatives are necessary for their replacement.

To improve interfacial interaction (natural-fiber/matrix), treatments on fibers, before manufacture of composites, have shown good results and many techniques have been developed during the last years. Methods as alkaline or mercerizing (figure 3) [11], agent silane coupling [12], acetylation [13], epoxy resins [14], induced radiation [15], have been studied with satisfactory results. In fact, treatments with organo-alkoxy-silane products show a fire retardant behavior alongside the improve of the interfacial interaction [16],[17].

To perform the ignifugation of the composites it is important to know that it is carried out before composite processing and that it must be done directly on the fibers. Ignifugation can be done by two routes, direct application on the textile or application on the textile after a pretreatment. Notably, alkaline pretreatment enables the reactive surface to be increased by eliminating fats, impurities, hemicellulose, and lignin from flax (Figure 3).

**FIGURE 3. Work of alkaline pretreatment on the fibers. (Left) Action of NaOH on flax fibers (before and after). (Right) Addition of FR on fibers after NaOH pretreatment.**



Source: KABIR, M. M., et al. Chemical treatments on plant-based natural fibre reinforced polymer composites: An overview. *Composites Part B: Engineering*, 2012, vol. 43, no 7, p. 2883-2892.

The UMET (Unité Matériaux Et Transformations) laboratory develops these methods of ignifugation of materials, and the present work seeks to study the flame retardancy of mixed fibers of flax and PLA, through the grafting of organo-alkoxy-silane compounds in fibers with an alkaline pretreatment and the impregnation of a sulfur base flame retardant.

# 1. MATERIALS AND METHODS

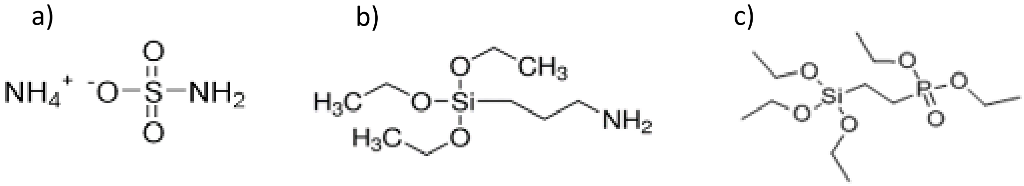
## 1.1 Materials

**1.1.1. Flax/PLA fabric.** A commingled Flax/PLA provided by Depestele Group and having a nominal mass of: 1760 g/m2 (Flax and PLA woven fibers in 50/50 forming a 2x2 fabric) was used for manufacture of the composite. Fibers were cut a size of 12x12 cm2. Prior to use, fibers were dried for 12h at 70°C.

**FIGURE 4. Commingled FlaxPLA fibers**

**1.1.2 Flame retardant tested.** Silanes have been evaluated as flame retardants (figure 5): Aminopropyltriethoxysilane (APTES, 98%, provided by Sigma Aldrich) and Diethyl phosphatoethyl triethoxysilane (DEPTES, 92%, Abcr). A more classical FR Ammonium Sulfamate (AS, Sigma Aldrich) has also been tested.

**FIGURE 5. Used Flame Retardants. a) AS b) APTES c) DEPTES**


a) b) c)

Source: SIGMA ALDRICH, Organoalcoxisilane reactives. [Online]. Merck, Darmst, Germany. (Recuperado 13 Enero 2018). Disponible: https:www.sigmaaldrich.com

## 1.2 Treatments of fibers

### 1.2.1 Silane treatments

**1.2.1.1 Pre-treatment using sodium hydroxide (NaOH).** After 12h drying, fibers were immersed in a 5% wt. solution of NaOH, for 3h, under stirring. They were also treated for 24 hours to assess the level of soda attack on the fibers. After the treatment, they were neutralized with tap water to pH 7.0 and oven dried at 50°C for 48h.

**1.2.1.2 Grafting of silane.** Three different silane treatments have been tested as explained in the following. The dried fibers were immersed under stirring for 1h in a 70/30 (v/v) ethanol/water solution containing:

(i) 10 wt. % of APTES,
(ii) 10 wt.% DEPTES, or
(iii) 5 wt. % of APTES and 5% of DEPTES.

After the treatment they were dried for 48h at 50°C.

**1.2.2 Ammonium Sulfamate treatment.** 57.08 g of powdered Sulfamate had been dissolved in 500 ml of distilled water. Then the sample was immersed in 100 ml of this solution for 10 min until a color change in the fiber was obtained, then the sample was passed through padding rollers in order to remove the excess of solution from the fiber.

### 1.3 Composites consolidation

Four plies composites were prepared using a vacuum bagging technique. Four layers of comingled flax/PLA fabrics were stacked between two steel plates. 5 different stackings have been prepared (Table 1). Either the stacking contains only untreated fabrics, or they are composed of one treated fabric and 3 untreated ones. A bag (Nylon 66, Tf=232°C, 50µm thick, 17.4m²/kg, from Cytec) were packed around this mold and the vacuum were maintained inside the bag throughout the process using a pump. The assembly was put in a press applying the simultaneously temperature and pressure cycles. The temperature cycle consists in: maintaining the sample 5 min at 180°C, then the temperature is increased to 60°C in 8 min and then maintained constant 60°C for 1 min. The pressure cycle is the following: 10 kN are applied for 3 min, then it is increased to 20 kN in 1 min and finally the pressure is kept constant at 20 kN for 10 min.

Table 1 summarizes the treated fibers and the composites made and studied in this work.

**TABLE 1. Summary of the samples**

| | Treated Fabrics | Composites |
|---|---|---|
| **FlaxPLA** | X | X |
| **FlaxPLA+NaOH** | X | X |
| **FlaxPLA +NaOH 24h** | X | |
| **FlaxPLA+AS** | X | X |
| **FlaxPLA+APTES** | X | X |
| **FlaxPLA+NaOH+APTES** | X | X |
| **FlaxPLA+DEPTES** | X | |
| **FlaxPLA+NaOH+DEPTES** | X | |
| **FlaxPLA+NaOH+APTES+DEPTES** | X | |

## 1.4 Characterization techniques

### 1.4.1 Evaluation of the fabrics

**1.4.1.1 Infrared spectroscopy with Fourier transform (FTIR).** Infrared spectroscopy with Fourier transform is a technique that allows to see the interaction between matter and electromagnetic fields in the infrared region. Light is absorbed at distinct frequencies in a liquid, solid or gas, which corresponds to the vibrational frequencies of the bonds in the sample. The absorption or emission spectrum obtained shows what kind of bonds are present. Reflective infrared spectroscopy was performed in a Nicolet iS50 (ThermoScientific) infrared spectrometer and was used in a wavelength range between 4000 and 500 cm$^{-1}$ with a spectral resolution of 4 cm -1, and all spectra were performed on 32 scans.

**1.4.1.2 Scanning Electron Microscope (SEM).** This microscopy technique is capable to give high resolution images of the surface of a sample thanks to electron-matter interactions by an electron beam emitted on the sample. Give morphological information of the analyzed material. The samples were metallized with carbon fiber before analysis. Samples were then analyzed on a HITACHI S-3400N microscope in which a voltage of 10 kV was applied to the metalized samples.

**1.4.1.3 Differential Scanning Calorimetry (DSC).** Differential Scanning Calorimetry is a thermoanalytical technique used for polymer characterization. Properties such glass transition temperature, crystallinity and melting temperature can be measured by this technique. These measurements were performed on the TA Instrument DSC Q100 equipment and the results were analyzed in TA Universal Analysis Software. Samples were prepared on small aluminum pans in which 3x4 mm composite sample was placed, after sealing, the samples were subjected to a heating/cooling cycle at a rate of 20°C/min from 25 to 160°C and vice versa with an isotherm time of 5 min after each temperature change.

**1.4.1.4 Nuclear Magnetic Resonance (RMN).** $^{31}$P NMR measurements had been performed on a Bruker Avance II 400 at 40.5 MHz using a 4 probe, without crossed polarization (CP) 1H-31P, with dipolar decoupling (DD) and magic angle spinning (MAS) at a speed of 12.5kHz. The spectra were acquired as a result of 16 scans for all the samples. The reference used was 85% H3PO4 in aqueous solution. $^{29}$Si NMR measurements had been performed on a Bruker Avance II 400 at 19.6 MHz using a 7 probe, without crossed polarization (CP) 1H-31P and dipolar decoupling (DD), with magic angle spinning (MAS) at a speed of 5kHz. The number of scans were chosen as a compromise between the signal to noise ratio and the occupation of the spectrometer. The reference used was TMS.

### 1.4.2 Thermal decomposition and combustion tests

**1.4.2.1 Thermogravimetric Analysis (TGA).** It is a technique that allows to follow the thermal degradation of materials as a function of temperature or time. It gives specific information such as: Degradation temperature of a material, start of degradation, percentage of residual mass. For the present sample analysis, a TGA equipment provided by Netszche was used under a Nitrogen atmosphere at a flow rate of 50 mL/min, between a temperature range of 30 to 800°C and a heating rate of 10°C/min. For each analysis, 10-12 mg of sample were used.

1.**4.2.2 TGA-FTIR.** The degradation of the material was carried out on a TA Instrument TGA Q5000. The analysis was performed after an isotherm of 120 min at 50°C, followed by a ramp of 10°C/min to 800°C, with a purge of 100 mL/min and under nitrogen atmosphere. The gas products were identified in a ThermoScientific

Nicolet iS10 FTIR spectrometer, 1 mm diameter gas line was used to transport gas from the TGA to the infrared cell, the line was held at 225 ° C to avoid condensation of degradation products. A wavelength range between 4000 and 400 $cm^{-1}$ and a number of 32 scans and an optical resolution of 4 $cm^{-1}$ were used. For each sample, 15 mg of fiber were placed in an Alumina basket.

**1.4.2.3 Pyrolysis-Combustion Flow Calorimeter (PCFC).** This equipment allows to assess the pyrolysis/combustion of a material, it measures the rate at which the heats of the combustion gases are released from a material during controlled pyrolysis in an inert environment. The capability of the flame retardant to limit the release of degradation gases was evaluated by this equipment supplied by Fire Testing Technology Ltd. Fibrous samples between 10 and 15 mg were deposited in an Alumina crucible and degraded under a nitrogen atmosphere in a pyrolizer with heating of 1°C/s and nitrogen flow of 80 cc/min. Then the degradation gases were mixed with nitrogen/oxygen in a combustor with an 80/20 ratio, respectively.

**1.4.2.4 Mass Loss Cone Calorimeter (MLC).** It is a modern equipment used to study fire behavior on a small scale. It provides information of the material thermal properties such as: ignition time, mass loss, heat generation rate and parameters associated with combustion. The center of the equipment is a truncated cone electric heater giving a heating flow of 35 $kW/m^2$, simulating a real fire condition. Ignition was achieved with a lighter 13 mm above the sample. The equipment was calibrated with a flow of methane. Measurements were made on a Fire Testing Technology in 50x50 $mm^2$ samples and all measurements were repeated at least 2 times to ensure their good repeatability. The margin of error of the results is estimated to be 10%.

# 2. RESULTS AND DISCUSSION

## 2.1 Pre-treatment with NaOH

**2.1.1 Material Characterization.** After the pretreatment with NaOH, the final weight of the sample was measured. Results are reported in Table 2. After alkaline pretreatment there was a mass loss of about 25% of the initial mass of the fabric, which may present a disadvantage in the composite manufacture. At 24h of pretreatment a loss of 66% of mass is observed, taking into account that the material is 50% PLA and 50% flax, there is a possibility of total destruction of one of the present components, this fact will be discussed in the FTIR analysis.

**TABLE 2. Decreased mass after treatment with NaOH**

| Sample | Increased/Decreased mass after treatment [%] |
|---|---|
| **FlaxPLA** | 0.00 |
| **FlaxPLA+NaOH** | -25.16 |
| **FlaxPLA +NaOH 24h** | -66.23 |

Likewise, by means of the Keyence microscope, the diameter of the fibers of PLA and flax were measured before and after the alkaline pretreatment. Table 3 shows a larger reduction in the diameter of PLA (8.15%) fibers compared to flax (0.83%), which makes it possible to say that PLA is affected more significantly with alkaline pretreatment than flax.

**TABLE 3. Fiber diameter decrease after NaOH pretreatment.**

| Material | Diameter [µm] | | |
|---|---|---|---|
| | Before Treatment | After Treatment | Reduction [%] |
| **Flax** | 23.99 | 23.79 | 0.83 |
| **PLA** | 18.41 | 16.91 | 8.15 |

**2.1.1.1 Infrared Analysis.** In order to know the chemical composition of the treated material after the alkaline pretreatment the infrared analysis of the samples was carriedout (figure 6). In figure 6, the increase in peaks at 3300 $cm^{-1}$ for NaOH treated fibers corresponds to the vibration of the OH bonds in the samples. In addition, there is a disappearance of the peak corresponding to the lignin, assigned by Xia et al. [11] at 1600 $cm^{-1}$. This clearly demonstrates the elimination of lignin and the increase of the hydroxyl groups of cellulose in the fibers by the action of sodium hydroxide. It generates a greater area for the possible grafting of FR. The grafting is expected to be placed between the hydroxyl group of the flax fiber and one ethyl groups from the silane molecule, consolidating a Si-O-C bond. For the alkaline pretreatment after 24

**FIGURE 6. Infrared spectrum of samples with and without alkali pretreatment**

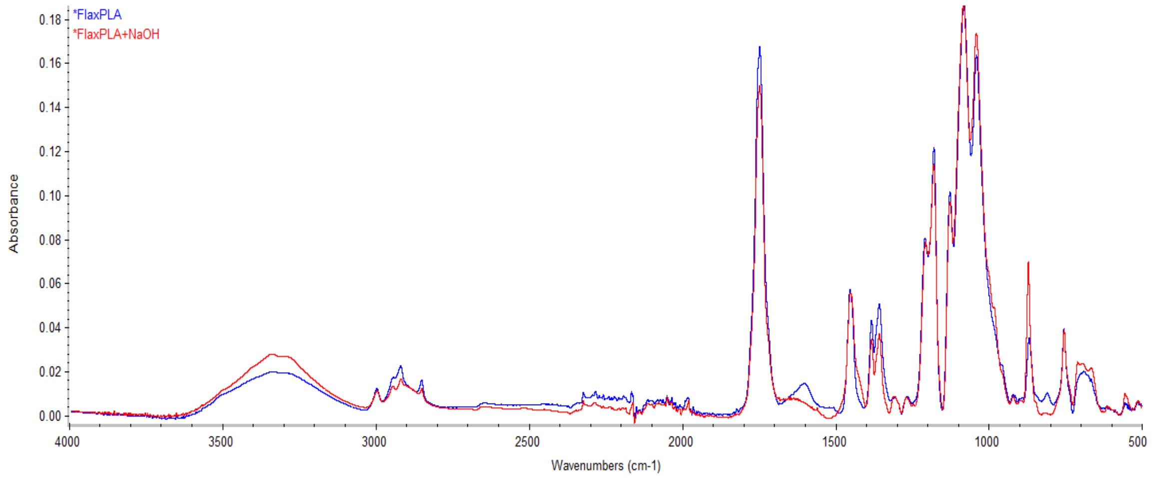
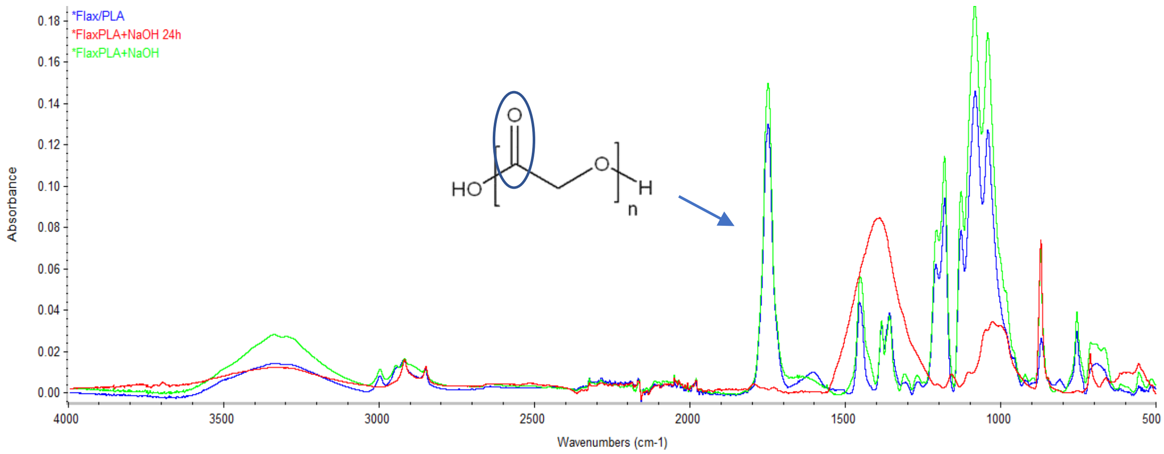


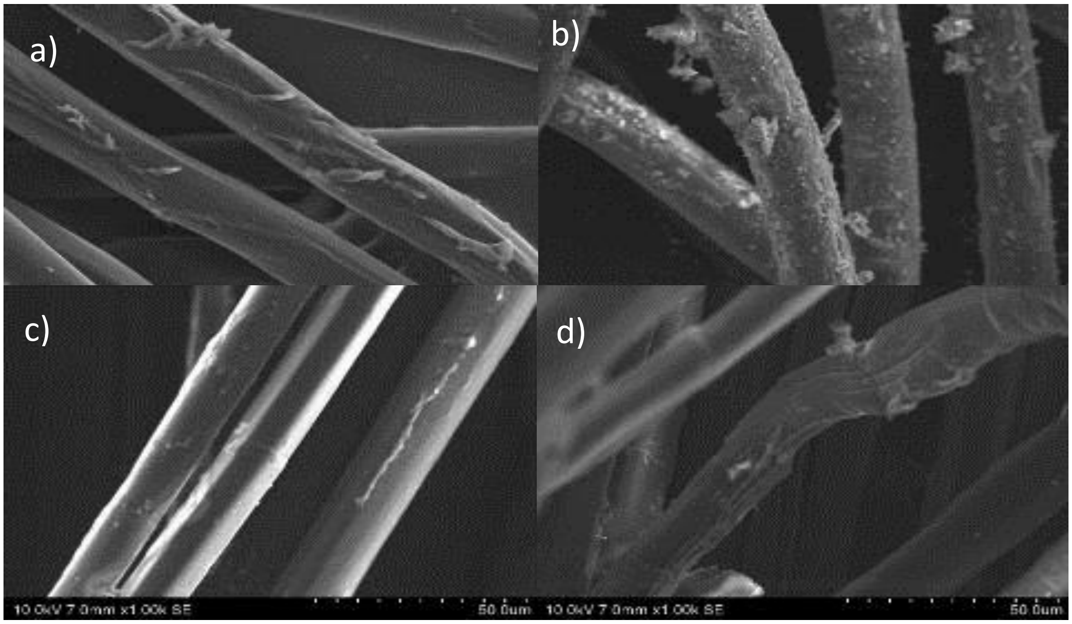
**FIGURE 7. Infrared spectrum of samples with and without alkali pretreatment after 24h**



hours, an elimination of the carbonyl group between 1800 and 1700 $cm^{-1}$ corresponding to PLA (figure 7). That makes clear the complete degradation of the polymer, as well as the characteristic groups of the flax between 1200 and 1000 cm.

**2.1.1.2 Scanning Electron Microscopy.** The response of flax and PLA fibers to pretreatment with NaOH can be seen more clearly by the Scanning Electron Microscope. After the action of NaOH in flax (figure 8.c and 8.d), flax gets a rougher surface and opens in layers (Annex A) and an increase in the roughness of the fiber's surface is observed, confirming the destructive action of the sodium hydroxide on the fibers. As for PLA (figure 8.a and 8.b), a kind of erosion is observed on the fibers and small particles deposited on the surface, probably the Na+ ions adhered to the carbonyl groups of the PLA.

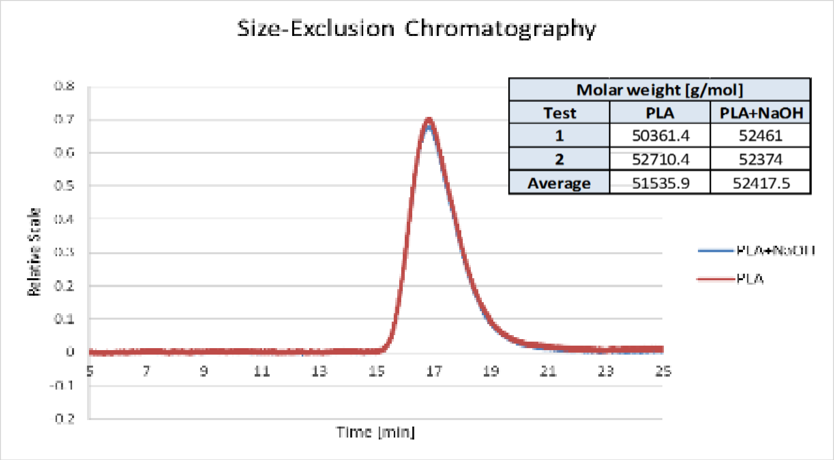
**FIGURE 8. Fibers morphology of a) PLA, b) PLA+NaOH, c) Flax and d) Flax+NaOH**



**2.1.1.3 Size Exclusion Chromatography (SEC).** Size exclusion chromatography showed that the molecular weight before and after the alkaline pretreatment of the PLA fibers was kept constant and the poly dispersion was the same in both samples as seen in Figure 9. This chromatographic analysis shows that, although there is a destruction of the PLA fibers, there is not a considerable change (Range error 7%)

in the molecular weight of the polymer.

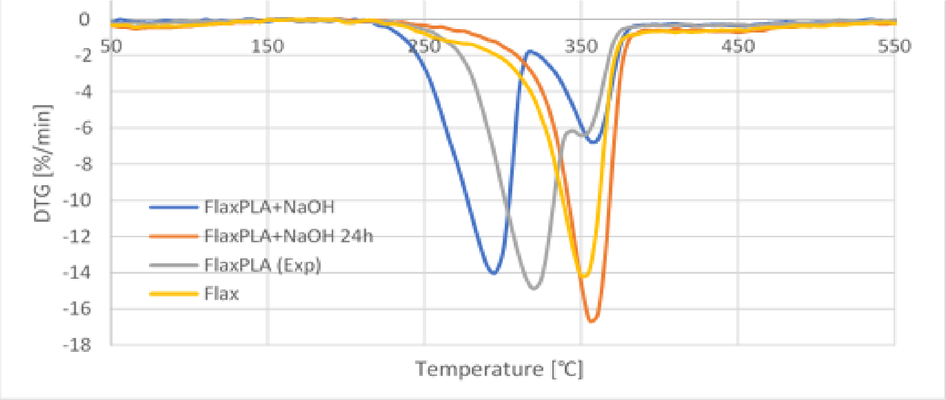
FIGURE 9. SEC of PLA fibers before and after pretreatment



| Molar weight [g/mol] | | |
|---|---|---|
| **Test** | **PLA** | **PLA+NaOH** |
| **1** | 50361.4 | 52461 |
| **2** | 52710.4 | 52374 |
| **Average** | 51535.9 | 52417.5 |

**2.1.1.4 Thermogravimetric Analysis (TGA).** This analysis of treated samples was done to verify the thermal stability before and after the alkaline pretreatment of the fibers. In figure 10, it is observed that, when doing the pretreatment, the degradability of the material changes, accentuating a second stage of degradation. This could be explained by the elimination of a few quantity of PLA present in the sample, somewhat reducing its interaction with flax fibers. After the 24-hour pretreatment, a degradation identical to the degradation of pure flax is noted, which leads to the conclusion that the alkaline pretreatment completely degrades the PLA in the commingled fabric.

FIGURE 10. Thermogravimetric analysis of FlaxPLA before and after treatment



## 2.2 Treatment with Flame Retardants

### 2.2.1 Material Characterization

**2.2.1.1 Percentages of adhesion/mass loss.** The loss/increase mass was monitored before and after each treatment (Table 4) where it is observed that treatment with all flame retardants increases the mass of the sample. Specially, the treatment with AS is the lowest with 2.02 % and the treatment with the highest percentage of “grafted” retardant is the sample treated with NaOH plus DEPTES with 41.67%. For both alkoxy-silane compounds the percentage of mass increase is higher after the alkaline pretreatment, clarifying that the increase of addition is given by the greater surface area made by the action of NaOH. Taking into account that the pretreatment reduces the mass of the sample by 25%, the treatment of the flame retardant increases it by the same magnitude and higher.

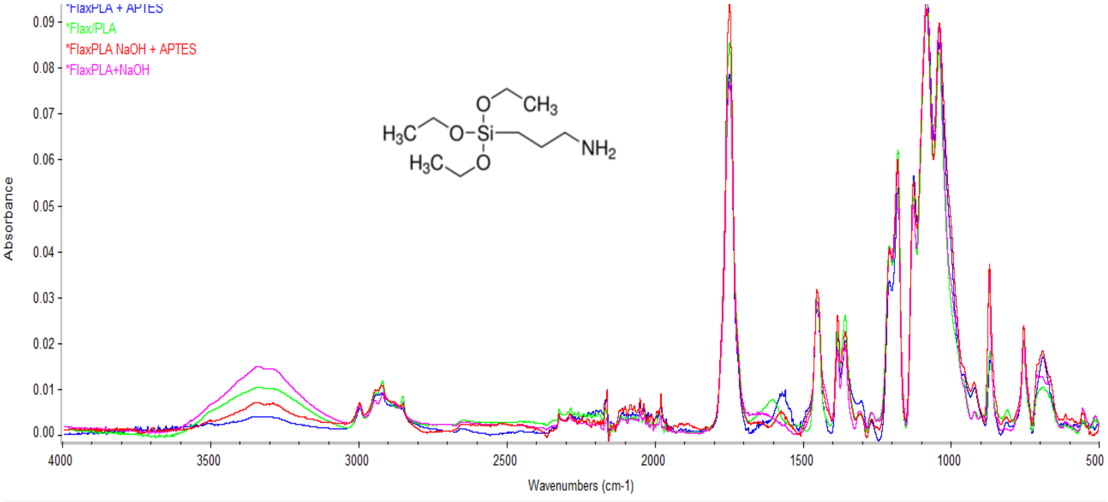
**TABLE 4. Increase in mass after treatment with flame retardants**

| Sample | Increased/Decreased mass after treatment [%] |
|---|---|
| **FlaxPLA** | 0.00 |
| **FlaxPLA+AS** | 2.02 |
| **FlaxPLA+APTES** | 23.83 |
| **FlaxPLA+NaOH+APTES** | 29.19 |
| **FlaxPLA+DEPTES** | 28.91 |
| **FlaxPLA+NaOH+DEPTES** | 41.67 |
| **FlaxPLA+NaOH+APTES+DEPTES** | 27.83 |

#### 2.2.1.2 Infrared spectroscopy with Fourier transform (FTIR)

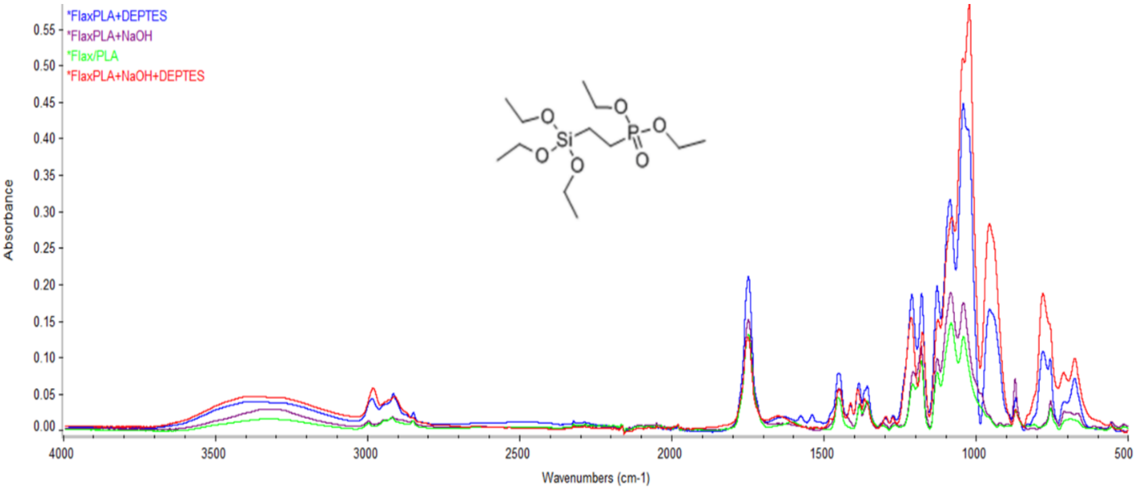
**APTES**: For samples treated with APTES, a reduction in the peak representing the hydroxyl group at 3300 cm$^{-1}$ is observed, this could suggest the disappearance of these groups. Such disappearance could be due to the grafting of the APTES molecules on the fibers. The peak observed at 1600 cm$^{-1}$ is attributed to lignin and the one at 1550 cm$^{-1}$ is identified as the amine group characteristic of the APTES molecule (figure 11). Finally, the peaks at 930 cm$^{-1}$ and 700 cm$^{-1}$ represent respectively Si-O-Cellulose [18] and Si-O-Si [11] bond. These peaks could indicate both the grafting and some condensation of the organoalkoxysilane at the surface of the fibres.

**FIGURE 11. Infrared spectrum of fibers under APTES treatment**



**DEPTES**: Likewise, samples treated with DEPTES, peaks appear between 3000 and 2900 cm$^{-1}$, which represent the large amount of C-H bonds present in the flame retardant. Other important peaks are the peaks belonging to the Si-O-Cellulose and Si-O-Si bonds present at 950 and 710 cm$^{-1}$ respectively. As with APTES, these two bonds are characteristic of grafting and condensation of the organo-alkoxy-silane compounds on the fibers [11]. Finally, the last major peak is at approximately 680 cm $^{-1}$ and represents the phosphorus-oxygen (P-O) bond found exclusively in the DEPTES molecule.

**FIGURE 12. Infrared spectrum of fibers under DEPTES treatment**



**2.2.1.3 Surface morphology of fibers.** The Scanning Electron Microscope has been used to observe the deposit of FR on the surface of Flax fibers, PLA fibers and comingled fabrics. In Annex B, a detailed comparison of the deposits done on flax and PLA can be seen according to the type of treatment performed: with APTES and DEPTES. It should be noted that, morphologically, all treatments affect PLA much more than flax.

**FIGURE 13. SEM images of a) FlaxPLA+APTES b) FlaxPLA+NaOH+APTES c) FlaxPLA+DEPTES d) FlaxPLA+NaOH+DEPTES.**

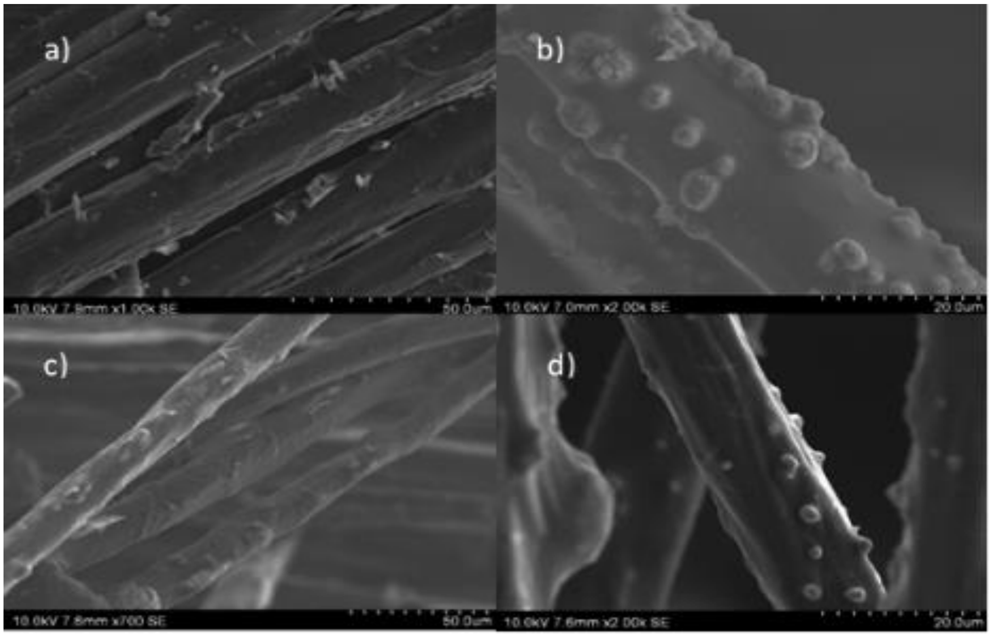
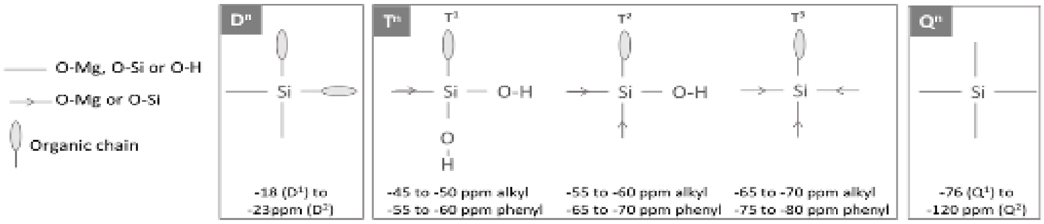


Figure 13 shows the results treatments of FlaxPLA with either APTES or DEPTES and with and without NaOH pretreatment. It can be noticed that the deposits morphologies are very different. For the fibers treated directly with APTES (figure 13.a), the fiber's surface is rather smooth even if some particles are observed on its surface. On the other hand, if an alkaline pretreatment is done prior to APTES treatment, particles are not observed anymore on the surface but instead, it looks like a kind of swelling/bubbles in the fiber, which may be the result of the reaction of the flame retardant on the reactive surface of the material (figure 13.b). With DEPTES (figure 13.c), the surface without alkaline treatment is rough and there are no little particles onto the fibers but with pretreatment (figure 13.d) presents the same type of swelling on the surface of the material is perceived. For both cases, the pretreatment changes the arrangement of the reagents on the surfaces.

**2.2.1.4 NMR.** The level of condensation of the silicon on the treated samples is observed on figure 15. The nomenclature for Si environment is the one described on figure 14 [19].

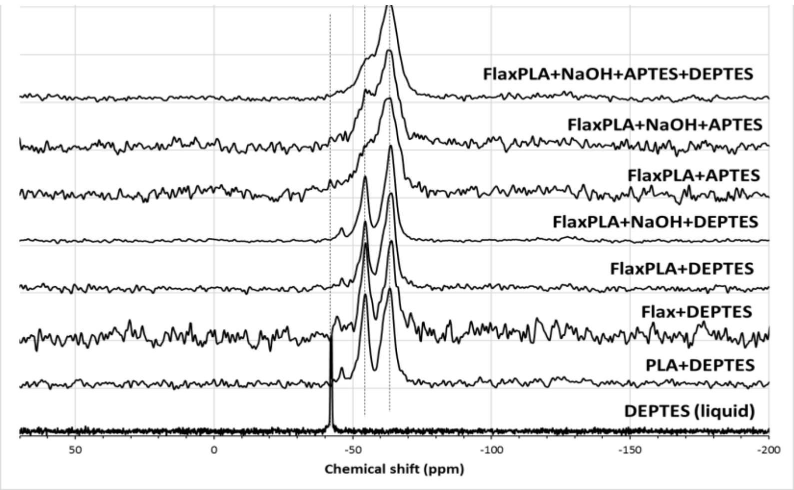
**FIGURE 14. Nomenclature for Si condensation.**



Source : UKRAINCZYK,et al. Template synthesis and characterization of layered Al− and Mg− Silsesquioxanes. *The Journal of Physical Chemistry B*, 1997, vol. 101, no 4, p. 531

In figure 15, all treated samples exhibit peaks between -50 and -75 ppm representing a T2 and T3 Si environment. This shows that one silicon atom condenses together with two other silicon atoms through the ethyl group beside him. According to the previous figure the fabrics present a condensation of silicon on its surface, however, there are differences in the condensation depending on the APTES or DEPTES. What is possible to affirm is that the presence of condensation of the molecules in

**FIGURE 15. $^{29}$Si RMN spectrum of samples treated with APTES and DEPTES**

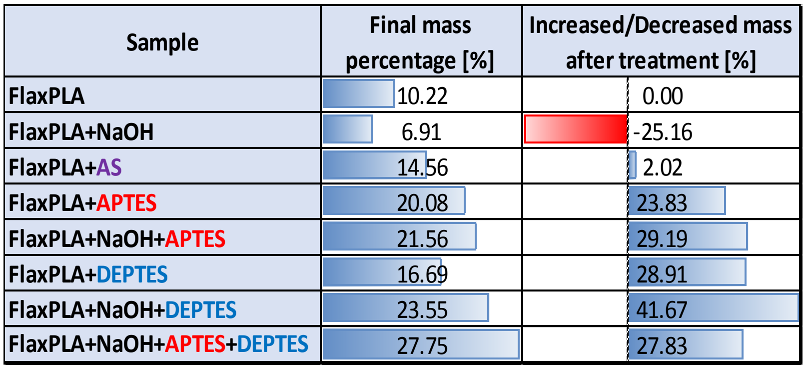


the fibers is a fact, favorable aspect for the ignifugation of the material. In Annex C, it is possible to see the 31P RMN spectrum which, as the Si spectrum show the presence of the phosphorous group in the samples, obviously if there is silicium condensation in the fibers, there will be a phosphorous signal.

### 2.2.2 Thermal degradation and fire test

**2.2.2.1 Thermal stability of fibers.** In Table 5, the residual mass percentages of all the samples studied are found, where almost all the fibers treated with organo-alkoxy-silane compounds have final mass percentages higher than 20%. It is important also to notice that all the samples treated with NaOH have a higher final mass percentage compared to their pair (figure 16 and 18).

**TABLE 5. Final mass percentage after TGA vs FR treatment addition**



| Sample | Final mass percentage [%] | Increased/Decreased mass after treatment [%] |
|---|---|---|
| FlaxPLA | 10.22 | 0.00 |
| FlaxPLA+NaOH | 6.91 | -25.16 |
| FlaxPLA+AS | 14.56 | 2.02 |
| FlaxPLA+APTES | 20.08 | 23.83 |
| FlaxPLA+NaOH+APTES | 21.56 | 29.19 |
| FlaxPLA+DEPTES | 16.69 | 28.91 |
| FlaxPLA+NaOH+DEPTES | 23.55 | 41.67 |
| FlaxPLA+NaOH+APTES+DEPTES | 27.75 | 27.83 |

For fibers treated with APTES (figure 17), the degradation temperature increases with respect to the reference FlaxPLA. Theoretically and according to Wilkie (2010) is due to the thermal decomposition of the condensed network of silane on the fibers, which, when degraded, form a layer of silane ash on the surface, limiting the flow of heat to the interior of the material and decelerating the production of volatiles.

The treatment with AS has two stages of degradation (figure 17): the generation, sulfation and carbonization on the fibers and the degradation of the remaining organic material. The first stage occurs rapidly and at a low temperature. The second stage is given at a higher temperature due to the carbonized layer which also fulfills the thermal barrier function [20].

FIGURE 16. Thermogravimetric analysis of APTES samples

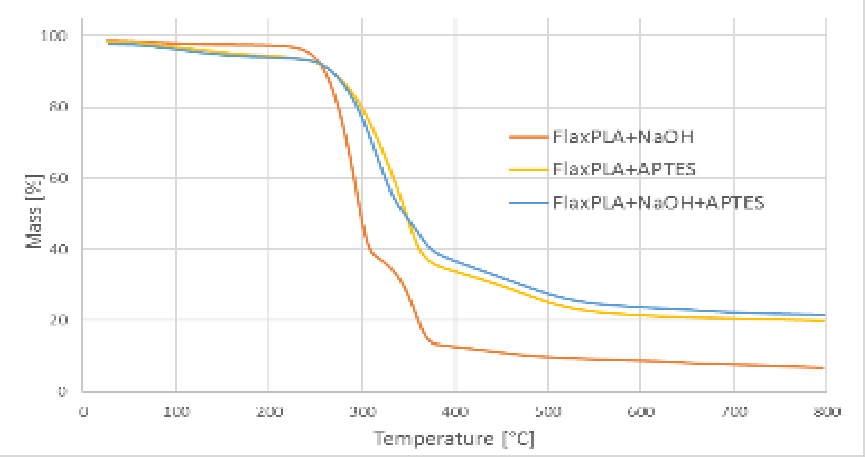


FIGURE 17. Comparative thermogravimetric analysis of fibers with FRs

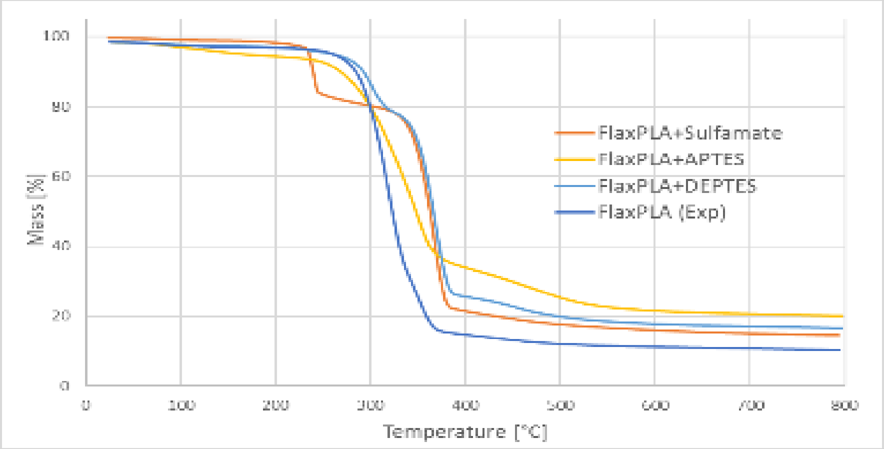
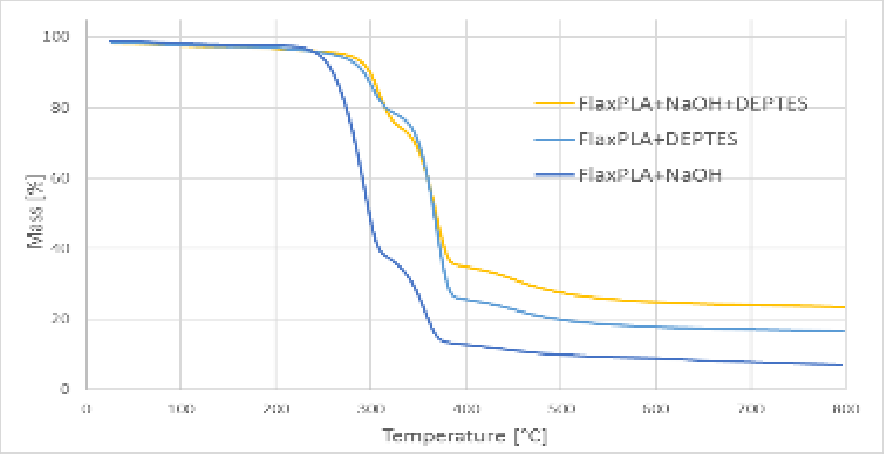


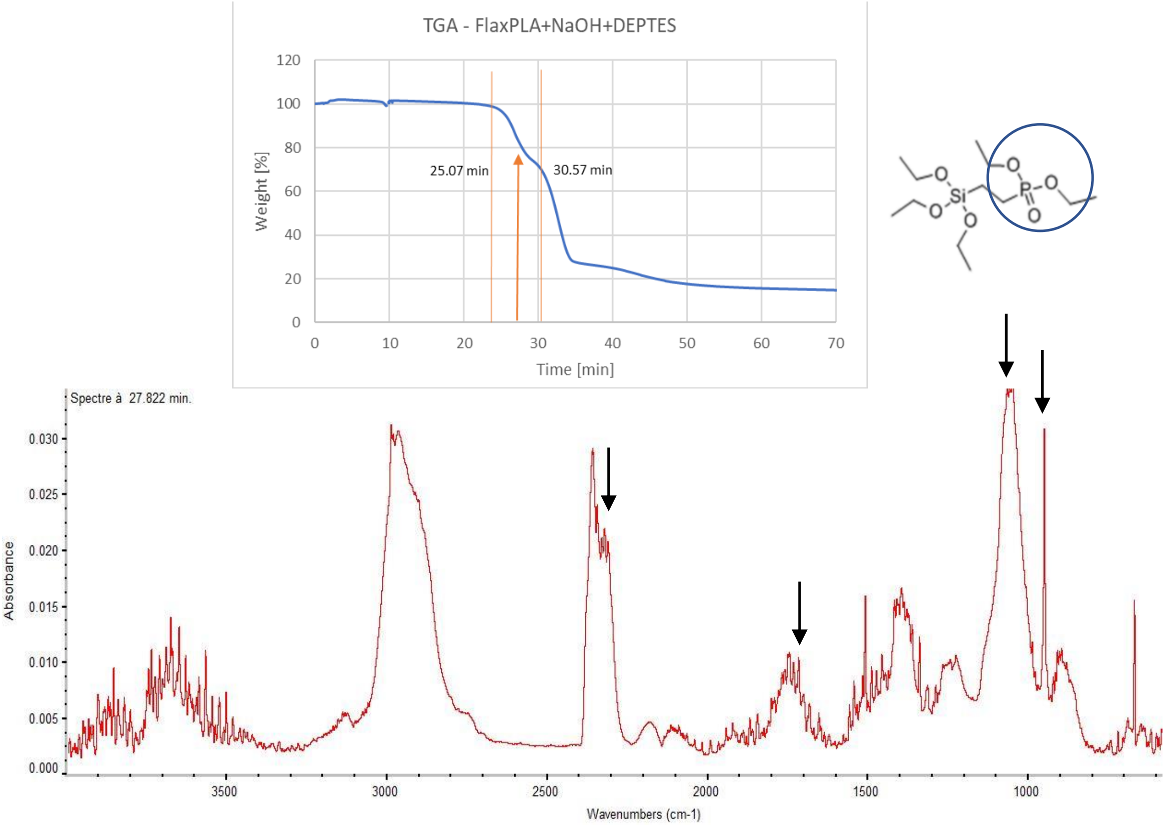
FIGURE 18. Thermogravimetric analysis of DEPTES samples



Finally, the treatment with DEPTES shows two stages of degradation according to figure 18. The first one, possibly, due to the degradation and performance of the phosphorus group. The second one by the action of the silane. As with AS treatment, the phosphorous group decomposes its initial molecule, and condenses on the fibers, according to Wilkie, 2010, the ester group of phosphorus formed after condensation, catalyzes the dehydration of cellulose instead of giving the depolymerization of natural fiber. Lastly, as with APTES treatment, the material is degraded at a near temperature and the greater mass is degraded in this second stage.

**2.2.2.2 TGA-FTIR.** The spectrum of the gaseous phase of the fabric treated with DEPTES shows that after 28 minutes from the temperature increase (Figure 19.1), it starts to appear distinct peaks. The hypothesis is that phosphoric acid is released from the DEPTES attached to the sample. In the spectrum it is possible to see the

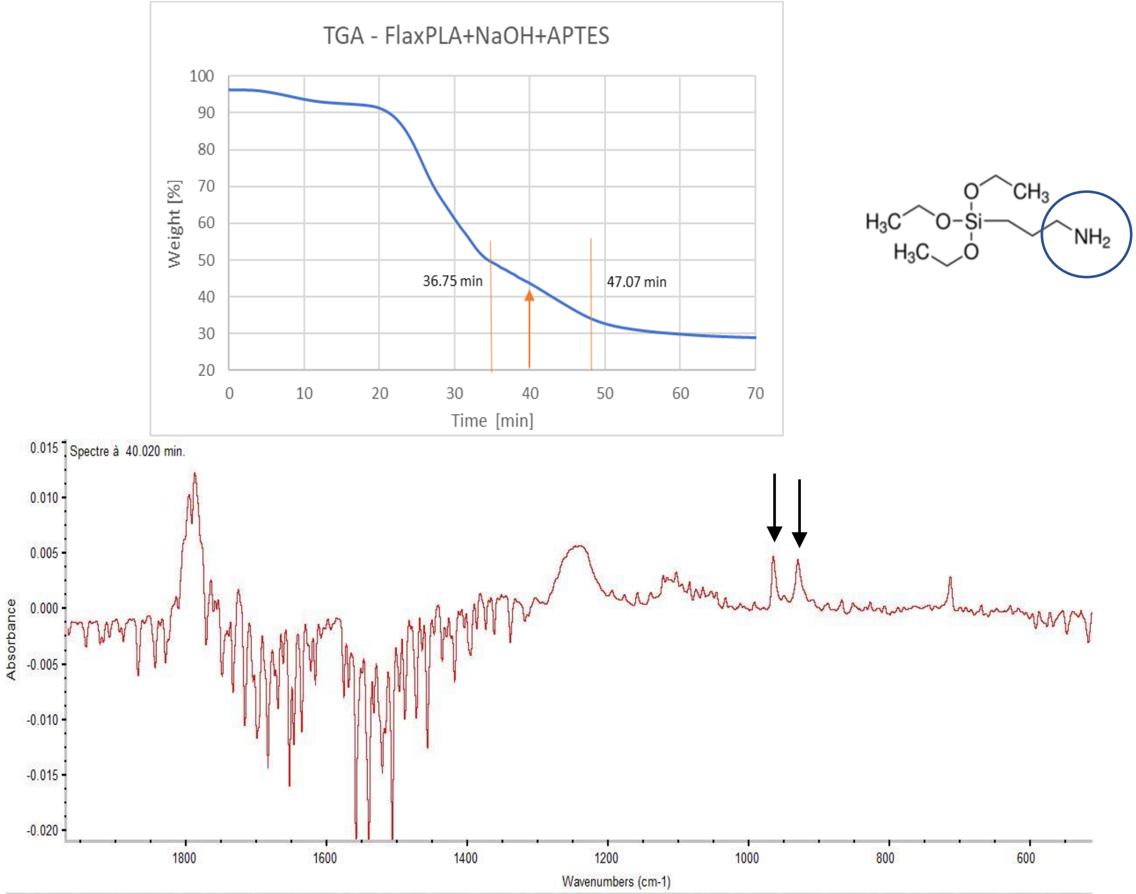
**FIGURE 19.1 DEPTES treated fabric (*up*) TGA and (*down*) FTIR at 28 min**



following peaks: 2300 cm$^{-1}$ corresponding to HO-P=O bonds; in 1730 cm$^{-1}$, 940 cm$^{-1}$, and 1010 cm$^{-1}$ which represent both the HO-P and P-O bonds. Those peaks correspond to the phosphoric acid, confirming that this compound is first released from the fibers, increasing the temperature at which the fibers degrade. When comparing this spectrum with the spectrum of fibers treated with APTES there is no similarity in the same range. In the APTES fiber, the protection is given by the condensed silicon network and in the fiber with DEPTES the protection is given by the condensation of silicon and phosphoric acid on the fibers.

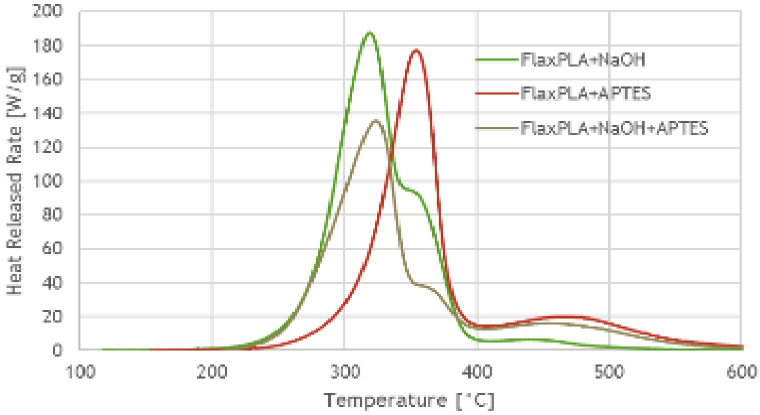
In figure 19.2 it is possible to see the following interesting peaks: at 965 cm$^{-1}$ and 930 cm$^{-1}$ which correspond to ammonia in gas phase, the beginning of this change is at 36 min. So, at this time it starts the liberation of the $NH_2$ group as ammonia and its forms is a shoulder in the weight percentage curve.

**FIGURE 19.2 APTES treated fabric (*up*) TGA and (*down*) FTIR** at 40 min



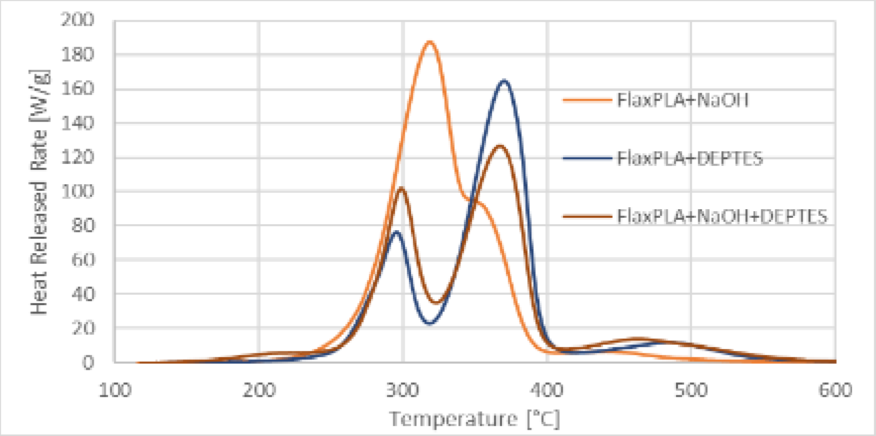
**2.2.2.3 Pyrolysis-Combustion Flow Calorimeter (PCFC).** When comparing the treatment with APTES as presented in figure 20, a considerable reduction of the Heat Released Rate (HRR) in the fiber with alkaline pretreatment is noted. Approximately, there is a reduction of 23% of the HRR. This is possibly due to the increased protection generated by an increase in APTES condensation on the fibers, this is also a proof in favor of alkali processing.

**FIGURE 20. PCFC of samples treated with APTES**



In the same way, the fibers treated with DEPTES have a reduction in the rate of heat release of the fiber pretreated with NaOH that correspond to a 25% less. As can be seen in the first heat release peak, it is possibly due to the release of the phosphorus group from the DEPTES molecule. This is equivalent in the two samples, but in the second peak it is clear the protection due to the greatest amount of addition of reagent in the fibers. Figure 21.

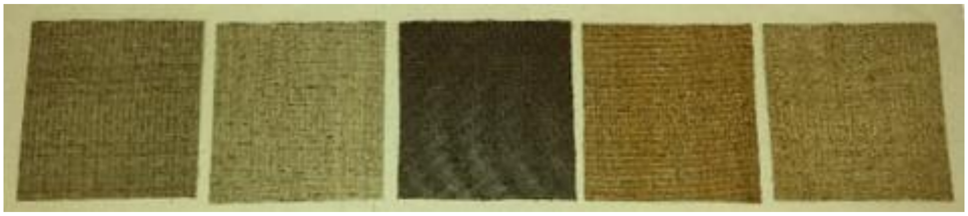
**FIGURE 21. PCFC of samples treated with DEPTES**



### 2.3 Construction of composites

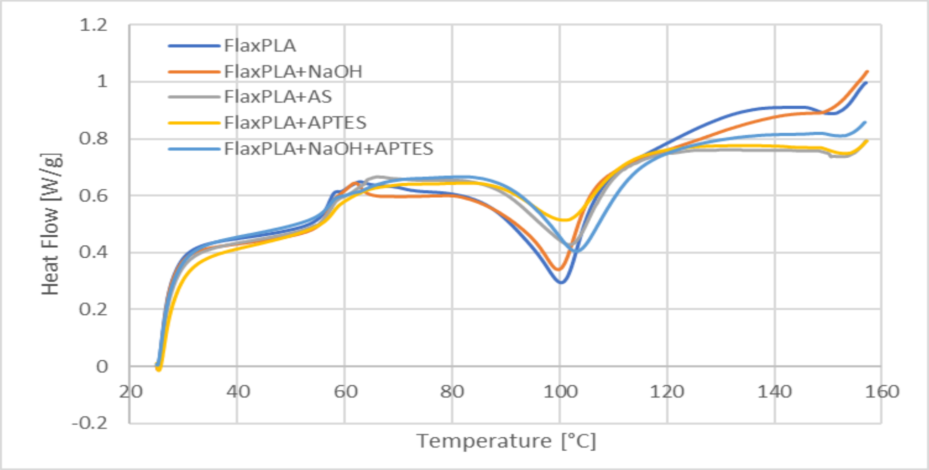
**2.3.1 Composites Characterization.** Using the molding press, the composites were constructed (figure 22) and the different treatments gave a different color to the composite. Notably, the treated with AS presents a very dark color compared to the other composites, this is given by the temperature cycle used for the construction of the material, which goes up to 180°C and according to the thermogravimetric curve, there is a small degradation of the sulfide group, before the average degradation of all the fibers. The alkaline pretreatment fibers are slightly clearer than their reference clearly by the elimination of lignin, fats and oils that pigment the fibers. Due to delivery delays it was no possible to make the DEPTES composites.

**FIGURE 22. Composites. *From left to right:* FlaxPLA, FlaxPLA+NaOH, FlaxPLA+AS, FlaxPLA+APTES, FlaxPLA+NaOH+APTES**



**2.3.1.1 DSC.** Differential Scanning Calorimetry analysis determined the glass transition temperatures of the samples, which did not show a significant difference between 56 and 58°C. Naturally these temperatures vary between 44 and 62°C. As

**FIGURE 23. Differential scanning calorimetry of composites**



shown in figure 23, the changing point near 60°C is the Glass transition temperature of the polymer. It does not change with the addition of the FR, but it is certainly different in the area under the curve which represents the melting process.

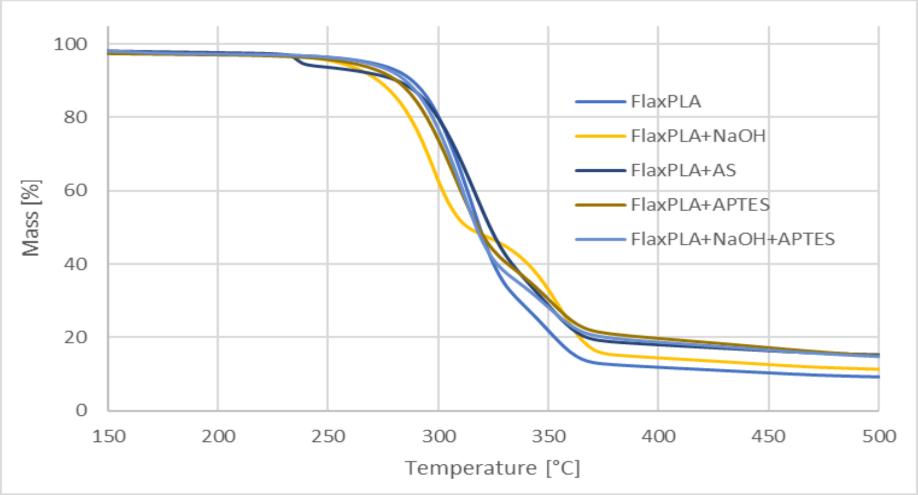
**2.3.1.2 Hydrophobicity test.** In order to corroborate if there was indeed an adhesion of the silane groups on the fibers, the hydrophobicity test was performed (figure 24). It is observed that the fibers treated with APTES are maintained in the non-polar part, corresponding to the oil. This is due to the reduction of polar hydroxyl groups belonging to the fibers.

**FIGURE 24. Hydrophobicity test oil/water. *From left to right:* FlaxPLA, FlaxPLA+APTES, FlaxPLA+NaOH+APTES**

### 2.3.2 Thermal decomposition and Combustion test

**2.3.2.1 Thermogravimetric analysis.** After the manufacture of the composites, the degradation temperatures are closer together and do not have a representative

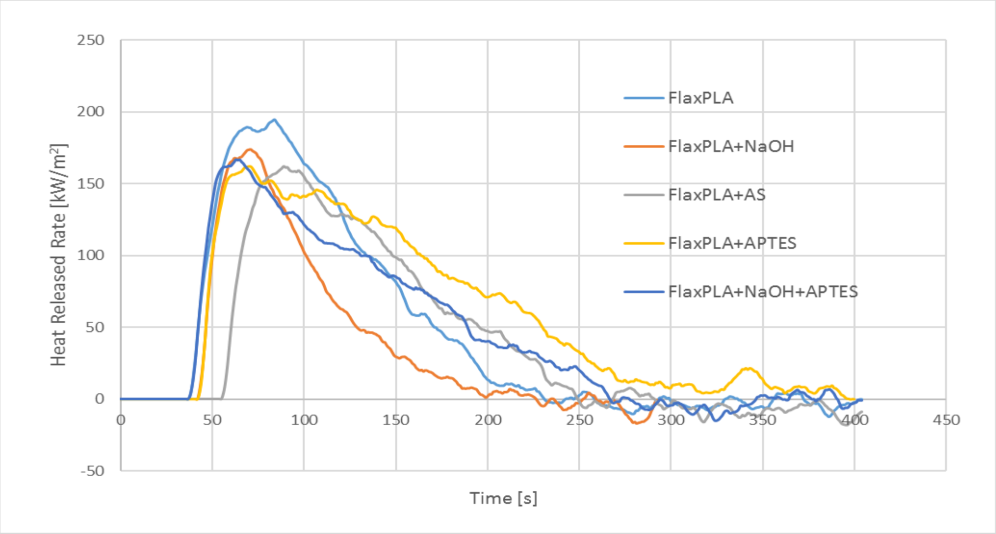
**FIGURE 25. Composites thermogravimetric analysis.**



difference in their degradation temperatures, as seen in figure 25. However, protection against the material is still present, as a larger residual mass is observed. Even the AS treated fiber shows a slight reduction in comparison to fiber degradation show in figure 17.

**2.3.2.2 Mass Loss Cone.** As seen in the figure 26, the ignition time is considerably higher for the sample treated with AS, unlike those treated with APTES that even though they have the same ignition time, there is a reduction of the rate of heat release. So, it is possible to infer that there is a mechanism of protection on fibers in a real condition of combustion, unlike the analysis by PCFC. In table 6 is the information of the tests of combustion done to the composites, where the greater mass loss occurred in the treated fiber with NaOH + APTES. Also, it is possible to notice a decrease in the peak of HRR of the FR fibers in comparison with the reference fiber. And finally, the Total Heat Released (THR) is lower in the fibers having pre-treatment with NaOH, than the ones that does not have it.

**FIGURE 26. Mass loss cone curves of the composites**



When the calorimetric test was carried out, the char residues observed in figure 27 were obtained. In these residues a different coloratura is observed, where the white residues correspond to the composites without FR and the rest ones are those treated with it. During the combustion process a swelling is observed in the fibers treated with FR.

**TABLE 6. Summary of MLC analysis data**

| Sample | Size [cm$^2$] | Weight [g] | | PHRR [kW/m$^2$] | THR [MJ/m$^2$] | Mass loss [%] | Ignition time [s] |
|---|---|---|---|---|---|---|---|
| | | Before | After | | | | |
| **FlaxPLA** | 19.14 | 5.32 | 1.93 | 193.85 | 18.32 | 63.7 | 41 |
| **FlaxPLA+NaOH** | 19.14 | 4.00 | 1.58 | 173.78 | 14.25 | 60.7 | 45 |
| **FlaxPLA+AS** | 19.14 | 5.31 | 2.05 | 161.56 | 16.54 | 61.4 | 58 |
| **FlaxPLA+APTES** | 19.14 | 5.53 | 2.05 | 162 | 23.33 | 63.0 | 45 |
| **FlaxPLA+NaOH+APTES** | 19.14 | 5.07 | 1.61 | 166.58 | 18.23 | 68.3 | 40 |

**FIGURE 27. Composite residues after MLC. *View from top. From left to right*: FlaxPLA, FlaxPLA+NaOH, FlaxPLA+AS, FlaxPLA+APTES, FlaxPLA+NaOH+ APTES**

# 3. CONCLUSIONS

There is a minimum level of degradation of PLA by the alkali treatment even though a PLA diameter reduction of 8% was evidenced in comparison with the 1% reduction in flax. This reduction does not mean a depolymerization of the structure is held, as it shows a constant carbonyl peak and a similar molar weight after 3h treatment. At 24h treatment, there is a complete destruction of the polymer. Likewise, all the silane treatments affect the PLA more than flax.

Grafting of silane groups in the fibers is high probable achieved due to the Silane condensation shown in NMR spectrum and the presence of Si-O-Cellulose bonds in FTIR spectrum at 950 $cm^{-1}$.

Alkali treatment increased the reactive surface and the grafting percentage of APTES and DEPTES treated fabrics in an 18% and 30% respectively. Besides, it helps to flame retard the fibers as shown in the HRR reduction of more than 20% and the increase of 15% of residual mass after thermal degradation of both silane treated fabrics.

Even though the mass addition of AS to the fibers does not get over 3%, the protection of the fibers is as good as with the silane treated fabrics, having one of the highest temperature of degradation initiation (235°C) and degradation temperature (371°C).

# 4. RECOMMENDATIONS

- Make the TGA-FTIR of the samples treated with AS to see if there is a similar action of sulfur in gaseous phase as shown in the small stage in the degradation curve before the complete degradation of the fibers, as the phosphoric acid does.

- Make the SEM analysis of the samples after the MLC test to check the type of carbonized layer that is formed around the fibers, also to check the major compounds present in the char after combustion.

- Prepare the composites treated with DEPTES and compare them with APTES and AS samples in order to corroborate the influence of NaOH pretreatment in the Heat Released Rate and Total Heat Released from fibers.

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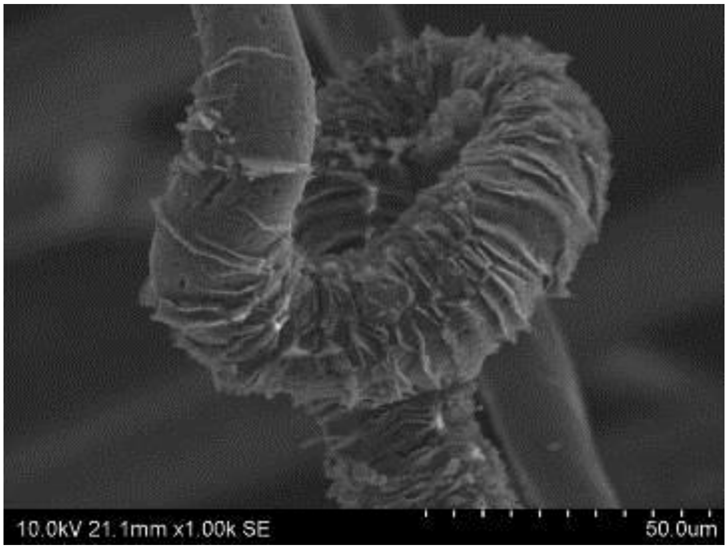
# ANNEX

## **Annex A** Flax fiber after alkali pretreatment

**FIGURE A.1 Flax fiber treated with NaOH**



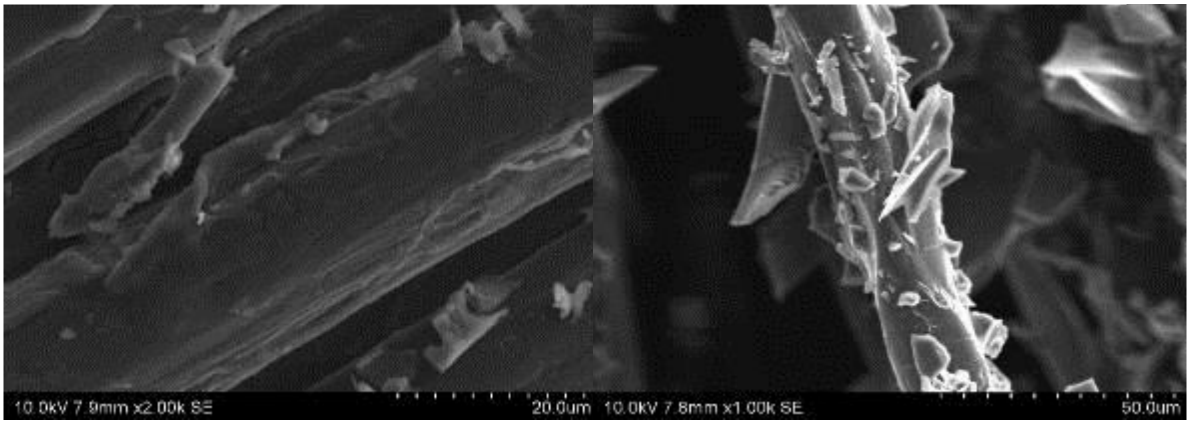
As it was discussed, when flax fibers are treated with NaOH, generally, fibers start to get rougher and start to open in layers as it’s seen in the annex figure. This particularly form of respond is probably due to the destruction of lignin, hemicellulose, and cellulose layers. This type of layers may show an aggressive attack of NaOH to the fibers, so the time of exposure of fibers before the solution must be controlled and watched carefully.

## **Annex B** Flax and PLA after APTES, DEPTES treatment.

As it is possible to see in next images, the respond of flax and PLA is different at the presence of APTES and DEPTES.

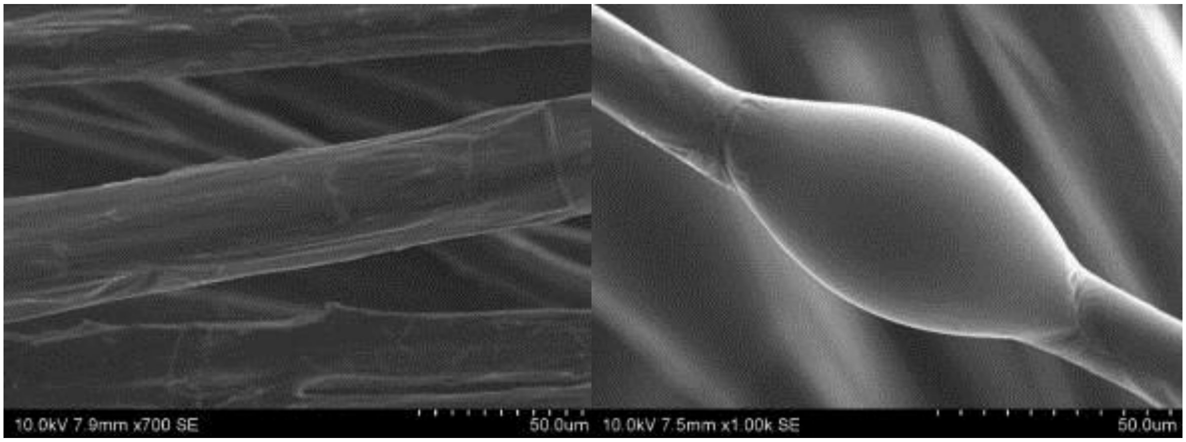
Flax respond after APTES makes the surface rougher, on the other hand, in PLA it is noted the high quantity of particles deposed on the fiber or maybe the alteration of the fiber.

**FIGURE B.1. Flax (*left*) and PLA (*right*) fibers after APTES treatment**



In DEPTES treatment case, the difference is further clear, PLA after treatment shows a swelling in the fiber which can make thing a grafting is taking place there. In flax fibers there is more difficult to see the respond but is noted some marks made in the fibers and a changing in the fiber morphology.

**FIGURE B.2 Flax (*left*) and PLA (*right)* after DEPTES treatment**



## **Annex C**. RMN spectrum of DEPTES treated samples.

All the peaks are placed in the same range and show a similar intensity peak for the phosphorous presence in the fibers. As it was discussed, the presence of the phosphorous bonds evidence also the presence of the silicium molecules, this is because of the molecules structure of DEPTES.

**FIGURE C.1 RMN spectre of samples treated with DEPTES**