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# Silazanes, a novel flax fibers functionalization: Effect on silicone-based composites

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## A B S T R A C T

The natural fibers use as reinforcement for composites is a topical subject. Usually, chemical functionalization is used in order to improve the compatibility between natural fibers and polymer matrices, for cross-linkable systems, the grafting agent used for fiber modification can also participate in the three-dimensional network formation and therefore improve the composite mechanical properties. In this study, a silazane: 1,3-divinyltetramethyldisilazane (DVTs) was used for the first time as a flax fibers modification to introduce at their surface vinyl groups, via covalent bonds, that can react during the polysiloxane system cross-linking. The reaction conditions for the flax functionalization were investigated, especially the alkaline pre-treatment impact of the fibers before grafting and the nature of solvent used during the reaction. Scanning electron microscope (SEM) analyses shown a high interfacial adhesion functionalized fibers/matrix.

Finally, tensile tests showed a significant increase of composites Young's modulus containing functionalized flax fibers.

## Keywords:

- A. Natural fibers
- A. Polymer-matrix composites (PMCs)
- B. Interface/interphase
- B. Fibre/matrix bond

## 1. Introduction:

In recent years and due to the growing environmental concern, the use of natural fibers instead of synthetic fibers as reinforcement for polymer matrices have become a solution of great interest to introduce new composites with reduced environmental footprint [1–11].

Flax fibers are one of the most widely used natural fibers [1], due to their advantages such as: low density [12], good mechanical properties [13,14], better specific tensile strength compared to glass fibers [15] and reasonable cost [16,17]. Furthermore, flax fibers have a lower environmental impact than glass fibers depending on the energy source in the producing country [18,19].

Flax fibers have been used to reinforce many kinds of thermoplastic and thermosetting polymer matrices such as polypropylene, epoxy, bio-epoxy, bio-phenolic resin [13], poly- $\beta$ -hydroxybutyrate [16], polylactic acid [20]. Moreover, the surface treatment of flax fibers such as atmospheric pressure plasma [21], epoxy [22], alkali and silane treatments [22,23] was performed in order to improve the interfacial adhesion between flax fibers and polymer matrices. This in turn enhances the mechanical properties of the composites.

To increase even more the interfacial adhesion, the fibers treatment with coupling agents bearing a functional group able to react with the

polymer matrix is very effective, it leads to a further increase in the mechanical properties [1]. Silane coupling agents are commonly used to modify the surface of cellulose fibers due to their ability to react with hydroxyl groups of cellulose chains. This modification leads to an improvement in the mechanical properties and a greater interfacial compatibility of the cellulose fibers with the matrix by forming covalent bonds, which contributes to better adhesion [24,25]. For example, Abdelmouleh et al. [26,27] have modified cellulose fibers by (3-aminopropyl)triethoxysilane (APTS) and 3-(trimethoxysilyl) propyl methacrylate (MPS) to reinforce epoxy and natural rubber composites, respectively. These modified fibers bearing amine or methacrylate groups can then participate to the formation of a three-dimensional connected network between fibers and matrix by condensation or radical reactions. The formation of covalent bonds between the fibers surface and the polymer chains of the matrix allows the improvement of the fibers/matrix interface and mechanical properties of the obtained composite. The surface treatment of cellulose fibres with MPS and APTS increases the Young modulus (E) up to 10 MPa comparing with 3.6 MPa for the untreated fibers-natural rubber composite and to 3.2 GPa instead of 2.55 GPa for the untreated fibres-epoxy composite.

Since flax fibers contain about 70 wt% of cellulose [28–30], it is possible to take advantage of the presence of cellulose hydroxyl groups

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in order to modify the surface fibers with a coupling agent.

From this point of view, silazane functions may be useful because they have the same ability as silanes to react with hydroxyl functions due to the reactivity of Si-NH groups [31]. Nguyen [32] have mentioned that silazane molecules have an excellent adhesion on a wide variety of polar substrates. He has attributed this strong adhesion to the formation of covalent bonds Si-O by reaction of the Si-NH groups with the hydroxyl groups of the substrate, releasing NH<sub>3</sub> as a by-product.

Nevertheless, to the best of our knowledge, silazane compounds have never been used as coupling agents for natural fibers using as reinforcement in polymer composites. Such compounds appear to be, nevertheless, very attractive for the surface modification of hydroxyl-rich cellulosic fibers.

Silazanes are usually used as ceramic precursors to prepare coatings [33–35]. As an example, Shayed et al. [36] have coated glass and carbon fibers with silazane molecules to protect the fibers against thermooxidation. Polysilazanes can be also involved for the development of light-emitting materials [37], fire-retardant polymers [38] or transparent reinforced composites [39].

On the other hand, silicone rubber is highly used for various applications such as automotive, aerospace industry, electronics, injection molding [40] and medical industry [41] due to its excellent properties including high elasticity, thermal stability [42], good chemical resistance [43] and electrical insulation [43,44]. The reinforcement of silicone rubbers with functionalized flax fibers would be useful in order to improve the mechanical properties of these materials and thus, expand their application field.

In the present study, 1,3-divinyltetramethyldisilazane (DVTS) was used to modify flax fibers. Thanks to the reaction between hydroxyl groups of the flax and silazane groups, functionalized fibers bearing vinyl groups were prepared and used to reinforce a silicone rubber matrix (polydimethylsiloxane (PDMS)). Indeed, in a second step the vinyl groups of the functionalized flax fibers can react with Si-H functions of the silicone chains in presence of Karstedt's catalyst to form covalent bonds between fibers and matrix. The effect of conditions on the grafting reaction has been studied in detail. Moreover, the effect of the functionalization of flax fibers on the mechanical properties for the flax/silicone composite was investigated.

## 2. Materials and methods

### 2.1. Materials

1,3-divinyltetramethyldisilazane 97 % (DVTS), was purchased from ABCR, dimethylsulphoxide (DMSO) 99.9 % and Toluene 99.8 % were supplied by Sigma-Aldrich, Acetic acid was purchased from Fisher Scientific Co. Sodium hydroxide (NaOH) was purchased from PanReac AppliChem. A two-component silicone elastomer BLUESIL RTV 141 A&B was kindly provided by Elkem Silicone France. Short flax fibers (L = 5 mm, Ø = 16 ± 2 µm) were obtained from Terre de Lin Groupe France. All the chemical products in this study were used as received without any further purification.

### 2.2. Preparation and pre-treatment of flax fibers

2 g of pristine flax fibers were dipped into a 200 ml of NaOH solution (0.5 M) at 70 °C for 3 h under stirring. Then, a neutralization process was performed with 200 ml of acetic acid (0.6 M) for 30 min at 70 °C followed by rinsing with deionised water until pH neutral to remove all acetic acid traces. The obtained pre-treated fibers were dried for 2 h at 60 °C.

### 2.3. Functionalization process of flax fibers

4 g of DVTS was dissolved in 16 g of (DMSO/Toluene) (35/65 wt%) co-solvent mixture. The prepared solution was added into a bottom flask

of 50 ml fitted with a reflux condenser. Then, 0.6 g of pre-treated fibers were dipped in this solution for 3 h at 80 °C under stirring. Finally, the fibers were filtered, squeezed by paper towel and washed twice with 20 ml of toluene over 10 min to remove non-reacted and non-grafted molecules.

After reaction, the obtained flax fibers are functionalized with vinyl groups via -Si-O-C- covalent bonds due to the reaction between DVTS and hydroxyl groups of the flax fibers. Furtat et al. [45] have mentioned a proposed mechanism for the decomposition of Si-N backbone of polysilazanes in the presence of hydroxyl groups: the hydroxyl function reacts with the Si-N bond to forms a Si-O-C bond, releasing NH<sub>3</sub> gas. When DVTS is used, for each molecule of coupling agent that reacts, two vinyl groups are assumed to graft onto the flax fibers (Fig. 1).

The functionalization rate (R<sub>F</sub>) was calculated according to the percentage ratio between the mass of grafted molecule and that of corresponding pre-treated fibers.

$$R_F = \left( \frac{\text{Functionalized fibers weight} - \text{pretreated fibers weight}}{\text{pretreated fibers weight}} \right) \times 100$$

This calculation is not accurate but gives an indication of the amount of ((CH<sub>3</sub>)<sub>2</sub>Si-CH = CH<sub>2</sub>) groups that are grafted onto the fibers during the functionalization process.

### 2.4. Preparation of silicone composite

The composites based on a crosslinked silicone elastomer were prepared using short flax fibers.

The silicone matrix was obtained by mixing a PDMS part bearing Si-H groups (0.39 wt%) and a PDMS part bearing vinyl groups (0.22 wt%). The system reacts by hydrosilylation and forms a cross-linked network in the presence of Karstedt's catalyst at room temperature. The vinyl groups grafted on the flax fibers can participate to the formation of this network by reaction with one part of the Si-H functions to form covalent bonds with PDMS chains of the cross-linked network (Fig. 2).

A series of silicon-based composites were prepared by mixing 3 g of each type of flax fibers (pristine /pre-treated/functionalized) with 180 g and 18 g of BLUESIL RTV 141 A and B, respectively. Then, the obtained mixtures were molded using a dog bone shape mold, after removing all gas bubbles under vacuum (Fig. 3). The mold was kept at room temperature for 24 h before samples were removed. The fibers / silicone matrix ratio for the composite products was 1.5 /100 (wt/wt).

### 2.5. Measurements

#### 2.5.1. Fourier transform infrared spectroscopy (FTIR)

Fourier transform infrared spectra were obtained using a Bruker VERTEX 70 spectrometer used in attenuated total reflectance mode, at a resolution of 4 cm<sup>-1</sup>, with 32 scans between 400 and 4000 cm<sup>-1</sup>.

#### 2.5.2. Scanning electron microscope coupled with energy dispersive X-ray spectrometry (SEM-EDS)

The fibers section was analysed using a scanning electron microscope (FEI Quanta 200 FEG). After being cut with a single edge blade, the samples were placed on a vertical sample holder under high vacuum at a voltage of 12.5 kV and a working distance of 10 mm. To locate the presence of vinyl groups associated with silicon element grafted on the flax fibers, SEM analysis was coupled with an energy dispersive X-ray spectroscopy, EDS, (Oxford INCA Energy system).

Scanning electron microscope was also used to perform a cross-sectional survey of the composites in order to observe the interface between the fibers and the silicone matrix. The samples were prepared using cryofracture method.

#### 2.5.3. Swelling of flax fibers

Swelling behaviour of elementary flax fibers in DMSO, Toluene and

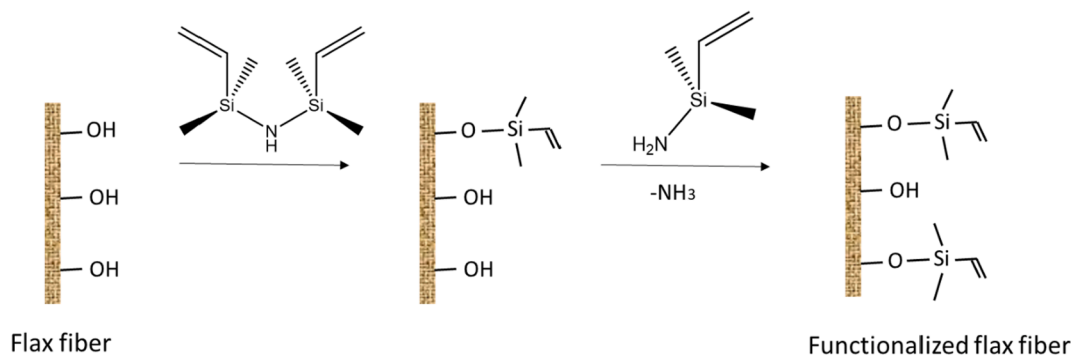


Fig. 1. Mechanism proposed for DVTS grafting on the flax fibers.

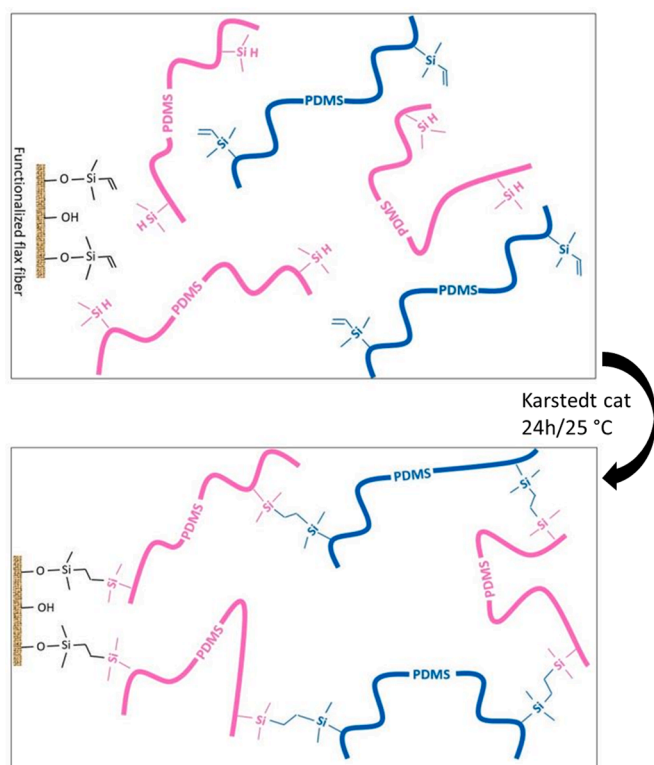


Fig. 2. Scheme representing the crosslinking step with formation of covalent bonds between silicone matrix and the functionalized flax fibers.

co-solvent (DMSO/Toluene) (35/65 wt%) mixture was observed between two glass plates by optical microscopy in transmission mode with a Laborlux 11 Pol (Leica, Germany) equipped with a mono-CDD Sony digital camera (resolution  $1600 \times 1200$  pixels) and an image acquisition software Archimed® (Microvision Instruments, France). The flax fiber was fixed on the bottom glass plate between two double-sided tapes with around 1 cm apart. The solvent was then injected by capillarity between the two glass plates.

A measurement of apparent diameter was carried out before and after wetting, five times along the fiber in order to calculate an average diameter. Then, the swelling rate was calculated as follow:

$$\text{Swelling rate\%} = \left( \frac{\text{Average diameter after wetting} - \text{Average diameter before wetting}}{\text{Average diameter before wetting}} \right) \times 100$$

This measure was done for all samples with each solvent four times. The standard deviation was calculated according to the swelling values obtained for these four samples.

#### 2.5.4. Thermogravimetric analysis (TGA)

A thermogravimetric analyser instrument (Setaram Setsys) was used to study the fibers thermo-oxidative decomposition. In alumina ceramic crucibles,  $10 \text{ mg} \pm 1 \text{ mg}$  of each kind of fibers (pristine, pre-treated and functionalized fiber) was heated from 30 to  $900^\circ\text{C}$  (heating rate of  $10^\circ\text{C}/\text{min}$ ) under air atmosphere (40 ml/min). During the analysis, 15 min of isotherm at  $100^\circ\text{C}$  was done in order to remove adsorbed water and facilitate the comparison between samples.

#### 2.5.5. Rheology measurements

Rheological instrument MCR 702 (Anton Paar) equipped with parallel plates (PP25, 25 mm diameter) was used to investigate and measure the storage and loss modulus of the silicone matrix during the curing reaction of the different formulations. The oscillation experiments were conducted at constant temperature, frequency and deformation of  $25 \pm 1^\circ\text{C}$ , 1 Hz and 1 %, respectively for 24 h.

#### 2.5.6. Tensile test

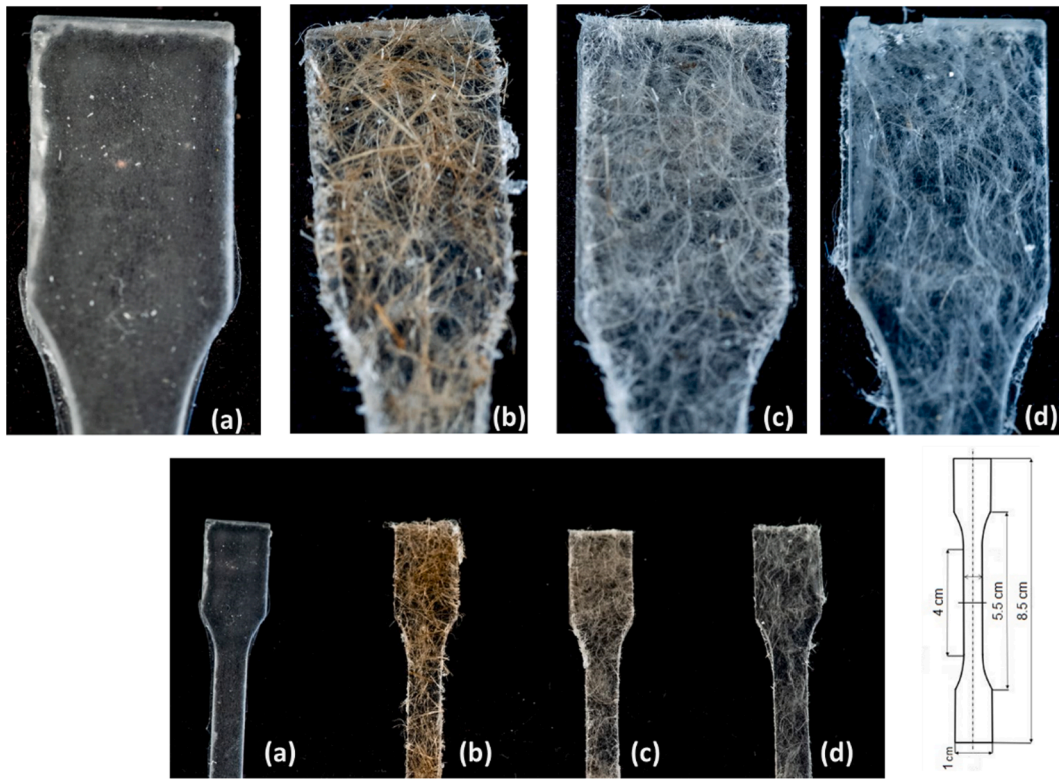
The tensile test of prepared composites was performed on a tensile machine (Zwick/Roell) equipped with a 2.5 kN load cell and a clip-on extensometer with a reference length of 30 mm at room temperature ( $25^\circ\text{C}$ ). The equipment is calibrated according to ISO 7500-1 and ISO 9513 methods for force and displacement sensors, respectively.

A crosshead speed of 50 mm/min was applied. The Young's modulus was determined by tangent method between 0.05 and 0.25 % of elongation. Each test was carried out at least 4 times.

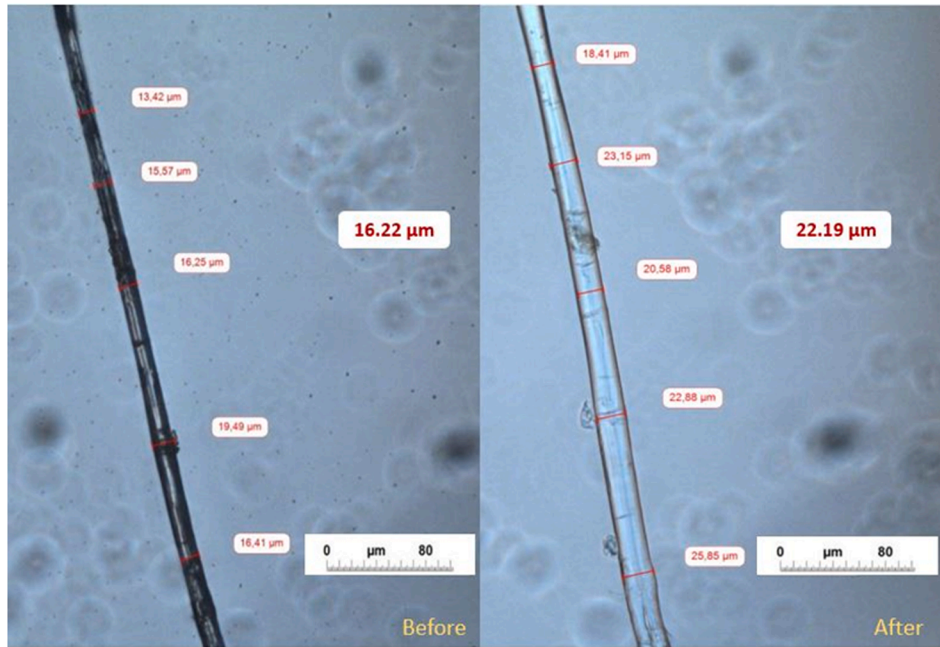
### 3. Results and discussion

#### 3.1. Solvent and pre-treatment step effect on the functionalization process

Firstly, the functionalization process was applied directly on the pristine fibers without pre-treatment step using toluene as a solvent. The obtained functionalization rate was negligible (0.1 %) and the reaction almost did not occur. This result is assumed to be due to the low accessibility of the silazane agent to the hydroxyl groups onto flax fibers when toluene is used.



**Fig. 3.** Dog bone test specimens obtained for the different flax/silicone formulations. (a) fiber-free silicone matrix, (b) silicone matrix/pristine flax fibers, (c) silicone matrix/pre-treated flax fibers, (d) silicone matrix/functionalized flax fibers.

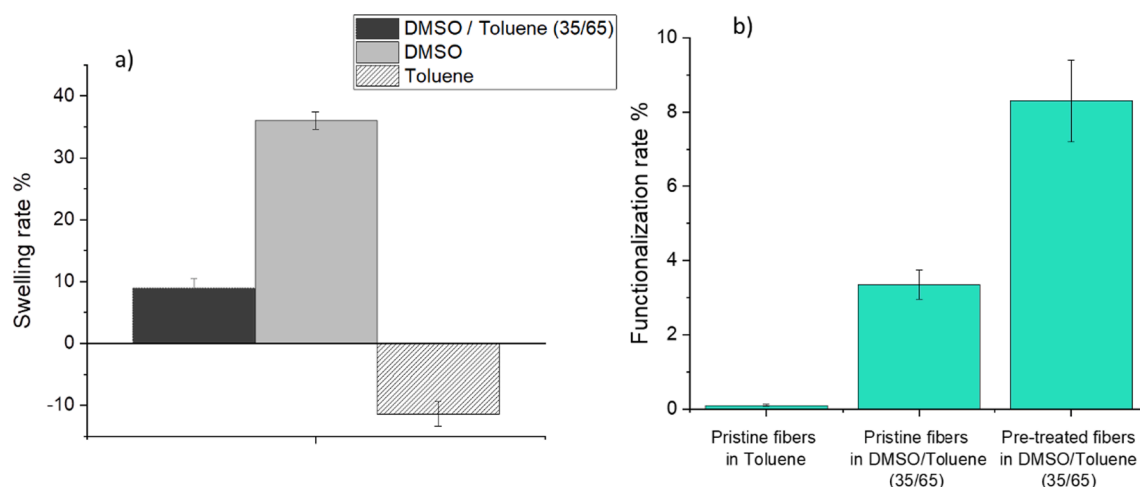


**Fig. 4.** Microscopy images of pristine flax fibers before and after wetting with DMSO.

The hypothesis is that the swelling of flax fibers is linked to their affinity with the used solvent. In order to define the solvent influence on the fiber swelling [46], the measurement of apparent fiber diameter for different solvents was performed using microscopy analysis. Pristine fibers were impregnated with DMSO, DMSO/toluene (35/65 wt%) mixture and toluene. DMSO was chosen because of its high polarity and toluene because it is a very good solvent for DVTS. The microscopy

analysis allows measuring the average diameter of fiber before and after solvent wetting (Fig. 4).

The average of flax fiber diameter increased from 16.2 to 22.2  $\mu\text{m}$  that corresponds to a swelling of 36.7 % when DMSO is used and from 21.0 to 22.8  $\mu\text{m}$  that corresponds to swelling of 8.8 % when it is wetted with the solvent mixture. Oppositely, the flax fiber diameter decreased from 26.1 to 23.2  $\mu\text{m}$  corresponding to a shrinkage around  $-11.4$  %

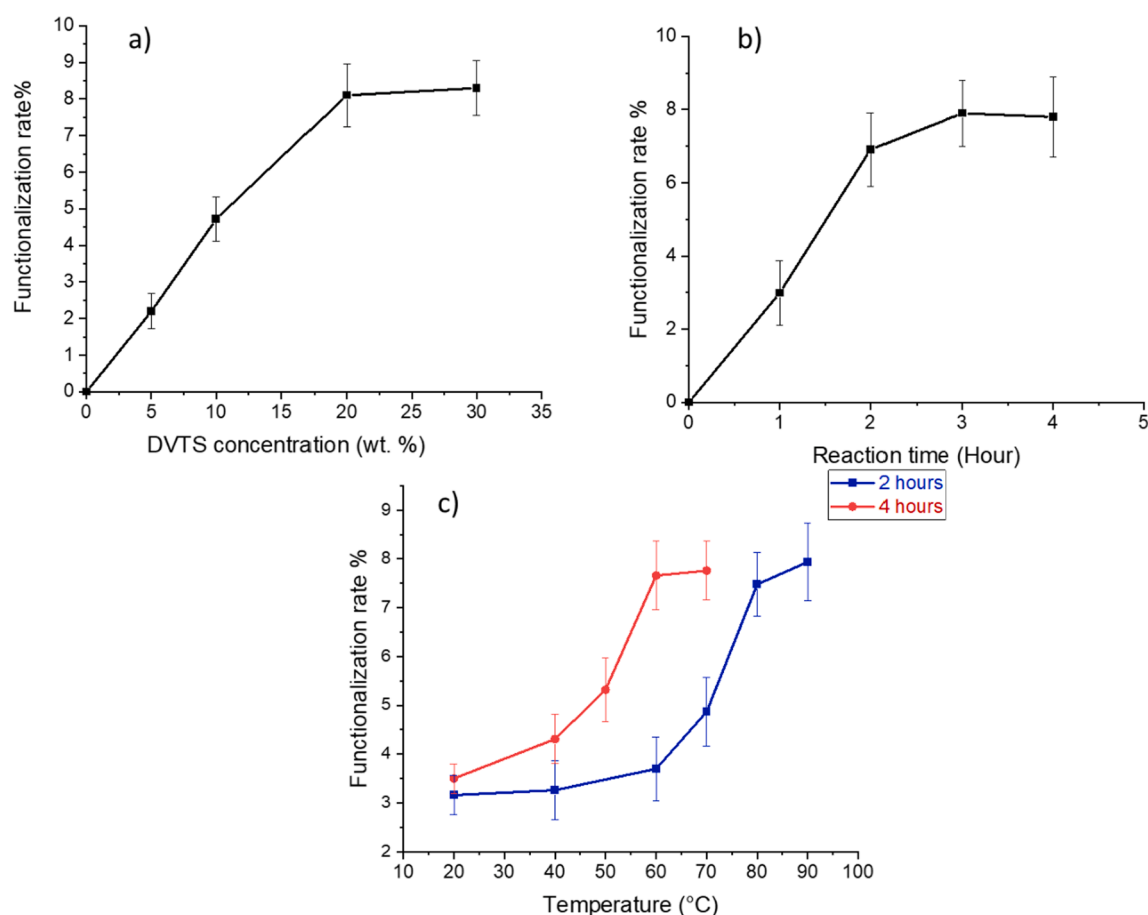


**Fig. 5.** (a) swelling measurement of pristine fiber impregnated with toluene, dmsol and (dmsol/toluene) (35/65 wt%) mixture. (b) Functionalization rate according to the used solvent and the pre-treatment.

when it is wetted with toluene (Fig. 5a).

In order to improve the RF, the toluene was replaced by the solvent mixture, DMSO/Toluene (35/65 wt%) tested previously, and RF value increased up to  $3.35\% \pm 0.4$  in the same conditions. The diameters difference measured by microscopy can explain the increase of RF with the DMSO/toluene mixture in comparison to toluene used alone. However, DMSO alone cannot be used because of its immiscible with DVTS and the DMSO/toluene ratio (35/65 wt%) is the highest at which DVTS remains soluble.

Finally, the pristine fibers were replaced by pre-treated ones. The pre-treatment by NaOH solution removes one part of the lignin product from flax fibers [47]. Then, the RF increased up to  $8.3\% \pm 1.1$  (Fig. 5 b). Generally, the lignin removal from the natural fibers promotes the availability of the cellulose-silane interaction sites. Furthermore, the pre-treated fibers surface is rougher than the surface of pristine ones which results in a larger effective contact surface. Moreover, the lignin elimination permits to facilitate the diffusion of the coupling agents inside the fibers [48]. For example, Valadez-Gonzalez et al [49] have



**Fig. 6.** The effect of (a) solution concentration, (b) reaction time and (c) temperature on the functionalization rate.

used vinyltris (2-methoxy-ethoxy) silane as a coupling agent to modify heneken fibers, it was found that the amount of silane adsorbed onto the alkali treated fibers was higher than that absorbed by the pristine ones.

### 3.2. The effect of reaction conditions on the functionalization process

The effect of solution concentration, reaction time and temperature on the functionalization process were investigated.

Three series of pre-treated fibers were functionalized with various concentrations of DVTS, for different reaction time and at several temperatures (Table S1).

In series 1, pre-treated fibers were functionalized with different concentrations of DVTS at 80 °C for 3 h. It was found that the  $R_F$  increases up to around (8.3 %) when the DVTS concentration increases up to 20 wt%. The relationship between  $R_F$  and the DVTS concentration is linear in this range. After this value, no further increase in  $R_F$  was observed (Fig. 6 a).

In series 2, pre-treated fibers were functionalized with different reaction times at 80 °C considering 20 wt% DVTS concentration. The  $R_F$  increases during the first 3 h. The relationship between  $R_F$  and reaction time is also linear in this range. Beyond this time, any prolongation of reaction time is useless. (Fig. 6 b).

In series 3 and 4, pre-treated fibers were functionalized at several temperatures for 2 and 4 h, respectively with 20 wt% DVTS concentration. The same behaviour was observed, the  $R_F$  increases with the rise in the reaction temperature. For 2 h of reaction, the  $R_F$  is approximately stable up to 60 °C. Thereafter, a sharp increase appears with the rise in temperature. For 4 h of reaction, the same behaviour is observed but less intense (Fig. 6c).  $R_F$  of 7.5 % could be achieved at 60 °C for 4 h and at 80° for 2 h.

According to these results, the highest  $R_F$  achieved was (8.3 %) at 80 °C for 3 h in the DMSO/toluene mixture using pre-treated flax fibers with 20 wt% DVTS concentration that are considered as the optimal conditions for the functionalization process.

### 3.3. Characterizations of functionalized fibers

All characterizations were performed on the functionalized fibers prepared under the optimal conditions allowing to obtain the maximum  $R_F$  (20 wt% of DVTS, 80 °C, 3 h, in the DMSO/Toluene co-solvent using pre-treated flax fibers) and after filtering, squeezing and washing twice with toluene during 10 min.

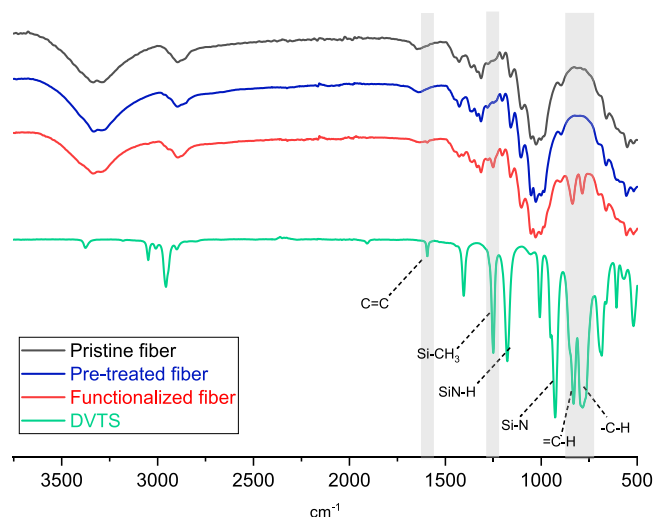


Fig. 7. FTIR spectra of DVTS, pristine and functionalized flax fibers.

#### 3.3.1. FTIR spectroscopy

DVTS, pristine, pre-treated and functionalized fibers were analysed by FTIR spectroscopy to confirm the reaction between silazane and hydroxyl groups, and to detect the presence of vinyl groups on the functionalized fibers surface (Fig. 7). The bands corresponding to the vinyl group (C=C stretching at 1592  $\text{cm}^{-1}$ , =C-H bending at 830  $\text{cm}^{-1}$ ), the Si-CH<sub>3</sub> groups at (1250  $\text{cm}^{-1}$ /780  $\text{cm}^{-1}$ ) and the silazane groups (N-H at 1175  $\text{cm}^{-1}$ , Si-N at 925  $\text{cm}^{-1}$ ) are highlighted in the DVTS spectrum.

The pristine and pre-treated fibers have exactly the same spectrum, the bands corresponding to the hydroxyl group (-OH at 3330  $\text{cm}^{-1}$ ) and the ether group (-C-O-C- at 1025  $\text{cm}^{-1}$ ) of the cellulose were observed. Concerning the functionalized fibers spectrum, vinyl and Si-CH<sub>3</sub> bands are present while the silazane bands are not observable. The disappearance of the characteristic bands of the Si-N-H and Si-NH bonds confirms the elimination of the silazane functions, while the presence of vinyl and Si-CH<sub>3</sub> bands confirms the grafting of Me<sub>2</sub>Si-CH=CH<sub>2</sub> on the flax fibers surface (Fig. 1).

#### 3.3.2. Scanning electron microscopy (SEM) with energy dispersive X-ray spectroscopy (EDS)

A cross-section of pristine, pre-treated and functionalized fibers were analysed by SEM/EDS with silicon mapping spectroscopy to confirm the presence of the grafted silicon part after DVTS grafting (Fig. 8). As it is clearly in EDS images, silicon is naturally present in flax fibers but only in trace amounts. The percentage of Si was  $\leq 1$  wt% according to the statistical calculation of EDS device. On the other hand, for the pre-treated fibers, silicon is almost non-present due to the pre-treatment with NaOH solution. The pre-treatment seems to remove the main silicon compounds from the fibers. Finally, for the functionalized fibers, silicon is highly concentrated about 4.1 wt%  $\pm$  0.7. The presence of this silicon is implicitly linked to the presence of the grafted vinyl groups.

#### 3.3.3. Thermogravimetric analysis (TGA)

Fig. 9 shows the TGA/DTG curves of pristine, pre-treated and functionalized fibers. The initial decomposition temperature ( $T_{in}$ ), the temperature of the maximum degradation rate ( $T_{max}$ ), and the ash yield ( $Y_{ash}$ ) are listed in (Table 1). A clear difference was observed in  $T_{in}$  and  $T_{max}$  between the pristine fiber on the one hand and the pre-treated and functionalized fibers on the other hand. The temperature at 5 wt% weight loss of pristine fiber is 256 °C, while for pre-treated and functionalized fibers, it is almost the same value 300 and 298 °C, respectively. Moreover, the highest rate of degradation of pristine fiber occurs at 355 °C, while for pre-treated and functionalized fibers, it occurs at 340 and 342 °C, respectively. This shift in  $T_{in}$  and  $T_{max}$  can be attributed to lignin removal from the flax fiber during the pre-treatment process. Indeed, it is mentioned in the literatures that alkali treatment of flax fibers leads to a slight improvement in thermal stability [50] which corresponds to the increase of  $T_{in}$  for the pre-treated fibers. Furthermore, DTG curve of pristine fiber displays a second peak at 490 °C while, this peak is too weak in the curves of pre-treated and functionalized fibers. The second peak represents the degradation of lignin [51]. The decrease of this peak confirms the lignin removal for pre-treated and functionalized fibers.

The value of  $Y_{ash}$  gradually increases from pristine and pre-treated fibers to functionalized ones. The lignin removal is probably responsible for the increase in  $Y_{ash}$  concerning the pre-treated fibers. While TGA was performed in air (aerobic pyrolysis), the oxygen allows the formation of silicon dioxide compounds from the pyrolysis of functionalized fibers which leads to a further  $Y_{ash}$  increase [52,53]. The silicon present in the functionalized fibers at a concentration of 4.1 wt% should react with oxygen to increase  $Y_{ash}$  up to 6.4 wt% if the reaction was complete. In our results, the presence of this initial amount of silicon increases  $Y_{ash}$  up to 5.8 wt%. This result is therefore of the same order as expected.

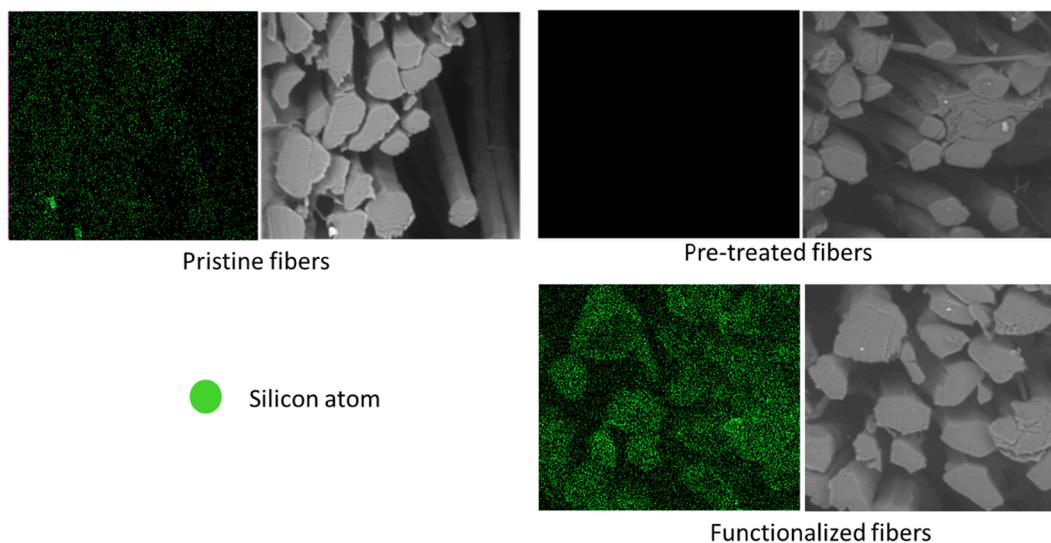


Fig. 8. SEM/EDS images of pristine, pre-treated and functionalized flax fibers.

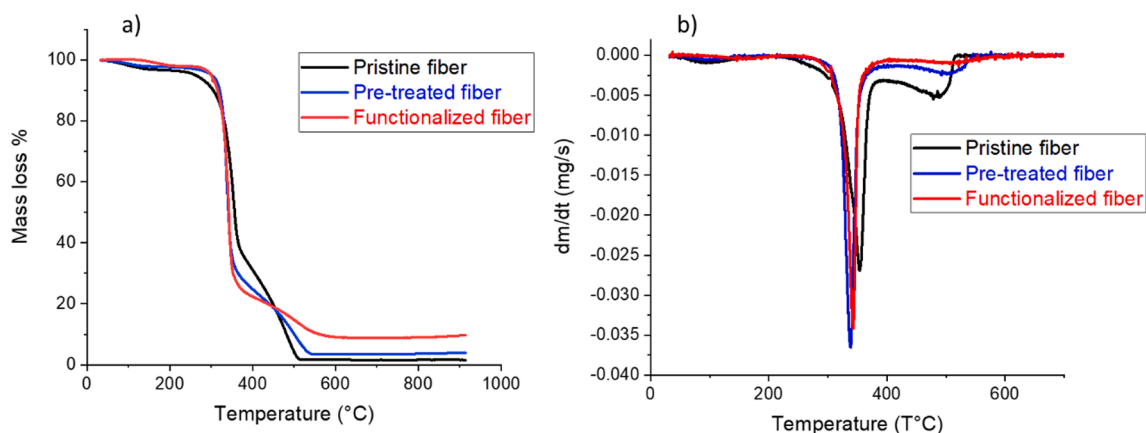


Fig. 9. (a) TGA and (b) DTG curves of pristine, pre-treated and functionalized fibers.

Table 1

TGA results of pristine, pre-treated and functionalized flax fibers.

Samples	$T_{in}$ (°C)	$T_{max}$ (°C)	$Y_{ash}$ (%)
Pristine fiber	256	355	1.5
Pre-treated fiber	300	340	3.9
Functionalized fiber	298	342	9.7

### 3.4. Effect of fibers presence on the curing reaction of PDMS formulations

Formulations of PDMS matrix, PDMS matrix with pristine fibers and PDMS matrix with functionalized fibers were prepared and then studied by rheological measurements in order to follow the evolution of the storage and loss modulus of the silicone system during the curing reaction (Fig. 10). Before the start of the crosslinking reaction, the  $\log G'$  value for the silicone matrix filled with pristine or functionalized fibers is greater than the unfilled one. This difference of rheology is attributed only to the presence of the flax fibers. After 3 h for unfilled matrix and 4 h in presence of flax fibers,  $\log G'$  starts to increase sharply until 12 h of reaction. Then,  $\log G'$  get close values for all formulations until the end of the reaction. Thus, the presence of the flax fibers has little influence on the crosslinking kinetic of the silicone matrix. Moreover, the grafting of vinyl groups on the flax fibers does not affect this crosslinking either. In addition, before the start of the crosslinking reaction, the  $\tan \delta$  value

for the unfilled matrix is greater than those of the formulations filled with pristine or functionalized fibers. At the gelation point ( $\approx 9$  h), the  $\tan \delta$  values for all silicone formulations are very close and this until the end of the crosslinking reaction. These results also confirm that the presence of flax fibers and their grafting with vinyl groups do not disturb the crosslinking reaction of the silicone system.

### 3.5. Characterisations of prepared composites

Pristine, pre-treated and functionalized fibers - reinforced silicone composites were characterized in order to observe the influence of flax fibers functionalization process on the adhesion with the matrix following the improvement of mechanical properties.

#### 3.5.1. Tensile test

The values of maximum tensile force stress ( $F_{max}$ ), elongation at maximum force ( $dL(F_{max})$ ), breaking point, elongation at break and Young modulus ( $E$ ) obtained by tensile test for the silicone composites filled with the different flax fibers are listed in (Table S2).

Stress strain curves of samples (Fig. 11) displayed the difference between prepared composites in terms of mechanical properties compared to the fiber-free matrix.

Young modulus  $E$  (Fig. 12) increased for the composites with pristine and pre-treated fibers from  $0.62 \pm 0.05$  MPa to  $2.42 \pm 0.12$  MPa and  $2.5 \pm 0.08$  MPa, respectively. Both of them have approximately the same

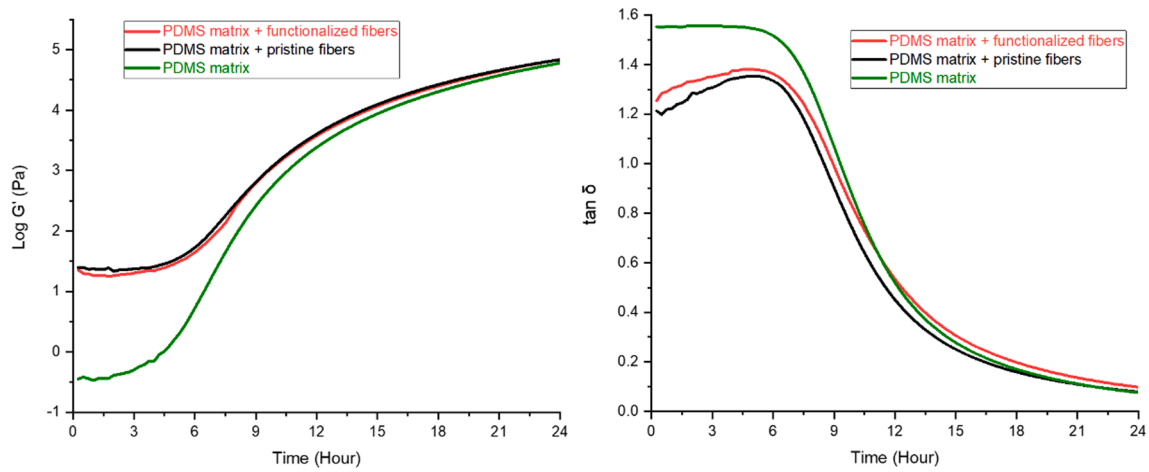


Fig. 10. Log  $G'$  and Tan  $\delta$  vs crosslinking reaction time for the PDMS matrix, PDMS matrix with pristine fibers and PDMS matrix with functionalized fibers.

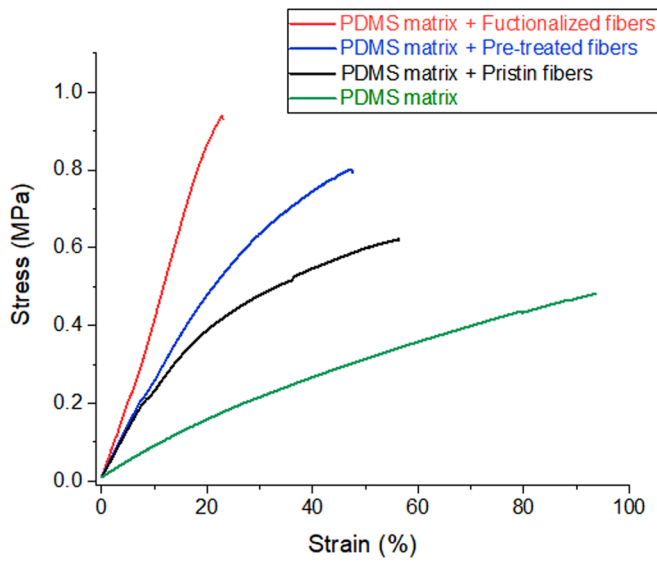


Fig. 11. Stress strain curves of silicone composites filled with pristine, pre-treated and functionalized fibers.

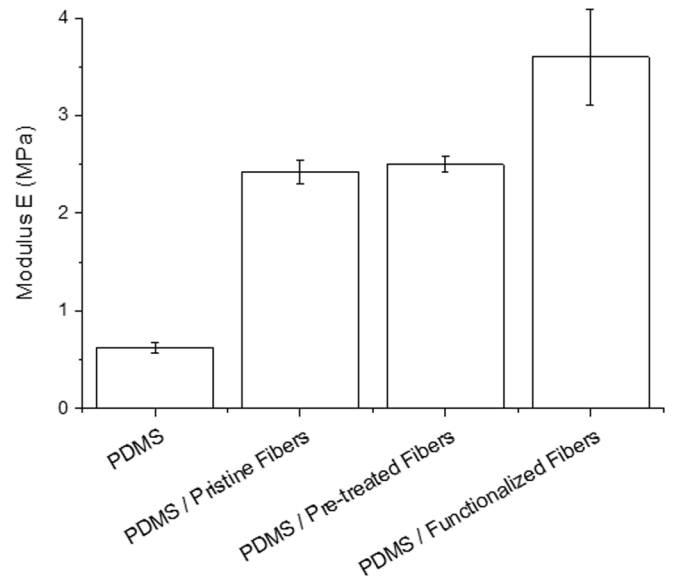


Fig. 12. Young modulus  $E$  of silicone composites filled with pristine, pre-treated and functionalized fibers.

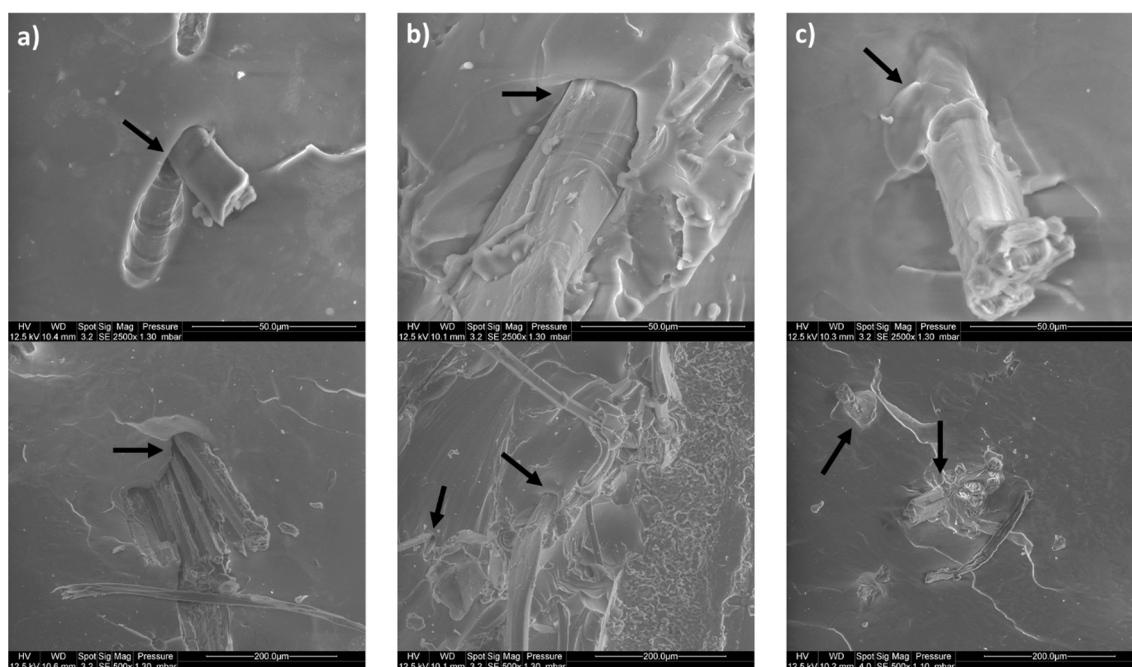
Young modulus  $E$  value, while composite with functionalized fibers has a much higher Young modulus  $E$ , close to  $3.6 \pm 0.5$  MPa. The flax fibers increased the stiffness of elastomer composite about 4 times but the functionalized one increased it about 5.8 times. The difference in Young modulus  $E$  between the pristine fibers-reinforced composite and the functionalized fibers-reinforced composite is about 40 %. Oppositely, elongation values at maximum force decreased for the composites filled with pristine and pre-treated fibers from  $91 \pm 7$  % to  $53 \pm 16$  % and  $45 \pm 10$  %, respectively. The elongation values for both composites are very close to each other, while composite with functionalized fibers has a highly decreased elongation about  $27 \pm 4$  %. These values are fully consistent with the evolution of the Young  $E$  modulus values.

Unlike Young modulus and elongation at maximum force (dL%), breaking point values of composites with pristine and pre-treated fibers are not identical and not even close to each other. Breaking point value of the composites has a progressive increase with pristine, pre-treated and functionalized fibers, respectively. Breaking point increased from 470 kPa for fiber-free silicone matrix to 550, 750 and 910 kPa for pristine, pre-treated and functionalized fibers-reinforced composite, respectively. It means that the pre-treatment of flax fibers increases the tensile strength of the silicone matrix but the functionalized ones increase it even more. Wu and Zuo [54], have prepared basalt fibers-

reinforced silicone composites, they found that the treatment of basalt fibers by APTS coupling agent improves the compatibility between fibers and silicone, resulting in an increase in the tensile strength of composites.

### 3.5.2. Scanning electron microscope (SEM)

SEM analysis (Fig. 13) was used to observe the fibers-matrix interface in cross-section of broken composites by cryofracture method. For composites reinforced with pristine and pre-treated flax fibers (Fig. 13 a and b, respectively), the adhesion between fibers and the matrix is very weak. The traces of fibers pull-out at the matrix surface are easily noticeable. The compatibility of pristine and pre-treated fibers with the silicone matrix is almost the same; the fibers are well dispersed in the matrix with very poor adhesion. Oppositely, there are not voids at the interfacial zone between fibers and matrix in composite reinforced with functionalized fibers. The ability of vinyl groups to react with the matrix during the curing process and to form covalent bonds between fibres and the matrix can explain this result. As it is showed in (Fig. 13c) the fibers are integrated in the matrix with a high level of adhesion. This could support the tensile test results that showed a great improvement in the mechanical properties of the functionalized fibers-reinforced composite.



**Fig. 13.** Cross-sectional SEM micrographs of prepared fibers-reinforced composites: (a) pristine fibers, (b) pre-treated fibers and (c) functionalized fibres.

#### 4. Conclusion

Flax fibers have been successfully functionalized with vinyl groups using DVTS.

The used solvents nature for the grafting reaction and the use of a fibers alkaline pre-treatment play a great role for the functionalization efficiency. The solvent can promote the swelling of the flax fibers while the pre-treatment removes lignin from fibers, both of which increase the functionalization rate.

Temperature, reaction time and DVTS concentration have also an influence on the  $R_F$  of flax fibers. The optimum  $R_F$  is 8.3 % and it was achieved at 80 °C for 3 h with 20 wt% of DVTS.

The functionalized fibers are effective to prepare a composite material based on silicone elastomer with high fibers/matrix adhesion.

The functionalized fibers is supposed to participate to the formation of the cross-linked network due to the presence of the vinyl groups on flax that can react with PDMS chains.

The mechanical properties increase when the silicone matrix was reinforced with functionalized flax fibers in comparison with pristine ones.

This study permitted to confirm the possibility to functionalize efficiently natural fibers via covalent bonding, using a silazane molecule. These first results open novel way possibilities in order to functionalize easily natural fibers with numerous added functional groups.

#### CRediT authorship contribution statement

**Antoine Ishak:** Methodology, Investigation, Formal analysis, Writing – original draft. **Rodolphe Sonnier:** Writing – review & editing, Conceptualization, Supervision. **Belkacem Otazaghine:** Writing – review & editing, Conceptualization, Supervision. **Claire Longuet:** Conceptualization, Writing – review & editing, Supervision.

#### Declaration of Competing Interest

The authors declare that they have no known competing financial interests or personal relationships that could have appeared to influence the work reported in this paper.

#### Data availability

No data was used for the research described in the article.

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#### Appendix A. Supplementary material

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