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Influence of Wear on the Sizing Layer and Desizing of Single Carbon Fibre-to-Fibre Friction

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A B S T R A C T

Carbon fibres are sized for use in the reinforcement of composite materials. The purposes for sizing include improving yarn cohesion, which is necessary for the weaving process, and increasing the adhesion between the fibres and the matrix. Nevertheless, during weaving, some fibrillation can occur, and that has detrimental effects on the weaving productivity and on the composite's properties. The purposes of this research were: (a) to determine whether abrasive wear between sliding fibres would modify the sizing and (b) to study the influence of sizing on the friction between fibres. The same type of carbon fibre was subjected to different desizing processes. The coefficient of friction between single fibres was obtained before and after desizing. The effects of sizing and sliding distance on frictional behaviour were investigated, and are related to the observed the wear of sizing layer. In fact, it increased with sliding distance and induced a decrease in the coefficient of friction. Moreover, an efficient desizing process induced a decrease of the coefficient of friction.

1. Introduction

In the field of composite materials, the significant role of sizing on the carbon fibre–matrix adhesion, and thus on the mechanical properties of composite materials, is very well known. In fact, carbon is extremely inert and, naturally, the adhesion of carbon fibres with polymer matrices is relatively low. In order to improve the adhesion between the carbon fibres and the polymer matrix, different surface treatments of carbon fibres can be done, such as plasma treatment or surface oxidation; the most common is the use of polymer sizing [1–5]. In that case, the sizing must be compatible with the matrix [6–10]. Moreover, the mechanical behaviour of the sizing has an influence on the mechanical properties of the final composite in terms of fatigue performance [11], flexural strength and fracture toughness [12].

The role of sizing is important for the interfacial properties between fibre and matrix, but also for tow or yarn cohesion. In fact, sizing is necessary for reinforcement manufacturing processes, such as during weaving, braiding or knitting processes. When yarn or tow cohesion decreases, fibrillation occurs and increases after several machine cycles, forming free fibres and fibril clusters, which can continue until the fibre breaks [13,14], inducing degradation of the composite's properties [15,16].

In another way, friction between yarns or tows influences the mechanical behaviour of plies during extension, shear [17] or compaction [18], and forming [19–21]. In these studies, the coefficient of friction between carbon fibres is arbitrarily chosen.

Cornelissen et al. showed an influence of sizing or desizing on the coefficient of friction (COF) between tows by the use of the capstan method [22]. Moreover, relative humidity has a great influence on the tow–tow COF with sizing, but not without sizing. Sizing has also been shown to have an influence on the creep compaction behaviour of dry fabric when the temperature varies (25 and 160 °C), while the behaviour of unsized fabric does not change [23].

The influence of the stages of production of a carbon fibre on the friction between single fibres and stainless steel has been studied by Kafi et al. using the capstan method [24]. The results obtained show a higher COF for sized carbon fibres than for oxidised and unoxidised ones. To the best of our knowledge, there are no other studies regarding the influence of sizing on the friction between two single fibres. However, Roselman and Tabor studied the influence of an oxidation treat-

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Table 1
Different desizing processes used.

Name of the process	Acetone	THF-5	THF-10
Solvent	Acetone	Tetrahydrofuran	Tetrahydrofuran
Boiling temperature	56 °C	65 °C	65 °C
Number of times siphoned	10	5	10

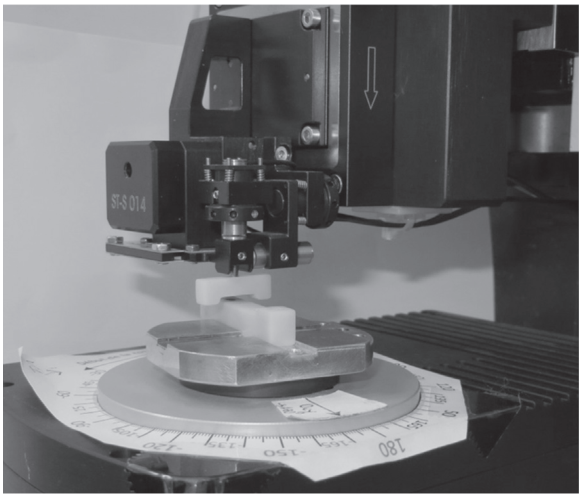

Fig. 1. Picture of the nanotribometer in the specific fibre carrier developed in the laboratory.

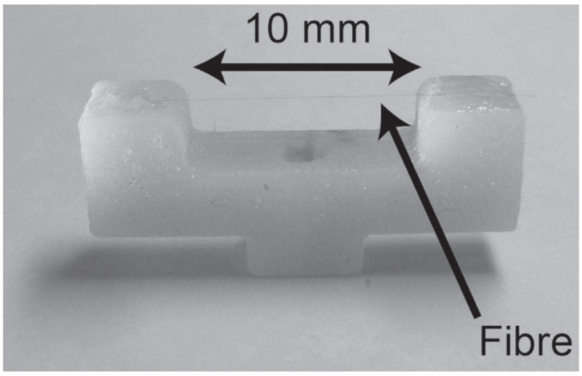

Fig. 2. Fibre sample on the specific sample carrier.

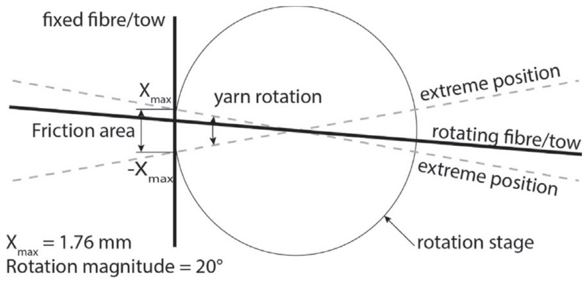

Fig. 3. Schematic of friction experiment.

ment on the friction between single fibres [25]. In that experiment, the lower fibre was clamped by its two ends and the upper fibre was clamped at one extremity, and free at the other. In this old but very interesting paper, the normal load applied on the fibre was not measured, but was calculated from the fibre's mechanical properties and its

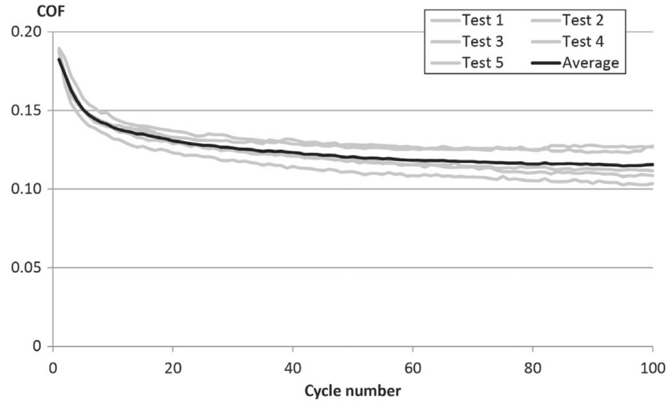

Fig. 4. Repeatability of the measurement of coefficient of friction relative to the number of friction cycles for carbon fibres sized.

deformation in the normal contact plane, and the friction force was measured from the deformation of the upper clamped-free fibre. Therefore, the results depended on the Young modulus of the fibre, in both its axis and transversal directions. The results obtained by this method showed that non-oxidised carbon fibres had a slightly lower coefficient than the oxidised ones.

As is mentioned in the literature, yarn cohesion due to sizing is very important during the reinforcement manufacturing process, for example, during weaving. A failure of the sizing film induces a defibrillation of the yarn and the formation of fibril clusters. It can be supposed if interaction and friction between fibres increase because of sizing damage, the defibrillation is enhanced and the damage will propagate. The purpose of the present study was to determine whether the friction between fibres that occurs during weaving modifies the sizing due to the wear phenomenon, and whether it influences the friction value between fibres. In the present study, the influence of different types of sizing was not considered, but the difference between fibres with sizing and fibres subjected to different desizing processes were studied.

2. Experiments

2.1. Investigation of carbon fibre

The carbon fibre was extracted from a 12 K type HTS40 tow provided by Toho Tenax. A single fibre is very fine with 7 µm in diameter. The sizing was based on polyurethane.

2.2. Desizing processes

The fibres are generally sized with high molecular weight polymers, which can be removed by extraction with hot solvent. The best means of extraction is the Kumagawa extractor, which consists of a bulb equipped with a siphon. The fibres were placed carefully in the bulb. The bulb was put into a round-bottomed flask. The solvent in the flask was heated gently and evaporated in a reflux condenser. The hot solvent dripped slowly into the bulb, falling onto the fibres, until it was siphoned off. The fibres were rinsed in hot pure solvent each time the bulb was siphoned. Two solvents were tested experimentally: acetone and tetrahydrofuran (THF). Filling and emptying the bulb took about 4 minutes for acetone and 5 minutes for THF, as they have different boiling temperatures of 56 and 65 °C, respectively. Table 1 shows the different conditions of extraction tested experimentally on the carbon fibres.

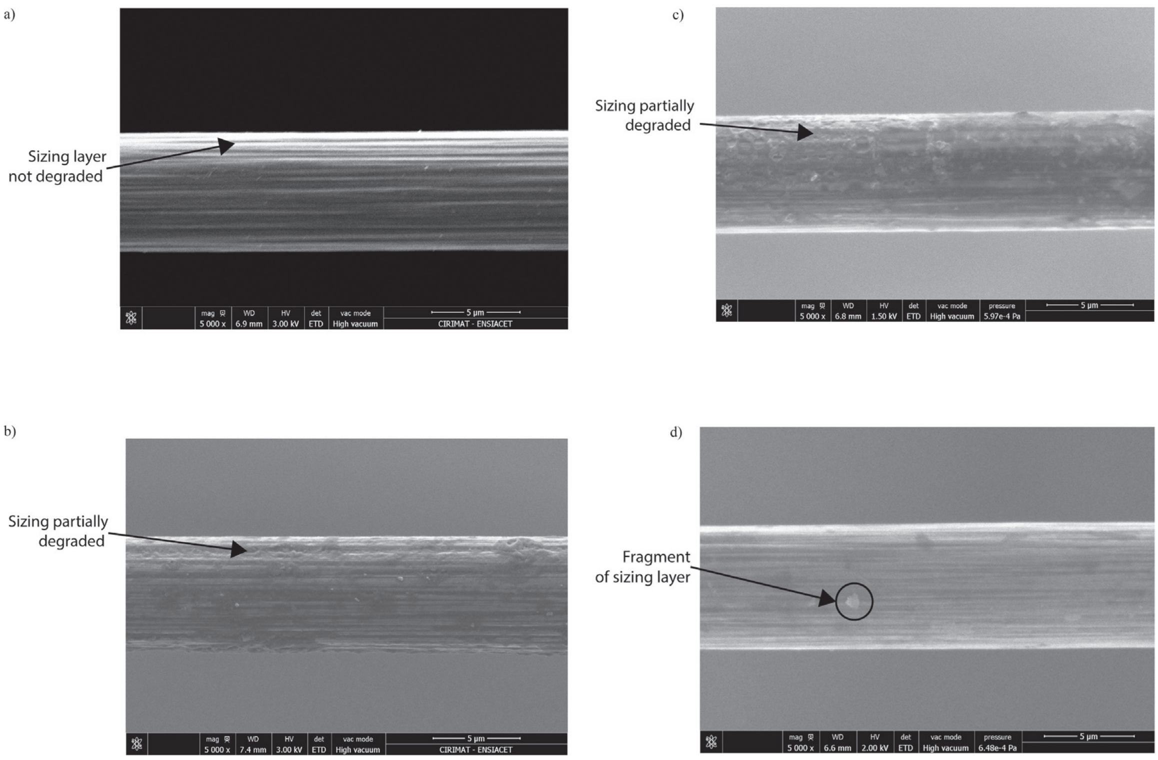

Fig. 5. SEM pictures of the different carbon fibres before friction: a) sized, b) desized with acetone, c) desized with THF siphoned 5 times, and d) desized with THF siphoned 10 times.

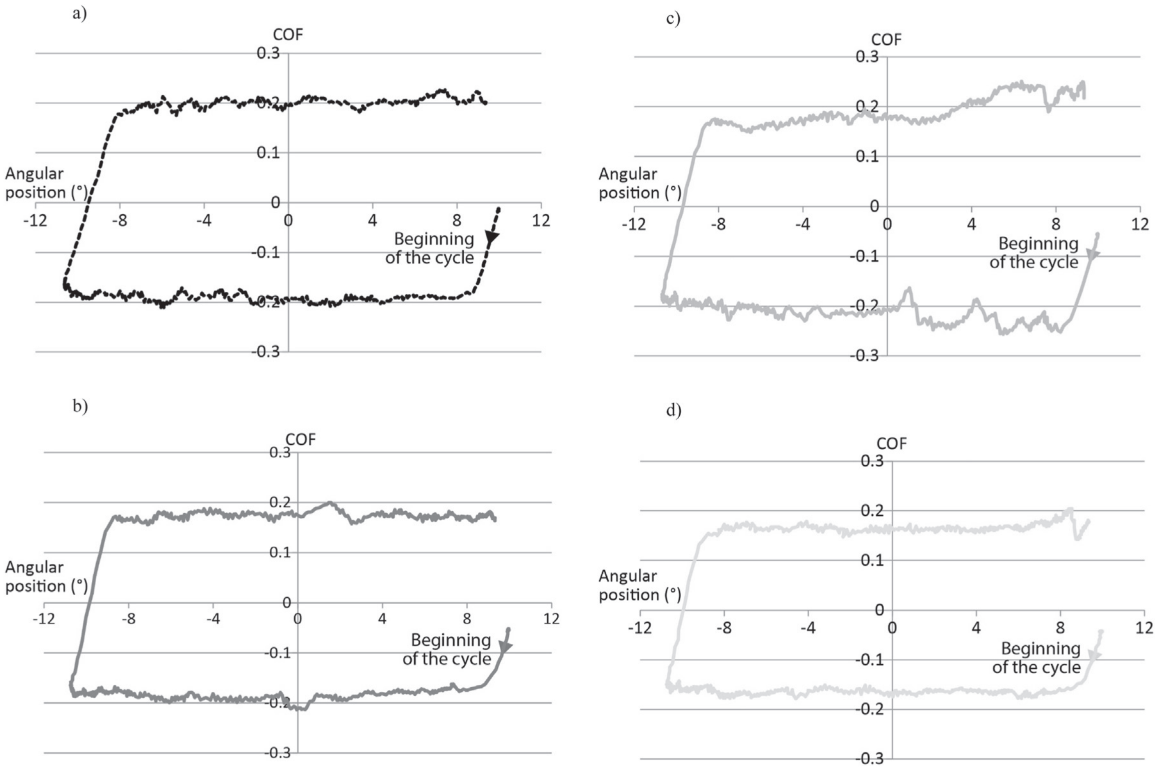

Fig. 6. First friction cycle (average of five friction measurements) relative to angular position for the carbon fibres a) sized, b) desized with acetone, c) desized with THF siphoned 5 times and d) desized with THF siphoned 10 times.

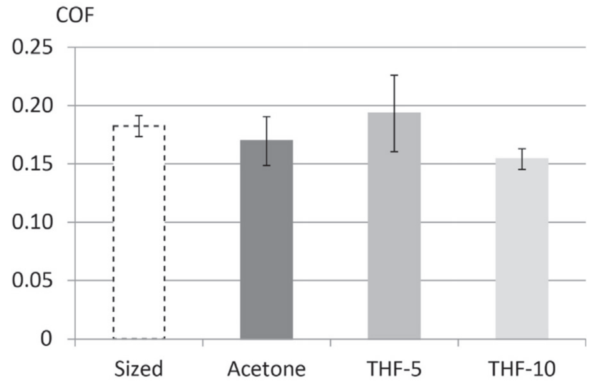

Fig. 7. First cycle coefficients of friction (average value for friction measurements with standard deviation) for the carbon fibres sized and desized with acetone, with THF siphoned 5 times, and with THF siphoned 10 times.

Table 2
First cycle coefficients of friction, standard, deviation and coefficient of variation (CV%) for the carbon fibres sized and desized with acetone, with THF siphoned five times, and with THF siphoned 10 times.

COF	Fibre			
	Sized	Desized with acetone	Desized with THF-5	Desized with THF-10
Mean value	0.182	0.170	0.193	0.154
Standard deviation	0.009	0.021	0.033	0.009
CV%	5%	12%	17%	6%

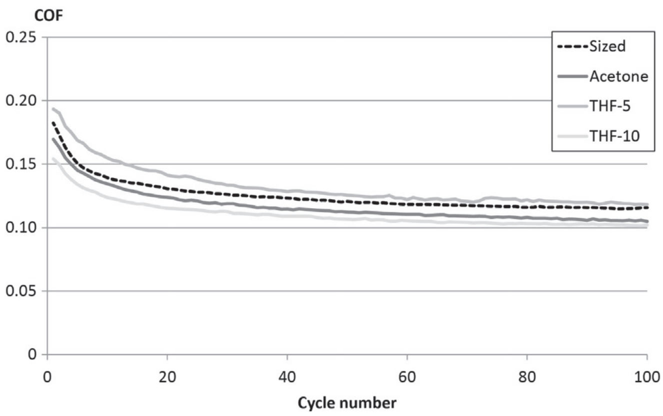

Fig. 8. Coefficient of friction relative to the number of friction cycles for the different carbon fibres sized and desized with acetone, with THF siphoned 5 times, and with THF siphoned 10 times.

2.3. Friction experiment

The objective was to rub two perpendicular single fibres together and to measure the contact forces. The experimental method and adjustments were described and argued elsewhere [26,27]. In fact, no other method has yet been proposed to measure the static and/or kinetic friction properties between single carbon fibres. Some other methods are proposed in the literature, but they are for tow-to-tow friction [22,28].

Measurements were performed by means of an NTR2 nanotribometer (CSM Instrument Company, Peseux, Switzerland). This device was originally a pin-on-disk tribometer and allowed reciprocating movement (Fig. 1). Specific sample carriers have been designed for this experiment to affix the single carbon fibres (Fig. 2). The first (and lower) sample was fixed onto the rotation stage. It followed a circular motion and allowed the fibre to move relative to one another with an alternative movement. The upper sample did not move and was orthogonal to the first one in its central location (Fig. 3), so the device led to perpendicular friction of the lower fibre against the upper one. This second sample carrier was fixed to a cantilever, which made it possible to measure the normal and friction forces during the experiment by means of capacitive sensors, whose range of force in each direction as 100 mN.

In this study, the distance between the upper and lower samples was chosen at the beginning of the test and remained unchanged during the whole test. The normal force is a parameter that was adjusted at the beginning of the experiment to the value of 5 mN. The vertical position of the upper sample carrier was then fixed during the whole friction test. The evolution of Fn was recorded during the test.

The oscillation motion was limited to $\pm 10^\circ$, and the friction occurred at 10 mm from the rotation centre. Due to this small angular amplitude, the motion between the samples was assumed to be orthogonal, even if the specific kinematic of the device induced a small lateral displacement (Fig. 3). This displacement was estimated to have a value of 0.15 mm, and was therefore neglected. The length of the sliding distance was about 3.4 mm for half of a cycle.

During a friction test, the normal and friction forces were recorded and the COF was computed from these two signals. The data acquisition frequency was 400 Hz for both forces.

Each test corresponded to 100 friction cycles, with a rotation stage oscillation frequency of 0.5 Hz. That corresponds to several centimetres in a weaving machine. The velocity followed a sinusoidal profile, and this test frequency corresponded to a maximum velocity of 5.5 $mm.s^{-1}$. This sliding velocity as the maximum linear velocity between the two samples, which corresponded to the central location (Fig. 3).

The most delicate operation was gluing the fibres on the sample carrier without breaking them and with the target pre-tension. Because of the small diameter of a carbon fibre, handling it remains a difficult task. During the setting up of the sample, one end of the fibre was glued and the pre-tension was obtained by suspending the desired mass of around 0.2 mN at the other end by a small piece of adhesive tape. Then, this end was also glued (Fig. 2). The same steps were done for the upper and lower fibre carriers. Friction tests were realized after the glue was dry, that is, after approximately 2 hours at room temperature, as the glue used was Loctite Super Glue-3®.

The upper fibre sample was 10 mm in length and the lower one 14 mm.

The friction test began as the rotating sample carrier was located at an extreme angular position, and the starting rotation direction was the same for each test.

Five friction tests were done for each kind of fibre. The results were expressed by the instantaneous evolution of the friction force, the normal force and the COF versus the angular position during a friction cycle. The average cycle relative to the angular position was also computed and studied. The averages of the friction force (Ft), the normal force (Fn) and the COF were computed for each cycle. The evolution of these average values during the cycles were also followed during a friction test.

All measurements were carried out under a standard atmosphere of 20 °C and 65% (relative humidity).

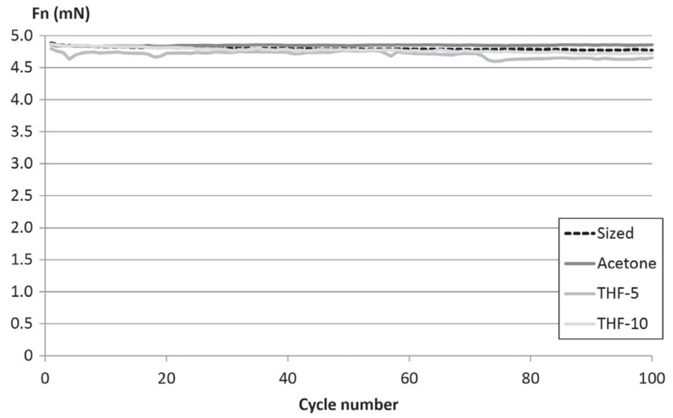

Fig. 9. Normal force Fn relative to the number of friction cycles for the different carbon fibres sized and desized with acetone, with THF siphoned 5 times, and with THF siphoned 10 times.

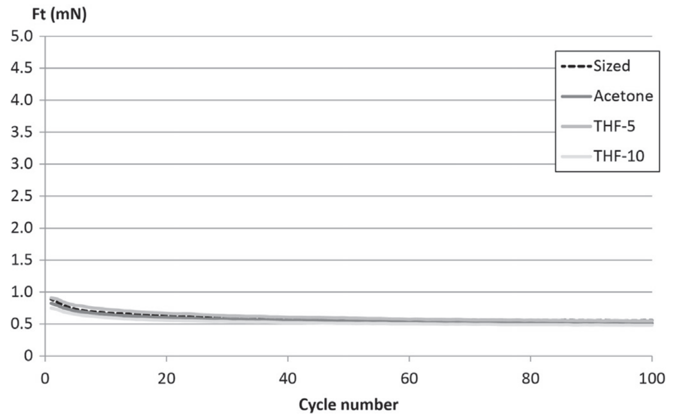

Fig. 10. Friction force Ft relative to the number of friction cycles for the different carbon fibres sized and desized with acetone, with THF siphoned 5 times, and with THF siphoned 10 times.

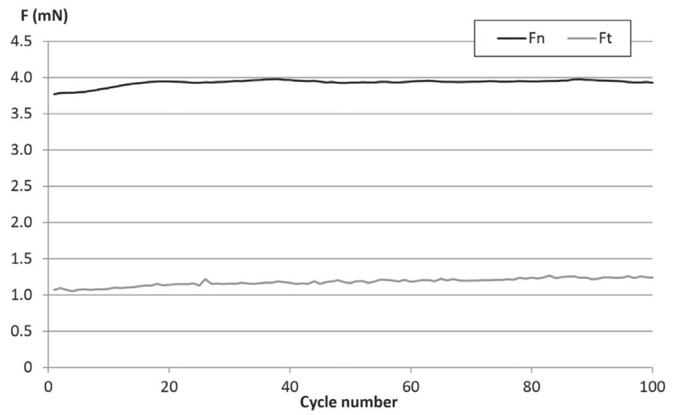

Fig. 11. Friction force, Ft, and Normal force, Fn, relative to the number of friction cycles for the steel cord samples.

3. Results and discussion

3.1. Repeatability of the measurement

The same friction cycle curves were plotted for five sized fibres in Fig. 4. This graph highlights the good repeatability of the measurements for single fibres. This repeatability during a friction cycle was also proved in a previous study [26].

3.2. Influence of the desizing process before friction

From Fig. 5, it can be seen the desizing process was not complete after acetone and THF have been siphoned 5 times. In fact, the sizing layer was only partially degraded by these two processes. A desizing process in which THF was siphoned 10 times seems to be more efficient, as only a few fragments of sizing layer were visible on the surface of the fibre (Fig. 5d).

Figs. 6 and 7, respectively, illustrate the first cycle of friction relative to rotation angle and the COF value for the different fibres with sizing, or after the three desizing processes. The variations of the COF can be due to stick slip mixed with fibre roughness effect. No trend can be observed before and after the different desizing processes, except for the THF-5-treated fibre, which had the highest COF. However, the coefficient of variation (CV%) of the COF (Table 2) is obviously linked to the fibre surface state before or after desizing (Eq. 1).

$$CV\% = \frac{Standard deviation}{Mean value} \tag{1}$$

In fact, the CV% is very low for the fibre with a smooth surface such as before or after desizing with THF-10 and is higher after the acetone and THF-5 processes. When the state surface was homogeneous, the normal CV% was about 5%, which is the value obtained for the sized fibre.

3.3. Influence of the number of friction cycles

The evolution of the COF is plotted relative to the number of friction cycles (Fig. 8), which is linked to the sliding distance. Whatever the kind of fibre, sized or desized, the COF decreased drastically during approximately the first five cycles. Because the COF is a ratio between the friction force and the normal force, an analysis of the evolution of these forces is interesting.

First, Fig. 9 illustrates the normal force, Fn, relative to the number of cycles. It can be observed that the normal force was not influenced by the number of cycles.

Second, Fig. 10 shows the friction force, Ft, decreased with the number of cycles. Therefore, it can be concluded that the evolution of the COF with the number of cycles was only due to a change of the friction force, and therefore of the surface state of the fibre. It was verified with steel cords that neither the friction force, nor the normal force, decreased with the number of cycles between 1 and 100 cycles (Fig. 11). Therefore, this effect was indeed due to the carbon fibre.

Fig. 12 shows the surface state of the different fibres after 100 cycles of friction. It can be observed that after 100 cycles, the sizing layer is worn and some fragments of the sizing layer can be observed. It can be seen that wear due to friction is visible even for the THF-10-treated fibre. It can be concluded that even with this process, the sizing layer was not totally removed.

Fig. 13 shows that after 100 cycles, the COF has the same evolution overall as for the first cycle (Fig. 6). In fact, the THF-10-treated fibre has the lowest COF, followed by the acetone-treated fibre and then the sized fibre, for which the value is very close to that of the THF-5-treated fibre. It can be observed that the value for the THF-5-treated fibre is close to that of the sized fibre, which may be due to the abrasive wear of the sizing. Except for the sized fibre, the CV% of the COF at the 100^{th} cycle decreased, probably because the wear of sizing layer induced a smoother surface, and thus a lower variation between measurements (Tables 2 and 3). For the sized fibre, the sizing layer was initially regular and then gave a smooth surface; after 100 cycles, the surface

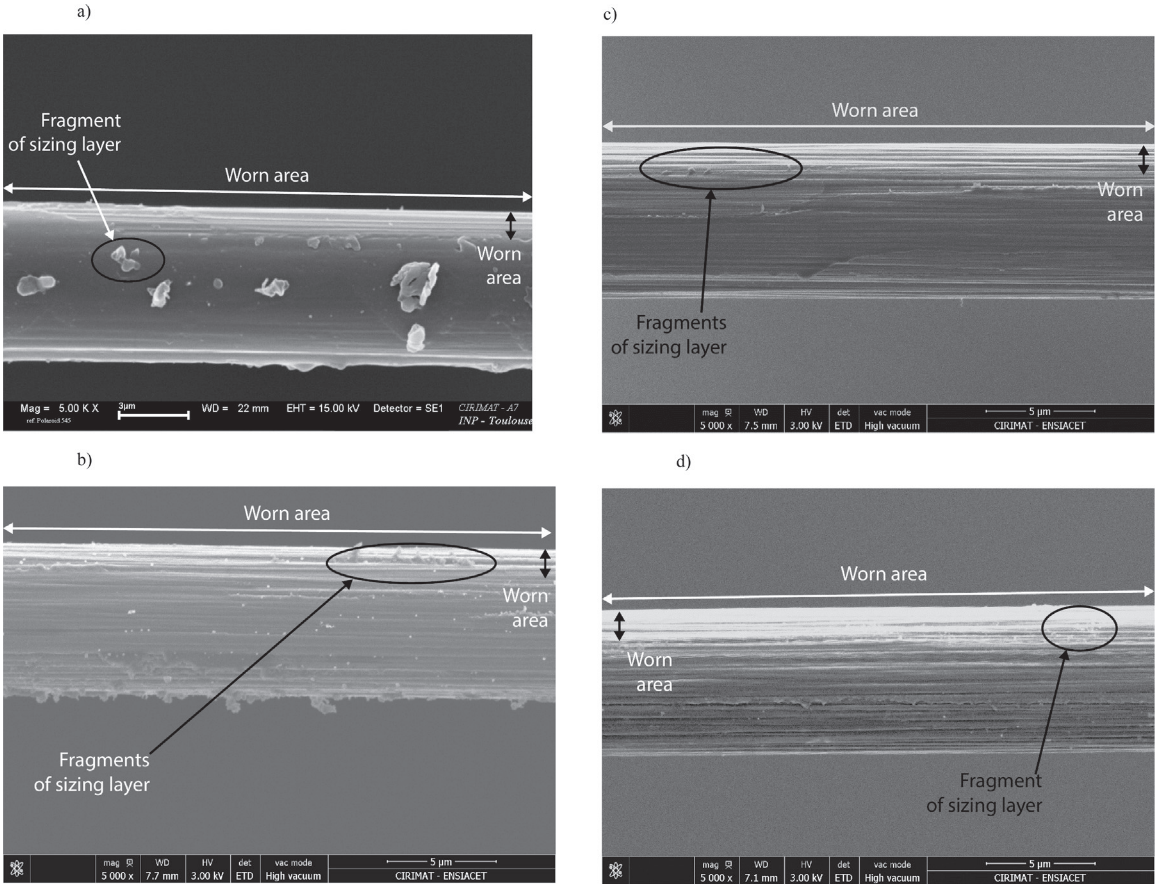

Fig. 12. SEM pictures of the different carbon fibres after 100 cycles of friction: a) sized, b) desized with acetone, c) desized with THF siphoned 5 times, and d) desized with THF siphoned 10 times. For each picture the worn area is delimited by the vertical and the horizontal double arrowed lines.

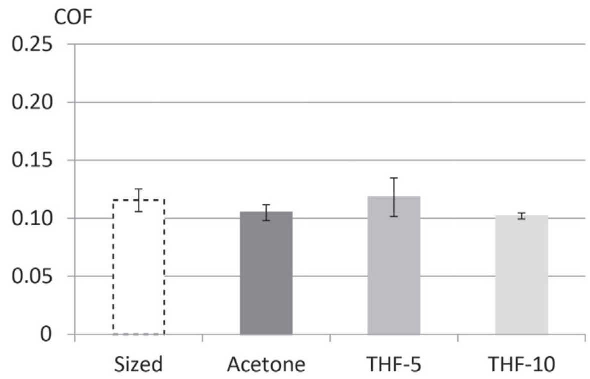

Fig. 13. Coefficients of friction at the 100th friction cycle (average value for friction measurements with standard deviation) for the carbon fibres sized and desized with acetone, with THF siphoned 5 times, and with THF siphoned 10 times.

Table 3
Coefficient of friction, standard deviation, and coefficient of variation (CV%) at the 100th friction cycle for the carbon fibres sized and desized with acetone, with THF siphoned 5 times, and with THF siphoned 10 times.

	Fibre			
COF	Sized	Desized with acetone	Desized with THF-5	Desized with THF-10
Mean value	0.116	0.105	0.118	0.102
Standard deviation	0.010	0.007	0.017	0.003
CV%	8%	6%	14%	3%

became rougher due to the wear of sizing layer.

By comparing the sized fibre and the efficient desizing process, i.e. THF-10, a higher COF for sized fibres can be observed. This result is in correlation in the study reported by Kafi et al. [24].

4. Conclusions

This study concerns the friction between fine single fibres, that is, carbon fibres 7 µm in diameter, and the influence of the sizing and desizing processes. The results obtained show that the single fibre-to-fibre friction measurement is sensitive to the sizing surface state. In fact, the coefficient of friction, and particularly its coefficient of variation, were linked to the sizing surface state and more precisely to the homogeneity of the sizing coating. Nevertheless, the greater the wear of sizing layer, the lower the coefficient of variation. The wear of sizing layer increases with sliding distance, inducing a decrease of the coefficient of friction.

In the future, the effect of the wear of sizing layer on the wettability of the surface should be analysed to evaluate the impact on the composite material manufacturing, i.e. during the weaving process, the shaping operation and fibre matrix adhesion.

Acknowledgements

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