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MECHANICAL CHARACTERISATION OF SIMULATED LONG DISCONTINUOUS FIBRE REINFORCED COMPOSITE FOR RECYCLING POTENTIAL ASSESSMENT

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Abstract:

In order to simulate a recycling process applied to a carbon/epoxy composite, thermal oxydation was performed on discontinuous virgin carbon fibres to remove sizing and binder from their surface. Differences between thermally treated and virgin fibres were evaluated by mechanical and chemical characterization both at the fibre scale and at the composite scale. It appeared that the thermal treatment had no major influence on the mechanical properties and wettability of fibres. Nonetheless, the composite based on thermally treated fibres suffered a significant loss in tensile strength compared to untreated fibres, while the interlaminar shear strength was not significantly impacted.

Keywords: recycling; carbon fibre composite; discontinuous long fibre; mechanical characterization

1. Introduction

Technical composites materials and especially those made of carbon fibres and thermosetting matrix are of great interest today to produce high performance, stiff, lightweight and corrosion very resistant structures in aeronautics, aerospace and general transport sector [1] [2].

For several decades many studies have been carried out on the recycling of these composite materials in view of the large amount of composite structures reaching their end of life. 70% of all composite materials produced every year are made of thermosetting matrix, which means that they cannot be recycled by melting or moulded. According to Jiang [3], it can be expected that 15 000 aircrafts will need to be retired in the next 20 years and this represents at least 200 000 tons of composite materials. For this reason, different valorisation techniques were developed, such as mechanical and chemical recycling and thermal valorisation [4][5][6]. Carbon fibres are very high-quality fibres. The aim of recycling these fibres is to try to keep their physical and mechanical properties intact for re-use in high performance structures. In particular, the conservation of the fibre length is a priority in order to produce new composite materials reinforced with long recycled fibres, offering the best mechanical performance. Among the three valuation techniques mentioned above, only the chemical and thermal recycling can keep the fibre length intact since the mechanical shredding leads to important length reduction [7]. Even though recycling techniques exist to remove thermosetting resin from carbon fibres, it is still extremely difficult to obtain recycled fibres longer than 20 mm.

For this reason, in this work, composite laminates made of long discontinuous carbon fibres of a specific length distribution is investigated. A thermal treatment was chosen to simulate the recycling of fibres. In order to fully characterize the behaviour of the composite, tests at the fibre scale, such as single fibre tensile tests, wettability measurements and atomic force microscopy characterizations

(AFM), were first carried out. Then, composites made of virgin of thermally treated long discontinuous carbon fibres and epoxy matrix were characterized by tensile tests and interlaminar shear strength tests (ILSS). Tests were performed on a continuous non-woven UD fabric used as reference and on both untreated and treated discontinuous non-woven UD fabrics.

2. Materials and Methods

2.1. Materials under investigation

The material under investigation is an unidirectional carbon fibre reinforced epoxy matrix composite. The Infugreen SR810 epoxy resin and hardener SD 8824 used at a ratio of respectively 100/32 were provided by Sicomin. As reinforcements, two different non-woven fabrics were used. First, a non-woven unidirectional carbon fibre reinforcement T700 Infusion (UD T700 I) provided by Sicomin was used as the reference. The second fabric (UDS) is a non-woven discontinuous STS 40 carbon fibre reinforcement made by Schappe Techniques which fibres length follow a distribution between 20 and 170 mm with an average length of 45mm. The UD T700 I has an areal weight of around 300 g/m² while the areal weight of the UDS is 160 g/m².

In order to simulate the recycling process of carbon fibres, the UDS was thermally treated in an Enitherm DP46 oxygen hoven. The temperature is increased from 30°C to 350 at a rate of 5°C/min, and then hold for 15 min. Finally, the temperature is increased from 350°C to 450°C at 5°C/min. This thermal process was adapted from the ISO 6964 standard. The fibres are hold for 30 min at 450°C in order to remove any organic sizing that can be found on the fibre surface. After thermal treatment, samples are cooled in the hoven at a slow speed. The treated non-woven fibres are reused for composite manufacturing by infusion process instantly after being taken out from the hoven.

Unidirectional laminates of 4 and 10 plies using the UD T700 I with sizes of 150x600 mm² and 150x150mm² respectively were produced by resin infusion at room temperature. The same process was repeated for UDS with 8 and 20 plies of 150x600 mm² and 150x150 mm² respectively. The number of layers was doubled for UDS in order to obtain a similar areal weight for both composites. After a curing time of 24 hours, the infused plates were demoulded and conditioned at 23°C. The composites plates were then cut with a water diamond saw for mechanical testing at the standard sample dimensions according to the ISO 527-4 (250x25mm²) for the larger plates and the NF EN 2563 (40x10mm²) for the smaller ones. The porosity of each plate was determined thanks to a density characterization using a Micrometrics gas pycnometer (AccuPyc 1330 Model).

2.2. Characterization methods

2.2.1. Single fibre tensile strength test (STS)

STS tests were performed to provide detailed information on the mechanical properties before and after a treatment of fibres. First, the diameter of each carbon fibre was determined using a Diastron FDAS 770 machine that allows to determine the diameter of the fibre on all its length. Then the fibre was placed into a Diastron LEX 820 apparatus to carry out the tensile test according to the standard ISO 11566:1996. The minimum number of tested samples was set to 20. The Young's Modulus was corrected using a compliance calculated on 12 and 30-mm fibre gauge length. All samples were analysed according to a Weibull model for both gauge lengths of 12 and 30 mm. All fibre ends were glued on plastic tabs with a Dymax Ultra-light weld 3193 UV glue.

During their manufacturing and/or the simulated recycling process performed in this study, defects may appear on the surface or in the core of fibres. Considering a constant diameter for all fibres, the Weibull approach treats these two types of defects indifferently. These flaws may lead to a dispersion of break strength of carbon fibres. For this reason, it was decided to analyse these data using the Weibull's probabilistic model. In a volume V , the flaw population is modelled by the parameter λ corresponding to a density of flaw activation under a certain load σ as follows:

$$\lambda = \frac{1}{V_0} \left(\frac{\sigma}{\sigma_0} \right)^m \quad (1)$$

for which m is the Weibull's modulus.

The failure probability of the fibre can be written as followed:

$$P_f = 1 - \exp\left(-\frac{V}{V_0} \left(\frac{\sigma}{\sigma_0} \right)^m\right) \quad (2)$$

To determine the Weibull's modulus of the fibres, a large number of fibres (superior to 20 according to the literature) must be tested. A non-linear optimisation procedure based on the Generalized Reduced Gradient (GRG) algorithm was used to adjust the material parameters.

2.2.2. Wettability measurements

A single carbon fibre was attached to one plastic tab using the same UV glue used in single fibre tensile test. A high precision force tensiometer, the K100SF from Krüss, was used with different liquids: water, diiodomethane and the Infugreen SR 8100 epoxy resin. During the procedure, the carbon fibre is dipped into the liquid at a speed of 1mm/min, reaching a defined immersion depth. This allows to determine an advancing capillary force. Then the fibre remains at this position for 60 s in order to obtain a static force. Finally, the fibre is withdrawn up to the initial position at a speed of 1mm/min and a receding force is measured. The static force will be used in this work to determine the static contact angles and then the surface energies as made in previous works of Garat et al [8]. The contact angle between the fibre and the liquid is calculated using the Wilhelmy's law as follows:

$$\theta = \arccos\left(\frac{\gamma_L \times p}{F}\right) \quad (4)$$

where F is the measured force, γ_L is the surface tension of the liquid and p is the fibre perimeter. Once the contact angle θ is calculated for each liquid, the Owens-Wendt's [9] formula which is a 2nd degree linear equation can be used to determine the fibre surface energy.

$$\frac{\gamma_L \times (1 + \cos(\theta))}{2 \times \sqrt{\gamma_L^d}} = \sqrt{\gamma_s^p} \times \frac{\sqrt{\gamma_L^p}}{\sqrt{\gamma_L^d}} + \sqrt{\gamma_s^d} \quad (5)$$

where γ_L^p is the polar component and γ_L^d is the dispersive component of liquid surface tension and the γ_s^d and γ_s^p are the dispersive and the polar component of fibre surface energy respectively.

In order to obtain the surface energy of the fibres, a fit of the equation for four different liquid was done according to previous work by Pucci et al [10].

2.2.3. Topographical Analysis

The nanoroughness of fibres was characterized with an Oxford Asylum Research MFP-3D Infinity AFM using a tapping mode. In order to observe the fibre surface, each end of the fibre was stuck to a glass sheet using a silver glue. Each sample was scanned on $5 \times 5 \mu\text{m}^2$ area at a scan speed $3.8 \mu\text{m/s}$. All

measurements were performed with an AC160TS-R3 silica tip. Thanks to the IGOR Pro 6.37 Software the roughness of the topography can be characterized by the means of two values. The first one is Ra which represents the average roughness of the surface as the second one, Rq, is the quadratic value roughness of the whole surface sample.

2.2.4. Mechanical Tensile Test

Axial tensile test specimen of 250 x 25 x 1.5 mm³ were produced from the composite plates using a water-cooled diamond saw. Aluminium tabs of 50 x 25 x 2 mm³ were bonded on each composite end using one-component cyanoacrylate Loctite Super Glue 3. All tests were performed with an MTS Criterion C45.105 tensile machine equipped with a 100 kN load cell at a crosshead speed of 1mm/min according to ISO 527-4 standard requirements. An additional high-resolution camera is placed in front of the sample, and images of its speckled surface are recorded at frequency of 1 Hz. A digital image correlation technique allows measuring the in-plane plane strain tensor and thus the Poisson's coefficient.

2.2.5. Short beam shear test (SBS)

The SBS test is a well-known and used method to study the interlaminar shear strength (ILSS) of laminates. For this test, specimens were cut from the 8 plies plate of UD T700 I and 20 plies plate of UDS in order to have a span of around 20 mm. A Z010/TH Zwick-Roell testing machine equipped with 3 points bending device and a 10 kN load cell was used to apply a load at 1mm/min. The apparent ILSS τ , expressed in MPa is calculated using the following equation:

$$\tau = \frac{3}{4} \times \frac{P_m}{b \times h} \quad (6)$$

Where P_m is the maximum load observed during the test (N), b and h are the measured width and thickness (mm) respectively.

3. Results and Discussion

3.1. STS tests

Single fibre tensile test results are shown in Table 1 as average value for at least 20 tests. All the tests were carried out in the pure elastic domain of the fibre. Differences between the treated and untreated fibres are not very significant. There was no change on the diameter of the fibres but a loss of 5% of the tensile strength was observed for thermally treated fibres. Considering the Young's modulus, the corrected one is a bit higher than the provider value (around 290 GPa against 250GPa for 12k STS40 EP) but this could be explained by a difference in the fibre holding. In the ISO Standard 11566:1996 the fibre is stuck onto by a paper frame whereas in this work each fibre is glued onto plastic tabs.

Table 1: STS results for UD T700 I, UDS Untreated and TT fibres

Sample Name	d [μ m]	σ_{\max} [MPa]	E_{corr} [GPa]	m
UD T700 I	6.61 \pm 0.33	4150 \pm 920	278 \pm 20	5.3
UDS Untreated	6.51 \pm 0.35	4000 \pm 1200	286 \pm 18	3.3
UDS TT	6.45 \pm 0.37	3800 \pm 870	292 \pm 17	4.4

The TT seems to have little impact on the mechanical behaviour of fibres except on the standard deviation of the maximum strength which is a bit lower for treated fibres. A Weibull's analysis also

reveals interesting differences with a slight decrease of the fibre strength at $P_f = 50\%$ and of the Weibull modulus as it can be seen on the Figure 1.

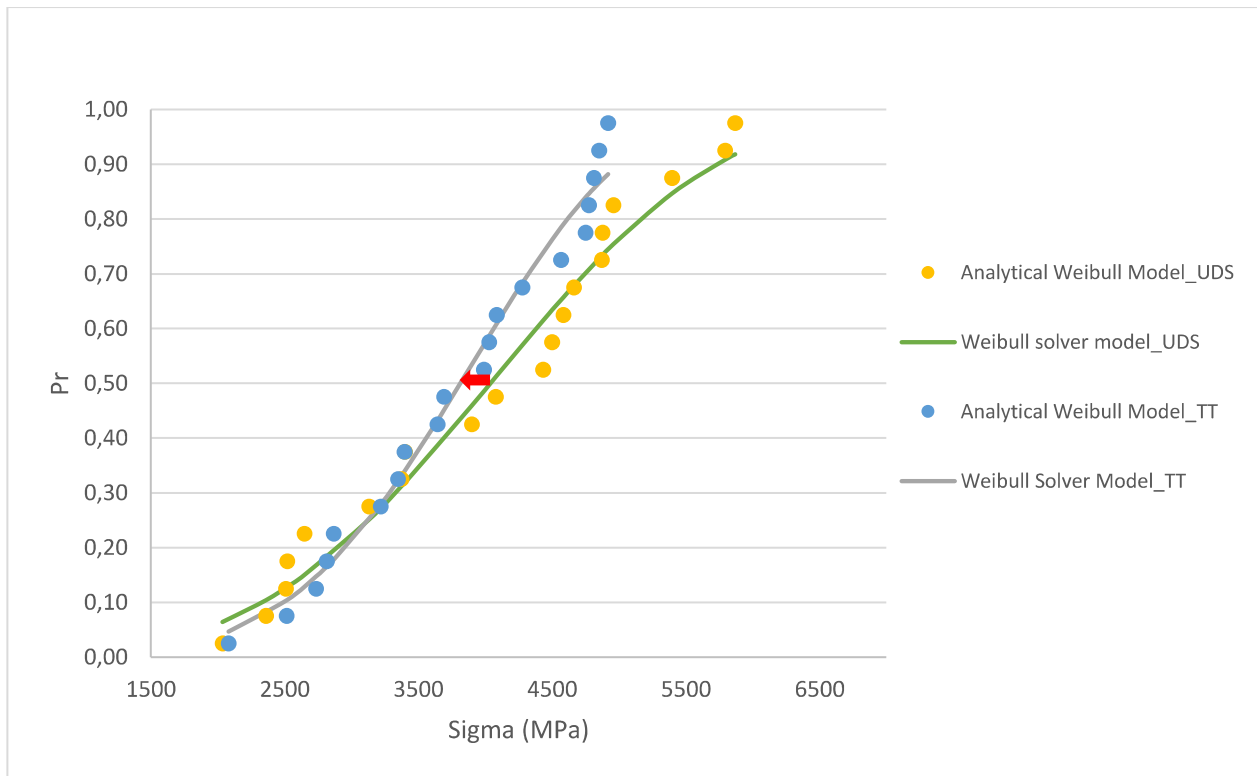


Figure 1. Probability of failure as a function of tensile stress for TT and untreated UDS carbon fibres

The plotted point and solver calculation of the Weibull modulus show that the treated and untreated fibres have a close slope which is observable on the small differences of the Weibull modulus. Nonetheless the deviation of the values is a bit lower for the treated fibres which could be a result of a surface change. It is possible that the heat treatment has made the surface flaws more uniform but these must be proven using surface characterization as with AFM measurements for example.

3.2. Wettability measurements results

3.2.1. Determination of the contact angle

The average results of the tests carried out with the K100SF Tensiometer for 8 single carbon fibres can be found in Table 2. Since the UD T700 I and UDS are not made of the same reference fibres, only untreated and treated UDS fibres were analysed with this method. It appears that treated and untreated have slight differences on contact angles especially with water and diiodomethane, whereas the contact angles values for the Infugreen epoxy shows similar results.

Table 2: Contact angle of treated and untreated fibre for various liquid

Sample Name	Water contact angle [°]	SR 8100 Infugreen Contact angle [°]	Diiodométhan Contact Angle [°]
UDS untreated	51.91 ± 8.5	50.19 ± 5.5	49.94 ± 7.97
UDS TT	61.02 ± 5.2	52.42 ± 5.1	53.94 ± 4.03

3.2.2. Determination of the fibre surface energy

According to the Owens Wendt equation (Eq.6), the static contact angle of the three liquid was used to obtain the fibre surface energies and components. The dispersive component of fibres after treatment remained the same but a small change was observed in the polar component. Nonetheless the values are really close taking the standard deviation in consideration.

Table 3: Surface energy of UDS Untreated and UDS TT

Sample name	Polar component [mJ/m ²]	Dispersive component [mJ/m ²]	Total component [mJ/m ²]
UDS untreated	27.3 ±6.6	22.0 ±1.5	49.3 ±5.8
UDS TT	20.9 ±4	21.6±1	42.5±3.4

3.3. Topographical Analysis

The variation of surface roughness after a desizing treatment have been studied by Yao et al [11] who demonstrated that sizing removal conducts to an increase in roughness. Some topographical analysis were performed by means of AFM on untreated and thermally treated carbon fibres. Measured roughness on both fibres seems to be coherent with results found in the literature. These results will be discussed during the oral presentation.

3.4. Mechanical tensile test

In order to investigate the influence of both the fibre distribution length and the TT on fibre, tensile tests were conducted at composite scale on UD T 700I laminate and both untreated and treated material. To ensure possible differences in the mechanical property tests were carried out on at least 5 samples until failure.

Table 4: Mechanical tensile tests results for Reference, UDS Untreated and UDS TT composites materials

Sample name	Tensile strength R _e [MPa]	Young modulus [GPa]	Poisson coefficient	Porosity [%]
UD T700 I	2145.172	106.8 ± 2.0	0.31 ± 0.02	4
UDS Untreated	1403 ± 85.1	98.6 ± 16.0	0.39 ± 0.1	2.5
UDS TT	1059 ± 112.9	77.9 ± 8.8	0.38 ± 0.1	6.0

On the first hand, the results presented in Table 4 show a good conservation of the Young modulus and Poisson ratio when considering the standard deviation. On the other hand, an important decrease of 25% of the maximum strength was observed for the thermally treated carbon fibres. Since no major differences exist between the two reinforcing non-woven, the adhesion between fibre and matrix after a thermal treatment can be the cause of such loss of properties. The discontinuity of the reinforcements also shows a significant loss of 35% in tensile strength compared to continuous fibres.

3.5. SBS test results

During the SBS test, is the specimen is subjected to longitudinal shear, but also to tension and compression. It is important to confirm the shear failure mode of the specimen by calculating the maximum tensile stress at failure and comparing it to the tensile strength R_e measured previously (Table 4):

$$\sigma_{max} = \frac{3}{2} \frac{FL}{be^2} < R_e \quad (7)$$

With F the load at failure, L the span, b and e the width and thickness of the sample.

It can be seen in the following table that the failure of samples was completely in the shear mode since maximum stress was always lower than the composites tensile strength.

Table 5: SBS test results for UD T 700 I, UDS Untreated and UDS TT composite materials

Sample name	ILSS τ [MPa]	Load at failure [N]	Maximum stress [MPa]	Composite tensile strength [MPa]
UD T700 I	48.1 \pm 2.61	1912	386	2145
UDS Untreated	52.4 \pm 2.14	2359	420	1403
UDS TT	52.6 \pm 1.86	2422	415	1059

Taking the dispersion into account, ILSS displayed in Table 5 does not vary much between the 3 composites. The fact that the discontinuity of fibres has little impact on ILSS is not very surprising since this test is mainly driven by the behaviour of both matrix and interfaces. It can also be observed that the thermal treatment does not influence much the adhesion between fibres and matrix since the ILSS value is 52 MPa for both composite materials.

3.6. Discussion

According to all test carried out, the three type of fibres tested (UD T 700 I, UDS untreated, UDS treated) have similar properties. From a mechanical point of view, only tensile strength and Weibull modulus seem to be impacted by thermal treatment. Tensile strength slightly decreases, while the Weibull modulus increases, reflecting the decrease in the dispersion of the strengths. The major differences between the fibres have been observed for surface topography which is more etched after thermal treatment. This could explain the small difference observed in wettability measurements.

At the composite scale, on one hand, it is understandable that the ILSS showed no evolution when using discontinuous fibres instead of continuous ones as explained previously. On the other hand, it is more surprising not to observe variation with the change in surface of fibres after thermal treatment. This could be explained by a change in the adhesion mode. Before thermal treatment, chemical bond between sizing and matrix were mainly responsible for the adhesion, while after treatment, the rougher surface allows a better mechanical adhesion thanks to interlocking. However, for a better understanding of the shear behaviour of the composites additional characterization needs to be done on the treated fibre such as XPS to observe the sizing removal.

Finally, the 25% drop in strength observed when switching from continuous to discontinuous fibres is directly attributable to the reduction in fibre size. Actually, the mechanical properties of both type of fibres are almost identical. Such a result has been shown several times in the past and was therefore expected. It is all the more important as we are interested in the recycling of these fibres whose size will be reduced after each recycling phase. After heat treatment, an additional drop of 25% is observed and is this time attributed to the change in the adhesion mode. While this change appears to maintain the SBS properties, it is not sufficient for the tensile failure properties.

4. Conclusion and perspectives

In this study, the recycling process of carbon fibres was simulated by testing the impact on the composite properties of the fibre length reduction and the fibre surface state after heat treatment. It was found that the heat treatment did not significantly influence the intrinsic mechanical properties of the fibres, but rather its surface properties in a small but noticeable way. Concerning the composite, modifications are more important, especially on the tensile properties. We note here that the length of the fibres has a predominant impact, as well as the modification of the surface condition of the fibres. These results are all the more important as recycling carbon fibres is an important objective for many companies. It is therefore mandatory to find a solution to compensate for these losses of properties with specific surface treatment such as plasma treatments, and to find weaving techniques to produce high quality reinforcements for laminates from long discontinuous fibres.

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