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Recovery and reuse of discontinuous carbon fibres by solvolysis: Realignment and properties of remanufactured materials

Géraldine Oliveux [a, *], Jean-Luc Bailleul [b], Arnaud Gillet [c], Olivier Mantaux [c], Gary A. Leeke [a, d]

[a] School of Chemical Engineering, University of Birmingham, Edgbaston, Birmingham, B15 2TT, United Kingdom
[b] Laboratoire de Thermocinétique de Nantes (LTN), UMR CNRS 6607, Ecole Polytechnique de l'Université de Nantes, UNAM, Rue Christian Pauc, BP 50609, Nantes, 44306, Cedex 03, France
[c] Institut de Mécanique et d'Ingénierie (I2M), UMR CNRS 5295, IUT de Bordeaux, 15 Rue Naudet, Gradignan, 33175, Cedex, France
[d] School of Water, Energy and Environment, Cranfield University, Cranfield, Bedfordshire, MK43 0AL, United Kingdom

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ABSTRACT

Discontinuous carbon fibre tows were recovered after solvolysis of an aeronautic type composite made with RTM6 epoxy resin. A Sohxlet extraction method was used to quantify the organic residue on the fibre tows and showed that less than 3 wt% was remaining on the surface. The recovered tows were therefore reused directly to manufacture a plate with randomly distributed carbon fibres and then three plates with realigned carbon fibres. The latter were then characterised and tested and the results obtained were compared to the material manufactured using the same type of virgin fibres by the same method. The materials made from recycled carbon fibres showed very good properties in comparison to the virgin fibre material, despite the presence of flaws such as quality of the fibre surface after solvolysis, alignment and voids). This is the first time in the open literature that carbon fibres recovered from solvolysis were reused in this way together with characterisation of the resulting materials.

1. Introduction

The usage of carbon fibres is increasing year after year, especially in transport applications. Currently aeronautics is the biggest consumer due to the recently developed planes (Boeing 787, Airbus A380 and A350), whereas the automotive industry seems rather reluctant to use them because of the expense and the slow manufacturing processes. In order to see more widespread usage, the cost of the carbon fibre would need to decrease to about $5 to 6 per pound (10–12 € per kg) [1]. Forecasts have also indicated that the current carbon fibre production volume would not be able to satisfy an increase in demand over the coming years. If every car manufacturer in the automotive industry attains a high-volume use of carbon fibre reinforced polymers (CFRP), the current carbon fibre production would not satisfy the demand according to experts at the JEC Americas 2014 [1]. Furthermore, these materials are still not recycled in a closed loop. Their wider usage in transport, and especially in automotive depends on their recyclability and their reuse in accordance with EU regulations. The recovery of carbon fibres by recycling end-of-life materials or production waste represents therefore a substantial resource that could fulfil these three issues (availability, recyclability and cost). Two technologies have particularly been studied and developed to recycle CFRP: pyrolysis and solvolysis. Both techniques have demonstrated the feasibility of separating efficiently the fibres from the resin and of producing very good quality fibres [2]. The main difference between these both techniques lies in what results from the resin degradation; pyrolysis mainly produces gases and oils, and in solvolysis the organic products from resin degradation are dissolved in the solvent system.

When single carbon fibres recovered from either pyrolysis or solvolysis are tested, the results show that their reinforcement properties are almost fully retained. Globally decreases of less than 10% have been observed for their tensile strength and their tensile modulus is unaffected [2]. Recycled and virgin carbon fibres (rCFs

* Corresponding author. School of Chemical Engineering, University of Birmingham, Edgbaston, Birmingham, B15 2TT, United Kingdom.
E-mail addresses: g.oliveux@bham.ac.uk, geraldine.oliveux@free.fr (G. Oliveux), jean-luc.bailleul@univ-nantes.fr (J.-L. Bailleul), arnaud.gillet@u-bordeaux.fr (A. Gillet), olivier.mantaux@u-bordeaux.fr (O. Mantaux), Gary.A.Leeke@cranfield.ac.uk (G.A. Leeke).

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and vCFs, respectively) are therefore similar, except that rCFs are no longer sized after the recovery treatment and in general are currently available in a discontinuous shape [2].

Different approaches have been studied to reuse the recovered fibres into new composite materials. These mainly are carbon fibres in random short fibre mats, pellets and realigned fibre mats, including reshaping into yarns [2]. However the only way to really benefit from the reinforcement capability and the value of the rCFs, is to at least align them. Indeed the alignment of discontinuous carbon fibres can considerably increase both the tensile stiffness and strength, and furthermore, the longer the fibres, the better the alignment and the higher the stiffness and the strength [3]. A few methods have been tried to align recycled carbon fibres in the United States, the United Kingdom and in France in particular [2]. The American company MIT-LLC (now known as Carbon Conversions) have developed a process called 3-DEP enabling the manufacture of three-dimensional preforms and the control of fibre placement and orientation according to the authors [4]. However the alignment quality has not been measured and was based only on a visual assessment. Furthermore the fibre length ranged between approximately 6 and 25 mm and produced preforms leading to a final fibre volume fraction lower than 30%. Researchers from the University of Nottingham have investigated two techniques based on a modified papermaking process as well as a centrifugal alignment process [2]. The second process was further investigated as it gave more promising results in terms of fibre alignment [2,5]. However the fibre length was again quite limited (up to 5 mm), together with the resulting mat overall density [5]. A process named HiPerDiF has been developed at the University of Bristol and produced materials showing a fibre volume fraction between 55% and 67% of the fibres aligned within the range of ±3° [6]. Again the process design limits, the fibre length and the preform areal density were also quite low (219 g/m^2). Furthermore this technique has not been tested on real recycled carbon fibres as yet. Researchers from the University of Bordeaux have recently patented a process to unweave pieces of recycled carbon fibre fabrics and align the fibre tows. The process can work with any fibre length, which is advantageous if one considers that the longer the fibres, the better the alignment [2]. Carbon fibres from other types of material could also be used as long as they are not fluffy. It was possible to produce a preform with 50 mm length fibre tows giving an areal density of 600 g/m^2 [2].

In this article, the Bordeaux process was used to align discontinuous recycled carbon fibre tows after unweaving of pieces of fabrics recovered by a solvolysis process [7–9]. According to the open literature, it is the first time that recycled carbon fibres recovered after solvolysis were reprocessed to make a new material. The other known work (not published as an article) in which solvolysed carbon fibres were reprocessed was realised in the AERDECO project [2]. However the amount of available recycled carbon fibres was too low to make a substantial mechanical characterisation. In this study, a material with randomly distributed carbon fibre tows and a material with aligned carbon fibre tows were manufactured and the mechanical properties (tensile and shear) were then measured. The results of mechanical testing are presented and discussed in relationship with the material structure and composition. The objective of this work was to assess the effect on the mechanical properties of flaws such as the presence of an organic residue coating the discontinuous recycled fibres recovered from solvolysis, fluffy fibres and not perfectly aligned fibre tows.

2. Material and methods

2.1. Materials

Plates of composite material made of RTM6 epoxy resin and 20 plies of T700 6 K carbon fibre woven fabric were cut into pieces of (50 × 50) mm^2 to (50 × 80) mm^2. Solvolysis was used to recover the carbon fibres as described in our earlier work [7]. The plates had a thickness of (6 ± 0.1) mm and a fibre volume content of (53 ± 1)%. Pieces of Prime Tex 48194 C1270S fabric from Hexcel, made with T700SC 12 K 50C carbon fibres, were cut in sizes similar to the pieces of RTM6 composite materials and manually unwoven to retrieve the virgin fibre tows. In this case, the fibres are sized but the sizing is not known.

A new plate was manufactured in the Laboratoire de Thermocinétique de Nantes (LTN) using the carbon fibres recovered after solvolysis and a commercial epoxy resin, SR 1500 cured with SD 2503 hardener from Sicomin. Four plates were also manufactured at the Institut de Mécanique et d'Ingénierie (I2M) in Bordeaux using carbon fibres recovered after solvolysis and another commercial epoxy resin, Araldite® LY 5052 cured with Aradur® 5052 hardener from Huntsman. Plates using virgin fibre tows of the 48194 C1270S fabric were also manufactured for comparison.

Grilon® polyamide powder (a mixture of polyamides PA6 and PA66, grain size 100 μm) from EMS-Grivory was used to bind the fibre tows together after alignment.

Acetone (analytical grade) was purchased from Sigma Aldrich. Water used in solvolysis experiments was unfiltered mains water.

2.2. Fibre recovery by solvolysis

The experiments were realised in a 5 L hastelloy batch reactor from Parr Instruments. The samples were placed into a stainless steel basket to avoid any contact with the reactor walls and therefore pyrolysis. Seven experiments were conducted with a 2.2 L mixture of water and acetone at 20:80 vol ratio. The composite loading rate was determined to give a resin concentration of (30 ± 1) g/L. The heating phase required about 75 min to reach 320 °C, inducing a pressure of (180 ± 10) bar. The system was maintained at this temperature for 2 h. Due to the weight of the reactor, it was not possible to lift it from the oven to cool, therefore the cooling phase required about 2 h for the temperature to decrease below 200 °C and approximately 18 h to reach 35 °C. After this time the reactor was opened and the pieces of fabrics and the liquid fraction containing the dissolved organic products from the degraded resin were recovered.

2.3. Fibre characterisation

The fibres were analysed by Environmental Scanning Electron Microscopy (ESEM) using a Philips XL30 FEG ESEM. Samples were cut and then mounted to adhesive stub mounts. Although carbon fibres are conductive, the samples were coated in platinum to improve image quality using and EMSCOPE SC500 low-vacuum sputter coater. Once mounted and coated on the stubs the samples were loaded individually into the ESEM and the sample chamber was evacuated. The images were taken at varying magnification levels at an acceleration voltage of 20 kV.

The organic residue on the recovered fibre bundles was measured on samples using a Soxhlet extraction method. The fibre bundles were put into a single thickness cellulose extraction thimble (25 mm diameter x 100 mm length from Whatman) and then placed in a Soxhlet extractor with 110 mL of an acetone carrier solvent. Each extraction cycle took 15 min, and the washing totalled 6 cycles giving an overall rinsing time of approximately 100 min. The mass of the fibre bundles was measured before and after washing, and the proportion of organic residue was determined using equation (1).

$$R\% = \frac{initial\ mass - remaining\ mass}{initial\ mass} \times 100 \quad (1)$$

The length distribution was measured on 118 recycled fibre tows and on 155 virgin fibre tows.

2.4. Fibre alignment

Both virgin and recycled fibre tows were manually unweaved from fabric pieces and an alignment process, patented by the I2M [10], was fed with the tows, which then fell into a U-shape channel that was manually displaced to produce 25 mm width tapes. Grilon polyamide powder was manually spread on the obtained tapes (about 2 wt%) and melted under infrared heating and then manually roll-pressed to bind the fibres together. A 150 × 280 mm^2 unidirectional ply was then obtained using 6 pieces of tapes (Fig. 1).

Each ply was photographed to measure the orientation of the fibres using a method developed at I2M and based on work from Ref. [10]. The comparison of the area of one ply with the area of a carbon fibre allowed to assume that at least 20% of the fibres in volume can be detected, which is statistically representative. The angle deviation and the length were measured on detected fibres as shown in Fig. 1b.

2.5. Remanufacture

A first plate was manufactured at LTN with carbon fibre bundles after manually unweaving of (240 ± 5) g fabric pieces recovered after solvolysis. The fibre tows were manually randomly spread on the surface of a prepared mould and impregnated using a brush with SR 1500 epoxy resin prepared according to manufacturer's specifications. The bagging was then finalised before air vacuuming at minus 1 bar. The epoxy resin was then cured during 16 h at room temperature, demoulded and post-cured at 75–80 °C for 1 h.

Three plates were manufactured at I2M with either four or six unidirectional plies of recycled carbon fibres. The plies were hand-laid at 0° on the prepared mould and each ply was impregnated with Araldite® LY 5052 using a brush. The plates were cured at 60 °C in a heating press (MIB-Hydro 20 kW) for 5 h under 35 bar. One of the plates was manufactured with recycled fibre tows that became fluffy during the unweaving process to measure the effect of the tow shape quality (Fig. 2). The methodology was also applied to manufacture a plate with four unidirectional plies of similar 12 K virgin carbon fibres. The details and characteristics of the four manufactured plates are summarised in Table 1.

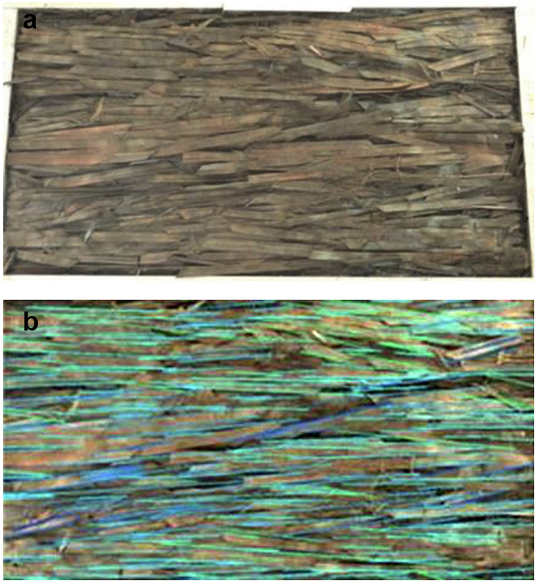


Fig. 1. A unidirectional ply of realigned carbon fibres recovered after solvolysis (150 × 280 mm^2); a) raw image and b) image with detected fibres (green lines). (For interpretation of the references to colour in this figure legend, the reader is referred to the web version of this article.)

2.6. Composite characterisation

2.6.1. Microscopy and composition

The cross section was observed under an optical microscope for each plate. The fibre content was determined for each plate using a calcination method developed by I2M on five samples of (10 × 10) mm^2. The weight of each sample was first measured in the air (M_a) and then in water (M_w) to calculate the composite density ρ_c using equation (2), with ρ_w being the water density. Each sample was then dried, placed into a crucible, covered to avoid fibre losses and weighed before being heated in a furnace at 500 °C for 145 min to burn off the resin.

$$\rho_c = \frac{\rho_w}{1 - M_w/M_a} \quad (2)$$

The crucible was weighed after calcination of the resin and provided the mass of remaining fibres (M_f). The fibre mass fraction W_f was then calculated using equation (3).

$$W_f = \frac{M_f}{M_a} \quad (3)$$

The fibre volume fraction V_f can be calculated using equation (4), considering the density ρ_f of T700 carbon fibres to be 1.80 g/cm^3 according to Toray's data sheet.

$$V_f = \frac{\rho_c}{\rho_f} \cdot \frac{M_f}{M_a} \quad (4)$$

2.6.2. Mechanical tests

For each plate manufactured with realigned recycled or virgin carbon fibres, 4 tensile 280 mm length x 20 mm width coupons were machined, with the longitudinal direction parallel to the fibre direction, and end-tabbed with glass fibre composite material. The longitudinal strain was measured with a contact-type extensometer equipped with knife edges (MTS Alliance RF/100). Both the tensile strength and modulus were determined for each coupon and averaged.

For each plate, 3-point bending tests were also performed on five 25 mm length x 10 mm width coupons (the exact dimensions

Fig. 2. One ply of recycled carbon fibres incorporating fluffy tows (150 × 280 mm^2).

Table 1
Details and characteristics of the plates manufactured with realigned recycled carbon fibres; *the thickness was measured at 3 different points on 4 coupons taken from each plate and then averaged.

Plate#	Fibre type and shape	Number of plies	Measured thickness* (mm)
GO1	Solvolysed, fluffy	4	1.64 ± 0.10
GO2	Solvolysed	4	2.44 ± 0.03
GO3	Solvolysed	6	3.44 ± 0.07
GO4	Virgin	4	2.09 ± 0.06

were measured for each coupon), with the longitudinal direction parallel to the fibre direction. The coupon was positioned on two fixed roller supports at a distance of either 14 or 20 mm and was then mounted on an MTS testing machine. A controlled displacement (2 mm/min) of the loading pin was then applied at equidistance from the two fixed supports. The applied force and displacement were recorded at a frequency of 10 Hz. For each plate, the first three coupons were always tested until failure and both remaining coupons were submitted to four bending cycles with a force lower than the failure force determined by the first coupons, the fifth cycle being done until failure. The shear strength was determined for each coupon.

3. Results and discussion

3.1. Fibre characterisation

Solvolysis experiments realised in the conditions given in section 2.2 enabled the recovery of fabric pieces that were perfectly separated from resin and from each other and retained their woven architecture (Fig. 3). No washing post-treatment was applied. Some fibres were imaged by ESEM (Fig. 4a and b) and showed very clean surfaces with small organic residue coating the fibres. Some resin dust was also observed and could be mostly removed thanks to a light washing with acetone as shown in Fig. 4c and d.

The measurement of the amount of organic residue after solvolysis by a Soxhlet extraction method led to a low value of 3 wt% maximum for unwashed fibres and less than 1 wt% for fibres that were rinsed for a few seconds with acetone. At the boiling temperature of acetone it was not possible to remove the entire residue even after 6 cycles. The Soxhlet extraction method therefore enabled the removal of resin dust that was present on the fibres, but not the residue coating the fibre surface. This implied that the remaining residue was adhered to the fibre surface and might lead to poor adhesion with a new resin. A semi-continuous solvolysis process, however, in which the solvent mixture is continuously renewed with purified solvent mixture, would enable a total removal of organic residue.

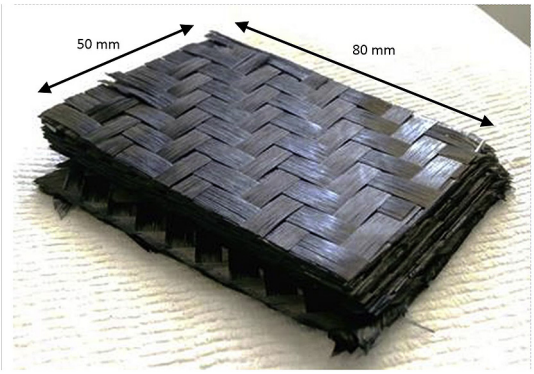


Fig. 3. Pieces of carbon fibre fabrics after solvolysis.

A previous study showed that virgin T700 carbon fibre bundles processed at 350 °C for 30 min in the mixture of acetone/water at a volume ratio of 80:20 did not lose more than 10% of their nominal tensile strength [8]. Furthermore the lower the temperature, the less affected were the fibres as there was no measurable decrease in the tensile strength after solvolysis at 300 °C [8]. It can be assumed therefore that the fibres recovered after solvolysis at 320 °C would have been little affected.

The measurement of the fibre length gave a mean length of 65.2 mm with a standard deviation of 19.0 mm for the recycled fibres, and a mean length of 54.9 mm with a standard deviation of 29.5 mm for the virgin fibres.

3.2. Composite material with recycled carbon fibre tows randomly distributed

A first plate was manufactured with recycled carbon fibre tows randomly distributed by hand and vacuum moulded (Fig. 5). Under vacuum the excess resin was absorbed by the bleeder. Some organic residue on the fibres was also displaced by the new resin as shown in Fig. 5b and c. A washing treatment prior to remanufacture would have removed this residue. Furthermore, it can be assumed that the fibre wetting with the new resin was therefore hindered by the presence of the organic residue, which was not chemically bounded to the fibre surface. It can therefore be assumed that this organic residue can be detrimental to the fibre/matrix interface and to matrix mechanical properties. The obtained plate showed a quite smooth mould surface. However the bagging surface was very wavy and the thickness was not constant (Fig. 5d). This can be explained by a non-homogeneous fibre tow distribution and tow overlap due to the unusual wide range of fibre length (20–80 mm). This was also observed in previous research work [3]. The mass fibre content was estimated to be approximately 53 wt%. Due to the varying thickness, it was not possible to cut coupons for mechanical testing, however this trial showed that it could be better to use shorter fibres to make this type of material in order to avoid fibre rich areas. Similarly, sheet moulding compounds, it would be better to use fibres with lengths less than 50 mm. When considering industrial quantities of recycled fibres and reuse, it might therefore be necessary to sort the recovered fibres according to length ranges that are suited to the target applications.

3.3. Composite material with realigned carbon fibre tows

3.3.1. Characterisation: fibre alignment and volume fraction

The quality of the realignment was evaluated using an image analysis method developed by the I2M. The obtained values are given in Table 2.

The frequency distribution of the fibre tow in-plane orientation angle is given in Fig. 6 for one ply of plate GO3 as an example representative of the average quality of realignment (excluding plate GO1, in which fluffy fibres were incorporated). Data for the other plates are shown in the table immediately below the chart in Fig. 6.

Except for plate GO1, the fibre orientation angle is between ±10° for the detected fibres, and as can be seen from Fig. 6, 76% of the fibre tows are within this range for plate GO3, among which 23% are aligned at ± 2° and can be considered as perfectly aligned [11]. Among the remaining 24%, the majority are between ±10 and ± 20° and the rest (2%) is outside ±20°. A work by Bednarcyk et al. [11] showed that a fibre misalignment can induce a dramatic loss of tensile strength of a unidirectional composite, the Young's modulus being almost unaffected. It showed that a reduction of more than 50% in the strength can be predicted when all the fibres of a unidirectional epoxy composite with a fibre volume fraction of 60% are

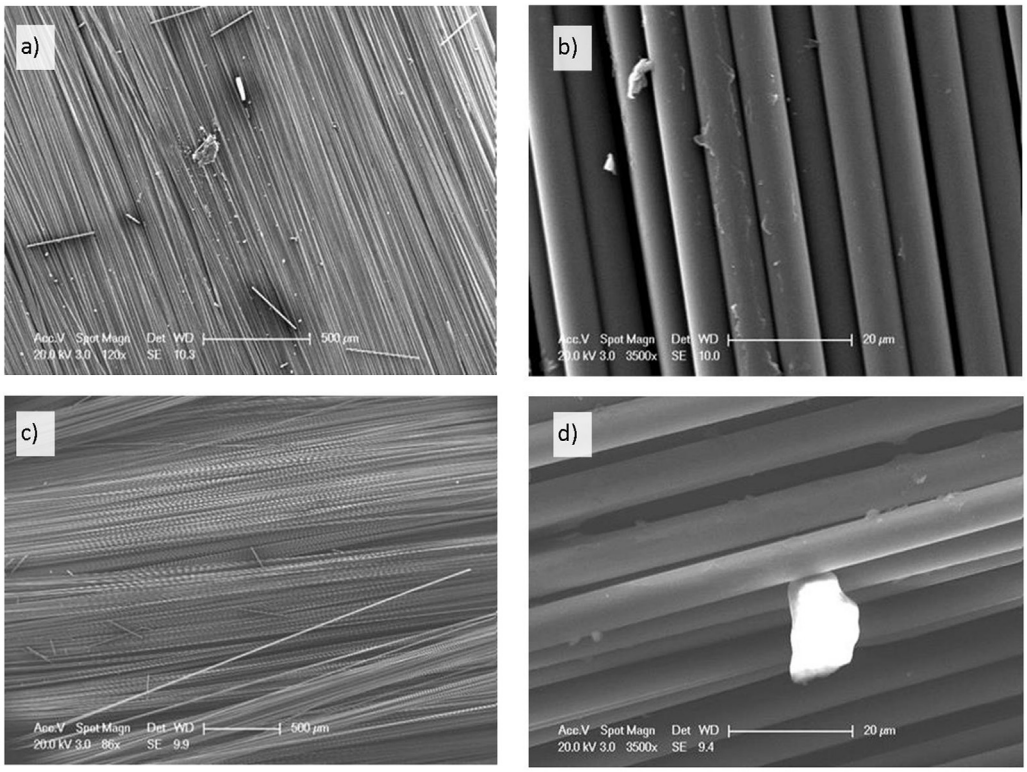


Fig. 4. ESEM images of: a) and b) unwashed carbon fibres recovered after solvolysis; c) slightly washed carbon fibres and d) solid particle of partially degraded resin on slightly washed carbon fibres.

misaligned by 10°. It can be said therefore that the mechanical properties of the composite materials manufactured for this work could be significantly lower than those of a composite material with fibre aligned at ± 2°. The presence of fluffy fibre tows in plate GO1 (Fig. 2) explains the poor alignment. The method would also detect more easily the longer fibres. Furthermore, the more dense the tapes and the plies, the more difficult the fibre alignment to detect.

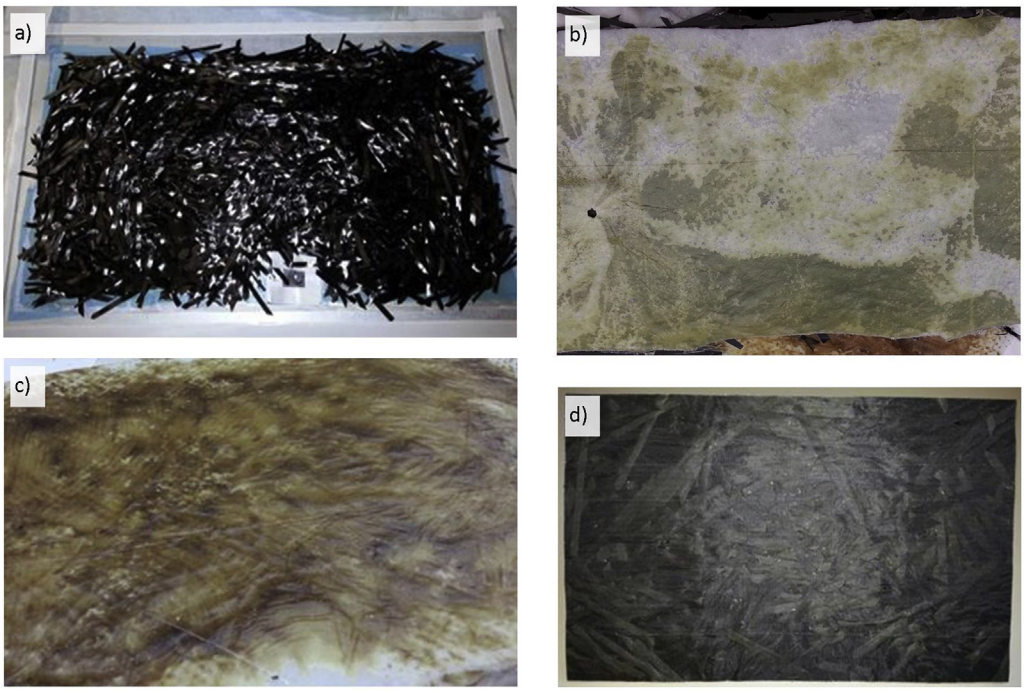
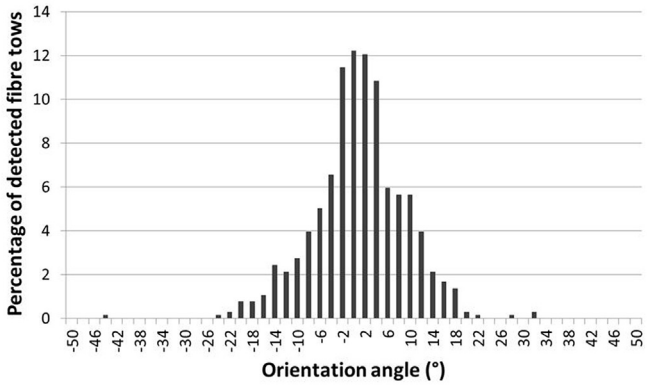


Fig. 5. Manufacture of randomly distributed fibre plate: a) recycled carbon fibre tows on the mould surface; b) bleeder impregnated with resin after curing of the plate made with virgin CF; c) bleeder impregnated with resin and organic residue after curing of the plate made with rCF and d) obtained plate after curing and edge trimming (bag surface).

Table 2
Physical properties of the plates. Values in brackets represent the standard deviations. Fibre areal weights were calculated from each ply weighed for each plate.

Plate#	Measured thickness (mm)	Measured fibre angle standard deviation (°)	Fibre volume fraction (%)	Porosity volume fraction (%)	Fibre areal weight/ply (g/m^2)
GO1	1.64 ± 0.10	13	46.6 (14.5)	4.5 (5.3)	359 (54)
GO2	2.44 ± 0.03	5	55.6 (7.8)	1.1 (1.1)	704 (106)
GO3	3.44 ± 0.07	8	53.9 (10.5)	1.7 (1.1)	605 (63)
GO4	2.09 ± 0.06	6	57.9 (8.5)	0.7 (0.1)	771 (29)



	≥ ± 20°	± 20° <...< ± 10°	≤ ± 10°
GO2	1	10	89
GO3	2	22	76
GO4	0	9	91

Fig. 6. Frequency distribution of the fibre tow in-plane orientation angle for plate GO3 and data for plates GO2 and GO4.

On the other hand, the tape density was not repeatable, leading to materials with heterogeneous tow density (Fig. 7). Fluffy fibres were incorporated in plate GO1 and produced more expanded plies, leading to a lower fibre content and areal weight and higher porosity (Table 2 and Fig. 8a). Plate GO1 showed wide dispersions in its physical properties (Table 2), indicating that the material was quite heterogeneous in terms of fibre distribution. For plates GO2, GO3 and GO4, the fibre tow distribution was quite heterogeneous within the material as well as within a ply, but in a less extent to that in plate GO1 (see fibre volume fraction and fibre areal weight/ply in Table 2). However plate GO4 was slightly more homogeneous. The recycled carbon fibre tows were stiffer than the virgin tows due to the presence of the organic residue and they also showed a tendency to stick to each other although they were not sticky. The friction between the fibres during their manipulation is suspected to induce static electricity. They produced more expanded tapes and the U-shape channel in which the fibres fell during the alignment step was filled faster. As an analogy recycled carbon fibre tows could be compared to matches that one would try to put back into their box. The plies and preform were consequently also more expanded.

Fig. 7. First ply of plate GO3 in the mould; the red circle indicates a lower tow density. (For interpretation of the references to colour in this figure legend, the reader is referred to the web version of this article.)

The resulting plate thickness and the number of plies, enables the ply thicknesses to be estimated which were 0.57 mm for plate GO3 and 0.61 mm for plate GO2 after compaction. The difference arises from the higher fibre tow density in GO2 plies. The virgin tows in plate GO4 did not show this expansion characteristic; therefore more tows could be loaded into the U-shape channel, leading to denser tapes, plies and preform. As they do not expand, the ply and preform thickness (estimated ply thickness of 0.52 mm after compaction) was also lower, and explains why the resulting material thickness is lower than that of plate GO2 despite the same number of plies. This phenomenon was also observed by Pimenta and Pinho [12]. They also observed that it was necessary to apply more pressure during manufacturing of a plate with recycled fibres coated with organic residue (areal weight 4% higher than the dry virgin fabric) to reach a good compaction and reduce the voids, because of the rigidity of the fabric after pyrolysis.

The micrographs in Fig. 8c and d show that the fibre/resin distribution is comparable for both plates GO3 and GO4, but shows more heterogeneous zones and voids in plate GO3. Furthermore, the micrographs in Fig. 8 are quite in consistency with the porosity deduced from the calcination results for each plate and given in Table 2.

3.3.2. Mechanical properties

The tensile properties obtained from the mechanical tests are shown in Fig. 9a and b. The results were obtained using four coupons for each plate, and so the dispersion values must be considered as coarse indicators. Plate GO1 indicated fibre volume content and fibre areal density per ply was much lower than for both plates GO2 and GO4, and therefore results in a lower thickness for the same number of plies. This was explained previously by the presence of fluffy fibres and justifies why the mechanical properties are lower than those of both plates GO2 and GO4.

Plates GO2 and GO3 both showed a higher tensile modulus than plate GO4 (which contains virgin fibres). The higher stiffness might be explained by the different tow widths between recycled and virgin fibres. Harper at al [3]. also observed that more narrow fibre tows induced a higher stiffness in the resulting material. It could also be explained by the presence of slightly longer recycled fibres (65.2 mm, standard deviation 19 mm) compared to the virgin ones (54.9 mm, standard deviation 29.5 mm) and a more homogeneous fibre length distribution for recycled fibres. Furthermore, plates GO2 and GO3 both resulted in close tensile strengths (about 7% lower for plate GO2). Plate GO4 had a higher tensile strength (see Fig. 9a) than the three other plates. The virgin fibres were sized and had no organic residue on the surface, which would give a better fibre-to-resin adhesion and therefore better resistance in the final material.

In order to allow a good comparison of the results, the strength and modulus values were normalised to a fibre volume fraction of 50%, as shown in Fig. 9c. The properties were normalised to a fibre volume fraction of 50% using a linear fit through the unreinforced

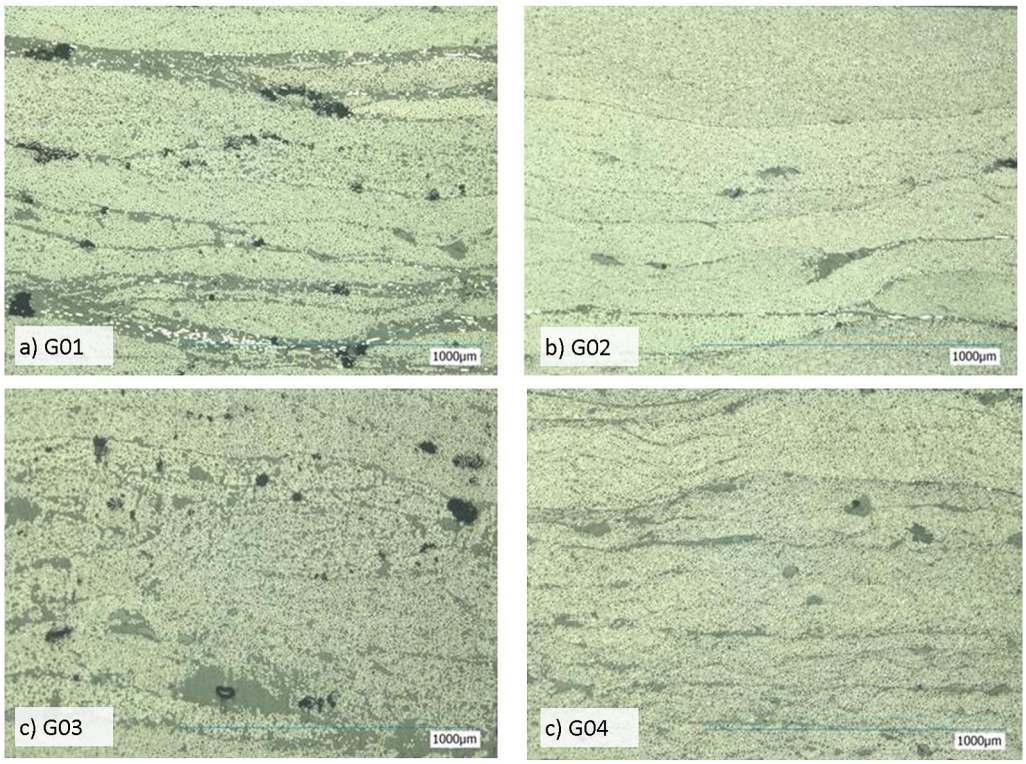


Fig. 8. Micrographs of cross sections of the plates manufactured either with recycled carbon fibres (a, b and c) or virgin carbon fibres (d).

resin properties to be consistent with the method used by Harper et al. [3]. Due to a higher thickness, plate GO3 was slightly stiffer and stronger than plate GO2. Surprisingly, plate GO1 showed a similar strength to plate GO2 despite the incorporated fluffy fibres, but its stiffness was significantly lower than that of plate GO2.

The failure profiles of the tested coupons indicated that the failure was mainly due to tow pull-out for plates GO2 and GO3 and to a less extent for plate GO4 (Fig. 10b, c and d). Instead of being of inter-laminar or intra-laminar type as classically observed for unidirectional laminates, the failure appeared to be more of an inter-tow type due to the specific characteristics of the manufactured materials. For plates GO2 and GO3, made with recycled carbon fibres, no fibre or tow breakage was observed (Fig. 10b and c), indicating that the inter-tow resin rich region and/or the fibre/resin interface was tested, more than the fibre strength. This can be explained by the presence of the residual fibre coating after solvolysis for plates GO2 and GO3, and the presence of the thermoplastic binder for plates GO2, GO3 and GO4. The presence of voids and the discontinuity of the fibres would have also induced a preferred failure pathway.

For plate GO4, some fibre and tow breakage was also observed (Fig. 10d) and a small amount of inter-tow failure and tow pull-out for plates GO2 and GO3,. The fibre/resin interface performed better thanks to the sizing on the virgin fibres and the absence of organic residue. However the sizing may have degraded due to the thermoplastic binder used during the production of the tapes, which could have affected the chemical reaction between the sizing and the epoxy resin during curing.

For plate GO1, the failure profile was modified due to the presence of fluffy fibres (Fig. 10a) and showed a combination of inter-tow failure and fibre breakage. The broken fibres appeared to be the fluffy ones.

The results were compared to results obtained for a composite manufactured with recycled unwoven and continuous fibre fabrics and labelled *r-D2* by Pimenta and Pinho [12] and to results obtained on a composite manufactured by a directed carbon fiber preforming (DCFP) robotised process using discontinuous virgin fibres by Harper et al. [3]. Pimenta and Pinho's material was manufactured with 8 plies of AS4 3 K recycled continuous carbon fibre fabrics. The plates were manufactured with Hexcel M56 epoxy using resin film infusion, leading to a fibre volume content of 50%. The fabric was recovered from M56/37%/280H5/AS4-3 K prepreg having a nominal fibre areal weight of 280 g/m^2. AS4 and T700 carbon fibres (used in this work) have quite comparable tensile properties: 4619 MPa and 4900 MPa for the tensile strength, respectively and 231 GPa and 230 GPa for the tensile modulus, respectively according to the manufacturer's data. Harper et al.'s material was manufactured using a robot-mounted chopper head, which sprayed carbon fibre tows and a thermoset binder onto a tool. 24 K STS-J and 6 K HTA carbon fibres from Toho Tenax were used. Their respective tensile properties are 4000 MPa and 4100 MPa for the tensile strength and 240 GPa for the tensile modulus.

The virgin fibres used in the present work had a higher strength (4900 MPa) than those used by Pimenta and Pinho (4619 MPa) and Harper et al. (4000 and 4100 MPa). In earlier work we showed that the recycled fibres after solvolysis also had a higher strength, based on the assumption of a decrease of 10% maximum due to the recycling treatment [8]. The resin used in this work was also stronger (strength of 80 MPa and modulus of 3 GPa) than that used by Harper et al. (strength of 60 MPa and modulus of 3 GPa). Fig. 9c shows the comparison of the tensile properties of the three types of materials. Pimenta and Pinho's r-D2 material [12] showed a 30% higher strength than that of plate GO2 (for similar thickness and material), however their material was less stiff (about 44% lower). As the woven architecture was retained, there were fewer fibres in the longitudinal direction, but they were perfectly aligned and continuous; furthermore the material was homogeneous. This would explain the higher tensile strength and the lower tensile

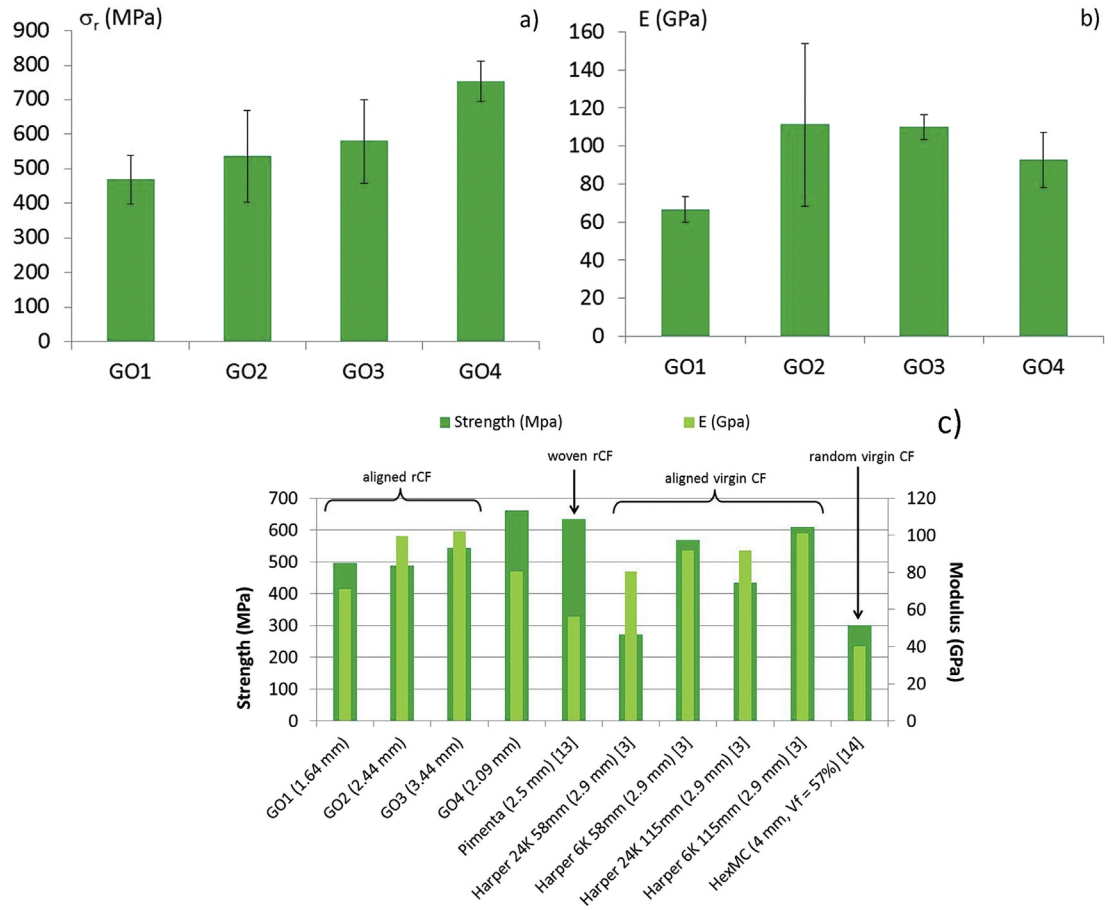


Fig. 9. Tensile strength (a) and modulus (b) measured on four coupons for each plate; c) Comparison with results obtained by Pimenta and Pinho [11] for laminates manufactured with pieces of recycled carbon fibre fabrics (AS4 3 K fibres, 8 plies and epoxy resin film infusion for a total thickness of 2.5 mm, the plate is named *r-D2*) in the warp and weft directions (respectively represented as 1 and 2) and results obtained by Harper et al. [3] for materials manufactured by RTM with preforms made by a Directed Carbon Fiber Preforming (DCFP) robotised process (resulting thickness of 2.9 mm). The values were normalised to a fibre volume fraction of 50% using a linear fit through the virgin resin properties. The values in brackets are the material thickness. Values obtained for a 4 mm thick material made with HexMC containing 57% of high strength carbon fibre in volume according to Hexcel technical datasheet [10] are also indicated.

modulus. Pimenta and Pinho's recycled fibres were reclaimed from ELG Carbon Fibres' pyrolysis process and retained a significant amount of organic residue (Fig. 5e in Ref. [12]). This comparison therefore enables the effect of the fibre physical properties (continuity, shape and distribution) to be appreciated. Continuous and well aligned and distributed fibres would give better reinforcement, however it can be seen from the results obtained in this work that without trying to be perfect the resulting materials exhibited very satisfying properties. It can therefore be expected that by improving the solvolysis process to remove the organic residue and the production of preforms, very good properties could potentially be achieved. This is even more noticeable when the comparison is made with Harper et al.'s results. Although their preform production process was more efficient in terms of alignment (94% of the fibres within ±10° against 89% for plate GO2, 76% for plate GO3 and 91% for plate GO4 in this work) and fibre distribution, the resulting properties were up to half that for 24 K fibres and only 15–20% higher for 6 K fibres than those obtained in this work (Fig. 9c). They used slightly less strong fibres (about −10% in the tensile strength) and resin (about −30% in the tensile strength) than in our present work, giving a resulting tensile strength up to 50% lower with 24 K fibres and up to 25% higher with 6 K fibres than with the recycled fibres in plates GO2 and GO3. Furthermore, they used virgin fibres having all the same length (either 58 mm or 115 mm), whereas in this work the fibre length varied between less than 10 mm–100 mm, with a 60 mm average; and the fibres were recycled. Considering all these differences, the present materials and Harper et al.'s materials were quite comparable. This confirms that the recycled fibres were of good quality and that they could replace virgin discontinuous fibres. The results obtained for a HexMC based material [13], made with high strength carbon fibre bundles of 8 mm width, 50 mm length and giving a 4 mm thick plate with a fibre volume fraction of 57% were also added in Fig. 9c. The fibre bundles are randomly distributed in the epoxy prepreg material. These results confirm again that the recycled fibres were of quality and that their alignment enhanced significantly the tensile properties despite the presence of the residual organic coating and the fibre length distribution.

The shear properties were also measured for the four plates with realigned fibres. The apparent interlaminar shear strength (ILSS) was determined by averaging the values obtained for the failure of the five coupons for each plate and using equation (5), where F is the maximum applied load, b the coupon width and t its thickness.

$$\tau = \frac{3F}{4bt} \tag{5}$$

The failure for each coupon was considered when a crack

Fig. 10. Failure profiles of the tensile-tested coupons: a) GO1, b) GO2, c) GO3 and d) GO4.

occurred inside the material, leading to a loss of stiffness and can be noticed on the curve by a slope change. The results are shown in Fig. 11.

Plate GO4 showed a higher apparent ILSS than plate GO2. It is comparable to plate GO3 although plate GO3 is thicker. As the remanufacturing process was the same for all the plates, it can be assumed that the difference between plates GO2 and GO4, having similar physical properties (Table 2) in terms of ILSS was due to the presence of the residual coating on the fibres and is in accordance to what could be observed from the failure profile after the tensile tests (Fig. 10). Globally the ILSS for the four plates are quite low compared to values from literature, which can be attributed to the discontinuity of the fibres, their length distribution and their alignment. Indeed the comparison of the results obtained for plate GO2 to that obtained by Pimenta and Pinho [12] indicates that the discontinuity, the various lengths and the alignment of the fibres affected significantly the shear properties of the material, considering that the amount of organic residue on the fibre was similar for both materials. Feraboli et al. [14] recovered T700 12 K carbon fibres after acid digestion. The 200 mm long fibres were randomly distributed to produce a 4.3 mm thick plate. The obtained shear strength is comparable to that obtained for 3.44 mm thick plate GO3 despite a much lower fibre volume content of 33%. The values were also in the same range as, although slightly lower than, for a material made with HexMC prepreg as shown in Fig. 11. This lower value, in spite of the alignment of the recycled fibres, can be attributed to a weaker fibre/resin interface due to the presence of the organic residue.

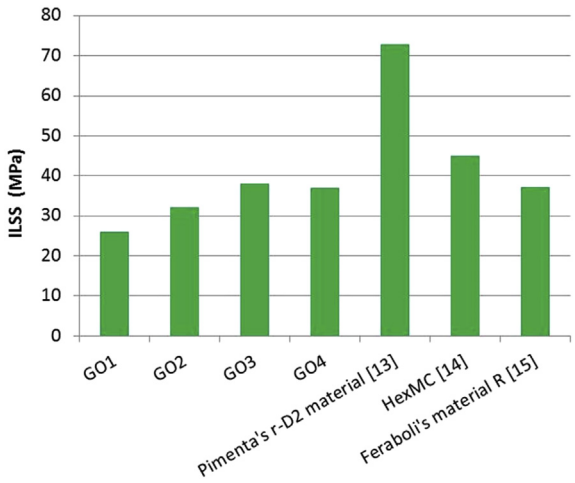


Fig. 11. Measured interlaminar shear strength and comparison with Pimenta's r-D2 material [11], HexMC material [12] and Feraboli's R material [13].

Further investigations are necessary to more deeply understand the effect of the different parameters. These include the fibre orientation distribution, the fibre length distribution and the presence of organic residue at the surface of the recycled fibres.

4. Conclusion

This work has demonstrated that the recycled fibres recovered by solvolysis offer a very good potential of reinforcement and could compete with virgin fibres providing there is a good fibre surface and a good alignment. The intention in this work was not to use perfect conditions (perfectly clean and aligned fibres and no defaults such as fluffy fibres). In these conditions, the obtained materials showed very good properties and that these recycled fibres could replace discontinuous virgin fibres, and even continuous virgin fibres in applications with complex shape, at a lower price. In order to improve the results, it appears necessary to improve the solvolysis process to remove the organic residue at the surface of the recycled fibres and enable a good adhesion with a new resin, and to improve the unweaving/alignment process to make more homogeneous material and a better controlled fibre alignment and distribution. The results could even be further optimised by sorting

the fibres according to their length range, keeping the shorter ones for random mats and the longer ones for realignment, as the alignment level is a function of fibre length [3].

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Access to data can be requested by emailing researchdata@cranfield.ac.uk.

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