A NOVEL TECHNIQUE FOR THE INTERFACIAL CHARACTERIZATION OF GLASS FIBRE -POLYPROPYLENE SYSTEMS

S. Cabral-Fonseca[a], M. C. Paiva[b], J. P. Nunes[b], C. A. Bernardo[b*]

[a] *National Laboratory of Civil Engineering (LNEC), 1700-066 Lisboa, PORTUGAL*

[b] *Department of Polymer Engineering, Universidade do Minho, Campus de Azurém, 4800-058 Guimarães, PORTUGAL*

[*]**Corresponding author:** *C. A. Bernardo*
Department of Polymer Engineering, Universidade do Minho, Campus de Azurém, 4800-058 Guimarães, PORTUGAL

ABSTRACT

In the present work, a new technique was developed to determine by fragmentation tests on single-filament model composites the interfacial properties of two opaque glass-fibre/polypropylene (GF/PP) systems. Fragmentation tests usually require the fibre inside the composites to be completely aligned in the traction direction. Since polypropylene matrices are non-transparent, it is not possible to guarantee *a priori* this condition. Hence, a novel technique was developed to determine the inclination of the filaments imbedded in the composites. The fibre-polymer systems were also evaluated by comparing their interfacial properties with the overall mechanical properties determined on pultruded GF/PP composites. The present work shows that the knowledge of the interfacial properties is important, not only to compare alternative fibre/matrix systems, but also to assess whether the level of adhesion in these systems is adequate to fabricate composites with good mechanical properties.

Keywords: Interfacial properties; adhesion; fragmentation; mechanical properties; composites

1. Introduction

In recent years, thermoplastic matrices have progressively replaced thermosetting ones as reinforcements of continuous fibre composites. In this way, it was possible to obtain more durable and recyclable materials, with good thermal and mechanical properties, without the need to involve chemical reactions [1]. On the other hand, thermoplastic matrix composites require melting and solvent-based processes to pre-impregnate the fibres (prepregs), which are costly and potentially aggressive to the environment. Recently, however, new technologies became available that allow substituting thermoplastic prepregs by low cost powder pre-impregnated materials, that are considered to be environmentally clean [2-4].

To develop technologies such as these it is necessary to know the properties of the materials with which they are going to be utilised. In the case of polymer-fibre systems, the quality of the interface is certainly one such property, as it controls the mechanical properties of the resulting composites. The fragmentation test has been widely used to characterise (ou "characterize"?) the interface of those systems [5, 6]. In this test, a tensile load is applied to a model composite consisting of a single filament embedded in a polymeric matrix and aligned in the loading direction. As the strain increases, the filament reaches failure prior to the matrix due to its much lower strain-to-break. The fragmentation process continues and the filament breaks repeatedly, until the stress transfer through the interface is no longer enough to induce further rupture. The fragments then reach a critical length, l_c, which characterises the interface. When the polymeric matrices are transparent, the fibre fragment lengths can be measured by bright field transmission microscopy. However, when the matrices are non-transparent, this cannot be done directly. In this case, more elaborate techniques, like the dissolution or the burn-off the matrix, or the use of acoustic emission methods, are required. A non-transparent matrix also makes direct verification of the fibre alignment impossible.

In this work, the interfacial characteristics of the GF/PP system were determined by means of the fragmentation test done on model composites. As the polypropylene matrix is non-transparent, a novel technique had to be developed to verify *a priori* the alignment of the fibre embedded in it. In spite of the poor adhesion that normally occurs between polypropylene and glass fibres, the values of the interfacial parameters determined in the present work were quite adequate for the fabrication of engineering composites. To validate this conclusion, GF/PP pre-impregnated materials in tow form (towpregs) were done in a dry-coating powder machine [7, 8] and later pultruded, using a pultrusion-head developed by some of the authors [9]. The mechanical properties of these composites were measured and compared with those theoretically predicted from the properties of the fibres and the matrix. In this case, however, in spite of the adequate value of the adhesion, the mechanical properties were not good, suggesting that the towpreg and the pultrusion processing conditions are yet to be optimised.

2. Theoretical background

2.1. Fragmentation tests

The micromechanical analysis of the fibre-matrix interface was done according to a method based on the Kelly-Tyson approach [10], developed in a previous study of carbon fibres [11]. The method considers that the tensile force acting on a fibre and the shear forces transferred through the interface are in static equilibrium [6], leading to a value of the average interfacial shear strength, $\bar{\tau}$, through the following relationship:

$$\bar{\tau} = \frac{d}{2.l_c}\sigma(l_c) \tag{1}$$

where d is the fibre diameter, and $\sigma(l_c)$ is the tensile strength of the fibre with a length l_c. On its turn, the value of the critical fragment length can be determined from the average length,

$\bar{l}$, assuming that the distribution of the fibre fragment lengths at the end of the rupture process is quasi-symmetrical:

$$l_c = \frac{4}{3}\bar{l} \tag{2}$$

2.2 Single filament tensile tests

It is evident from equation 1 that the calculation of $\bar{\tau}$ implies the determination of the dependence of the fibre strength on the length. In the present work, this dependence was determined performing single filament tensile tests [12] at several gauge lengths, and fitting a two-parameter Weibull distribution to the data, adopting the "weakest link" approximation. This approximation assumes that the fibre is formed by *L* independent links of arbitrary unit length, each link failing or surviving at a given stress level, independently of its neighbours. The strength distribution of each independent link is also described by a simple Weibull distribution, characterised by identical parameters. Then, the Weibull cumulative distribution function $F(\sigma,\sigma_0,m)$, and the corresponding mean strength ($\bar{\sigma}$), are given, respectively, by:

$$F(\sigma;\sigma_0,m) = 1 - \exp\left[-L\left(\frac{\sigma}{\sigma_0}\right)^m\right] \tag{3}$$

$$\bar{\sigma} = \sigma_0 L^{-1/m}\Gamma\left(1+\frac{1}{m}\right) \tag{4}$$

where Γ represents the gamma function.

The parameters of the Weibull distribution were estimated with data determined at all gauge lengths simultaneously, using the "maximum likelihood" method, as developed by Stoner [13]. In this way, a single set of parameters that fit all the gauge lengths tested was obtained. The tensile strength at any gauge length, needed for the calculation of $\bar{\tau}$, was finally calculated from equation 4.

2.3. Mechanical properties of the composites

The tensile strength and modulus of the GF/PP composites in the fibre direction (σ_1 and E_1,) were calculated from the properties of the fibres and the polymer applying the law of mixtures:

$$\sigma_1 = \sigma_f \left(1 - \frac{l_c}{2\,l}\right) v_f + \sigma_m \left(1 - v_f\right) \tag{5}$$

$$E_1 = E_f \left(1 - \frac{l_c}{2\,l}\right) v_f + E_m \left(1 - v_f\right) \tag{6}$$

where σ_f, E_f, v_f and l are, respectively, the tensile strength, modulus, volume fraction and total length of the glass fibres, and σ_m and E_m the tensile strength and modulus of the polymer.

3. Experimental

3.1. Materials

E-glass fibres with 2400 Tex from two different suppliers were used in this work: 357D-AA from *Owens Corning* and P 227 from *Vetrotex*. In the text these fibres are termed "GF-Type 1" and "GF-Type 2". The polymer utilised was 9184B P, a polypropylene from *ICO Polymers France*, black in colour and in powder form, with a density of 0.905 Mg/m^3 and a particle size between 150 μm and 750 μm.

3.2. Polypropylene mechanical properties

The polypropylene tensile properties were determined in an Instron 4302 universal testing machine equipped with a 10 kN load cell and a clip strain gauge extensometer at a cross-head speed of 5 mm/min. The tests were done according to the ISO 527 standard [14], using type 1A "dog-bone" samples cut from compression moulded plates.

3.3. Single filament tensile tests

The mechanical properties of the fibres were measured by tensile testing single filaments, according to a method adapted from the ASTM standard [12, 13], and their diameters determined by laser diffraction with a 10 mW He-Ne laser beam [15 (porque foi retirada a referência do Tzeng?)]. The tensile tests were performed in an Instron 4505 machine equipped with a 2.5 N load cell, at a crosshead speed of 0.5 mm/min, and three different gauge lengths (20, 40 and 60 mm). At least 40 filaments were tested at each gauge length. Fibre modulus and elongation-at-break values were corrected to account for the compliance of the testing system [7].

3.4. Fragmentation test

Polypropylene is a semi-crystalline, non-transparent, polymer. Moreover, a grade with a black pigment was chosen in the present study, so the matrix was quite opaque. Hence, since the fibres in the fragmentation specimens should be aligned in the loading direction, a new method was developed to determine their inclination inside the matrix.

Polypropylene plates were prepared by compression moulding. Six glass filaments were positioned, parallel to each other, straight across a steel frame, glued to the metal in both extremities. Two polypropylene plaques were assembled in both sides and the set compressed in a hot press at 230°C, and then cooled, under constant pressure (100 kN). Six different plaques were prepared, each with six filaments, equally spaced and positioned at their middle thickness. Test specimens, with a “dog-bone” shape and one single filament aligned in the centre, were cut from the plates according to the DIN 53504 standard [16]. The specimens were then stretched in an Instron 4505 testing machine at a speed of 0.5 mm/min, to bring about the repeated breakage of the fibre.

The technique developed to determine the fragment length distribution, characteristic of the fibre-matrix bond, is described in the following paragraphs (see also figure 1):

i) A sample, 10 mm in length, was cut from the central, “dog-bone” shaped, part of the tensile specimen.

ii) The two parts that remain after the cut were used to determine the fibre alignment inside the opaque matrix. For that purpose, the extremities close to the central part were microtomed perpendicularly to the axis of the tensile specimen, and the sections observed by optical microscopy. The position of the glass fibre in the cross-section could be detected, as shown in figure 2. The knowledge of the exact position of both extremities of the fibre allows the verification of its alignment in relation to the axis.

iii) The samples in which the fibre was misaligned more than 2.5° were rejected. The matrix of the remaining samples was then burnt-off inside a ceramic cup. The fibre fragments remaining in the cup were carefully placed under an optical microscope to measure their length. This new procedure made it possible to use only fragmentation data obtained from specimens with well-aligned fibres.

3.5. Composites' fabrication and characterisation

As stated before, composites were produced in two stages. First, towpregs were prepared with polypropylene powder and two different glass fibres (GF-Type 1 and GF-Type 2) in a proprietary dry-coating powder machine [8]. Then, the towpregs were pultruded continuously into composites in a line to which the specifically made pultrusion-head had been adapted [9].

3.5.1. Physical characterization

The composites were analysed for glass fibre and void content, and density. The glass fibre content (weight fraction, w/w) and density were determined by calcination (ISO 1172

standard [17]) and immersion (ISO 1183 standard [18]), respectively. The void content was determined from the experimental density and that calculated from the components' fractions and their individual densities.

3.5.2. Mechanical characterization

The composites were tensile tested according to the ISO 527 standard [14] in an Instron 4483 testing machine equipped with a 100 kN load cell, at a cross-head speed of 2 mm/min.

4. Results and discussion

4.1. Polypropylene tensile tests

The tensile tests generated results typical of a polypropylene matrix. The modulus, yield strength and ultimate strain data were 1.46±0.10 GPa, 23.3±0.5 MPa and 4.8±0.2 %, respectively.

4.2. Single filament tensile test

Table 1 presents tensile data for the glass fibres. For both fibre types a large variation in diameter is observed. As expected, the tensile strength decreases slightly with increasing gauge length. The strength values are marginally lower than those usually reported in the literature for E-glass fibres [19]. The same occurs with the tensile modulus. These small differences between the mechanical properties taken from manufacturer data sheets and those experimentally determined by single filament tests are quite common [7, 15]. They often result from the use of different testing methods (e.g. the tensile testing of “fibre-bundles” instead of single fibres) or from the publication by the manufacturers of values obtained at very short fibre lengths (usually, near the fibre critical length).

The estimated Weibull parameters that fit the experimental strength data at all gauge lengths are presented in table 2. The Weibull parameters allow the estimation of the fibre strength at small lengths, for each fibre type, using equation 4. As figure 3 shows, the predicted Weibull strength varies significantly with the fibre length, especially at small lengths.

4.3. Fragmentation tests

The length of 74 and 44 glass fibre fragments, obtained from well aligned GF-Type 1 and GF-Type 2, respectively, were measured. The corresponding histograms are shown in figure 4 (a) and (b). As can be seen in the figure, the fragment length results correspond reasonably well to a normal distribution. Additionally, the distributions were tested for normality using the normal probability plot and the Kolmogorov-Smirnov test, and statistically accepted as symmetrical [20]. The value of l_c was then determined according to equation *2*. The fragmentation results are presented in Table 3, together with the Weibull strength at the critical fibre length, and the corresponding value of $\bar{\tau}$, calculated from equation 1.

The $\bar{\tau}$ values obtained in this work, 12.7 MPa and 13.8 MPa for the GF-Type 1/PP and GF-Type 2/PP systems, respectively, are slightly larger than those reported in the literature for a similar system [21]. These values are not high, as was to be expected, given the low physical and chemical interactions occurring between the glass fibres surface and an inert matrix such as polypropylene. On the other hand, the results are very close to the theoretical shear strength of polypropylene that would provide an upper limit for $\bar{\tau}$. In fact, the concurrent application of the Tresca and Von Mises [22] criteria leads to values of 11.8 MPa and 12.8 MPa for the GF-Type 1/PP and GF-Type 2/PP systems, respectively. This allows the conclusion that the adhesion of both systems, albeit low, is suitable for the production of composites with good mechanical properties. Moreover, it may be possible to

enhance the interactions between the fibres and the matrix by functionalisation of the latter, grafting polar monomers, as proposed by Mäder and Pisanova [23].

4.4. Characterisation (ou "characterization"?) of the composites

4.4.1. Physical characterisation (ou "characterization"?)

The values of the fibre and void content and the density of the composites are presented in table 4. A high fibre content was observed, especially for GF-Type 1/PP. The void content is also considerably high for both types of composites, indicating a heterogeneous distribution (and possibly insufficiency) of the matrix.

4.4.2. Mechanical characterization

The tensile properties of the composites are shown in table 5, together with the estimated values of the corresponding tensile properties, obtained from equations 5 and 6. A high discrepancy is observed between experimental and theoretical results, namely for the tensile strength. A possible cause for this is the high void content, as well as the irregular distribution of matrix around the fibres detected by Scanning Electron Microscope examinations. In spite of this, the properties, namely the modulus, seem adequate for many engineering applications.

5. Conclusion

The interactions between two types of glass fibres from two different manufacturers and a polypropylene matrix were studied by means of fragmentation tests on single filament model composites. Since the matrix was opaque, a novel technique was developed to determine the inclination of the glass fibre and the fragment length distribution inside the test specimen. The glass fibres were characterised mechanically by single filament tensile tests, and showed similar strength and modulus and a wide diameter variation. Fitting a

two-parameter Weibull distribution to the strength results allowed their estimation at small gauge lengths, as required for the calculation of the interfacial shear strength, $\bar{\tau}$. The values of $\bar{\tau}$ for the two GF/PP systems, that characterise the quality of their interfaces, were similar and relatively small, as expected for the interaction of glass fibres with a matrix that is almost inert from the physical and chemical point of view. However, as the values are close to the theoretical shear strength of the matrix, it can be concluded that the adhesion of the systems is adequate for the production of composites with good mechanical properties. Moreover, it may be possible to improve the level of fibre-matrix adhesion by using an appropriately modified PP matrix.

A high discrepancy was observed between the experimental and theoretical values of the mechanical properties of the composites. Density analyses and SEM observations indicate that this may be due to the many voids generated by the pultrusion process, which still needs to be optimised. The preparation of towpregs with higher polymer contents will probably also improve the quality of the final composites. In any case, the properties of the composites, namely the modulus, still seem adequate for many engineering applications.

Acknowledgements

The authors gratefully acknowledge the support of the Praxis XXI Program to the present work, through the project PULTRU - *Development of New Technologies of Production and Characterisation of Polymer Matrix Composites*. The contribution of the Fundação Luso - Americana para o Desenvolvimento (FLAD) for the mobility of the researchers involved in this project is also acknowledged.

References

[1] Brandt J, Drechsler K, Richter H. In: *The use of high-performance thermoplastic composites for structural aerospace applications*. Proceedings of the 9th International Conference on Composite Materials (ICCM-9), Vol. VI, Madrid, 1993. p. 143-150

[2] Gant BW, Edie DD, Lickfield GG, Drews MJ, Ellison MS. Thermoplastic coating of carbon fibres. ASTM STP 1004 1989; p. 50-61

[3] Iyer SR, Drzal LT. Manufacture of powder-impregnated thermoplastic composites. J. Thermoplastic Composite Materials 1990; 3(4): 325-355.

[4] Miller A, Wei C, Gibson, AG. Manufacture of polyphenylene sulfide (PPS) matrix composites via the powder impregnation route. Composites Part A 1996; 27A(1): 49-56.

[5] Drzal LT, Herrera-Franco P. Composite fibre-matrix bond test. In: Engineered materials handbook, volume 3: Adhesives and sealants, ASM International. 1991.

[6] Fraser WA, Achker FH, di Benedetto AT. In: Proceedings of the 30th Annual Technical Conference on Reinforced Plastics, Vol. 22^{A}, Society of the Plastics Industry, Washington DC, 1975. p. 1-13.

[7] Nunes JP, Bernardo CA, Pouzada ASD, Edie DD. Formation and characterisation of carbon/polycarbonate towpregs and composites. Journal of Composite Materials. 1997; 31(17): 1758-1777.

[8] Nunes JP, Silva JF, Silva F, Marques AT, Novo, PJ. In: Proceedings of the 9^{th} European Conference on Composite Materials (ECCM-9), Brighton, 2000. CD-ROM.

[9] Mota JN, Nunes JP, Pouzada, ASD. In: Proceedings of Annual Technical Conference (ANTEC'2000), SPE, Orlando, 2000. CD-ROM.

[10] Kelly A, Tyson WR. Tensile properties of fibre-reinforced metals: copper/tungsten and copper/molybdenum. J. Mech. Phys. Solids 1965; 13: 329-350.

[11] Paiva, MC, Bernardo CA, Nardin M. Mechanical, surface and interfacial chracterisation of pitch and PAN-based carbon fibres. Carbon 2000; 38: 1323-1337.

[12] ASTM D3379-1975 (Reapproved 1989)

[13] Stoner EG. The Effect of Shape on the tensile strength of pitch-based carbon fibres, USA: Clemson University, 1991, PhD thesis.

[14] ISO 527 - 1993

[15] Paiva MC. Study of mechanical, surface and interfacial characteristics of pitch and pan-based carbon fibres, Portugal: Minho University, 1998, PhD thesis.

[16] DIN 53504 - 1994

[17] ISO 1172 - 1996

[18] ISO 1183 - 1987

[19] Murphy J. Reinforced plastics handbook. Elsevier Advanced Technology. 1998

[20] Cabral-Fonseca SB. Caracterização de interfaces em compósitos de matriz termoplástica reforçada com fibras de vidro longas, Portugal: Minho University, 2001, MSc thesis.

[21] Pisanova EV, Zhandarov EV, Dovgyalo VA. Interfacial adhesion and failure modes in single filament thermoplastic composites. Polymer Composites 1994; 15: 147-155.

[22] Beer FP, Johnston ER. Mechanics of materials. SI Metric Ed. McGraw-Hill. 1987

[23] Mäder E, Pisanova EV. Characterisation and design of interphases in glass fibre reinforced polypropylene. Polymer Composites 2000; 21(3): 361-368.

FIGURE CAPTIONS

Figure 1. Schematic representation of the determination of the fragment lengths and fibre alignment inside a non-transparent fragmentation test specimen. The two micrographs shown, although sketched, correspond to real specimens (note that in this case the fibre is misaligned)

Figure 2. Optical micrograph of the cross-section of a fragmentation test specimen showing the fibre position as a bright circle

Figure 3. Dependence of the strength on the length of the glass fibre, predicted using a two-parameter Weibull distribution

Figure 4. Histograms of the fibre fragment lengths measured on fragmentation specimens. (a) “type 1” glass fibres/PP; (b) “type 2” glass fibres/PP

TABLE CAPTIONS

Table 1. Tensile test data of single filaments.

Table 2. Parameter estimates for the Weibull distributions (experimental strength vs. gauge length data).

Table 3. Critical fibre length, Weibull tensile strength at critical length and corresponding interfacial shear strength.

Table 4. Physical characteristics of the composites.

Table 5. Tensile properties of the composites.

S. Cabral-Fonseca, M.C. Paiva, J.P. Nunes, C.A. Bernardo, *A novel technique for the interfacial characterization of glass fibre - polypropylene systems*

Figure 1

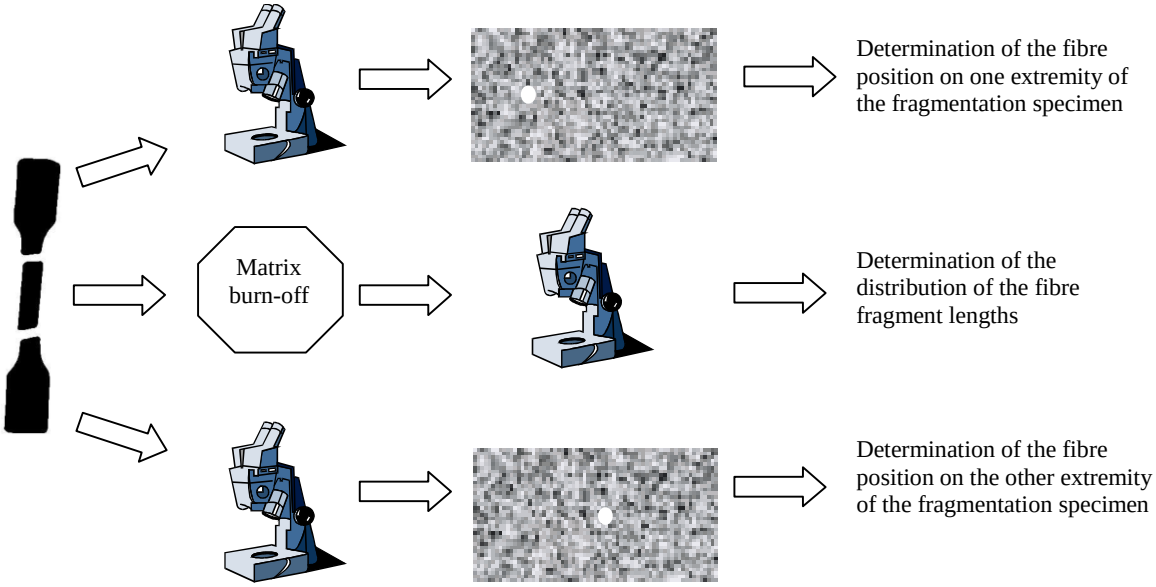


Figure 2

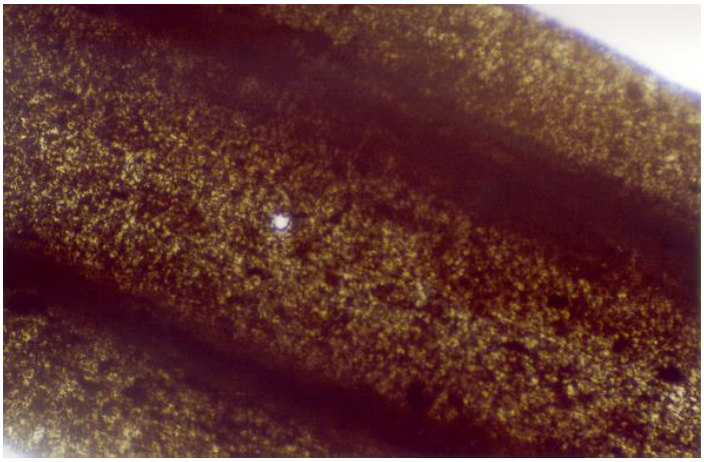


Figure 3

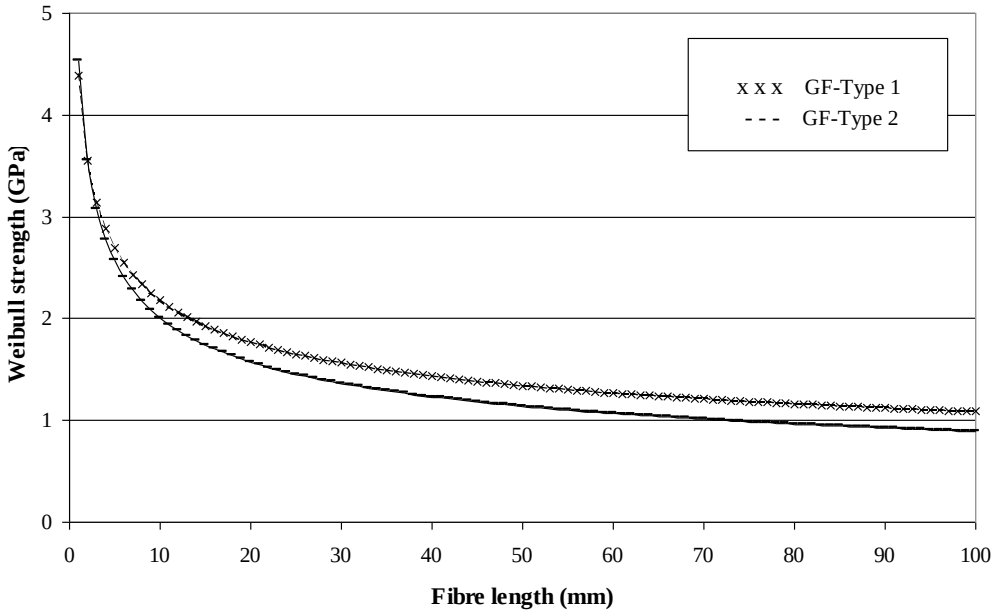
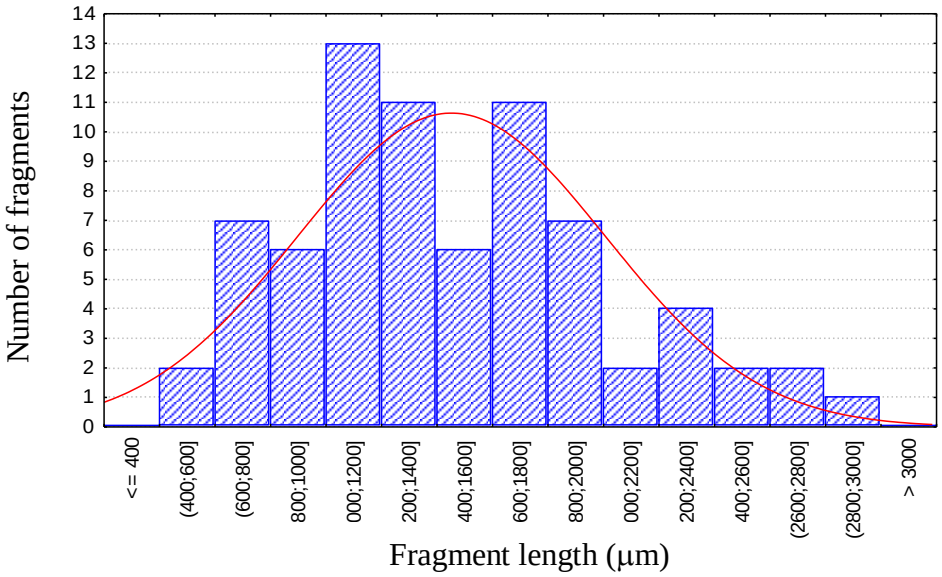

x x x GF-Type 1
- - - GF-Type 2
Weibull strength (GPa)
Fibre length (mm)
0
1
2
3
4
5
0
10
20
30
40
50
60
70
80
90
100

Figure 4

a) 'Type 1' glass fibres/PP



b) 'Type 2' glass fibres/PP

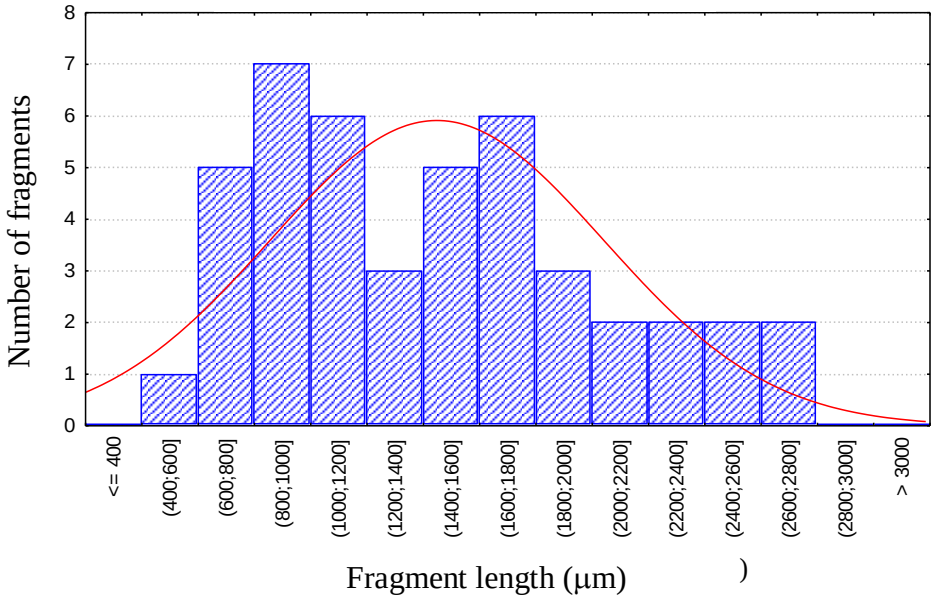


Table 1

Table 1. Tensile test data of single filaments

Sample	No. of fibers tested	Diameter (μm) ± S.D.	Gauge length (mm)	Tensile strength (GPa) ± S.D.	Tensile modulus (GPa) ± S.D.
GF–Type 1	43	13.7 ± 2.0	20	1.7 ± 0.5	62 ± 12
	48		40	1.4 ± 0.5	
	42		60	1.3 ± 0.5	
GF–Type 2	38	14.8 ± 2.4	20	1.5 ± 0.5	60 ± 13
	41		40	1.2 ± 0.5	
	36		60	1.1 ± 0.4	

Table 2

Table 2. Parameter estimates for the Weibull distributions (experimental strength *versus* gauge length)

Sample	m (shape parameter)	σ_0 (scale parameter)
GF–Type 1	3.301	4.888
GF–Type 2	2.827	5.092

Table 3

Table 3. Critical fibre length, Weibull tensile strength at critical length and corresponding interfacial shear strength

Sample	lc (μm)	$\sigma_{Weibull}(l_c)$ (GPa)	$\bar{\tau}$ (MPa)
	± 95% confidence interval		
GF-Type 1/PP	1936 ± 129	3.59 ± 0.1	12.7 ± 1.2
GF-Type 2/PP	1931 ± 180	3.59 ± 0.2	13.8 ± 1.9

Table 4

Table 4. Physical characteristics of the composites

Sample	Glass fiber content (%)		Density	Void content (%)
	w/w	v/v		
GF-Type 1/PP	86.0	68.7	1.75	14.1
GF-Type 2/PP	76.5	53.8	1.55	13.6

Table 5

Table 5. Tensile properties of the composites

Sample	Tensile Strength (MPa)		Tensile Modulus (GPa)	
	Experimental	Estimated	Experimental	Estimated
GF-Type 1/PP	292	900	25.4	42.6
GF-Type 2/PP	305	602	22.3	32.4