Paulina Latko-Durałek*,
Kamil Dydek,
Emila Golonko,
Anna Boczkowska

Mechanical Properties of PETG Fibres and Their Usage in Carbon Fibres/Epoxy Composite Laminates

Faculty of Materials Science and Engineering,
Warsaw University of Technology,
ul. Woloska 141, 02-507 Warsaw, Poland
* E-mail: paulina.latko@inmat.pw.edu.pl

Abstract

This paper reports on a melt-spinning process of glycol-modified poly(ethylene terephthalate) PETG and regranulate of PETG. The effect of the processing temperature and winding reel velocity on the diameters of fibres was examined. It was observed with a scanning electron microscope that the surface of fibres produced from recycled PETG are thicker but smoother than fibres made of fresh PETG. Applying a higher drawing velocity helped to decrease the diameters, which were between 75-150 μm. Under static deformation, fibres showed different behaviour, with higher flexibility and lower strength observed for fibres made of PETG regranulate. Both types of fibre were chopped and added to carbon fibre reinforced polymers as interlayers to investigate their effect on mechanical properties. It was found that the flexural strength decreased in the presence of PETG fibres, while interlaminar shear strength improved, but only in the case of fresh PETG fibres.

Key words: *PETG, fibres, CFRP, mechanical properties, SEM, recycling.*

Introduction

The ability of poly(terephthalate ethylene) PET to undergo strain-induced crystallisation results in its higher density and stiffness, but also reduces its transparency. Therefore for applications in which both strength and appearance are important, glycol-modified poly(ethylene terephthalate) PETG copolymer is more suitable. This is an example of an amorphous polymer in which strain-induced crystallisation does not occur and the polymer remains transparent [1]. PETG is a perfect candidate for thermoforming, extrusion, and injection moulding into different shapes such as sheets, films or fibres. It has good optical properties as well as high chemical and impact resistance. Moreover it is easy to dye and print on, thus it is also used as coloured foil on many types of packaging as a barrier against gas, moisture and solvents. Hence an increasing amount of printed PETG foil waste is being produced. On the one hand, PETG is a fully recyclable polymer, but on the other it cannot easily be processed due to the colours used on the surface, which consist of inorganic chemical compounds. Therefore, to make post-consumer PETG foils transparent, it is necessary to remove all of the colours without destroying the polymer. Depending on the chemical character of the inks, they can be washed out by cationic or anionic surfactant solutions [2, 3]. It is also possible to use another solvent, as applied in this work, which effectively removes all types of ink from PETG foils without destroying their structure [4]. In the next step, the transparent and dried foil flakes were extruded into regranulate pellets, as in a typical mechanical recycling process.

The main goal of this paper is to present one possible application of rPETG as an initial material for the production of fibres in melt-spinning processes. Furthermore fibres produced not only from regranulate PETG but also from fresh PETG were used as interlayers in Carbon fibre reinforced polymers (CFRP). This idea stems from the fact that thermoplastic polymers in the form of fibres [5] or nonwovens [6] are a known way to improve the fracture toughness and interlaminar properties of CFRP [7]. There is also an example of introducing PET [8] into CFRP, but there is a lack of data concerning the usage of PETG, especially regranulate PETG.

Materials and methods

Two types of material were used to produce fibres: PETG with the trade name Eastar™ Copolyester 6763 (Eastman Chemical Company, USA), and pellets of regranulate PETG (rPETG) produced by mechanical recycling of post-consumer printed foil. Both types of fibre were obtained directly from pellets using a laboratory twin-screw extruder (HAAKE MiniLab, Thermo Scientific, Germany), a round shape nozzle with a diameter of 0.75 mm, and a winding reel. Two temperatures were applied (200 °C and 210 °C) and two winding reel velocities (600 rpm and 1000 rpm), while the screw's rotation was kept constant at 40 rpm. An example designation of fibres produced is PETG/200/600, meaning that they were made from fresh PETG at 200 °C and a winding reel velocity of 600 rpm. In total, 8 types of fibres were produced.

Three types of carbon fibre and epoxy resin laminate were produced. A mould consisting of a glass plate was coated with perforated foils instead of a release agent. 16 layers of carbon-epoxy UD prepreg MTM46/HTS5631 (Cytec Industrial Materials, UK) were cut to a size of 300 mm x 150 mm with a lay-up $[0]_{16}$. The prepreg had an areal weight of 150 g/m², containing 35% epoxy resin and 12,000 carbon fibres. Again on the top layer of the prepreg, perforate foil was placed, along with a polyester mat to drain the rest of the epoxy resin. Finally the laminate was covered with nylon foil as a vacuum bag. The mould was placed
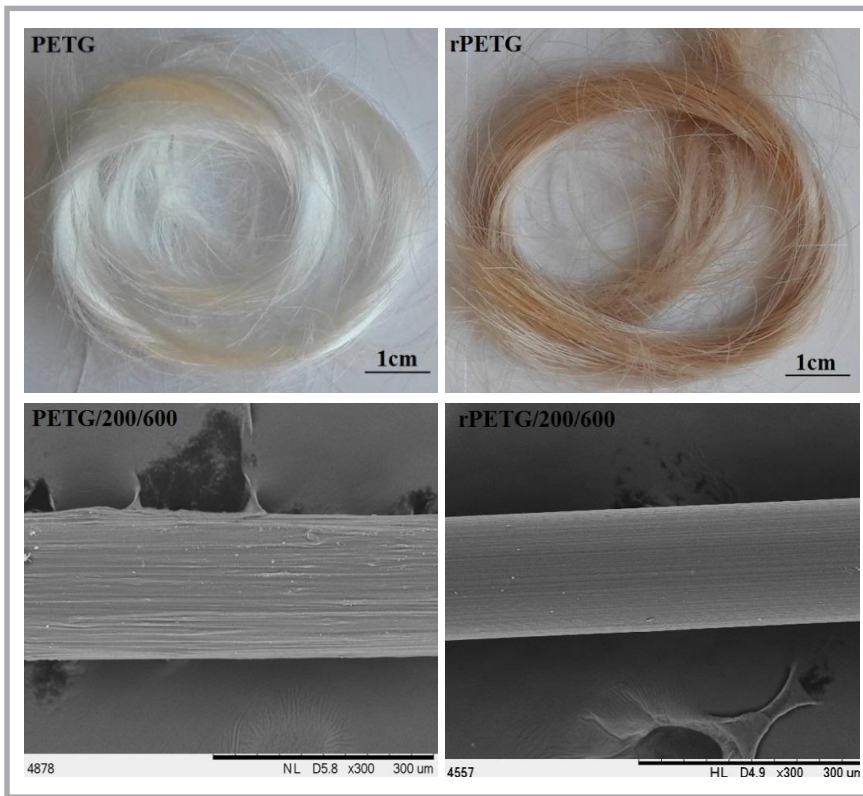
Figure 1. *Appearance of PETG and rPETG fibres.*

in a vacuum oven, heated to 130 °C, and cured for 90 minutes. This laminate is referred to as the reference panel and has a thickness of 2.2 mm. Composite laminates with PETG fibres and rPETG fibres were manufactured in the same conditions as the reference panel. In these cases, the fibres were cut to a length of 7 cm and then distributed randomly by hand between each layer of the prepreg. The amount of PETG and rPETG fibres in each layer corresponds to an areal weight of 12 g/m² and 5 wt% of the total matrix content of the laminate. The volume fraction of PETG/rPETG fibres in the laminate was 0.5 and the thickness was 2.4 mm.

For microscopic observations, fibres were first coated with a thin layer of gold. The diameters of single fibres were measured using a scanning electron microscope (TM 3000 Hitachi, Japan) at a voltage of 5 kV. The average diameters were calculated from at least 100 measured fibres. The quality of composite laminates produced was also analysed by SEM. For this, a small piece of laminate was cut and finished using a polishing machine. The porosity of each laminate was determined from minimum 8 SEM images using ImageJ software. SEM was also applied to analyse the laminates after the ILSS test.

Mechanical properties of the fibres were characterised using a standard tensile machine (EZ-SX Shimadzu, Japan). A single fibre was fixed to a special thick paper frame equipped with metal disks using an epoxy glue. After solidification, the frame with the fibre was clamped to the machine's holder with glue and cut directly before the test. Of each type of fibre, 10 samples were measured at a constant cross-head displacement rate of 10 mm/minute at room temperature. Taking into account the diameter of the fibres, the average tensile strength, elongation at break and Young' modulus were calculated.

Mechanical properties of the laminates were characterised in a three-point bending test (ASTM D790-17) and short beam shear test (ASTM D2344) using an MTS Q/Test 10 universal testing machine. From each test, 8 specimens were cut from different places in the laminates in the direction of the carbon fibres. For the short beam shear, the dimensions of the specimen was 25 mm x 10 mm x 2.2 mm, and for the three-point bending, the dimensions were 42 mm x 12.7 mm x 2.2 mm for the reference panel and 46 mm x 12.7 mm x 2.4 mm for the laminates with inserted fibres. All samples were tested at room temperature at a speed of 1 mm/min.

■ Results and discussion

PETG and rPETG fibres

The melt-spinning process of PETG and rPETG was uncomplicated and fibres had a rather low tendency to break during winding. The noticeable difference between the colour of the fibres produced is presented in ***Figure 1***. Those made from PETG were white, while those from rPETG were slightly pink. Moreover fibres made from rPETG were significantly smoother and flatter on the surface, as is visible from the SEM images presented in ***Figure 1***.

The effect of the processing conditions on fibre thickness was observed by measuring their diameters using SEM (***Table 1***). For PETG, the melt-spinning process was continous when the extrusion temperature was 210 °C. The fibres obtained at 200 °C had smaller diameters. In the case of rPETG fibres, the application of a higher extrusion temperature of 210 °C resulted in a much more difficult process and thicker fibres with diameters over 200 µm. This was caused by a strong Barus effect, enhanced by remaining traces of solvent [9]. Except for these fibres, the rest had diameters around 150 µm. Applying a higher winding reel velocity re-

Table 1. *Mechanical properties and average diameters of fibres produced.*

| Fibre	Average diameter, µm	Tensile strength, MPa	Elongation at break, %	Young's modulus, MPa
PETG/200/600	138 ± 26.9	122 ± 22.9	136 ± 21.0	2437 ± 294.4
PETG/200/1000	126 ± 41.5	157 ± 20.8	111 ± 21.1	3384 ± 696.1
PETG/210/600	151 ± 24.9	92.7 ± 27.5	142 ± 35.9	1555 ± 451.2
PETG/210/1000	75.1 ± 3.87	205 ± 26.5	48.4 ± 11.8	4678 ± 656.9
rPETG/200/600	157 ± 33.9	24.5 ± 4.37	195 ± 56.2	1656 ± 284.2
rPETG/200/1000	139 ± 22.9	25.1 ± 4.05	137 ± 59.7	1467 ± 250.0
rPETG/210/600	272 ± 47.9	8.26 ± 1.45	171 ± 41.6	532.2 ± 96.01
rPETG/210/1000	238 ± 58.7	7.77 ± 2.56	136 ± 21.2	669.2 ± 237.7
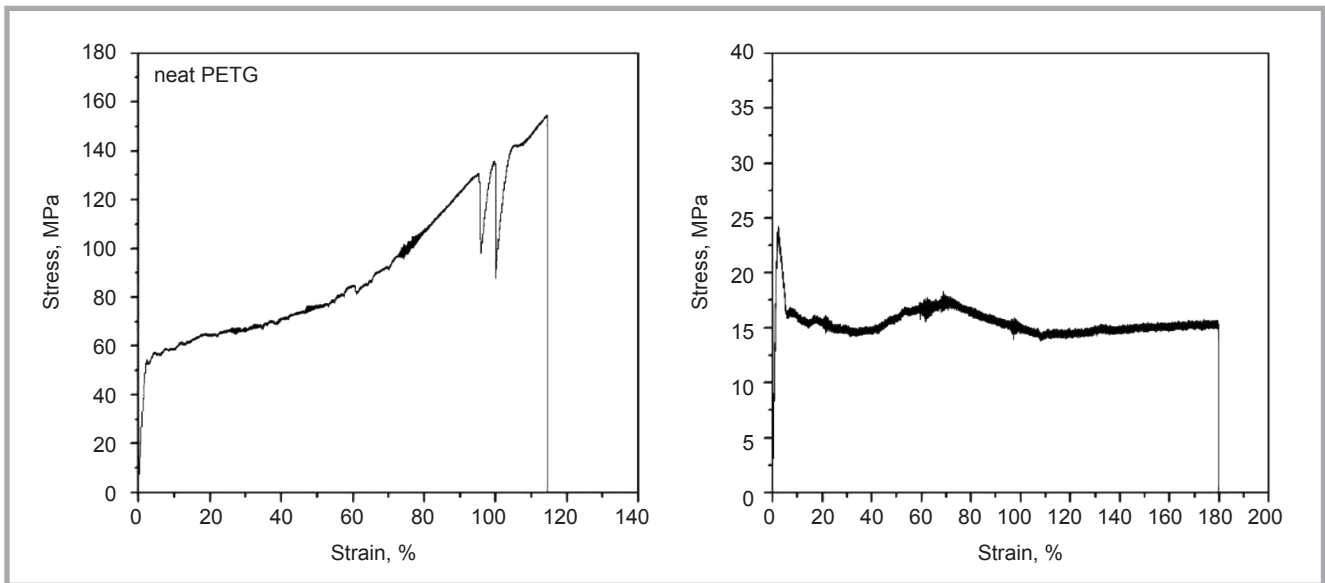
Figure 2. Examplary strain-stress curves for fibres made of neat PETG and rPETG.

sulted in thinner fibres, as was especially observed for PETG processed at 210 °C and 1000 rpm. Decreasing the diameters of fibres is an important step in their further application in CFRP. Using fibres that are too thick decreases the volume fraction of carbon fibres and, consequently, the mechanical properties of the laminates.

Representative strain–stress curves for both types of fibre are presented in *Figure 2*. The first section of the curve is rectilinear and indicates the elastic deformation of the fibres. From this part, Young's modulus was determined. After the yield point was reached, the fibres started to deform more plastically, which is associated with the orientation of the amorphous phase and the formation of a neck in the sample. Interestingly, in PETG, this resulted in strain hardening and increased stiffness, while rPETG fibres deform and become softer, wihout hardening. This difference in mechanical deformation may be related to the shorter polymer chains in regranulate and the effect of plasticisers from the solvent used to remove inks from the PETG foils.

It was noticed that rPETG fibres are more flexible than PETG fibres, as is confirmed by the higher elongation at break values obtained for rPETG in comparison to PETG fibres produced under the same processing conditions (*Table 1*). Moroever fibres which have high elongation also possess lower stiffness. For PETG fibres, the highest Young's modu-
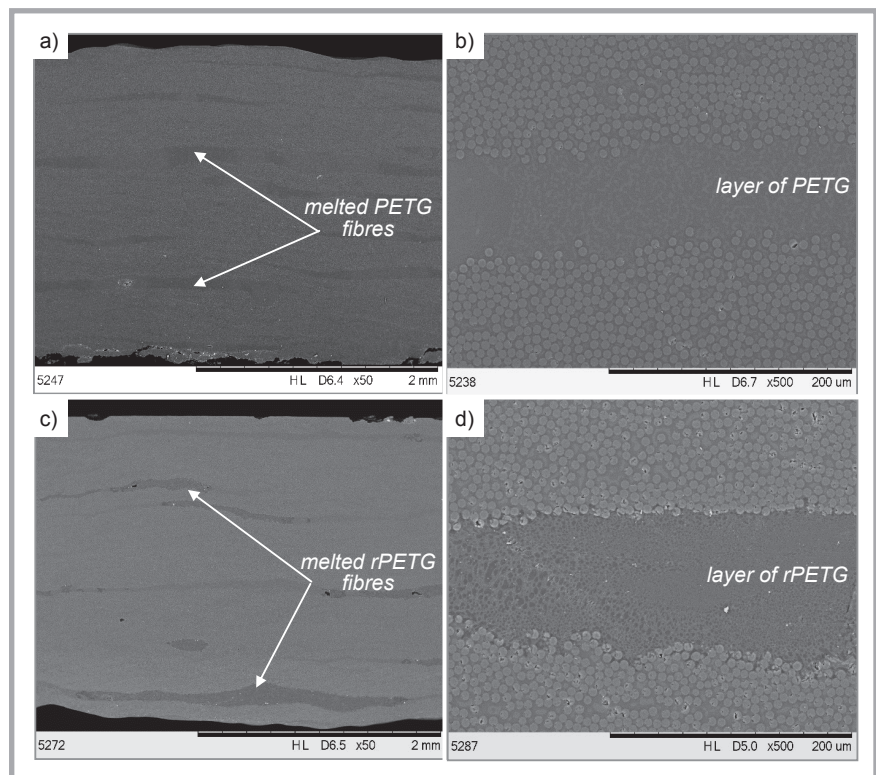

Figure 3. SEM images of laminates reinforced with neat PETG fibres (a, b) and recycled PETG fibres (c, d).

lus achieved was 4.7 ± 0.6 GPa when the processing temperature was 210 °C and the winding velocity 1000 rpm. Increasing the fibre strength by applying higher rotational speed was observed for cotton yarns [10]. For fibres made from rPETG this is only 1.7 ± 0.3 GPa for a processing temperature of 200 °C and winding speed of 600rpm. As expected, the tensile strength is higher for PETG fibres

(205 ± 26.5 MPa) and much lower for rPETG fibres (25.1 ± 4.05 MPa). The reduced strength of fibres fabricated from PETG after recycling is related to shorter polymer chains and the lower molecular weight. However, the values of elongation at break obtained for rPETG fibres are much higher than for recycled PET fibres, for which the elongation was around 22% [11].
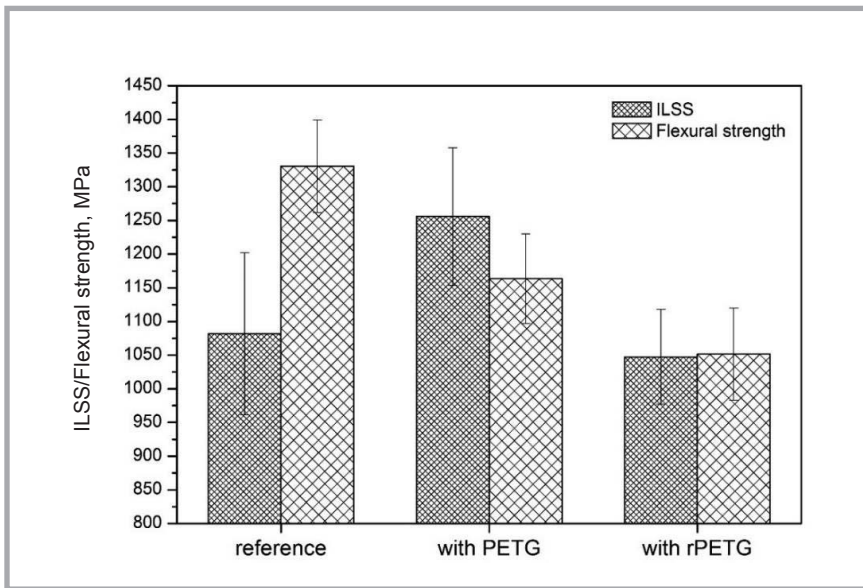
Figure 4. Mechanical properties of CFRP reinforced with fibres of neat PETG and rPETG.
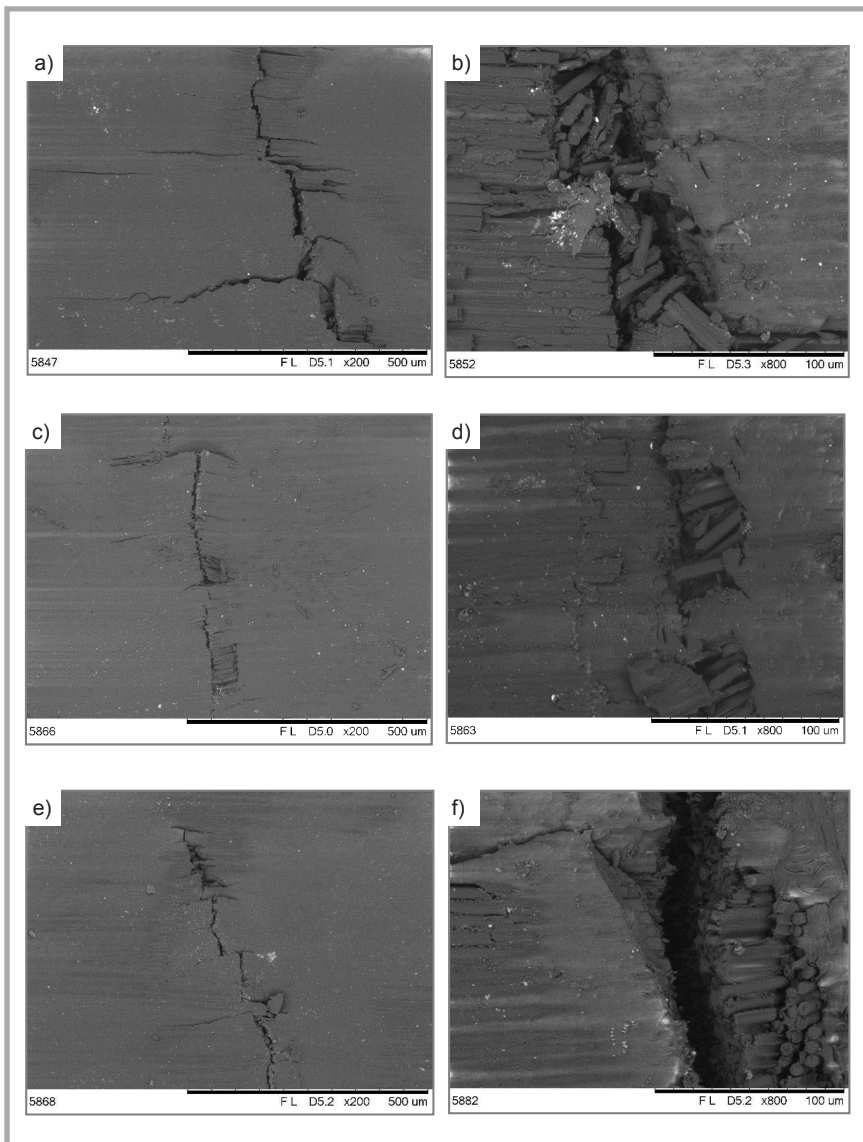

Figure 5. SEM images of laminates after ILSS. Reference panel (a, b), panel with PETG fibres (c, d), panel with rPETG fibres (e, f).

Composite laminates

The incorporation of thermoplastic fibres into CFRP should not affect the quality of laminates, especially as it does not cause the formation of many pores. The value of porosity calculated was 0.14% for the reference panel, 0.01% for the panel with PETG fibres and 0.02% for that with rPETG fibres. It is confimed by the cross-section of the laminates produced with layers of PETG and rPETG fibres, checked by SEM and presented in *Figure 3*. Generally neither laminates have pores or other defects, which means that the usage of thermoplastic fibres as additional layers does not disturb the fabrication process of laminates. The curing temperature and pressure applied resulted in the melting of both types of fibres and the formation of continous layers between carbon fabrics (*Figures 3.a, 3.c*). Images created at a higher resolution (*Figures 3.b, 3.d*) also showed a lack of delamination and cracks in the composites, as well as satisfactory compatibility between PETG or rPETG, carbon fibres and epoxy resin.

The main goal of the introduction of thermoplastic polymer into CFRP is to improve the mechanical properties. *Figure 4* shows that the flexural strength is highest for the reference panel, and is about 200 MPa and 300 MPa less in the case of laminates with PETG and rPETG, respectively. In the case of ILSS, there was a visible improvement of about 20%, but only when PETG fibres were inserted. For laminates reinforced with rPETG fibres, there was no improvement in interlaminar properties. The lack of a significant increase in the mechanical properties of CFRP by insertion of PETG and rPETG fibres could be related to the fact that the diameters of these fibres were too large, which strongly affects the effectiveness of strengthening due to insufficient wetting of carbon fabrics by the thermoplastic resin [12, 13]. The other possibility reported in the literature is inhomogeneous distribution of fibres in each layer, which leads to the formation of a local higher concentration of polymer [14].

SEM images of the laminate's surface after the ILSS test is shown in *Figure 5*. In each case the laminate was not totally destroyed, but there is a visible difference in the broken area. The highest is for the reference panel (*Figure 5.a*). while the highest cohesion was exhibited by the

laminate with PETG fibres (*Figure 5.c*). Moreover in the reference panel the fracture is brittle, showing a lot of broken fibres in the destroyed area. Modification of CFRP with both thermoplastic fibres leads to less brittle fracture and better cohesion of the sample (*Figures 5.d, 5.f*) due to the reinforcement of weak interlaminar regions of the laminates [15]. Interestingly the application of rPETG fibres as interlayers did not result in the same improvement in ILSS but in even lower values of ILSS than for the reference CFRP. From the SEM images (*Figure 5.f*), much deeper and sharp fracture of fibres is seen, which could be related to a trash amount of solvent remaining in rPETG fibres, and consequently with lower adhesion of the polymer to the carbon fabric, or due to higher fibre brittleness.

■ Conslusions

In this study, a melt-spinning process was applied to produce fibres directly from fresh PETG and from regranulate of PETG obtained by washing out the printing from post-consumer foils. It was found that for fresh PETG, a suitable processing temperature is 210°C, which is too high for rPETG. The diameters of PETG fibres were lower than for rPETG, but they have a smoother surface and higher flexibility. Application of both types of fibres as interlayers in CFRP resulted in good quality laminates, but with lower flexural strength, while there was significantly improved ILSS in the case of fresh PETG fibres. SEM images of laminates after the ILSS test confirms that the application of thermoplastic polymer reduced the cracking area of CFRP.

References

 1. Dupaix RB, Boyce MC. Finite strain behavior of poly(ethylene terephthalate) (PET) and poly(ethylene terephthalate)-glycol (PETG). *Polymer* 2005;46: 4827-38.
 2. Gecol H, Scamehorn JF, Christian SD, Riddell FE. Use of surfactants to remove solvent-based inks from plastic films. *Colloid Polym Sci.* 2003; 281: 1172-7.
 3. Songsiri D, Min SS, Scamehorn JF, Osuwan S, Ellis JW. Use of cationic surfactant to remove solvent-based ink from rigid high density polyethylene surfaces. *Colloids Surfaces A Physicochem Eng Asp.* 2002; 204: 261-9.
 4. Piesowicz E, Boczkowska A, Latko P, Putynkowski G, Przetakiewicz W, Paszkiewicz S, et al. A method for recovering polymer from printed PETG substrates. EP 2987822 B1. 2014.
 5. Hogg PJ. Toughening of thermosetting composites with thermoplastic fibres. *Mater Sci Eng A.* 2005; 412: 97-103.
 6. Zhu L. Investigations on damage resistance of carbon fiber composite panels toughened using veils. Chinese J Aeronaut. Chinese Society of Aeronautics and Astronautics; 2013; 26: 807-13.
 7. Ramirez V a, Hogg PJ, Sampson WW. The influence of the nonwoven veil architectures on interlaminar fracture toughness of interleaved composites. *Compos Sci Technol. Elsevier Ltd*; 2015; 110: 103-10.
 8. Mureau AS, Peijs MT. Blends of poly(ethylene terephthalate) and epoxy as matrix material for continuous fibre reinforced composites. *Plast Rubber Compos.* 2001; 30: 213-21.
 9. Elias HG. Filaments and Fibers. Chapter 38-Filaments Fibers Macromol. 1-Structures Prop. Second Ed. Springer; 1984.
10. Yang R, Gao W, Xue Y. Airflow Characteristics During the Rotor Spun Composite Yarn Spinning Process. *FIBRES &TEXTILES in Eastern Europe* 2017; 25: 13-17.DOI:10.5604/01.3001.0010.4621.
11. Vadicherla T, Saravanan D. Effect of blend ratio on the quality characteristics of recycled polyester/cotton blended ring spun yarn. *FIBRES &TEXTILES in Eastern Europe*. 2017; 25: 48-52. DOI: 10.5604/12303666.1227875.
12. Beckermann GW, Pickering KL. Mode I and Mode II interlaminar fracture toughness of composite laminates interleaved with electrospun nanofibre veils. *Compos Part A Appl Sci Manuf. Elsevier Ltd*; 2015; 72: 11-21.
13. Xu H, Tong X, Zhang Y, Li Q, Lu W. Mechanical and electrical properties of laminated composites containing continuous carbon nanotube fi lm interleaves. *Compos Sci Technol. Elsevier Ltd*; 2016; 127: 113-8.
14. Wong W Y D, Lin L, McGrail PT, Peijs T, Hogg PJ. Improved fracture toughness of carbon fibre/epoxy composite laminates using dissolvable thermoplastic fibres. *Compos Part A Appl Sci Manuf.* 2010; 41: 759-67.
15. Nash NH, Young TM, McGrail PT, Stanley WF. Inclusion of a thermoplastic phase to improve impact and post-impact performances of carbon fibre reinforced thermosetting composites – A review. *Mater Des. Elsevier Ltd;* 2015; 85: 582-97.