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Recycling effects on microstructure and mechanical behaviour of PEEK short carbon-fibre composites

J. R. SARASUA*, J. POUYET
Laboratoire de Mécanique Physique, CNRS URA n 867, Université de Bordeaux I,
33405 Talence, France

The effect of recycling on microstructure and mechanical properties has been evaluated for injection-moulded poly-ether-ether-ketone (PEEK) composites reinforced with 10% and 30% short carbon fibres. Microstructure characterization was carried out by determining fibre length distributions, PEEK molecular weight, and by SEM observations of fracture surfaces before and after processing. These studies reveal degradation of fibres and matrix during recycling. Tensile Young's modulus and strength, as well as impact strength reductions are presented for recycled composites.

1. Introduction

Recycling of plastic wastes, with or without reinforcement, is an interesting possibility from an ecological and economical point of view. The recycling studies carried out with unreinforced polymeric systems have usually focused on the role of macromolecular chain degradation in the loss of mechanical properties [1, 2].

However, in the case of short fibre-reinforced thermoplastics (SFRTP), the applicability of the recycled material will not be only limited by the hypothetical thermo-mechanical or chemical degradation that the polymeric matrix might experience, but also by the effects that such an operation could have on the whole structure of the composite involving matrix, fibres and fibre–matrix interface [3].

Injection-moulded short-fibre composites are structurally complex materials whose microstructure is set up during the manufacturing process. For that reason their properties are hardly predictable. Studies concerning the orientation state of fibres [4–6], fibre length [7, 8] fibre–matrix interface [9] and matrix crystallinity [10–12] demonstrate, for the understanding of final mechanical properties of the SFRTP pieces, that the relationships between processing, microstructure, and properties are of greatest importance.

In this work, the possible use of recycled short carbon fibre-reinforced composites of poly-ether-ether-ketone (PEEK) was evaluated. With this aim microstructure characterization was first realised. Then, static and impact mechanical behaviour was determined. Results are discussed relating the manufacturing process, structure and properties.

2. Experimental procedure

2.1. Materials and manufacturing

The materials studied were poly-ether-ether-ketone (PEEK) reinforced with 30% and 10% (weight content) of short carbon fibres. The 30% composite and the unreinforced PEEK supplied by ICI (trade names "Victrex PEEK 450 CA 30" and "Victrex PEEK 450 G", respectively), were melt blended by extrusion to obtain the 10% carbon fibre-reinforced composite. Blending was carried out in a Brabender Plasticorder PLE-650 extruder machine with a screw aspect ratio $L/D = 25$ at 400 °C. Extruded bands of 0.5 mm thickness were obtained and then pelletized by grinding. The composite materials studied in this work were named CPEEK30 and CPEEK10, respectively. In order that both composites should be processed under the most similar conditions, the 30% reinforced materials were also previously extruded.

CPEEK10 and CPEEK30 were submitted to one ($n = 1$), three ($n = 3$), five ($n = 5$) and ten ($n = 10$) successive injection cycles in a Battenfield BA230 preplasticizing injection machine at a barrel temperature of 380–390 °C. Injection pressures and speeds were kept constant and the mould temperature was fixed at 120 °C. The crystallinity degree of PEEK under these processing conditions is $X_c = 30\%$ [13]. At the end of each cycle, tensile specimens (ASTM D-638, type IV) and impact specimens (ASTM D-256) were obtained.

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* Author to whom all correspondence should be addressed.
Present address: Department of Science and Technology of Polymers, Chemistry Faculty, University of Basque Country, PO Box 1072, 20080 San Sebastian, Spain.

2.2. Microstructure characterization

2.2.1. *Image analysis of optical micrographs*

A fibre suspension was prepared with washed and filtered fibres in a diluted poly (methyl methacrylate) solution in chloroform after dissolving the matrix in concentrated sulphuric acid. A microscope slide was filled with this suspension. Then the solvent was evaporated and a good dispersion of fibres in a transparent polymer film was obtained. Fibre images were taken from a Leitz Aristomet optical microscope, recorded in a Sony magnetoscope and then analysed by a commercial Image Analysis software (SAMBA 20005 from ALCATEL). Measurements were carried out counting at least 500 fibres for each sample. Finally, a statistical software was used to obtain fibre length distribution histograms.

2.2.2. *Scanning electron microscopy (SEM)*

Fracture surfaces of tensile tested specimens were observed in a scanning electron microscope (SEM) Hitachi S-2700 at 15 kV. Samples were previously gold-coated to avoid electrical charges in a sputter coater SC 500 from Bio Rad Microscience Division.

2.2.3. *Viscosimetry*

The molecular weight, $\bar{M}_w$, of PEEK matrix in the injection-moulded composite pieces was determined before and after recycling by viscosimetry of concentrated sulphuric acid solutions before and after recycling. Mark–Houwnik coefficients reported in the literature [14] were used as follows:

$$[\eta]_{25\,^\circ\mathrm{C}} = 6.195 \times 10^{-5}\,(M_w)^{0.94}(\mathrm{d}l/g) \qquad (1)$$

The intrinsic viscosity at 25 °C, [4] 25 °C is given in decilitre per gramme units.

2.3. Mechanical characterization

2.3.1. *Tensile tests*

Tensile tests of injection-moulded specimens (ASTM D-638, type IV) were conducted in an Instron 4301 universal testing machine at 5 mm min^{-1} and 25 °C to determine their stress–strain behaviour. Young's moduli, E, yield and break stress, σ_y, σ_b, their respective strains, ε_y, ε_b, and the ultimate energy were determined as the mean value of at least six determinations.

2.3.2. *Impact tests (IZOD)*

IZOD impact tests (ASTM D-256) were carried out with a 25 J pendulum equipped with a ATS/MK3 fractoscope system (from CEAST) on notched specimens. The impact strength was determined as the mean value of the energy to break by unit thickness over ten determinations.

3. Results and discussion

Fig. 1 shows the fibre-length distribution histogram of commercial granules of 30% short carbon fibre PEEK composite. The study of the effect of processing on fibre length was carried out for CPEEK30 and CPEEK10 comparing the average values obtained from composite fibre-length distribution histograms at different numbers of cycles, n. These histograms showed the fibre-length distribution was narrowed and the average fibre-length values decreased as the number of injection cycles increased. Fig. 2 represents the average length of carbon fibres in 10% and 30% composites submitted to a different number of injection cycles. It is noted that carbon fibres are significantly abraded during the processing. At $n = 3$ the fibre length had fallen to half of the initial value in the granules. Between $n = 1$ and $n = 3$ the fibre of CPEEK10 exceeds that of CPEEK30.This is attributed to the fibre attrition produced by fibre–fibre interactions. At a higher number of cycles, the role of fibre-reinforcing content is not as relevant as other factors leading to fibre degradation, such as fibre contact with processor surfaces, viscose forces developed in the polymeric melt, or grinding between two subsequent processing cycles. No differences could be found in fibre length between CPEEK10 and CPEEK30. At $n = 5$, fibre length was reduced to around a quarter of the value in CPEEK30 granules. Subsequent injection cycles do not substantially modify the value obtained at $n = 5$.

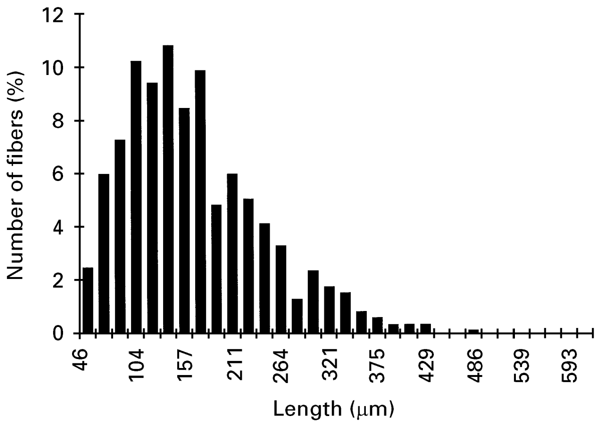

Figure 1 Fibre-length distribution histogram of raw 30% short fibre-reinforced PEEK.

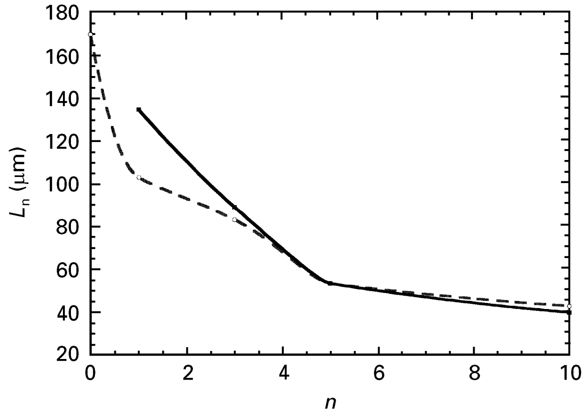

Figure 2 Average fibre length of PEEK carbon fibre composites versus the number of injection cycles, n. (– – –) CPEEK30, (——) CPEEK10.

Fibre orientation and fibre–matrix adhesion were studied by SEM. Fig. 3 shows the fracture surface

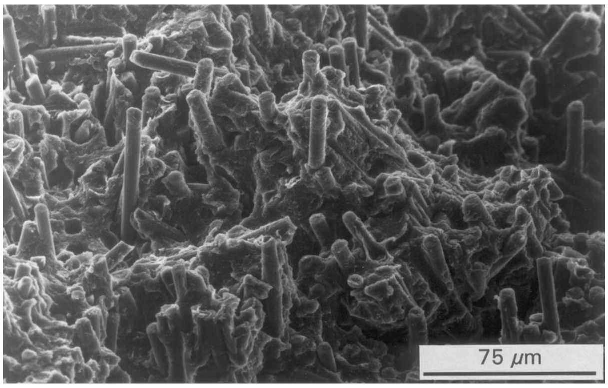

Figure 3 Fracture surface scanning electron micrograph of 10% carbon fibre composite (CPEEK10, $n = 1$).

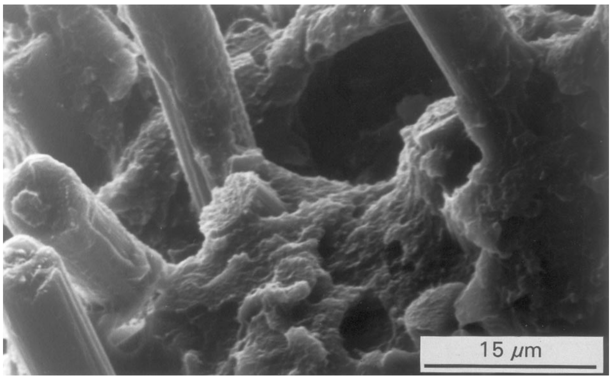

Figure 4 Fracture surface scanning electron micrograph of 30% carbon fibre composite (CPEEK30, $n = 1$).

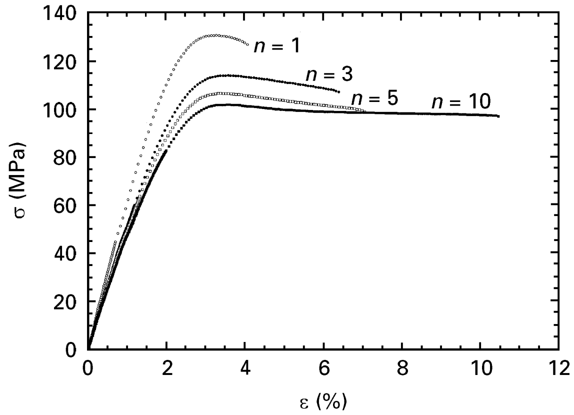

Figure 5 Stress–strain curves of recycled CPEEK10.

TABLE I Tensile properties of CPEEK10 at different numbers of injection cycles, *n*

	n			
	1	3	5	10
E (GPa)	6.2 ± 0.1	5.3 ± 0.2	5.1 ± 0.2	4.9 ± 0.1
σ_y (MPa)	130 ± 1	113 ± 1	107 ± 1	101 ± 1
ε_y (MPa)	3.2 ± 0.1	3.4 ± 0.1	3.3 ± 0.1	3.5 ± 0.1
σ_b (MPa)	125 ± 3	105 ± 1	100 ± 1	95 ± 1
ε_b (MPa)	3.5 ± 0.2	6.4 ± 0.5	7.0 ± 0.6	11.4 ± 0.8

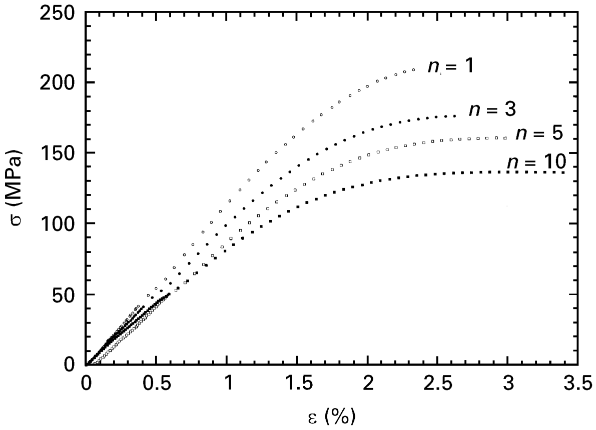

Figure 6 Stress–strain curves of recycled CPEEK30.

micrograph of CPEEK10 submitted to one injection cycle. As can be observed, most of fibres lay in the perpendicular direction with regards to the plane of the micrograph. This indicates that, in these composites constituted of three layers [15], there is a high fibre alignment along the melt-flow direction which corresponds to the direction of strain during the tensile tests. Moreover the pullout length is seen to be small. The magnified fracture surface in Fig. 4 shows the carbon fibres recovered by the matrix. This is a demonstration of the good adhesion of PEEK to carbon fibres. Reprocessing seems to be unfavourable for fibre alignment because of the lower inertia and higher mobility of short fibres [16]. At the fibre–matrix interface of recycled materials, a comparison of micrographs of composites submitted to one and ten injection cycles indicated no substantial modifications in fibre–matrix adhesion.

3.1. Mechanical properties

The tensile stress–strain curve of 10% carbon fibre-reinforced PEEK at different numbers of injection cycles is shown in Fig. 5. The evolution of stress at $n = 1$ shows an initial linear increase of stress followed by shear yielding, after which fracture is produced rapidly. As the number of injection cycles is increased, the tensile behaviour approaches that of unreinforced PEEK: Young's modulus and tensile strength are reduced, and quantitatively important improvements are obtained in ductility (see Table I).

The tensile behaviour represented in Fig. 6 shows the 30% carbon fibre composites near the ductility threshold defined by the yield point. In this case the key factor determining the failure mode is fibre content, and recycling does not significantly modify the high deformation properties of these materials. For that reason the improvements of elongation at break are not remarkable, and the main effect of recycling is to reduce stiffness and strength (Table II).

The most important evolution of the mechanical properties described above is produced during the initial five injection cycles. Taking into account that fibre attrition took place principally between $n = 1$ and $n = 5$, it is demonstrated that fibre length plays a major role in the mechanical behaviour of recycled composite pieces. The contribution of matrix

TABLE II Tensile properties of CPEEK30 at different numbers of injection cycles, n

	n			
	1	3	5	10
E (GPa)	12.1 ± 0.1	10.3 ± 0.4	9.7 ± 0.2	8.5 ± 0.2
σ_b (MPa)	211 ± 1	178 ± 1	160 ± 1	138 ± 1
ε_b (MPa)	2.4 ± 0.1	2.7 ± 0.1	2.9 ± 0.2	3.4 ± 0.3

TABLE III Ultimate energy (static tensile ASTM D-638) and impact strength (dynamic IZOD ASTM D-256) short carbon fibre composites at different numbers of injection cycles

n	CPEEK10		CPEEK30	
	Ultimate energy (J)	Impact strength ($\mathrm{J\,m^{-1}}$)	Ultimate energy (J)	Impact strength ($\mathrm{J\,m^{-1}}$)
1	2.8 ± 0.1	83 ± 6	2.3 ± 0.1	86 ± 8
3	4.4 ± 0.4	65 ± 4	2.4 ± 0.1	84 ± 3
5	4.2 ± 0.9	57 ± 16	2.3 ± 0.4	80 ± 3
10	6.3 ± 2.4	51 ± 5	2.6 ± 0.3	65 ± 4

degradation during recycling plays a secondary role (PEEK molecular weight was found to decrease from, $\bar{M}_w = 25\,000$ at $n = 1$ to $\bar{M}_w = 18\,000$ at $n = 10$) as is reflected by the quantitative small differences found in stiffness and tensile strength between $n = 5$ and $n = 10$ when fibre length is nearly constant. In a previous work in which PEEK was unreinforced or reinforced by short glass fibres, recycling was not observed to degrade the PEEK matrix [17]. The degradation of PEEK in the presence of carbon fibres could suggest a chemical reaction between PEEK chemical structure and some product of the pyrolysis of carbon fibres (unstable at these high processing conditions). Finally, the possibility of misalignment of fibres induced by recycling is also likely to contribute to some extent to the observed reduction of low deformation properties.

Table III shows the impact resistance (IR) behaviour of CPEEK10 and CPEEK30 with recycling as well as the values of ultimate energy obtained from tensile measurements (UTE). UTE of these composites is seen to increase both as the number of reprocessing cycles is increased and as the fibre content is decreased. We have seen above that recycling leads to ductility improvements and strength reductions in tensile tests. These improvements in UTE evince the sensitivity of this energetic parameter to ductility changes induced by microstructure variations during recycling.

Impact results show the impact strength is reduced by reprocessing and by low fibre contents. Thus, inverted trends are found between these two impact and tensile energy parameters with recycling. The differences are attributed to fragility produced by high strain rates, and notches present in impact tests that make IR basically a strength-dependent parameter.

4. Conclusion

The effects of recycling on microstructure and mechanical properties of injection-moulded PEEK short carbon fibre composites have been studied. Although matrix degradation and some misalignment of fibres during recycling could contribute to some extent to the evolution of tensile properties, the observed reductions in Young's modulus and tensile strength and ductility improvements must be explained principally in terms of fibre degradation occurring during the process.

The impact strength of 30% carbon fibre PEEK is higher than that of 10% carbon fibre-reinforced PEEK, and both are decreased by recycling. This is attributed to brittleness induced by the high strain rates involved in the impact tests which make the impact strength a strength-dependent property.

Recycling of PEEK reinforced with short carbon fibres is a way of manufacturing new composite materials. The microstructure–mechanical properties relationships show that, despite the fact that damage to the fibres can be important during the process, properties are good enough for these materials to be useful for some specific uses.

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