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Mechanical characterization of melt spun fibers from recycled and virgin PET blends

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Abstract In this study two Poly (Ethylene Terephthalate) (PET) polymers obtained from mineral water bottles and a virgin fiber grade PET polymer were investigated. In order to improve their properties when reprocessed at high temperatures, recycled polymers were blended with virgin one. Thermal and rheological properties of extruded recycled/virgin (PET-V/R) blends showed a good microstructural stability compared to extruded pure recycled polymers. Mechanical behaviour of melt spun fibers obtained from recycled/virgin blends were investigated in static (tensile) and dynamic (DMA) modes and gave interesting properties. Fatigue failure of fibers was also studied and resulting fracture morphologies were analysed by Scanning Electron microscopy (SEM).

Introduction

A major problem faced by the plastics industry is that of waste disposal. Recycling material would appear to offer a solution which is satisfactory in terms of preventing environmental pollution. Increasing interest has recently, been focused on the recycling of plastic wastes, especially Poly (Ethylene Terephthalate) (PET). PET recycling represents one of the most successful and widespread examples of polymer recycling. The main driving force responsible for the increased recycling of post-consumer PET is its widespread use particularly in the beverage industry [1].

Recycling of PET can be carried out according to different strategies. In particular, the post-consumer PET can be depolymerised to re-use the regenerated monomers as raw materials for a new polymerisation process (chemical recycling) or can be reprocessed after washing and grinding (mechanical recycling). Otherwise, a common problem faced during mechanical recycling of PET is the degradation of the polymer that leads to a reduction of its average molecular weight (MW) [2], as well as to mechanical properties deterioration, [3]. In fact, during processing, PET undergoes three different degradation phenomena, namely thermal, mechanical and hydrolytic chain scission. According to Regel [4], hydrolytic chain scission is the fastest and the most dangerous degradation process. Thermal exposure, as well as shear degradation with the simultaneous presence of retained moisture and physical contaminants (PE, PVC, adhesives…), will also lead to a remarkable MW loss during reprocessing at high temperatures. These losses will result in plastic material with reduced rheological and mechanical properties. Using recycled polymer in blend with virgin polymer of the same nature is a common solution for upgrading post-consumer materials. Scarfato and La Mantia [5], has studied blends of recycled PA6 and virgin PA. They found that the blends prepared in specific conditions show rheological and mechanical properties close to those of the virgin polymer. Kukaleva et al. [6], investigated blends of recycled and virgin HDPE polymers. They stated that mechanical properties (modulus and elongation) of the blends have predictable linear behaviour. Earlier, Wenguang [7]

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prepared and characterised homopolymer blends of recycled/virgin PVC. He found that the properties of the blends are between those of the pure compounds.

The aim of this work is the processing by mechanical recycling of PET polymers in order to obtain melt spun yarns. Our method consists in using blends of recycled and virgin PET polymers to maintain the properties of the recycled polymer sufficiently high during different processing steps (extrusion, spinning, drawing…).

Experimental

Materials

Three types of materials were investigated in this study: two PET bottle waste polymers and a virgin one. Chips of crushed and cleaned bottles, purchased from an industrial plastic waste collector, were used as the source for recovered PET materials. Recycled PET (PET-A) comes from blue post-consumer bottles and recycled PET (PET-B) arises from heterogeneous deposits of various coloured PET bottles (white, green …etc). A fiber grade PET (PET-C), kindly provided by Rhodia, was used as the virgin PET resin. The characteristics of these three starting polymers are recapitulated in Table 1.

It should be pointed out that PET chips or flakes have to be dried before extrusion. otherwise the molecular weight will be considerably reduced. The moisture content of PET should not exceed 0.005%. So, recycled chips and virgin pellets were dried under vacuum during 12H at 100 °C in order to eliminate the residual moisture content. Then, blends of virgin/recycled PET were obtained using a Haake–Rheocard twin screw extruder under the following conditions: die temperature 270 °C, extrusion speed 40 rpm and residence time of 5 mn. The extrudate is cooled in water then passed through a pelletizing unit. We considered the following compositions of blends: 90/10, 70/30, 50/50 and 25/75 (PETV/ PETR w/w).

The blends' pellets thus prepared were used to spin PET filaments. A laboratory scale melt spinning unit was employed for this study with the following configuration: 1–10 cm/min extruder speed, single-hole spinneret type, 1 mm spinneret die dimension, a take-up speed of 150 m/min, and an extrusion temperature of 270 °C. A further hot drawing (λ = 10×) of ''as spun'' filaments at 110 °C is then processed to enhance their mechanical properties. The drawing ratio is calculated from the ratio of the winding roll speed on the delivery roll speed.

Methods of analysis

A TA Instruments calorimeter was used to study the thermal behaviour of blended PET polymers. The swept temperature lies between 30 and 280 °C under nitrogen atmosphere and an empty capsule as reference. The calorimeter is attached to a thermal analysis data station that calculates crystallisation temperature, T_c, melting temperature, Tm, enthalpy of crystallisation, ΔH_c, enthalpy of melting, ΔH_m and cold crystallisation enthalpy ΔH_{cc} of samples. The percent of crystallinity, χ, for all PET samples was calculated from Eq.1 [8], whenever a crystallisation exotherm was present during heating:

$$\chi(\%) = \frac{\Delta H_m - \Delta H_{cc}}{\Delta H_m^0} * 100 \tag{1}$$

where ΔH_m is the melting heat of the polymer, ΔH_{cc} is the cold crystallisation heat and $\Delta H_m^0 = 32.5\,\text{cal/g}$ [9], is the heat of fusion of a 100% crystalline PET.

Steady shear rheological measurements on PET blends were carried out on a dynamic rheometer MCR500 from Physica. The rheological properties of molten materials were determined using 25 mm parallel plates geometry. Shear rate ranging from 0.1 to 300 s^{-1} was investigated.

Tensile mechanical properties of blends' fibers, such as tensile modulus, elongation and stress at break, were measured on an MTS Instron dynamometer. During tensile test a constant length gauge of 25 mm was loaded at constant crosshead speed of 100 mm/mn. A high sensitive captor of 10 N was used to obtain mechanical data.

Apart from tensile behaviour, dynamic mechanical analysis of PET fibers was also performed on dynamic viscoelastometer module of the MCR500 apparel from Physica. One single filament is fixed by extremities in two clamps and passed through a vertical bar. When carrying DMA tests, a static strain of 5% is applied to prevent the fibre from becoming slack. Then, a sinusoidal strain with an amplitude of 50 μNm is applied at a constant frequency of 5 Hz. The temperature is scanned between 30 and

Table 1 Intrinsic Viscosity, molecular weight and MFI of the three PET polymers

	$[\eta]$ (dL/g)	M_w (g/mol)	T_f (°C)	MFI	η_0 (Pa.s)
PET-A	0.67	35,500	249.4	26	832
PET-B	0.63	32,300	248.5	30	807
PETC	0.74	42,100	253	20	1280

230 °C at a heating rate of 3 °C/mn. Temperature dependence of dynamic mechanical properties, such as storage modulus (E') and tangent of loss factor (tanδ) are then analysed.

Monofilaments of PET-V/R blends have been subjected to fatigue tests on our Universal Fiber Tester machine. This device consists of two clamps, one being directly fixed on the frame, and the other on a mobile crosshead. The crosshead displacement, thus the distance between clamps, is controlled by an electric motor and measured with a LVDT transducer. In order to apply a sinusoidal cyclic load to fibres, the machine is equipped with a vibrator. This allowed the operator to choose the minimum and the maximum values of the cyclic load. The minimum load was set to zero and the maximum load was expressed as a percentage of the mean breaking stress determined by the tensile tests. A servo system permitted the machine to compensate for creep and preserve exactly the same sinusoidal load throughout the test. The main data obtained through this test were the number of cycles to failure. Only fibre failures occurring in the gauge length were considered and failures in the grips were discounted. All tests were run under controlled humidity and temperature (60% and 21 °C) at a constant frequency of 50 Hz. The broken ends of the fibers were then examined with SEM micrography.

Results and discussion

Thermal and rheological properties of recycled/virgin PET blends

Thermal analysis

DSC analysis of PET-V/R pellets was carried out following this experimental protocol: a heating step from 20 to 280 °C at a rate of 10°/mn, then a thermal treatment at 280 °C for 3 min follwed by a crystallisation step from 280 °C down to 20 °C at 10 °C/mn. The thermograms recorded during DSC run of PET-C/A blends are reported on Figs. 1 and 2. The same behaviour was also observed for PET-C/B blends. On Figs. 1 and 2 we can see that PET-V/R blends show various changes on the positions of melting and crystallisation process. The melting temperature, which corresponds to the maximum of the melting peak, shifts to high values with the increase of virgin PET content. On the other hand, the crystallisation temperatures (T_c), which correspond to the minimum of the crystallisation peaks during quenching run, of the blends decrease with the increase of PETV composition. This indication of the higher temperature at which crystallinity begins to appear is related to the thermal cycles that tend to have a higher T_c value, that is the crystallization of PET begins at higher temperature. The crystallinity increases slightly with increasing percentage of recycled PET in the blends. These results are in accordance with the finding by Fann et al. [10], that the thermal cycling process releases the entanglement and increases the crystallinity.

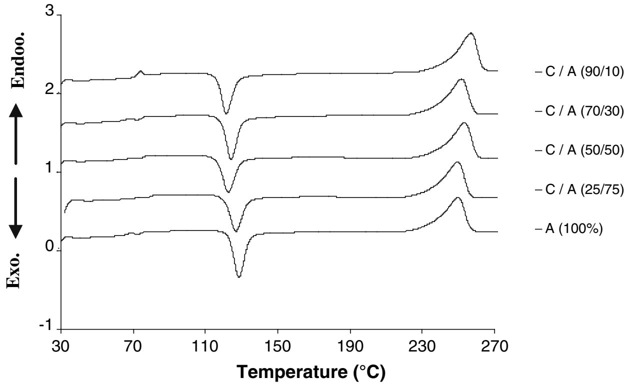

Fig. 1 Thermal behaviour during heating run of PET-C/A blends

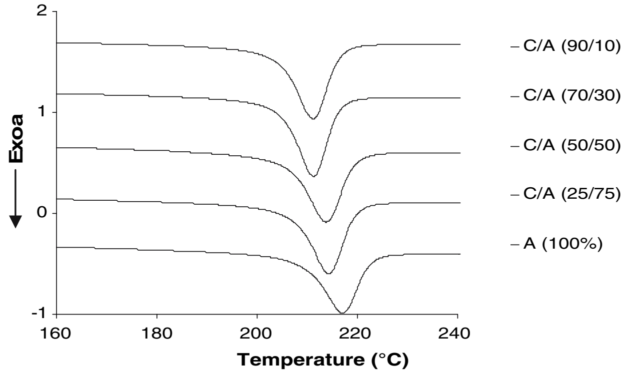

Fig. 2 Thermal behaviour during crystallisation run of PET-C/A blends

The presence of single melting and crystallisation peak reveals, as predicted, that PET-V/R blends are single phase homopolymer blends of the same material (PET). Thermal behaviour of blends of virgin/recycled PET points also out the good microstructural morphology of our blends.

Rheological behaviour of PET-V/R blends

Steady state rheological properties of virgin/recycled PET blends were determined at shear rates ranging between 0.1 and 300 s^{-1} at constant temperature. The flow curves obtained for different blends are reported on Figs. 3 and 4. Note that the apparent viscosity increases with the increase of virgin PET percentage for the two types of blends PET-C/A and PET-C/B. Also the viscosities of all the blends lie between those of pure PET materials. Furthermore, it can

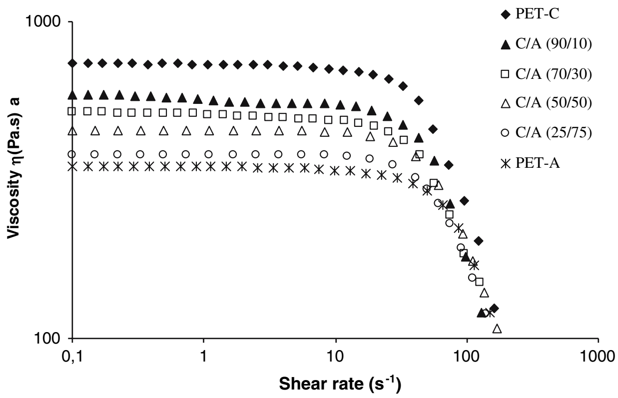

Fig. 3 Flow curves of PET-C/A blends

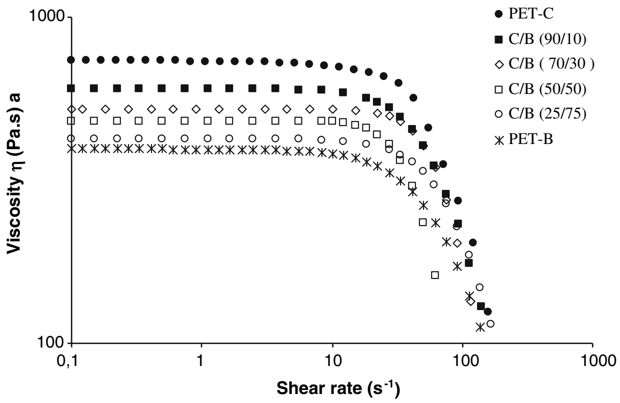

Fig. 4 Flow curves of PET-C/B blends

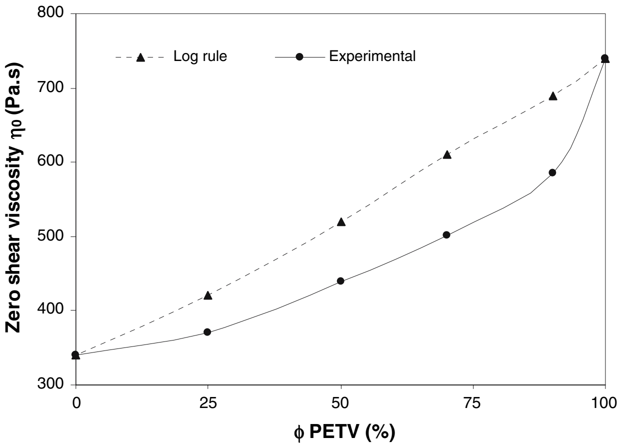

Fig. 5 Negative deviation of viscosity versus composition for PET-C/A blends

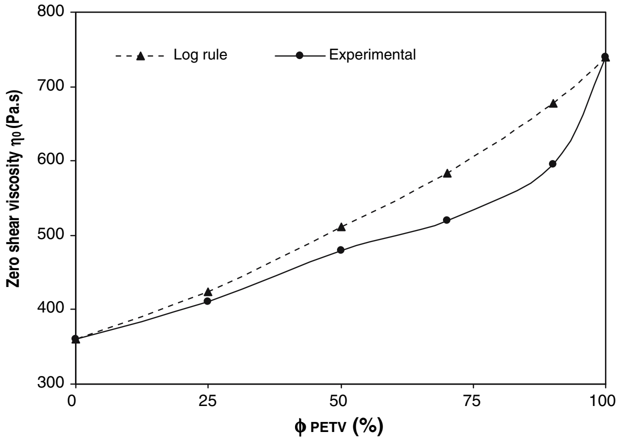

Fig. 6 Negative deviation of viscosity versus composition for PET-C/B blends

be noted that the viscosity of the blends PET-C/B is slightly higher than that of the blends PET-C/A.

Kamal and Utracki [11] suggested that viscosity of polymer blend systems can be divided into three classes by experimental observations: positive deviation blends (PDB), negative deviation blends (NDB) and positive-negative deviation blends (PNDB) from the logarithmic rule frequently used to model polymer/polymer blends viscosity. The logarithmic rule is written as [12]:

$$\ln \eta_{\mathrm{m}} = \sum_{\mathrm{i}} \phi_{\mathrm{i}} \ln \eta_{\mathrm{i}} \qquad (2)$$

where η_{m} is the viscosity of the blend; ϕ_i the weight fraction of constituent i (i = 1, 2) and η_i the viscosity of component i.

The zero shear viscosity of our blends is plotted against the PETV weight fraction (Figs. 5 and 6). The experimental curves show negative deviating viscosity.

As obtained by thermal analysis, the negative deviation reveals the absence of phase separation that would mean that PETV and PETR are miscible down to the macromolecular level. The PET-V/R blends would so form an isotropic medium that has no separate domains occupied by the respective constituent components.

From the thermal and rheological characterization of the different blends of recycled/virgin PET, it can be observed that they can present good feed stock for melt processing and may be expected to yield fibers with good properties. We performed melt spinning of the blends to study the effect of blending on the mechanical properties of the recycled PET polymers.

Mechanical behaviour of blends' fibers

Tensile Mechanical properties

As a measure of fibers performance, we studied the tensile mechanical behaviour of the PET-V/R drawn fibers (draw ratio $\lambda = 10$). The stress-strain curves of the produced fibers in various blend ratios obtained at a constant

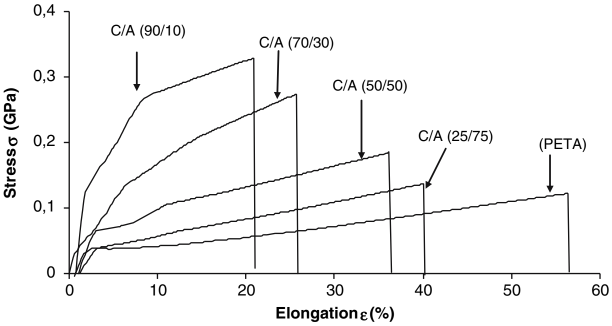

Fig. 7 Stress–Strain curves for PET-C/A fibers

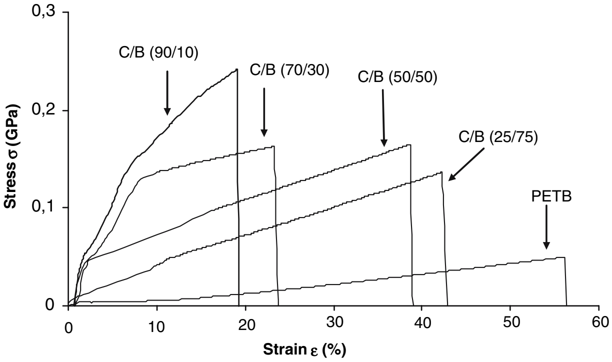

Fig. 8 Stress–Strain curves for PET-C/B fibers

crosshead speed of 100 mm/mn are reported on Figs. 7 and 8. The breaking stress (σ_B) and elongation (ε_B) are obtained at the breaking point and the elastic modulus was calculated from the initial linear part of the stress-strain curves (under 1% of elongation). The tensile properties of the fibers thus obtained are detailed in Table 2.

Fibers from pure recycled polymers have the lowest tensile mechanical characteristics. These properties are progressively improved by adding virgin PET to recycled PET matrix. In order to evaluate the effect of virgin PET content on the mechanical properties of the blends, we reported on Fig. 9 the variations of the stress and elongation at break with virgin PET percentage for PETC/A fibers. The PET-C/B fibers (not reported on figure) have almost the same behaviour. We note that an increasing of the virgin PET composition from 25 to 90%, the breaking stress of the blend fibre is nearly the double. The breaking elongation decreases by the increase of the virgin moiety.

Table 2 Tensile properties of PET-V/R fibers

	Breaking elongation (%)	Breaking stress (MPa)	Elastic Modulus (GPa)
C/A (90/10)	20.3	339	7.6
C/B (90/10)	18.8	242	6.8
C/A (70/30)	25.9	293	5.4
C/B (70/30)	22.6	153	4.8
C/A (50/50)	35.1	194	4.9
C/B (50/50)	38.3	164	5.7
C/A (25/75)	39.6	151	3.4
C/B (25/75)	39	131	2.8
PETA	55.4	98	1.6
PETB	56	67	0.8

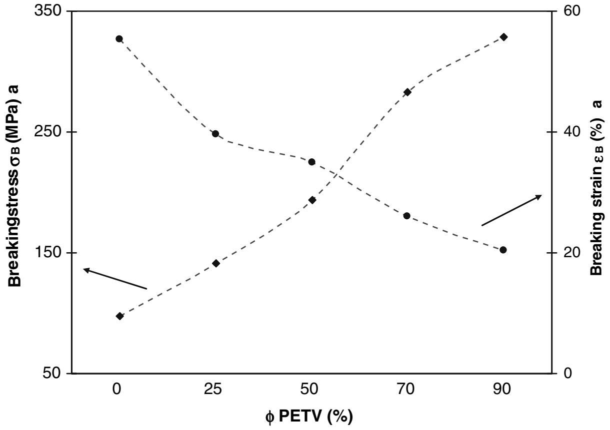

Fig. 9 Evolution of σ_B and ε_B with virgin PET content for PE-TC/A fibers

Dynamic mechanical analysis

One of the most powerful methods used to investigate the variations of viscoelastic properties within temperature of solid polymeric materials is dynamic mechanical analysis. It consists at applying a very small sinusoidal strain to a test sample at a constant frequency whilst the temperature is scanned is increased at constant rate. The stress is measured and the viscoelastic properties such as storage or real modulus E′ and loss factor tanδ are calculated.

We realised dynamic mechanical analysis in solid state on single PETV/R filament samples. During the test a constant strain (5%) is applied to the sample at a frequency of 5 Hz. Obtained variations of the storage modulus (E′) of the blends' yarns are reported on Fig. 10.

The real modulus E′ is decreasing along the temperature range investigated. The characteristic evolution of E′ occurs in a temperature ranging between 70 and 100°C. It manifests by a severe drop of *E*′ along the viscoelastic zone until temperatures close to 150 °C. This transition, called α transition, is associated to the mobility of amorphous region of the material. On the other hand, there is an increase in the total storage modulus with the increase of the virgin PET proportion in the mixture. This increase of *E*' can be explained by a gradually shifting of the molecular weight distribution as one progresses from pure recycled PET (low molecular weight) to pure virgin PET

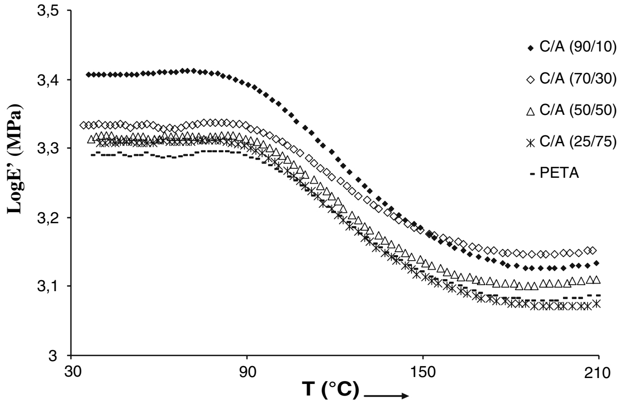

Fig. 10 Storage modulus E' versus temperature of PET-C/A fibers

(high molecular weight). It is well known that the spinning/drawing behaviour of PET is sensitive to molecular weight via its influence on the intrinsic viscosity.

The values of the low temperature limit of real modulus E' and the peak values of tanδ of PET-V/R monofilaments are reported on Table 3. From the obtained values we note that for all the blends the temperature T_α (obtained at the maximum of the peak and assimilated to glass transition temperature T_g) increases with PETV content. Contrary to T_α, tan$\delta_{\max}$ values decrease with the virgin PET percentage indicating an improvement of the mechanical resistance of the fibers.

Fatigue failure of PETV/R fibers

Loading conditions in cyclic fatigue tests for PET fibers has been extensively studied in literature [13–15]. The authors stated that in order to obtain a fatigue failure of polyester fibre, the maximum sollicitation load must be near 70% of the mean tensile breaking stress. Nevertheless, this sollicitation criterion was established within virgin PETs' fibers, thus, for our PET-V/R fibers we performed fatigue tests with two different maximal sinusoidal loads: 70 and 75% of mean tensile breaking stress. The life times (in cycles number) of the PET-V/R fibers subjected to these maximum cyclic loads, but each with zero minimum load, are compared on Table 4. The notations NF meant that no failure was observed after a threshold sollicitation time of 180 min and IF meant that an immediate rapid failure was observed (in less than 2 min). From Table 4 we depict, that fatigue failure for PET-C/A fibers is obtained at a maximum load of 70% of the mean breaking load, but for PET-C/B fibers the failure occurs frequently at a maximum load of 75%. These values of maximum cyclic load will so be used for fatigue fracture morphology analysis.

Scanning electron microscopy of broken ends reveals that fatigue fracture morphologies for PET-V/R fibers are similar to those of virgin PET fibers described in literature [16]. As can be seen on Fig. 11, the failure after fatigue cyclic test leads to a typical fracture morphology with a tongue of material (Fig. 11a) in a part of the fiber and the corresponding hollow (Fig. 11b) on the other part of the broken fiber. When the PET fiber is subjected to cyclic loading the fracture mechanism can be described as follows: fatigue starts with a transverse crack on the fibre surface. Then the crack turns and runs along the fibre at a slight angle to the fibre axis. As it proceeds, the crack gets deeper until eventually the tensile stress on the reduced cross-section is large enough to cause a ductile tensile break to become the final stage of fiber failure. As seen on Fig. 12, the tongue of a fatigued polyester fiber is extremely long and generally curved outside the fiber axis. This is a consequence of the fact that the axial crack runs closely parallel to the fibre axis. In some tests, a number of separate fatigue cracks develop along the fibre, as shown in Fig. 13 with one crack failing first.

Table 3 DMA characteristics of PET-V/R fibers

	Tan(δ)$_{\max}$	T_α (°C)	$E'_{\max}$ (MPa)
C/A (90/10)	0.09	128	2560
C/B (90/10)	0.1	131	2070
C/A (70/30)	0.11	121	2150
C/B (70/30)	0.117	125	1870
C/A (50/50)	0.116	120	2030
C/B (50/50)	0.125	123	1730
C/A (25/75)	0.117	113	1850
C/B (25/75)	0.124	118	1670
PETA	0.12	114	1830
PETB	0.131	105	1600

Table 4 Mean lifetimes MLF (in cycles number) of PET-V/R fibers subjected to different maximum cyclic loads

	0–70%			0–75%		
	MLT (10^{-5})	Samples' Number	CV (%)	MLT (10^{-5})	Samples' Number	CV (%)
C/A (90/10)	5.1	21	4.3	3.3	26	3.8
C/A (70/30)	4.5	27	4.7	2.4	22	4.6
C/A (50/50)	3.8	17	6.2	IF	4	–
C/A (25/75)	4.1	24	5.6	IF	5	–
PETA	2.8	19	7.4	IF	4	–
C/B (90/10)	4.9	23	5.5	3.7	21	8.1
C/B (70/30)	NF	4	–	3.1	17	7.4
C/B (50/50)	NF	3	–	2.85	23	5.4
C/B (25/75)	3.05	19	6.5	IF	26	4.3
PETB	3.1	24	4.2	2.6	20	6.6

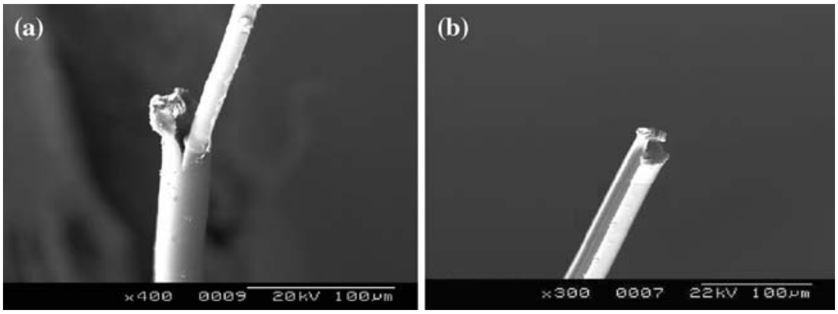

Fig. 11 Typical fatigue fracture morphology of PET-V/R fibers

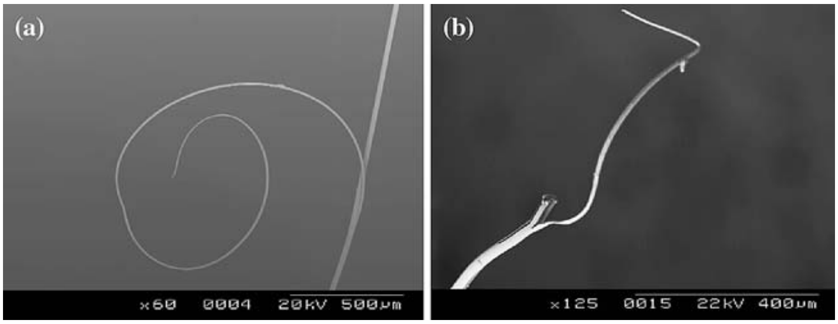

Fig. 12 Long tongues of fatigue failed PET-V/R fibers

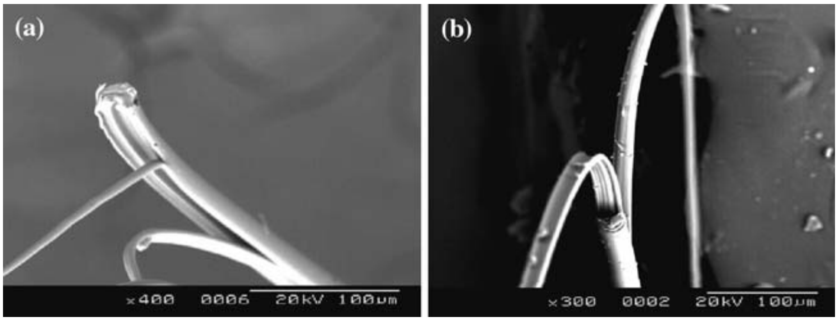

Fig. 13 Multiple fracture cracks in fatigued PET-V/R fibers

Conclusions

The analysis of thermal and rheological behaviour of PET-V/R blended polymers showed the absence of phase separation. That would mean that PETV and PETR are miscible down to the macromolecular level. In addition, recycled and virgin PET are compatible polymers that would form an equilibrate PET polymer with intermediate molecular weight when melt blended.

The study reveals also that melt spun fibers of PET-V/R blends present reliable dynamic and static mechanical properties until high recycled PET content. Thus, the mechanical blending of recycled PET chips and virgin PET pellets improves the melt processing of recycled PET and allows to obtain fibers with mechanical characteristics close to those issued from virgin PETs. Regarding cyclic fatigue tests, the recycled/virgin PET fibers could be used at the same applications than those spun from pure virgin PET polymers and would so achieve a good resistance level to cyclic loading sollicitation.

On the other hand, this study demonstrates that melt spinning fibers form PET-V/R blends is a suitable manner to recycle plastic PET wastes and then preserve environment.

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