*Manufacture and rheological behavior of all recycled PET/PP microfibrillar blends

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Abstract

For several years, new plastic bottles made from opaque polyethylene terephtalate (PET) have been on the market. When their waste is mixed to those of recycled clear PET, the obtained material cannot be recycled anymore due to a loss of properties. Moreover, because of an important grade variety, the large number of additives used and poor homogeneity, the processing and recycling of opaque PET appears as a challenge. The way chosen to revalue this recycled opaque PET (r-OPET) is its microfibrillation in a recycled polypropylene (rPP) matrix. The effects of the concentration of r-OPET were studied by rheology, supported by SEM images and related to the morphology of the mixture. It was demonstrated that $(20/80)_w$ r-OPET/rPP blend was the best ratio to favor microfibrillation, as it offers the appropriate amount of solid filler to obtain a sea-island morphology.

Thereafter, the influence of the temperature of microfibrillation is presented. The thermomechanical curve of the $(20/80)_w$ r-OPET/rPP blend suggests that microfibrillation should be more effective around the Tg of r-OPET. The optimum temperature was found, where an improvement of rheological and mechanical properties is observed. A Cross model with yield stress is proposed to describe the rheological behavior of this material.

Keywords: recycled, polymer composite, microfibrillar reinforcement, incompatible blends, opaque PET

Introduction

From the 1950's, the consumption of plastics has considerably grown until global production almost reached 360 million tons in 2018. [1] This evolution, added to a long tradition of single-use or disposable plastics, naturally leads to a substantial increase of plastic waste and the development of post-consumer recycling industry as a result of environmental pressure. [2,3]

Polyethylene terephthalate (PET) is widely used in manufacturing of soft-drink beverage bottles, packaging films and textile fibers. Compared to others resins, the recycling of this thermoplastic polymer is one of the most effective in Europe. In this respect, more and more recycled PET (rPET) consist of regenerated food packaging or fibers (e.g. sport shirt).

Nevertheless, in the last few years, a new kind of PET has appeared on the market essentially for milk bottles and packaging: Opaque PET (OPET). Its composition differs to clear PET by the addition of TiO_2 particles in various amount (up to 15%) depending on the application. The aim of such a polymeric material is to protect the packaging content from UV degradation thanks to the addition of these particles. Titanium dioxide is, indeed, a well-known UV-barrier [4] in addition to its coloring properties.

When opaque PET was launched at the beginning of the 2010's, the manufacturer's declared ambition was not only economical but also ecological. Actually, OPET was up to 20% lighter, thinner, and produced with less water and electricity than the material previously used. But the issues occurred during the end of life that have not been anticipated. According to various reports of COTREP (center of resources and expertise on the recyclability of plastic household packaging in France), the presence of more than 15% of OPET in the PET waste source disrupts the using recycling process of this plastic.

Like all the recycled deposits, this material results from the crushing of a lot of kind of OPET bottles collected in recycling centers. And, because of its important grade variety, the large number of additives used to give the plastic its properties (color, mechanical or thermal properties, UV-barriers…) and its poor homogeneity, the OPET processing and recycling appears to be a real challenge. Indeed, not only there are different grades of PET within the material but also several pollutants such as PE or others inorganic elements (Al, Cu, P, Ca…). Added to this, the shape of material is diverse just like the size. All these characteristics result into instability during processing and, by extension, a drop in properties. Adding a chain extender, like Joncryl for r-OPET for instance, is an approach for the polymer to get its properties back. However, it's not the only one. [5]

The blending of polymers is considered as an economical and practical method to obtain new material with improved properties. [6] Nevertheless, usually, the polymers are immiscible in the melt state [7,8] on account of phase separation and low adhesion between two phases. [9] Two different approaches are often employed to avoid the immiscibility drawbacks. The first one involves adding a compatibilizer such as copolymers. The second one entails transforming the blend into a microfibrillar composite (MFC) - considering that shape and size of the dispersed phase strongly affect the properties of the final polymer blend. The first investigations in this field were performed by Evstatiev and Fakirov during the 1990s. [10,11,12] Their work dealt with microfibrillar reinforced composites based on blends from recycled PET, PP and a compatibilizer and highlighted an improvement of thermal and mechanical properties.

The processing of microfibrillated blends is usually done in three steps: firstly, the blending of the compounds to obtain a sea-island morphology; secondly, the cold or hot stretching in order to microfibrillate the dispersed phase of the blend; finally, the isotropization of the matrix thanks to an ultimate processing step, generally translate into compression or injection moulding.

Among the polymers used in the context of microfibrillar mixtures, PP/PET blends are widely studied. [13-18] The interest of these mixtures comes from the differences between both polymers melting temperature (Tm) and glass transition temperature (Tg). On the one hand, PP's Tg is around -10°C whereas PET's one is around 80°C. As a consequence, at ambient temperature, PET can be used as a solid reinforcement in a vitreous matrix (PP). On the other hand, PP's fusion temperature is around 160°C whereas PET's one is around 245°C. Hence, after microfibrillation, if the blend is reprocessed where matrix is molten (i.e. 200°C) PET fibers are not impacted as its melt temperature is higher; provided that the processing window is not too close to the Tm of PET fibers, otherwise they will melt and return into spherical shape.

The objective of this paper is to study the ability of recycle opaque PET (r-OPET) to fibrillate within a recycled PP matrix (rPP), *i.e.* to manufacture a blend of two polymers that are both recycled and one of them which is also opaque in a revaluing spirit. The first part is dedicated to the evaluation of the optimal ratio between r-OPET and rPP. Then, the microfibrillation parameters will investigate through hot and cold stretching (that is to say either directly thanks to the extruder or in the tensile machine). Finally, the influence of microfibrillation on the thermal, mechanical and rheological properties of the blends will be measured.

1. Material and methods

1.1. Materials

The recycled opaque poly(ethylene terephthalate) flakes (r-OPET) were provided by SUEZ (SUEZ RV plastiques, BAYONNE, FRANCE). The molecular weight of the r-OPET was 69400 g/mol, while the inorganic content was around 1.9% and mainly related to the presence of TiO2. The glass transition temperature of r-OPET is 80°C, and the melting temperature is 244°C.
The recycled polypropylene (rPP) was provided by Quality Circular Polymers under the reference QCP™ EXPP 152A (QCP polymers, GELEEN, NETHERLANDS). This product contains a minimum amount of 95% of recycled polypropylene. The melting temperature of this rPP is around 170°C and melt flow index (MFI) around 16 g/10 min at 230°C and 2.16 kg.

Before processing and characterization, both polymers were dried at 80°C for 24hours in an oven under air atmosphere.

Figure 1. Mixed recycled OPET flakes (a) and recycled PP pellets (b)

1.2. Processing

1.2.1. Extrusion

The r-OPET and the r-OPET/rPP blends were processed thanks to a co-rotating twin screw extruder from LABTECH engineering company Ltd (LABTECH engineering company Ltd, SAMUTPRAKAN, THAILAND), with a ratio L/D (length/diameter of screw) equal to 40. The screws diameter is 16 mm including 10 different heating zones (**Table 1**) and a die diameter of 3 mm. The extruder screw profile is assembled from modular screw elements, including transporting elements, kneading and mixing elements. The extrusion temperature profile of r-OPET and the blends, in the majority of the paper (except for §2.1), are shown in **Table 1**. The twin-screw speed is fixed at 150 rpm. The feeding rate was adjusted at 1.5 kg/h.

Table 1. The extrusion temperature profile

Die Z (°C)	Z9 (°C)	Z8 (°C)	Z7 (°C)	Z6 (°C)	Z5 (°C)	Z4 (°C)	Z3 (°C)	Z2 (°C)	Z1 (°C)
265	265	275	275	275	275	275	265	200	150

In order to evaluate the penchant for r-OPET to fibrillate directly during the extrusion process, six temperature variations were performed on the zones Z8, Z9 and Die Z (§2.1). The other ones were set, as shown in Table 1.
The six temperature profiles were determined as follow (from Die Z to Z8 in °C):

- T1: 260 / 265 / 275
- T2: 240 / 245 / 260
- T3: 235 / 245 / 260
- T4: 230 / 245 / 260
- T5: 225 / 240 / 260
- T6: 220 / 240 / 260

The twin-screw speed is fixed at 150 rpm and the feeding rate was adjusted at 1 kg/h.

1.2.2. Microfibrillation

The manufacturing of MFC include three steps. Firstly, the blend is melted thanks to extrusion of r-OPET and rPP (which have different melting temperature). The filament obtained (with a diameter around 3mm) is immediately plunged in a cold bath to set OPET droplets. Secondly, the filament is drawn by a tensile machine MTS (MTS, MINESOTA, USA) equipped with an oven (MTS CE42), in our case at 3 different temperatures, with a speed of drawing of 100 mm/min. The initial length and diameter of the filament were respectively of 100mm and 3mm. During stretching, the filament was subjected to a strong necking. The final length is 223mm with a diameter around 0.3mm in the part where the necking occurred. Thirdly, the final processing step (*i.e.* a thermal treatment between the melting point of the two components) is done by compression or injection molding in order to give the matrix an isotropic nature.

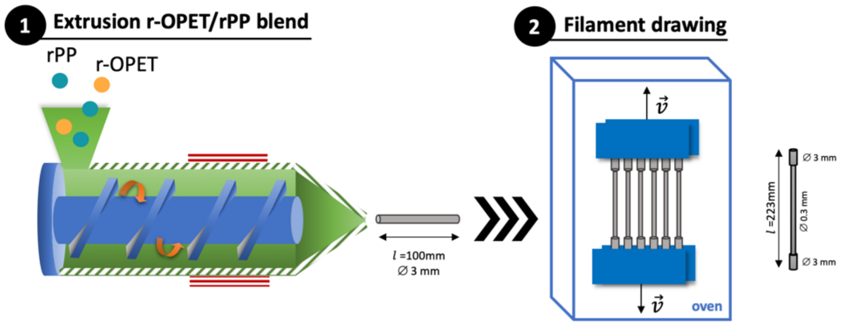

Figure 2. Microfibrillation consists in the manufacture of micron scale fibers of a first polymer (r-OPET) in a second one making up the matrix (rPP).

1.2.3. Processing of samples for rheological measurements

Samples for rheological measurements were pressed by heating press at 210°C and 40 bars. Spots of 25mm diameter and 2mm thickness were manufactured in this way.

1.2.4. Injection moulding of tensile test specimens

In order to quantify the mechanical properties of the different blends, specimens were injected in a microinjection machine HAAKE MiniJet 2 to obtain a standard tensile specimen ISO 527-5A. The injection temperature was set at 210°C and the mould maintained at 45°C.

1.3. Characterization

1.3.1. Rheology

All the rheological measurements were performed on an Advanced Rheometric Expansion System (ARES, Rheometrics) using a 25 mm diameter parallel plate geometry (with a gap of around 1.7mm) for the mechanical spectra. The analyses of all the samples were determined in the linear viscoelastic regime at 200°C. This temperature allows to keep the morphology of r-OPET phase unchanged, thanks to the high melting temperature of r-OPET (244°C). Injected parallelepiped sample has been used for the thermomechanical analyses. The experimental conditions were fixed at 2°C/min and 1rad/s in the linear viscoelastic regime.

1.3.2. SEM Microscopy

Cryo-fractured samples were covered with a 20 nm carbon layer (Leica EM ACE200 coater) to allow backscattered electrons observations. Samples were analyzed by CSEM-FEG Inspect F50 field emission gun scanning electron microscope operated at 5-10 kV.

1.3.3. Tensile tests

The tensile tests were performed with an INSTRON 5582 equipped with a video extensometer INSTRON AVE2, at room temperature.
The crosshead speeds were 1 mm/min with the extensometer and the 100 mm/min without.
The tensile moduli were calculated between 0 and 0,5% of elongation.

2. Results and discussion

2.1. Blends of (10/90), (20/80) and (30/70) (w/w) r-OPET/rPP

The morphology of a blend depends significantly on the composition ratio of the components. The general objective is to obtain a blend made of r-OPET microfibrils in a rPP matrix. r-OPET microfibrils are obtained by stretching out r-OPET droplets in a rPP/r-OPET blend. Therefore, sea-island morphology is the most appropriate morphology of the blend that will be processed prior to microfibrillation.

A first step is thus to determine the maximum amount of r-OPET that can be introduced in rPP while guaranteeing a sea-island morphology. In order to do so, a spectromechanical measurement of the properties of the rPP/r-OPET blends in the linear viscoelastic regime has been processed at 200°C. At this temperature, the r-OPET behaves like a solid fiber and constitute therefore a filler of the rPP matrix.

Figure 3 presents the results obtained for blends containing 10, 20 and 30% of r-OPET in a rPP matrix.

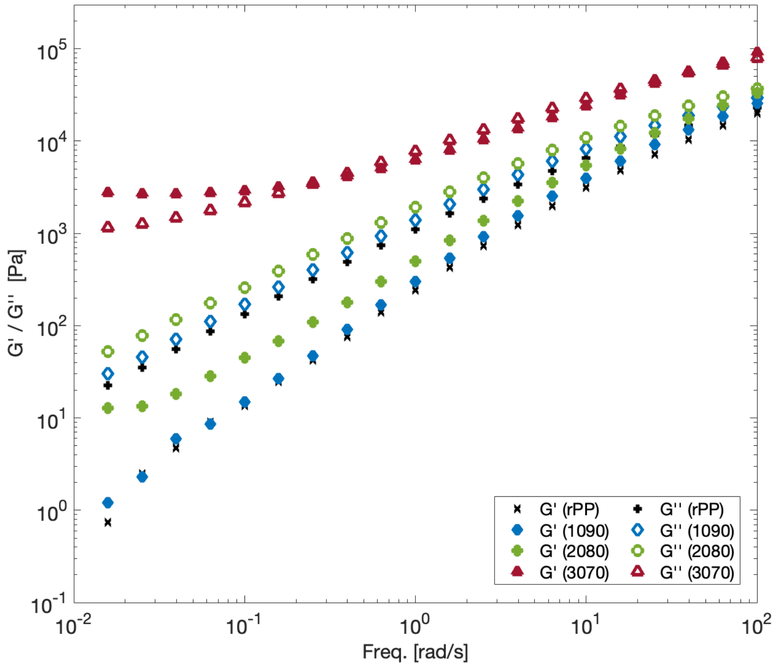

Figure 3. Storage and loss moduli versus the frequency of the rPP matrix and the three r-OPET/rPP blend ratios within a rheometer equipped with a parallel plate geometry at 200°C

For the (10/90) (w/w) r-OPET/rPP blend, the rheological response is the one of a viscoelastic liquid : the loss modulus is higher than the storage modulus, which characterizes a liquid like behavior. In addition, it is clear that the behavior of this blend is very close to the one of the pure matrix (rPP). The SEM image of this sample is shown on **Figure 4A**: we can see that it presents a sea-island morphology.

On the contrary, in the case of the (30/70) r-OPET/rPP blend, the composite behaves like a viscoelastic solid at the lowest frequencies. The solid behaviour of this material is associated with the high amount of r-OPET which is solid at the temperature of the analysis. The system morphology shows a strong anisotropy (**Figure 4 C).** This could be linked to a high amount of solid r-OPET, which creates percolated paths. This assumption is supported by the spectromechanical curve which reaches a rheological percolation threshold. With some continuous zones of r-OPET, the (30/70) r-OPET/rPP blend thus does not present the appropriated morphology for microfibrillation.

Finally, the (20/80) (w/w) r-OPET/rPP blend shows a behaviour that is halfway between the previous two ones. At intermediate frequencies, the behaviour of this blend is the one of a viscoelastic liquid. At the lowest frequencies measured, a slight increase of the storage modulus is visible, which is characteristic of filled polymers at low contents of fillers. For this blend, the SEM image shows a sea-island morphology (**Figure 4 B**).

As a conclusion, relying on both SEM's images and rheological characterisation, we can consider that the blend containing 30w% of r-OPET is very close to reach a percolation threshold and a start of continuous r-OPET zones, which is not suitable for further microfibrillation of r-OPET domains. On the opposite, at 10w% there is not enough r-OPET in the blend to obtain significant effects related to the addition of r-OPET, according to the rheological results. Moreover, the van Gurp Palmen (vGP) plot (Figure 8 b) is in very good accordance with these assumptions. Indeed, Li *et al.* have shown that a curve with a plateau close to 90° and a slight hollow in the low moduli is the classical behavior of a sea-island morphology whereas when a maximum appears, it can be identified as a clue of co-continuity. [19]

It thus appears that the best ratio to favour microfibrillation is (20/80) (w/w) r-OPET/rPP.

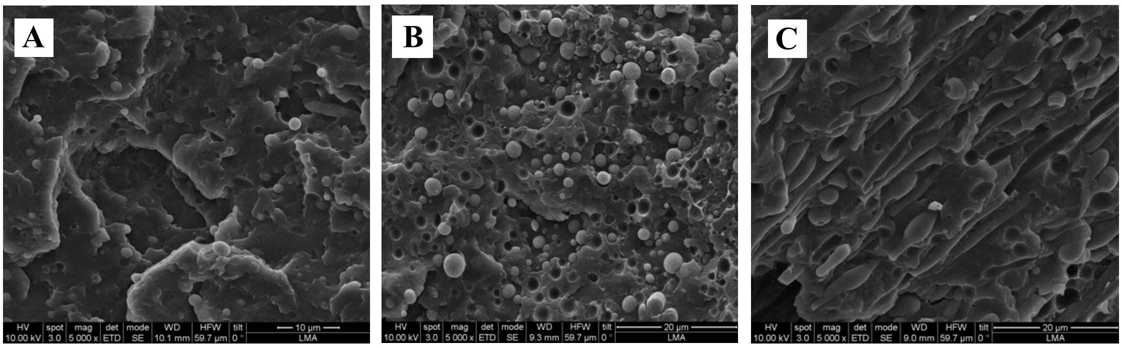

Figure 4. SEM images of r-OPET/rPP blends for different ratios of r-OPET. (A) 10/90. (B) 20/80, (C) 30/70

2.2. Influence of the temperature of the extrusion die on flow properties

It is possible to stretch out a polymer through the extrusion process. In order to evaluate the efficiency of a direct fibrillation during this processing step, six temperature profiles were tested, decreasing the last three extrusion zones temperatures from T1 to T6 (cf §1.2.1). Spectromechanical analyses were, then, performed to characterize the possible modification in the microstruture.

The rheological behaviour of microfibrillated blends depends on several factors such as fiber volume fraction or aspect ratio. The viscosity is sensitive to the concentration of microfibrils during low shear rates as fibers are quite disoriented whereas at higher shear rate, they remain more oriented. [20]

To evaluate quantitatively the appearance of a viscosity increase at low frequency, Lertwimolnun and Vergnes used a modified Cross model introducing a yield stress term (Equation 1): [21]

$$\eta(\omega) = \frac{\sigma_0}{\omega} + \frac{\eta_0}{[1 + (\omega\tau)^n]} \qquad (1)$$

with the yield stress σ_0 the zero-shear viscosity η_0, the mean relaxation time τ, and the power law index n.

Experimental data were fitted according to this equation, using a Nelder-Mead simplex method. The adjusted parameter yield stress, thanks to the minimization parameter, is plotted in **Figure 5** as a function of the die zone temperature.
By using the Nelder-Mead simplex method that minimize χ^2 (Equation 2), the four optimal rheological parameters values, previously described, were determined. [22]

$$\chi^2 = \frac{1}{n_{exp}} \left(\sum_{i=1}^{n_{exp}} \frac{\left[\log(\eta_{exp,i}) - \log(\eta_{theo,i})\right]^2}{\left[\log(\eta_{exp,i})\right]^2} \right) \qquad (2)$$

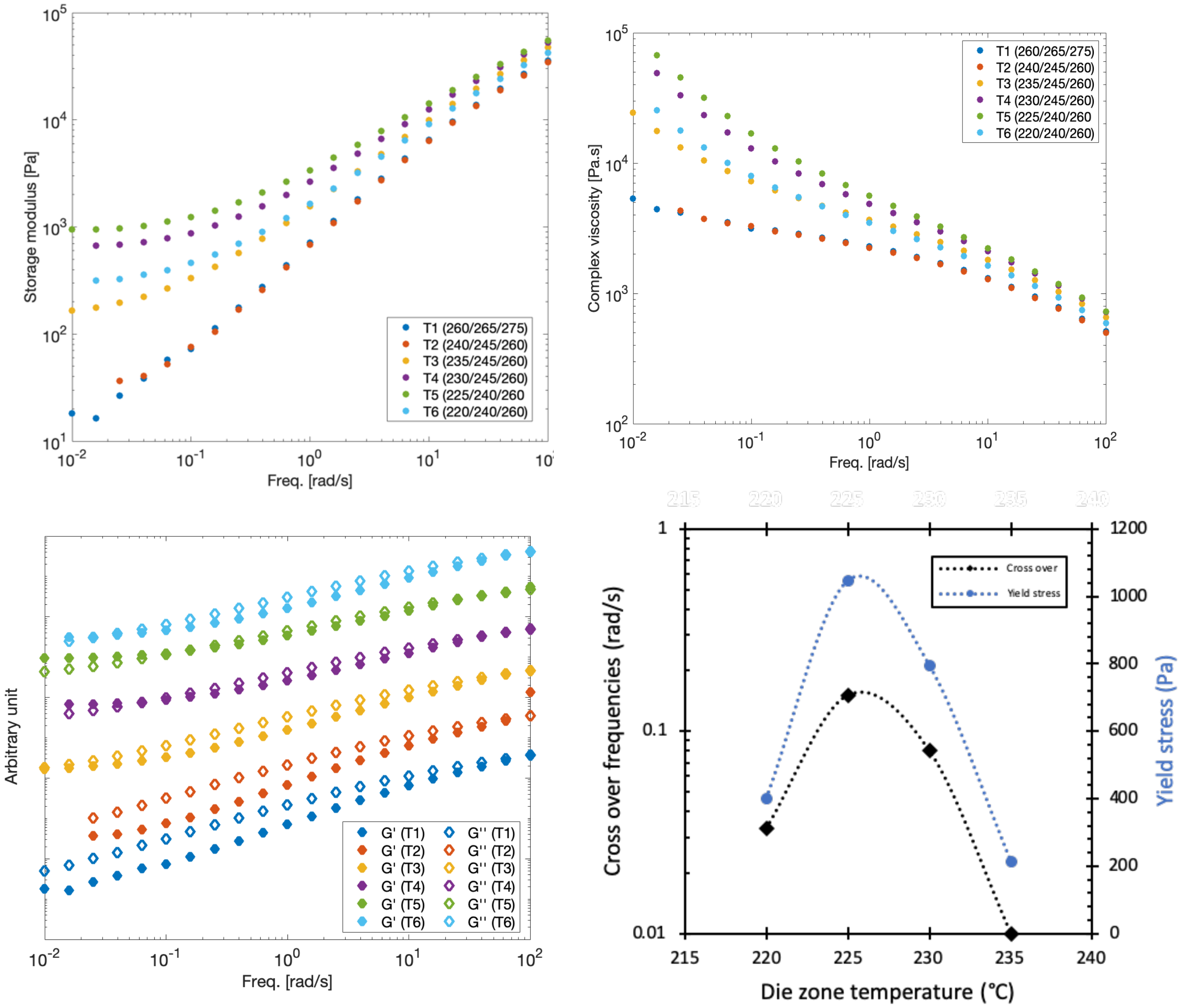

Figure 5. Spectromechanical analyses (at 200°C) of (20/80)w r-OPET/rPP depending on the extrusion temperature profile presented in terms of (a) storage moduli and (b) complex viscosity. (c) Complex moduli G' and G'' shifted on the Y-axis to be able to observe the cross-over frequencies. (d)Yield stress and cross over frequency extracted from the spectromechanical analyses presented in (a) and (c)

The extrusion temperature profile clearly modifies the rheological behaviour of the blend. If a liquid-like behaviour characterizes the samples with the hottest die zone temperatures (*i.e.* T1 and T2, corresponding to 260°C and 240°C), the four others samples present a cross over spread on a frequency range between 0.01 and 1 rad/s. Moreover, the relaxation times are not the same depending on the profile. An optimum temperature can be detected thanks to Figure 5 (b).

Indeed, an increase of yield stress and cross-over frequency highlights a more pronounced morphology structuration. Furthermore, the tendency is almost the same for these two parameters with a maximum reached around 225°C (T5). At this temperature, the cross-over occurs nearly one decade earlier than for the sample extruded with a 260°C die zone and its yield stress is five times more important. Nethertheless, some SEM images don't agree wholeheartedly with a real structuration of the minor phase (r-OPET) as fibrils.

In the case of the highest extrusion temperatures, the shape of the blend is the one of a sea-island morphology (Figure 6.A). From 230°C, r-OPET drops seem to be slightly stretched without actually being able to fully turn into fibers. However, at 225°, even if none fiber is detected, a strong anisotropy and orientation can be observed as much for the matrix as for the dispersed phase (Figure 6.B).

Finally, the last heating zones of the extrusion process (and so the manufacturing temperature) modify the morphology and the rheological behaviour of the blends from sea island to something more oriented and anisotropic. However, the obtained morphology is not the one of a microfibrillar blend.

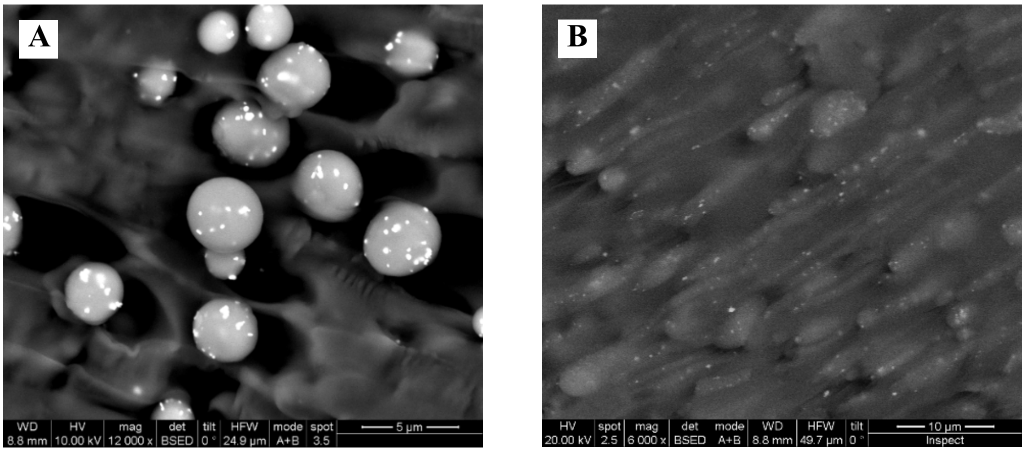

Figure 6. SEM images of the two blends with the extreme rheological behaviours, *i.e.* extrudated at T1 (A) and T5 (B)

2.3. Thermomechanical analysis of r-OPET

Thanks to the previous experiments, it was clear that the fibrillation of the r-OPET phase was not effective directly through the extruder. So the process needed to be changed and the cold stretching of the blend is a second option in order to obtain the expected morphology.

In this context, the microfibrillation of the r-OPET must be performed in the rubbery state, at a temperature slightly above the glass transition temperature (Tg) of this material in order to stretch it without breaking, [23,24] and well below the Tm of the r-OPET to be able to retain its fibrillar form. Actually, close to the Tg, relaxation times are relatively long what avoid capillary instabilities while preserving some deformability. Researchers noticed that the processing temperature range should be located between Tg and Tcc (corresponding to cold crystallization). [25]

To determine the temperature providing the better result, a thermomechanical analysis of the r-OPET has been done. The temperature range at which microfibrillation should be performed was enlightened by the thermomechanical characteristics of r-OPET, presented on **Figure 7**.

It can be seen, that the Tg of r-OPET is around 80°C, while a cold crystallization occurs at 120°C. DSC measurements were also performed, corroborating the thermomechanical analysis results (*i.e.* characteristic temperatures) but without bringing new information. As a conclusion, the microfibrillation process has to be done between 80 and 120°C.

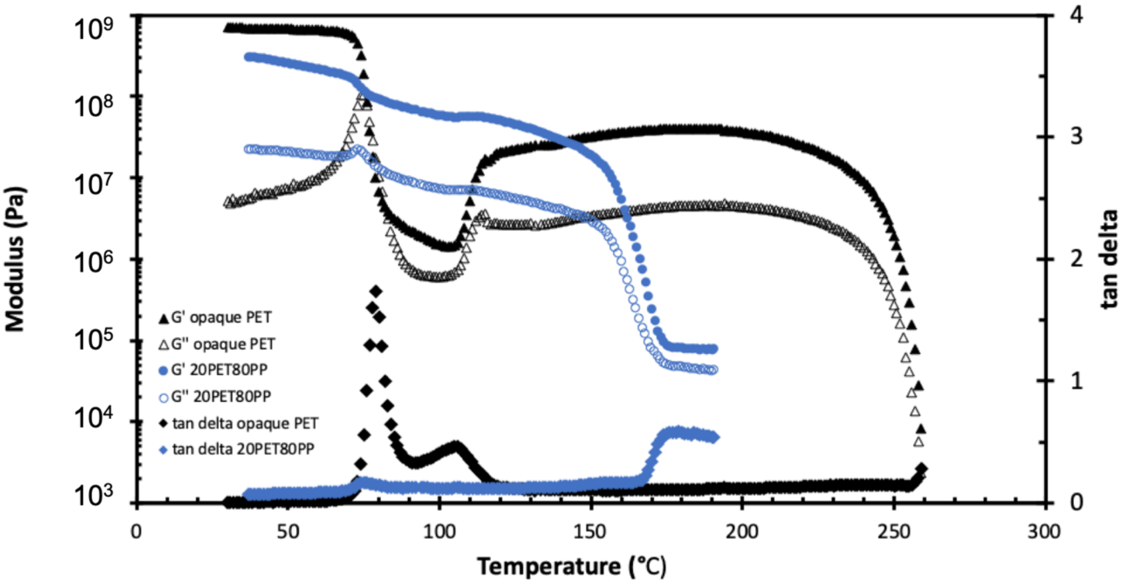

Figure 7. Thermomechanical analysis of r-OPET and (20/80)w r-OPET/rPP blend between 30°C and 260°C (at 1 rad/s, 2K/min)

2.4. Influence of the drawing temperature on microfibrillation

(20/80) (w/w) r-OPET/rPP blends were microfibrillated at 3 different temperatures in the range determined from the thermomechanical analysis: 80°C, 100°C and 120°C. The objective of this part is to evaluate the effect of this processing temperature on the morphology and on the rheological properties of the microfibrillar blends.

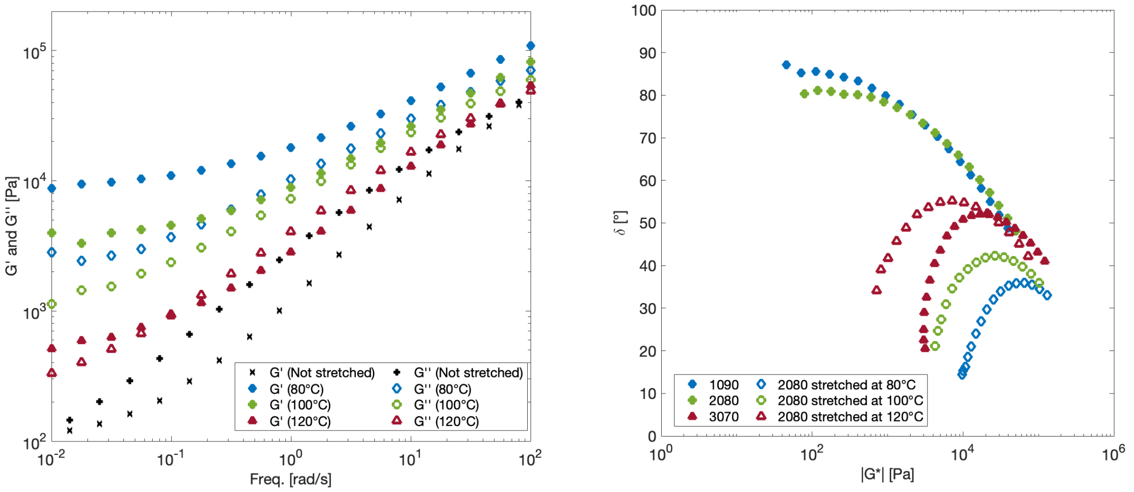

Figure 8. (a) Superposition of G’ and G’’(at 200°C) of (20/80) (w/w) rOPET/rPP of classical and microfibrillated samples as a function of temperature of microfibrillation. (b) van gurp Palmen plots of the samples before and after microfibrillation process

The spectromechanical properties of (20/80) (w/w) r-OPET/rPP blends processed at 80°C, 100°C and 120°C were measured in the linear viscoelastic regime (**Figure 8**) and compared to the behaviour of the blend before microfibrillation. This study of the rheological properties was performed at 200°C: this temperature is well below the melting temperature of the r-OPET; the r-OPET domains will thus retain their microfibrillated shape, and the rheological behaviour observed is directly related to the morphology of the dispersed phase domain. What’s more, some authors have demonstrated that the van Gurp Palmen plot shape depends on the microstructure of the material. More precisely, an introduction of fibers in a matrix produces a maximum in the vGP plot (contrary to the matrix or a blend without co-continuous zones which reach a plateau close to 90°) and a shift of this maximum toward high moduli was observed with the amount of fibers added. Thanks to Figure 8b, one can observe this evolution suggesting that the blend fibrillated at a temperature close to 80°C contains the larger amount of fibers.[18,26] In addition, a more classical interpretation of vGP plot rests on the evolution of the angle value. At 90°, the viscous state is dominant (what corresponds to a Newtonian liquid) whereas for a null phase angle, the material deforms elastically like a solid. Thus, the composition ratios lower than 30%w r-OPET are the closest to a liquid like behavior whereas a higher input of PET solid filler or a drawing at a temperature close to the Tg lead to lowest angles, thus to a more solid behavior.

Before microfibrillation, the blend presents a liquid-like behaviour at 200°C, with a loss modulus G” higher than the storage modulus G’. On the contrary, all the microfibrillated blends exhibit a solid-like viscoelastic behaviour at low frequencies, whatever the processing temperature.

Nevertheless, variation in the microfibrillation processing temperature results in noticeable differences in the rheological properties of the blends. The closer the temperature is to 80°C, the more the moduli increase. This observation can be related to the morphology of the microfibrillated blends. **Figure 9** shows SEM micrographs of the blends microfibrillated at the 3 different temperatures.

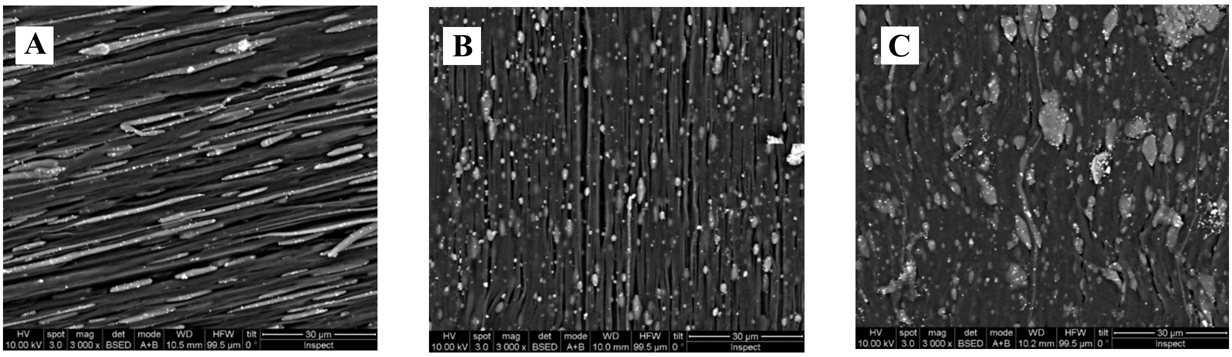

Figure 9. SEM images of (20/80) (w/w) rOPET/rPP realized after drawing the filaments by tensile machine at 80, 100 and 120°C, at 100mm/min. (A) At 80°C, the polymer mixture seems to be heterogeneous but the PET fibers are long and oriented. (B) At 100°C, the polymer mixture is not homogeneous: PET phase consists of fibers of different length but some droplets appear, all oriented. (C) At 120°C, the polymer mixture is not homogeneous: PET phase consists of small drops, large drops and other geometries. But, an orientation of the phase is observed.

Fibers of r-OPET appear longer and thinner at 80°C, whereas some droplets are still there at 100°C. The fibrillation is even less effective at 120°C, where most of the r-OPET domains have a quite-spherical shape.

Moreover, the curve of tan δ reaches a peak around 80°C both for the (20/80) (w/w) rOPET/rPP blend and r-OPET (**Figure 7**). The higher tan δ, the more the viscosity exceeds the elasticity. Indeed, this element could explain that, at the temperature corresponding to the maximum of tan δ, the microfibrillation is better. Actually, the PET droplets are deformable enough to be stretched without for all that they are subjected to relaxation and get their drop shape back. During the stretching process, the strength necessary to the tensile machine to elongate the filament was measured. Around ten filaments were used and the signal has been recorded during the fibrillation. The shape and size of the filament do not correspond to any standard, but the engineering stress versus the strain has been plotted (Figure 10): it clearly indicate that at 80°C, a much more important tensile force is needed. This parameter could be linked with the rheological behavior and the formation of the fibrils which seems to be enhanced close to the Tg of PET.

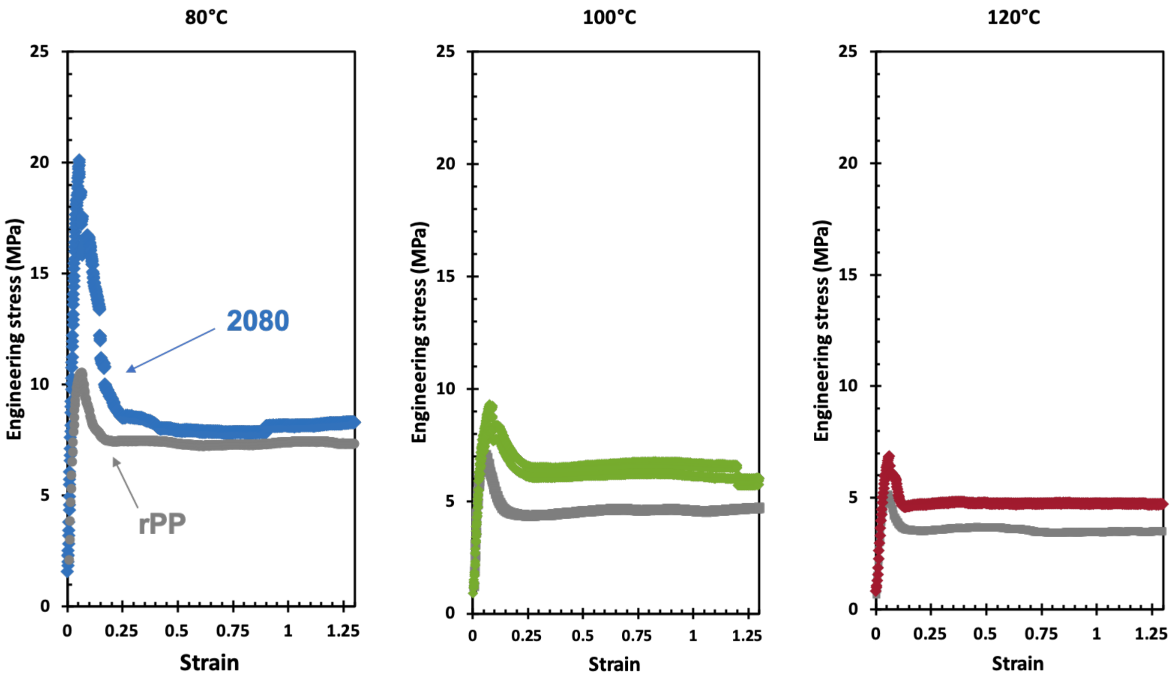

Figure 10. Engineering stress versus strain (normalized for one filament with an average diameter of 3 mm) recorded by the testing machine during the stretching of r-OPET/rPP blends at the 3 temperatures and compared with the matrix

In order to better quantify the effects of the temperature of the microfibrillation process on the rheological behaviour of the blends, the spectromechanical results can be plotted in terms of the complex shear viscosity versus frequency (**Figure 11**). If the complex viscosity exhibits a decrease with the frequency, the rheological behaviour is not only shear-thinning. The influence of microfibrillation is more pronounced in the low frequency region where a yield stress can be measured.

As for the study of the influence of the extrusion temperature, a Cross model with yield (Eq. 1) stress was used to fit experimental data (with a Nelder-Mead simplex method, Eq. 2) and precisely evaluate the increase in the structuration of the microfibrillated and non microfibrillated blends.

A very good accordance between experimental values and the adjusted model was obtained.

Table 2. Results of the fitted Cross model with yield stress

Parameters	(20/80) (w/w) rOPET/rPP non-microfibrillated	(20/80) (w/w) rOPET/rPP microfibrillated at 80°C	(20/80) (w/w) rOPET/rPP microfibrillated at 100°C	(20/80) (w/w) rOPET/rPP microfibrillated at 120°C
σ_0 (Pa)	123	9 170	3 720	545
η_0 (Pa.s)	5 200	35 900	18 800	10 500
τ (s)	0.48	3.58	1.79	1.77
$\boldsymbol{n}$	0.51	0.57	0.56	0.50
χ^2	0.009	0.009	0.01	0.01

The variation of σ_0 is significant: this value decreases with the microfibrillation temperature. This can be related to a better structuration of the material. Actually, a higher value of the yield stress is the signature of an increase in the structuration.

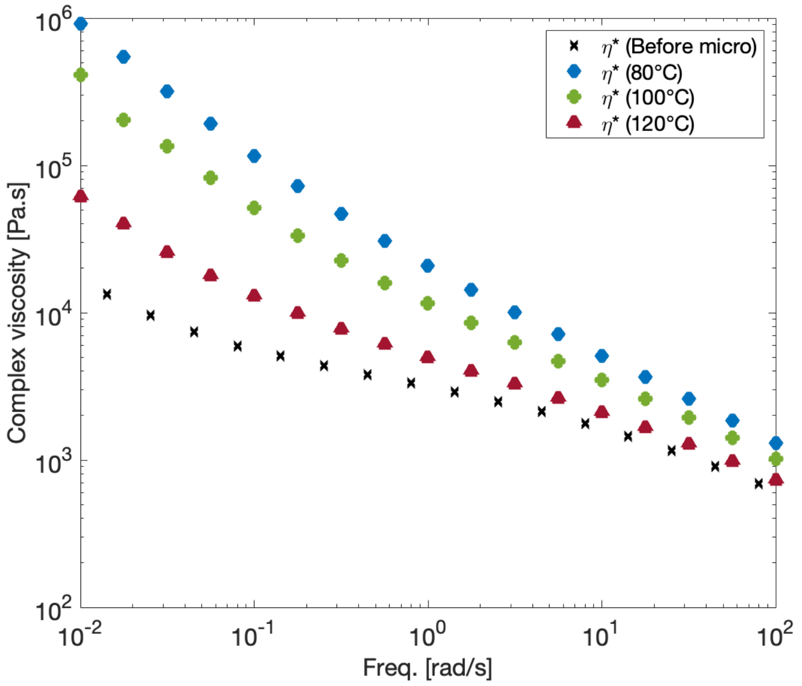

Figure 11. Superposition of complex viscosity as a function of temperature of microfibrillation at 200°C

To relate the morphology highlighted by SEM with rheology and more precisely, connect the increase of structuration with the one of yield stress, an aspect ratios measurement has been performed for each stretching temperature.

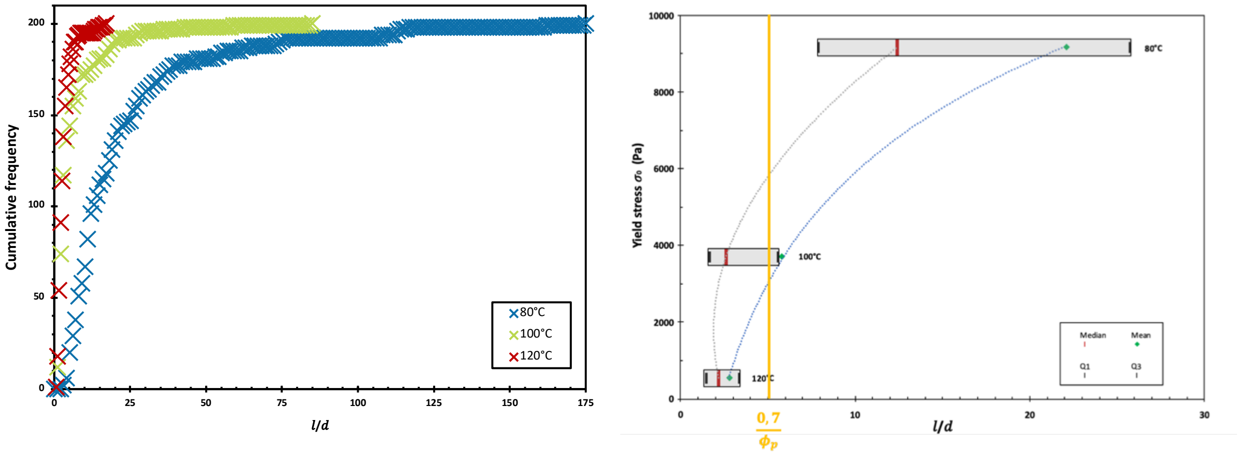

Figure 12. (A) Cumulative frequency of l/d ratios versus stretching temperature; (B) Yield stress versus l/d ratios (statistical parameters) with two guidelines for eyes (means in blue, median in grey)

The aspect ratio of an individual r-OPET fiber is the ratio of its length to diameter, which is an important parameter affecting the properties of a microfibrillated polymer composite. The diameters and lengths of 200 fibers were measured, thanks to ImageJ, under SEM observation. **Figure 12** displays the cumulative frequencies of r-OPET fibers with the stretching temperature and the statistical parameters that flew from it.

From the three curves plotted in **Figure 12A,** two elements can be extracted. Firstly, the more the temperature is close to the Tg of r-OPET (i.e. 80°C), the more the distribution is spread out on high values of l/d. Secondly, the standard deviation increases following the same tendency: in other words, the more the temperature is close to the Tg of r-OPET, the broadest is the distribution of fibers lengths in the blend and so the strongest is the anisotropy. This result confirms, on a more representative sample, the impression of intensifying the drawing of initial r-OPET drops' when the material is near the r-OPET Tg, emerging from SEM images (**Figure 9**).

Figure 12 B points out the relationship between aspect ratios and yield stress. To clarify the layout of data, the mean, median, first and third quartiles have been plotted rather than only the mean and standard deviation (because of the large dispersion of the measurements). The shift of aspect ratios with the stretching temperature is clearly visible: the mean of l/d at 80°C is almost four times more important than the mean at 100°C and eight times more than the one of 120°C. Concerning the median, the values at 120°C and 100°C are equivalent and six times lower than the median at 80°C. This kind of increase could remind the curves of percolation phenomena.

It is common to find in the literature about polymers loaded with high aspect ratios fillers (like carbon nanotubes) a relationship between the volume fraction of fillers required to reach the percolation threshold and their aspect ratios (Equation 3): [27-30]

$$\begin{cases} \alpha = \dfrac{l}{d} \\ \phi_p \cong \dfrac{1}{\alpha} \end{cases} \qquad (3)$$

where α (length/diameter) is the aspect ratio of a filler and ϕ_p the volume fraction required to reach the percolation threshold.

Usually, with an aspect ratio remained constant, the volume fraction of fillers is modified to determine the percolation threshold: the more α is important, the less ϕ_p necessary to percolate is significant. In our case, two components are different. First, instead of maintaining the aspect ratio constant, the loading rate (determined by the ratio of r-OPET integrated in the blend, *i.e.* 20%$_m$) is the same in each 20/80 blend. Then, the Equation 3 is not totally suitable. Indeed, the relation is preferentially used for very high aspect ratio fillers.

Favier et al. determined the volume fraction of whiskers needed to get a geometric percolation assuming that they had a cylindric shape and were randomly placed (in location and orientation). [30] In their case (0< α <200, close to our results), the percolation threshold was determined by:

$$\begin{cases} \alpha = \dfrac{l}{d} \\ \phi_p \cong \dfrac{0{,}7}{\alpha} \end{cases} \qquad (4)$$

The density of rPP given by the supplier is 0.915 g/cm^3. For r-OPET, a mean density value of 1.40 g/cm^3 has been taken into consideration. [31] Thus, for a 20%m r-OPET content in the blend, the volume fraction associated is around 14% what correspond to a percolation threshold from an aspect ratio of 5 (**Figure 12 B**) that is to say between 120°C and 100°C.

It is clear that this approach doesn't give a very formal indication but the order of magnitude is in good accordance with rheological results. Actually, the spectromechanical analysis (**Figure 8**) shows a liquid-solid transition between the two highest stretching temperatures. At 120°C, a cross-over of G' and G'' is visible. At 100°C, and at low frequency, G' and G'' are nearly parallel what corresponds to a rheological percolation.

More generally, with a constant volume fraction of fillers, shear thinning effects appeared at lower shear rate for higher values of aspect ratios and complex viscosity increase when increasing aspect ratios. [33-35]

As a consequence, 80°C appears to be the best drawing temperature in order to favour the appearance of r-OPET microfibrils and the improvement of the rheological properties of the (20/80) (w/w) (r-OPET/PP) blend.

2.5. Comparison between microfibrillated and non-microfibrillated blends

The impact of r-OPET into rPP on the mechanical properties of r-OPET/rPP blends was previously studied. [36] It has been demonstrated that the tensile properties and fatigue life of rPP were significantly increased (30% for elastic modulus) by the addition of 20 or 30% of r-OPET.

Here, we compared the rheological and mechanical properties of the (20/80) (w/w) (r-OPET/PP) blend before and after microfibrillation at the optimal temperature of 80°C determined previously.
According to **Figure 8**, both blends exhibit radically different rheological properties at 200°C. The microfibrillated blend has a solid-like behaviour, with rather high G' and G" moduli,

whereas its non-microfibrillated equivalent is at the frontier between solid and liquid-like behaviour. SEM results allow to correlate this difference with a difference in morphology (**Figure 9**). These differences in rheological behaviour for those two blends, having exactly the same composition, reveal the strong effect of the morphology (going from a drop to a fiber) on the viscoelastic properties, and allow to identify the solid-like behaviour of this blend as a rheological signature of the morphology.

Moreover, we can note that the rheological behaviour of the microfibrillated (20/80) (w/w) r-OPET/rPP is close to the one of a percolated filled polymer. It puts forward a possible percolation of the fibers in the microfibrillated blend. Hence, it seems that the fibers take more space and thus have a higher probability for the drops to connect to each other.

Furthermore, the real interest of microfibrillation is to obtain better mechanical properties than the "sea-island" morphology. Mechanical tests were thus performed to measure the effect of microfibrillation on the blend properties.

The mechanical behaviour of a composite depends of various factors: the compatibility between the fillers and the matrix, the dispersion of the fillers in the blend, the quality of the interfaces between fillers and matrix. [37]

Table 6 shows the detailed values obtained by tensile tests on different blends. To start with, because of their poor homogeneity, and the presence of nanofillers, the deformation at break is rather low for r-OPET and rPP, which may have contributed to the behaviour of the blends based on these two materials.

Moreover, the results regarding the temperature of drawing are also in a good accordance with the mechanical analysis: the tensile modulus of 80°C microfibrillated blend is significantly higher than that at 100°C.

For microfibrillated (20/80) (w/w) r-OPET/rPP, the tensile modulus is higher than that of the non-microfibrillated blend and the pure rPP. On the other hand, the deformation at break is lower than the one of the non-microfibrillated compound and of the pure rPP. The microfibrillation process thus appears as an efficient way to obtain an all-polymer composite with improved tensile modulus, but a slightly more fragile behaviour.

However, in the case of the microfibrillated blend the standard deviations are better (38% for rPP, 50% for 20r-OPET/80PP non microfibrillated and only 20% for (20/80) (w/w) r-OPET/rPP microfibrillated). As explained before, r-OPET is an inhomogeneous material with lot of different grades of OPET and fillers. Thus, the standard deviation can be important especially in the case of deformation at break and tensile modulus. The same phenomenon happens with rPP: recycled material can have various properties due to their various origins.

Table 3. Results of tensile tests

Designation	Tensile strength(MPa)	Tensile modulus (MPa)	Deformation at break (%)
r-OPET	60 ± 10	2300 ± 600	15 ± 15
rPP	31 ± 1	1300 ± 70	40 ± 15
(20/80) (w/w) rOPET/rPP non microfibrilated	26 ± 1	1535 ± 75	30 ± 15
(20/80) (w/w) rOPET/rPP microfibrilated at 80°C	32 ± 1	2000 ± 215	10 ± 2
(20/80) (w/w) rOPET/rPP microfibrilated at 100°C	29 ± 1	1570 ± 50	25 ± 10

2.6. Influence of the temperature treatment on the rheological behavior of the microfibrillated blend

In the previous parts, the rheological properties of the microfibrillated blends were studied at 200°C, which is well below the r-OPET melting point (T_M=250°C). Kuzmanovic et al. [38] showed that the microfibrillation was lost when the blend was heated above the melting temperature: the microfibrils relaxed back to a “sea-island” morphology. The objective in this part is to melt the blend thanks to an isotherm at 265°C for 10 minutes, in order to confirm this result.

Two spectromechanical experiments were performed on the same (20/80) (w/w) rOPET/rPP microfibrilated sample. The first one consisted in realizing a spectromechanical analysis at 200°C. After this first test, the temperature was increased at 265°C for 10 minutes in order to melt the r-OPET fibers. Finally, during the second one, the temperature was returned to 200°C to make a new spectromechanical test. To make sure no degradation of rPP occurs during these two spectromechanical analysis, a time sweep was realized at 270°C (extrusion temperature), 1 rad/s for 1 hour 30 minutes. This time sweep indicated that under those conditions only 20% modulus deviation can be observed. Hence, the obtained differences are not due to any degradation in the material.

The complex modulus of the microfibrillated blend before and after melting measurements are available in the Supporting information. Two different behaviours can be observed. The non-molten blend behaves as a viscoelastic solid, while the molten has a liquid-like behaviour. Melting results in the loss of the rheological signature of microfibrillation: the mechanical spectrum of the molten blend superimposes with the one of the blends that was not microfibrillated (**Figure 8**). This experiment thus confirms the importance of the temperature treatment during processing: heating the blend to temperature higher than the r-OPET melting temperature results in the loss of the microfibrillation.

Conclusion

Blends of (20/80)w r-OPET/rPP, that appear as the best ratio to obtain a favourable fibrillation morphology (*i.e.* a sea-island morphology), were manufactured and stretched either directly through the extruder or thanks to a tensile machine. With the first method, called hot stretching (because of a temperature range included between 220 and 260°C), the r-OPET droplets were not be able to fully turn into fibers contrary to the cold stretching (at a temperature close to the Tg of r-OPET) that has produced defined fibers. Their aspect ratios were measured from SEM images and compared to the rheological experiments which have presented a good accordance with a Cross model with yield stress.

The yield stress is a good indicator of the structuration of a blend. The experiments carried out directly during the extrusion process have shown an interesting increased of this parameter: from 123 to 1000 Pa with an optimized temperature (around 225°C). But this method is ten times less effective than the use of the testing machine. At 80°C, where the l/d ratio is the more important, the yield stress reaches almost 10 000 Pa.

In the context of European Commission strategy aiming for more circular economy, the plastic wastes reduction through more recycling and reusing seems to be a long-term solution. With the modification of the morphology (from drops to fibers and so from a liquid viscoelastic to a solid viscoelastic) and the increase in mechanical properties in comparison with non-microfibrillar blends, the composites obtained (with a smart response as a function of the temperature: appearance of optimized fibers at 80°C and loss of the morphology over 265°C) could appear as a part of the answer.

Acknowledgement

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Supporting information

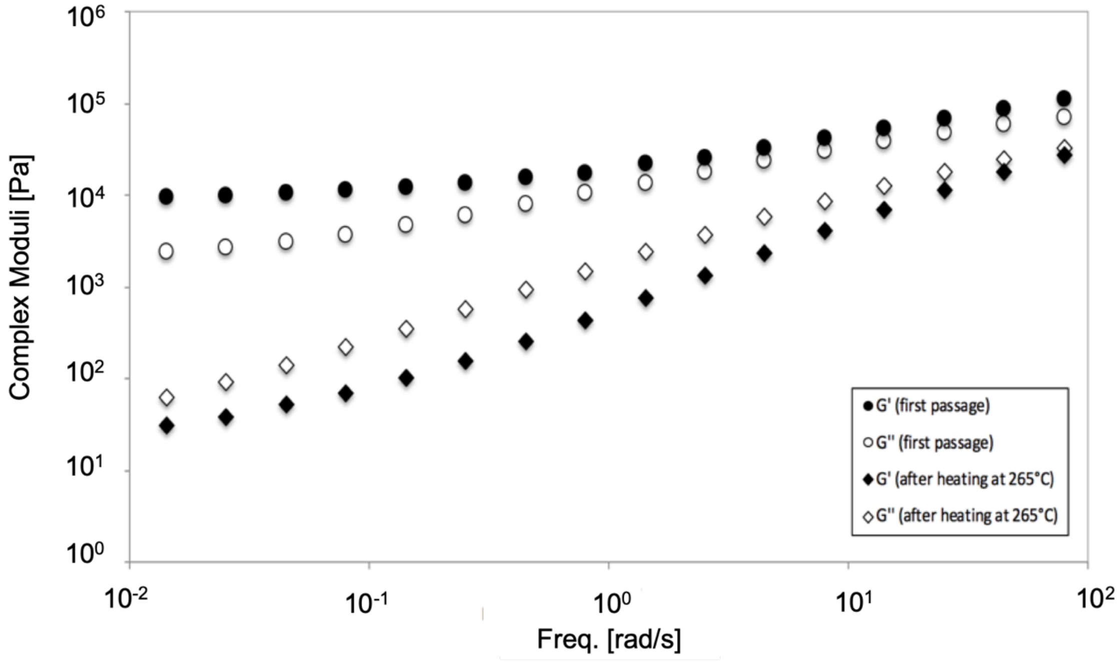

Figure A. Superposition of spectromechanical analysis of (20/80) (w/w) rOPET/rPP blend before and after thermal treatment (265°C, 10 min) at 200°C

Table of content

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Rheological, Thermal and Mechanical Behavior of all Recycled Opaque PET/PP Microfibrillated Composite (MFC)

Microfibrillation consists in the manufacture of micron scale fibers of a first polymer (recycled opaque PET) in a second one making up the matrix (rPP) to improve the properties.