Preliminary note

The impact of the increase in white opaque PET on the recycling of PET packaging

1/ Context

Conventionally, long-life dairy drinks (milk, drinking yoghurts, etc.) have been packaged in HDPE bottles, but this market now has access to a new material, in the form of white opaque PET (**150 million bottles sold in France in 2012, representing 5000 to 6000 tonnes**).

Opaque PET has UV and gas diffusion barrier properties that are comparable to those of HDPE. It also has a processability compatible with the increase in production output rates, allows for bottle weight reduction and for eliminating the aluminium seal on bottle caps.

Barrier properties required for preserving dairy drinks are provided by opacifiers, the most frequently used being titanium dioxide (TiO_2). These opacifiers may be added in varying concentrations, either on their own or mixed with other additives (carbon black, mica, silica, etc.).

Without the addition of opacifiers, PET is one of the resins best suited to the recycling process. The use of titanium dioxide calls for enquiry into the impact of a growing and increasingly significant proportion of this opaque PET on current recycling chains and outlets. Opacifiers are present in many types of HDPE packaging, and are well known to recyclers. However, there is a marked difference between the applications and markets for recycled HDPE and those for PET, which tolerate opacifiers to a much lesser degree.

The main outlets for recycled PET are bottles, fibre and sheet. The presence of the various additives contained in opaque PET prevents it from bring used in bottles and sheet applications, made from clear PET. Fibre has fewer constraints and can tolerate a small proportion of opaque PET in certain applications. However, to date there are no specific outlets for opaque PET alone or opaque PET in high concentration.

On a practical level, the current PET packaging sorting system produces two streams of PET, which are directed to two different processes:

- **the pale coloured PET stream**, the main applications of which are sheet and bottles, cannot accept opaque PET, even in small quantities. This will necessitate taking measures during the sorting process to ensure the absence of opaque PET pollutants in the pale coloured PET stream; this is even more important where the technology used includes a layer of carbon black; however, a proportion of pale coloured PET is also used in the fibre industry.
- **the dark coloured PET stream,** to which opaque PET is directed, a large number of recyclers systematically remove and reject bottles made of opaque PET, as their systems are completely unable to tolerate them. Some recyclers accept opaque PET in its current proportions, even though it brings no added value to the quality of the recycled material produced.

At its current level of dilution within the dark coloured PET stream (5% across all sectors - dairy, oils, detergents, cold drinks, etc.), the impact of opaque PET as yet remains moderate: to date there has been no particular technical problem or impact on the quality of recycled dark coloured PET, and recyclers are successful in extracting opaque PET bottles prior to the recycling process itself. However, PET bales bought by recyclers lose some of their initial value, since a proportion of the material is not currently recycled.

These impacts are limited for the moment, but will be exacerbated by any increase in the quantity of opaque PET. The outlook for the possible increase in market share of opaque PET is outside Cotrep's control but, for the purposes of this analysis, the following scenarios are put forward on a hypothetical basis[1]:

- *Current situation: for the estimated 6000 T of opaque PET placed on the market, and based on a calculation of one in two bottles selectively sorted per inhabitant, representing 3000 tonnes to be recycled, the proportion of opaque PET in dark coloured bales should currently stand at 7%; in fact, composition analyses show a proportion that does not exceed 3%, since some opaque PET also enters other streams (pale coloured PET and HDPE);*

- *By 2015, based on predicted growth of 45% in market share, the quantity of opaque PET placed on the market will increase to nearly 9000 tonnes; the quantity sorted will therefore be 4500 tonnes and the proportion in dark coloured bales will exceed 11%*

- *In the event that the dairy industry replaces HDPE entirely with PET (approximately 50,000 tonnes placed on the market), the proportion of opaque PET in the dark coloured PET stream would rise to about 40%.*

It is in this context that COTREP has carried out various preliminary studies on the recyclability of opaque PET packaging in the PET stream, in order to give a precise technical assessment of the impact of the presence of opacifiers and carbon black on the recycling of PET.

2/ Recyclability study: Results and initial conclusions

Since fibre is the only application that can accept a small proportion of opaque PET, this is the outlet for which we studied the behaviour of opaque PET during the recycling process. During the two tests, firstly in the laboratory and then under industrial conditions, fibre quality was assessed based on the two parameters of colour and mechanical properties.

For these tests, four "technologies" available on the French market were introduced in equal proportions into a pale coloured PET stream and a dark coloured PET stream[2]. Two types of opacifier were also tested, one based on titanium dioxide and the other on silicon dioxide. These trials also enabled us to assess the impact of the carbon black layer present in one of the technologies.

The laboratory tests and industrial tests concurred in terms of the following conclusions:

- For pale coloured PET fibre applications, and in concentrations of up to 15-20% opaque PET in the material, the mechanical properties of the fibres are maintained and remain the same as those of the control fibres. However, **the presence of the carbon black layer** caused greying of the fibre, rendering it **non-compliant with user specifications.**

- For dark coloured PET fibre applications, the mechanical properties were maintained up to concentrations of 15-20%, as above, while variations in colour - at these same concentrations - were not discernible, as a result of the initial colour of the incoming material. **Above a proportion of 15-20% opaque PET**, **recycling of the PET blend to produce fibres is no longer possible**, since the excessive proportion of opacifier in the incoming material creates processability problems and a reduction in the mechanical properties of the resulting fibres.

3/ Outlook

The tests carried out confirm that, in the event of significant growth in opaque PET, and without an increase in the existing number of outlets, its presence is extremely likely to result in the following consequences:

- From an economic point of view, the presence of a significant proportion of non recyclable PET in the main applications is likely to reduce the market value of PET bales;

- From a technical point of view, at proportions of over 15% within the dark coloured PET stream, opaque PET is detrimental to the processability and quality of the resulting fibres and is unsuitable for any further

[1] Sources: Eco-Emballages and ELIPSO, 2010 figures
[2] Conditions and protocol in the technical report

applications. Two solutions may be considered according to projected outlets (which, at this stage, have yet to be developed):

- o Sort the streams for recycling in order to remove a proportion of the opaque PET and thus return below this threshold. This solution would nevertheless increase the proportion of irretrievable material;
- o Create a specific stream for opaque PET, taking into account any colour restrictions.

In addition, any failure on the part of sorting techniques to extract opaque PET correctly and/or control the proportions would damage the credibility of the overall recycling process for dark coloured PET in fibre applications.

CONCLUSION

These initial findings may usefully contribute to other projects on the same subject. The information gathered to date is incomplete, and requires further study on the possibility of implementing, in the longer term, a recycling process including opaque PET, taking into account the specific properties of the material and oriented towards its own, customised outlets. COTREP is continuing its study to identify some outlets that should be confirmed by several industrial tests and an economic evaluation.

Technical report

The impact of incorporating white opaque PET into the PET stream

This technical report endorses the preliminary note of the same title, and describes the conditions and protocols that were implemented for the recyclability study on opaque PET, as well as the main conclusions in terms of fibre processability and quality.

1/ Analysis principle and criteria

The study focused on assessing the impact of the various additives contained in opaque PET on PET recyclability in the pale and dark coloured streams. Four technologies were selected from the main technologies identified in the production of TiO_2 -opacified PET bottles for use in the dairy industry, and these four technologies underwent recyclability tests.

In the first instance, Bottle-to-Fibre (BtF) regeneration tests were conducted on each technology in the laboratory, with each test conducted independently of the others. Following this, an industrial scale test was carried out to confirm the results obtained in the first test, both in the pale and dark coloured PET streams, for the four technologies combined.

During the laboratory tests, various homogeneous mixtures of opaque PET and recycled PET (R-PET) were prepared. For each mixture, a number of physical criteria, including mechanical, visual and thermal criteria, were assessed. We should note that the proportion of TiO_2, the size of the particles included in the material and their bonding properties during the processing of flakes are key factors in the variations seen in these technical specifications.

The procedure followed during this study was as follows:

1. **Determination of concentrations of opaque PET within the dark coloured PET stream** to simulate the replacement of HDPE by opaque PET at levels of 10%, 25%, 50% and 100% of the market (see above);
2. **Determination of viscosity indices and thermal characteristics** for the granules obtained;
3. **Assessment of fibre utility** (processing, product manufacture);
4. **Physico-chemical analysis of fibres**: viscosity index, colour of the products obtained, mechanical properties (tensile strength, fibre tenacity, etc.).

2/ Test protocols and results

a. *Laboratory tests*

1. *Types of sample*

The four selected technologies differed in terms of the size and proportion of the additives incorporated into the master batch. As a general rule, white opaque PET is composed of the following components:

- a **PET matrix** in a single or double layer;
- an **opacifying charge** of titanium dioxide (TiO_2), the percentage of which may vary between **5 and 10%** and of which the particle size is between **0.2 and 3 µm**;
- a protective **layer of carbon black,** which is not systematically present: only one of the chosen technologies included this.

The differences in the technical specifications of the fibres were assessed using several concentrations of opaque PET in the dark coloured PET stream. The selected concentrations represent the potential penetration of dairy industry opaque PET on the French market, and have been set at **10, 20 and 40% according to the following table:**

REPLACEMENT RATE	CONCENTRATION OF WHITE OPAQUE PET (STREAM Q5)
10%	≈ 7%
25%	≈ 15%
50%	≈ 25%
100%	≈ 40%

Calculation of the concentration of opaque PET in the dark coloured PET stream based on the replacement rate for dairy industry HDPE

2. *Results analysis: technical feasibility and measurement of physical quantities*

The full set of results is given in the table below. The values obtained have been compared to those of a control sample composed of 100% recycled PET from a standard dark coloured PET stream. Any variation in properties below 5% compared to the control was considered insignificant.

For blends containing between **10% and 40%** opaque PET, the resulting fibres mainly presented the required physico-chemical properties, and could therefore be incorporated into the existing dark coloured PET stream.

However, given the loss of sheen and the colour variations ranging from greenish to grey (in the case of the technology containing a layer of carbon black), **only concealed applications, or applications in which appearance is of secondary concern, may be foreseen.**

Samples / Physical quantities	Control (granules)	Granules	Fibres
Viscosity index (measured on granules)	0.87	0.5<VI<0.6 ⇨ VI<0.87	Reduction in VI generally proportional to the concentration of opaque PET ⇨ Impact on the processing parameters (adaptation required)
Thermal constants (°C)	Tf ~ 245 Ct ~ 185	243<Tf<250 180<Ct<190	-
Technical feasibility	-	-	High level of processability
Colouration	-	-	Greenish and dull tinge proportional to the opaque PET content and therefore the incorporated TiO_2
Mechanical properties	-	-	No significant variation from the control

b. *Tests under industrial conditions*

1. *Types of sample and tests carried out*

Based on the positive results previously obtained in the laboratory, the behaviour of flakes obtained from opaque PET dairy bottles was assessed **under actual industrial conditions**, at two concentrations.

The four selected technologies were subsequently used in the manufacture of three tonnes of bottles, each from blends containing concentrations of up to 25%. These were then ground into flakes and tested in blends in the **pale coloured PET stream (Q4)**[3] **and dark coloured PET stream (Q5)** in proportions of **20% and 25%** respectively.

2. Results analysis

The full set of results is given in the table below.

Physical quantities \ Samples		Streams tested	
		Pale coloured PET (Q4)	**Dark coloured PET (Q5)**
TiO_2 Content		**1.5%**	**1.9%**
Proportion of opaque PET		**20%**	**25%**
Rate of replacement of HDPE		**50%**	**62.5%**
Fibres	**Technical feasibility**	**High level of processability**	**Deterioration of extrusion proportional to the opaque PET content (and therefore the TiO_2 content)** **At maximum incorporation the product is non-compliant**
	Colouration	**Visible colour difference in comparison to the control => non-compliant with the usual specifications**	**No significant variation from the control**
	Mechanical properties	**No significant variation from the control**	**A reduction in mechanical properties proportional to the increasing TiO_2 content**

- **Pale coloured PET stream (Q4)**

The material, comprising 20% opaque PET and 80% pale coloured PET, underwent a conventional extrusion process. The recycler's usual protocol is to add a very small quantity of virgin TiO_2 to the mixture. In our case, this stage was rendered unnecessary by the presence of TiO_2 in the opaque bottles: after dilution of the material, the concentration of TiO_2 stood at 1.5%.

The fibres in the test had a distinct grey colour, and were therefore non-compliant: **even in very low concentrations in the material (1.25%), the impact of the internal black layer is too great to enable any applications for fibre obtained from the pale coloured stream.**

However, a high level of processability is observed in the recycled mixture, and a good stretch ratio in the resulting fibres. **In small quantities, titanium dioxide would appear not to alter the quality of recycled fibres. Opaque PET bottles, incorporated in controlled amounts and without a layer of carbon black, may consequently provide a useful source of titanium dioxide in recycling processes requiring the addition of an opacifier.**

- **Dark coloured PET stream (Q5)**

The proportion of opaque PET incorporated into the dark coloured PET stream has reached 25%, the equivalent of 50% HDPE replacement. The additional concentration of TiO_2 incorporated is a maximum of 1.9%.

With 25% opaque PET added to the incoming stream, the mixture does not have a high level of processability, mainly due to a drop in viscosity and a reduction in mechanical properties in fibres. The colour of the fibres is, however, comparable to that of the control, since colouration is limited by the dark colour of the stream.

Given the results obtained and the risk of supply variations (with the percentage of opaque PET varying between individual bales), the maximum acceptable proportion of opaque PET in the dark coloured PET stream is 15%.

[3] The pale coloured PET stream is not the natural destination for opaque PET: the test conducted under these conditions aimed to give an assessment of the processability of the blend according to the defined protocol.

3/ IMPACT OF THE TYPE OF OPACIFIER ON THE QUALITY OF FIBRES

The influence of TiO_2 on fibre quality has been demonstrated above.

In order to establish whether the impact observed is linked to the actual particle type, PET dairy bottles containing a different opacifier were exposed to the same laboratory test conditions as those previously described. In this opacifier, titanium dioxide was replaced by a silica derivative.

The sample in question comprised PET with an opacifier charge. Particle size was of the order of a µm, while the incorporation rate within the material (blend) was particularly high. As in the previous case, the various technical specifications for the fibres obtained were assessed at concentrations of **10, 20 and 40%** opaque PET blended with recycled dark coloured PET.

At 10% and 20%, the trials showed a high level of processability, allowing the production of fibres with satisfactory technical specifications. However, the results were non-compliant at a concentration of 40%, due to the excessive opacifier particle content in the material.

Consequently, irrespective of whether TiO_2 or a different opacifier is used, the industrial scale test results show that, under the conditions for size and percentage of opacifier charge defined above, in dark coloured PET streams containing more than 20% opaque PET the fibres obtained no longer meet technical criteria, and no longer comply with the rules in force in the profession[4].

TECHNICAL CONCLUSIONS

The main results of this study have enabled an assessment to be made of the impact of dairy industry opaque PET on the recycling process for pale and dark coloured PET.

At the quantities tested, opaque PET does not technically disrupt the recycling process for the pale coloured PET stream, but the colour of the fibres obtained does not comply with the expectations of users of regenerated fibres. Opaque PET is therefore excluded from this stream.

Opaque PET does not present a problem for the main applications within the dark coloured PET stream, since it currently remains at low concentrations (2%): consequently, it may be either removed by the recycler or kept in the stream.

However, **above concentrations of 15% opaque PET** (in other words, **1.125% TiO_2**), the resulting fibres have inadequate mechanical properties, and this factor prevents the integration of opaque PET in larger proportions. This observation is unaffected by the type of opacifier used (at the tested concentrations), since silica derivatives show the same results.

[4] These results concur with two empirical rules defining the impact of the charge according to the size and proportion of the particles incorporated into the resin, which are summarised in the following table:

RULE \ TECHNOLOGIES	OPACIFIER: TiO_2	OTHER OPACIFIER (BASED ON SiO_2)
The particle ratio should be below 5%, in order to favour processability	For 40% opaque PET introduced in dilution ⇨ < 5%: TESTED	For 40% opaque PET introduced in dilution ⇨ >5%: UNTESTED
Particle sizes (and size distribution) or particle agglomerates should not exceed 1/3 of the final diameter of the fibre	Size of fibres obtained in the laboratory: 6.25 to 5 dtex. Particle or agglomerate size should be below 7.24 µm ⇨ TESTED FOR THE 5 TECHNOLOGIES	