Guidelines on Acceptability of Additives and Barrier Materials in the PET Waste Stream for an Effective Recycling of PET

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In the development of these guidelines Petcore was supported by the PET industry and worked with national organisations in charge of recovering post-consumer plastic waste (in particular Valorplast, France).

1. Introduction

Recycling of PET bottles in Europe represented, in 2001, a volume of over 350 Kt and is still increasing.

The impressive recycling rates contribute to both public and legal acceptance of PET bottles in Europe while they are also beneficial to the entire plastics packaging industry.

PET keeps expanding in new beverage segments as new bottles providing outstanding barrier properties are being developed.

These new «high-tech» bottles, incorporating additives or barrier materials, will, at some point, challenge existing recovery schemes.

Petcore has studied the question and, in order to help the PET production, filling and recovery chain evaluate the impact of such bottles, it has developed these guidelines.

The guidelines take into consideration :

- The specific European market for PET barrier bottles.
- The assumption that, sorting of clear barrier bottles will be performed alongside clear bottles and sorting of coloured barrier bottles will be performed alongside coloured bottles.
- Technical know-how at the time of evaluation.
- Potential technical improvements in automatic bottle sorting and reclamation technologies (bottle grinding and washing, flake washing and flake sorting).

It must be noted that, these guidelines may evolve according to the progress of the above elements at the time of evaluation.

2. Objectives of the guidelines

- Present the PET industry with a tool that will help them evaluate the constraints and limitations linked to recovery and recycling of containers incorporating additives and barrier materials.
- Allow meeting material recovery legal requirements of both Packaging and Packaging Waste Directive 94/62/EC and CEN standard prEN 13430.
- Help national post-consumer plastics waste recovery organisations to decide on the most appropriate technique for waste collection and sorting.
- Demonstrate the responsible attitude of the PET industry with regards to recycling.

Additives and barrier material tested against these guidelines will reveal their behaviour in current recycling processes. The results of the tests will not only provide a rough indication on threshold ▸

values of the additive/barrier material tolerated in the end application, but will also provide indications regarding suitability of a particular additive/barrier material in the current R-PET stream.

3. Basic principles

Bottles containing a particular additive or barrier material must be acceptable to both current reclaim processes and to R-PET end applications.

Testing will be requested by either the

- bottle manufacturer or the
- barrier material supplier or the
- company promoting or commercialising the bottle (hereafter «the company»).

Petcore or any national organisation in Europe will provide all the necessary support and guidance to whomever decides to perform the tests.

Investigations are carried out under secrecy agreements and property rights of the results of the tests belong to the company only.

It is the sole right of the company to publish these results.

Tests and evaluations are carried out by well-known companies involved in either the R-PET reclaim process or in the R-PET end applications manufacture (hereafter «the experts»).

Details on testing procedures are agreed, prior to the testing process, between Petcore, the company and the experts.

4. Factors influencing the introduction of new materials in the PET recovery and recycling chain

To evaluate the possible consequences of a given barrier bottle, the following information is essential :

- Packaging description (shape, colour, content, weight, trade mark, distinctive features).
- Ease of visual identification for manual or automatic sorting (IR, UV, ...).
- Type of polyester (thermal stability and discolouration during solid stating).
- Type of barrier material/additive (physical properties : melt temperature, density, thermal stability during extrusion and solid stating).
- Amount of barrier or additive per bottle in % of weight, layer thickness.
- Quantitative analytical methods for the additive/barrier.
- Estimated amount of new bottles, growth rate and return rates in introduction area (country/region).
- Removal rate of barrier material/additive in the reclaim process (friction washing and chemical washing).
- Negative impact on the reclaim process or its water treatment
- Threshold concentration of barrier material/additive that can be allowed in the R-PET flake steam. ▸

5. R-PET applications

The R-PET applications these guidelines centre on are :

- Fibres (padding, carpets, isolation, non-wovens and textiles)
- Sheet and film.
- Strapping.
- Bottles.

The following properties of the additive/barrier material must be checked prior to the testing :

- **Food contact compliance**
  Additives/barrier materials must comply with food contact regulations in Europe.
- **Thermal stability of additives**
  If the additive causes fumes or smells it will be prohibited for many applications.
- **Discolouration**
  When reprocessed, additives must neither lead to any yellowness nor to grey effects and colours must remain stable.
  Information on discolouration can be obtained by performing simple tests (See appendix P-0).

6. List of appendixes

The appendixes to these guidelines describe how to determine threshold concentrations and removal rates of additives and barrier materials.

P-0 Yellowness index and determination of flake colour.
P-1 Evaluation of the influence of additives or barrier materials in the production and properties of R-PET fibres.
P-2 Evaluation of the influence of additives or barrier materials in the production and properties of R-PET strapping.
P-3 Evaluation of the influence of additives or barrier materials in the production and properties of R-PET sheet.
P-4 Evaluation of the influence of additives or barrier materials in the production and properties of bottles containing R-PET.
R-1 Evaluation of delamination and removal of barrier materials or additives during the reclaim process.

7. Approved Petcore protocols

The following protocols have been discussed both within the Technical Committee of Petcore and with EuPR :

- «*Evaluation of the influence of barrier materials on the production of R-PET fibres*». Dr.G. Salvio, Montefibre - Acerra Research Centre
- «*Protocol to evaluate the influence of a barrier material on the production of bottles*». Dr. A. Roulin, PTI Europe

The testing procedures given in both protocols are in line with the Petcore guidelines. ▸

I. Colour of Flakes and Powder After Heat Treatment - Yellowness Index (YI)

Property		Specification
Flake Colour	YI	19 max. (2)
	a	-
	b	9 max. (2)
	Δb	4 max. (3)

Notes :

- *Material must comply with all legal requirements applicable to the country where the bottles are going to be used. In several countries, the authorization for multilayer technology containing recycled material in the middle layer requires specifically that food grade PET or PET from beverage bottles is only to be used as the source for recycled material.*
- *Colour : The new pre-heated flake powder method is used as the reference. YI is the yellowing index, which is a combination of L, a, b values. YI can be easily measured by spectrophotometers.*
- *For Δb, an alternative colour determination test procedure is described below.*

A. REQUIRED EQUIPMENT

Hot air oven : temperature required 235+/- 5°C

- Precision balance (0.01g)
- Stainless steel container
- Chronometer
- Plastic shovel
- Plastic container
- DEWARE container
- Liquid nitrogen
- Grinder DAVENPORT with a screen of 1 millimetre
- Minolta Colour measurement equipment - Spectrophotometer Minolta CM 3500 D or newer model.

Parameters :

- Light : Day light 6500° Kelvin - 10° CIE 1964
- Hunter lab method
- L, a, b colours and YI Yellowness index (DIN 6167)

Safety : use special gloves for low and high temperature and goggles when you handle liquid nitrogen.

B. PROCEDURE

1) Preparation of the sample

a) Verify that the hot air oven is adjusted at 235°C +/- 5°C ;
b) Weight between 300 and 500 grams of flakes in the precision balance ;
c) Put the flakes in the stainless steel container ;
d) Put the container in the hot air oven. It has to stay 30+/- 2 min. in the oven ;
e) After completion of heating, remove the sample and let it cool down.

2) Colour measurement

a) Completely fill the spectrophotometer glass container with the flakes. Shake it 30 seconds. Add flakes to the glass container during shaking with your other hand because flakes fall out ;
b) The sample is ready to be measured ;
c) Put the glass container on the Minolta instrument. Start the measurement ;
d) After the first measurement, turn the container 90 degrees and perform the measurement again. Repeat the procedure at 180 and 270 degrees.
e) The instrument automatically averages the three measurements results ;
f) Empty the glass container ;
g) Measure two other samples with the same method from a) to g).

3) Grinding of flakes

a) Put the cooled flakes into the DEWARE container ;
b) Cover them completely with liquid nitrogen ;
c) Leave the flakes in the DEWARE for a minimum of 2 minutes ;
d) Open the grinder and remove the screen ;
e) Fill the screen with frozen flakes ;
f) Put the screen in the grinder and close it ;
g) Start it up and grind during the time the powder falls into the reception container ;
h) Stop the grinder ;
i) Continue from d) to i) in order to grind all the quantity of flakes frozen in the liquid nitrogen.

4) Colour measurement

a) Fill the glass container of the spectrophotometer with the powder. It must be totally full ;
b) When the glass container is full, shake it for 10 seconds ;
c) The sample is ready to be measured ;
d) Put the glass container on the Minolta instrument. Start the measurement ;
e) After the first measurement, turn the container 90 degrees and perform the measurement again. Repeat the procedure at 180 and 270 degrees.
f) The instrument automatically averages the three measurements results ; ▸

g) Empty the glass container ;

h) Measure two other samples with the same method from a) to h).

C. RESULTS

We obtain three measurements of colours L, a, b and YI -yellowness index- of the flakes and powder of flakes after thermal treatment.

Determine the average and the standard deviation of colours L, a, b and YI.

II. Determination of flake colour & Δb

A. PURPOSE

To outline the procedure for determining the L, a, b and Δb colour values for both washed flake and oven aged flake.

A first colour reading of the washed flake is taken prior to oven aging and a second reading is taken once the sample is oven aged.

High Δb values may be the result of residual caustic or glue contamination of the flake.

B. SCOPE

This procedure is suitable for :

- Spectrophotometer : Minolta, Model 3500D.
- Laboratory Oven : Conterm, Model 260M.

C. DEFINITIONS

- *Colour* : is a measurement based on the level of yellow within a sample.
- Δ*b Colour* : is a calculated result based on the colour b difference, before and after oven aging.

D. SAFETY

As sample trays are extremely hot after the test time required in the oven, this procedure must be carried-out wearing heat protective gloves, full-length arm coverings and safety glasses.

If, during removal from the oven, the skin comes in contact with the internal components of either the oven or the sample trays, the area affected must be placed under running cold water for at least 15 minutes.

The affected area may be bandaged, but not with wet bandages.

After the burn has been treated, seek further assistance with the fist aid officer and make sure that the incident is registered. ▸

E. METHOD

1. Sample Preparation

a) To ensure homogeneity of the sample, mix the flakes thoroughly prior to testing.

b) Weigh out one kilo (1kg) of flake onto an oven tray and spread the sample evenly.

c) Put the sample in the oven (set at 220°C) and leave for 45 minutes.

d) After the required time, remove the sample tray from the oven.

2. Colour Determination (Pre-oven aging)

a) Put approximately three hundred grams (300g) of washed flake in a beaker.

b) The sample must be ground using the laboratory course-grinding mill.

Grinder set-up :

- There are two screen passes available for the course grinder, one bearing 7mm diameter holes, and the second bearing 10mm diameter holes.
- The standard screen to be used in preparation for colour determination is the screen pass bearing 7mm diameter holes.
- To remove the screen from the grinder, remove the two screws on the front of the grinder. Once the screws have been removed, the screen will fall from the bottom of the grinder.
- To reinstall a new screen, insert the new screen from the bottom of the grinder, hold it in place and insert the screws.

c) Set up the spectrophotometer for flake measurement.

d) Put a sample of the ground flake in a petri dish and take a reading for colour. Record on the QA worksheet the L, a and b colour results for the washed flake.

3. Colour Determination (Post-oven aging)

a) After the one-kilo (1kg) sample has been removed from the oven, put approximately three hundred grams (300g) of oven-aged flake in a beaker.

b) The collected sample must be ground using the laboratory course-grinding mill.

c) Put a sample of the ground oven aged flake in a petri dish and take a colour reading. Record on the QA worksheet the L, a and b colour results for the washed flake.

Note :

- *Course flake does not provide with uniform coverage of the reading surface for colour determinations. As a result, deviations between readings are significant ! !*
- *To ensure an even coverage of the measuring surface, all course flake samples must be ground to a 4mm-particle size. Better coverage of the measuring surface reduces the variability of results between readings. (The ground flake particle size distribution will lie between 0 and 7mm).*
- *If flake samples are not ground, the variability of results increases. Consequently, negative Δb values may be obtained.* ▸

4. Calculation (Δb)

Δb = (Post-oven aging) Colour b - (Pre-oven aging) Colour b.

F. SPECIFICATION

The maximal limit value for Δb for washed flake is 4 ! ▸

Evaluation of the influence of additives or barrier materials in the production and properties of R-PET fibres.

Introduction

Fibres made from R-PET have a wide range of applications. These include production of textiles, non-wovens, carpets and insulation fibres. All these applications have a variety of performance requirements. As it is impossible to predict in which application a barrier bottle will end up, the barrier material or additive must not affect any of the mentioned applications.

To avoid that producers set their own testing conditions, the present testing guidelines intend to cover all applications and to be acceptable to all producers.

Target

The results of these spinning test procedures will give an indication on the threshold value that an additive or barrier material may reach without affecting either the spinning process or the fibre properties.

Experimental procedures

The procedures are based on a comparative approach where standard PET is substituted, little by little and at increasing rates, with additives/barrier bottles. In line with a typical production situation, the test samples will contain 50% regular textile-grade PET chips combined with a varying mixture of standard grade R-PET flakes. The flakes from the additives/barrier bottles make up the remaining 50% of the sample. Flakes can be taken from normal bottle production and bottles do not need to undergo the recovery plant's washing operations. However, material from a recycling plant is allowed.

Testing relates to a standard volume of barrier bottles of 20% in weight.

Evaluation of spinning behaviour

Each mixture is dried according to standard procedures and is fed to a laboratory device for staple fibre samples production.

No irregularities must occur.

No sticking, degradation fumes or smells.

The flake dimensions and the apparent density must allow transportation to drying and extrusion units.

The acceptable apparent density of the feed must be 0.28 g/cm^3 or higher.

The material must have good filterability in the spinning pack.

Pressure build up should be limited and there should be no increase in fibre breaks.

Evaluation of the properties of the fibre ▸

- **Mechanical properties**. These include tenacity, elongation, tenacity at 5% elongation and heat shrinkage. These properties should stay within 25% of the reference.
- **Discolouration**. Some fibre producers do not require a discolouration test. However, it is still recommended to perform such a test.
- **Dye uptake** : For this evaluation, it is recommended that the comparative measurement of the yellow index (Cielab System), be carried out on lab-dyed fibre samples. The fibres are dyed in a dispersed-blue dye bath and the dyeability is evaluated as a yellow index difference appearing when samples are compared to the reference. The maximum value allowed for the yellow index difference is 1.
- **Fluorescence**. Fluorescence is unacceptable as it raises problems in some end-applications. Quantitative evaluation can be obtained by comparing the yellow indexes (Cielab system) of non-dyed samples in the presence and in the absence of UV light. The maximum yellow index difference in both situations allowed is 1.

Conclusions

The maximum concentration of barrier material or additive allowed in the flake stream is obtained from the highest concentration fulfilling both production conditions and end-application properties requirements.

The maximum concentration of barrier bottles allowed in the reclaimer's feed stream can be calculated if the removal ratios of the reclaim process are known (see Appendix R-1). ▸

Evaluation of the influence of additives or barrier materials in the production and properties of R-PET strapping.

Introduction

Strapping made out of R-PET achieved a considerable market share. It is an important application for coloured bottles (green). R-PET strapping is a high performance product that can only be manufactured from high viscosity PET and low PVC content. Solid stating (post condensation) is essential in the production process to increase the molecular weight of R-PET. Solid stating is usually carried out after flakes are extruded into granules. Strapping and drawing of the extruded tape is obtained through a second extrusion. The properties of strapping are partly determined in the laboratory but, given its complicated quality criteria, they also need to be determined by performance tests during actual use.

Target

The results of the strapping test procedure will provide indications on the threshold value that a barrier material or additive can reach without affecting either the production process or the strapping properties.

Experimental procedures

These procedures are based on a comparative approach where standard R-PET is substituted, little by little and at increasing rates, with barrier bottles. Regular R-PET is replaced by a range of grinded barrier bottles making up to 20 % of total weight.

The barrier bottle material can be taken from normal bottle production and bottles do not need to undergo the recovery plant's washing operations. However, material from a recovery plant is allowed.

If most of the additive or barrier material is removed during the washing process, the suggested test levels of grinded barrier bottles into R-PET might be unrealistically high. A lower concentration range can then be discussed.

The following steps need to be evaluated :

- **Extrusion of flakes**. No sticking, degradation fumes or smells. The flakes must have a specific weight/volume ratio suitable for transportation to the drying and extrusion units. (> 0.28 g/cm^3)
- **Solid stating**. Barrier material must not affect post condensation reactions aimed at increasing the molecular weight of PET. The increase in molecular weight realized in a certain reaction time must not be reduced. The maximum deviation accepted is 5%. Specialized laboratories can perform small-scale tests.
- **Extrusion into strapping**. No process deviations. During the drawing process, special attention must be given to possible splitting of strapping as splitting is unacceptable.
- **Mechanical properties**. These include tensile strength and elongation at break, tensile modulus, notched izod tests and flexural strength and modulus. Moreover, specifications regarding ▸

water absorption, relative permeability, surface resistance and electric strength must be met. This test must be preferably performed in cooperation with a strapping producer.

Conclusions

Acceptable levels of barrier material or additive will result from the simultaneous fulfilment of the processing conditions and end-application properties specifications.

Some strapping producers will require a full performance trial in an actual application before they accept deviations from the current ISO 9000 standard flake production. ▸

Evaluation of the influence of barrier materials or additives in the production and properties of R-PET sheet

Introduction

Sheet production is an important application for R-PET. Its potential market, in Western Europe, is of 150 Kt a year. Sheet is produced in clear, green and black. The market for black is currently small but still relevant with regards to the brown/amber beer bottles expected to increasingly appear on the market.

Production process

Sheet production does not require any viscosity increase. The sheet is produced either directly from the flakes or after extrusion of flakes into granules. This extrusion process is less demanding than the extrusion processes required for both strapping and bottle production. Any barrier or additive passing the filterability test for fibre spinning is acceptable for sheet extrusion. If a new bottle must be evaluated for sheet extrusion only (and not for production of either strapping or bottles) a production trial is the only alternative.

Test should preferably be carried out in cooperation with a producer.

Barrier bottle flakes are added, little by little and at increasing rates, to the R-PET feed (up to 20% in weight). Any deviations (smells, degradation fumes, sticking effects or increased number of pinholes included) must be recorded. Particular attention must be drawn to discolouration and haze. It will be the producer who will judge whether deviations are acceptable.

Sheet properties

- **Mechanical properties.** These include measurements in both the extrusion direction and perpendicularly to it. Tensile modulus, tensile strength, elongation at break and tear strength are important. Barrier materials that passed the strapping tests are not expected to raise any problems in these mechanical tests.
- **Sheet appearance.** Colour deviations from standard R-PET sheet colour are difficult to judge. If colour deviations occur because of the barrier material, acceptability will need to be discussed with sheet producer. The barrier material must not cause black spots or surface irregularities. ▸

Evaluation of the influence of additives or barrier material in the production and properties of bottles containing R-PET

Introduction

Use of R-PET in food contact approved bottles is an excellent example of closed loop mechanical recycling. At present, the market is still limited but a large growth is expected. Given its potentially large volume, this application offers a valid alternative outlet to R-PET as its «classical one» (the fibre market) is gradually being transferred from Europe to Asia.

The process aimed at introducing post-consumer PET into food contact applications requires careful purification of the input material. Any pollutant the bottle might have come in contact with, subsequent to its original content, must be carefully removed. After thorough washing and grinding, flakes are extruded into granules. In order to remove the very last traces of pollutants, the granules go through a prolonged treatment under vacuum and at high temperatures. This process is called solid stating. Solid stating is also needed to increase the molecular weight of R-PET that will guarantee the technical properties of the bottles manufactured with recovered material.

It is important to ensure that any barrier material or additive introduced does not affect the solid stating process nor that it put in jeopardy food contact approvals.

Target

The results of this test will provide indications on the threshold value that an additive or barrier material can reach in the R-PET stream without affecting either the production process or the technical properties of the new bottle.

Experimental procedures

These procedures are based on a comparative approach where standard R-PET is substituted, little by little and at increasing rates, with barrier bottles. It is recommended that regular R-PET be replaced by a range of grinded barrier bottles up to 20 % of total weight. New bottle material can be taken from normal bottle production and bottles do not need to undergo the recovery plant's washing operations. However, material from a recovery plant is allowed.

If most of the barrier material is removed during the washing processes, the test levels of grinded barrier bottles into R-PET suggested might be unrealistically high. A lower concentration range can be then discussed.

The following processes need to be evaluated :

- **Extrusion of flakes into granules.** No sticking, degradation fumes or smells. The flakes must have specific weight/volume ratio suitable for transportation to the drying and extrusion units. (> 0.28 g/cm^3)
- **Solid stating of granules.** Barrier material must not affect post condensation reactions ▸

necessary to both increase the molecular weight of PET and to remove impurities. The molecular weight increase achieved in a certain reaction time must not be reduced. The maximum acceptable deviation is 5%.

- **Injection moulding and bottle blowing**. No process deviations. No filtration problems.
- **Bottle properties**. Bottle appearance (colour deviations and haze included) is a critical factor. The effect on acetaldehyde formation needs to be determined. Mechanical properties like burst pressure, top load, drop impact, stress crack resistance and creep need to stay within agreed limits.

It is recommended to cooperate with a specialised laboratory.

Conclusions

The acceptable levels of additives or barrier material in the flake stream will depend on both processability and on the properties specifications of the new bottle. The acceptable concentration of barrier bottles allowed in the reclaimer feed stream can be calculated if the removal ratios of the reclaim processes are known (See Appendix R-1). ▸

Evaluation of delamination and removal of barrier material during the reclaim process and possible effects of additives.

Introduction

European PET bottle reclaimers use a wide variety of processes. Moreover, the European processes are slightly different from the ones used in US.

The major difference between European and American processes relate to the pre-treatment and washing of bottles. In Europe, dry grinding without a pre-wash has now been almost completely abandoned and will surely not be considered for barrier bottles. Almost all European reclaimers use a hot bottle pre-wash followed by flakes grinding and either friction washing or chemical washing of flakes. After the washing process, a float/sink process removes low-density plastics like PE and PP from the PET. Some recyclers also use a counter current flow to remove those particles that either sink slowly or float. The next steps involve water separation, drying of the flakes and air separation. Due to delamination of multilayer flakes, particular attention must be drawn to a possible increase in the apparent density of the dry flake as this has an impact on its transport. In the dry stage, the flake passes through an air separator in order for fine particles to be removed. To increase the removal rate of thin barrier layers, it can be necessary to discuss the optimisation of this step with the reclaimer.

To remove PVC flakes, some reclaimers use either an electrostatic separator and/or flake sorters based on colour detection. To increase their removal ratio, some barrier materials could require a specific flake detector.

It is necessary to discuss with the experts as to whether any effect of an additive are to be expected. If not, there is no need to carry out this test.

Barrier bottles that passed the «Champions for change» programme of American Plastics recyclers (APR) will delaminate satisfactorily.

Test procedures

A. Laboratory trials

Small-scale experiments can give good indications as whether delamination of multilayers or removal of coating/plasma layers actually occurs. Some specialized laboratories undertake this kind of testing. They use, for the chemical wash, a detergent with 1% NaOH. So far, no laboratories test friction washing.

B. Plant trials

Barrier bottles must replace part of the regular feed during the regular production run. The percentage of barrier bottles replacing regular bottles will depend on the quantity of new bottles expected on the market. The feed can take up to 20 % in weight of barrier bottles. A feed composed of 80% regular bottles and 20% barrier bottles must be obtained during a period of half an hour. Samples must be taken at 5 minutes intervals as of the first (expected) appearance of barrier bottles flakes. The various waste streams should, if possible, also be sampled. The fraction removed during the air separation phase can be relevant. ▸

An analytical procedure is required to determine the concentration of barrier material in the flakes. With this data it is possible to calculate the removal ratio.

If the study centres only on the presence of very thin plasma coatings or on delaminaton of a multi-layer, it is sufficient to add a small amount of coloured barrier bottles to the clear bottle stream and to collect the coloured flakes at the end of the process. A microscopic examination of the flakes, or a partical size analysis in solution (Partisol test), will reveal to what extend the barrier layer has been removed or delamination has occurred. It will not be possible for the very thin barriers to be traced back in the waste steam.

During trials, the production process needs to be carefully observed as for apparent density effects of the dry flakes or increased wastewater problems. The composition of the air separation waste must be checked with regards to increased levels of PET as that might lead to a reduction in the R-PET recovery ratio.

Conclusion

Acceptability of a barrier bottle in the current recovery process will depend on : barrier/additive removal ratio, threshold values and market shares expected for the new bottle. ▮

Protocol to Evaluate the Influence of a Barrier Material on the Production of Fibres from R-PET

Introduction :

In order to evaluate the *maximum or threshold concentration* of the new barrier PET material in a R-PET stream at which Bottle to Fibre Recycling is still possible, in terms of spinning processability and fibre end-properties, this MONTEFIBRE's lab-scale test protocol can be followed.

This proposed protocol is basically structured on a COMPARATIVE APPROACH consisting in different evaluations carried out by substituting (at increasing levels) the New Barrier-PET material for the Standard R-PET in a test feed stream for the production of polyester fibre.

Other determinations must be done in an ABSOLUTE way with the aim of having a wide characterization of the new material useful for its best suitable transformation into fibre by the drying, extrusion, spinning and drawing processes.

On the basis of the experimental results a positive/negative judgment about the possibility of the new barrier material to be recycled into fibre can be formulated, indicating a maximum amount in mixture with the Standard R-PET.

Experimental session :

Part I

Some properties of the new Barrier- PET material have to be measured on pure material (100 %, not mixed).

A positive result for each of the following items (P) is required :

- **P1= Flakes Dimensions** : the new material flakes must have dimensions suitable for feeding to drying and extruding units.

  Acceptable range is
  0.5 cm < **P1**< 1.5 cm. for the maximum length.

- **P2 = Apparent density** : the new material must have a specific weight/volume ratio suitable for transportation and feeding to drying and extruding units. P2 is the weight of a defined volume of flakes.

  Acceptable range is
  P2 > 0.28 g/cm^3.

- **P3 = Intrinsic Viscosity** : the new material must have a intrinsic viscosity high enough to permit its re-extrusion in the transformation to fibre.

  Acceptable range is
  0,60 < **P3** < 0,80 dl/g.

- **P4 = Melt Viscosity** : the new material must have a melt viscosity compatible with spinning processability.

  Acceptable range is
  2000 < **P4** < 4000 poises at 270°<T(°C) < 280°.

- **P5** = **Heat Stability** : during drying and extrusion the new material must show a behaviour similar to the standard R-PET.

  Acceptable behaviour is

  P5 = NO STICKING, DEGRADATION FUMES, SMELLS.

- **P6** = **Filterability** : the new material must have a good filterability in the spinning pack. The pressure increase in a filtration pack during an extrusion test (Filter Test - annex) is evaluated for the pure new barrier material. P6 is a value of the time-pressure increase for filtration surface unit in the pack (ΔP) after 90 min of extrusion.

  Acceptable value is

  P6 = (ΔP) 40 bar/h*cm^2.

Part II

The determination of the maximum acceptable concentration of New Barrier-PET in a PET feed stream for polyester fibre production is evaluated by lab-scale spinning of test mixtures. These mixtures (Ci) are composed of Textile Grade PET Chips (T) Standard Bottle Grade PET Chips (S) and New-Barrier PET (N) in different percentages according to the following scheme :

Tab.1

Mixture	% T	% S	% N
C0	50	50	0
C1	50	40	10
C2	50	30	20
C3	50	20	30
C4	50	10	40
C5	50	0	50

Each of these mixtures is dried and fed to a lab-spinning device for the production of staple fibre samples of 6.7 dtex (6.35(0.35) count. The samples are characterized by the following items (M) to define the maximum allowable concentration of Barrier-PET in the R-PET stream.

- **M1** = **Mechanical Properties (Tenacity, Elongation, Tenacity at 5% Elongation)** : these measurements are carried out on the staple fibre samples obtained from mixtures C0 to C5.

Acceptable value for each sample (Cn for n = 1,2,3,4,5) is

M1(Cn) =

Tenacity (Cn) > 0,75 * Tenacity (C0)

0,75 * Elongation (C0) < Elongation (Cn) < 1,25 * Elongation (C0)

Tenacity 5% (Cn) > 0,75 * Tenacity (C0)

- **M2** = **Heat Shrinkage (BWS)** : this measurement is carried out on 10 m. of yarn (before heat -setting and cutting) in boiling water for 30 min. Then the percentage difference in the length before and after the heat treatment is evaluated and reported as BWS for each sample.

Acceptable BWS value for each sample (Cn for n = 0,1,2,3,4,5) is
M2(Cn) = 0.75 * M2(C0) < BWS(n) < M2 * (C0) 1.25 %

- **M3** = **Discoloration** : A significative fibre yellowing has to be avoid in the production from new barrier bottle. The yellow index difference among C0 not- dyed sample and Cn not-dyed samples has to be checked.($\Delta Yi(n) = Yi(Cn)-Yi(C0)$ with n= 1,2,3,4,5 not dyed samples)

Acceptable value is
$\Delta Yi(n) = \pm 5$

- **M4** = **Dye-Up-take** : this evaluation is a comparative measurement of yellow index (CIELAB System) carried out on lab-dyed fibre samples. The staple-samples obtained from the mixtures C0 to C5 are dyed in a dispersed-blue-dye bath and the dye-ability of the samples from C1-C5 is evaluated as yellow index difference ($\Delta Yi(n) = Yi(Cn)-Yi(C0)$ with n = 1,2,3,4,5) towards to the C0 sample.

Acceptable ΔYi value for each sample (Cn for n = 1,2,3,4,5) is
M4(Cn) = $\Delta Yi(n) = \pm 1$

- **M5** = **Fluorescence** : this phenomenon must be absent to avoid problems in some end-uses. A quantitative evaluation can be obtained by comparison of the yellow index (CIELAB system) of non-dyed samples in the presence and in the absence of UV light. Thus, the yellow index difference ΔYi^{F}= Yi (UV-on)-Yi (UV-off) measured for each fibre sample has to be calculated.

Acceptable $\Delta Yi^{F}(Cn) = [Yi\ (UV\text{-}on)\ (-Yi\ (UV\text{-}off)]_{Cn}$ value for each sample
(for n = 1,2,3,4,5) is
M5(Cn) = $\Delta Yi^{F}(Cn) = \pm 1$

Conclusions

A positive judgment on the processability of the New-Barrier PET will result from the simultaneous fulfilment of items P1, P2, P3, P4, P5, P6.

The maximum allowable concentration of the New-Barrier PET in the feed stream will be the highest still simultaneously fulfilling of items M1, M2, M3, M4, M5 for the different test mixtures according to the scheme of Tab.1. ▮

Protocol to Evaluate the Influence of Barrier Materials or Additives on the Production of PET Bottles

Introduction

PETCORE is in the process of formulating guidelines to evaluate the influence of barrier materials or additives on the R-PET recycling processes. Commercially, the barrier materials are either applied as a coating or introduced in a co-injected multilayer configuration. Additives are generally incorporated into the preform during injection moulding in the form of liquid or solid masterbatches. In order to judge the influence of these materials on the recycling process, production of bottles containing recyclate from such bottles is recommended. The following protocol can be followed to determine acceptability.

A positive test result will indicate the acceptance of the material for this recycling application at the level conducted in the test. In combination with other test protocols (e.g. Montefibre for fibres) the acceptability of the bottle containing barriers or additives for R-PET recycling can be judged.

Acceptability of a particular material is determined by comparing bottles made with clean washed flake from the test material and similarly cleaned, washed flake from identical bottles which do not contain the barrier material, coating or additive. In order to avoid the influence of extraneous variables like adhesives, labels or of the recycling process, the standard flakes and the flakes containing the material under test should be produced from unlabeled preconsumer bottles. If (partial) removal of the barrier material during a reclaim step is required, both the standard flake and the barrier containing flakes should follow the same procedure in line with the appendix R1 of the guidelines describing the study of delamination and removal of barrier material during the reclaim process. If this reclaim process cannot be carried out for practical reasons, as a second alternative a mixture of barrier material and regular bottles might be composed representing the composition after the reclaim process. Proof has to be delivered that the chosen composition is realistic.

In this protocol the assumption is made that during the next decade the R-PET content in a food contact bottle will not exceed 25% and that the penetration of bottles containing barriers, coatings or additives in the PET bottle market will not exceed 7 %.The second assumption will require testing at 20 % levels to account for fluctuations in concentration and cumulative effects. The first assumption only applies for R-PET obtained via curbside collection. Industrial bottle waste or bottles collected via deposit systems might be applied at higher concentrations if suited.

Flake specifications

1. Apparent density

Transportation to drying and extruding units should not cause problems.

Required : apparent density > 0.28g/cm^3

2. Colour

Required : The b* value should not exceed a value of 4.

Evaluation of processing

The following processing steps have to be distinguished :

Extrusion and pelletisation.

This will require the following test mixtures :

Sample A	Standard flake - 100%	Barrier/additive flake - 0%
Sample B	Standard flake - 80%	Barrier/additive flake - 20%

Specifications to be met are :

3. Intrinsic viscosity

Required : After extrusion, the IV of sample B should be within 0.02 units of the control sample A.

4. Heat stability

Required : No sticking, fumes or odors should be noticed when compared to control sample A. In addition, no additional thermal degradation, in the form of black specks or other inclusions should be noticed.

5. Filterability

The filterability of sample B must be compared with sample A under identical conditions representative of the actual production situation.

Required : The pressure increase in a filtration pack during an extrusion test should be identical for both samples.

Standard conditions for control and test samples will be defined and designed to mimic actual production situations. All process parameters for each sample will be monitored and reported. Screens from control sample and study sample will be analysed for any variations.

Solid stating

Materials A and B should both be solid stated under identical conditions to increase the molecular weight until a final IV of 0.82 ± 0.02 is reached. The increase should be monitored via hourly checks during the solid stating process.

6. Time of processing

Required : Sample B should reach this viscosity in a time equal to the time needed for sample A or to a maximum of 1 hour longer.

7. Pellet colour

Required : The pellets should not increase more than 10% in colour (L,a,b should have a maximum value of 1.) ▸

8. Acetaldehyde content

Required : The AA content should not increase more than 0.5 ppm

Injection moulding of preforms

The following compositions should be injection moulded into an appropriate preform :

Sample C	75% virgin bottle PET + 25% *(or 50%)* Sample B (after solid stating)
Sample D	75% virgin bottle PET + 25% *(or 50%)* Sample A (after solid stating)

9. Injection processing

Required : No significant differences in processing between C and D under identical conditions.

10. Preforms

The preforms of sample D should be compared to the preforms of sample C and meet the following requirements :

Required :

10a. Visual inspection : No increase in black spots, particulates or gels.

10b. Intrinsic Viscosity : IV of the preforms of sample D should be within ± 0.02 units

10c. Acetaldehyde concentration : The preforms from sample D should not exhibit an acetaldehyde increase of more than 1ppm above that of the preforms from sample C.

10d. Colour : The preforms from sample D should not exhibit a colour value DELTA CMC of greater than 2.

10e. Haze : The preforms from sample D should not exhibit an increase in haze of more than five per cent above that of the preforms from sample C.

Blow Moulding

The preforms produced from samples C and D should be blow moulded into appropriate bottles for the preform design.

11. Processing

Required : No significant differences in the resulting containers between samples C and D under identical processing conditions. It is understood that small differences in process settings are generally necessary between different batches of preforms. ▸

Container properties

12. Bottle properties

Required : A reduction in performance of Sample D when compared to Sample C should not exceed 5% when the bottles are tested for the following performance criteria :

Visual inspection for black spots, particulates or gels.
Section weights
Brimful and fillpoint volumes
Headspace AA - a maximum increase of 0.5 µg/L
Burst strength
Drop impact
Top load
Stress crack resistance
Thermal stability
CO2 loss by FTIR

Conclusion

The material is deemed to be acceptable for bottle-to-bottle recycling when each of the above performance criteria is met.

Please note : Should a material meet all of the above specifications, this procedure only substantiates the fact that the material is suitable to be re-used as a food container. Prior to its use for this application, it is necessary to verify that the material is in compliance with all governmental regulations for use as a food container. This procedure does not certify compliance with any legal authority.

Note : *The levels of flake containing barriers, coatings or additives and the permissible differences in properties between the control sample and the materials under evaluation were defined during discussions within the PETCORE technical committee.* ▮