Maisons-Alfort, 27 November 2006

OPINION

of the French Food Safety Agency (Afssa) on the assessment of health risks associated with the use of materials made from recycled poly(ethylene terephthalate) intended for or placed in contact with foodstuffs and drinking water

LA DIRECTRICE GENERALE

On 8 November 2000, Afssa made a self-request on the health risks associated with the use of materials made from poly(ethylene terephthalate) (PET) intended for or placed in contact with foodstuffs and drinking water.

CONTEXT

In 1993, the French Higher Council for Public Hygiene (Conseil Supérieur d'Hygiène Publique de France/CSHPF) was consulted with regard to registrations requesting authorisation of use of materials containing recycled PET. In response, a favourable opinion and general opinion on recycling were issued the same year. Two registrations were subsequently sent to the CSHPF in 1996. Afssa assessed them and issued a favourable opinion in 2000, the year in which a number of similar registrations were sent to Afssa.

In view of this initial experience and the growing number of requests, it seemed necessary to develop an overall approach ensuring systematic and uniform assessment of the potential risks associated with PET recycling for contact with foodstuffs or drinking water, fields for which there are distinct regulations.

METHODOLOGY AND EDUCATED QUESTIONS

In this context, a working group (WG) "Health assessment of materials composed of recycled PET used as a material in contact with foodstuffs or drinking water" was created at Afssa. The objectives of this group was to identify critical points of PET recycling, propose a methodology for assessing the health risks associated with the use of recycled PET and draw up guidelines for constituting registrations submitted by manufacturers.

The working group heard professionals, recycling technologists, potential users of recycled PET and scientists, specialist in materials or in risk assessment. The WG considered the previous work, and particular attention was paid to the work from a European research programme (the conclusions for which were published by ILSI in 1997). Since then, some recent work providing a more detailed risk assessment (European FAIR programme "recyclability" 1998 - 2002) and a method for predicting migration on the basis of recycled PET (ADEME programme - Eco-Packaging 1997 - 2001) have become available. The working group took account of this new information and adapted it within its assessment procedure.

The working group also examined the potential risk of chemical contaminants present at very low levels. This has led to a concern threshold being **set**, one that is essential for drawing up guidelines.

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OPINION

After consultation of the working group "Health assessment of materials composed of recycled PET used as a material in contact with foodstuffs or drinking water" and the specialist expert committees "Water" and "Food Contact Materials", Afssa is issuing the following opinion, completed by the appended report:

Whereas the requirements of European Directive 94/62/EC on packaging waste management and objectives on the rate of recycling of plastic materials;

Whereas European Regulation 1935/2004 on materials intended to come into contact with food which states that food contact materials must not transfer substances to foodstuffs in sufficient amounts to endanger human health;

Whereas finished packages and materials obtained from recycled materials must present all the guarantees of consumer safety, as recommended by the CSHPF in 1993[1];

With regard to recycling processes

Whereas selective sorting and collection of waste enable materials initially designed for contact with food to be selected at the start of recycling processes;

Whereas several steps of recycling processes result in PET decontamination, with yields reaching up to 99 % for substances of lower molar mass;

Whereas the substances that are the easiest ones to be eliminated during these recycling steps are also those are able to migrate faster (volatile substances, low molecular mass);

With regard to the assessment of potential health risks associated with the use of recycled PET

Whereas the possible health risk associated with the use of recycled PET in contact with food is associated with the presence of chemical contaminants that may arise from an unsuitable re-use of packaging materials by consumers or contact with waste;

Whereas the FDA believes that if an authorised molecule turns out to be carcinogenic, the risk excess associated with daily exposure throughout a person's lifetime of 1.5 µg/person/day would be less than 1 in 1 million [2], which represents a very low level of risk;

Whereas the specific features inherent in PET recycling and considered for the risk assessment conducted by Afssa (type, concentration and low frequency [3] of potential contamination of recovered PET, decontamination process, reactivity of potential contaminants, *etc.*) [4], an exceptional exposure of 1.5 µg of contaminant from recycled PET/person/day represents a tolerable health risk, even when the chemical structure of the contaminant has not been identified;

Whereas a migration limit less than or equal to 1.5 µg of contaminant from recycled PET/kg food or water is considered to be without significant risk for consumer health;

Whereas a migration model, where each parameter has been assessed with a safety margin, enables an over-assessed migration to be predicted, and links this migration limit of 1.5 µg/kg food to a maximum tolerable concentration of pollutant in the materials composed of recycled PET, this maximum concentration depending on the molar mass of the contaminant, conservation temperature and shelf life of the products;

Whereas the risk assessment involves ensuring that the materials resulting from the recycling process do not contain any contaminant at a higher concentration than this maximum tolerable concentration in the recycled PET;

Whereas in practice it is impossible to check the absence of all contaminants with a lower concentration than this maximum tolerable concentration in each batch of recycled PET;

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[1] CSHPF opinion of 7 September 1993 on materials recycled from used packaging in contact with foodstuffs. It states that recycled materials must present the same guarantees as virgin material.

[2] Food and Drug Administration, Department of Health and Human Services, 1995, "Food Additives; Threshold of Regulation for Substances used in Food-Contact Articles", Federal register, Vol. 60, N° 136, 36582-36596.

[3] Statistically exceptional character of such a contamination, which could be assessed as one bottle in several thousand in recent studies: WELLE F. & FRANZ R. (10 and 11 February 2002), "Typical contamination levels and patterns in and analytical recognition of postconsumer PET recyclates", Presentation in Varese Italy, EU – Project FAIR-CT-98-4318 "recyclability".

[4] *Cf.* report appended to this Opinion.

Whereas a decontamination yield of 99 % (measured on model substances for which the list is proposed) guarantees that the maximum tolerable concentration of a contaminant in recycled PET will not be exceeded and therefore that the migration of these contaminants will be less than or equal to 1.5 µg/kg of food or water in drinks;

Whereas the studies [5] conducted on thousands of PET bottles collected in different countries showed that the contamination rate is 20 mg/kg of recovered PET at the most [6], and that the main pollutants identified are food flavourings;

Whereas the recycling processes with a decontamination rate of 99 % bring this value of 20 mg/kg below the maximum tolerable concentrations,

In view of these analytical elements, Afssa considers that the use of materials in poly(ethylene terephthalate) (PET) intended for or placed in contact with foodstuffs and water in drinks does not represent a health risk for consumers once the recycling process:

- is assessed from the collection of the used PET to the production of recycled PET. For this, Afssa proposes guidelines (*cf.* Annex I) for constituting registrations requesting authorisation of use.
- guarantees its capacity to eliminate potential contaminants, particularly by complying with the decontamination criteria (*cf.* Annex I).
- complies with the recommendations for production monitoring (*cf.* Annex II).

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[5] BAYER F. (2002), "Polyethylene terephthalate recycling for food-contact applications : testing, safety and technologies: global perspective", *Food additives and contaminants*, Vol. 19. supplement 111-134.
FRANZ R., MAUER A. AND WELLE F. (2004). "European survey of post-consumer poly(ethylene terephthalate materials to determine contamination levels and maximum consumer exposure from food packages made from recycled PET", *Food Additives and Contaminants*, Vol. 21, 265-286.

[6] Recovered PET: collected, sorted and washed used PET.
Recycled PET: recovered PET that has undergone a recycling or decontamination process.

Annex I

Guidelines for constituting registrations requesting authorisation of use of recycled Poly(ethylene terephthalate) (PET) intended for contact with food

Preamble

These guidelines regard materials made exclusively from PET and recycled PET. Finished products made from recycled PET must comply with the regulations set for materials in contact with food and/or drinking water (Regulation 1935/2004 and Directive 2002/72/EC [7]).
The guidelines apply in the most common cases, corresponding to contacts at temperatures less than or equal to 40 °C. If different requests are made, other conditions for use may be envisaged.

I.1- Subject of request

Manufacturers wishing to recycle PET for food use must indicate, in detail, the subject of the request, conditions for use and, in particular, the maximum percentage of recycled PET that will be used in the composition of the finished articles. Manufacturers must also state if they are targeting applications for drinking water or not.

Afssa may only take account of the conditions stated by manufacturers in this paragraph "subject of request".

All the steps must be laid out in details, specifying in particular their technological function (sorting, regeneration, elimination of metallic materials, decontamination, *etc.*).

Manufacturers must also:

- specify the steps over which they have direct control (on a production site under their responsibility) and those which they control through a document of specifications (materials purchased). In the event that they do not carry out the collection or sorting of used bottles, they must indicate their origin and attach the specifications that they give to their suppliers,
- undertake to set up a quality assurance and traceability system of raw materials, their finished products and the recycled PET transformation process (to prevent derivatives of the process). If the steps of the recycling process are certified, the certificate from the certifying body must be included in the request dossier,
- undertake to subsequently declare any significant modification to the decontamination process that is likely to have an impact on the quality of their finished products. They must then provide a new request dossier containing all the elements which will enable a new assessment of the health risks to be conducted.

I.2- Collection, sorting and regeneration

The means of collecting input materials and successive sorting operations must be described in details by manufacturers. They must also refer to the specifications laying down the conditions for recovering sorted recyclable materials. The specifications document must be included in the dossier and the specifications described.

After regeneration (washing, grinding, *etc.*), the PET flakes must contain less than 0.05 % of materials other than PET (wood, metals, PVC, *etc.*). The regeneration step must be described, with particular mention of how it eliminates possible contaminants. The composition of detergents

[7] In practice, reference must be made to the most recent regulations. These may be verified by office C2 of the Direction Générale de la Consommation, de la Concurrence et de la Repression des Fraudes (DGCCRF)/General Directorate of Fair Trading, Consumer Affairs and Fraud Control – Ministry for the Economy, Finance and Industry.

used during the cleaning steps must be indicated, and must be compatible with food contact (ministerial order of 8 September 1999 – Brochure 1227 - DGCCRF).

For these three steps, manufacturers must prove that they control all of these criteria and explain how they obtain the finished product.

I.3- Assessment of the capacity of the treatment process to decontaminate PET

I.3.1- Decontamination rate

The main requirement of these guidelines, the ultimate objective of recyclers, must be to ensure and prove that the migration of any contaminant cannot exceed 1.5 µg/kg of food.

The capacity of the recycling process to decontaminate will be assessed using an experimental decontamination test. The decontamination yield of the process will be calculated and must be more than or equal to 99 %. For benzophenone, whose molar mass is high and diffusion coefficient is lower, a decontamination yield of 90 % must be achieved.

This test may be conducted on materials made on a pilot line (particularly for authorisation requests prior to the construction of an industrial site). Manufacturers must then prove that the real production unit performs in the same way as the pilot unit in terms of chemical decontamination.

Virgin PET must be spiked in the mass by model substances, to a concentration of around 500-1000 mg/kg of PET for each substance after the PET is dried (the total amount of concentrations of model substances must not exceed 5000 mg/kg). These concentrations are much higher than realistic pollutant concentrations, but necessary for estimating the decontamination rate, through analytical procedures.
These flakes (or granules) thus contaminated will then be introduced into the treatment process and undergo the full process. The concentration of model substances will be checked by extracting the PET before introduction into the process and after each step.

The model substances to be used are given in the table below [8].

Table 1: List of model substances used in the experimental PET decontamination test.

Model substances	CAS number	Molar mass (g/mol)
Toluene	108-88-3	92
Phenol	108-95-2	94
Chlorobenzene	108-90-7	113
Limonene	138-86-3	136
Benzophenone	119-61-9	182

Manufacturers must describe:

- the method used to impregnate PET flakes. For example, soaking the flakes in a solution of model substances in the dichloromethane allows the flakes' pollution throughout[9]. Other protocols described in literature may be used if they lead to a similar percentage of contamination throughout. Protocols that impregnate the surface of materials, flakes or granules only should not be used as, in this case, the model substances would be eliminated during the washing or drying steps, preventing the decontamination yield from being measured. Thorough impregnation results in the conservation of a sufficient concentration of the model substances in the materials after these steps.

[8] Their choice of substances in Table 1 is guided by:
- their volatility and molar mass: substances with a lower molar mass are generally eliminated during the PET drying step; higher molar masses migrate more slowly,
- their solubility: some of these substances are soluble in aqueous simulants, which is essential for assessing migration studies.

[9] PENNARUN P.Y., DOLE P., FEIGENBAUM. A. (2004). "Functional barriers in PET recycled bottles. Part I: determination of diffusion coefficients in bi-oriented PET with and without contact with liquids" . Journal of Applied Polymer Science, 92, pp. 2845-2858.

- the detailed conditions for producing the material or, where applicable, the finished product.
- Extraction and dosage methods must be validated and may be based on standard AFNOR NF V03-110 or, where applicable, AFNOR NF T 90-210 (for analyses in water). The protocols used should be described in detail.

I.3.2- Migration of model substances

Migration studies do not replace assessment of the capacity of the recycling process to decontaminate (decontamination rate) as specified in the previous paragraph.

Contact with food simulated by water and acetic acid at 3 %:
If a PET contains 400 mg of a model substance/kg PET after washing and 4 mg/kg at the end of the recycling process (decontamination yield 99 %), the model shows that migration after 10 days at 40 °C will not exceed 1.5 µg/kg of food, whatever the contaminant mass (Figure 2).

Contact with other simulants:
The predictive model corresponding to Figure 2 is only applicable for water and acetic acid at 3 %. For other simulants, the finished products (spiked with model substances) must undergo migration studies of model substances so as to determine the maximum concentration in the PET (after decontamination) compatible with a migration lower than 1.5 µg/kg of alcoholic or fatty food.

These tests are conducted on finished products (bottles for example) made from spiked PET having undergone the recycling process (the same as in I.3.1). The simulants and migratory conditions used must be suitable for the type of food to be packaged and comply with directives 97/48/EC and 85/572/EC laying down the “basic rules necessary for testing migration” (see note 7). The protocol should be described in details. Manufacturers must:

- give the concentration of model contaminants in the PET subject to migration testing (in principle about the same as in paragraph I.3.1),
- describe the migration tests,
- give the migration values (µg/6dm²).

On the basis of these elements, a maximum contaminant concentration in the PET will be determined using the usual proportionality rule between the migration of model substances and their concentration in the material.
For example, if a PET containing 4 mg of model substance/kg of PET (after decontamination) gives a migration of 15 µg/kg of ethanol (random example), a maximum of 0.4 mg pollutant/kg of PET must be guaranteed after decontamination. With account taken of a decontamination rate of 99 %, this amounts to 40 mg contaminant/kg of PET after the washing steps and before decontamination.

Manufacturers must describe all the methods implemented so as to guarantee that this maximum concentration is not exceeded.

<u>Comments</u>

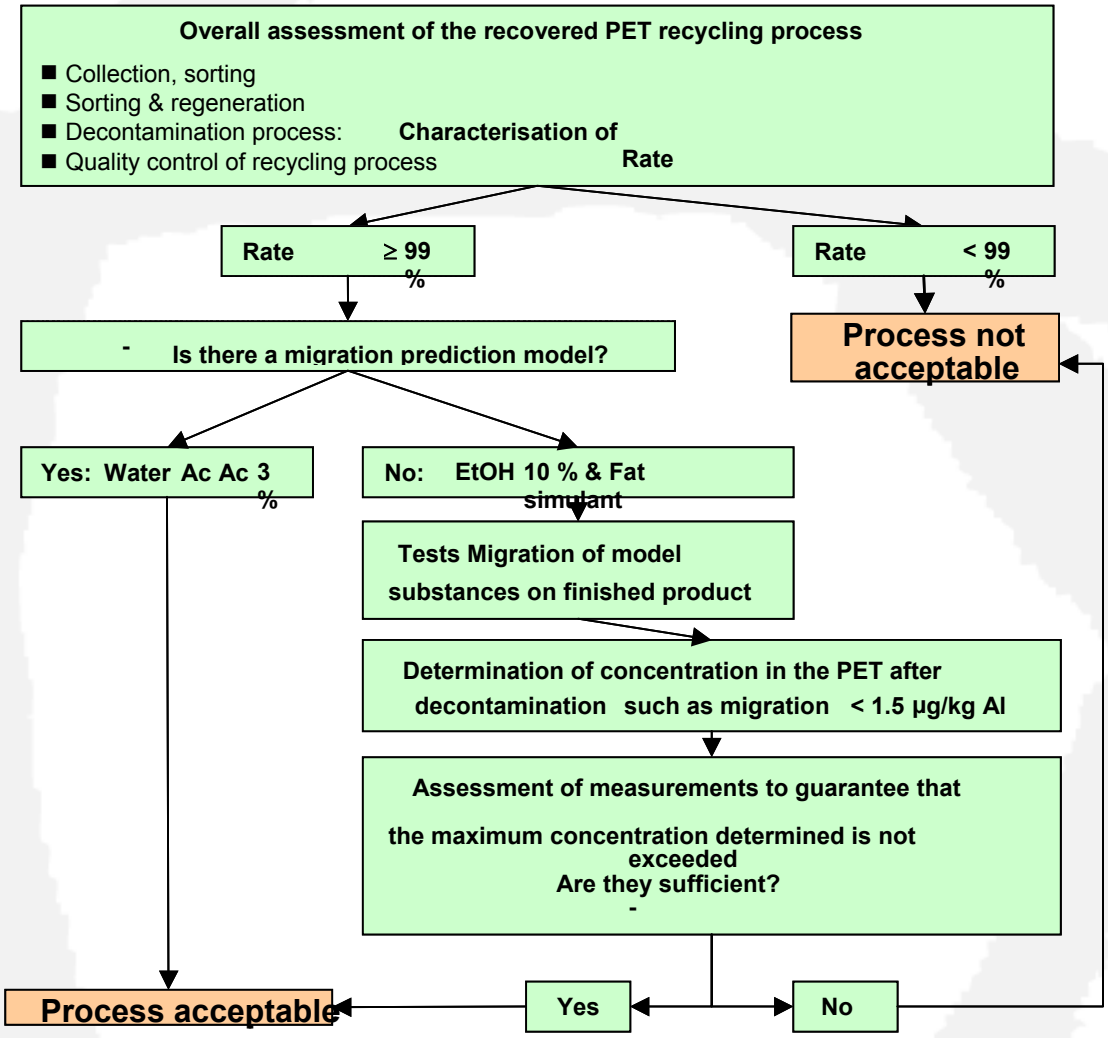
The guidelines are meant to meet the most common requirements as regards the majority of drinks or foodstuffs.

However, manufacturers may propose another means of assessment or other scientific elements that have not been considered in the general guidelines. In this case, they must specify all the arguments justifying their choice in a specific document. The scientific publications on which the chosen methodology is based must be enclosed with this document. In view of the scientific justifications put forward, the standard dossier may be required.

The migration conditions are suitable for single and multi-layer materials where the recycled PET is in the contact layer.

This assessment framework is only fitting for exceptional contamination. For recurring contamination, contaminated batches may not come into contact with food.

Figure 1: Organisation chart of the overall assessment of the PET recycling process



Annex II

Recommendations on monitoring recycled PET production

In the case of authorisation, quality control of recycled PET production must be set up, so as to:

- guarantee that the quality of the recycled PET is and will stay equivalent to that of virgin PET, and that it meets the assessment criteria forming part of a request for authorisation of use,
- enable the detection of any serious drift in the recycling process (exceptional pollution, failure during any step of the process) and **remove non-conforming batches.**

II.1- Physico-chemical monitoring

Manufacturers must undertake to monitor physico-chemical elements themselves. They must indicate the physico-chemical characteristics that they intend to monitor through this quality control and to reveal any drift in the process: viscosity index when melted, glass transition and melting temperatures of the recycled and virgin PET (suitable for food contact).

For the viscosity index, all batches must be tested.
Manufacturers must check the glass transition temperatures of the recycled PET (in comparison with the virgin PET) at least once a week.
Should there be a drift in the process, none of the batches produced since the last inspection may come into contact with food.

II.2- Monitoring of contaminant concentration in the PET

For current production, manufacturers must guarantee that the quantity of possible contaminants in the recycled resin is such that migration cannot exceed 1.5 µg/kg of food. Tests should therefore be conducted on the recycled PET, in comparison with the virgin PET.
These analyses are to be performed on the granules obtained during routine production (not to be confused with model materials containing model substances).

Manufacturers must conduct inspections at least once a week on samples from clearly identified batches. The samples from each batch must be measured separately.
Should a contaminant be detected at a level such that migration would exceed 1.5 µg/kg of food, none of the product batches between the two inspections may come into contact with food.

II.2.1- Contact with aqueous environments

The molar mass of any substance not present in the virgin PET but present in the recycled PET at over 4 mg/kg of PET must be determined systematically. Using the figure below, manufacturers must ensure that this molar mass is compatible with a concentration in the recycled PET resulting in a migration that is less than or equal to 1.5 µg/kg of food.
If the migration calculated exceeds 1.5 µg/kg of food, the contaminated PET batches must not come into contact with food.

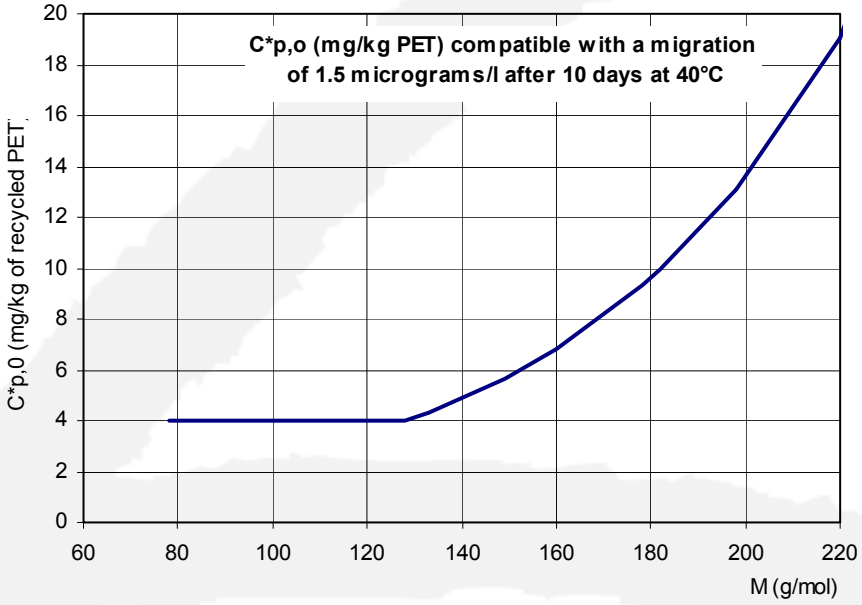


Figure 2: Tolerable contaminant concentration in the PET, compatible with a migration limit of 1.5 µg/l after 10 days at 40 °C (calculated for 6 dm²/l of simulant). This figure is calculated for aqueous foodstuffs; it applies to single and multi-layer materials where the recycled PET forms the layer that is in contact with the food. For information, the surface/volume ratios are 6, 7 9 and 10 dm^{-1} for 1.5 l, 1 l, 0.5 l and 0.33 l bottles respectively[10].

Analyses will be performed on granules from the decontamination process or on finished products. Protocols must be validated in accordance with standard AFNOR NF V03-110. Contaminants may be searched for in recycled PET materials as follows:

- **Analysis of extractable substances**: the material may be extracted using dichloromethane, in a balloon under reflux, using Soxhlet apparatus or a pressurised solvent extraction system. The material will be divided to facilitate extraction (finished products will be cut into flakes for example). The extract will then be concentrated by evaporation or reduction under moderate vacuum.
  The concentrate may be analysed by gas-phase chromatography (GPC) and/or high performance liquid chromatography (HPLC) coupled with mass spectrometry (MS). The concentration corresponding to the peaks will be determined using a series of similar hydrocarbons with similar retention times as standards. A comparison with the available mass spectral libraries will also be made.
- **Analysis of volatile substances**: in principle, the most volatile substances are eliminated during the drying steps and do not pose a health risk. If necessary, they may be extracted from the material (divided into flakes, for example) by dynamic headspace, coupled with GPC/MS.

II.2.2- Contact with alcohol or fat media

Extraction will take place as indicated above. The concentration must not exceed the maximum tolerable contaminant concentration in the PET after decontamination determined using the migration study in paragraph I.3.2.

[10] Internal surfaces and volumes of bottles 1.5: 9.2dm²; 1: 7dm²; 0.5: 4.5dm²; 0.33: 3.3dm² (source: Syndicat des eaux minérales)

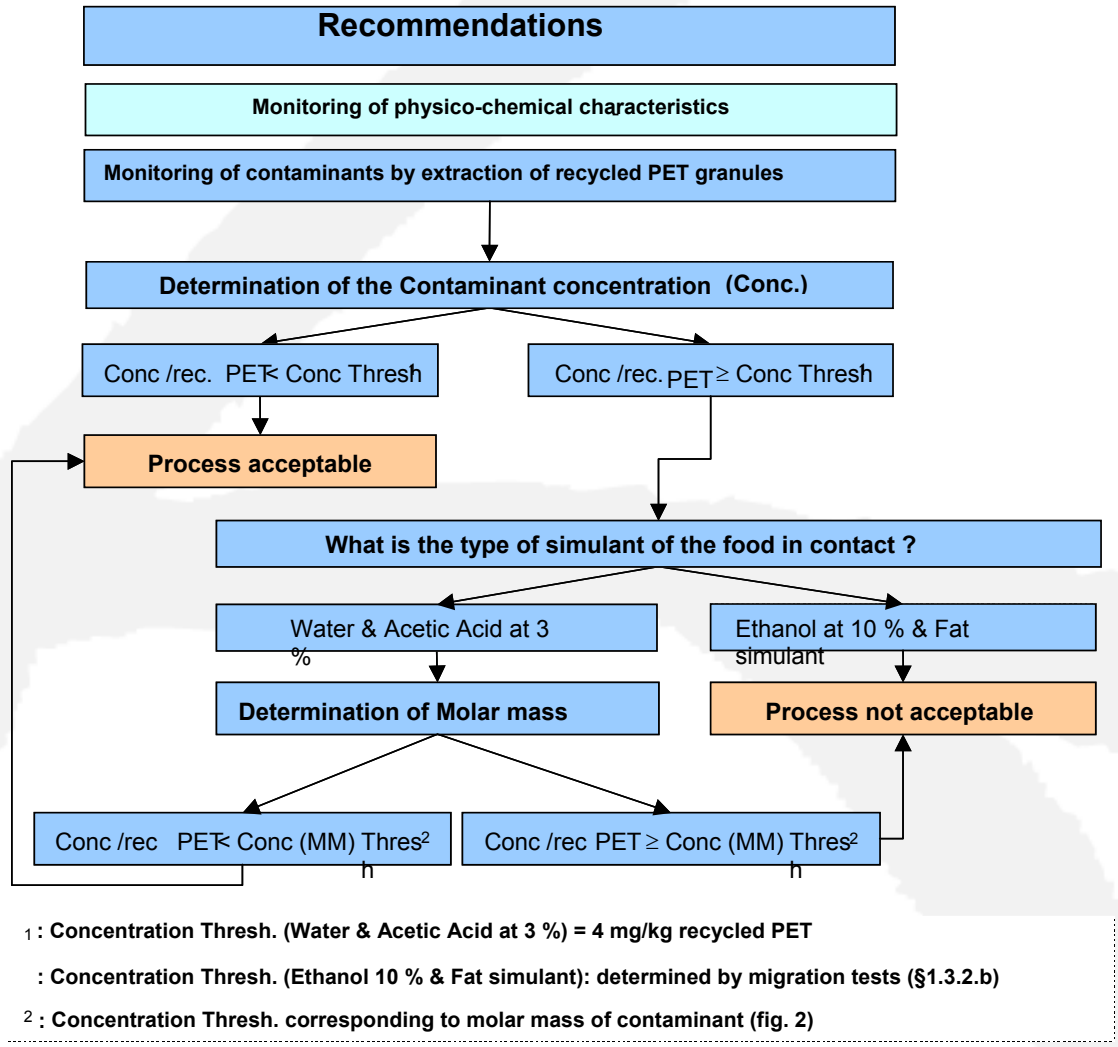


Figure 3: Protocol for searching for contaminants and testing the inertia of the decontaminated PET within the framework of monitoring carried out by manufacturers.

Other recommendations concerning manufacturers using recycled PET

Recycled PET producers must indicate to manufacturers using it what the maximum recycled PET level is that may be used to compose their materials or products. The maximum useable level may not exceed the one mentioned in the assessment request (paragraph I.1 Subject of request).