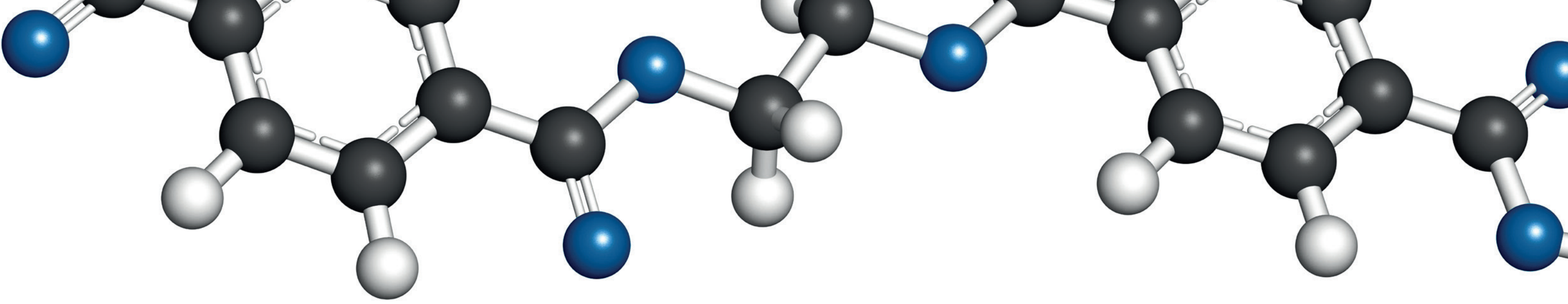


The Facts about PET

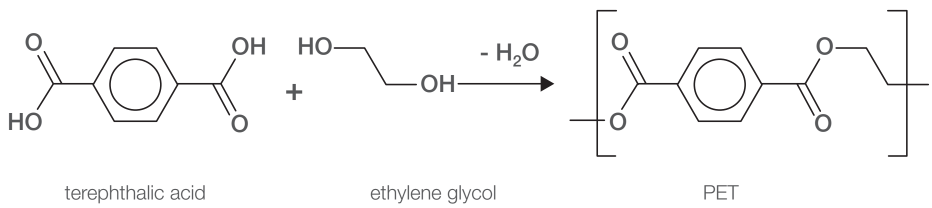
Dr. Frank Welle

What is PET?

The abbreviation PET stands for polyethylene terephthalate, a polymer that, from a chemical point of view, is a polyester. Polyesters were first manufactured in the 1930's, for use as synthetic fibres. Much of the PET produced today is used to produce fibres either for industrial or clothing applications and usually mixed with natural fibres like cotton and wool for the latter. Fleece sweaters, for example, are made of PET fibres. In the early 1950's, PET use expanded to packaging films. Film and magnetic tape also use PET film as a carrier. In the 1970's, a production process for PET bottles was developed. PET bottles were initially used for soft drinks, but gradually their use for bottled water expanded.

PET is manufactured from terephthalic acid (a dicarboxylic acid) and ethylene glycol (a dialcohol). The two substances react together to form long polymer chains, with water as a by-product (Figure 1). As in most processes of polymerisation, a catalyst is used to speed up the reaction kinetics.

Figure 1: Structure and chemical equation of PET



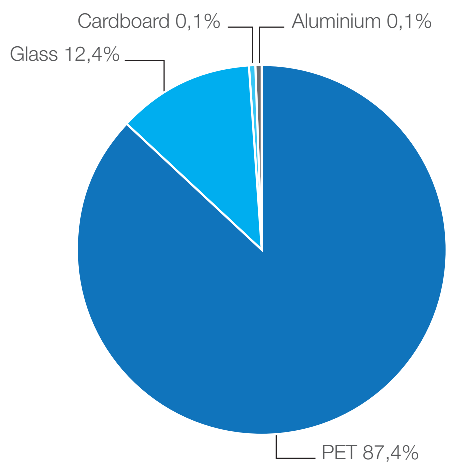
Why use PET?

PET bottles are very strong, colourless and lightweight. PET is transparent and it allows the content of the container to remain visible. The strength and lightweight of PET is very important for beverage packaging since it makes the bottles safe for on-the-go or sports use. Over the years, the weight of PET bottles has been reduced and today a 1.5L bottle can weigh as little as 20 to 30 grams. This process of light weighting represents a true benefit with regard to the environmental performance a bottle will have during its lifetime: production, transport to the consumer and end of life cycle. With its excellent material properties, PET is widely used today as a packaging material for liquids such as carbonated beverages and is one of the most suitable materials for the packaging of natural mineral and spring water.

Use of PET in packaging applications

PET is used in the packaging sector in the form of films, trays or bottles, its principle use being in bottles. In 2016, the global uses of PET packaging (excluding fibre) amounted to a total of 21.7 million metric tonnes (Source: PCI Wood Mackenzie). As far as bottles are concerned, 87.4% of bottled water sold in Europe in 2016 (Source: GlobalData) was supplied in PET (Figure 2).

Figure 2: Packaging use by the European bottled water industry (Source: GlobalData)



The manufacturing of PET bottles

PET bottles are usually manufactured in a two-stage process. PET granulates melted at about 280°C and processed into preforms. These preforms already have the bottle cap thread and are small and easy to transport. Shortly before the filling process, the preforms are heated to about 110°C and blown into their final bottle shape. “One stage” process can also be used where the preform goes directly from the injection to the blowing stage. After cooling bottles are filled with the beverage. The “stretch blow-moulding process” causes the PET to partially crystallise, which improves the stability of the bottle and enhances its thermal properties and barrier against oxygen and carbon dioxide. Non-crystalline PET is highly transparent while fully crystalline PET is opaque and is used, for example, to make microwavable dishes and trays.

The interaction of PET with food and water

No packaging material is fully inert and so there will always be some kind of interaction with the beverage or foodstuff it contains. In the case of food, mild oxidation may occur due to oxygen permeation. Likewise, carbon dioxide from carbonated beverages can permeate through the packaging material. In certain instances, there may also be a small degree of migration of components from the plastic packaging into the content. For consumer health protection, all such interaction must be reduced to a minimum. As with all other material in contact with food, PET packaging does comply with all European and national legal requirements. Such requirements include an assessment of the initial raw materials employed (i.e., monomers and additives) and the compliance with any restrictions that are established, such as migration limits. The requirements for the migration of monomers and additives according to the European Packaging Legislation is given in Table 1 (EU 2011).

Table 1: Requirements according to European Packaging Legislation (EU 2011)

Substance	Specific migration limit in mg per kg food
Acetaldehyde	6
Terephthalic acid	7.5
Isophthalic acid	5
Mono- and diethylene glycol	30
Antimony	0.04
2-Aminobenzamide	0.05

Acetaldehyde

Acetaldehyde is a by-product of the PET manufacturing process. It is produced when PET is heated to a high temperature to produce bottles. Many beverages and foodstuffs contain natural acetaldehyde (Table 2). The trace quantities of acetaldehyde that may migrate from PET into bottled water are totally harmless, although they may cause the water to have a slightly fruity off-taste. When the concentration exceeds 0.02 mg of acetaldehyde per litre, the consumer may be able to taste it. Based on consumers' acceptance and local regulation, this is something that should be avoided in some countries whereas it is well accepted in others. PET bottle manufacturers have worked closely with the bottled water companies to optimise the PET bottle production process with a view to minimising levels of acetaldehyde migration (Welle 2018). Also acetaldehyde reducing additives are applied in the preform manufacturing process (see Chapter below).

Table 2: Concentration of acetaldehyde in different food stuffs (Nijssen et al. 2009)

Foodstuff	Concentration in mg per kg food
Vinegar	20 to 1060
Bread	4.9 to 10.0
Wine, sparkling wine	2.5 to 493
Citrus fruit	1.2 to 230
Orange juice	0.7 to 192
Yoghurt	0.7 to 76
Beer	0.6 to 63
Apple juice	0.2 to 11.8
Natural mineral water in PET bottles (typical value)	<0.01
Taste threshold for acetaldehyde in water	0.01 to 0.02
Limit value in Europe for migration from packaging materials (see Table 1)	6

Acetaldehyde reducing additives

Traces of acetaldehyde can migrate from the PET bottle wall into natural mineral water. The main goal in preform and bottle manufacturing is to reduce the acetaldehyde concentration in PET. From migration theory, the bottle wall concentration of acetaldehyde is directly proportional to the migration under the same storage conditions. This means that the reduction by a factor of two results in half of the migrated amount of acetaldehyde into bottled water (Welle 2014a). 2-Aminobenzamide, also known as anthranilamide, is the most popular acetaldehyde reduction additive and called an acetaldehyde scavenger used in PET preform manufacturing. This additive reacts chemically with acetaldehyde to form a non-odorous and higher molecular weight substance (Mrozinski et al 2012 and 2013, Franz et al 2016, Gehring and Welle 2017). As any other additive, 2-aminobenzamide must be approved for the application in PET bottles and the specific migration limit of 2-aminobenzamide of 0.05 mg per kg food (Table 1) has to be controlled in routine tests by the mineral water filling company.

Monomers (ethylene glycol and terephthalic acid)

In general terms, the migration of monomers from plastics can never be totally prevented. PET, however, is highly inert compared to other plastics. Thus, only extremely small quantities of monomers may migrate into bottled water. For example, a study (Störmer et al. 2004) has shown that the level of migration of the monomers ethylene glycol and terephthalic acid from PET bottles is far below statutory limits. Nonetheless, water bottling companies constantly monitor levels of monomer migration from PET bottles.

Antimony

Antimony trioxide is the major catalyst used to polymerise PET. In principle, the catalyst will remain in the PET after polymerisation. Typically, concentrations of antimony in PET bottles are below of 300 mg per kg PET (Welle and Franz 2011). Alternative catalysts for the polymerisation of PET have also been developed, mostly based on titanium, aluminium or germanium. However, to date the alternatives developed have not succeeded in making a major commercial breakthrough and antimony trioxide remains by far the dominant catalyst employed by resin suppliers.

As with all the substances employed in the manufacture of PET, antimony is subject to strict statutory regulations in Europe. The maximum permitted level of antimony migration from a PET bottle into the finished product is 0.04 mg per litre (Table 1). Under normal storage conditions, the level of antimony migration from PET bottles is extremely low. The limit value for antimony migration from PET packaging may not be exceeded during the shelf life of the beverage, even when bottles are stored in warm climates for many months (Welle and Franz 2011).

The limit value for antimony in water is considerably lower than the limit value for migration from PET packaging. In Europe, for example, a maximum of 0.005 mg of antimony may be present in one litre of natural mineral, spring or drinking water at the time of packaging. Even if, from a legal point of view, the migration limit of 0.04 mg per litre is valid for bottled water, natural mineral and spring water companies evidently comply with the lower value established for water, taking it as the maximum acceptable level of antimony.

PET does not contain plasticisers
Plasticisers are additives employed in various polymers to alter their properties and make them "softer". Amongst the most commonly used plasticisers are phthalic acid esters and adipic acid esters. It can be definitively stated that plasticisers are not used in the PET resin formulation for making bottles.

The name of one of the monomers used to make PET, terephthalic acid, does sound like to phthalic acid, the material used as a starter for many plasticisers, and this often leads to the mistaken belief that PET contains plasticisers.

There is no bisphenol A in PET
Bisphenol A is a monomer used in the production of some polymers such as polycarbonate (PC). Bisphenol A is never used in the manufacture of PET bottles.

Do any endocrine disruptors from PET bottles leach into the water they contain?
In 2009 it was reported in the media that endocrine disruptors were migrating from PET bottles into natural mineral water. Endocrine disruptors have a similar effect on humans to the naturally produced hormone, estradiol. For this reason, the concentration of such endocrine disruptors is expressed as estradiol-equivalents (EEQ). It has been alleged that a peak value of 75,000 pg estradiol-equivalents was detected in natural mineral water contained in PET bottles (Wagner and Oehlmann 2009). The substances responsible for this were, however, never found. The German Bundesinstitut für Risikobewertung (Federal Institute for Risk Assessment) immediately reported on said allegations and concluded that there was no evidence to indicate that the origin of the endocrine disruptors was the PET bottles (BfR 2009). Several subsequent studies by national monitoring laboratories, such as the Swiss Federal Office of Public Health, were unable to confirm the presence of such exceedingly high values, nor find any significant difference between the water contained in glass and PET bottles, or even between bottled and tap water (Brüschweiler and Kunz 2011, Bopp et al. 2010). The concentrations found were of the order of 5 pg per litre of natural mineral water, a factor approximately 15,000 lower than the value originally reported (75,000 pg). Interestingly, even the work group that published the report stating the original high value were later unable to verify it in a follow-up study (Wagner and Oehlmann 2011). The sample preparation was shown to be one of the major factors to avoid false positive or false negative results (Chevolleau 2016). It is also interesting to compare the estrogenic activity found in bottled natural mineral water with natural occurring estradiol activity in milk and beer (Table 3). A review article with all relevant literature data on potential endocrine substances in PET bottles has been published in 2014 (Welle 2014b).

Table 3: Concentration of estradiol (equivalents) determined in bottled natural mineral water compared to natural concentrations in milk and beer

Foodstuff	Concentration in pg per kg food
Natural Mineral water in PET, first study of Frankfurt researchers (Wagner and Oehlmann 2009)	75,000 (EEQ)
Natural Mineral water in PET, follow-up study of Frankfurt researchers (Wagner and Oehlmann 2011)	1 to 11 (EEQ)
Natural Mineral water in PET and glass, studies of food control authorities (Bopp et al. 2010, Brüschweiler and Kunz 2011)	5 to 10 (EEQ)
Milk (Courant et al 2007)	24,000 (estradiol)
Beer (Blendl 2011)	2,000,000 (EEQ)

In 1999, the WHO Joint FAO/WHO Expert Committee on Food Additives (JECFA) panel set the Acceptable Daily Intake (ADI) value for estradiol at 0.05 µg per kg body weight per day, but as a veterinary drug (JECFA 2000, FAO/WHO 1999). On the basis of the abovementioned exposure scenario, the 10 pg estradiol-equivalent found in maximum by national public health authorities still remains beneath the recommendation by a factor of 50,000.

Bio-PET

Traditionally, the monomers of PET are manufactured from fossil-based resources. However, a synthetic route for ethylene glycol, one of the two monomers, was developed from biomass as early as in the late 1980's. Sugar-cane is transformed to bio-ethanol. In the second step, bio-ethanol is oxidized to the monomer ethylene glycol, which is subsequently used for the polymerisation of PET. A mass fraction of about 30% by weight is realized when using bio-ethylene glycol as monomer for PET. The second monomer of PET, terephthalic acid, is not commercially available using bio-based resources. However, synthetic routes from biomass to terephthalic acid are available in laboratory/pilot scale.

From a chemical point of view, bio-PET is indistinguishable from fossil-based PET. Therefore, the same manufacturing facilities for PET pellets, preforms and bottles can be used. Also, bio-PET is fully recyclable along with fossil-based PET. Such bio-based equivalents to fossil-based polymer are called "drop-in" bio-polymers.

Background information on concentrations:

1 mg per litre (milli gram)	0.001 g per kg food	parts per million (ppm)
1 µg per litre (micro gram)	0.000,001 g per kg food	parts per billion (ppb)
1 ng per litre (nano gram)	0.000,000,001 g per kg food	parts per trillion (ppt)
1 pg per litre (pico gram)	0.000,000,000,001 g per kg food	parts per quadrillion (ppq)

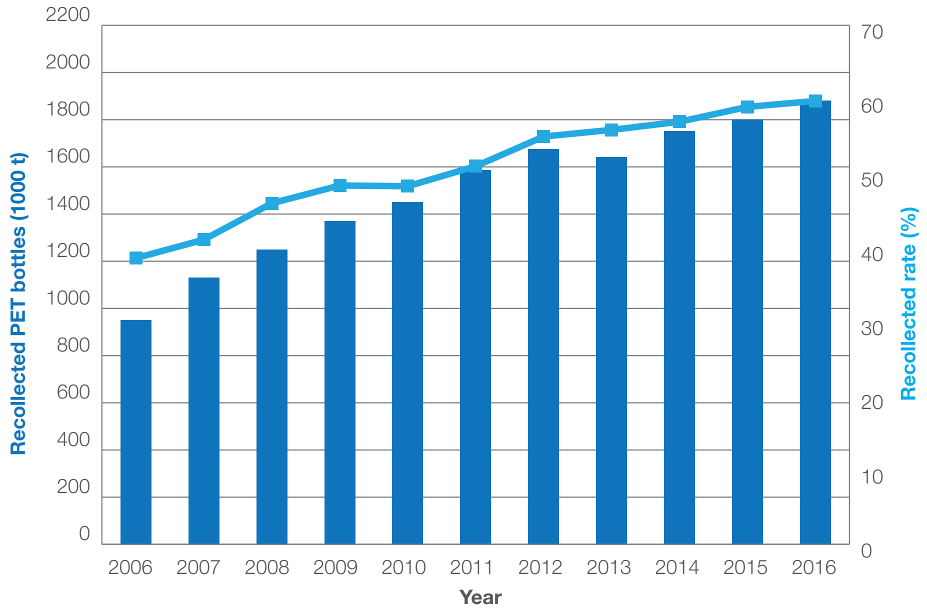
Recycling of PET bottles

Selective bottle collection
PET is identified by its polymer code 01 (Figure 3). In terms of recycling, PET bottles are a special case in all respects. PET bottles represent a significant fraction of total use of packaging and are easy to sort. Large quantities of (post-consumer use) bottles are available and can be economically recycled. Blue, green and clear PET water bottles can be colour sorted and each colour fraction can be recycled separately. Over the last decade, the number of bottles collected for recycling in Europe has grown significantly. In 2016, out of 3.15 million tonnes of PET bottles and containers placed in the European market, a remarkable 59.8% - in total 1.88 Million tonnes - were collected and 1.77 million tonnes mechanically recycled (Figure 4). In certain countries, such as Germany, Iceland, Norway and Switzerland, the amount collected accounted for approximately 90% of the total. PET is fully recyclable and can be re-melted and mechanically recycled as often as required, particularly when mixed with virgin resin.

The PET bottle recycling industry is well-established. Collected PET bottles can be recycled into fibres and textiles or processed into new PET bottles. Thus, with recycling, PET forms part of a closed material cycle, significantly reducing the net utilisation of valuable resources such as crude oil.

Figure 3: PET polymer code

Figure 4: Growth in the amount of used PET bottles collected in Europe (Source: Petcore Europe)



Bottle-to-bottle recycling
The recycling process first involves removing the labels and closures and shredding the PET bottles. After an intensive wash process, the PET recyclate can be used as the raw material for high-quality products such as fleece sweaters, sleeping bags and insulating materials. Constant improvement of recycling processes over the last two decades has resulted in PET recyclates of such high quality that they are used to manufacture new PET bottles (Welle 2011). In 1998 the first recycling plant for the production of PET preforms, from post-consumer PET bottles, was installed. Collected PET bottles are thus turned into new PET bottles.

This requires a so-called "super-clean" recycling process, a process yet to gain full European Food Safety Authority (EFSA) approval. A total of 110 recycling processes and plants across Europe were given an approval from the EFSA by end of 2017. The EFSA concluded for all these processes "that the recycled PET obtained from this process intended to be used up to 100% for the manufacture of materials and articles for contact with all types of foodstuffs for long-term storage at room temperature, with or without hotfill, is not considered of safety concern." Only some recycling companies that employ a high effective decontamination process and possess adequate quality assurance procedures are allowed to manufacture the "super-clean" recyclate which, on analysis, should not be distinguishable from virgin PET. Thus, PET bottles made from recyclate are as good and "safe" as bottles made from virgin PET. The current amount of recyclate used to make new PET bottles is between 25% and 50%. Technically, it is feasible to make PET bottles from 100% recyclate but in most cases this may result in a slight discoloration of the bottles.

Further Information

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About the author

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Frank is a chemist who received his PhD from the University of Freiburg, Germany. In 1997 he moved to the Product Safety and Analytics Department of the Fraunhofer Institute for Process Engineering and Packaging (IVV). The research work of his group, consisting of around 35 scientists, engineers and technicians, focusses on the interaction of food packaging materials and food and on consumer exposure to packaging related migrants. Frank is an expert in the migration testing of PET bottles and in the food law compliance evaluation of the PET bottle-to-bottle recycling processes. His laboratory is fully equipped with the latest analytical equipment for migration and permeation testing. The migration laboratory is accredited in accordance with DIN EN ISO/IEC 17025.

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