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On the Origin of Microplastics in Bottled Water

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Abstract. Microplastics contamination of bottled water has been reported in several published investigations. Detection and identification is usually based on FTIR and Raman methodologies. Reported microplastics counts vary widely due to experimental detection limitations and laboratory contamination. There is no definite information on the impact of microplastics ingestion to human health, but awareness in the general public is increasing and consumers are concerned. It is argued that microplastics generation can be traced to injection molding of bottle preforms and caps. Injection mold cavity gate marks, flash and surface porosity are the main sources, due to break off and shedding during subsequent transportation, handling, blow molding of the preforms and during bottling and filling operations. Plastic dust in polymer processing factories is also a contributing factor. Intake by humans increases from opening and closing due to stress and abrasion. There is ongoing research on detection in various laboratories around the world, but hardly any attempts to relate microplastics generation to material properties or processing conditions.

INTRODUCTION

Microplastics (MPs) are defined as synthetic polymer contaminants, having sizes in the range 1 μm–1 mm, occasionally up to 5 mm. In sizes less than 1 μm they are referred to as nanoplastics. They have been detected in oceans, lakes, rivers, reservoirs, groundwater, tap water, bottled drinking water and wastewater. A review [1] of several publications and an extrapolation based on typical consumption data, reported a maximum yearly human intake of 458,000 MPs from tap water and 3,569,000 MPs from bottled water. Other investigations also concluded that the presence of microplastics per litre of bottled water is much higher than per litre of tap water. Significant health concerns have been raised, even though in a report published in 2019 by the World Health Organization [2] it is stated that microplastics in drinking water "don't appear to pose a health risk at current levels" based on the information available. It was also concluded "that it is possible that some smaller plastic particles may be able to pass through the gut wall and translocate to tissues remote from the mucosa, although this may not necessarily translate to a health risk". Careful reading of the report shows that the conclusion is not that there is no risk, but rather that there is limited information available to assess the risk level and calls for more research. Part of the problem is the doubtful quality of available data on the occurrence of microplastics in drinking water. In a critical review, Koelmans et al [3] concluded that only four out of 50 studies "received positive scores" in their proposed quality criteria.

Research on microplastics in bottled water was very limited till 2018 when four impactful papers were published [4-6]. The publication by Mason et al [4] attracted considerable attention not only from researchers, but also from mass media and aroused public awareness. They examined 259 PET water bottles from 11 well-known brands from 9 countries, using Nile Red tagging and FTIR. Microplastic contamination counts ranged from 0 to over 10,000 per litre with 95% of particles being between 6.5 and 100 μm with an average of 325 per litre of water. Schymanski et al [5] tested water from 22 different returnable and single-use plastic bottles, 3 beverage cartons and 9 glass bottles purchased from grocery stores in Germany. They used micro-Raman spectroscopy. They found 118±88 microplastics per litre in returnable, but only 11±8 microplastics per litre in single-use bottles. Almost 80% had a particle size between 5 and 20 μm. Oßmann et al [6] used special membrane filters combined with micro-Raman spectroscopy and detected particles as low as 1 μm in 32 samples of bottled mineral water. The microplastics count varied from 2649±2857 per litre in single use PET bottles and up to 6292±10521 per litre in glass bottles. Over 90% of the detected

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microplastics and pigment particles were smaller than 5 μm, which were not detectable by the methods used in prior investigations.

The above-mentioned studies were very carefully carried out in terms of analytical detection protocols, but it is impossible to determine the origin of microplastics contamination from them. Mason et al [4] found that 54% of the particles over 100μm, were identified as polypropylene (PP) and stated that it "matches a common plastic used in bottle caps". In the work of Schymanski et al [5] involving returnable plastic bottles, most of the particles were identified as polyethylene terephthalate (PET, 84%) and polypropylene (PP, 7%). They concluded that "this is not surprising since the bottles are made of PET and the caps are made of PP". Neither in [4] nor [5] the caps were explicitly identified as PP. In fact, it is highly unlikely that they were, because the vast majority of the common screw caps of bottled water are made of high-density-polyethylene (HDPE) having melt flow index between 1-2. Oßmann et al [6] reported that it was extremely difficult to prevent sample contamination completely. On average 384±468 microplastics per litre were found in blank samples, consisting mainly of PP, some of polystyrene (PS), PE and PET. Also, in the work of Mason et al [4] Nylon (PA) and PS were detected, which implies that a fraction of the microplastics is not related to bottle or cap material.

Winkler et al [7] purchased PET bottles having HDPE caps from Italian supermarkets. They used a combination of scanning electron microscopy imaging (SEM) and energy-dispersive X-ray spectroscopy (EDS) with size detection limit of 3μm. They concluded that PET bottle necks and HDPE caps are responsible for releasing large number of microplastics, especially after opening and closing many times. PET bottle squeezing and crushing did not significantly affect the microplastic count. Weisser et al [8] used FTIR with detection limit of 11μm. They attributed the presence of microplastics mainly to bottle capping of returnable glass bottles. 81% of MPs detected "resembled the PE-based cap sealing material" of the aluminum caps.

In the present paper, the main emphasis is on providing information of certain aspects of injection molding (IM) of PET bottle preforms and HDPE caps which can generate microplastics. Some microplastics might be generated at the injection molding machine or they might be produced during subsequent operations in conveying, blow molding, bottle filling and bottle capping.

DETECTION AND IDENTIFICATION

From the various published investigations, it is evident that detection of microplastics in bottled water is a challenging task. The reported microplastics counts per litre vary widely due to methodologies followed and instrument limitations. The severe criticism by Oßmann et al [9] and the subsequent rebuttal by Zuccarello et al [10], is indicative of the situation.

The most common methods to reliably detect and identify MPs are Fourier Transform Infrared (FTIR) and Raman micro-spectroscopy (RM). Using FTIR spectroscopy, different approaches can be followed: for relatively large particles (approximately greater than 100 μm), clean individual particles can be measured by an attenuated total reflection accessory and the method is usually abbreviated as ATR-FTIR. In micro-FTIR (μ-FTIR), the spectrometer is attached to an optical microscope. The limit of detection (LOD) in this case is approximately 10 μm. For MPs in the range of 1-10 μm (and perhaps less than 1 μm), the preferred choice is RM. After MPs are collected on a filter (filter material choice must not interfere with measurements), image and absorption or emission spectra analysis are performed, producing information for the particle number, size, shape and chemical identity. Thermal degradation methods can also be used to analyze MPs (e.g. pyrolysis gas chromatography mass spectrometry, Pyr-GC/MS) if they occur in large numbers, rather than single particles. The sample is pyrolyzed, under inert conditions, so that specific decomposition products of the individual polymers can be analyzed. In this case, their total mass (one polymer type) must exceed the LOD of the method (in the range of μg).

There are challenges not only in the analytical methods for detection and identification, but also in experimental setups for sampling. There is frequently lack of quality assurance. Schymanski et al. [11], highlighted the significance of the challenges by presenting a consensus paper of 12 European analytical laboratories and institutions dealing with MPs identification and quantification with spectroscopic methods and give a guidance towards a harmonized MPs analysis.

INJECTION MOLDING AND HANDLING OF CAPS AND BOTTLE PREFORMS

The PET bottle industry experienced a very rapid growth from the late 1970s. This was partly due to the convenience for water and soft drinks and also to banning of 1.5 litre glass Coca Cola bottles from some jurisdictions, due to their tendency to explode with dangerous consequences, when dropped. According to STATISTA [12] 583.3

billion PET bottles were produced globally in 2021. Caps are usually made of HDPE having Melt Flow Index in the range of 1-2 g/10 min (2.16 kg, 190°C). Combination of PET bottle and HDPE cap is excellent for recycling, because it is easy to separate them in a water bath where PET with specific gravity 1.38 sinks and HDPE (sp.gr. 0.95) floats. A few years ago, PP caps were also introduced which pose a problem for recyclers because PP also floats in water. HDPE and PP cannot be repurposed together for high quality plastic products. However, the vast majority of caps for PET bottles, in technologically advanced countries, are made of HDPE.

The injection molded one-piece HDPE cap was invented by Albert Obrist in Switzerland and patents were issued in several countries in the 1970s. The invention was originally intended for returnable glass bottles, but it was quickly applied to PET bottles. Fig. 1(a) shows the top of a PET bottle and a HDPE opened cap. Both the cap and bottle preform are injection molded. Fig. 1(b) shows a typical mold cavity and the location of the cavity gate mark, which is a slightly protruding surface discontinuity. Flash is excess material that can escape from the mold cavity and remains stuck on the molded part. In Fig. 1(b) the gate mark is shown on the outer surface of a product looking like a cap, but frequently water bottle caps have a gate mark inside. Whether the gate mark is inside or outside it can be a source of microplastics which can easily break-off during the various handling operations of the caps. While molders try to eliminate flash from molded products, a tiny amount of flash capable of producing numerous micron sized microplastics is practically unavoidable. Caps exhibit surface porosity, easily visible with the help of a magnifying glass, and they are intentionally grooved on the outside to facilitate grip by the consumer's hand. Porosity and the grooves contribute to increased shedding of microplastic particles.

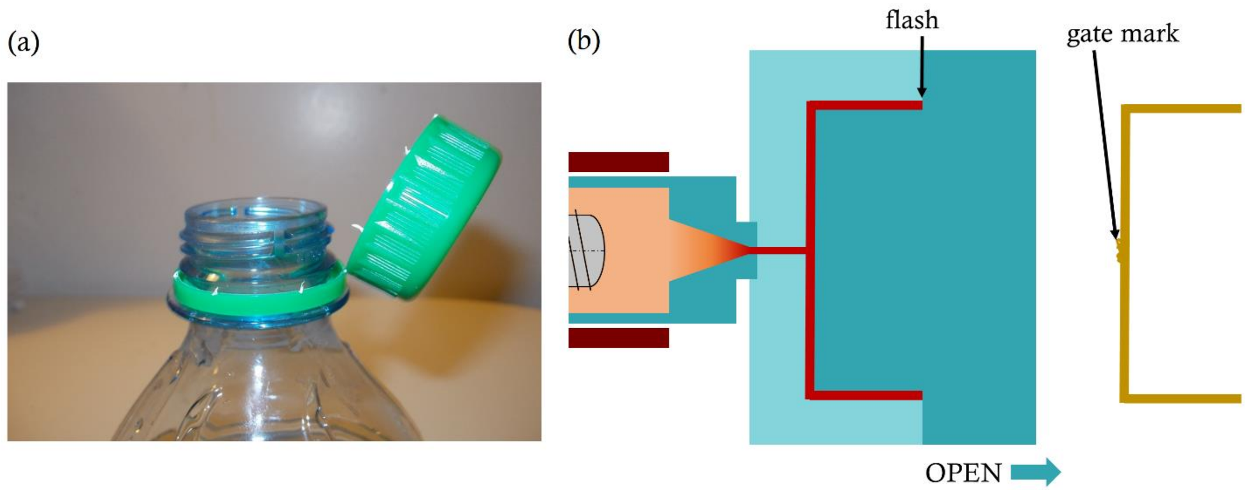

FIGURE 1. (a) PET bottle and HDPE opened cap and (b) schematic representation of a typical injection mold cavity

In Fig. 1(a) the bottle was opened after applying a small amount of torque, sufficient to break off all but one of the "bridges" that were holding the two cap parts together. During cavity filling the molten polymer flows into the mold cavity gate, filling the upper part first and then flows through the bridges to fill the bottom ring. In a simulation of flow in a cavity of an actual production mold, the authors determined a shear rate of about 90,000/s on the wall of eight 0.3 mm diameter bridges. The calculated wall shear stress was about 0.85 MPa assuming no-slip. Under such conditions HDPE melt is known to slip at the wall. Despite the slip at the wall, it was impossible to fill the bottom part of the cavity to form the ring in the injection molding machine, using a particular proprietary grade of HDPE. A slip agent was then compounded with HDPE before injection molding. The slip agent resulted in increase of slip velocity as measured by the Mooney method [13] and subsequently enabled the production of good quality HDPE screw caps. Typical slip agents for HDPE are erucamide or behenamide, which are primary fatty amides.

The slip agents are also helpful in application of a reduced level of torque by the capping machine and for easy removal by the hand of the consumer. HDPE has high coefficient of friction (COF). Erucamide migrates to the surface as some sort of plate-like crystals [14], forms a thin deposit and reduces COF. A certain length of time is required for the migration of the slip agent to the surface. For this reason, manufacturers store the caps for a period of time before capping the PET bottles. Reduction of COF means less abrasion and perhaps fewer microplastics. However, the microplastics produced contain also a certain amount of a fatty amide, which might also have some toxicity.

Fig. 2(a) shows a bottle preform having a clearly visible gate mark. Bottle preforms are injection molded simultaneously in molds having numerous cavities (perhaps 144 or more). They are usually dropped to a conveyor belt when the two parts of the mold open and subsequently transported to a blow molding machine. Obviously, small pieces of plastic can easily break off from the protruding gate marks and end up as PET microplastics inside the bottle. The authors have investigated the operation of a 96-cavity mold in an attempt to explain why two of them were producing short shots. Before rectifying the operation, the incomplete parts appeared to easily generate plastic fragments, which could end up as microplastics before sorting them out of the production stream. Also, during blow molding of preforms, PET fragments may shed from good quality bottles. PET bottles are usually produced by stretch-blow molding for increasing the degree of crystallinity and improving physical properties. There have been no studies as to whether stretch-blowing has any impact on microplastics generation, but it might increase tiny fragment shedding, due to the high speed of stretching/production. Also, plastics processing factories are known to have plastic dust related to pneumatic transportation of polymer pellets and to bumping of plastic parts to each other. Plastic dust in injection molding and extrusion factories is frequently a fire and explosion hazard. It also, contributes to the generation of microplastics which may get stuck on the surface of caps, preforms or end up inside water bottles.

Fig. 2(b) shows a typical PET bottle neck. The upper part is threaded, while in the lower part is designed for the purpose of trapping the bottom ring of the cap during removal by twisting to break off the "bridges". This means that the capping machine must be capable of screwing the cap on to the neck and subsequently pushing it down. Such procedures involve considerable amount of stress and abrasion between the cap and the bottle neck and they are likely to contribute to generation of microplastics which will end up in the water.

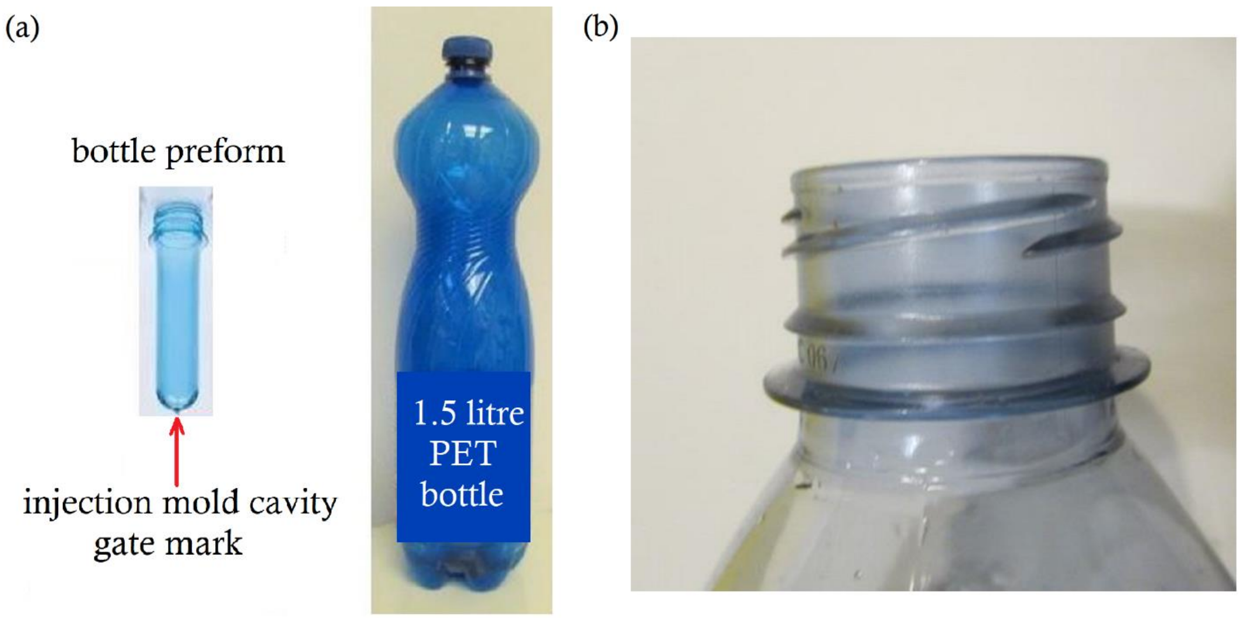

FIGURE 2. (a) Bottle preform with a clearly visible mold cavity gate mark and a 1.5 litre PET bottle and (b) typical PET bottle neck. Notice the upper threaded part and the design feature for trapping the bottom cap ring.

The material properties of PET and HDPE (or PP), the processing conditions and the actual design of preforms, caps and bottles are expected to have a significant effect on generation of microplastics. There are no industry standard requirements. The authors examined several bottles of water purchased in Canada. The weight of PET was in the range 14-24g for 500 ml bottles. Winkler et al [7] reported bottle weight as low as 9.61 g. The bottle weight is determined by structural requirements and also by consumer preferences. The corresponding cap weights examined by the authors were in the range 1.5-3g, while those by Winkler et al about 1.5 g. These differences are expected to have an impact on the microplastics count, but there have not been any studies on this matter. It is not known whether light-weighting in the PET bottle industry results into more or less microplastics.

During injection molding high packing pressures applied are likely to reduce surface porosity (less microplastics shedding) and at the same time may increase flash (more microplastics). There have not been any studies on molecular weight and molecular weight distribution effects. Also, there have not been any studies on the impact of bottle neck thread design. It can be conjectured that existence of sharp corners are likely to result in more microplastics shedding.

CONCLUSION

From several analytical investigations available in the open literature, it is apparent that the number of microplastics per litre of bottled water is much higher than in tap water. The microplastics counts reported vary widely due to the different detection limits of the various methods used. The impact on human health has not adequately studied, but it is believed that microplastics of smaller size are likely to have the most detrimental effects. Even though harmful human health effects have not been fully documented, the estimated annual intake from bottled water and other sources is very large and it is causing great concern among consumers [15].

Surface porosity, cavity gate marks and flash of injection molded caps and bottle preforms are likely the main sources of microplastics. Micron sized fragments break off and shed from bottles (PET) and the caps (mainly HDPE, some PP) and end up in the water during the various handling and bottling operations. Intake by humans also increases in daily use due to abrasion while opening and closing. Also, other polymers have been detected which are likely to be due to plastic dust in injection molding plants or laboratory contamination.

While the analytical investigations for detection and identification are improving there is hardly any research on the impact of material properties, processing conditions or bottle and cap design. Generally speaking, there remain several unanswered questions regarding the relative importance of the various root causes of microplastics generation.

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