Does sunlight change the material and content of polyethylene terephthalate (PET) bottles?


ABSTRACT

A simple water treatment process called SODIS (solar water disinfection) consists of filling polluted water in PET bottles that are exposed to sunlight for 5–6 hours. However, sunlight does not only destroy disease-causing microorganisms found in the water but also transforms the plastic material into photoproducts. Laboratory and field tests revealed that these photoproducts are generated at the outer surface of the bottles. No indication for migration of possible photoproducts or additives from PET bottles into water was observed with the applied analytical methods.

Key words | PET (polyethylene terephthalate), photoproducts, solar radiation, water disinfection

INTRODUCTION

An important reason for the transmission of infectious diseases in developing countries is the lack of adequate and safe water and sanitation systems. The poor in rural areas, in rapidly expanding urban slums and in squatter settlements are the most affected by this lack of infrastructure. Water supply monitoring programmes indicate that more than 1 billion people have no access to safe water (approximately 800 million people in rural areas and 300 million in urban settlements) (WHO et al. 1996). This situation in developing countries has negative effects on public health. Diarrhoeal diseases cause approximately 2.5 million deaths per year, 2 million children die before the age of five (WHO 1998). In spite of the efforts made at international and national level, water supply coverage is a long way from the target of ‘safe water for everybody’. The world’s growing population also enhances the absolute number of people without a proper water supply. Programmes designed to provide safe water to the unserved cannot keep pace with the ever-growing populations in many rural cities and conurbations in developing countries.

Conventional rural water treatment plants in developing countries often fail to produce safe drinking water. Smooth operation and maintenance of the installations are often hindered by a lack of trained operators, by an unreliable supply of chemicals and spare parts, and by financial problems. Since major urban water supplies are also not always capable of maintaining a regular supply of qualitatively good water, the distributed water is often considered unsafe for direct consumption. Treatment of water at household level (e.g. boiling) or purchase of mineral water for consumption is more a reality than an exception in urban areas of developing countries.

Solar Water Disinfection (SODIS) is one treatment option for small quantities of drinking water at household level. This simple treatment technology uses solar
radiation to inactivate and destroy pathogenic microorganisms present in the water. The treatment basically consists of filling transparent containers with water and exposing them to full sunlight for several hours. The efficiency of SODIS was examined by comprehensive laboratory research and field tests (Wegelin et al. 1994; Sommer et al. 1997). The SODIS technique of bacterial inactivation has been shown to be highly effective in reducing the pathogenicity of contaminated drinking water in Maasai children (Conroy et al. 1996).

The most important advantages of SODIS are its simple application and low costs. However, to attain sustainability, locally available material should be used whenever possible. Glass or plastic bottles are generally available at local markets. Glass bottles are gradually being replaced by polyethylene terephthalate (PET) or polyvinyl chloride (PVC) bottles. Since glass is inert and not transformed into photoproducts, glass bottles with good UV-A transmittance would be ideal for SODIS use. However, glass breaks more easily, is heavier and more expensive than plastic bottles. PET bottles should be used for SODIS application, as this material is supposed to have less additives (photo-stabilisers, plasticisers) than PVC.

PROBLEM AND APPROACH

Exposing water in PET bottles to intense conditions of heat and light over prolonged periods raises questions regarding the formation of photoproducts and the migration of compounds from the containers into the water. These photoproducts might reduce the efficiency of SODIS and, when migrating into the water, possibly cause health hazards to the consumers of the treated water.

The aspects studied are also of general interest to the soft drink industry. Although fewer additives are used for PET than for other polymers (such as PVC), UV-stabilisers (Monteiro et al. 1998), brighteners (Di Pasquale et al. 1996) and tougheners (Meyer & Leblanc 1995) were used to improve the PET characteristics and to increase its applicability. Furthermore, investigations are necessary to determine whether recycled PET, as used for carbonated soft drinks, contains compounds from the recycling process.

An interdisciplinary research team from Switzerland carried out laboratory tests to examine type and location of the formed photoproducts as well as their influence on the quality of the water stored in PET bottles. These studies were complemented by field tests carried out by a joint Irish and Malaysian collaborative research group.

EXPERIMENTAL SECTION

Samples and experimental setup

Ageing of bottles used in SODIS demonstration projects

Plastic bottles used in the countries participating in the demonstration projects were selected according to the following criteria: (1) availability on the retail market of the specific country; (2) good transparency to UV-A light. Ageing of such bottles was checked at EAWAG by UV-vis spectrophotometry after they had been used for several months in these SODIS projects, taking unused bottles of the same kind as a reference.

Ageing of PET bottles in Switzerland

Two tests were carried out in Switzerland. The first preliminary test (referred to as ‘EAWAG-1’) consisted in exposing three small pieces (about 2 cm × 5 cm) of a PET bottle to sunlight for several months from late spring to late summer. The second test (referred to as ‘EAWAG-2’) was carried out using four full and four empty 1.5 l Evian® mineral water bottles made of PET and purchased on the retail market. The bottles were stripped off their paper label, mounted onto a black-painted corrugated iron rack, inclined at a 45° angle with respect to the horizontal position, oriented south, and exposed to natural sunlight on the roof of EAWAG (latitude 47.4°N) on 25 May 1998. After a period of 15, 30, 63 and 126 days, respectively, a full and an empty bottle were removed from the rack and stored in the dark at room temperature (21–25°C) along with a full and an empty control bottle kept there during
the entire period of the experiment. The water in the bottle contained (according to consumer information): calcium 78 mg/l, magnesium 24 mg/l, sodium 5 mg/l, potassium 1 mg/l, bicarbonate 357 mg/l, sulphate 10 mg/l, chloride 4.5 mg/l, nitrate 3.8 mg/l, silica 13.5 mg/l, pH 7.2. The original content of the bottles was used to avoid contamination through opening of the bottles. Straight after irradiation of all the PET bottles, water samples were filled into clean glass bottles, previously rinsed with bi-distilled water and stored in the dark at 4°C until analysis. Due to shipping, the samples for aldehyde analysis were stored at higher temperatures for about one day. PET material samples 0.25–0.30-mm thick for analysis by UV-vis spectrophotometry were cut out from the upper smooth part of the bottle; i.e., from the side most exposed to the sun.

Material: PET04 (full and exposed to sunlight), PET05 (full, dark control), PET10 (empty, dark control), internal and external refers to our join experiment with the Evian® bottles.

Daily sunlight intensity data was obtained from the Swiss Meteorological Institute (SMI) in Zurich (i.e., from its two observation stations nearest to Duebendorf: Zurichberg and Kloten).

The tests in Malaysia used non-carbonated mineral water stored in PET bottles exposed to light. Two test bottles were placed in a horizontal position on a wide balcony where they were exposed to full sunshine for a period of 99 days in sub-equatorial Malaysia (Penang, latitute: 5.3°N). Controls consisted of a similar number of bottles of the same water stored in darkness.

Analytical methods for PET bottles

UV-visible spectrophotometry

UV-visible transmittance spectra at EAWAG were recorded on a Kontron Instruments model Uvikon 940 spectrophotometer in the spectral range of 300–500 nm. Plastic samples of about 1 cm × 3 cm were cut out from a smooth area of the bottle and taped to the back slit of the sample compartment. No reference was used. Transmittance reading with this method is affected by different factors:

- reflection from both material/air surfaces accounts for about 8% of transmittance losses;
- refraction due to some curvature of the plastic sample;
- scattering due to inhomogeneities of the polymer material and scratches on the surface (important for used bottles);
- absorption by the plastic material.

Since typically unused, clear, colourless or slightly bluish PET bottles exhibited a maximum transmittance of >85% at about 500 nm, refraction and scattering contribute less than 7% of the loss in transmittance in the absence of absorption at this wavelength. The typical lower limit of 85% transmittance compares well with the transmittance values of 88.5% (average) obtained by UV-vis spectrophotometry for PET material using an integrating sphere (EMPA 1997). To assess the transmittance losses due to absorption, the transmittance values were corrected by dividing the transmittance of the same sample at 500 nm (such spectra will be referred to as ‘corrected’).

Two-step mass spectrometry

Two-step laser mass spectrometry (L2MS) proved to be a powerful tool for direct analysis of polymers additives (Wright et al. 1996). In contrast to secondary ion mass spectrometry (SIMS), merely used for surface analysis (Lang et al. 1997), L2MS allows penetration of most polymers, thereby, providing three-dimensional information. A home-built L2MS system was used as already described in detail elsewhere (Voumard et al. 1993). Only its major features are given hereafter.

Pieces of the Evian® bottles (approx. 13 mm × 13 mm, test ‘EAWAG-2’) were mounted onto the tip of a sample holder before their introduction into the vacuum chamber. A remote-controlled motor-driven sample rotator allowed, if necessary, exposure of a new spot for each laser pulse.

A CO₂ laser (Alltech 853 MS, Luebeck, Germany, 0.6 J/cm², 100 ns) was used for ablation of the bottle material. An iris and a ZnSe lens (f = 50 mm) mounted on a micrometer screw allowed control of the energy density
of the beam and size of the ablation spot. The settings used for this project correspond to about 6 J/cm² on an elliptic spot of about 100µm × 150 µm.

The ionising laser radiation, delayed by 10 µs in relation to the desorption laser, was produced by an optical parametric oscillator laser (MOPO-730D10, Spectra Physics Lasers Inc., Mountain View, CA, 10 ns, 0.001 nm line width) pumped by the third harmonic of a pulsed Nd:YAG laser (GCR-230, Spectra Physics Lasers). A 220 nm wavelength, corresponding to a photon energy of 5.64 eV, was used for this project. The UV beam passed through the plume of ablated bottle material 2.5 mm above the sample's surface after being focused by a cylindrical lens (∠ = 250 mm). A pyroelectric detector (Gentec ED-100) was placed behind the ionising source to measure the energy of each UV pulse to normalise the respective ion signals.

Mass spectrometric analysis of the thereby ionised compounds was performed by a reflectron time-of-flight instrument (R.M. Jordan Co., Grass Valley, CA).

### Analytical methods for water samples

#### Extraction

Water samples of the dark control and of 15, 30, 63 and 126 days of sunlight (test ‘EAWAG-2’) were analysed. Graphitised carbon black material (ENVI-Carb) for enrichment of substances in irradiated bottles containing drinking water, 6 ml solid-phase extraction tubes (polypropylene) and polyethylene frits were commercially available from Supelco SA (Bellfonte, PA, USA).

500 mg of ENVI-Carb material was filled in 6 ml polypropylene cartridges. A 75 ml polyethylene reservoir was connected to each tube. All glassware was rinsed with methanol. The pH of the samples was 7.4–7.5. The solid phase was conditioned with 7 ml of dichloromethane/methanol (70/30), 7 ml of methanol and 10 ml of bi-distilled water. The water samples (800 ml) were filled into the reservoir and the samples enriched. After washing with 1 ml bi-distilled water, the retained compounds were eluted with 2 ml of methanol and 5 ml 50 mM ammonium acetate in dichloromethane/methanol (70/30). The combined eluates were evaporated on an aluminium heating block (50–60°C) under a gentle stream of nitrogen. The dry residues were redissolved in 2 ml of dichloromethane, dried overnight with sodium sulphate and again evaporated to dryness. Glassware blanks with HPLC water (800 ml) (Scharlau, Barcelona, E) were analysed simultaneously.

The analytical techniques chosen for the study in Malaysia was the solid-phase microextraction (SPME), a method that integrates sampling, extraction, concentration and sample introduction in a single step, and which has been shown to be effective for the extraction of phthalates from aqueous media (Kelly & Larroque 1999). The SPME method consisted of immersing the fibre in 10 ml of the water sample at 35°C for 15 min, with stirring at 400 r.p.m. The fibre, which was obtained from Supelco Bellefonte, PA, USA was coated with partly cross-linked polydimethylsiloxane/divinylbenzene in a film thickness of 60 µm. It was previously established that this type of fibre extracts more compounds than fibres coated with either carbowax or polydimethylsiloxane alone.

#### Analysis

UV-vis. absorbance was used in Malaysia to identify changes of the water quality. For UV analysis, ultraviolet visible absorbance of the samples was examined between 190 and 800 nm, using fresh glass-distilled water as a blank.

Quantification of aldehydes present in the Swiss water samples was performed by high-performance liquid chromatography (HPLC) after derivatization with 2,4-dinitrophenylhydrazine in the laboratory of the University of Muenster, Germany (Vogel 1998).

In the SPME method the enriched fibre was placed in the injector port (at 270°C) of a gas chromatograph fitted with an OV 17 column (15 cm × 0.53 mm i.d., film thickness 1 µm) with nitrogen as carrier gas at a flow rate of 10 ml/min. The temperature program was 50°C for 5 min, heat to 240°C at 10° per minute and maintenance at this temperature for 5 min. The separated compounds were detected by mass spectrometry. Local drinking water was not used, since the SPME technology is sensitive to interferences that could block the sorption sites on the
fibre, thus preventing extraction of the dibutylphtalate that may be present. In all cases, fresh glass-distilled water was used as a control.

For the analysis by GC/MS, the extracts were derived by adding 50 µl of the derivation mixture (Sylon BTZ (Supelco SA, Bellefonte, PA, USA)): N,O-bis(trimethylsilyl)acetamide (BSA)/trimethylchlorosilane (TMCS)/n-trimethysilylimidazole (TMSI): 3/2/3). After a reaction time of 15 min at 80°C, the solution was evaporated to dryness by a gentle nitrogen stream and the residue was dissolved in 150 µl of toluene.

Separation and detection of the analysis was achieved using a GC/MS system (Fisons GC 8000 coupled to a Fisons Autospec Q magnetic sector mass spectrometer) equipped with a 15 m home-made DB-5 column (dimethyl 5% diphenylsiloxane, 0.25 i.d., 0.134 µm film thickness).

GC injection parameters: 1 µl splitless; GC temperatures 110°C, −210°C, 2.5°C/min, −245°C, 245°C isothermal 2 min.

MS parameters: temperature of transfer line (GC interface): 255°C, ion source: EI positive mode, electron energy 70 eV, ion source temperature 255°C, trap current: 300 µA, mass range: 50–600 D, cycle time: 2.1 s.

RESULTS AND DISCUSSION

PET samples

UV and visible transmittance is a key factor when assessing the suitability of containers for solar water disinfection. Ideally, the walls of such containers should be fully transparent to light in the entire spectral range of terrestrial sunlight, extending from about 290 nm to the infrared range. Owing to the presence of UV stabilisers and light absorption properties of the PET material itself, it is difficult to obtain plastic bottles with a transparency below 320 nm. The plastic bottles for the SODIS demonstration projects in different parts of the world were selected for their UV-vis spectra. Typically clear PET bottles have a transmittance of >60% above 340 nm. As the bactericidal effect of light is important not only in the UV-B (280–320 nm), but also in the UV-A (320–400 nm) and violet (400–450 nm) spectral ranges (Wegelin et al. 1994; Webb et al. 1976), such bottles were successfully used for SODIS (Sommer et al. 1997). A general decrease in UV-vis transmittance of these bottles was observed after several months. Figure 1 illustrates the change in transmittance spectrum due to ageing of the bottle. The uncorrected spectrum exhibits a strong decrease in transmittance in both UV-A and visible spectral ranges. The corrected spectra, which account for changes in absorption properties of the material, reveal that the aged bottle absorbs more light in the UV-A spectrum than the unused one.

To confirm that the change in absorption properties of the material was induced by sunlight, three samples of colourless PET material from a single bottle were exposed to sunlight for 1, 2 and 4 months, respectively. The spectra of such samples exhibited a decrease in transmittance in the UV-A range with increasing sunlight exposure time (see Figure 2). Transmittance spectra of the
exposed samples were similar to the corrected spectra of used bottle material. Factor analysis of the difference in absorbance between the three exposed samples and unexposed sample (using the same data as in Figure 2) revealed one single spectral component, corresponding to 99.9% of the variance. The maximum change in absorbance was detected at 331 nm.

Exposure of full and empty bottles (as described in the Experimental Section) resulted in spectral changes (Figure 3) similar to those already observed with the samples cut from PET bottles. Transmittance changes of the samples irradiated for the same period of time were identical within the accuracy range of the measuring method, regardless of the content of the bottle. With the only exception of the samples irradiated for 63 days, which can probably be attributed to a difference in thickness of the two samples. Factor analysis of the difference in absorbance between the eight exposed and the reference samples revealed two spectral components amounting to 91.9% and 8.0% of the variance, respectively. The maximum change in absorbance was detected at 334 nm. Although the spectral change in both experiments is similar, a detailed analysis revealed that the sunlight-induced chemical transformation of the material was not identical, which might be attributed to the use of possibly different additives. The additional component detected by UV-vis spectrophotometry in this experiment is possibly caused by a fading of the dye or transformation products of the dye used to give the bluish colour.

Figure 4 illustrates the evolution of absorbance of the PET samples as a function of exposure dose. The increase in absorbance at different wavelengths within the 330–360 nm range is most likely to be directly proportional to the dose received by the PET material up to an exposure dose of 320,000 W h m$^{-2}$ (corresponding to about two months). The increase in absorbance at a 560,000 W h m$^{-2}$ dose is somewhat less than expected from these proportions. This may be attributed to the protecting effect (inner filter effect) of the photoproducts building up in the exposed PET material, but also to a decrease in the UV-B and UV-A relative component of sunlight when approaching autumn.
Figure 5 (PET5 and 10 internal and external) depicts the average L2MS spectra of 13 individual shots on different spots of an Evian® PET bottle stored in the dark (as described in the sunlight irradiation experiment). All prominent peaks can be rationalised as PET fragments, as shown in Figure 6. Moreover, the mass spectra obtained corresponded well with the ones from pure PET foils, and with the literature data (Voumard et al. 1993). No peaks that could possibly be assigned to additives were observed.

Figure 7 illustrates the ion signal of mass 149 of the series of shots on the same spot with the three bottles examined during the long-term study. PET10 external and internal (dark control) and PET05 external and internal (dark control filled with water) exhibit a distinct decrease in the ion signal with increasing shot number. However, ion signals m/z = 149 of the PET04 bottle (full bottle exposed to sunlight for 126 days) are markedly reduced on the outer surface. Similar results were obtained with a used PET bottle from Thailand (data not included). Analysis of the inner side showed a somewhat different picture, as a reduction of the ion signal was not always observed, and most probably caused by surface heterogeneity (Figure 7 internal (1) vs. internal (2)). Note that the relative abundance of varying ion signals did not differ significantly, neither with depth, nor with sample. The low ion signals resulted from reduced ablation of sample material with the CO2 laser. This could have been caused by the external surface exposure to mechanical stress, its extended contact with water in the bottle, or by a possible alteration in cross-linking of PET polymers as a consequence of their intensive exposure to sunlight.

The results obtained with L2MS do not allow to draw any conclusions concerning substantial leaching of either PET or, if present at all, its additives into the aqueous phase. PET seems to undergo slight changes in degree and type of polymerisation. This could be attributed to its extended exposure to sunlight and, probably even more so, to mechanical stress. Since these findings correlate with UV-absorbance spectra, the efficiency of microbial deactivation might be reduced when using old bottles.
Water samples

Analytical evaluation of water samples stored in PET bottles in Malaysia revealed that the spectra for the control and test samples were virtually identical. No UV-absorbing compounds that might possibly be released in concentration lower than the detection limit into the water could be detected (Table 1).

While exposure has no influence on the acetaldehyde content, the formaldehyde content seems to correlate with exposure time, except for the longest exposed sample exhibiting the same concentration as the unexposed one. For more conclusive results, measurements of a statistically significant number of samples are required. In any case, the aliphatic aldehyde content of all tested water samples is well below the limits for safe drinking water (according to Swiss legislation, this limit is set at 15 mg/l for formaldehyde).

SPME-GC-MS analysis of the Malaysian samples revealed that compounds in both control and tests samples were identical and hence, there is no real evidence that there are compounds leaching from PET into the water. The samples from the ‘EAWAG-2’ test were compared with each other to determine whether organic photoproducts and/or additives leach from PET material into the aqueous phase during sun exposure. No significant differences between dark control, sun-exposed samples (15, 31, 63 and 128 days) and blank samples were identified. In all samples, only some phthalates, probably leached from the polypropylene cartridges (Bucheli et al. 1997), were detected. Therefore, the analytical methods used did not reveal any organic substances leaching from PET material. However, the analytical method was not replicated as only one bottle was exposed and the whole sample volume enriched at once for each irradiation time. Risk assessment and determination of photoproducts required additional comprehensive databases, including careful quality control (recoveries, blanks, detection limits, and replicates) and different enrichment and detection methods.

CONCLUSION

The different analysis examining the PET material and the water stored in the bottles and carried out independently in Switzerland, Germany and Malaysia reveal that photoproducts are formed at the outer surface of the PET bottles. These products increase with progressing sunlight exposure time the absorbance of the solar UV-spectrum. Furthermore, photochemical ageing of the bottles does not change the quality of the water stored in the bottles.
with regard to aldehyde, organic photoproduct, additive or phthalate concentrations. All these substances were if at all detected at low concentrations well below the limits for safe drinking water.

The tests were run with water stored in the bottles up to 126 and 99 days, respectively, and hence, possibly harmful substances could accumulate over these test periods. However, in the SODIS water treatment method the water is usually exchanged every day and thus, the concentrations of the analysed substances are lower, presumably by a factor of 10 or 100. Hence, PET bottles are considered adequate for SODIS use.

The health effects to the community, of long term SODIS exposure on other types of plastic, especially those containing additives (e.g. in PVC bottles), remains to be examined. Furthermore, sunlight irradiation might accelerate the migration of PET-components or the generation of products through (thermo-activated) chemical reactions.

Finally, the results of these studies also suggest that PET bottles are excellent containers for soft drinks quite often exposed to sunlight over extended periods of time.

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