542

Egypt. J. Chem. **Vol. 66** No. 11 pp. 573-583 (2023)

Egyptian Journal of Chemistry

Migration of Acetaldehyde and Formaldehyde from PET-bottled Water Under Hot Climate Conditions

Abdelhakim A.A [1] **Abdel-Aziz M.S** [2] **and Maha Sultan** [3]

[1,3]Packaging Materials Department, [2]Microbial Chemistry Department
National Research Centre, 33 El Bohouth St. (former El Tahrir st.), Dokki, Giza, Egypt, P.O. 12622

Abstract

This study focused on how sunlight exposure affects the mount of antimony that leached into polyethylene terephthalate-bottled water as well as the amount of formaldehyde and acetaldehyde that leached from egyptian weathering after a certain period of time. The change in the mechanical properties, chemical composition, and water vapor permeability of bottles were also investigated. Bottles from the markets of two different companies were gathered and used in this experiment. A market of recently filled bottles served as the source for the reference groups. The second group originated from bottles that had been kept in the laboratory for different amounts of time. The third group was made up of bottles that had been in varying intervals of solar exposure for 386 days. The leached substances (formaldehyde, acetaldehyde, and antimony) as well as the water's toxicity and the presence of microorganisms in the water were all evaluated in the bottles' water. According to the findings, the bottles' ir spectra under varied exposure situations do not significantly differ from each other. Under a variety of weathering storage circumstances, bottled water does not demonstrate toxicity because the half maximum effective concentration (E_c50) values were less than 100 mol/L.

Keywords: Polyethylene terephthalate, Formaldehyde, Sunlight exposure, Acetaldehyde

1. Introduction

The utilization of food packaging materials has contributed to risks due to the leaching of dangerous migrants from packaging material to the packed food. In the last decades, the employment of bottled water has grown rapidly. PET-based bottled water is widely utilized in our country and around the world. PET is a great material for water packing because of its chemical resistance, lightweight, low water gas permeability, strong mechanical qualities, and transparency, as well as the fact that it is easily recyclable [1]. As a result, PET can be used to modify glass [2]. Hazardous contamination may be present in plastic bottles; these contaminants may diffuse into the water contained in the bottles, causing diseases such as mutagenic or carcinogenic effects [3]. PET is frequently used in packaging, particularly for bottled foods including water, beverages, and fruits. Antimony, oligomers, formaldehyde, and acetaldehyde are the primary components that remain in PET after processing or packaging [3]. The materials released into bottled PET starting reactants (catalysts), reaction by-products, and plastic additives

were the subject of these investigations. Migration-controlled processes that simulate actual storage conditions are used to monitor several substances. The diffusion of carbonyl compounds from the PET bottle wall to water was studied to see whether conditions, such as contact duration, temperature storage, light exposure, and the physicochemical features of drinking water, could increase their migration from the polymer into bottled water [4,5]. The primary source of formaldehyde and acetaldehyde in bottled drinking water was PET bottles. Their concentrations in the PET bottle will be determined by the raw material compositions and manufacturing technology used (production of granules, preforms, and bottles). The diffusion of formaldehyde and acetaldehyde was influenced by temperature and storage period, according to most kinds of literature. Wegelin et al. [6], Nawrocki et al. [7], Mutsuge et al. [3] have come to opposing results about the rise or decrease in the quantities of these two chemicals after exposure to sunlight. Trace levels of acetaldehyde, formaldehyde, and other organic and inorganic elements have been identified in water packaged in PET bottles, where it is genotoxic in biological effect and a human

_____

carcinogen [8]. The safety of PET bottles for drinking water is currently under debate. The contaminations produced from PET bottles are dependent on the storage circumstances, such as temperature, time spent in the temperature, and exposure to sunlight [9]. Bottled water has become part of everyone's daily existence. It's critical to look into its impact on human health and the environment. The main source of concern is antimony leaching from PET water bottles. In an investigation, the bottled water was exposed to various times and temperatures in experiments. Longer exposure, as well as greater temperatures, showed more antimony leaching in most samples [6]. Acetaldehyde is produced during the polymerization reaction, as well as during the melting process during the production of PET bottles. The production of carboxyl and vinyl ester chain endings is caused by the scission of polymer chain bonds. As a reaction sub-product, acetaldehyde is generated by combining these two end groups [8].

An internal breakage of the polymeric chain produces formaldehyde [10]. The early migration research focused on acetaldehyde to clarify why bottled water tastes and smells undesirable.

The levels of acetaldehyde and formaldehyde in industrial PET were strongly dependent on the molecular weight of the polymer and the bottle-blowing temperature [1]. Because PET bottles are employed for packaging products such as mineral water, the packing materials must have high degrees of odor and flavor neutrality for this application. Because acetaldehyde is observable at low concentrations in mineral water as a fruity flavor, the migration of acetaldehyde is of particular interest. Acetaldehyde is a dissociation product of the PET polymer that is produced during use or manufacture. Acetaldehyde is trapped in the PET bottle wall after cooling down and migrates into the mineral water after filling and storage.

The goal of this study was to assess the amount of formaldehyde, acetaldehyde, and antimony in PET drinking water bottles, as well as the change in odor or taste of water, and bottled water toxicity, and the change in PET material attributes. 2.Experimental

2.1. Materials

Dimethoxymethane with a purity of 99 percent was manufactured. Formic acid and pure ethanol (99 %) were acquired from ADWIC, Egypt. Merck, Germany, provided the formaldehyde solution (37%), as well as the acetaldehyde (90%). Sigma-Aldrich in Japan provided the P-toluene sulfonic acid monohydrate (98.5%). Two samples of bottled water in PET from

two separate firms were purchased from Cairo retail outlets and were assigned the letters N and S.

2.1.1. UV exposure of PET sheets
The PET sheets were exposed to UV. Accelerating weathering Tester; Model QUV- Q- LAB Test suspended Cycle ASTM G 154 CYCLE for 50 and100 hours.

2.2. FTIR Spectroscopy
The FTIR spectra were investigated using the FTIR in the range of 4000-400 cm-1 by preparing samples from the bottles fresh packed to water and taking symbols (NI, SI). Samples after storage without exposure to light were recorded for time intervals and take the symbol of (NII, SII). The last samples exposed to sunlight get the symbols (NIII, SIII).

2.3. Mechanical properties of PET Bottles
PET material mechanical testing is significantly different from other types of plastics, and there is very little preceding knowledge. To conduct the testing, follow the ISO 527-3- 1995 guidelines: Plastics. The testing was guided by the determination of Tensile Properties - Part 3: Test Conditions for Films and Sheets. The mechanical testing involved gathering standardized commercially emptied bottles, which resulted in a curled flat sheet. For testing, a minimum of five specimens per combination were employed. All mechanical qualities were determined using an Intron machine type 34 SC- 5 Universal Testing Machine (chosen testing speed = 50 mm/min) that was made in the United States.

2.4. Preparation of formaldehyde stock solution
The thiosulfate-iodide technique was used to standard an aqueous formaldehyde stock solution (100 µg mL-1) made by diluting 2.4 mL of 37% (w/v) stock formaldehyde solution to 1 L with DDW.

2.5.Preparation of diethoxymethane and diethoxyethane
The diethoxymethane and diethoxyethane were produced by reacting formaldehyde and acetaldehyde with the chemicals specified in the following strategy (1). In ethanol, 10 µL of acetaldehyde and formaldehyde were combined with 480 µL of 1% (w/v) Para toluene sulphonic acid as described in Scheme (1) [11].
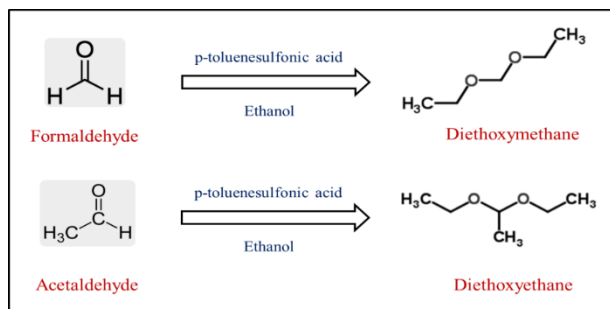
Scheme 1: Preparation of dimethoxymethane and diethoxyethane

2.6. Sample preparation

1 mL of the water sample was mixed with 4 mL of 1% para- toluene sulphonic acid. Formaldehyde is detected as diethoxymethane. Acetaldehyde is detected as 1, 1-diethoxy ethane.

2.7. Determination of acetaldehyde and formaldehyde concentrations in water samples by gas chromatography-mass spectrometry analysis (GC-MS)

The GC-MS system (Agilent Technologies) included a gas chromatograph (7697A), mass spectrometer detector (5977A), and ahead space autosampler with a Headspace temperature program of 70°C ovens, 90°C loops, and 110° transfer line temperature for a 20-minute equilibrium time. A DB-624 column (30 m x 320 m, 1.8m) was used in the GC. The following temperature program was used with hydrogen as the carrier gas at a flow rate of 1.8 ml/min and a split mode of 25:1, injection volume of 1 l, and the following flow rate: 35°C for 5 minutes; 40°C/min rise to 220°C, then hold for 1 minute. The injector and detector were both kept at 170°C and 230°C. Electron ionization (EI) at 70 eV was used to obtain mass spectra with a spectral range of m/z 20-400 and a solvent delay of 2.0 min. The spectrum fragmentation pattern was compared to those recorded in Wiley and NIST Mass Spectral Library data to identify various constituents.

2.8. Water vapor permeability

Water vapor transmission rate (WVTR) was carried out using GBI W303 (B) Water Vapor Permeability Analyzer (China) using the cup method. The water vapor permeability was measured as the amount of water vapor passes through the tested film. Also, WVTR was measured as the mass of water vapor transmitted throughout a unit area in a unit time under controlled conditions of temperature (38oC) and humidity (4%) according to the following Standards (ASTM E96, ISO 2528, ASTM D1653, TAPPI T464, DIN 53122-1, JIS Z0208).

The water vapor transmission rate (WVTR):

The water vapor transmission rate (WVTR):

$$WVTR = S\frac{1}{A} \dots \dots (1)$$

S is the slope (g/h) and A is the film`s area (m^2).

$$WVP = L \times \frac{WVTR}{\Delta P} \dots . \dots \dots .. \ (2)$$

WVP (g. mm. m^{-2}. kPa^{-1} .h^{-1} , L is film`s thickness (mm) and ΔP (38 °C) is the partial pressures of water vapor in saturated air at100% to relative humidity and air (5 .942 kPa), respectively.

2.9. Microbiological analysis

To control the microbiological quality of the natural spring bottled water during the 386 days of storage, the sample was done at 1, 29, 70, 103, 160, 210, 313, and 386 days of storage in both incubation settings and sunlight exposure. A pour plate method was used to determine total bacterial counts as colony forming units (CFU), and the plates were incubated at 37 oC for 48 hours. Total coliform counts were measured using eosin methylene blue agar plates incubated for 24 hours at 22 oC and 37 oC. Lurial Broth [12] was used to determine the E.coli count, which was kept at 37°C for 24 hours [13].

2.9.1. The total bacterial count of drink bottled water (N and S samples)

Water samples were used to inoculate solid agar medium (total count agar) with the following constituents (g/l): tryptone (5), yeast extract (2), glucose (1), and agar (18), and the final pH was adjusted to 7±0.2. 100μL from each water sample was used to inoculate the agar plate with 20ml of solidified medium using a glass swab.

2.10. Microtox® test

The toxicity of unconcentrated mineral waters was determined by the Microtox® test [13], using lyophilized cultures of a bioluminescent bacterium, V. fischeri NRRL-B-11177 [13]. In the Microtox® technology, bacterial light emission inhibition is proportional to sample toxicity. The reading was taken at a wavelength of 490 nm after 30 minutes of incubation at 15 °C. Five replicates of unconcentrated water samples were compared to five replicates of blank control samples using the comparison test protocol (NaCl2 %). Microtox® data collecting software revealed whether there was a significant difference (>5%) between samples and controls.

3. Result and discussion

3.1. FTIR studies of PET films under exposure of sunlight

Photo-degradation during storage, caused by UV radiation exposure and temperature variations, results in the formation of carboxyl end-groups [14], which

affects both the mechanical characteristics and fracture behavior of the bottles, as well as their water vapor penetration barrier qualities. For each type of bottle and the storage circumstances, the bottles were divided into three groups (N and S). The first investigated groups, NI and SI, were taken as reference samples after being collected from the market and freshly filled. The second group (NII, SII) was stored in a carton box in the lab for various time intervals up to 386 days, while the third group was exposed to sunlight for 386 days in a carton box for various time intervals (NIII, SIII). ATR-FTIR spectroscopy was conducted on the PET bottle samples to determine the changes in functional groups attributable to the exposure to different environmental conditions and to investigate the influence of weathering conditions in packed water contained in the bottles. The main absorption bands in the ATR –FTIR spectra of freshly filled bottles (SI and NI), samples kept in the lab for 386 days (SII and NII), and samples stored for 380 days outside in direct sunlight (SIII and NIII) are shown in Figure (1). The primary peaks of PET were shown in Table (1) at 1714cm-1, 1243 cm-1, and 1096 cm-1 and were found to be unaffected by the varied circumstances employed in this work. The band at 1714 cm-1 corresponds to C=O in conjugation with the aromatic ring. Asymmetric C–C–O stretching involving the carbon in the aromatic ring is represented by the band at 1243 cm-1. Aromatic C–H out of plane bending, O–C–C asymmetric, stretching, trans and gauche conformations, C–H asymmetric stretching, aromatic C–C stretching, C–H bending, and C–H alkane deformation were seen at 872 cm-1, 1093 cm-1, 2963 cm-1, 1504 cm-1, 1455 cm-1, 1408 and 1338 cm-1, respectively. The first clear alteration in FTIR spectra was observed after 380 days of storage (Figure 1). Small peaks were observed in different regions: near1713 cm−1, and 1577–1453 cm−1. These bands could be assigned to the formation of the carboxyl end-groups and alkenes end-group in addition to the oxidation process during processing [15,16], where the principle band appeared at 1713 cm−1 assigned carbonyl group of the carboxylic group. The small peaks around it could be also assigned to the carboxyl band, but the shifting is due to both the oxidation and the formation of possible substitution on the closest benzene ring as well [17,18]. The appearances of these peaks approve the suggestion of photo-oxidative degradation of polymer i.e. chain scission and formation of alkenes end-groups. On other hand, SI, SII, and SIII samples showed no significant change, where the bottles display bands at 1714cm-1, 1243 cm-1, and 1096 cm-1. Other bands at 871 cm−1 and 723 cm−1 have reduced relative intensity. We can conclude that there are no significant differences among the IR spectra of the bottles under the different circumstances of

exposure. Likely, the degradation of PET bottles has not occurred under normal sunlight or during storage inside the markets. Possibly, the changes in PET bottle structure cannot be detected by IR or the change occurrence may be related to oxidation and carboxylic group formation accumulated during bottle processing and employing high temperatures during that, thus the change accrues for fresh bottles before filling.
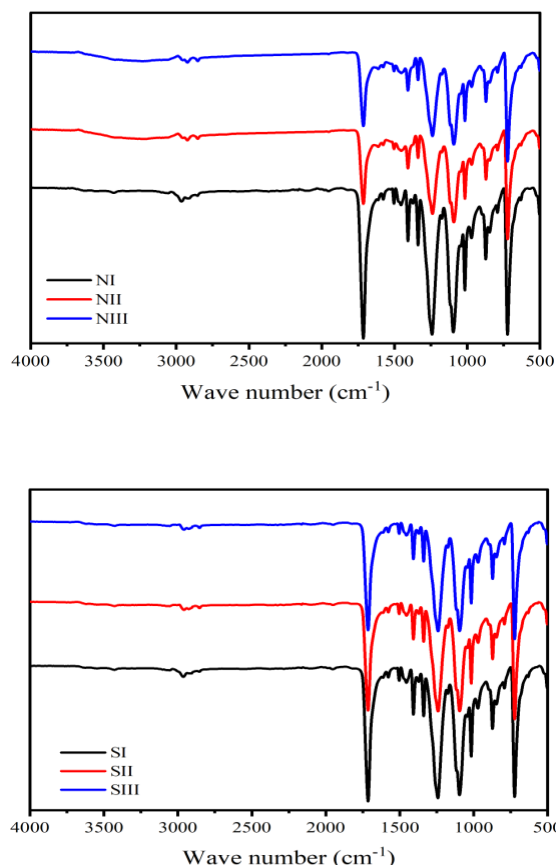

Figure 1: ATR –FTIR spectra for PET samples: SI, NI: freshly filled bottles, SII, NII: samples kept in the lab for 386 days, and SIII, NIII: stored for 380 days outdoor under direct sunlight

3.2. Mechanical properties of mechanical properties of PET films under sunlight exposure

Average stress-strain curve results of PET Reference tests plastic sheet were determined. These results are comparable to those found in materials data books (CUE, 2003), which show that PET's maximum tensile strength ranges from 48.3 to 72.4 MPa. The following results were discovered for the mechanical properties of bottled N-type, as shown in Figure (2): the tensile strength of the PET bottle polymer material rose with increasing sunlight exposure time. It was increased from 83 ± 1.5 to 143 ± 3.8 MP increasing the sunlight exposure time up to 100 hours. The tensile strength of

PET of bottled S type has the same behavior, the tensile strength increased from 114.3±1.35 to 155±3.38 MPa up to 100 hours of sunlight exposure. The change in the elongation % was the opposite. The PET N and S sample types decreased from 122.5±2.5 %to 96±3.76 % and 150±2.33% to 104±4.04%, respectively. But for the modulus of elasticity, the PET N and S sample types increased from 1579±15.5 to 2714±21.8 N/m2 and 1707±19.35 to 2809±27.98 N/m2, respectively

Table 1: The main IR peaks (cm-1) for the groups N and S

| Symbol	Description	C=O	C-O aromatic	C-O aliphatic	C-H aromatic	C-H aliphatic
NI	Freshly filled bottles	1713	1239	1096	871	723
NII	Bottles are stored in the lab. For 380 days	1713	1239	1092	871	723
NIII	Bottle exposed to sunlight for 380 days	1714	1242	1096	873	723
SI	Freshly filled bottles	1714	1243	1096	871	723
SII	Bottles are stored in the lab. For 380 days	1714	1241	1092	872	723
SIII	Bottle exposed to sunlight for 380 days	1714	1242	1096	872	723
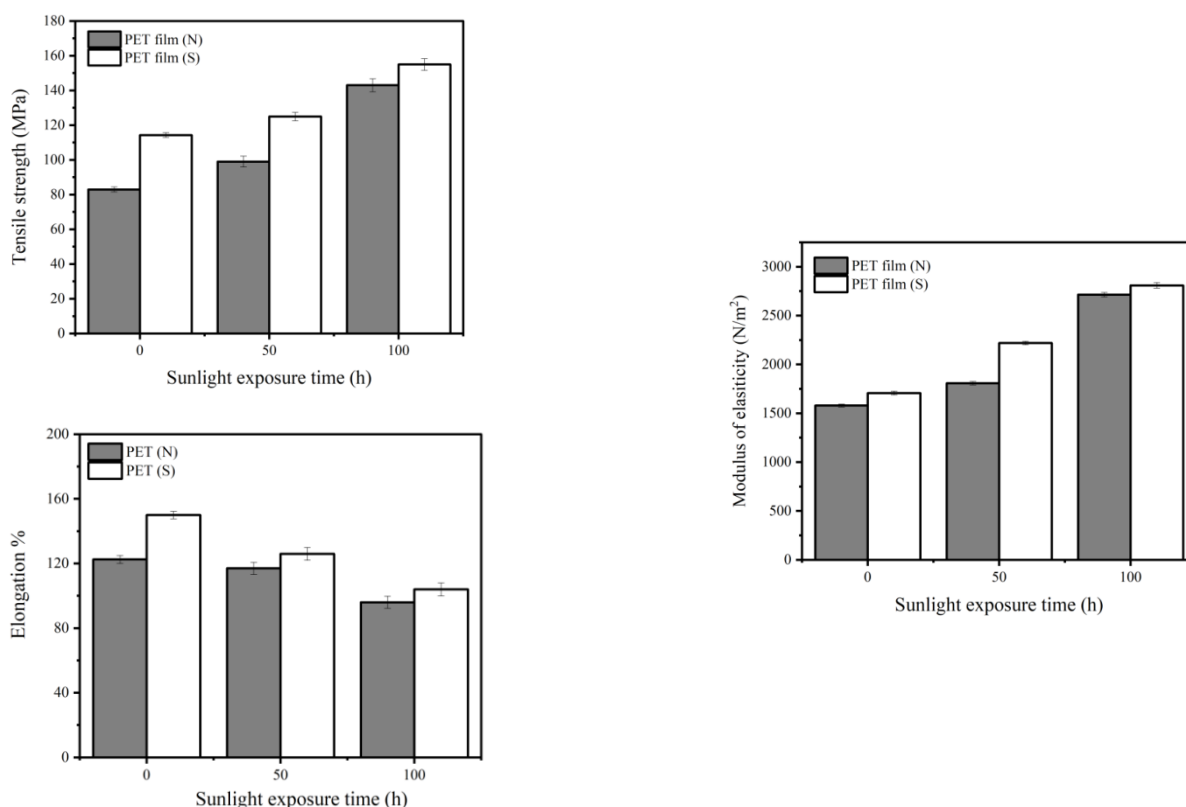
Figure 2: Mechanical properties of PET films as a function of sunlight exposure time

3.3. Water vapor permeability

Figure (3) illustrates WVP of fresh-packed water PET bottles (NI, SI), exposed PET bottles for UV lamps (NII, SII), and exposed PET bottles for the sunlight (NIII, SIII). It's worth noting that the behavior of water vapor permeability in the two types of bottles (N and S) is nearly identical, with minor differences. In addition, the effect of long-term storage versus exposure to sunlight and high temperatures in Egyptian weathering has a minor impact on water vapor permeability. The WVP of fresh-packed water PET bottles (NI, SI) were 1.619±0.033 and 1.603±0.04, and exposed PET bottles for UV lamp (NII, SII) were 2.473±0.051 and 2.315±0.054 and exposed PET bottles for the sunlight (NIII, SIII) were 2.657±0.055 and 2.677±0.044 g.mm.h-1.m-2 KPa^{-1}.
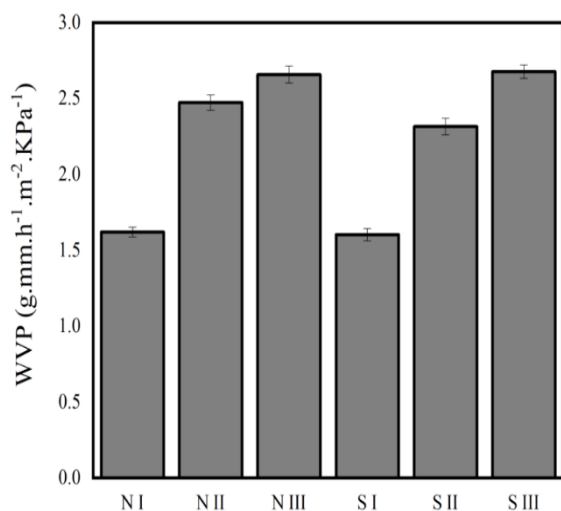

Figure 3: WVP of fresh-packed water PET bottles (NI, SI), exposed PET bottles for UV lamp (NII, SII), and exposed PET bottles for the sunlight (NIII, SIII)

Table 2: Leached formaldehyde and acetaldehyde concentrations after sunlight exposure using GC-MS

Sample symbol	Exposure time (day)	Formaldehyde (mg/L)	Acetaldehyde (mg/L)
N1	0	ND	1.65
N2	126	ND	1.73
N3	189	ND	2.12
N4	267	5.15	4.16
N5	322	12.3	ND
N6	378	ND	ND
N7	441	ND	ND
S1	0	ND	1.27
S2	126	ND	1.32
S3	189	ND	2.05
S4	267	0.96	7.16
S5	322	1.96	ND
S6	378	ND	ND
S7	441	ND	ND

3.4. Influence of sunlight exposure on formaldehyde and acetaldehyde leaching

The most important carbonyl chemicals migrating from PET bottles are formaldehyde and acetaldehyde. Thermo-mechanical and thermo-oxidative degradation of PET produce them.

The proportion of formaldehyde and acetaldehyde in the PET wall is determined by the chemical quality of the raw material, the polymer's molecular weight, and the manufacturing process (granule manufacture, preform production, and bottle blowing temperature) [1].

The influence of sunlight exposure on formaldehyde and acetaldehyde leaching into bottled water was measured with waters for both brands of PET bottles NIII and SIII using GC-MS for 386 days. The quantity of formaldehyde and acetaldehyde leached from PET bottles (NIII and SIII) to bottled water was determined using gas chromatography (GC-MS) after the bottles were exposed to sunlight in Egyptian weathering for varied timeframes. Table (2) displays the results obtained. In brand NIII bottle type formaldehyde was not detected for up to 189 days. However, acetaldehyde was detected immediately after sunlight exposure; the leached acetaldehyde was 1.65 mg/L and exceeds 4 mg/L up to 267 days. The leached formaldehyde content was 5.15 mg/L up to 267 days and exceeds 12 mg/L up to 322 days. The leaching of formaldehyde and acetaldehyde continue to increase with time until 378 and 322 days, respectively, and no leached formaldehyde and

acetaldehyde were detected. However, in brand SIII bottles, formaldehyde leaching was observed only after 267 days given 0.96mg/L while acetaldehyde release was already observed immediately (1.27m/L). Formaldehyde concentration of bottle NIII brand was still higher than of bottle brand SIII (6.2 times higher) up to 322 days of exposure. However, at day 267 day, acetaldehyde concentration of bottle brand SIII was still higher than acetaldehyde in bottle brand NIII (1.7 times higher). The results revealed that formaldehyde and acetaldehyde were not detectable with long-term exposure. There are extensive studies on migration of acetaldehyde and its effect on undesirable taste and odor in bottled water after 386 days. Porretta and Minuti (1995) [19] detect trace amounts of acetaldehyde in different brands of drinking water purchased from retail. It was proposed that traces of metal ions or oxygen in still water could facilitate the

degradation of acetaldehyde and formaldehyde. May be all the organic are likely products resulted from oxidation and/or reduction of acetaldehyde. Mutsuga et al. (2006) [20] studied the stability of formaldehyde and acetaldehyde in sterilized and unsterilized mineral water. The scientists noticed that these two chemicals disappeared over time in commercial mineral water stored in sunlight and attributed it to heterotrophic bacteria that may degrade them. Another study evaluated the effects of UV irradiation from the sun. As a result, the possibility that sun irradiation might induce organic compound breakdown via photoreactions cannot be ruled out [21]. Tolerable quantities of acetaldehyde and formaldehyde were fewer than 6 mg/kg and 15 mg/kg, respectively, according to the European Union's declared specific migration limits of certain chemicals (expressed in mg/kg food) (EU 2011). The amounts of leached formaldehyde and acetaldehyde were clearly within the European Union's declared particular migration limitations [22, 23].

3.5. Antimony releasing

As a result of the catalysts or additives used to generate PET, inorganic species may be present. The most essential catalyst in the production of PET is antimony trioxide (Sb_2O_3) (EU, 2008). Sb values in PET are normally between 170-300 mg/kg. However, only a small percentage of the Sb in PET is released into the water [1]. The amounts of Antimony leached from the two brand bottles (NIII and SIII) into the water were determined according to the Standard method of examination of water (2012) 22nd American Public Health Association, Washington, D.C. The concentrations of Antimony leached from PET into water results are shown in Table (3). The impact of exposure to sunlight on the migration of Sb for diverse timeframes was investigated. Table (3) shows that the quantities of Antimony contained in

packed water migrated at low levels (less than 10 mg/L) in the two PET samples (SIII, NIII). These findings might be due to the use of a different type of catalyst or the use of minuscule quantities that are undetectable by this methodology. The Sb concentrations in this investigation are similar to those found in a study by Westerhoff et al. [24] who found no significant changes in samples held at 22°C after 3 months. They did, however, discover that high-temperature storage had a considerable impact on Sb release. Keresztes et al. [24] and Cheng et al. [26] also validated these findings [26]. Both authors, on the other hand, led to the realization that solar irradiation had a lesser impact on Sb leaching than temperature when it comes to the impact of bottle color Westerhoff et al [24].

Table 3: The amounts of Antimony leached from PET into water

Samples	Unit	Sb
N1	mg/L	<0.01
N2	mg/L	<0.01
N3	mg/L	<0.01
N4	mg/L	<0.01
N5	mg/L	<0.01
S1	mg/L	<0.01
S2	mg/L	<0.01
S3	mg/L	<0.01
S4	mg/L	<0.01
S5	mg/L	<0.01

3.6. Microbiological studies

Table 4 shows the images of colony forming units (CFU) of Staphylococcus aureus inoculated water of bottle N and S brands and the effect of Egyptian weathering storage conditions on their survival and counts. Also, Figure (4) shows the effect of different weathering storage circumstances on colony-forming unit counts (cells/mL). As shown in Figure (4), the bacterial count of the utilized contained water samples in bottles N and S brands indicated that both water samples had less than 100 cells/mL of bacterial growth. The standard suspension of Staphylococcus aureus (4 x 105 cells/mL) was subsequently injected into both water samples. Under aseptic circumstances, one milliliter of this stock solution was suspended in 1.5 milliliters of each water sample. Both samples inoculated were exposed to direct sunlight (keeping

_____

freshwater sample inoculated with Staphylococcus aureus in a dark cold environment) for 18 months and colony forming units (CFU) were quantified directly for well-shaken samples. The control water sample: Staphylococcus aureus water inoculated N brand sample had a CFU value of 2×10^2 cells/mL, whereas the S brand water sample had a CFU value of 2.4×10^2 cells/mL. The CFU value of the freshwater inoculated with S. aureus of N brand sample was 9×10^1 cells/mL, while the CFU value of the light exposed sample was 3×10^1 cells/mL. The CFU value of the S sample was 14×10^1 cells/mL, but the CFU value of the light exposed samples was 6×10^1 cells/mL. According to these findings, exposure to sunlight has contributed to more bacterial growth inhibition than keeping in cold and dark conditions.
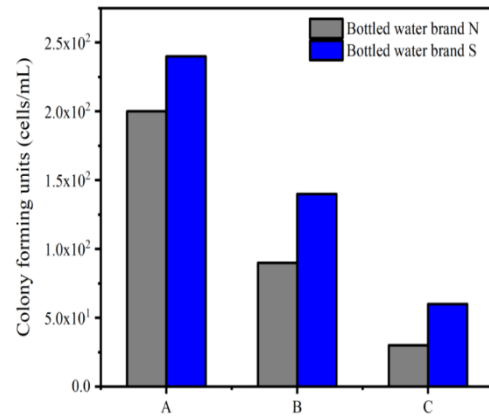

Figure 4: Colony forming units of bottled water brand N and S (A: freshwater inoculated with S. aureus, B: freshwater inoculated with S. aureus kept in the cold and dark environment, and C: freshwater inoculated with S. aureus exposed to sunlight for 18 months

Table 4: Effect of sunlight exposure on colony forming units (cells/ml) of S. aureus inoculated fresh bottled waters (N and S)

Sample	N	S
Fresh bottled water (N and S)		
S. aureus inoculated fresh bottled waters (N and S)		
S. aureus inoculated fresh bottled waters (N and S) in a dark and cold environment		
S. aureus inoculated fresh bottled waters (N and S) exposed to sunlight		

_____

3.7. Toxicity

The toxicity of bottled water results after UV exposure using Microtox analyzer 500 [27] was shown in Table. The results were calculated according to BS EN-ISO (2008) and NSF-BS (2016): [28, 29]. The half maximum effective concentration (EC50) values were ≥100 mol/L. According to the toxicity results, there is no toxicity in drinking water in PET bottles under various weathering storage conditions, such as high temperature and sunlight or a long period of exposure, which means that despite these conditions, some organic matter leached to bottles, changing the odor or taste of water, but not to the point of toxicity. Exposing PET bottles to sunlight, which also increases the water's temperature, raises questions about the formation of by-products and their migration into water, as a possible source of health hazards for the consumers. The carbonyl groups were detected may be due to presence of aldehydes, phthalates and others in PETbottled waters following sunlight exposure [28].

Table 4: Toxicity of bottled water after UV exposure using Microtox analyzer 500

Sample name	Half maximum effective concentration (EC50 in mol/L)	Toxicity results
N1	≥100	Non-toxic
N2	≥100	Non-toxic
N4	≥100	Non-toxic
S1	≥100	Non-toxic
S2	≥100	Non-toxic
S4	≥100	Non-toxic

Conclusion

Based on the foregoing findings, it can be inferred that there is no marked change between the IR spectra of the bottles under various exposure circumstances, indicating that there is no deterioration of the PET in natural sunlight or during market storage. It could be related to oxidation and carboxylic group formation accumulated during bottle processing and employing high temperatures during that, thus the change accrues for fresh bottles before filling. The lack of antimony detection could be due to the use of a new type of initiator during the preparation of PET polymer materials, or it could be due to the low levels of Sb in the samples. Depending on the results, IR spectra of the bottles do not differ significantly under various exposure conditions. The half maximum effective concentration (EC50) values were ≥100 mol/L, and bottled water does not exhibit toxicity under various weathering storage conditions.

Conflicts of interest

There are no conflicts to declare".

Formatting of funding sources

Acknowledgments

References

[1] Al-Tayyar, N.A., Youssef, A.M., Al-Hindi, R.R.; Antimicrobial packaging efficiency of ZnO-SiO$_2$ nanocomposites infused into PVA/CS film for enhancing the shelf life of food products, *Food Packag. and Shelf Life*, 25, (100523) 2020. doi.org/10.1016/j.fpsl.2020.100523

[2] Bach, C., Dauchy, X., Chagnon, M.-C., Etienne, S., Chemical compounds and toxicological assessments of drinking water stored in polyethylene terephthalate (PET) bottles: A source of controversy reviewed, *Water Res.*, 46, (571-583) 2012a. doi.org/10.1016/j.watres.2011.11.062

[3] Cristina , B., Xavier, D., Marie-Christine, C., Serge, E., Chemical compounds and toxicological assessments of drinking water stored in polyethylene terephthalate (PET) bottles: A source of controversy reviewed, *Water Res*, 46(3): (571-583) 2012. https://doi.org/10.1016/j.watres.2011.11.062

[4] Bulich, A.A., Isenberg, D., Use of the luminescent bacterial system for the rapid assessment of aquatic toxicity, *ISA trans.*, 20, (29-33) 1981. PMID: 7251338

[5] Ceretti, E., Zani, C., Zerbini, I., Guzzella, L., Scaglia, M., Berna, V., Donato, F., Monarca, S., Feretti, D., Comparative assessment of genotoxicity of mineral water packed in polyethylene terephthalate (PET) and glass bottles, *Water Res.*, 44, (1462-1470) 2010. 10.1016/j.watres.2009.10.030

[6] Cheng, X., Shi, H., Adams, C.D., Ma, Y., Assessment of metal contaminations leaching out from recycling plastic bottles upon treatments, *Env. Sci. and Pollut. Res.*, 17, (1323-1330) 2010. 10.1007/s11356-010-0312-4

[7] Commission, E., 2011. Commission Regulation (EU) No 10/2011 of 14 January 2011 on plastic materials and articles intended to come into contact with food. Off. J. Eur. Union 12, 1-89.

[8] polyethylene terephthalate bottles, preforms, and resins by automated headspace gas chromatography, *J. Chrom. Sci.*, 18, (242-246) 1980. doi.org/10.1093/chromsci/18.5.242

[9] Franz, R., Welle, F., Can migration of endocrine disruptors from plastic bottles be the cause of estrogenic burden recently determined in bottled mineral water, *Dtsch Lebensmitt Rundsch*, 105, (315-318) 2009. 20093157776

[10] Depaolini Andrea R., Elena F., Giancarlo B., Roberto F., Enrico D., Acetaldehyde in Polyethylene Terephthalate (PET) Bottled Water: Assessment and Mitigation of Health Risk for Consumers, *Appl. Sci.*, 10(12), (4321) 2020. doi10.3390/app10124321

[11] Wiwiet, Y., Tasia, A., Slamet, I., Sophi, D., Analytical Method Development for Determining Formaldehyde in Cream Cosmetics Using Hyphenated Gas Chromatography. *ACS Omega.*, 6, (28403-28409) 2021. DOI: 10.1021/acsomega.1c04792

[12] Victor, J. , Michael H.R-B., David J.B., Assessing chemical toxicity with the bioluminescent photobacterium (*vibrio fischeri*): a comparison of three commercial systems Water Res, 35(14): (3448-3456) 2001. https://doi.org/10.1016/S0043-1354(01)00067-7

[13] ISO, W., Determination of the inhibitory effect of water samples on the light emission of vibrio fischeri.(luminescent bacteria test), Iso 11348-1, 2 and 3, (1-21) 1998.

[14] Keresztes, S., Tatár, E., Mihucz, V.G., Virág, I., Majdik, C., Záray, G., Leaching of antimony from polyethylene terephthalate (PET) bottles into mineral water. *Sci. of the Total Env.*, 407, (4731-4735) 2009. doi.org/10.1016/j.scitotenv.2009.04.025

[15] Delilah, L., Jeanette, D., Göran, D., Åke., L., Leachates from plastic consumer products – Screening for toxicity with *Daphnia magna, Chemosphere*, 74(9): (1195-1200) 2009. https://doi.org/10.1016/j.chemosphere.2008.11.022

[16] Mutsuga, M., Kawamura, Y., Sugita-Konishi, Y., Hara-Kudo, Y., Takatori, K., Tanamoto, K.,. Migration of formaldehyde and acetaldehyde into mineral water in polyethylene terephthalate (PET) bottles, *Food Addit and contam.*, 23, (212-218) 2006. https://doi.org/10.1080/02652030500398361

[17] Mutsuga, M., Tojima, T., Kawamura, Y., Tanamoto, K., Survey of formaldehyde, acetaldehyde and oligomers in polyethylene terephthalate food-packaging materials, *Food Addit and contam*, 22, (783-789) 2005. doi.org/10.1080/02652030500157593

[18] Nawrocki, J., Dąbrowska, A., Borcz, A., Investigation of carbonyl compounds in bottled waters from Poland, Water Res, 36, (4893-490) 2002. 10.1016/s0043-1354(02)00201-4

[19] Neamţu, M., Frimmel, F.H., Photodegradation of endocrine disrupting chemical nonylphenol by simulated solar UV-irradiation, *Sci. of the Total Env.*, 369, (295-306) 2006. 10.1016/j.scitotenv.2006.05.002

[20] No, R., 10/2011 of 14 January 2011 on Plastic Materials and Articles Intended to Come into Contact with Food. Official Journal of the European Union L 12.

[21] Marleen van, A., Susan, E. D., Dianne, B., Joseph, E. M., Timothy, E. L., Cameron, R. H., Cheryl , H., Flavor Threshold for Acetaldehyde in Milk, Chocolate Milk, and Spring Water Using Solid Phase Microextraction Gas Chromatography for Quantification, J. Agric. Food Chem., 49(3): (1377–1381) 2001. https://doi.org/10.1021/jf001069t

[22] Prasad, S.G., De, A., De, U., Structural and optical investigations of radiation damage in transparent PET polymer films, International

Journal of Spectroscopy, 1(7) 2011. doi.org/10.1155/2011/810936

[23] Silverstein, R.M., Bassler, G.C., Spectrometric identification of organic compounds. J. of Chem. Edu., 39, (546) 1962. doi.org/10.1021/ed039p546

[24] Standardization, I.O.f., Water Quality: Determination of the Inhibitory Effect of Water Samples on the Light Emission of Vibrio Fischeri (Luminescent Bacteria Test). Method Suring Liquid-dried Bacteria. ISO 1998.

[25] Steckenreiter, T., Balanzat, E., Fuess, H., Trautmann, C., Chemical modifications of PET induced by swift heavy ions. Nuclear Instruments and Methods in Physics Research Section B: Beam Interactions with Materials and Atoms, 131, (159-166) 1997. 10.1016/s0168-583x(97)00364-9

[26] Vijayakumar, S., Rajakumar, P., Infrared spectral analysis of waste pet samples. International Letters of Chemistry, Physics and Astronomy, 4, (58-65) 2012. https://doi.org/10.18052/www.scipress.com/ILCPA.4.58

[27] Wegelin, M., Canonica, S., Alder, C., Marazuela, D., Suter, M.-F., Bucheli, T.D., Haefliger, O., Zenobi, R., McGuigan, K., Kelly, M., Does sunlight change the material and content of polyethylene terephthalate (PET) bottles? Journal of Water Supply: *Res. and Tech.—AQUA*, 50, (125-135) 2001. doi.org/10.2166/aqua.2001.0012

[28] Welle, F., Franz, R., SiO x layer as functional barrier in polyethylene terephthalate (PET) bottles against potential contaminants from post-consumer recycled PET, *Food Addit and contam*, 25, (788-794) 2008. doi.org/10.1080/02652030701704755

[29] Westerhoff, P., Prapaipong, P., Shock, E., Hillaireau, A., Antimony leaching from polyethylene terephthalate (PET) plastic used for bottled drinking water, *Water Res*, 42, (551-556) 2008. 10.1016/j.watres.2007.07.048