Songklanakarin J. Sci. Technol.
41 (2), 259-264, Mar. – Apr. 2019

http://www.sjst.psu.ac.th

Original Article

Degradation of polyethylene terephthalate bottles after long sunlight exposure

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Received: 23 June 2017; Revised: 8 October 2017; Accepted: 3 November 2017

Abstract

Effects of sunlight on PET bottles degradation and liquid filled inside the bottles were studied. Three types of soft drinks filled in Polyethylene terephthalate (PET) bottles; drinking water in clear bottle, carbonated water in green, and pink bottles was left on the rooftop of building for 8 months. After long exposure to sunlight, the bottles' shapes were not changed, but the tensile strength of plastics decreased. Moreover, the enthalpy of fusion which corresponds to molecular rearrangement of plastics increased. The results from FTIR showed slightly increased of peak hydroxyl group at 3,400 cm^{-1} on outer surface of PET bottle. Sunlight slowly degraded the chemical structure on outer surface of PET bottle by photo-hydrolysis reaction. The pH of water for all samples changed from acid to base. By using Tollen's reagent, aldehyde was found clearly in drinking water after sunlight exposure, but was not observed in green and pink water.

Keywords: polyethylene terephthalate, degradation, PET bottle, contamination, carbonated soft drinks

1. Introduction

Drinking water is very important for all living organisms, especially for humans. Medically, each person should drink clean water at least eight glasses per day or approximately two liters per day. Due to the change of lifestyles in modern society, bottled water and soft drinks are convenient for carrying and more hygienic than drinking from tap water. PET is the material of choice for beverage packaging because of its possessing some superior properties, such as good mechanical and barrier properties, excellent clarity, easy transport and processing, and light weight compared to metal and glass (Ewender, Franz, Mauer, & Welle, 2003; Welle, 2011).

Polyethylene terephthalate (PET) is formed by polymerization of ethylene glycol and terephthalic acid or terephthalic acid methyl ester with the present of antimony trioxide (Sb_2O_3) as catalyst (Duh, 2002). In some cases, germanium and titanium oxides are used as catalyst or co-catalyst (Duh, 2002). PET is classified as a thermoplastic, when heated to melting temperature (255 ºC); it can be reprocessed to new plastic bottles or other products. PET bottles are considered to be safe for bottling drinking water, carbonated soft drinks, as well as for more sensitive beverages like beer, wine and juices. PET also has good barrier properties towards moisture and oxygen (Ewender *et al.*, 2003). PET is also resistant to acidic beverage such as carbonated soft drinks and juices.

PET undergoes photo-degradation when it is exposed to sunlight for a long time. PET absorbed sunlight at a wavelength range located at the end of ultraviolet light spectra (UV with wavelength between 300 nm and 330 nm). The absorbed UV light has enough energy to break the carbon-carbon bonds and create free radicals, which causes degradation of PET through thermomechanical and thermo-oxidative processes, generating non-intentionally added sub-

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stances (NIAS), which can migrate into the bottled water. The degradation process usually accelerates by external factor such as oxygen content, moisture, and temperature (Bach *et al.*, 2013). The degradation of plastic can be observed from the paling or yellowish color of the products. The degradation decreases physical and mechanical properties of plastic. Energy absorbed from UV light will break the covalent bonds in polymer molecules leading to photolysis reaction and finally degraded. The photochemical process causes change in molecule different ways including cleavage, elimination of small molecule, forming unsaturated bonds, rearrangement, cyclization, cross-linking, oxidation, and photo hydrolysis (Chaisupakitsin, 2008).

Fechine, Rabello, Souto Maior, & Catalani (2004) investigated surface characterization of photodegraded poly-ethylene terephthalate films obtained by bi-axial extrusion. After exposed to ultraviolet light in a laboratory weathering chamber for periods of up to 1,100 h, the unstabilized films are very susceptible to the degradation effects causing a large deterioration, especially in surface layers. The presence of an ultraviolet light absorber effectively reduced the formation of carboxyl end-groups at the surface as well as in the bulk of the films. In the case of samples with UV absorber the fluo-rescence data showed a barrier imposed by this additive in the formation of the monohydroxy-terephthalate. Scanning electron microcopy (SEM) of fracture surfaces showed that film ductility is highly reduced after exposure.

Compounds from PET bottle, such as degradation products of the polymer, catalyst residues and other contaminants, can migrate into water or liquid inside. The most important degradation products present in PET are aldehydes such as formaldehyde and acetaldehyde (Wegelin *et al.*, 2001). Environmental factors and storage time have effects on the release of chemical substances from PET. In sunlight exposure tests, PET degradation products such as terephthalate monomers and dimers are primarily formed at the outer surface of the bottles. The water sample stored in the bottles showed higher formaldehyde and acetaldehyde levels after longer storage times. However, sunlight exposure has no effects on these compounds levels (Bach *et al.*, 2013; Wegelin *et al.*, 2001). Temperature and the presence of CO_2 increased the release of formaldehyde, and acetaldehyde. A degradation compound of phenolic antioxidants, 2,4-di-tert-butylphenol, and an intermediary monomer, bis (2-hydroxyethyl) terephthalate, were found in PET-bottled waters (Bach *et al.*, 2012).

Schmid, Kohler, Meierhofer, Luzi, & Wegelin (2008) studied the migration of organic substances from PET to water by using used colorless transparent beverage bottles of different origin. The bottles were exposed to sunlight for 17 hrs at geographical latitude 47 ºN. In a general screening of treated water, only food flavor constituents of previous bottle contents could be identified above a detection limit of 1 mg/L. Maximum concentration of plasticizers di (2-ethylhexyl) adipate (DEHA) and di (2-ethylhexyl)phthalate (DEHP) were 0.046 and 0.71 mg/L, respectively, which is in the same range as these plasticizers found in commercial bottled water.

Thailand, like most other countries, uses PET as the packaging for drinking water and carbonated water. These bottled water and carbonated water are left in the sun for a long time at high temperature during distribution process to the consumers. Recently, there are many concerns about the degradation quality of beverage inside and the migration of degradation products from PET bottles after exposure to sunlight and stored at high temperature. Therefore, the effects of sunlight exposure to the degradation of PET bottles and quality of liquid in side were investigated in this study. Three different types of bottled water and carbonated water with different color were compared.

2. Materials and Methods

2.1. Experiment

Three types of polyethylene terephthalate bottles filled with drinking and soft drinks, i.e., clear PET bottles (filled with drinking water), green PET bottles (filled with green carbonated soft drinks), and pink PET bottles (filled with pink carbonated soft drinks), six bottles of each type were placed on the roof top of building for eight months from May 20, 2016 until Jan 20, 2017. The temperature and relative humidity were recorded every day except holidays. After 0, 1, 3, 4, 6, and 8 months, one bottle from each type of beverages were photographed to record the physical characteristics of the bottles and kept in dark cabinet for further analysis. The functional groups of bottle materials were characterized using Fourier transform infrared spectroscopy (FTIR, Spectrum GX, Perkin Elmer) at wave number 400-4,000 cm^{-1}. The thermal properties and mechanical properties of the bottle after light exposure were analyzed by Differential Scanning Calorimeter (DSC, Pyris Diamon, Perkin Elmer) and Tensile Testing Machine (Universal Testing Machine; model LR1K, LLOYD Instruments Ltd.) respectively. The pH of liquid inside bottles was measured using pH meter (Metrohm). The carbonyl functional groups of liquid inside bottles were determined using 2, 4-Dinitrophenylhydrazine (2, 4-DNP) and Tollen's reagent. The concentration of ion in liquid was analyzed by Ion chromatography technique.

2.2. Analytical methods

2.2.1. FTIR

Samples were taken by scratching the PET material from bottles after sunlight exposure for 0, 1, 3, 4, 6, and 8 months. The samples were ground with potassium bromide and formed into thin sheet for measuring light transmission and analyzing by FTIR technique.

2.2.2. Differential scanning calorimeter

The heat of fusion and melting temperature of PET materials were determined using a Differential Scanning Calorimeter (DSC, Pyris Diamon, Perkin Elmer) with heating rate of 10 ºC/min and cooling rate of 10 ºC/min Measurement temperature start from 50 ºC up to 350 ºC.

2.2.3. Tensile strength test

Samples were cut into a drum bell shape with the size of 2 × 10 cm. Each sample was tested for the tensile strength using Universal Testing Machine (model LR1K LLOYD Instruments Ltd.) under following conditions; load cell 2 KN, test speed 50 mm/min and gauge length 25 mm.

2.2.4. Analytical method for stored beverage

Concentrations of anion were determined using Ion Chromatography, IC technique according to method no. 4110B in standard method of water and wastewater examination (APHA, AWWA, & WEF, 2012). The concentration of carbonyl functional group in aldehyde and ketone were determined by adding 2 ml of 2, 4-Dinitrophenyl hydrazine (2, 4-DNP) into 10 ml sample. Then, the precipitate was filtered, dried and weighed.

The carbonyl groups of aldehyde were tested using Tollen's reagent. Tollen's reagent was prepared by adding 1 ml of 10% silver nitrate ($AgNO_3$) in a clean and dry test tube. After adding one drop of sodium hydroxide (NaOH), the brown color of silver oxide (Ag_2O) appeared; then gradually adding NH_4OH dropwise until the brown precipitate of (Ag_2O) disappeared. To test with the sample, five drops of Tollen's reagent were added into 10 ml sample, the silver mirror formed at the test tube wall was observed if there was carbonyl group of aldehyde in the samples.

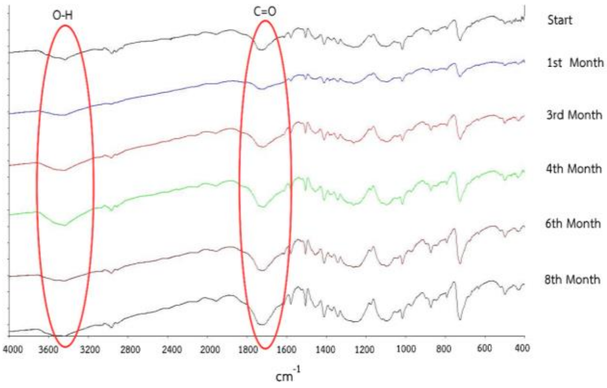
3. Results and Discussion

3.1. PET bottles characterization

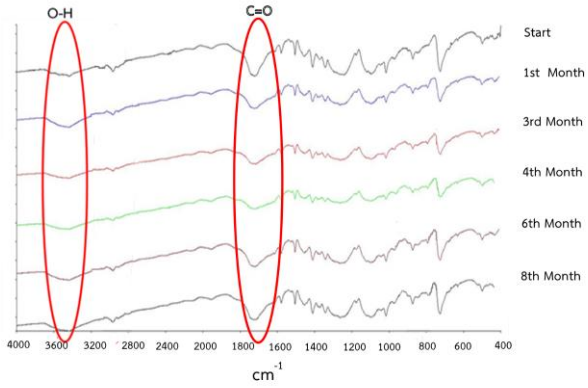
Three types of polyethylene terephthalate bottles filled with drinking and soft drinks, i.e., clear PET bottles (filled with drinking water), green PET bottles (filled with green carbonated soft drinks), and pink PET bottles (filled with pink carbonated soft drinks), six bottles of each type were placed on the roof top of building for eight months from May 20, 2016 till Jan 20, 2017. After 0, 1, 3, 4, 6, and 8 months, the functional groups of bottle materials were characterized using Fourier transform infrared spectroscopy at wave number 400-4,000 cm^{-1}. The FTIR result was shown in Figure 1.

The results from Figure 1 indicated that hydroxyl groups at 3,400 cm^{-1} and carbonyl groups at 1,700 cm^{-1} slightly increased with longer exposure time. Similar results were found by Wegelin *et al.* (2001), and Fechine *et al.* (2004). Increasing of hydroxyl groups means polyethylene terephthalate (PET) bottle undergoes the hydrolysis reaction. PET is a condensation polymer between terephathalic acid and ethylene glycol; therefore, it contains an ester bond. Sunlight and moisture in the weather induces hydrolysis reaction at the ester bond of PET as shown in Figure 2.

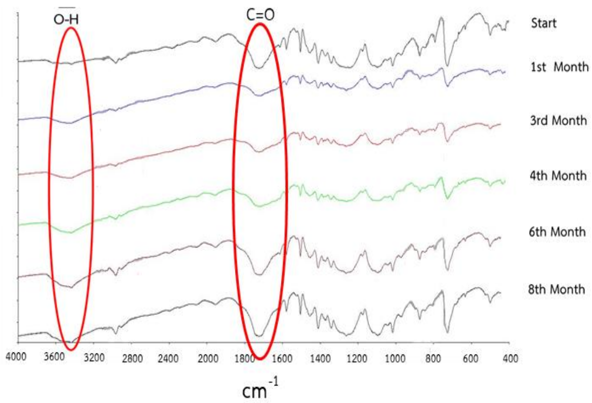
The melting temperature and heat of fusion of bottle material were determined using DSC (Pyris Diamon, Perkin Elmer). The observed melting temperature and heat of fusion of PET material before and after exposed to sunlight were shown in Table 1. The melting temperature (T_m) of PET bottles is normally at 250 ^oC, as shown in Table1. The melting temperature did not change after exposure to sunlight for 4 and 8 moths. However, the enthalpy of fusion (ΔH_m) increased. This means that heat from sunlight induces molecular rearrangement of polymer chain which similar to annealing process of polymer. The observed enthalpy of fusion for clear PET bottle was 13.8 J/g to 23.3 J/g, from the beginning to the end of melting state. The enthalpy of fusion at the beginning of melting state for Green PET bottle and Pink PET bottle was 21.3 J/g and 17.3 J/g, respectively. These enthalpy values are higher than that of clear PET bottle because pigment in bottle



(a)



(b)



(c)

Figure 1. Transmittance (%) of hydroxyl and carbonyl group of PET at different exposure times: (a) Clear bottle, (b) Green bottle, (c) Pink bottle.

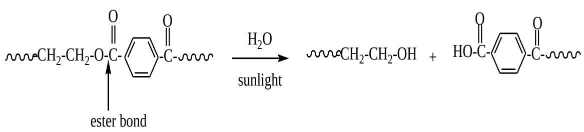


Figure 2. Hydrolysis reaction of PET.

Table 1. Thermal properties of PET bottles.

Type of bottle	Time(month)	T_m (ºC)	ΔH_m(J/g)
Clear	0	250	13.8
	4	249	20.6
	8	249	23.3
Green	0	250	21.3
	4	250	22.0
	8	250	23.3
Pink	0	250	17.3
	4	251	21.4
	8	250	22.5

material induces polymer crystallization leading to the higher enthalpy.

3.2. Physical property of PET bottles

As can be seen in Figure 3, the maximum tensile forces of green and pink PET bottles are higher than clear PET bottles before the experiment. The maximum tensile force correlates with the degree of crystallinity of polymer. This means that the green and pink bottles are stronger than clear PET bottle. However, all kinds of bottles showed slightly decreased in maximum tensile force after eight months sunlight exposure. These results suggested that the degradation took place in polymer chain. Chain lengths and molecular weight of polymer decreased under hydrolysis reaction, as discussed in the FTIR analysis section.

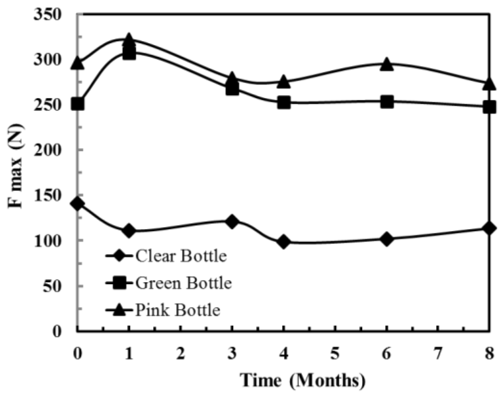


Figure 3. Maximum tensile force (kN) of PET bottles at various exposure time.

3.3. Water analysis

Before exposed to sunlight, the pH of drinking water in this experiment was 4.5. And, the pH of green water and pink water was 3.9 and 3.5, respectively. After exposure to sunlight for 8 months, pH of drinking water in clear PET bottle changed from 4.5 to 6.5. The pH of water in Green and Pink PET bottles are change from 3.9 and 3.5 to 4.2 (Figure 4). The change in pH resulted from the reaction of anion (F^-, Cl^-, NO_3^-, $SO_4^=$) in beverage and water then produced OH^- and acid, as shown in the following equations.

$$F^- + H_2O \longrightarrow HF + OH^- \quad (1)$$
$$H_2O + Cl^- \longrightarrow HCl + OH^- \quad (2)$$
$$H_2O + NO_3^- \longrightarrow HNO_3 + OH^- \quad (3)$$
$$H_2O + SO_4{=} \longrightarrow HSO_4^- + OH^- \quad (4)$$

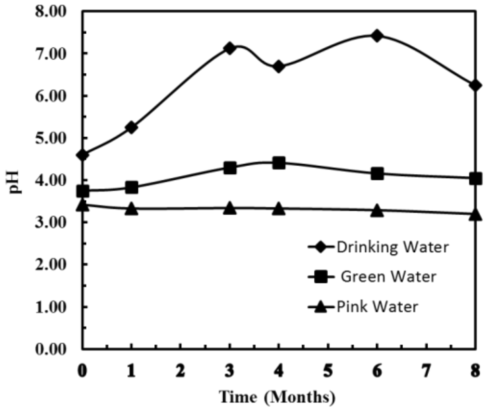


Figure 4. pH of beverage in PET bottle at various exposure time.

From Figure 4, pH of water in Green and Pink PET bottles were slightly changed from acid to base when compared to drinking water. This suggested that green and pink pigments which were mixed with water can reduced or retarded the extent of the above reactions.

3.4. Anion concentration analysis

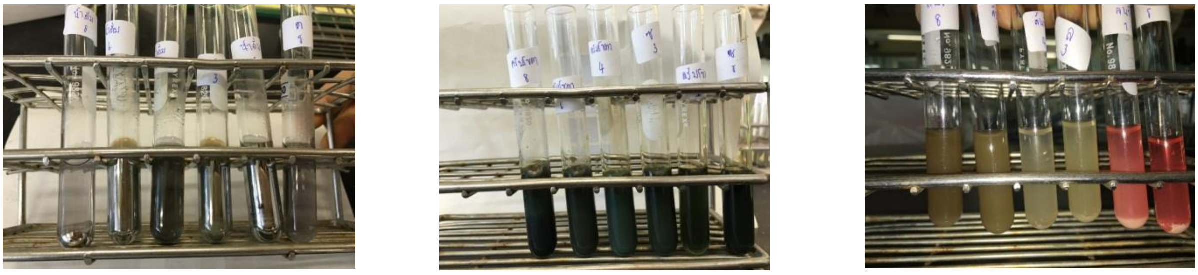
The concentration of anions, i.e. F^- Cl^-, NO_3^- and $SO_4^=$ in water was analyzed by using ion chromatography followed the standard methods for the examination of water and wastewater (APHA, AWWA, & WEF, 2012). The data shown in Table 2 indicated that the concentration of F^-, Cl^-, NO_3^- and $SO_4^=$ for all samples was influenced by sunlight. The concentration of these anions in all samples was fluctuated during outdoor sunlight exposure time. These results are in agreement with the observation of Sulaiman, Lawen. & Shelear (2011). Sunlight accelerated the chlorination and fluorination reactions. Moreover, it also altered organic compounds in water to NO_3^- and $SO_4^=$ (Sulaiman *et al.*, 2011). It should be noted that pink water in pink PET bottle had the highest total anions concentration and did not change much after 8 months sunlight exposure. On the other hands, total anion concentration of drinking water and green water were obviously changed. Total anion concentration of drinking water was decreased, while it was increased in case of green water.

3.5. Aldehyde detection

Acetaldehyde is produced during the polymerization reaction and the melting process in PET bottles manufacturing, and during thermal degradation. In this experiment, Tollen's reagent was used for qualitative test to check the forming of acetaldehyde in water which probably migrated from PET bottles during sunlight exposure. The results shown in Figure 5 indicated an obviously silver mirror coated on the test tube's wall of drinking water sample. This pointed out

Table 2. Anion concentration found in beverages.

Type of Beverage	Exposure Time (Months)	F^- (mg/l)	Cl^- (mg/l)	NO_3^- (mg/l)	SO_4^{2-} (mg/l)	Total (mg/l)
Drinking Water	0	12.63	203.16	20.31	18.36	254.46
	4	55.38	55.38	13.2	65.97	189.93
	8	2.73	109.98	11.97	5.46	130.14
Soft Drink in Green Bottle	0	-	81.15	5.67	39.6	126.42
	4	20.19	79.83	7.38	41.73	149.13
	8	40.92	80.79	61.74	41.25	224.70
Soft Drink in Pink Bottle	0	14.52	99.87	112.17	79.26	305.82
	4	30.08	58.98	130.83	74.82	294.70
	8	57.99	56.85	126.24	67.20	308.28



(a) (b) (c)

Figure 5. Tollen's reagent test for (a) clear water (b) green water (c) pink water. (Note: Test tubes on the right hand side of each rack were sample before sunlight exposure and on the left hand side after sunlight exposure).

that there were trace amount of aldehyde and acetaldehyde in water which was migrated to drinking water from PET bottles and it was decreased over exposure time. On the other hand, the silver mirror was not formed when tested with the carbonated water sample, but the turbidity of carbonated water increased after exposed to sunlight as shown in Figure 5. These might be the results of the interference of colored water in Tollen's reagent test. However, the decrease of silver mirror formed on the test tube of clear water sample over exposure time indicated that sunlight does have significant effects on the migration of aldehyde and acetaldehyde into drinking water.

4. Conclusions

Under this experiment, it was found that sunlight induced change both in plastics container and filled water. Moreover, plastic pigments, food additive pigments, and carbon dioxide filled in water affect the pH, total anion concentration and also, aldehyde content**.**

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