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Original Article

Exposure Hazard to Bisphenol A for Labor and Particle Size Distribution at Polycarbonate Molding Plants

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Abstract

Background: This research provides an insight into exposure information and particle size distributions of Bisphenol A (BPA), a common environmental hormone, at polycarbonate (PC) molding plants in southern Taiwan.

Methods: The inhalable dust sampler as IOM and the micro-orifice uniform deposition impactor (MOUDI) were used for samples collection to evaluate the level and particle size distribution of BPA in PC molding plants. All collected samples were analyzed by high performance liquid chromatography (HPLC) for BPA concentrations.

Results: BPA concentrations detected from the plant using optical grade PC material ranged from 32.28 to 44.97 μg/m^3, which were significantly higher than BPA concentrations (16.16 to 19.39 μg/m^3) detected from the plant using food grade PC material. Under working environment, the particle size distribution showed a single mode distribution, with a MMAD of 0.84μm and a GSD of 1.97. Emission of BPA increased during heating process and most of BPA particles deposited in the nasal cavity (63.37%), following by alveolus (30.7%), and trachea-bronchus (5.93%).

Discussion: It is of importance that proper personal protection should be taken upon the BPA particulates released during the molding process at PC molding plants.

Keywords: Bisphenol A, Polycarbonate, Respiratory tract, Particle size distribution

Introduction

Bisphenol A (BPA) is an environmental hormone and an endocrine disruptor bearing estrogenic efficacy. BPA will bond to the receptor of estrogen to disturb the reaction of normal hormones in human body through release, transport, metabolism, and bonding, and it will react with some certain hormones that regulate and maintain constant human growth, to pose adverse health effect (1). It will cause a variety of diseases including cancer, infecundity, heart disease, prematurity, inhibiting androgen, and enhancing estrogen (2).

BPA is one of the most important industrial chemicals in the world, which is a major raw material for producing epoxy, polycarbonate, and fire inhibitors (3-5). After BPA was primarily synthesized in 1891, it (Bisphenol A) has been widely used in manufacturing food cans, drinks vessels, and even in baby's bottles since 1950 (6, 7). The production of BPA, in year of 2010 reached 4 million metric tons and the demand was still growing. Of BPA products, polycarbonate (PC) becomes an important plastic material having great demand in Taiwan and the yield is recorded to be 335

thousand metric tons in 2010 (8). PC is characterized to be a tough, uniform, and transparent material that is used for making food packing materials, transparent containers, baby bottles, compact disks, and protective glasses.

A Chinese male worker was exposed to BPA at an average level of 5.97 μg/cm^3 in an epoxy manufacturing plant and resulted in suffering from sexual disorder(9). There are many researchers focused extensively on BPA exposure to soil and wastewater to date and on the study for dissolution of BPA from food containers, canisters, and dental sealants (10, 11), which may subsequently enter human body. However, study of BPA exposure to the air is still lacking, particularly on the study for BPA exposure to worker in a plastic plant is relatively rare, and not to mention the study of particle size distribution of BPA.

It is of importance to analyze particle size distribution of organic compounds whose chemical and physical properties may affect human health (12), because the tiny aerosol particles may easily enter the deep region of respiratory tract system and pose adverse effect to human health. Burning plastic in city or its outskirt caused BPA spreading in the air and formed an environment for human exposure to BPA (13). The size of BPA particle was smaller than 1.9 μm; however, such study was lack of estimation of exposure concentration of BPA in different regions of respiratory tract.

This study investigated the BPA exposure to worker in two polycarbonate molding plants and estimated the amount of BPA deposition in various regions of respiratory tract based on the result of BPA particle size analysis. Additionally, BPA extraction from PC product was also tested to study the relationship between the residual BPA content in PC product and the BPA concentration exposed to the air under the working environment.

Materials and Methods

Aerosol Sampling

Sampling of Airborne BPA

This study employed the inhalable dust sampler as IOM to collect BPA particulates in the air. The sample time was 36 to 48 hours; sampling medium was 25 mm-diameter fiberglass filter with particle retention of 0.3 μm; and the sampling flux was set at 2 *l*/min. Four samples were taken from each of production lines: one from the inlet of heating unit, two from the outlet of heating unit, and one from worker's operational area. A total of 28 samples were collected in this sampling event of which 24 samples were taken from plant A and 4 samples from plant B, and 2 field blank samples were also prepared in place for quality assurance purpose.

Sampling of BPA Particulates for Particle Size Analysis

Micro-orifice uniform deposition impactor (MOUDI) was used as the dust sampler to collect BPA particulates under the worker operational environment to estimate the particle size distribution that workers were exposed to, and the sampling time was 36 to 48 hours. The interior of MOUDI consists of 10 47 mm-diameter impactors, with 50% cut-off sizes ($d_{50\%}$) being 18 μm (inlet), 10 μm, 5.6 μm, 3.2 μm, 1.8 μm, 1.0 μm, 0.56 μm, 0.32 μm, 0.18 μm, 0.1 μm, and 0.056 m, respectively. The sampling medium is 47 mm-diameter fiberglass filters with the particle retention of 0.3 μm. To prevent particulates from bounce of and re-suspension during the course of BPA sampling, the filters on the 10 impactors are painted with sticky, inertia substance and the sampling activities proceed after such substance is dry thoroughly. The sampling flux is set at 30 *l*/min and there are eight sets of samples collected (six sets from A plant and two sets from B plant).

Extraction and HPLC/UV Operating Conditions

Each of the samples was first stored in 10ml glass test tubes awaiting laboratory analysis. Subsequently, methanol (HPLC grade, 99.9%, Echo Chemical Co.) was added to the test tubes and stirred with an ultrasound vibrator for 30 minutes and then the test tube was centrifuged for 10 minutes. The suspension was taken from the tube and directly injected to HPLC for analysis. The BPA standard (HPLC, 99.9%) was obtained from Taiwan Prosperity Chemical Co.

The BPA analysis was run by HPLC (Waters 2690, Hitachi) which was equipped with Mightysil RP-18 column (250 mm by 4.6 mm ID), ultraviolet detector was set at 273 nm, ratio of methanol/DI water was 70/30 (v/v), and the flow rate was 0.5 m//min. Correlation coefficient of the calibration curve, using six readings, was calculated to be 0.9996 within the concentration range from 0.025 ppm to 1.0 ppm.

Residual BPA Analysis

Samples of PC raw material were obtained from two PC plants (Plant A and Plant B) for residual BPA analysis. Of these samples, PC raw material from Plant A was optical grade while that from Plant B was injection grade. At first, PC sample was placed in a triangular glass container and added with 20 m/ of methylene chloride. The sample was then stirred with an ultrasound vibrator for 60 minutes, and then 50 m/ of methanol was added slowly. The sample was left undisturbed to alleviate polymer precipitation. The suspension was then concentrated to 2 m/ of volume through evaporation under 40 ℃ coupled with decrease in pressure. Then methanol was added to the suspension to a fixed volume and filtered prior to injection into HPLC for analysis.

There were two types of PC raw materials (optical grade) used at Plant A and were identified as OG-1 and OG-2, respectively. Only one type of PC raw material was used at Plant B and was identified as IG-1.

Quality Control

After completion of sampling, each of samples was placed in a glass test tube with a threaded, Teflon lined cap. The mouth of the test tube was sealed with tape and stored in a -20 ℃ refrigerator pending analysis. All samples were analyzed within one week of sampling. During each of sampling events, field blanks were prepared simultaneously. As a result, eight field blanks and two medium (laboratory) blanks were stored in glass test tubes which were also analyzed, following the same procedures as previously described. The analytical results of these blanks indicated that the target compound was not detected, meaning no cross contamination of samples.

Detection limit (DL) of the BPA extract for HPLC was 1.79 μg/l (S/N=3) (14). Recovery rate of BPA of the spiked samples was 95.6 % (n=6) and BPA remained in the fiberglass filter was measured to be 0.475 μg. The test data of this study were corrected by using the recovery rate.

Statistical Analysis

Estimate of Exposure Level of Airborne BPA

The estimating procedures of exposure adopted the method recommended by American Industrial Hygiene Association (AIHA) of which W-test was first performed to examine if the distribution of airborne BPA concentrations was in agreement with a normal distribution or a logarithmic normal distribution. Then the mean (AM_{MUVE}), the standard deviation, and 95% confidence interval of Minimum Variance Unbiased Estimate (MVUE) were calculated to express the conditions of airborne BPA exposure in the working environment.

Extent of Airborne BPA Exposure to Different Regions of Respiratory Tract

The respiratory tract was divided into three regions: the region from mouth to throat is called as Nasal Region (N); the region from throat to tracheo is called as Tracheo-Bronchial Region (TB); and the region from tracheo to alveolar is called as Alveolar Region (A). The dust particulates might be deposited in different regions of the respiratory tract through breathing and caused various degrees of hazard. The amount of regional dust deposition was much dependent on the size of particulates; therefore, it was of importance to consider particulate distribution and the human inhale efficient of various sizes of particulate when performing assessment of exposure to airborne BPA.

This study used MOUDI sampler to collect data for grain size analysis. The test data were analyzed using the method developed by Vincent (2005) (15) for estimating the human inhale efficiency of inspirable aerosol, through which the amount of BPA deposited in different regions of respiratory tract was calculated.

Results

Analytical Result of PC Extraction

Inasmuch as the two experimental plants manufacture different products, Plant A uses raw optical grade PC material to manufacture the optical lens for protective glasses, while Plant B uses raw injection (or food) grade PC material to manufacture the water bottle. Different grades of raw PC material are different in BPA content; therefore, it is reasonable to say that the exposure level to BPA in the two plants will not be the same. This study performed PC extraction tests to evaluate the residual concentration of BPA for correlating the airborne BPA exposure levels at the plastic plants with the residual BPA concentration from raw PC materials.

The extraction tests were repeated three times on each grade of the raw PC materials obtained from the two plastic plants, following the procedures mentioned in previous section. The test data were analyzed by calculating the mean, standard deviation, and coefficient of Variant to assure the test met the precision criteria set for quality assurance purposes.

Table 1 shows results of BPA concentrations from the raw PC materials at Plant A and Plant B and indicates that the average BPA concentrations of samples OG-1 and OG-2 at Plant A are 47.11 μg/g and 42.26 μg/g, respectively which are greater than that of sample IG-1 from Plant B, which is 14.83 μg/g. The coefficients of variance for the three samples fall in between 0.77 % and 2.5 % (Table 1).

Table 1: Statistical results of BPA extracted from raw PC material

Plant	Sample ID	Concentration (μg/g)				SD	CV (%)
		1st Test	2nd Test	3rd Test	Mean		
A	OG-1	47.68	46.2	47.46	47.11	0.80	1.69
	OG-1	42.34	42.54	41.90	42.26	0.32	0.77
B	IG-1	14.84	14.41	15.25	14.83	0.42	2.85

Distribution of BPA Concentration in Working Environment

Samples collected by IOM were analyzed to evaluate the distribution of airborne BPA concentrations in the process area. As a result, the BPA concentration at the inlet of heating unit was identified to be relatively high as compared with those at the outlet of heating unit and in the worker operating area (Table 2 and Table 3). At Plant A, values of AM (MVUE) were 44.91 μg/m^3 at the inlet of heating unit, 40.89 μg/m^3 at the outlet of heating unit, and 32.28 μg/m^3 in the worker operating area. Furthermore, a *t*-test was conducted to examine the variation of the exposure levels in the three areas of concern. The test result revealed that there was no significant variation (P=0.203) between the inlet of heating unit (260 ℃) and the outlet of heating unit (280 ℃).

Additionally, BPA concentrations at the inlet (260 ℃) and outlet (280 ℃) of heating unit were much higher than that in the worker operating area, with p-values of 0.04 and 0.00047, respectively indicating significant variation in statistics.

Of the two plastic plants, the exposure level of BPA was apparently higher for Plant A than that for Plant B.

Table 2: Distribution of BPA concentrations at plant A

Process Area	n	AM (MVUE) (μg/m^3)	GSD	95% Confidence Interval	BPA Conc. (μg/m^3)
Heating Inlet (260℃)	5	40.89	1.16	35.92~47.83	31.18~43.51
Heating Outlet(280℃)	12	44.97	1.13	42.10~47.90	36.18~55.72
Worker Area	6	32.28	1.21	28.01~38.43	25.39~40.68

Note: The concentration distributions were all in logarithmic normal distribution through W-test.

Table 3: BPA concentrations at plant B

Process Areas	n	BPA Conc. (μg/m³)
Heating Inlet (260℃)	1	18.82
Heating Outlet (280℃)	2	19.39*
Worker Area	1	16.16

Note: the average BPA at heating outlet ranged from 19.28 to 19.5 μg/m³

Particle Size Distribution of BPA in Working Environment

This study used MOUDI as the sampler to collect airborne BPA particulates in the subject plants for analysis, and resulted that the BPA concentration in each level of the impactors (from 1st to 10th level) was detected at concentrations below the detection limit at Plant B. Therefore, results of the airborne BPA concentration and particle size analysis were discussed solely for Plant A (Table 4).

Figure 1 demonstrated the particle size distribution of the airborne BPA, and indicated that the particulates of BPA were in a single mode distribution with a mass median aerodynamic diameter (MMAD) of 0.84 μm and a geometric standard deviation (DSD) of 1.97.

As could be seen in Table 4, most of BPA particulates in the working environment were cumulated in levels of impactors from 4th through 8th levels while the large sizes of intercepted particulates of BPA (1st to 3rd levels) were not detected. Based on this result, BPA spreading in the working environment consisted mainly of the particle sizes ranging from 0.18 μm to 1.8 μm with a MMAD and a GSD of 0.84 μm and 1.97, respectively.

Table 4: Concentration distribution of BPA in the operating environment

Levels of Impactors	50% Screened Size ($d_{50\%}$, μm)	BPA Conc. (μg/m³)	
		Plant A (n=6)	Plant B (n=2)
Inlet	18	ND	ND
1st	10	ND	ND
2nd	5.6	ND	ND
3rd	3.2	ND	ND
4th	1.8	5.04±2.98	ND
5th	1.0	9.14±4.43	ND
6th	0.56	14.69±5.12	ND
7th	0.32	7.70±3.47	ND
8th	0.18	2.54±0.98	ND
9th	0.1	ND	ND
10th	0.056	ND	ND

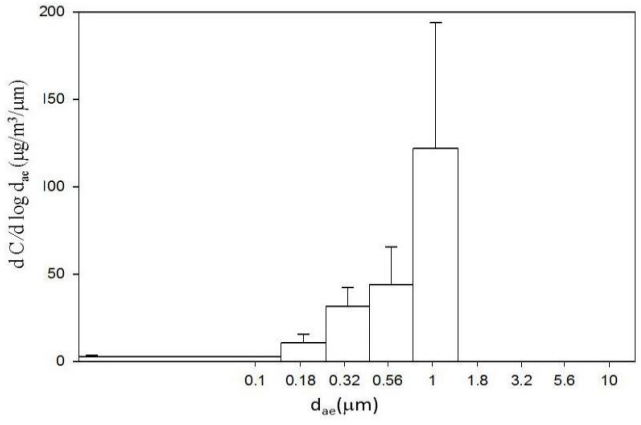

Fig. 1: Distribution of airborne BPA in the operating environment

Exposure Concentrations of BPA to Various Regions of Respiratory Tract

Accumulation and the ratio of BPA in different regions of the respiratory tract including Nasal, Trachea-Bronchia, and Alveolar, were quantified using the formula for calculation of particle inhaling efficiency in respiratory tract and particle size distribution using MOUDI sampler. The BPA concentration cumulated in Nasal region was the highest at 7.53±3.36 μg/m³, followed by BPA cumulated in Alveolar region was at 3.65±1.27 μg/m³, and BPA cumulated in Trachea-Bronchial region was the least at 0.7±0.3 μg/m³(Table 5).

The percentages of BPA accumulation in different regions of respiratory tract were calculated and resulted 63.37 % in Nasal region, 30.7 % in Alveolar region, and 5.93 % in Trachea-Bronchial region.

Table 5: BPA concentrations and the associated ratios in respiratory tract

Respiratroy Tract	BPA Conc. (μg/m³)	Percentage (%)
Nasal Region	7.53±3.36	63.37
Tracheo-Bronchial Region	0.70±0.30	5.93
Alveolar Region	3.65±1.27	30.70
Total	11.89±4.91	100.00

Discussion

It appears that the raw optical PC material contains relative high content of BPA as opposed to the raw injection PC material, and the sample OG-1 contains the highest concentration of 47.11 μg/g among the three samples tested.

The test result revealed that there was no significant variation (P=0.203) between the inlet of heating unit (260 °C) and the outlet of heating unit (280 °C). It appeared that the BPA's melting point (158 °C) and boiling point (220) are both lower than the temperature near the inlet and outlet of the heating unit (260 ℃ to 280 °C) such that BPA particulates tended to diverge into the air under warming condition. Because of no significant difference in temperature near the heating unit, BPA concentrations at the inlet and outlet of heating unit should not vary significantly.

During the course of heating process, BPA would be released from raw PC material. Concentrations of BPA would be increased with increasing heating temperature; as such, the worker should not be working near the heating unit to minimize the exposure to BPA.

The exposure level of BPA was apparently higher for Plant A than that for Plant B. According to the fact that the production volume of Plant B was less than that of Plant A (Table 1), and the sampling time for Plant B was on a 36-hour basis owing to small production volume, while sampling time of Plant A was on a 48-hour basis. The long sampling duration may result in relatively high BPA at Plant A. In addition, BPA concentration in the raw PC material from Plant B was detected to be lower than that in the raw material from Plant A and might lead to low exposure concentration as opposed to Plant A.

He et al. (16) conducted a test to measure airborne BPA concentration at an epoxy and BPA manufacturing plant and found that the average concentration of BPA exposure to the air was as high as 450 μg/m^3. Li et al. (9) also performed a test at a different epoxy manufacturing plant to quantify the exposure level of airborne BPA to workers and resulted in an average BPA exposure concentration of 5.97 μg/m^3. Results from the two studies depicted above indicated that BPA concentrations were both obviously higher than the BPA concentrations (32.28 to 44.97 μg/m^3) concluded in this study. Such significant variation was probably caused by different type of process train, and worker was subjected to more exposure to BPA because BPA was the main raw material for epoxy manufacturing. As to the subject study, BPA was polymerized in the raw PC material and it would be released in the air during the course of heating process, therefore, causing less BPA exposure when compared with the epoxy and BPA manufacturing plants.

Most of BPA particulates in the working environment were cumulated in levels of impactors from 4th through 8th levels while the large sizes of intercepted particulates of BPA (1st to 3rd levels) were not detected. Reasons of small particle deposition in the impactors were probably caused by the fact that the MOUDI samplers were placed close to the heating unit and quickly collected the fresh and newly formed BPA particulates emitted from the heating unit. Relatively high GSD was proba-

bly caused by numerous sampling events (two MOUDI samples per event) with sampling location near the heating zone. It was found that different batch of raw PC materials was used at each sampling event. BPA contents in the raw PC material from different batches were tested and concluded that BPA concentrations ranged from 42.34 μg/g to 47.11 μg/g by which it might lead to variation in analytical results.

According the percentages of BPA accumulation in Trachea-Bronchial region, it was believed that release of BPA particulates in the air would occur during the course of PC molding process and the majority of BPA would cumulate in Nasal region. Still, there were 30.7 % of the released BPA, which would be deposited in Alveolar region. Upon this finding, a proper personal protection should be taken upon BPA particulates generated in the PC molding process.

Conclusion

This study conducted a sampling and analysis plan for two polycarbonate (PC) molding plants, located in southern Taiwan to evaluate the exposure concentration of airborne bisphenol A (BPA), residual BPA in raw PC material, and BPA uptake in various regions of respiratory tract when exposed to workers. Results of this study are concluded as below:

1. Through extraction tests of raw PC material, it was found that un-polymerized BPA concentration in optical-grade PC raw material was greater than in injection-grade PC raw material.
2. The airborne BPA concentrations detected in the plant using optical-grade PC raw material ranged from 32.28 μg/m^3 to 49.97 μg/m^3, which were found to be higher than the airborne BPA concentrations detected in the plant using injection-grade PC raw material, from which the airborne BPA concentrations ranged from 16.16 μg/m^3 to 19.39 μg/m^3. This result was in agreement with the extraction tests.
3. Because of BPA analysis, exposure concentration of BPA was found to be relatively high in the close proximity of heating unit, which was probably caused by the fact that PC raw material facilitated the release of BPA in the course of heating process.
4. Under an operating environment, the distribution of BPA particulate sizes was in a single mode distribution with a MMAD and GSD of 0.84 μm and 1.97, respectively.
5. Through heating, BPA would be released in the air during PC molding process and the majority of BPA would be accumulated in Nasal region (63.37 %), followed by Alveolar region (30.7 %), and then followed by Trachea-Bronchial region (5.93 %).

Ethical considerations

Ethical issues (Including plagiarism, Informed Consent, misconduct, data fabrication and/or falsification, double publication and/or submission, redundancy, etc.) have been completely observed by the authors.

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